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## SAFETY MOTOR FUEL

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This invention has to do with a method of controlling inflammability of motor fuels for high-compression spark-ignition engines. More particularly, it is concerned with conferring upon hydrocarbon motor fuels high immunity to explosion and inflammability under a wide variation of aviation service conditions with the least possible detraction from the volatility and antiknock qualities of the fuel and without imparting undue corrosiveness to the fuel.

The importance of reducing fire hazard in aircraft is obvious, particularly for combat or long range transport units, but, the need of high octane safety fuels for aviation engines has presented some important problems with regard to avoidance of fire hazards.

The use of high flash point naphthas for reducing fire hazard is well known in cleaning, paint, and other industries which make use of solvents. Hitherto, it has been presumed that solvents like kerosene or Stoddard's solvent, and the like, with a minimum flash point of 105° F., have adequate safety from fire hazards, and accordingly, without further investigation, this same minimum flash point was generally regarded as an index of safety for motor fuels. By recent investigations applied particularly to motor fuels for aviation service, I have found that the tests for safety of these aviation fuels depend upon factors not present in the use of solvents and that, moreover, other significant characteristics of fuels must be taken into account, which makes the problem with respect to fuels quite distinctive.

The main object of the present invention is to control the explosiveness and inflammability of motor fuels with the least possible detraction from their desired volatility characteristics.

To accomplish the objects of the present invention it was determined by a number of special tests, what service conditions created a fire hazard in the use of the fuels and to what extent the fuels have to be modified with respect to their tendencies to flash, burn, and explode, so as to reduce these tendencies to a minimum. Further, in carrying out these tests, it was determined that the potential fire hazards are greatly reduced with less impairment of the volatility characteristics of the fuel by adding to the fuel proper amounts of selected noninflammable substances, more particularly, certain highly volatile organic halides.

Contrary to the long accepted belief that merely a removal of highly volatile fuel components to increase the minimum flash point of a fuel to about 105° F., or thereabove, insures the safety of the fuel against fire hazard, I have found that when the fuel becomes subjected to a variation of conditions brought about by change in altitude it becomes unsafe. As a matter of fact, the more volatile fuels, with flash points below 105° F. are less prone to form explosive mixtures in fuel tanks at certain high altitudes than are the commonly regarded safety fuels with flash points of about 105° F. or thereabove, which actually can form explosive mixtures under practical aviation service conditions. Thus, at high altitudes, the variable combinations of temperature and pressure imposed on a fuel in a supply tank have certain changing effects on the air to vapor ratio in the fuel tank. For instance, at atmospheric pressure of sea level, the fire hazard may be negligible for the ordinary safety fuel having a flash point of 105° F., but as the pressure is reduced by gaining of altitude, the temperature at which the fuel is subject to explosion drops sharply. At an altitude of 25,000 feet the ordinary safety fuel forms an explosive mixture in the tank at 68° F.

Another important property of a fuel, previously overlooked in evaluating safety characteristics of fuels, is the fire point and rate of burning. Those should be taken into account to decrease the danger from conflagration caused by a spark, open flame, or a hot metal surface in the case of a plane crash. Thus, in evaluating the safety factor of fuels, it was found necessary to make determinations on inflammability limits, spontaneous ignition temperatures, and burning characteristics.

From a long series of tests with variations of all practical factors, it was ascertained that an aviation fuel having a minimum flash point of 124° F. more properly obviates potential explosive hazards under all practical combinations of fuel temperature and altitude pressures. This determination took into consideration the initial fuel temperature, the rate of change in altitude, the rate of cooling, the degrees of agitation at the vapor-liquid interface in a fuel supply tank, and

was determined up to the altitude of 30,000 feet at 30° C. However, such a requirement seriously limits the availability of high octane number hydrocarbon fuels on account of manufacturing limitations and requires a fuel of such low volatility that difficulties in starting and engine operation may be encountered due to improper carburetting and the lack of a proper air to fuel ratio in the fuel induction system of the engine. It will be appreciated by those skilled in the art that the hydrocarbon fuels differ in their propensities for forming vapors at different temperatures. For example, an aromatic fuel with a flash point of 102° F. in the range of altitude from sea level to 25,000 feet forms a mixture which is too lean to burn in a fuel tank at 20° C., from 25,000 feet to 57,000 feet, it forms an explosive mixture, and above 57,000 feet forms a mixture which is too rich to burn.

To determine whether and how a noninflammable addition agent could be satisfactorily used to prevent the formation of an inflammable mixture in fuel tanks through a wide range of altitudes without impairing the volatility characteristics of the fuels, a number of determinations were made on different types of aviation fuels with varying amounts of the addition agents.

A hydrocarbon aviation fuel principally composed of hydrogenated tri-isobutylene, having a flash point of 104° F., was blended with 1 or 2% of methyl iodide, and no inflammable mixtures were formed at any reduced pressure for a temperature of 25° C. With 0.5% of methyl iodide added to the same type of hydrocarbon fuel, inflammation was obtained over a narrow range of pressure at 24° C. The highest absolute pressure at which inflammation was obtained was 238 mm. of mercury, corresponding to a minimum altitude of 29,200 feet.

The important advantage of the noninflammable addition agents is made apparent in tests of these agents added to naphthas lacking in the desired degree of safety. A valuable benefit of these addition agents is to make it permissible to use naphtha fractions of more desirable volatility and to greatly increase the availability of hydrocarbon fuel bases for use in safety fuels which were otherwise excluded.

It is indicated by the following data that the volatility of the addition agent significantly governs the ability of the agent to raise the flash point of the fuel blend to a safe minimum point. The indications from data of this kind are that only those compounds having boiling points below 60° C. are actually effective for accomplishing the purpose of this invention.

TABLE I

*Effect of non-inflammable compounds on the flash point of a naphtha*

| | Closed cup flash point, °F. | Boiling point of noninflammable compound | |
|---|---|---|---|
| | | °C. | °F. |
| 1. Petroleum naphtha | 102 | | |
| 2. Ditto+5% trichloro monofluoromethane | >175 | 23.7 | 74.7 |
| 3. Ditto+5% methyl iodide | >175 | 42.5 | 108.5 |
| 4. Ditto+5% trichloro trifluoroethane | >175 | 47.7 | 127.9 |
| 5. Ditto+5% ethyl iodide | 97 | 72.3 | 162.1 |
| 6. Ditto+5% n-propyl iodide | 102 | 102 | 215.6 |
| 7. Ditto+5% carbon tetrabromide | 102 | 189 | 372.2 |

The foregoing data are representative of the effects for different types of non-inflammable compounds and indicate that to raise the flash point of an ordinary petroleum naphtha through the margin of flash point safety so that the fuel has a flash point well above the minimum of 124° F. without sacrificing volatility, not all noninflammable compounds can be satisfactorily employed. For example, ethyl iodide, normal propyl iodide, and carbon tetrabromide are substantially ineffectual for raising flash point of the fuel. This same relationship of boiling point to effectiveness of the non-inflammable agent has been found to hold in all other instances including that of carbon tetrachloride (boiling point 76.8° C.), which is known to have been used in hydrocarbon solvents for decreasing fire hazards, but which is not suitable in aviation safety fuels.

Further observations prove that excessive concentrations of any completely noninflammable compounds are necessary to effect an appreciable increase in the flash point of ordinary motor fuels. In general, the less highly chlorinated compounds are not sufficiently non-inflammable and are required in excessive concentrations for any practical effect on increasing the flash point. But, high concentrations of the halogenated compounds are undesirable in the motor fuels, for they tend to give corrosion troubles and to decrease the lead susceptibility of the fuel in proportion to their concentration. Hence, it was found advisable to find the optimum types and concentrations of the agents and the most satisfactory type of fuels to be blended in forming practical aviation safety fuels.

In determining what types of hydrocarbon base fuels could be properly used with optimum and minimum proportions of the noninflammable compounds, various naphthas were blended with the noninflammable agents and in varying proportions. It was determined from these tests that about 0.5% by volume is the minimum of any suitable noninflammable agent which could be used to obtain a satisfactory elevation in the flash point of the fuels and that it was unnecessary to use amounts as high as 5% of the agent, so that the preferred concentration of the noninflammable agent of proper characteristics is in the range of 1% to about 2%. This concentration factor is illustrated in the following table with respect to a hydrogenated tri-isobutylene fuel and an aromatic safety fuel, which mark the two extremes in types of hydrocarbon bases.

TABLE II

| Fuel | Closed cup flash point, °F. | Boiling point of noninflammable compound, °C. |
|---|---|---|
| Hydrogenated tri-isobutylene safety fuel | 104 | |
| Ditto+2% methyl iodide | >175 | 42.5 |
| Ditto+1% methyl iodide | >175 | 42.5 |
| Ditto+0.5% methyl iodide | 112 | 42.5 |
| Aromatic safety fuel | 102 | |
| Ditto+5 vol. per cent methyl iodide | >175 | 42.5 |
| Ditto+1 vol. per cent methyl iodide | 111 | 42.5 |

To illustrate how the hydrocarbon fuel base must also correspond to a certain standard in order to make the use of the noninflammable agent practically effective, data are presented in the following table on the effects of the agent in fuel bases of varying volatility and flash point:

TABLE III

| Hydrocarbon fuel base | Approximate boiling range, °F. | Tag, flash °F. | | |
|---|---|---|---|---|
| | | Fuel alone | +5% methyl iodide | Increase |
| Gasoline | 100–300 | −30 | −22 | 8 |
| Naphtha No. 1 | 144–318 | −14 | +6 | 20 |
| Naphtha No. 2 | 208–318 | +30 | 46 | 16 |
| Naphtha No. 3 | 280–351 | 88 | [1] >175 | >87 |
| Aromatic safety fuel | 290–425 | 100 | >175 | >50 |

[1] Pensky-Martin flash >240° F.

From data such as that presented in Table III, it was found that it is important to have the initial boiling point of the hydrocarbon base stock substantially at a minimum of approximately 275° F. with the specific agent methyl iodide. However, the minimum boiling point, and similarly the minimum flash point, of the hydrocarbon base fuel can be varied with the boiling point of the selected noninflammable agent employed. This has been very clearly demonstrated. For example, methyl bromide which is more volatile than methyl iodide and has a boiling point of about 4.5° C. (40° F.) can be blended in small amounts with a hydrocarbon base stock having a flash point as low as from 15 to 25° F. (about 20° F.) to obtain true safety fuels having closed-cup tester flash points well above 124° F.

From investigations of the relationship between the boiling point of the noninflammable agent and the flash points of the hydrocarbon base stocks, and the blends, the conclusion was reached that the minimum flash point of the hydrocarbon base fuel should be limited, in that the boiling point of the noninflammable agent should be no more than about 30 Fahrenheit degrees above the flash point of the base fuel, and preferably this difference should be less than 20° F.

The relationship between the flash points and boiling points of the fuels and the blends are rather peculiar. As a rule, the flash point of the conventional petroleum distillate fuels varies directly in proportion to the initial boiling point of the fuel, and can be estimated approximately by use of the following formula:

$$\text{Closed-cup flash point (°F.)} = 0.73 \times \text{initial boiling point (°F.)} - 122$$

In contradistinction to this relationship, with the blended noninflammable agents having boiling points below 60° C. (140° F.), the flash points of the blends decrease with the boiling point of the agent quite markedly, this decrease amounting substantially to the difference between the boiling points of the agents employed. This is illustrated, for example, in the difference between methyl iodide and the lower boiling methyl bromide. The methyl bromide, boiling at 40° F., boils about 68 Fahrenheit degrees below the boiling point of the methyl iodide, and accordingly the hydrocarbon base fuel blended with methyl bromide can have a flash point about 68 Fahrenheit degrees below the flash point of the hydrocarbon base stock blended with the methyl iodide to form a blend of comparable high flash point above 124° F.

In general, the hydrocarbon base stock to be used with any of the inflammability controlling agents should boil substantially within the gasoline boiling range; i. e., should have volatility suitable for use as a carburant with an initial boiling point no lower than about 100° F. and an end point ordinarily less than 437° F.

Unless otherwise indicated, the flash point referred to is that determined with a tag closed tester (A. S. T. M. standard method).

By noninflammable compounds are meant those having substantially no explosive limits with air and which have flash points considerably above 175° F.

Due to the numerous factors involved in formulating aviation safety fuel safeguarded from all potential hazards in aviation service with a minimum lowering of volatility and with a minimum concentration of the noninflammable agent, it is somewhat difficult to state exact relationships. However, it can be safely stated that the desired safety fuels are formulated from naphtha or gasoline fractions having minimum flash points less than 30 Fahrenheit degrees below the boiling point of the noninflammable organic addition agent, which must have a boiling point below the critical upper limit of 60° C. and be added in a concentration between 0.5% and 5% by volume, and preferably between about 1.0% and 2% by volume.

One of the distinguishing characteristics of the preferred noninflammable addition agents is that they contain only 1 to 2 carbon atoms in the molecule and contain one of the halogens other than chlorine, e. g. iodine, bromine, or fluorine. Also, as a rule, the polyhalides are more reliably less inflammable than the monohalides, and this fact is indicated more strikingly in the case of chlorine compounds; e. g., chloroform ($CHCl_3$) which is a border line noninflammable agent which can be used in the present invention, is satisfactorily noninflammable, but methyl chloride ($CH_3Cl$, B. pt.—24° C.) and methylene chloride ($CH_2Cl_2$, B. pt. 40° C.) are not sufficiently noninflammable even though they have lower boiling points. Likewise, ethyl chloride and ethyl dichloride are not useful for the present purposes.

In a number of instances mixtures of the suitable noninflammable agents work more satisfactorily, e. g. methyl iodide with methyl bromide, etc. but with the same limiting proportions for the combined agents.

It is to be understood that the specific examples which have been given are for the purposes of illustration and are not intended to limit the scope of the invention. There are variations which come within the spirit of the invention as defined in the following claims.

I claim:

1. The method of controlling the inflammability in motor fuels for high-compression spark-ignition engines, which comprises blending from 0.5% to 5% by volume of a noninflammable organic halide boiling below the limit of about 60° C. (140° F.) with a hydrocarbon fraction boiling substantially in the gasoline boiling range having an end boiling point below 437° F. and having a closed-cup flash point less than 30 Fahrenheit degrees below the boiling point of said organic halide to raise the closed cup flash point of the blend to above 124° F.

2. A method as described in claim 1, in which said organic halide is a bromide.

3. A method as described in claim 1, in which said organic halide contains fluorine.

4. A method as described in claim 1, in which said organic halide is an iodide.

5. A safety aviation fuel for high-compression, spark-ignition engines, having a flash point above

124° F. and formulated by blending from 0.5% to 5% by volume of a noninflammable organic halide boiling below 60° C. with a hydrocarbon fuel boiling substantially within the gasoline boiling range having an end boiling point below 437° F. and having a flash point less than 30 Fahrenheit degrees below the boiling point of said organic halide.

6. A safety aviation motor fuel for high-compression spark-ignition engines with a closed-cup flash point substantially above 124° F., formulated by blending from 0.5% to 5% by volume of methyl iodide with a hydrocarbon fuel boiling substantially within the range of 280° F. to 425° F. and having a flash point of at least about 88° F., the proportion of methyl iodide being sufficient to raise the flash point of the blend to above 124° F.

7. A safety aviation motor fuel for high-compression spark-ignition engines, formulated by blending from 0.5% to 5% by volume of methyl bromide with a hydrocarbon fuel fraction boiling substantially within the gasoline boiling range having an end boiling point below 437° F. and having a flash point of at least about 20° F. to raise the flash point of the blend to above 124° F.

8. A safety aviation motor fuel for high-compression spark ignition engines having a flash point above 124° F. and formulated by blending from 1% to 2% by volume of a noninflammable organic halide, containing only 1 to 2 carbon atoms per molecule and containing fluorine, with a hydrocarbon fuel boiling within the gasoline boiling range having an end boiling point below 437° F. and having a flash point less than 20 Fahrenheit degrees below the boiling point of said organic halide, the boiling point of said organic halide being essentially below 60° C.

9. A fuel as described in claim 8, in which said organic halide is trichloro monofluoromethane.

10. A motor fuel having a flash point above 124° F. containing 0.5% to 5% by volume of a noninflammable organic halide having a boiling point below 60° C., and comprising a major proportion of a hydrocarbon liquid having an initial boiling point not lower than about 100° F. and an end boiling point below 437° F. and a flash point not lower than 30 Fahrenheit degrees below the boiling point of said organic halide.

11. Motor fuel according to claim 10 in which the organic halide has only 1 to 2 carbon atoms and contains at least 4 halogen atoms.

12. Motor fuel according to claim 10 in which the organic halide contains a halogen having a different molecular weight than that of chlorine.

13. Motor fuel according to claim 10 in which the organic halide is a fluorinated derivative of a hydrocarbon having only 1 to 2 carbon atoms.

14. Motor fuel according to claim 10 in which the organic halide contains only 1 to 2 carbon atoms and contains at least 3 fluorine atoms.

15. Motor fuel according to claim 10 in which the organic halide contains 1 to 2 carbon atoms and contains fluorine and another halogen.

16. Motor fuel according to claim 10 in which the organic halide contains 1 to 2 carbon atoms and contains fluorine and chlorine.

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