Sept. 17, 1946. R. F. MARSCHNER ET AL 2,407,718

AVIATION SUPER FUEL

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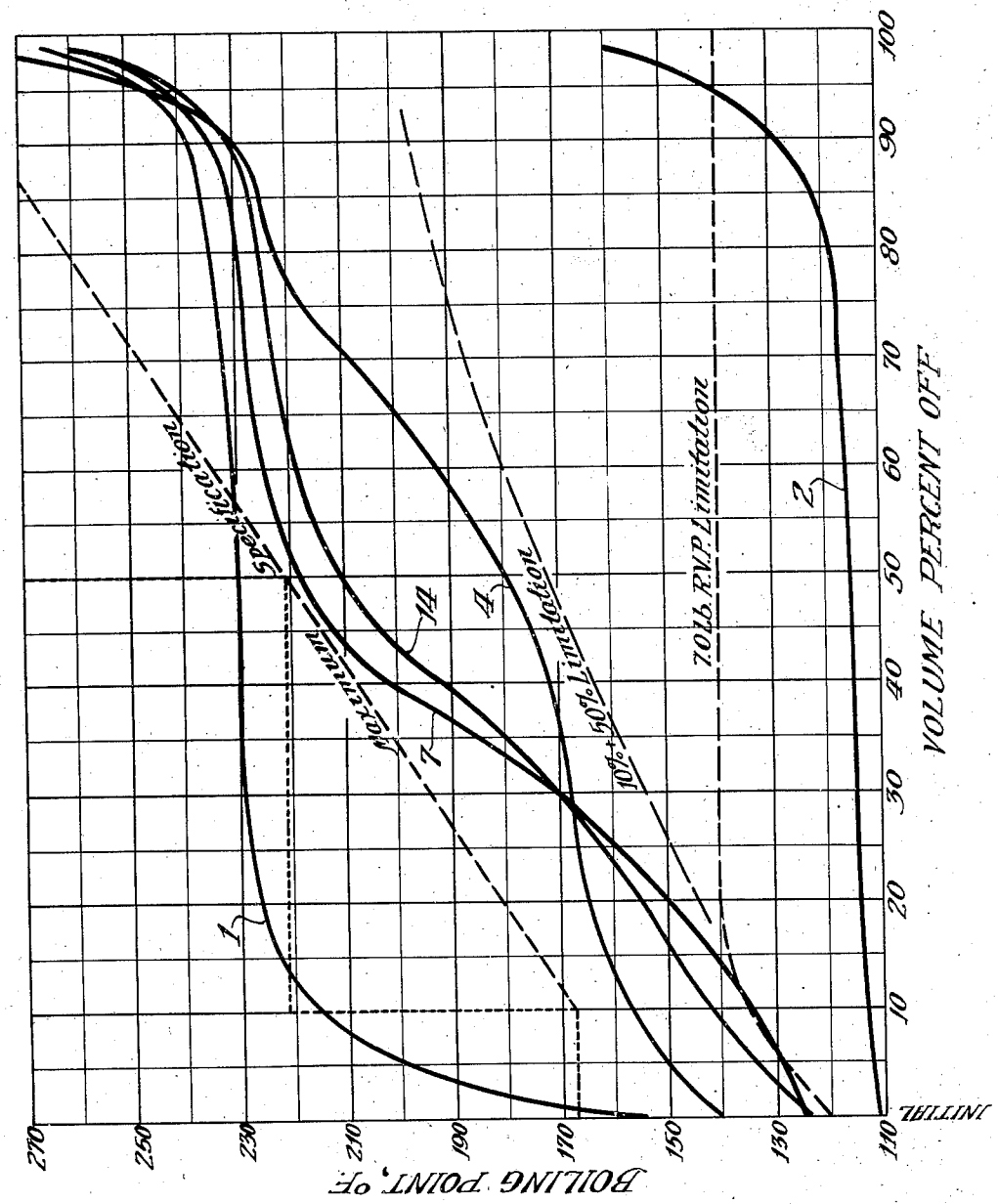


Fig. 1.

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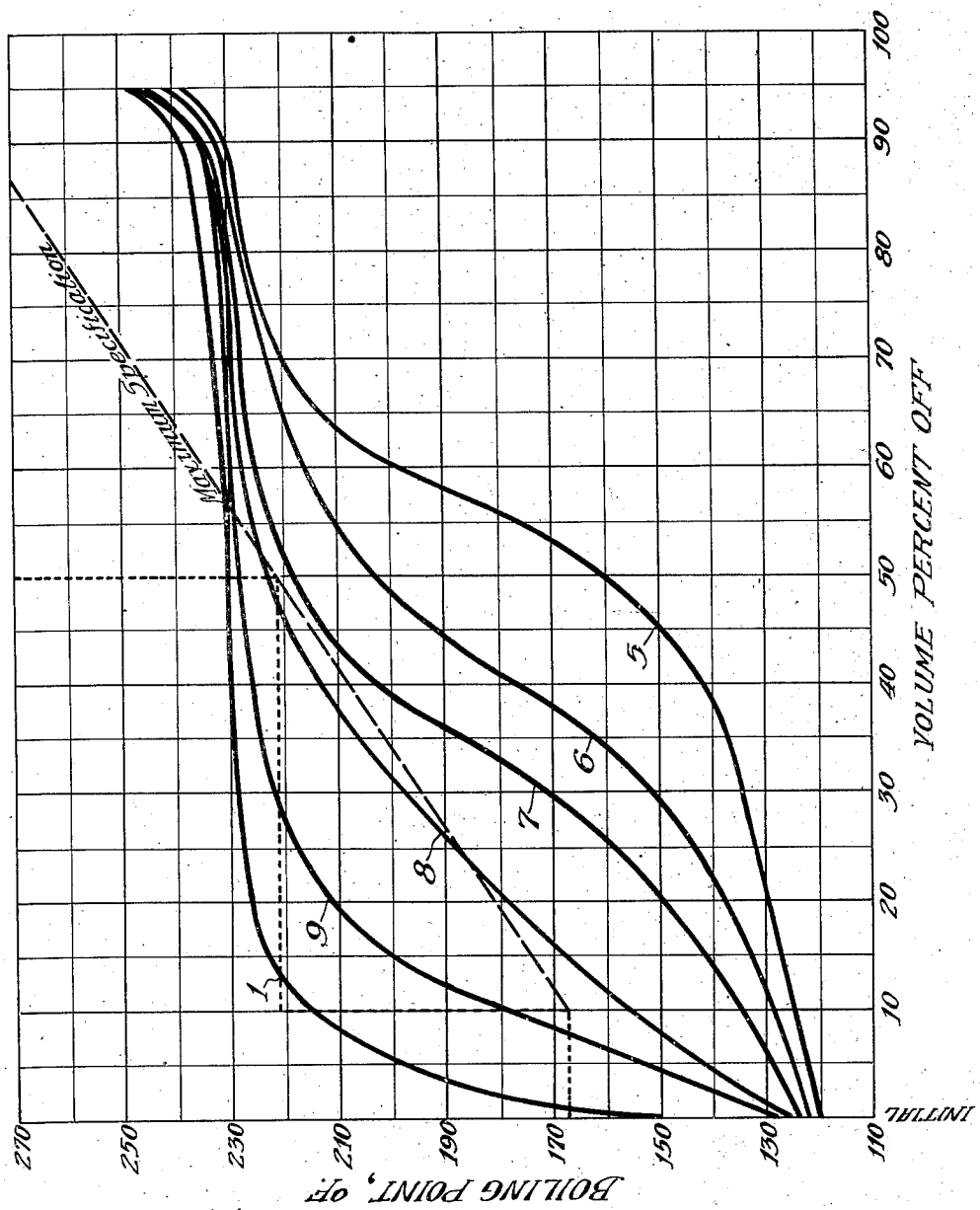


FIG. 2.

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AVIATION SUPERFUEL

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11 Claims. (Cl. 44—77)

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This invention relates to new and improved superfuels adapted for aviation purposes. It pertains more particularly to blends of which the major component is a high octane number base stock such as isooctane and the minor component is a blending agent exemplified by hydrocarbon-ketone azeotropes. The preferred low-boiling azeotropes are mixtures of acetone with diisopropyl, neohexane or cyclopentane but we may also employ other azeotropes such as mixtures of methylethyl ketone with benzene, cyclohexane or triptane and we may employ a ketone such as methylisobutyl ketone for forming an azeotrope with isooctane itself.

Ketones have been employed in ordinary gasolines and even in gasolines to which a minor amount of isooctane has been added but heretofore no such blend has met the strict present-day requirements for aviation superfuel. Furthermore, no prior blends have utilized the azeotrope-forming properties of ketones for solving the problem of making high octane number base stocks meet aviation volatility requirements.

For modern aviation engines the fuel must not only have a high antiknock value under all conditions of use, a high lead tetraethyl response, etc. but it must also meet certain initial, intermediate and overall volatility requirements. Volatility specifications for 100 octane number aviation fuels are summarized in the drawings. The dotted lines represent the literal maxima set on boiling point, but for practical purposes the dashed line defines the upper limit. If any point on the A. S. T. M. distillation curve of a fuel falls below the lowest dashed line, it probably will exceed 7.0 pounds R. V. P. If the fuel is to have a Reid vapor pressure approaching 7.0 pounds, however, the 10% point will be in the vicinity of 135° F. and the 10%+50% (307° F.) specification automatically sets the minimum 50% point at 172° F. For practical purposes the intermediate dashed line represents the lower distillation limit. This leaves a rather narrow band into which the complete distillation curve of aviation superfuel falls in meeting specifications.

Commercial isooctane can have an initial boiling point of about 165° F. but between the 10% and 90% points the boiling temperature is within the range of about 210 and about 240° F., and it has a Reid vapor pressure of only about 2 p. s. i.

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The isooctane described herein is the commercial product which can, for instance, be prepared by polymerizing a mixture of isobutylenes and other butenes, diluted with butanes, to isooctenes. Subsequently, the isooctenes are hydrogenated to produce a hydrocodimer isooctane fraction. Alkylate isooctane can be prepared by the alkylation of isobutane with butenes or by the dehydroalkylation of isobutane or by the destructive alkylation of higher branched paraffins, for example by the sulfuric acid process. The term "isooctane" as used in this specification and in the appended claims (unless more expressly defined in the specific instances) is hereby defined as including not only 2,3,4-trimethylpentane but also commercial isooctanes comprising primarily trimethylpentanes such as hydrocodimer isooctane, alkylate isooctane, etc., as such products are commercially produced and marketed. The manner in which a commercial isooctane alone fails to meet distillation specifications is illustrated by its distillation curve on Figure 1.

It is therefore an object of our invention to adjust the distillation characteristics of commercial isooctane. More specifically it is an object of our invention to adjust the vapor pressure and the volatility of an aviation gasoline comprising commercial isooctane. A further object is to lower the mid point of the aviation superfuel without adversely affecting the antiknock properties. Another object is to provide a blended isooctane aviation fuel having the desired initial and overall boiling characteristics. An additional object is to provide a tailor-made fuel of high lead response and lean and rich octane numbers.

An important object of our invention is to utilize maximum amounts of high octane number base stocks such as isooctane with available high octane number hydrocarbons such as cyclopentane, neohexane and diisopropyl so that a maximum amount of a superfuel passing all specifications can be produced with a minimum amount of these particular hydrocarbons. In other words, our object is to decrease the amount of cyclopentane, neohexane or diisopropyl which must be added to a base stock in order to meet the most rigorous specifications without decreasing overall performance while at the same time obtaining the desired volatility of the blend.

To attain these objects we propose a unique

aviation superfuel comprising between about 60 and about 90 volume percent of a base stock having a clear octane number of at least 85, for example commercial isooctane. The azeotropic mixture as the low boiling ingredient can be used in quantities ranging between about 10 and about 40 volume percent of the blend. This azeotrope comprises between about 30 and 50 volume percent of a hydrocarbon selected from the group consisting of cyclopentane, neohexane, and diisopropyl and between about 50 and about 70 volume percent of a ketone or mixture of ketones. The amount of the low-boiling azeotrope can be further lowered by employing a higher boiling azeotrope as exemplified by mixtures of benzene, cyclohexane or triptane with methylethyl ketone or by including a small amount of a higher ketone such as methylisobutyl ketone in the blend.

One outstanding feature of our invention is the use of azeotropes which boil below the boiling point of either ingredient thereof. Thus acetone boils at 134° F. and diisopropyl boils at 136° F. and both have about 7 p. s. i. Reid vapor pressure but a mixture of 57% acetone and 43% diisopropyl has a boiling point of only 114° F. and 11 p. s. i. Reid vapor pressure. Although cyclopentane and neohexane boil near 121° F. and have about 9 p. s. i. Reid vapor pressure, mixtures of about 35% cyclopentane or neohexane with about 65% acetone boil at only 105° F. and have about 13 p. s. i. Reid vapor pressure. In practicing our invention we utilize these phenomenal decreases in boiling point or increases in volatility which are thus provided by the azeotropes for obtaining results which could not be accomplished by the use of corresponding amounts of either ingredient by itself. In other words, the properties of the acetone and the hydrocarbons such as cyclopentane, diisopropyl and neohexane are not simply additive but a new and unexpected result is obtained by their conjoint use within the defined limits.

An antiknock agent e. g. lead alkyls, can be added in conventional quantities to the blends varying from small amounts up to the upper limit tolerated by other considerations having to do with engine design. This upper limit at present is fixed at about 4 cc. of lead tetraethyl per gallon of fuel. Our blends, however, have a high lead response and meet the octane number specifications without excessive amounts of lead.

We have found that certain blends comprising isooctanes with cyclopentane, neohexane or diisopropyl and certain azeotrope-forming ketones are excellent pursuit or combat aviation fuels, as such or with lead alkyls added. Selected low-boiling ketones can be used to form an azeotrope with cyclopentane, neohexane, and/or diisopropyl in order that the vapor pressure and volatility of the isooctane blend is adjusted. Certain other ketones boiling at temperatures in the vicinity of isooctane form an azeotrope with isooctane itself and thereby lower the end point of the isooctane and the mid point of blends. Mixed ketones can be included in the blend to affect both the initial and the middle boiling characteristics.

Broadly our invention contemplates an azeotrope-forming agent selected from the group of ketones having not more than six carbon atoms and boiling within the aviation fuel boiling range. Examples of such ketones, the composition of hydrocarbon azeotropes thereof and their properties are set out in Table I.

TABLE I

Hydrocarbon-ketone azeotropes of high octane hydrocarbons

Ketone	Hydrocarbon	V. percent	Boiling point, ° F.	
			Component	Azeotrope
Acetone			134	
	Cyclopentane	35	121	105
	Neohexane	33	121	105
	Diisopropyl	43	136	114
Methylethyl ketone.			176	
	Benzene	50	176	172
	Cyclohexane	33	177	159
	Triptane	24	177	159
Methylisobutyl ketone.			240	
	2,3,4-trimethylpentane.	47	236	225

Those hydrocarbon-ketone azeotropes which boil in the range of between about 90 and 135° F. are of great importance in aviation fuels because of the paucity of hydrocarbons which boil in this range and which when blended with isooctane yield a superfuel having a Reid vapor pressure approaching the specification maximum, 7.0 p. s. i., a high clear octane number, and a high lead response.

The addition of the low boiling ketones, for example, acetone, to form an azeotropic mixture with diisopropyl, neohexane and/or cyclopentane has several interesting effects. The boiling point of the hydrocarbon is lowered so that less blending agent need be added to commercial isooctane to reduce the 10% point below 167° F. The total volume of blending agent available is increased by the volume of ketone added and this together with the reduction in the 10% point permits for more aviation superfuel production from commercial isooctane and a limited amount of diisopropyl, neohexane, and/or cyclopentane. The Reid vapor pressure of the azeotrope is greater than the hydrocarbon addition agent alone, hence less blending agent is necessary to raise the R. V. P. of the isooctane to the desired level.

When a higher boiling ketone is added to isooctane the ketone-isooctane azeotrope formed lowers the distillation range of the commercial isooctane to pass the 50% point specification with less volatile hydrocarbon present. Ketones or mixtures thereof suitable for addition to commercial isooctane to lower the mid-point include ethylpropyl, methylbutyl and dipropyl ketones. The ketones may suitably be prepared from waste petroleum products such as propylene or butenes through reaction with sulfuric acid to produce isopropyl or secondary butyl alcohols, followed by dehydrogenation to acetone or methylethyl ketone. The higher ketones may be prepared by oxidation, for example, with air, of polymers of such olefins. One advantage of addition of such a ketone to commercial isooctane is that a smaller amount of a light hydrocarbon containing no more than six carbon atoms, as such or as an azeotropic mixture with a light ketone, need then be added to lower the 10% point below 167° F.

We have discovered that the azeotropes can be used according to our invention to bring both the boiling point range and vapor pressure of isooctane within the specifications illustrated in Figure 1. The distillation characteristic of various blends are shown in the drawings and are summarized in Table II.

TABLE II

Inspections of ketone blends

	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Diisopropyl	0	50	0	50	25	20	15	10	5	20	20	5	10	15
Acetone	0	50	50	0	25	20	15	10	5	0	0	5	10	15
Isooctane [1]	100	0	50	50	50	60	70	80	90	80	70	80	70	60
Methylisobutylketone	0	0	0	0	0	0	0	0	0	0	10	10	10	10
Distillation A. S. T. M., °F.:														
Init.	148	111	130	140	120	122	124	126	128	156	142	130	128	124
10	215	113	133	157	126	128	134	156	179	188	186	182	158	142
20	226	114	134	164	130	137	150	180	211	196	195	203	175	153
30	228	114	136	168	134	151	170	195	221	206	202	217	190	170
40	230	114	137	172	141	176	202	214	225	214	210	220	209	192
50	230	115	140	180	160	203	218	223	228	219	217	223	218	211
60	231	116	146	192	198	214	226	228	230	226	222	225	223	219
70	233	117	222	209	220	224	228	230	231	229	226	227	226	223
80	235	119	230	223	228	229	230	231	232	231	229	229	228	226
90	238	128	232	230	230	232	234	235	235	236	233	233	233	231
EP	266	160	256	280	264	268	276	267	258	270	259	256	265	261
10+50	445	228	273	337	286	331	352	379	407	407	403	405	376	353
Reid vapor pressure, p. s. i.	2.3	10.0	6.6	4.1	8.1	7.0	6.0	5.4	4.7	2.6	2.6	4.3	5.4	6.1
Octane number A. S. T. M. (clear)	93.1			94.0			94.5							95.2

[1] Hydrocodimer.

The drawings demonstrate graphically the nearly ideal way in which azeotropes can be used to bring the commercial isooctane within the present aviation superfuel distillation specifications. The reference numerals of the curves refer to the like-numbered blends set out in Table II, and the drawings should be read in conjunction with the table. These curves indicate the effects of the various ketones and in general illustrate our invention.

A suitable blending agent comprises an azeotropic mixture of between about 50 and about 70 volume percent ketone and between about 30 and about 50 volume percent of a high octane number 5 or 6 carbon atom hydrocarbon. Examples of such blends are illustrated in Table I. For example, a diisopropyl-acetone azeotrope having 57 volume percent acetone boils at 114° F. and has a Reid vapor pressure of about 10.3 p. s. i. The boiling point of the diisopropyl is lowered some 22° F. so that a greater percentage of isooctane can be used in preparing a blend whose 10% point is below 167° F. As shown in Table II, a blend of 50% isooctane and 50% diisopropyl has 94.0 octane number whereas a blend of 70% isooctane and 30% of a blend of equal volumes of diisopropyl and acetone has a slightly better octane number of 94.5 even though it contained far less diisopropyl. Such a blending agent is useful for modifying commercial isooctane to improve the volatility, lead response and the general suitability of the blend as an aviation superfuel.

Another blended fuel according to our invention comprises 70 volume percent isooctane and an azeotropic mixture of acetone and cyclopentane. An azeotropic mixture of about 65 volume percent acetone and about 35 volume percent cyclopentane has a lower boiling point of about 105° F. and a higher Reid vapor pressure of about 13 p. s. i., as well as a larger volume than cyclopentane itself. This permits the relatively limited amount of cyclopentane available to go further when blended with the base fuel such as isooctane since a finished aviation fuel having a higher vapor pressure can be made with a smaller percentage of azeotrope than of the hydrocarbon blending agent and the aviation fuel contains a smaller volume of cyclopentane. The neohexane-acetone azeotrope may be used equally well in this blend.

Another aspect of the invention consists of the addition of ketones, especially methylethyl ketone, to hydrocarbons of intermediate boiling range. Provided a suitable fuel were available, engines could be designed to operate far more efficiently than at present. Such an ideal fuel would be of constant volatility throughout and would consist, for example, of a pure hydrocarbon. Methylcyclopentane (B. P. 163° F.) passes all present day volatility specifications since its 10% point is below 167° F. and its 10+50% points total 326 which exceeds 307°. But in certain respects cyclohexane and triptane are superior fuel hydrocarbons to methylcyclopentane. These hydrocarbons are too high-boiling (176–7°) to be as suitable. By the addition of methylethyl ketone to cyclohexane or triptane an azeotrope shown in Table I results, which does pass all volatility specifications. Corresponding azeotropes of methylisopropyl ketone with cyclohexane and with triptane contain mainly hydrocarbon and likewise give flat lower-boiling distillation curves.

We contemplate a further modification of the invention. With the use of pentene and hexene alkylation, "iso-nonane" and "isodecane" aviation fuel bases are obtained which approach the 90% and end point specifications of aviation fuels. By the addition of the proper ketone which may actually exceed the specification points these temperatures may be brought into line. We also contemplate blending higher ketones, for example mixtures of C_6 ketones, to the reaction product described in our copending application S. N. 437,050, now United States Patent 2,308,562.

In this specification and in the accompanying claims the term "cyclopentane" is hereby defined as including not only the pure chemical compound but also as including technical or commercial grades of cyclopentane obtainable by close fractionation of naphtha. Preferably this cyclopentane should have an A. S. T. M. octane number of at least about 90, should have a narrow boiling range and should consist chiefly of cyclic C_5H_{10} (pentamethylene).

The term "neohexane" as employed in this specification and in the accompanying claims is hereby defined as including not only the hydrocarbon 2,2-dimethylbutane but as also including commercial neohexane as produced by the thermal alkylation of isobutane with ethylene at a pressure of about 4500 pounds per square inch

and a temperature of about 950° F., by the catalytic isomerization of hexanes with an aluminum chloride or aluminum chloride-hydrocarbon complex catalyst in the presence of hydrogen chloride and added hydrogen at temperatures of about 200 to 300° F. and at a pressure of about 850 pounds per square inch, or by any other commercial process. Preferably this neohexane should have an A. S. T. M. octane number of at least about 90, should have a narrow boiling range and should predominate in 2,2-dimethylbutane.

The term "diisopropyl" as used in this specification and in the accompanying claims is hereby defined as including not only the hydrocarbon 2,3-dimethylbutane but also includes commercial diisoproply produced by the alkylation of isobutane with ethylene effected in the presence of an aluminum chloride-hydrocarbon complex catalyst at a temperature within the range of about 50 to 150° F., under a pressure sufficient to maintain the reactants in liquid form, usually about 50 to 150 pounds per square inch, preferably in the presence of an excess of isobutane. The diisopropyl may, however, be obtained from any other commercial source. It should have an A. S. T. M. octane number of at least about 90, should have a narrow boiling range and should contain predominantly the hydrocarbon 2,3-dimethylbutane.

Likewise, the terms "benzene," "cyclohexane" and "triptane" are hereby defined to mean commercial products of relatively narrow boiling range and high octane number and these terms are not limited to the use of pure or even substantially pure hydrocarbons.

From the above it will be apparent that we have provided new aviation superfuels and methods of preparing the same. Although we have described in detail preferred embodiments of our invention, it should be understood that various modifications thereof will be apparent from the above description to those skilled in the art. Therefore it is to be understood that our invention is not limited thereto but only by the appended claims.

We claim:

1. A super aviation fuel comprising between about 85 and about 60 volume percent isooctane and between about 15 and about 40 volume percent of an azeotropic mixture comprising between about 40 and 60 volume percent of diisopropyl and between about 60 and 40 volume percent of acetone.

2. A superfuel which comprises a blend including between about 60 and about 90 volume percent of trimethylpentane and an azeotropic mixture of propanone and a hydrocarbon selected from the group consisting of cyclopentane, neohexane, and diisopropyl.

3. A superfuel comprising a blend of a major proportion of iso-octane and between about 10 and about 40 volume per cent of an azeotropic mixture of between about 50 and about 70 volume percent of acetone and between about 30 and about 50 volume percent of a hydrocarbon selected from the group consisting of cyclopentane, neohexane, and diisopropyl, said azeotropic mixture boiling in the range of between about 90 and about 135° F.

4. A superfuel comprising a blend of a major proportion of isooctane and between about 10 and about 40 volume per cent of an azeotrope of propanone and a high octane number hydrocarbon selected from the group consisting of cyclopentane, neohexane, and diisopropyl, said azeotrope boiling within the range of between about 90° and about 165° F.

5. A superfuel comprising a blend of between about 60 and about 90 volume per cent of isooctane and an azeotrope of butanone and a high octane number hydrocarbon selected from the group consisting of benzene, cyclohexane, and trimethylbutane, said azeotrope boiling within the range of between about 90° and about 165° F.

6. An aviation combat fuel which comprises a blend of between about 10 and about 40 volume percent of an azeotropic mixture of butanone and a high octane number hydrocarbon selected from the group consisting of benzene, cyclohexane, and trimethylbutane, between about 50 and about 80 volume percent of trimethylpentane and between about 5 and about 20 volume percent of an azeotropic mixture of trimethylpentane and a hexanone.

7. An aviation superfuel comprising between about 60 and about 80 volume percent of trimethylpentane, between about 10 and about 40 volume percent of an azeotropic mixture which comprises between about 30 and about 50 volume percent of a high octane number hydrocarbon selected from the group consisting of neohexane, diisopropyl, and cyclopentane and between about 50 and about 70 volume percent of propanone and between about 5 and about 20 volume percent of hexanone.

8. The method of adjusting the over-all distillation characteristics of commercial trimethylpentane comprising the steps of adding between about 15 and about 40 percent of a propanone azeotrope of a hydrocarbon selected from the group consisting of neohexane, diisopropyl, and cyclopentane to adjust the vapor pressure and the front end volatility and adding between about 5 and about 20 volume per cent of methyl iso butyl ketone to lower the mid-point of the blend.

9. An aviation superfuel which comprises essentially an isooctane and between about 10 and about 40 volume per cent an azeotropic mixture of trimethylbutane and butanone.

10. An aviation superfuel which comprises essentially an isooctane and between about 10 and about 40 volume per cent an azeotropic mixture of cyclohexane and butanone.

11. An aviation fuel comprising between about 60 and about 90 per cent of an isooctane and between about 40 and about 10 per cent of at least one of two classes of azeotropes, the first class comprising propanone and a hydrocarbon selected from the class consisting of neohexane, cyclopentane, and diisopropyl and the second class comprising butanone and a hydrocarbon selected from the class consisting of cyclohexane, benzene, and trimethylbutane.

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