

## UNITED STATES PATENT OFFICE

2,365,009

## MOTOR FUELS

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No Drawing. Application December 19, 1940,  
Serial No. 370,787

11 Claims. (Cl. 44—53)

In this invention selected alcohols properly blended with certain low molecular weight hydrocarbons provide valuable quick-starting fuels for high-compression spark-ignition engines. These fuels are of special value for developing maximum power and thermal efficiency in high output engines with freedom from vapor locking difficulties.

Although it has been known that alcohols, such as methyl or ethyl alcohol, either pure or blended with gasoline have some advantages as motor fuels, mainly that of high octane rating, they have only limited use in countries where adequate petroleum supplies are readily available. The alcohol-gasoline blends introduce certain operating difficulties; for example, a small amount of water causes separation of the alcohols from the gasoline, meaning that these blends have low water tolerance. These blends, moreover, are subject to vapor locking difficulties, which are more serious than such difficulties incident to the use of the gasoline without the addition of alcohol. The use of the pure alcohols would be advantageous for power, anti-detonating quality, and water tolerance, but the pure alcohols have poor starting characteristics.

In accordance with the present invention, disadvantages of alcohol-gasoline blends and pure alcohols as motor fuels are overcome by blending from 5% to 10% by volume of a selected low molecular weight hydrocarbon component having from 3 to 5 carbon atoms per molecule, with a major proportion of an alcohol having from 1 to 5 carbon atoms per molecule.

I have found that blends of these selected compounds in the proper proportions are not subject to phase separation, even if a considerable amount of water is added. I have also found that these blends satisfactorily keep in storage without excessive vapor loss and satisfactorily mix with intake air on being carbureted for obtaining quick starting of a cold motor. These blends exhibit extraordinary freedom from vapor lock in carbureting systems designed and set for use with ordinary hydrocarbon fuels. In comparison to all alcohol containing fuels hitherto proposed, the exceptional properties of the blends herein provided are of tremendous advantage.

In order to obtain a desired efficiency with these fuel blends, it is important that the volatile hydrocarbon component be blended in a proportion of at least 5% of the blended components and should be lower boiling, or of greater volatility, than hexanes or hexenes. Methane, ethane, and ethylene are at the other extreme, in

being too low boiling. Limitations on selection and proportioning of the hydrocarbon component are dependent on proper air to fuel ratios in average fuel induction systems.

Fuel blends of the present invention have certain peculiar characteristics in that the low boiling hydrocarbon and the alcohol blended in ascertained proportions do not form ideal solutions but exhibit abnormally large deviations from Raoult's law governing ideal solutions. These deviations appear significant for satisfactory air-fuel ratios with blends herein described. Small amounts of lower and higher boiling hydrocarbons, such as, ethane or hexane, incidentally present in the composition do not destroy the value of the fuel for the intended purpose.

The upper limit of the hydrocarbon component proportion restricted in accordance with empirical determinations on vapor lock tendencies of the blends; for example, a blend of more than 10% of isopentane in ethanol, or more than 10% butane in isopropanol or butanol, at ordinary atmospheric temperatures causes vapor lock in the average fuel system. Thus, about 10% by volume of the hydrocarbon component is the upper practical limit.

Blends of between 5% and 10% by volume of the volatile hydrocarbon component with 95 to 90% by volume of the alcohol component exhibit desirable properties of quick-starting, high anti-knock quality, low vapor-locking tendency and high-power output.

Alcohols used as a major ingredient of the blends are preferably monohydric aliphatic alcohols (alkanols) of 1 to 5 carbon atoms per molecule. Ethyl and methyl alcohols, on account of their availability and large deviations from ideal solutions in the desired blends are useful.

Of alcohols higher boiling than ethyl alcohol, isopropyl and secondary butyl alcohols are outstanding for present purposes. Other alcohols higher boiling than ethyl, but with less preference, are n-propyl, n-butyl, tertiary-butyl, isobutyl, ter-amyl, n-amyl, and sec-amyl alcohols. The preferred alcohols have normal boiling points below 150° C. It is desirable to omit alcohols boiling above 175° C.

Blends formulated for the practice of this invention have unusual distillation and vapor pressure characteristics, which enable them to form a vapor charge which undergoes quick ignition in cold motors at sub-zero temperatures. These blends remain homogeneous even with 10 or more volumes of water added per 100 volumes of the

blend. They remain satisfactorily constant in composition and purity for suitable periods of time for use under various operating conditions.

For illustration, characteristics of blends forming specific embodiments of this invention are presented in the following table:

TABLE I

Blend	Composition	Reid vapor pressure	Initial boiling point, °F.	90% distilled off at °F.	Dist. loss, percent	Water tolerance vols. of water/100 vols. of blend
1.....	5% n-pentane in methanol.....	7.9	122	149	1.0	22.4
2.....	10% n-pentane in methanol.....	11.4	88	149	0.8	11.9
3.....	5% isopentane in ethanol.....	5.7	135	178	1.7	38.5
4.....	10% isopentane in ethanol.....	9.4	97	178	1.5	29.5
5.....	5% butane cut in isopropanol.....	8.3	131	179	1.9	111.0
6.....	5% butane cut in butanol.....	7.6	185	241	5.0	16.7

The butane cut used in blends 5 and 6 is otherwise known as plant butane, which contains approximately 60 to 70% n-butane, 20 to 25% isobutane, and 10 to 20% butenes.

Another remarkable characteristic of the new fuels is that addition of water up to a certain extent enhances volatility characteristics of the blends. The water may replace a certain minor proportion of the alcohol in the blends without substantially changing the proportions of the hydrocarbon component to form a fuel blend of enhanced volatility characteristics especially suitable for carbureting. This phase of the invention is particularly useful for raising vapor pressures and volatility distribution of the blends. To illustrate this phase of the invention, the following examples are given:

#### Examples

Blends of n-pentane and isopropyl alcohol were made up with varying amounts of water then subjected to tests for determination of their volatility and vapor pressure characteristics. The compositions of the blends and the inspections obtained on them are summarized below:

TABLE II

	Blend No.			
	1	2	3	4
Vol. percent n-pentane.....	10	10	10	10
Vol. percent isopropanol.....	90	80	70	60
Vol. percent water.....	0	10	20	30
Inspections:				
Gravity.....°A. P. I.....	50.5	43.6	38.2	33.0
Reid V. P.....#/sq. in.....	5.0	6.7	11.1	13.5
A. S. T. M. dist.—				
I. B. P.....°F.....	122	97	95	91
Percent at 158° F.....	8.0	9.5	11.0	12.5
Percent at 212° F.....			94.0	84
90 % at.....°F.....	180	176	190	212
Dist. loss.....percent.....	2.0	1.0	1.0	1.0

By investigation of engine performance with blends described in Table II, it was ascertained that such blends combine desired properties for quick starting and increased power at low temperatures with avoidance of vapor lock in ordinary automotive engines. It is important to note, however, that to obtain the desired results in engine performance, the Reid vapor pressure of the blend should be at least of the order of 5 lbs./sq. in. and, in general, should not exceed 13 lbs./sq. in. Thus the added volume of water may be as high as about 30%.

It can also be observed that as the water replaces minor proportions of alcohol, in the limited amounts of about 10, 20, and 30%, the Reid vapor pressure is increased, while at the same time, the blend is given substantial improvement in volatility balance, the amounts of the fuel vaporized at different intermediate temperatures

throughout the boiling range of the fuel being increased. This balancing of the volatility is desirable for more uniform distribution of the combustible mixture. Thus, in characteristics of prime importance for engine performance, the aqueous alcoholic solutions containing correct

amounts of the highly volatile hydrocarbons are fully satisfactory.

As previously set forth, regardless of whether the fuel blend contains water or is substantially free from water, it should preferably contain a hydrocarbon component blended in a proportion of about 5 to about 10% by volume in order to give the blend the desired advantageous characteristics noted. The alcohol component constituted of one or more alkanols having 1 to 5 carbon atoms per molecule is the major ingredient of the fuel blend, i. e., the alcohol, whether anhydrous or aqueous is blended in an amount of at least 60%.

When water is present in the fuel blend to form what is termed an aqueous alcohol component, the proportion of water added should not exceed that amount which is above the water tolerance of the blend, moreover, preferably it should not exceed about 30% by volume.

The ordinarily most useful fuel blends of the present invention are formulated from ½ to 1 part by volume of the 3 to 5 carbon atom hydrocarbon component blended with 6 to 9 parts by volume of the 1 to 5 carbon atom alcohol component and with from 0 to 3 parts by volume of water, the combined parts by volume of the alcohol component and of the water being blended with the hydrocarbon component in a volume ratio of at least about 9 to 1, so that the aqueous alcohol forms at least about 90% by volume of the fuel.

It is not intended to limit the invention to the specific blends shown in the foregoing tables. It will be observed that these tables illustrate how the blends are obtained with varying characteristics so that for a specific purpose, the most efficient blend is provided.

If requirements of a carbureted engine are such that the Reid vapor pressure must come within the range of 7 to 7.5 or 8 pounds per square inch, as in the case of aviation motors, blends meeting this requirement are available among the foregoing types of blends. For example, a blend between 5% and 10% of isopentane in ethanol will clearly have a Reid vapor pressure meeting these requirements. Other properly chosen combinations of the hydrocarbons and alcohols also meet this requirement.

It is to be noted that the preferred blends are obtained by selecting a relatively higher molecular weight hydrocarbon for blending with a lower molecular weight alcohol, e. g., a C<sub>4</sub> to C<sub>5</sub> hydrocarbon with a C<sub>1</sub> to C<sub>2</sub> alcohol, vice versa, a lower hydrocarbon blended with a higher alcohol, e. g., a C<sub>3</sub> or C<sub>4</sub> hydrocarbon with a C<sub>3</sub> to C<sub>5</sub>

alcohol, or with modification by added water. However, for an average automotive engine, blends satisfactorily used have Reid vapor pressures ranging from 5 to as high as about 13 pounds per square inch at 100° F., or even slightly higher in cold climates.

One way of efficiently and economically using the disclosed blends is to supply the carburetor of the engine from an individual tank separate from the main supply tank, so that the alcohol blend can be fed to the engine for starting at low temperatures or acceleration at high power.

The advantageous blends described may also contain small amounts of other ingredients ordinarily useful in motor fuels, e. g., a fraction of 1% of an anti-knock agent, such as tetraethyl or tetramethyl lead. They may also contain a small amount of a dye, thickening agent, or lubricant. By a small amount is meant generally less than about 1%.

The volatile hydrocarbon component, as indicated, is preferably a 3 to 5 carbon atom paraffinic hydrocarbon which is resistant to oxidation and readily available in highly purified form; hence, in general, the disclosed blends are easily obtained in a chemically stable form.

The hydrocarbon component may also contain or be composed of unsaturated hydrocarbons having 3 to 5 carbon atoms per molecule. Such unsaturated hydrocarbons may be mono-olefins or diolefins, but preferably the unsaturated hydrocarbons should not contain more than one double bond, i. e., should not be more unsaturated than a mono-olefin. Also, the 3 to 5 carbon atom cycloalkanes or cycloalkenes may be used. Thus, in general, suitable hydrocarbons for the hydrocarbon component may be characterized as 3 to 5 carbon atom molecules containing no more than two double bonds and preferably no more than one double bond.

The alcohol component may contain small amounts of other low boiling oxygen-containing compounds, such as ethers, ketones, aldehydes, and esters, but ordinarily these should not be present in any substantial amounts to avoid upsetting the effective balance between the preferred components in the blend.

In the accompanying claims the term "branched alcohol" is intended to mean any alcohol having a branched molecular structure, such as isopropyl alcohol, secondary butyl alcohol, isobutyl alcohol, and tertiary butyl alcohol, in contradistinction to normal straight chain alcohols, such as n-propyl alcohol, n-butyl alcohol.

Fuels described above and comprising methanol in one case and a branched alcohol in another case, with a small amount of normally gaseous hydrocarbon without any water present are claimed in copending applications Serial Nos. 516,710-11, respectively.

There are obviously a number of modifications which come within the spirit of this invention and it is not intended that the invention as defined in the appended claims be limited to the specific examples that have been given for the purpose of illustration.

A portion of the subject matter disclosed in this application but not claimed herein is claimed in applications Serial Nos. 516,710 and 516,711, filed January 1, 1944; these applications claim motor fuels containing a major proportion of certain lower alcohols and a minor proportion of light hydrocarbon but without any water.

I claim:

1. A motor fuel combining desirable properties

of quick-starting and low vapor locking tendency for use in high-compression spark-ignition engines, comprising  $\frac{1}{2}$  to about 1 part by volume of 3 to 5 carbon atom hydrocarbons containing no more than two double bonds in the molecule blended with from 6 to 9 parts by volume of 1 to 5 carbon atom alkanols and with sufficient water up to 3 parts by volume to substantially raise the vapor pressure of the hydrocarbon-alkanol mixture to at least 5 lbs./sq. in. (Reid), the combined parts by volume of the alkanols and of the water blended with the hydrocarbons being at least in the ratio of 9 to 1 and less than about 10% of the total fuel volume being hydrocarbons.

2. A motor fuel having combined desirable properties for quick-starting, particularly in cold spark-ignition engine operation, low vapor locking tendency, high water tolerance, and good volatility balance formulated by blending from  $\frac{1}{2}$  to about 1 part by volume of a 3 to 5 carbon atom hydrocarbon having no more than one double bond with about 9 parts by volume of an aqueous alkanol having 1 to 5 carbon atoms per molecule, water being present in a proportion of less than 3 parts by volume but in sufficient amount to substantially raise the vapor pressure of the hydrocarbon-alkanol mixture to at least 5 lbs./sq. in. (Reid) and less than about 10% of the total fuel volume being hydrocarbons.

3. A motor fuel combining desirable properties of quick-starting and low vapor locking tendency for use in high-compression spark-ignition engines, said fuel being composed essentially of 5% to about 10% by volume of a 3 to 5 carbon atom paraffin component homogeneously blended with a 1 to 5 carbon atom alkanol component which, together with water present in sufficient amount to substantially raise the vapor pressure of the paraffin-alkanol mixture to at least 5 lbs./sq. in. (Reid), forms at least 90% by volume of the blend, the water being restricted to below 30% by volume and to prevent phase separation.

4. A motor fuel composition as described in claim 3, in which said alkanol component is mainly ethanol.

5. A motor fuel composition as described in claim 3, in which said alkanol component is mainly isopropanol.

6. A motor fuel composition as described in claim 3, in which said alkanol component is mainly secondary butyl alcohol.

7. A motor fuel combining desirable properties of quick-starting and low vapor locking tendency for use in high-compression spark-ignition engines, said fuel being composed essentially of 5% to about 10% by volume of a 4 to 5 carbon atom paraffin blended with about 60% to 95% by volume of a 1 to 2 carbon atom alkanol, said fuel also containing sufficient water up to 30% of the total volume to substantially raise the vapor pressure of the other portion of the fuel to at least 7 lbs./sq. in. (Reid).

8. A motor fuel combining desirable properties of quick-starting and low vapor locking tendency for high-compression spark-ignition engines, said fuel being composed of 5% to about 10% by volume of isopentane blended with from about 95% to 60% by volume of ethanol, said fuel also containing sufficient water up to 30% of the total volume to substantially raise the vapor pressure of the other portion of the fuel to at least 7 lbs./sq. in. (Reid).

9. A motor fuel composed essentially of about 5% to 10% by volume of pentane, about 70% to

90% by volume of an alcohol having 1 to 2 carbon atoms, and a sufficient amount of water up to 20% to substantially raise the vapor pressure to at least 7 lbs./sq. in. (Reid) and to substantially reduce the initial boiling point of the mixture.

10. A motor fuel composed essentially of about 5% to 10% by volume of pentane, about 70% to 90% by volume of isopropyl alcohol and a suffi-

cient amount of water up to 20% to substantially raise the vapor pressure to at least 7 lbs./sq. in. (Reid) and to substantially reduce the initial boiling point of the mixture.

11. Motor fuel according to claim 1 also containing a small amount of tetraethyl lead as anti-knock agent.

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