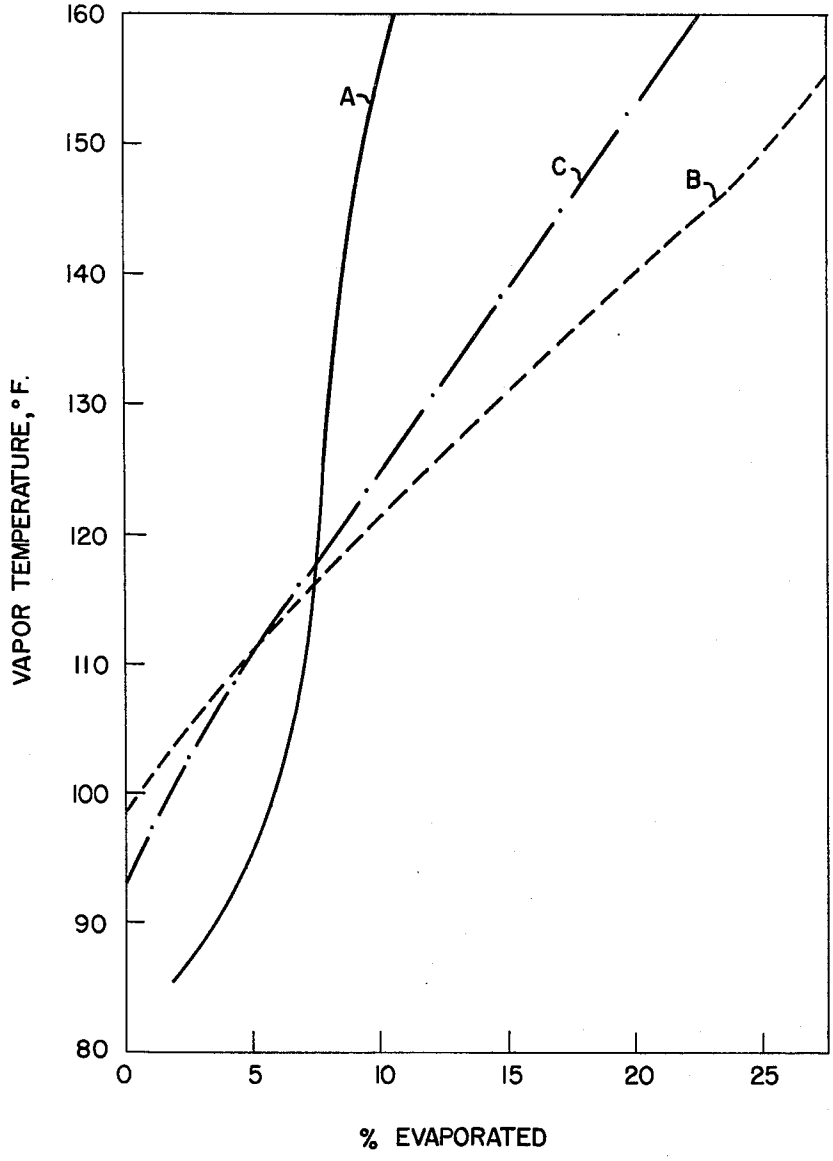
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MINIMIZING WEATHERING LOSS BY PROPANE-PENTANE PRIMING OF GASOLINE
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FIGURE-1

VAPOR TEMPERATURE - EVAPORATION CURVES FOR GASOLINES OF 11.6 TO 12.0 VLTR

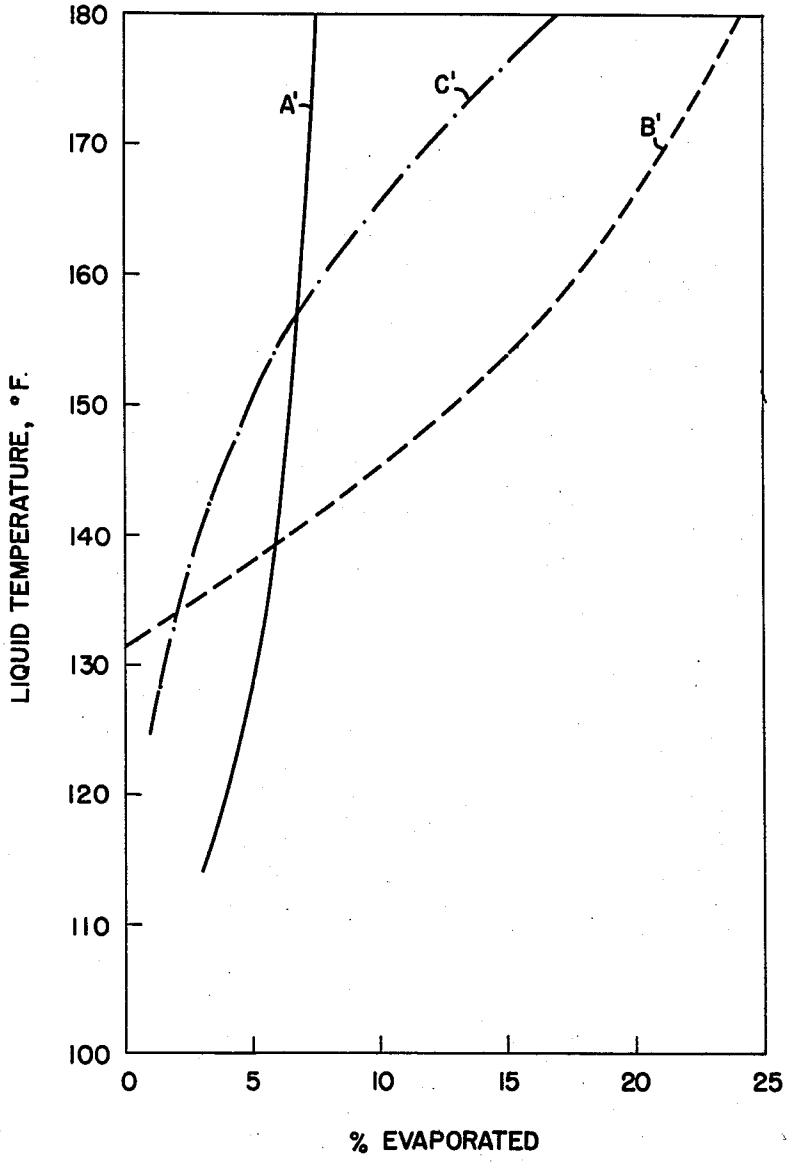


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FIGURE-2

LIQUID TEMPERATURE-EVAPORATION CURVES FOR GASOLINES OF 11.6 TO 12.0 VLTR



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MINIMIZING WEATHERING LOSS BY PROPANE-PENTANE PRIMING OF GASOLINE

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5 Claims. (Cl. 44—52)

The present invention relates to gasoline fuel compositions of balanced volatility primed with propane and pentane.

Gasoline is a complex mixture of hydrocarbons which should provide quick starting automobile engine performance in all types of weather and temperature conditions. A gasoline with ideal front end volatility characteristics would maximize starting ability, initial warm-up and light end component utilization, but minimize vapor losses and vapor lock. In commercially preparing a gasoline of predetermined volatility so as to satisfy the conflicting requirements of ideal front end volatility, the highly volatile butane and some butene fractions from modern refinery operations are blended as primers with the hydrocarbon base stock.

The content of butanes in gasoline generally varies from between about 4% to about 20% depending upon 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 11 p.s.i. and a C_4 content of 5–10%. Spring grade fuels are more volatile, having a Reid vapor pressure of 10 to 12 p.s.i. and containing about 8–12% C_4 hydrocarbons, while winter gasolines which are the most volatile have a Reid vapor pressure of 12 to 15 p.s.i. and a C_4 content of about 10–18%. The use of the C_4–C_5 hydrocarbon refinery cut generally referred to hereafter as "butane" as a priming agent has inherent disadvantages in regard to volatility characteristics, and does not lend itself to the best resolving of the ideal front end volatility requirements of gasoline.

It is among the objects of this present invention to provide a method whereby a critical mixture of propane and pentane in gasoline will give better front end volatility characteristics than the use of a gasoline conventionally primed with butane alone or butanes and pentanes. It is further an object of this invention to set forth a method whereby the addition of propane-pentane mixtures to debutanized gasoline will maximize starting ability, initial warm-up and light end component utilization, and, in particular, minimize vapor and weathering loss while maintaining a constant vapor lock tendency rating (VLTR) in the gasoline. Further objects of this invention, as well as the nature and scope of this invention will become more apparent from the subsequent description.

As herein defined the starting ability refers to that period of time between starting to turn the engine over and the time when the engine is operating under its own power. Starting ability is associated with the temperature point in degrees Fahrenheit at which about 20% of the fuel by volume (or 15% by weight) evaporates. Thus, for example, a fuel which has a 20% evaporated point of 125° F. will give better initial starting ability than a fuel whose 20% point is 135° F. With the choke of an automobile closed, an air/fuel ratio of about 3/1 by weight is supplied during cranking. Since an air/fuel weight ratio of at least 20/1 is needed for combustion, about 15 wt. percent or 18–22% by volume of the fuel must vaporize to satisfy the starting requirements of an automobile. The exact volume percentage depends upon the relative density of the less volatile components in the gasoline. The 20%

point represents the most suitable value of starting ability for typical fuels. Thus, the 20 vol. percent point on a vapor temperature basis as an indication of starting ability is now seen to be based upon technical considerations and is not an arbitrary figure.

Warm-up refers to that period of time between the time when the engine is operating under its own power to the time in which smooth performance (no hesitation on acceleration) is obtained. Soon after start-up, the operation may be very rough since the car is so cold that only a small portion of the fuel is vaporizing. As time progresses and the engine warms up, the vaporization approaches 100%. Thus, high front-end volatility is most important during the initial rough period of warm-up (initial warm-up) which usually lasts the first 3–5 minutes after cold start-up, although high mid-fill and back-end volatility become increasingly important thereafter. Initial warm-up is probably best associated with the 158° F. point of the fuel or, to the percentage evaporation by volume at a fuel vapor temperature of 158° F. Thus, a gasoline with a 158° F. point of 25% evaporation will give better initial warm-up than a fuel of 20% evaporation at 158° F.

Although fuels can be blended to give good initial start-up and warm-up by increasing the volatility characteristics of the fuel, increased volatility increases vapor locking tendencies and the vapor or weathering losses of the fuel. The vapor locking tendencies of the fuels can be predicted and expressed by the vapor lock tendency rating (VLTR) which utilizes the Reid vapor pressure (RVP) of the fuel and the 158° F. point of the fuel. The VLTR can be expressed as follows:

$$VLTR = RVP + 0.13 \text{ (percent evaporated at a vapor temperature of 158° F.)}$$

It has been found that fuels possessing equal VLTR values give equal protection from vapor lock. Vapor lock incidence at a given temperature increases with increasing fuel VLTR.

Vapor loss or weathering loss is here defined as the total amount of fuel loss from the refinery to the point of utilization in the automobile. As is apparent, the higher the volatility, the greater the vapor or weathering loss that can be expected. Relative vapor losses depend upon the liquid temperature in degrees Fahrenheit necessary to evaporate 2 to 4% of the gasoline, or the relative true vapor pressure at any percentage evaporated in this loss range. This is the typical loss range between the refinery and car engine. Thus, higher liquid temperatures for a given percentage evaporated or lower vapor pressures result in lower evaporation losses. The liquid temperature-evaporation loss concept becomes absolute rather than relative, for systems such as carburetor losses in which actual fuel boiling occurs, rather than air evaporation. In such cases, the liquid temperature in conjunction with the ASTM distillation data can be utilized to predict the actual percentage loss. In summary then, higher front end volatility of fuel gives better initial start-up and warm-up, but increases vapor losses or weathering losses and the vapor locking tendency of the fuel.

The hydrocarbon base stock to which the priming agent is added is normally a blend of a variety of individual stocks, notably pentanes or a C_5–C_6 cut including both paraffins and olefins; light virgin naphtha; dependanized and under cut catalytic naphtha; dependanized and under cut 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 reacting a C_3–C_5

olefin with an isoparaffin such as isobutane; and polymer gas obtained by thermal or catalytic polymerization of propylene, butenes, and pentenes and mixtures thereof. The blending of these components with light ends including propanes, butanes, and pentanes to meet the aforementioned specifications of the various types of gasoline 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. The specifications of course vary with the seasons. While the present discovery is applicable to all grades of gasoline, it is particularly valuable and its effect is particularly advantageous in connection with the more volatile winter grade type gasolines.

The solution to the problem of how to maximize the starting ability, initial warm-up, and light end component utilization, but minimize vapor losses and vapor lock, forms the basis of the present discovery. It has been discovered that by pressurizing or priming debutanized gasoline with a mixture of a propane and pentane primer within certain critical limits of percentage propane depending upon the type and volatility characteristics of the gasoline desired, to a constant VLTR, better initial start-up warm-up and lower vapor losses can be obtained, than by pressurizing the same gasoline with a conventional butane primer to the same VLTR. The term "debutanizing" is used in a manner to indicate the substantial removal of butane and butenes and similar C_4–C_5 hydrocarbons, but would excluded the accidental inclusion of minor amounts of some butane and butenes with the commercial propane-pentane mixture or the minor residual traces of butane-butenes left in the gasoline after debutanizing. Whereas the propane cut for refinery blending is predominantly propane and propene, traces of C_2 and some butanes may also be present. Pentanes or pentenes may be either wide boiling cuts including mostly pentanes, but having several percent of C_4 present in addition to perhaps up to 25% of high boiling hydrocarbons; or high purity cuts having over 95% of a particular C_5 compound such as isopentanes.

To more fully understand the results of this invention, attention is directed to FIGURES 1 and 2 in which FIGURE 1 illustrates three vapor temperature-evaporation curves and FIGURE 2 illustrates three liquid temperature-evaporation curves all for summer gasolines at a constant VLTR of 11.6–12.0 containing a butane primer, an isopentane primer and a propane-pentane primer. The distillation curves of winter and spring gasoline would be quite similar to FIGURES 1 and 2, but would have lower ordinate vapor and liquid temperatures. Referring now to FIGURES 1 and 2 with a more detailed description. Curves A and A' are the vapor (FIG. 1) and liquid (FIG. 2) distillation curves of a summer gasoline primed with 10% butane by volume and having a Reid vapor pressure of 10.3. Curves B and B' are the vapor (FIG. 1) and liquid (FIG. 2) distillation curves of a summer debutanized gasoline primed with about 26% by volume isopentane and having a Reid vapor pressure of 8.2. Curves C and C' are the vapor (FIG. 1) and the liquid (FIG. 2) distillation curves of a debutanized summer gasoline primed with about 24% by volume of a propane-pentane mixture where the propane constitutes about 1.1% by volume of the final gasoline composition, and which gasoline has a Reid vapor pressure of 9.2. These curves are based on actual laboratory experimental data.

A comparison of curves A, A', B, and B' will illustrate the practical and economical advantage of priming the same fuel with 20–25% pentane rather than the conventional 4–10% butane. In comparison to the butane primed gasoline of curves A and A', curve B in FIGURE 1 has a lower 20% vapor temperature for superior starting; higher percentage evaporated at 158° F. (by extrapolation) for better initial warm-up; the same VLTR, and in FIGURE 2, B' has a lower vapor and weathering loss as indicated by the higher temperature in the 2–4% evaporation range. A comparison of curves B and B' with C and C' will now illustrate that the use of a propane-pentane blend comprising propane in a certain definite percentage by volume will maintain most of the volatility benefits of pentane primed fuel, and still allow less weathering and result in a better gasoline from a quality standpoint. Curve C' has a lower vapor or weathering loss than either curve A' or B' as can be seen by the higher liquid temperatures in the 2 to 4% evaporation range in FIGURE 2. The better quality gasoline will be due to the use of the propane primer, since propane has a higher octane value than either butane or pentane alone. The utilization of a propane primer, besides decreasing the weathering loss and maintaining volatility benefits, will generally give gasoline blends of a higher initial octane number. Further, the utilization of propane as a priming agent is particularly advantageous to the refiners, since its use will present economic advantages along with broadening of the availabile base stocks for use in priming gasoline.

The amount of propane used to obtain the all-inclusive front end volatility advantages in the propane-pentane priming is critical. Propane substitution for pentane must be in the ratio of only 1 vol. of propane to 5 to 12 volumes of pentane backed out, preferably a ratio of 1/8–10, to maintain a constant VLTR. This substitution will result in the total composition of the gasoline having about 1 to 4% by vol. of propane and up to about 50% by vol. pentane, the ratio of the pentane to the propane in the final gasoline composition being about 5/1 to 50/1. Thus, increasing propane substitution tends to lower the fuel 158° F. point and to raise the fuel 20% vapor temperature. Thus, for a summer type of gasoline, the critical propane substitution point for pentane has been discovered to be limited to about 2% by vol., since this is about the percentage point at which the 158° F. evaporation point for the blend becomes lower or where the 20% vapor temperature exceeds that of the comparable butane primed gasoline (e.g., from 2 to 25% butane). This is the point at which the advantage of the propane-pentane priming of fuel over the butane primed fuel with respect to cold starting and initial warm-up is lost. Even greater advantages for propane-pentane primed fuels can be obtained in the winter grade of gasoline. In the winter gasoline, higher volatility levels are needed for good start-up and warm-up and thus, the more volatile butanes must be added to the pentane normally in the gasoline to reach the desired volatility level. The same problems exist in winter gasolines as previously discussed since higher VLTR levels up to or even above 19.0 are desirable. The use of propane-pentane priming of winter fuels has many advantages. The higher VLTR required cannot be reached with pentane priming alone since even 50% pentane in the base fuel would only result in a RVP of about 11 and a 158° F. point of perhaps 55%. This would give a maximum VLTR of 18.2. The use of 1 to 4% by volume propane in a ratio of between 5 to 12 volumes of pentane backed out for each volume of propane added with a preferred ratio of 8 to 10 volumes of pentane backed out to each volume of propane added has been discovered to provide a winter grade of gasoline superior in starting ability, initial warm-up and with low vapor loss in comparison to the same gasoline conventionally primed with butane and pentane. The discovered critical amount of propane added to the fuel blend and thus, consequently, the amount of pentane backed out, will once again be dependent upon the propane-pentane fuel maintaining a lower 20% vapor temperature point and a higher percent evaporated at 158° F. than the butane-pentane fuel. The propane-pentane fuel in order

to have the same VLTR protection as the butane-pentane fuel will necessarily have a Reid vapor pressure at least as low as the butane-pentane fuel. Furthermore, the propane-pentane primed fuel maintaining all the volatility advantages for start-up and warm-up will give better advantages than butane-pentane primed fuel in vapor losses, since it will only give high losses in the unusually low loss region of less than 1% evaporation. Even before this minor amount is evaporated, the true vapor pressure will be lower for the propane-pentane gasoline and, thus, the vapor loss rate will continue to be less thereafter.

The practical value of the present invention in regards to vapor loss protection can be further illustrated by the following experimental data in Example 1.

EXAMPLE I

Volume percent evaporation of gasoline after 10 minutes in constant temperature bath

Volume, percent	VLTR	RVP	Percent at 158° F. (vapor)	Bath temperature	
				135° F.	150° F.
C_3 2.0 C_4 0.3 C_5 12	11.7	10.0	13	2.0	4.2
C_4 10 C_4 0.8 C_5 26	11.6 11.8	10.3 8.2	10 28	2.7 1.5	4.8 9.2

The above data show the advantages of propane-pentane primed fuels and pentane primed fuels over butane primed fuel. In particular, the advantages of propane-pentane primed fuels over butane primed fuels in regards to the percentage evaporated at 158° F. and the low vapor losses at both temperatures (135° F. and 150° F.) are most significant. As expected from FIGURE 2, the pentane primed fuel has a low to normal vapor loss at the lower temperature but a much higher loss at the higher temperature. As known to those skilled in the art, typical losses between a refinery and an automobile engine are about 2 to 4% on commercial butane primed gasoline, of which 1–2% are between the refinery and service station pump and the remainder represents filling, car tank, and carburetor vapor losses.

The effect of the gasoline priming agent on summer and winter type gasolines can be further demonstrated by the following data of Example II.

EXAMPLE II

Effect of gasoline priming agent on car performance

SUMMER GASOLINE

Vol. percent [1] primer	RVP	Percent at 158° F. vapor temp.	VLTR	Min. temp. for [2] cold start ° F.	Rel. power [3] during initial warm-up at 40° F.	Percent car vapor lock protection at 100° F.	Est. rel. vapor losses (refinery to car engine)
2% C_3 20% C_5	9.0	25	12.3	−3	100	98	1.5
8% C_4 10% C_5	9.5	23	12.5	−2	90	96	2.5

WINTER GASOLINE

					At 15° F.	At 65° F.	
3% C_3 35% C_5	13.0	40	18.2	−21	100	98	1.3
17% C_4 18% C_5	13.6	37	18.4	−21	70	96	2.0

[1] In a depentanized base gasoline.
[2] Cars with poor choking action.
[3] 1959 Ford data and assuming that the 158° F. point is controlling

The above data indicate the utility and advantages both commercial and practical to be obtained in cold starting ability, initial warm-up ability, and in minimizing vapor losses at a constant VLTR when critical amounts hereinto before described, of propane in a propane-pentane primer are used to prime each type of gasoline, in comparison to the now prevalent commercial method of priming with butane and butane-pentane mixtures.

EXAMPLE III

To indicate the critical amount of propane in combination with pentane that can be added to winter grade gasoline before the advantage over the conventional C_4–C_5 priming is lost, the following data are presented.

Winter gasoline (estimated values)

Primer by volume			RVP	VLTR	Percent evap. at 158° F.	° F. at 20% evap.	Percent vapor loss at 115° F.[1]
Percent C_3	Percent C_4	Percent C_5					
1	1	50	12.4	18.3	46	120	2
2	1	42	12.8	18.0	40	124	3
3	1	35	13.2	17.9	36	127	4
4	1	28	13.6	17.8	32	135	5
5	1	23	14.3	17.2	18	160	6
------	20	8	13.9	18.3	34	127	[2] 5.4

[1] Estimated for standard evaporation test—10 min. in bath at 115° F.
[2] Measured value, also value of 1.3% was measured for gasoline containing about 50% pentane (VLTR of 18.1) and essentially no C_3 or C_4's.

From the above data, it can readily be seen that the actual limitation on the propane in the propane-pentane priming of the winter grade gasoline is about 4% by volume of propane. The addition of more propane-pentane primer results in the advantage over the conventional butane-pentane priming of winter grade gasoline being lost.

EXAMPLE IV

An improved gasoline of the instant invention can be prepared by the method of debutanizing a hydrocarbon base stock boiling in the gasoline boiling range in a conventional bubble column containing about 30 trays. The column is operated at about 200 p.s.i.g. and has a top temperature of about 165° F. and a bottom temperature of about 330° F. A reflux ratio of about 0.5 to 0.8 is used. The reflux ratio is the ratio of the weight of liquid returned to the tower, to the weight of vapor products from the tower less the weight of liquid returned to the tower. The characteristics of the charge to the tower and the resulting products are given below:

	Debutanize	
	Charge	Product
Volume percentage C_4	10	0
RVP, p.s.i.	10	4.5
Percentage distillate plus loss at—		
158° F	23	13.7
212° F	50	44.2
End point, °F	355	355

The above debutanized gasoline is then primed with a mixture of a propane and a pentane fraction, so that the resultant product has about 16.0 percent by volume of a pentane fraction and 1.6 percent by volume of propane.

The above demonstrate the inventive method of priming a debutanized gasoline with a propane-pentane mixture so as to minimize vapor loss at a constant vapor lock tendency rating.

In summary, the present discovery relates to the new concept of priming gasoline with pentane and up to a critical amount of propane, which is as much propane as possible, limited only so as to not exceed the Reid vapor pressure nor have less than the same percentage evaporated at 158° F. nor a higher 20% point on a vapor basis than a butane primed gasoline. The propane-pentane or pentane primed gasoline will then result in a gasoline com-

position having superior starting ability, superior initial warm-up and lower vapor and weathering losses than a conventionally primed gasoline of butane or butane-pentane, of substantially the same vapor lock tendency rating. It is apparent that the advantages of this invention, particularly in terms of the weathering and vapor losses can be obtained with all of the major types of gasolines including automotive, marine type as well as aviation gasolines.

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 lead anti-knock compounds, such as tetraethyl lead and conventional lead scavenging agents of the type well known to the prior art, as well as gum inhibitors, anti-icing agents, oxidation inhibitors, solvent oils and the like.

What is claimed is:

1. A method of pressurizing a motor fuel to minimize vapor loss while maintaining a substantially constant vapor lock tendency rating, which method comprises debutanizing a hydrocarbon base stock boiling in the gasoline boiling range, and priming said debutanized fuel with a mixture of propane and pentane so that the total resultant composition has from about 1 to about 4% by volume of propane and a ratio by volume of pentane to propane of between 5/1 and 50/1.

2. A method of pressurizing a motor fuel as defined in claim 1 wherein the amount of propane comprises an amount of propane which will give a percentage evaporation at a vapor temperature of 158° F. and a vapor temperature at which 20% by volume evaporates of more than that percentage and less than that temperature obtained when the said motor fuel is primed to the same vapor lock tendency rating with from 2 to 25% butane.

3. A method of pressurizing a summer type motor fuel to minimize vapor loss while maintaining a substantially constant vapor lock tendency rating which method comprises debutanizing a hydrocarbon base stock boiling in the gasoline boiling range; and priming said debutanized fuel with a mixture of propane and pentane, so that the total resultant composition has from about 1 to about 2 percent by volume of propane and a ratio by volume of pentane to propane of between 5/1 and 50/1 and a Reid vapor pressure of between about 7 and about 11 p.s.i.

4. A method of pressurizing a winter type motor fuel to minimize vapor loss while maintaining a substantially constant vapor lock tendency rating which method comprises debutanizing a hydrocarbon base stock boiling in the gasoline boiling range; and priming said debutanized fuel with a mixture of propane and pentane, so that the total resultant composition has from about 2 to about 4 percent by volume of propane and a ratio by volume of pentane to propane of between 5/1 and 50/1 and a Reid vapor pressure of between about 12 and about 15 p.s.i.

5. A method of pressurizing a motor fuel as defined in claim 1, wherein said fuel is a winter grade gasoline and where, for each volume of propane, between 5 and 12 volumes of pentane are backed out.

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