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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 stocks 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 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 neoheptane, which are highly desirable blending stocks. As a second component, base stocks comprising isohexanes, isooctanes, 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 isopentane 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

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as a source of volatility to adjust the vapor pressure of the blend and to produce desirable distillation characteristics, especially in the initial portion of the distillation curve.

Since the synthetic isoparaffin blending stocks are ordinarily available in somewhat smaller volume than base stocks prepared from naturally-occurring distillates, blending formulas which require minimum volumes of such synthetic stocks are 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 isoparaffins, such as the isohexanes, etc., as being more valuable than a full boiling range naphtha, unless the naphtha is deficient in normal (low octane number) paraffins or has unusually high octane number as a result of its content of naphthene hydrocarbons.

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 C_4 hydrocarbons, and preferably containing only minor amounts of C_5 to C_9 normal paraffins. The content of naphthenes 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 C_5 , C_6 , and C_7 paraffins from the isoparaffins 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 number reference fuel, the relative improvement being stated in ml. of tetraethyl lead.

While laboratory tests and octane 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 isoparaflinic 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 isoparaflinic 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 isoparaflin blending formulas insofar as possible. This procedure requires that such special performance characteristics as lean and rich mixture ratings be obtained through the inclusion of 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 effective operation and power output of the engines are improved. It is a further object of this invention to provide an improvement in the blending formulas for preparing predominantly isoparaflinic aviation fuels whereby the rich mixture deficiencies of said isoparaflin 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 isoparaflinic aviation fuel of 100 octane number rating or better containing a relatively minor proportion of an added compound providing 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 essentially isoparaflin hydrocarbons have greatly improved octane number ratings at high fuel-air ratios when minor proportions of isopropylbenzene are added. The isopropylbenzene is employed as the substantially pure compound since its efficacy is highly specific and definitely superior to other

aromatic homologues which might be present in crude or impure alkylated benzene mixtures. A further purpose served by the use of the substantially pure compound is the elimination of associated impurities which may have deteriorative effects on the fuel and/or on aircraft fuel systems in which it is used.

In the investigation and testing of isoparaflin aviation fuel blends containing aromatic hydrocarbon additives for the purposes outlined above, it has been found necessary to disregard the conventional concepts of the use and properties of aromatics as a class. For example, whereas aromatics have been previously regarded as enhancing the octane rating of ordinary fuels, it is necessary in the present instance to limit the quantity of aromatic to avoid degradation of the octane number and response to tetraethyl lead antidetonant. Further, while aromatic hydrocarbons have heretofore been regarded as equivalents within the limits of their physical properties, such equivalency is entirely lacking in the present application as will be illustrated hereinafter.

While specific embodiments of the present invention may be invoked in a great variety of blending operations involving isoparaflinic blending and base stocks, one satisfactory procedure may be outlined in the following operations. A fuel is to be prepared, according to a blending formula, from iso-octane, isopentane and a naphtha comprising C_6 and C_7 isoparaflins in proportions which produce 100 octane number with 4 ml. of tetraethyl lead per gallon. This blending formula is altered according to the present invention to include isopropylbenzene by use of a predetermined volume per cent of an isopropylbenzene-isopentane mixture having a vapor pressure substantially equal to that of the finished fuel (usually 7 pound Reid vapor pressure). The volume of the mixture used replaces a corresponding volume of isoparaflin base stock and synthetic blending stock with the blending proportions of the latter usually being readjusted to produce the same octane number rating as before.

The isopropylbenzene may be added alone to fuel blends, but it is often more convenient to employ the isopentane mixture. The advantages lie in the maximum utilization of isopentane and less difficulty in blending to meet vapor pressure specifications. The amount of isopropylbenzene thus included in the finished fuel is further limited by its relatively high boiling point ($306.5^\circ F.$) which restricts the volume permissible in a fuel having a maximum 90 per cent evaporated temperature of $275^\circ F.$

The isopropylbenzene employed in the fuel compositions may be derived from any suitable source, provided a relatively pure product is obtained. In many cases, it is difficult to separate isopropylbenzene from complex mixtures of aromatic and other types of hydrocarbons such as may result from the non-selective alkylation of mixed stocks such as gasoline fractions. For this reason, the preferred source of isopropylbenzene for the present invention is the selective alkylation of benzene with propylene or its equivalent alkylating agents in the presence of suitable alkylation catalysts such as boron fluoride or hydrogen fluoride which produce the branched-chain derivative exclusively. The isopropylbenzene which may be thus produced in high yields is substantially free of undesirable impurities

and is readily separated from unreacted benzene and/or polyalkylated benzenes.

The amounts of isopropylbenzene added will obviously be dependent on the other fuel components and on the rich mixture octane rating which is desired in the final blend. In most cases, the isopropylbenzene will vary between about one and about 20 volume per cent of the blend, with a somewhat narrower range of about two to about 10 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 to 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 isopropylbenzene, perhaps because of the branched side-chain, exhibits quite different properties from those of benzene, toluene, xylenes and even ethyl and n-propylbenzenes. One way in which the different and more desirable properties of isopropylbenzene are evidenced is in reduced swelling of and diffusion through rubber or rubber-like materials with which the compounds or fuel compositions containing them are in contact. Comparative data are given below for an isoparaflinic aviation fuel (blend A) and for said fuel after

tane number ratings of 100 octane number 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 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 isopropylbenzene to isoparaflinic aviation fuels, the following examples are cited:

Example I

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

Formula	Isoparaflin components, volume per cent				Aromatic additive (5 volume 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	16.8	33.7	13.6	Ethylbenzene.
D.....	30.9	16.8	33.7	13.6	Isopropylbenzene.

addition thereto of 5 per cent and 15 per cent of benzene, ethylbenzene, and isopropylbenzene, in contact with a moderately oil-resistant synthetic rubber, as represented by Hycar O. R.

These blends were rated according to the Army-Navy test method AN-VV-F-746 and also according to the supercharged engine method AN-VV-F-748. Octane numbers above 100 are recorded

	Blend A	Aromatic additive					
		Benzene		Ethylbenzene		Isopropylbenzene	
Aromatic concentration (volume percent).....	None.....	5	15	5	15	5	15
Percent swelling (24 hours).....	Zero.....	2.2	3.43	0.5	2.4	0.5	.9
Diffusion (grams/hour).....	0.014.....	0.035	0.112	0.025	0.059	0.022	0.034
Increased solvency due to aromatic (mg./gm. rubber per 24 hours).....	(Reference).....	10.7	18.7	2.7	4.0	1.2	1.6

These results indicate that the swelling, diffusion, and solvency effects with the alkylated benzenes are appreciably less than with benzene itself. This effect is apparently due to decreased aromaticity resulting from the alkyl group, and varies particularly with the length of the side chain. This means that better service characteristics result from the use of isopropylbenzene and/or that larger concentrations of isopropylbenzene 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 Specification (Method for Knock-Test AN-VV-F-746), dated October 5, 1940. This method is utilized for determining ordinary oc-

as ml. of tetraethyl lead in 100 octane number iso-octane in the following table.

Blend formula	Antiknock rating		
	AN-VV-F-746	AN-VV-F-748	
		Lean mixture	Rich mixture
A.....	MI. TEL	MI. TEL	MI. TEL
B.....	0.03	0.20	0.65
C.....	100	0.30	0.80
D.....	100	0.20	0.80
E.....	0.03	0.30	1.25

These results indicate the substantially improved rich mixture rating provided by isopropylbenzene as compared to the fuel A alone and to formulas

B and C with benzene and ethylbenzene. The effect of the aromatic additives is very slight in the conventional (F746) rating, and also in the lean mixture supercharged ratings.

While a certain small improvement is indicated for benzene and ethylbenzene, the magnitude of the improvement is in most instances not sufficient to justify the use of these additives. The use of benzene in particular is questionable in view of other and undesirable effects on the qualities and properties of the fuels. On the other hand, the superior qualities of isopropylbenzene are clearly indicated since the rich mixture rating of fuel D is approximately twice that of fuel A when considered in terms of ml. TEL in iso-octane.

Example II

A special aviation fuel was prepared by blending commercial iso-octane, neohexane, and isopentane in proper proportions to meet vapor pressure and distillation specifications, and to meet octane number requirements with 3 ml. TEL per gallon. This composition was then modified by the inclusion of a mixture of 78 per cent isopropylbenzene (Boiling Range 305 to 308° F.) and 22 per cent isopentane to produce a fuel containing 10 per cent isopropylbenzene. The comparative octane ratings of these fuels with 3 ml. TEL per gallon were as given below in terms of ml. TEL in 100 octane iso-octane. Octane numbers by the AN-VV-F-746 method were approximately 100.

	Octane rating (AN-VV-F-746 method)	
	Lean mixture	Rich mixture
Reference blend.....	0.80	2.0
Ref. blend+10% isopropylbenzene.....	0.80	2.6

In this case, without appreciably affecting the conventionally determined octane number, the rich mixture rating of the fuel was raised 0.6 ml. TEL in iso-octane.

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 application to predominantly isoparaflinic fuel blends, it is broadly applicable to fuel compositions suitable for the purposes outlined and within the limits prescribed.

What is claimed is:

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 isoparaflin hydrocarbons having five, six, seven, eight and nine carbon atoms per molecule and about 10 per cent by volume of isopropyl benzene 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 isoparaflin hydrocarbons having not less than 5 and not more than 9 carbon atoms per molecule and about 10 per cent by volume of isopropyl benzene 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 essentially of a mixture of isoparaflin hydrocarbons having not less than five nor more than nine carbon atoms per molecule and isopropyl benzene in an amount between about 1 and about 20 per cent 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 isoparaflin hydrocarbons having not less than five nor more than nine carbon atoms per molecule and isopropyl benzene in an amount between about 2 and about 10 per cent 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.

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