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GASOLINE COMPOSITIONS

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This invention relates to an improved gasoline composition and more particularly to a gasoline containing substantial amounts of butanes and butenes and a mixture of isopropyl and secondary butyl alcohols.

It has been known in the past to include minor proportions such as about 1-2.5% of isopropyl alcohol in gasoline for the purpose of imparting anti-stalling properties by the prevention of carburetor ice formation. This property is particularly valuable for fuels used in operating internal combustion engines during cold, humid weather.

One disadvantage of employing small proportions of isopropyl alcohol has been its tendency to increase the vapor pressure of the gasoline composition in which it is included. Consequently, in order to produce a gasoline containing isopropyl alcohol which would be of sufficiently low vapor pressure as not to have an undesirable vapor-lock tendency, it has been found necessary to decrease the concentration of volatile hydrocarbons such as butanes and butenes. Such a decrease or backing-out of butanes is highly undesirable from an economic standpoint, since these highly volatile fractions are relatively plentiful in modern refinery operations and possess high octane characteristics.

The effect of small quantities of isopropyl alcohol on the vapor pressure of gasoline is somewhat unexpected. Isopropyl alcohol has a Reid vapor pressure of 1.9 p. s. i. and is miscible with gasoline in all proportions. Gasoline normally has a Reid vapor pressure of 7.15 p. s. i. so that the addition of a soluble component of lower vapor pressure would be expected to effect a net vapor pressure decrease. Actually, an abrupt vapor pressure increase occurs upon the addition of 1-4% by volume of isopropyl alcohol. One possible explanation of this anomaly is that the isopropyl alcohol molecules, which are known to exist as dimers or higher polymers because of co-ordinated valences, are broken down into individual molecules on being highly diluted by a non-polar medium such as gasoline. The individual alcohol molecules would be expected to exert a much higher vapor pressure than the polymer existing when the alcohol is in pure or highly concentrated form.

The content of butanes in gasoline generally varies between about 4% to about 20% by volume, depending on the season during which the gasoline is to be used. Summer grade gasoline intended for use and storage during warm weather should be of the lowest volatility, having a Reid vapor pressure of about 7 to 10 p. s. i. and a C₄ content of 4-8%. Spring grade fuels are more volatile, having a Reid vapor pressure of 11 to 12 p. s. i. and containing about 9-12% C₄ hydrocarbons, while winter gasolines, which are the most volatile, have a Reid vapor pressure of 13 to 15 p. s. i. and a C₄ content of 13-18%. Since the present invention makes it possible to retain substantial amounts of butanes in the gasoline while adding an effective amount of isopropyl alcohol, and, in some cases, to actually increase the butane

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content without raising volatility, the greatest advantages are to be gained in its application to the volatile winter grade gasoline. However, the present invention may also be used in preparing less volatile spring and summer grade fuels.

It has now been found that by the inclusion of small percentages of secondary butyl alcohol into gasoline fuels containing isopropyl alcohol, the undesirable vapor pressure rise usually associated with the presence of isopropyl alcohol can to a large extent be alleviated and in some cases a gasoline of overall reduced volatility produced, so that additional butanes may be included without adversely affecting the vapor-lock characteristics of the fuel. It may be that this unexpected effect is the result of re-association of the isopropyl alcohol molecules in the gasoline blend due to the addition of butyl alcohol. This explanation is presented as a hypothesis only.

It is an object of the present invention, therefore, to provide a gasoline fuel composition containing substantial amounts of butanes and at the same time possessing desirable anti-stalling characteristics and having sufficiently low vapor pressure as not to cause undesirable vapor lock when used in internal combustion engines.

It is a further object of this invention to provide a gasoline composition containing isopropyl and secondary butyl alcohols in which the fuel has improved octane rating characteristics.

A still further object of this invention is to provide a stable motor fuel containing isopropyl and secondary butyl alcohols having satisfactory power output characteristics when used in internal combustion engines.

These objects, as well as others which will be in part pointed out specifically and in part apparent from the subsequent description, are attained by providing a gasoline composition containing mixtures of from about 2 to 12% by volume of a blend of isopropyl and secondary butyl alcohols in which the ratio of isopropyl alcohol to secondary butyl alcohol is preferably from about 1:1 to about 1:3.

In the past, it has been customary to evaluate the volatility of hydrocarbon mixtures such as gasoline in terms of so-called "Reid vapor pressure." In measuring the vapor pressure of gasoline blends containing isopropyl alcohol, the introduction of either water or water saturated air into the system may seriously affect the total vapor pressure. In the regular Reid vapor pressure method for an all-hydrocarbon gasoline in which a water phase is present, the two immiscible liquids exert additive vapor pressures. However, when a water-soluble material such as isopropyl alcohol or secondary butyl alcohol is present, the distribution of such a component between the water and gasoline phases may have a pronounced effect on the total vapor pressure. Furthermore, in making up blends of gasoline with such compounds as alcohols, the mechanical loss of some of the butanes present is difficult to avoid, thus seriously affecting the vapor pressure of the final compositions. In view of this, a more exact method of measuring vapor pressure has been developed, and since the results of a number of tests utilizing the vapor pressures thus obtained are set forth in the ensuing description, the special apparatus and method of operation used will be described somewhat in detail. All of the vapor pressure data presented in the ensuing description for gasoline-alcohol blends are based upon this refined method as described below. When Reid vapor pressures are employed, they will be specified as such. It has been found that the Reid vapor pressures are generally proportional to those vapor pressures determined by the method to be described, so that an increase in vapor pressure produced by a particular combination of alcohols in a gasoline would also reflect an

increase in Reid vapor pressure, although possibly of a different magnitude.

The apparatus employed for the vapor pressure determinations comprised a metal jacketed Seltzer bottle of about 1300 ml. capacity fitted with a special adapter carrying a gauge reading from 0 to 15 p. s. i. pressure and a self-sealing rubber diaphragm assembly through which successive samples could be withdrawn from, or added to, a single charge of gasoline by means of a hypodermic needle. A calibrated blow case was used to introduce the original sample into the bottle (or the bomb, as it may be called) against a dry nitrogen atmosphere. A constant-temperature water bath fitted with an electronically controlled immersion heater and an air-driven stirrer was used to maintain the temperature in the bomb constant at 100° F.

Before each determination, a record was made of the room temperature, barometer reading and initial temperature of the bomb. The bomb was sealed at a pressure of one atmosphere after being thoroughly flushed with dry nitrogen. It was then heated at 100° F. to equilibrium pressure with respect to the room and the pressure was recorded in p. s. i. g. If the observed pressure corresponded to the pressure calculated due to temperature differential, the bomb was considered in suitable condition for use. It was then cooled in ice water and a 265 ml. sample was introduced into the bomb from the calibrated blow case. The sample was charged against the nitrogen atmosphere in the bomb. The bomb was then placed in the 100° F. bath and readings were taken in accordance with the procedure well known in the Reid method.

Equilibrium pressure was assumed when three successive five-minute periods gave the same reading. Blends of the gasoline were then made in the bomb by introducing a calculated amount of alcohol through the rubber diaphragm by means of a hypodermic needle. Before each addition, an equivalent volume of gasoline or blend was first removed from the charge in order to maintain a constant volume in the bomb. The direct reading in p. s. i. g. was observed on the gauge and observed values were corrected for initial temperature differential and compressibility of the nitrogen. These values, as stated before, are close to the true vapor pressures of the gasolines and generally comparable to Reid vapor pressure readings, although they are believed to be considerably more accurate.

The conventional Reid method for determining vapor pressures of petroleum products, ASTM designation D-323, Federal specification (VV-L-791) method: 1201, is based on the measurement of the vapor pressure of a hydrocarbon in the presence of water. Since the two components are mutually insoluble, they exist as separate phases and, consequently, the vapor pressures of the two components are additive. Thus the vapor pressure of the hydrocarbon can be obtained by applying the appropriate correction for the vapor pressure of water. However, if this method and procedure are applied to a system comprising a hydrocarbon, water, and a third, mutually soluble component such as a lower aliphatic alcohol, the vapor pressure will be in error, since the vapor pressures will no longer be additive. The water present will be distributed between a phase containing the major portion of the water, the mutually soluble component, and some hydrocarbon, and a phase containing the major part of the hydrocarbon, mutually soluble component, and water. Or, if there is a sufficient proportion of the mutually soluble alcohol added, it will solubilize the water and hydrocarbons to give one phase. The existence of such phases is dependent upon the water content, which in the Reid method is indeterminant. Thus the true vapor pressure of a hydrocarbon blended with a water-soluble component cannot be measured accurately by the Reid method.

The present method described measures the vapor pressure of the strictly dry components in a dry, inert atmosphere. This method also provides for the introduction to, or removal of samples from, a single charge of gasoline, a feature which minimizes sample errors due to opening of the bomb when charging due to loss of low boiling hydrocarbons during this process.

In preparing gasoline mixtures in accordance with the present invention, it is desirable to include in the fuel at least sufficient isopropyl alcohol to impart anti-stalling characteristics to the gasoline. This minimum amount has been found to be dependent to some extent on the type of gasoline employed. More alcohol is necessary to prevent stalling due to carburetor icing in high volatility winter grade gasoline than in the less volatile summer and spring grades. Thus, the amount of isopropyl alcohol included will vary between about 1-3% by volume. In some cases where the addition of only a small amount of isopropyl alcohol is necessary to prevent stalling, an even smaller amount, i. e., less than 1% by volume, may be employed by the inclusion of a small quantity of secondary butyl alcohol in the fuel. This will be illustrated in a subsequent example.

Contrary to expectations, it has been found that the effect of secondary butyl alcohol in lowering the vapor pressure of a gasoline-isopropyl alcohol blend to which it is added is not merely one of counteracting the corresponding higher vapor pressure effect of isopropyl alcohol. Data in the subsequent examples will illustrate that a marked synergistic effect takes place, resulting in much less increase in the vapor pressure of a gasoline than would be expected where alcohol mixtures predominantly isopropyl alcohol but containing some secondary butyl alcohol are employed.

EXAMPLE I

In this example, gasoline base stock having the following inspections was mixed with various percentages of 99% isopropyl alcohol and absolute secondary butyl alcohol respectively, but not with mixtures of the two.

Engler distillation, percent distilled	
8%	° F. 136
9%	° F. 139
10%	° F. 143
45	48% ° F. 238
49%	° F. 240
50%	° F. 242
88%	° F. 351
89%	° F. 356
50	90% ° F. 361
Percent recovery	
Percent residue	
Percent loss	
55	Gravity, API 58.9
Reid vapor pressure	

Various amounts of the two alcohols were added to the base stock and the vapor pressure measured in p. s. i. g. The values given as ΔP represent the change in vapor pressure in p. s. i. with respect to the base gasoline when the following percentages of the indicated additive were employed.

TABLE I

Composition	ΔP at volume percentage additive indicated (p. s. i. g.)			
	2	4	6	8
Gasoline+99% isopropyl alcohol	0.75	0.88	0.81	0.75
Gasoline+secondary butyl alcohol	-0.06	-0.12	-0.25	-0.31

From the above it might be expected that the addition to a base gasoline stock of 8% total alcohol comprising 75 a mixture of 6% isopropyl alcohol and 2% secondary

butyl alcohol based on the gasoline would result in a net vapor pressure increase of 0.75 p. s. i. (the sum of a +0.81 p. s. i. due to the isopropyl alcohol and -0.06 p. s. i. due to the secondary butyl alcohol). This is not the case, however, as is illustrated by Table II below. In obtaining the data for this latter table the same gasoline base stock was mixed with blends of isopropyl and secondary butyl alcohols in various volume percentages and using various ratios of isopropyl alcohol to secondary butyl alcohol. These results, in terms of changes in vapor pressure (ΔP), are given below.

TABLE II

Ratio of isopropyl alcohol to secondary butyl alcohol	Volume percent of additive used	Change in vapor pressure (ΔP) in p. s. i.
1/10	11	-0.50
1/5	12	-0.44
1/4	5	0.12
1/4	10	-0.19
1/3	4	0.18
1/3	8	-0.12
1/2	3	0.25
1/2	6	0.13
1	2	0.32
1	4	0.38
1	6	0.25
1	8	0.19
2	2	0.50
2	4	0.50
2	6	0.44
2	8	0.37
3	2	0.50
3	4	0.50
3	6	0.50
3	8	0.19

Thus, instead of an overall vapor pressure increase of 0.75 p. s. i., as would have been expected to have resulted from the addition of 8% of a 3:1 mixture of isopropyl and secondary butyl alcohols in the absence of a synergistic effect, a vapor pressure increase of only 0.19 p. s. i. resulted. It will be noted by making other comparisons that in all cases the increase in vapor pressure obtained by using the mixture of isopropyl and secondary butyl alcohols was less than would be expected on the basis of the individual alcohols themselves. This differential of 0.56 p. s. i. is equivalent to 1.1 volume percent of butanes. Therefore, instead of backing out 1.43% butanes, which would be necessary to maintain vapor pressure of the original base gasoline on the basis of the expected 0.75 p. s. i. increase due to the additive mixture, it is necessary to back out only 0.33 volume percent butanes to cancel the 0.19 p. s. i. actual increase. Thus, the advantages of the additives are obtained without the sacrifice of the expected amount of butanes.

In the most preferred embodiments of the invention, the alcohols are added in such quantities as to produce an actual overall decrease in the vapor pressure. This means that additional butanes can be added to the gasoline and the desired volatility still maintained. To obtain this result the mixture of alcohols added must contain more secondary butyl alcohol than isopropyl alcohol and a substantial amount of the mixture must be employed. This does not adversely affect the fuel value of the gasoline, since as much as about 12% by volume of the alcohol mixture may be employed without appreciably lowering the calorific content of the resulting blend. Secondary butyl alcohol also contributes to the elimination of carburetor icing, especially when used in conjunction with isopropyl alcohol. Mixtures of equal volumes of isopropyl and secondary butyl alcohols are as effective in preventing carburetor icing as is isopropyl alcohol alone. For this reason, it is not always necessary to include as much as 1-2.5% of isopropyl alcohol in the gasoline to prevent carburetor icing. It may also be desirable in some cases to employ blends containing less secondary butyl alcohol than isopropyl alcohol, even though a net vapor pressure increase results, since this

increase is less than the predictable value. In most instances 2-8% by volume of a blend of the alcohols will be incorporated into the gasoline. However, to obtain a vapor pressure decrease the use of blends containing at least about three times as much secondary butyl as isopropyl alcohol by volume is preferred.

EXAMPLE II

Although secondary butyl alcohol is the preferred additive for gasoline-isopropyl alcohol blends, it has also been found that mixtures of secondary and tertiary butyl alcohols also may be employed advantageously in some cases. The use of such mixtures is of great economic advantage, since in commercial operations mixtures of the secondary and tertiary butyl alcohols are commonly produced as such. The fact that mixtures of secondary and tertiary butyl alcohols may produce a net lowering of vapor pressure is an especially unexpected result, since the tertiary alcohol alone has a pronounced tendency to increase the vapor pressure of a gasoline to which it is added. In Table III below, a gasoline base stock was mixed with various percentages of isopropyl alcohol and various percentages of mixtures of isopropyl alcohol with mixed tertiary and secondary butyl alcohols. The Reid vapor pressures of these mixtures were determined and it was found that blends of isopropyl alcohol with the mixture of tertiary and secondary butyl alcohols often resulted in a net vapor pressure decrease.

TABLE III

	Composition	Modified ¹ Reid vapor pressure in p. s. i. g.
35	Base stock	14.2
	Base stock plus 2% isopropyl alcohol	14.6
	Base stock plus 4% isopropyl alcohol	14.3
	Base stock plus 8% isopropyl alcohol	14.2
	Base stock plus 4% of a 50/50 mixture of tertiary and secondary butyl alcohols	13.6
40	Base stock plus 2% isopropyl alcohol and 2% of a 50/50 mixture of tertiary and secondary butyl alcohols	13.7
	Base stock plus 4% isopropyl alcohol and 4% of a 50/50 mixture of tertiary and secondary butyl alcohols	13.2

¹ No water present.

The addition of the mixed butyl alcohols effects a net decrease in vapor pressure of 0.5 p. s. i. in one case and 1.0 p. s. i. in the other. Thus, 0.95% by volume and 1.90% by volume respectively of butane could be added to these blends while maintaining the volatility of the fuel at a constant value.

EXAMPLE III

In addition to providing a beneficial effect in regard to vapor pressure or volatility characteristics of gasoline, secondary butyl or tertiary butyl alcohols provide an improvement in performance characteristics, especially with respect to octane number. In Table IV given below, a base gasoline stock containing 2.2 cc. per gallon of tetra ethyl lead was mixed with various percentages of secondary butyl alcohol and tertiary butyl alcohol, giving the following results:

TABLE IV

	Composition	Research octane number	Research ¹ blending octane number
65	Base stock (containing 2.2 cc. T. E. L. per gallon)	90.1	120
	Base stock plus 4% secondary butyl alcohol	91.3	113
	Base stock plus 6% secondary butyl alcohol	91.5	115
	Base stock plus 8% secondary butyl alcohol	92.1	115
70	Base stock plus 6% tertiary butyl alcohol	91.4	112
	Base stock plus 8% tertiary butyl alcohol	91.6	109

¹ The research blending octane number is defined as the research octane number of the blend minus the value obtained when the research octane number of the base stock is multiplied by the fraction of base stock in the blend and the difference divided by the fraction of blending agent in the blend.

It will be understood, of course, that the secondary butyl alcohol may be supplied either pure or in admixture with other butyl alcohols such as isobutyl or normal butyl alcohols, as well as with tertiary butyl alcohol. The basic gasoline stock may also contain in addition to certain conventional materials such as tetraethyl lead or other alkyl lead anti-knock agents and conventional scavenging agents of the type conventionally employed when tetraethyl lead is used, such other additives as solvent oils, gum inhibitors, oxidation inhibitors, and the like.

While the invention has been described with respect to various specific compositions, it will be, of course, understood that it is not to be so limited but is to include such reasonable equivalents as may be included within the scope of the appended claims.

What is claimed is:

1. A gasoline composition consisting essentially of a hydrocarbon base stock boiling in the gasoline range, about 4% to about 20% by volume of C_4 aliphatic hydrocarbons, about 1% to about 3% by volume of isopropyl alcohol and about 1% to about 9% by volume of secondary butyl alcohol.

2. A gasoline composition consisting essentially of hydrocarbons boiling in the gasoline range, about 4% to about 20% by volume of C_4 aliphatic hydrocarbons, and about 1% to 12% by volume of isopropyl alcohol and secondary butyl alcohol in the ratio of about 1:1 to 1:3.

3. A gasoline as defined by claim 2 in which there is about 2% to 8% by volume of isopropyl alcohol and secondary butyl alcohol.

4. A gasoline defined by claim 2 in which the ratio of isopropyl alcohol to secondary butyl alcohol is about 1:3.

5. A gasoline having a Reid vapor pressure of not more than about 15 pounds per square inch consisting essentially of a hydrocarbon base stock boiling in the gasoline range, about 4% to 20% by volume of C_4 aliphatic hydrocarbons, and about 1% to 12% by volume of a mixture of isopropyl alcohol and secondary butyl alcohol, said mixture having three times as much secondary butyl alcohol as isopropyl alcohol.

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