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GASOLINE COMPOSITION CONTAINING ISOPROPYL ALCOHOL AND ISOPROPYL ETHER

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This invention relates to naphtha base gasolines, and more particularly to gasoline fuel compositions containing substantial concentrations of butanes and substantial quantities of isopropyl ether and isopropyl alcohol.

In the past it has been known that isopropyl alcohol in concentrations of between about 1% and about 2.5% have been useful in imparting so-called "anti-stalling characteristics" to gasoline. It has been found that in operating internal combustion engines of the type employed in present day automobiles, on cold moist days gasoline evaporates in the carburetor and exerts a sufficient refrigerating effect during the warm-up period to condense and freeze moisture present in the air entering the carburetor. It is also known to include in such anti-stalling gasoline a very small amount, such as 0.05 to 0.2 volume percent, of isopropyl ether. In these small, critical concentrations the ether assists the alcohol in retarding ice formation. The term "isopropyl ether" as used in this description and in the ensuing claims refers to di-isopropyl ether.

The presence of isopropyl ether in gasoline fuels has also been suggested with a view to utilizing the high octane rating of branched chain ethers. Such suggestions have dealt with the use of relatively large amounts of ethers up to and including 50% in gasolines of relatively low volatility and relatively low initial octane number.

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.

It has now been found that by adding both isopropyl alcohol and isopropyl ether to a highly volatile gasoline fuel of a high initial octane rating, a pronounced synergistic effect is exerted between the alcohol and the ether, especially with respect to the vapor pressure of the gasoline. The resulting alcohol-ether blends represent very substantial and desirable improvements in various performance characteristics of the gasoline. Among these characteristis are stability, octane rating, improvement in warm-up characteristics, cleaner burning, and an improvement in volatility characteristics allowing the inclusion of substantial amounts of C_4–C_5 hydrocarbons (generally referred to hereinafter as "butanes") in the fuel, thereby effecting substantial economies in the manufacturing process.

In preparing a gasoline of predetermined volatility, the inclusion of a constituent that has the effect of lowering the vapor pressure of the resultant blend by 0.5 p. s. i. below that of the base stock permits the inclusion of an additional 1.0% of butanes by volume. Conversely, the inclusion of a constituent that raises the vapor pressure of a gasoline necessitates the backing out of butanes to maintain a constant volatility.

The content of butanes in gasoline generally varies between about 4% to about 20%, depending on the season during which the gasoline is to be used. Summer grade gasolines 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 C_4 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% C_4 hydrocarbons, while winter gasolines, which are the most volatile, have a Reid vapor pressure of 13 to 15 p. s. i. and a C_4 content of 13–18%. Since the present invention makes it possible to retain substantial amounts of butanes in the gasoline while adding effective amounts of isopropyl alcohol and isopropyl ether, and in some cases, to actually increase the butane content without raising volatility, the greatest advantages are to be gained in its application to the more volatile winter grade gasolines. However, the present invention may also be used in preparing less volatile spring and summer grade motor fuels.

Thus the present invention relates to the economic as well as quality upgrading of gasoline hydrocarbon base stocks of relatively high volatility. In other words, the invention is applicable to hydrocarbon gasoline base stocks containing substantial amounts of C_4 and C_5 hydrocarbons and accordingly having a Reid vapor pressure between about 7 and 14 p. s. i. More specifically, the invention applies to gasoline base stocks having a gravity of about 55 to 60° API, containing about 4 to 20 percent butanes and butenes, and having an A. S. T. M. distillation such that about 15 to 30 volume percent of the gasoline stock, counting recondensed distillate as well as uncondensed distillation loss, is evaporated below 158° F., about 55 to 70 percent is evaporated below 257° F., and about 85 to 95 percent is evaporated below 356° F. It will be recalled that the 158° F. point is usually taken as a measure of front-end volatility or start-up and vapor lock characteristics whereas the 257° F. point is usually taken as a measure of intermediate volatility or performance of the fuel during engine warm-up; the 356° F. point gives an indication of the proportion of high boiling constituents and is taken as an indication of proper distribution and absence of excessive lubricant dilution to be expected from the fuel. The initial boiling point of the hydrocarbon base stock is between about 85 and 110° F., and the final boiling point at about 320 to 430° F., exclusive of any solvent oil which may also be present. For high anti-knock motor fuels, the Research octane number of the hydrocarbon base stock should

preferably be in excess of 80, and its net heat of combustion from about 116,000 to 130,000 B. t. u./gallon, depending on gravity and other considerations.

The hydrocarbon base stock normally is a blend of a variety of individual stocks, notably "butanes" or more properly a C_4 cut including both butanes and butenes; pentanes or a C_5–C_6 cut including both paraffins and olefins; light virgin naphtha; dependanized and undercut catalytic naphtha; dependanized and undercut reformed naphtha; dependanized 400° F. end-point reformed naphtha; dependanized 400° F. end-point thermally cracked naphtha from gas oil and reduced crude; catalytically cracked heavy naphtha boiling between about 300 and 420° F.; thermally cracked heavy naphtha; hydroformed naphtha; alkylate obtained by combining a C_3–C_5 olefin with an isoparaffin such as isobutane; and polymer gasoline obtained by thermal or catalytic polymerization of propylene, butenes and pentenes and mixtures thereof.

The blending of these components to meet the aforementioned specifications is a well-known art. Thus butanes are used to control Reid vapor pressure, pentanes and light virgin naphtha to control front-end volatility, while the volatility and octane level of the total available gasoline pool is usually controlled by the severity of the reforming operation so as to produce a balanced pool meeting the aforementioned specifications.

It has now been found that by including small amounts of isopropyl alcohol in a gasoline and at the same time adding at least one half volume of isopropyl ether per volume isopropyl alcohol, the increase in vapor pressure and light-end volatility normally associated with the addition of isopropyl alcohol to gasoline is substantially lessened, thus minimizing the amount of butanes that must be backed out of the gasoline when isopropyl alcohol is employed alone or in conjunction with a lesser proportion of ether in order to provide beneficial anti-stalling properties. It has also been found that using higher percentages of isopropyl ether and thus higher ratios of ether to alcohol, a net lowering of vapor pressure can be obtained, thus permitting the inclusion of more butanes than is possible in the base gasoline while keeping the fuel at a substantially constant level of volatility. In addition, the inclusion of substantial amounts of isopropyl ether, i. e., up to about 10–12% by volume, results in the production of a generally superior motor fuel.

It is an object of the present invention to provide a gasoline fuel containing isopropyl alcohol and at least one half volume of isopropyl ether per volume alcohol which fuel contains a substantial amount of butanes and which possesses desirable anti-stalling characteristics from the standpoint of preventing ice formation in the carburetor.

It is a further object of the present invention to provide an improved gasoline fuel containing isopropyl alcohol and isopropyl ether in which the storage characteristics are substantially improved.

It is a still further object to provide an improved gasoline fuel containing isopropyl alcohol and isopropyl ether having increased octane number and being particularly suited for use in internal combustion engines having high compression ratios in the order of about 10 to 1.

In the past it has been customary to measure the volatility, and hence the so-called "vapor lock tendency," of gasoline fuels by the so-called "Reid vapor pressure method" (A. S. T. M. designation: D–23; Federal Specification VV–L–791, Method: 1201). In this determination using an all-hydrocarbon gasoline, any water, which will inevitably be present, is substantially immiscible with the gasoline, and the two immiscible liquids exert additive vapor pressures. However, once a mutually-soluble component such as isopropyl alcohol is present, distribution of this soluble compound between

the water and gasoline phases may have a pronounced effect on the total vapor pressure. In order to determine this effect, a special method with far greater accuracy than is possible by the conventional Reid method of measuring true vapor pressure of gasoline containing water-soluble compounds has been developed, and in the ensuing description all of the vapor pressure determinations, unless otherwise specified, were determined by the method to be described below.

The vapor pressure apparatus employed consisted essentially of a metal jacketed seltzer bottle of approximately one quart capacity fitted with a special adaptor carrying a gauge for reading pressures of from 0 to 15 pounds per square inch, 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 bomb (as the bottle is usually 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 for maintaining the bomb 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 then sealed at a pressure of one atmosphere after being thoroughly flushed with dry nitrogen. It was then heated at 100° F. until equilibrium pressure was reached, and this pressure was recorded. If the observed pressure corresponded to the calculated pressure, that is, the increase in pressure due to the temperature differential, then the bomb was considered to be free from leaks and in suitable condition for use. It was then cooled in ice water and a sample of 265 ml. of gasoline was introduced into the bomb, which had a volume of about 1300 ml. The sample was charged from the blow case against the nitrogen atmosphere of the bomb. The bomb was then placed in the 100° F. constant-temperature bath and readings were taken in accordance with the procedure of the Reid method.

Equilibrium pressure was assumed when three successive five-minute periods gave the same reading. Blends of the gasoline were made directly in the bomb by introducing the calculated amount of alcohol or ether to be added through the rubber diaphragm by means of a hypodermic needle. Before each addition an equivalent amount of gasoline was first removed from the charge in order to maintain a constant volume in the bomb. The direct readings on the gauge in p. s. i. were recorded for each determination and corrected for temperature differential and compressibility. It was found that these readings, while generally lower than the corresponding Reid vapor pressure, would usually vary in the same direction as the Reid vapor pressure when such variation in vapor pressure was caused by the inclusion of the additive.

The increased use of high compression ratio internal combusion engines in commercial automobiles makes it necessary to provide a gasoline fuel possessing excellent anti-stalling performance with minimum tendencies to cause car octane-requirement increase and surface ignition. Volatility characteristics which insure vapor lock protection, ease of engine starting, and rapid engine warm-up must be maintained in such a fuel. It is also important to provide a fuel having anti-stalling characteristics because of the increased incidence of automatic transmissions, and because most cars are no longer provided with a manual throttle with the result that drivers can no longer increase the idle speed during the warm-up period to prevent stalling. The use of isopropyl ether in gasoline appears very attractive, since it has a research blending octane number of about 114 and a motor blending octane number of about 106 in present day fuels. Isopropyl alcohol provides an excellent research blending octane number of about 120. Because of the low solu-

bility of isopropyl ether in water, it will not serve to prevent carburetor icing when used alone, so that any motor fuel having desired anti-stalling characteristics may also contain some ispropyl alcohol. Usually, from about 1–3% by volume of isopropyl alcohol is included depending upon the volatility characteristics of the fuel. Generally, less alcohol is included in summer grade gasoline than in the more volatile winter grade.

As pointed out previously, the use of relatively small quantities of isopropyl alcohol has resulted in undesirable increases in vapor pressure, thus necessitating the backing out of low cost butanes from gasoline. When relatively high percentages of isopropyl ether are employed, however, and especially when three to four volumes of isopropyl ether are added for each volume of isopropyl alcohol, the vapor pressure increase resulting from the use of isopropyl alcohol is minimized and in some cases eliminated entirely. This is due partially to the fact that isopropyl ether when used by itself exerts a vapor pressure lowering effect upon gasoline, but, as the data in Table I below will illustrate, the over-all change in vapor pressure characteristics due to a combination of isopropyl alcohol and isopropyl ether is not the same as would be predicted from their individual effects. A pronounced synergistic action is exerted, resulting in a substantially lesser tendency to increase vapor pressure than could be predicted by numerical calculation alone. In the data of Table I a base gasoline stock having the following inspections was employed:

Gravity, API	58.9
Reid vapor pressure, p. s. i. g.	9.7
Engler distillation—	
Initial boiling point, ° F.	97
Percent distilled at 122° F.	4
Percent distilled at 140° F.	9.5
Percent distilled at 149° F.	12.5
Percent distilled at 158° F.	15.5
Percent distilled at 212° F.	35.5
Percent distilled at 238° F.	48.0
Percent distilled at 302° F.	75.0
Percent distilled at 374° F.	92.5
Final boiling point, ° F.	434
Percent recovery	97.0
Percent residue	1.0
Percent loss	2.0

In order to point out the effect of adding isopropyl alcohol and isopropyl ether blends on the change in vapor pressure of the gasoline, the absolute vapor pressures have not been recorded in Table I, but simply the change in vapor pressure resulting from the addition of various amounts of blends as indicated.

using the combined additives were much less. For example, the base gasoline blended with 2 volume percent of 99% isopropyl alcohol gave a vapor pressure increase of 0.75 p. s. i., and the same gasoline blended with 6 volume percent of isopropyl ether gave a vapor pressure decrease of 0.37. A 3 to 1 mixture of isopropl ether and isopropyl alcohol in an 8 volume percent concentration in the gasoline gave a vapor pressure increase of 0.18 p. s. i. However, if the individual components had acted independently of one another, the predicted vapor pressure increase would have been 0.75 minus 0.37, or a net increase of 0.38 p. s. i. The observed value of 0.18, therefore, is less than half the vapor pressure increase that would have been predicted. This effect can also be observed for other ratios and other concentrations.

In connection with this anomaly it is to be noted that although isopropyl ether is more volatile than is isopropyl alcohol, yet it lowers the vapor pressure of the gasoline. On the other hand, the higher boiling isopropyl alcohol increases the vapor pressure of the gasoline. Thus, at 75° F. the vapor pressure of the ether is 135 mm. while that of the alcohol is 40 mm. In order for the ether to have a vapor pressure of 40 mm. it must be cooled to 24° F. Nonetheless, as shown in Table I, addition of ether to a gasoline lowers its vapor pressure, while alcohol increases it.

The data in Table I also illustrate the effect the ratio of ether to alcohol has upon the vapor pressure changes. When a high ratio of ether to alcohol is employed, the total amount of additive necessary to effect a net lowering a vapor pressure is less than when a lower ratio is used. In general, the addition of isopropyl ether to motor fuel is more desirable from the standpoint of its effect on vapor pressure so that where sufficient alcohol is used to impart the desired anti-stalling effect, the remainder of the additive material is preferably isopropyl ether. As much as 10–12% by volume of non-hydrocarbon material may be included in gasoline without adverse effect on power output of the engine. Since only about 2% by volume of isopropyl alcohol need be included in the fuel to impart the desired anti-stalling characteristics, up to about 10% by volume of isopropyl ether may be employed. Table I shows that fuels in this composition range have particularly desirable volatility characteristics. For example, gasoline to which 8% isopropyl ether and 2% by volume of isopropyl alcohol have been added showed a net decrease in vapor pressure of 0.13 p. s. i. as compared with the base stock. Gasoline to which 10% isopropyl ether and 2% by volume of isopropyl alcohol had been added exhibited a net vapor pressure decrease of 0.38 p. s. i. An additional 0.7% of butane may then be added to the fuel without increasing its volatility or vapor lock tendency. Both of these fuel compositions are particularly desirable since they contain sufficient isopropyl alcohol to prevent stalling due to carburetor icing and are substantially improved as to

TABLE I

Composition	Volume ratio of isopropyl ether to isopropyl alcohol	Vapor pressure change in p. s. i. at volume percent additive indicated										
		2	3	4	5	6	7	8	9	10	11	12
Base stock+99% isopropyl alcohol	0	0.75		0.88		0.81		0.75				
Base stock+99% isopropyl alcohol+isopropyl ether	1/19	0.69										
	1/3	0.50										
	1/2		0.56									
	1	0.38		0.44		0.44		0.38				
	2	0.25		0.37		0.37		0.31				−0.19
	3	0.18		0.31		0.25		0.18		−0.13		
	4	0.06		0.12		0.06		0.00				−0.38
	5					0.00						
	6						−0.06					
	8								−0.31			
	10										−0.50	
Base stock + isopropyl ether	∞	−0.12		−0.24		−0.37		−0.50				

It is interesting to note that the blends of isopropyl alcohol and isopropyl ether gave lower vapor pressures than could be predicted from the values given by the individual components. That is, the increases as a result of

octane rating. At the same time, the addition of isopropyl ether and isopropyl alcohol in these ratios permits the inclusion of additional amounts of butane into the fuel while maintaining a constant level of volatility. Therefore, a particularly preferred embodiment of the present invention covers the use of an anti-stalling amount of isopropyl alcohol in conjunction with sufficient isopropyl ether to effect a net lowering of the vapor pressure of the resulting fuel mixture when compared to the vapor pressure of the gasoline base stock. Such preferred compositions may contain about 1 to 3% by volume of isopropyl alcohol and about two to four times that volume of isopropyl ether.

Another important characteristic of gasoline fuel beneficially affected by the addition of blends of isopropyl ether and isopropyl alcohol is that of storage stability as measured by the A. S. T. M. breakdown time test. Here again it is found that blends of isopropyl ether and isopropyl alcohol effect a substantially greater improvement in stability as measured by breakdown time than either of these components exerts individually. This is illustrated by Table II below, wherein data are presented that were obtained by the addition of various amounts of isopropyl alcohol and/or isopropyl ether to a hydrocarbon base gasoline useful as a motor fuel.

TABLE II

Composition:	A. S. T. M. breakdown time in minutes
Base gasoline	310
Base + 5% isopropyl ether	350
Base + 10% isopropyl ether	395
Base + 2% isopropyl alcohol	370
Base + 2% isopropyl ether and 5% isopropyl alcohol	480
Base + 5% isopropyl ether and 5% isopropyl alcohol	560

These same blends were thereafter subject to an accelerated storage test for four weeks. The test itself, by past experience, corresponds excellently with actual field results.

TABLE III

Effect of isopropyl alcohol-isopropyl ether mixture on gasoline stability

Composition	Gum, mg./100 ml.		Peroxide number, mg. O_2/l.	
	Initial	Storage test	Initial	Storage test
Base gasoline	3.2	21	0.10	17
Base+5% isopropyl ether	3.0	10.5	0.10	1.4
Base+2% isopropyl alcohol	2.2	14	0.11	2.6
Base+2% isopropyl ether Base+5% isopropyl alcohol	0.8	5.5	0.10	0.31
Base+5% isopropyl ether Base+5% isopropyl alcohol	3.6	5.0	0.10	0.18

The above data illustrate the advantages gained by using blends of isopropyl ether and isopropyl alcohol as compared with using either of these materials separately.

They also illustrate that a particular advantage is obtained when the amount of isopropyl ether employed is at least equal to one half the amount of isopropyl alcohol employed. It is of particular interest to observe that, though ethers are notorious peroxide formers, their inclusion in the composition of the invention diminished rather than increased the peroxide number of the stored fuel.

It will be understood that the isopropyl alcohol and isopropyl ether employed in making the improved fuel composition of the present invention may be derived from any source whatsoever, and that the process of manufacture plays no part in the present invention. However, it has been found that a suitable combination of isopropyl alcohol and isopropyl ether for such application may be produced by certain types of olefin hydration reactions, such as the hydration of propylene or gases containing propylene.

In addition to the hydrocarbon constituents and the isopropyl ether and isopropyl alcohol, it will, of course, be understood that the improved fuel composition of the present invention may also contain conventional amounts of other materials or additives, for example, various alkyl lead compounds such as tetraethyl lead and conventional lead scavenging agents of the type well known to the prior art, as well as gum inhibitors, oxidation inhibitors, solvent oils, and the like.

While the present invention has been described with respect to several specific embodiments thereof, it will be understood that the invention embraces also those equivalents known to those skilled in the art.

What is claimed is:

An improved motor gasoline with Reid vapor pressure between 7 and 15 p. s. i., which comprises at least 70% by volume of hydrocarbons boiling between 85° and 430° F. and a minor proportion of vapor pressure controlling agents consisting of between 4 and 18% by volume of butanes, between 1 and 4% by volume of isopropanol and between 2 and 12% by volume of isopropyl ether, the ratio by volume of said isopropyl ether to said isopropanol being between 2/1 and 10/1, said percentages being based on the volume of said motor gasoline.

References Cited in the file of this patent

UNITED STATES PATENTS

2,240,040	Hooton	Apr. 29, 1941
2,668,522	Hickok et al.	Feb. 9, 1954

FOREIGN PATENTS

486,631	Great Britain	June 8, 1938

OTHER REFERENCES

Aviation Gasoline Manufacture by Van Winkle, McGraw-Hill Co., Inc., 1944, first edition, pp. 212 and 216.

"Alcohol," A Fuel for Internal Combustion Engines by Pleeth, Chapman & Hall Ltd., 1949, pp. 83–85.

Industrial Solvents, Mellan, Reinhold Corp., 1950, second ed., pp. 56–62.