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MOTOR FUEL

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The present invention relates to a motor fuel composition adapted to provide distinctly improved motor operation when the fuel is carburetted under cool, moist atmospheric conditions. The motor fuel composition of the present invention comprises gasoline or a hydrocarbon mixture boiling in the gasoline boiling range and a very small percentage of C_1 to C_4 monoalkyl ether of mono- or di-ethylene glycol. In addition, the fuel compositions of the present invention may contain solvent oil and other additives such as lead alkyl anti-detonants, dyes, gum inhibitors, oxidation inhibitors, metal deactivators, rust-preventives and the like.

This application constitutes a continuation-in-part of Serial No. 169,074, filed June 19, 1950, and now abandoned.

The novel fuel compositions of this invention are primarily intended to overcome certain operational difficulties in connection with automotive, marine, stationary, and airplane engines. The difficulties referred to result in loss of power and frequently in stalling of the engine under idling conditions. This loss of power and stalling may be encountered whenever the weather conditions in which the engine is used are such as to provide a relatively high humidity, and a temperature below about 60° F. The difficulties have been encountered in all types of cars employing all types of carburetors and utilizing all commercial brands of gasoline. Table I gives a summary of the results obtained in a survey of 300 cars of 20 different models which were run on winter grade commercial gasolines. The substantial number of stalls encountered in the operation of the cars under the indicated conditions is noteworthy.

TABLE I

Temperature, ° F	32	35	37	52	56
Relative Humidity, percent	52	70	96	100	96
Weather	Clear	Overcast	Light rain	Heavy rain	Rain
No. of complaints of 2 or more stalls per 100 cars	11	53	60	63	9

This problem has of late become of increased importance due to certain specific factors. First, most postwar cars are not provided with a manual throttle so that car owners are no longer able to increase the idle speed during the warm-up period to prevent stalling. Second, the idle speed of cars with automatic transmissions is rather critical during a warm-up and the fastest idle which may be used must not be too fast, increasing the criticality of stalling conditions. Third, stalling of a car with automatic transmission frequently does not occur until the driver is ready to accelerate, so that just at this most inconvenient time it is necessary to shift the car to neutral, restart the engine, and shift back into drive; magnifying ing the inconvenience of frequent stalls. A fourth factor affecting the magnitude of stalling difficulties relates to the volatility of the fuels now provided for automotive use. The volatility of commercial fuels over a period of

years has been increased sufficiently so as to increase stalling difficulties as will be brought out herein.

On investigating this problem, it has been determined that the cause of repeated engine stalling in cool, humid weather is the formation of ice in the carburetor of the engine. On a cool, moist day, gasoline evaporating in the carburetor exerts sufficient refrigerating effect to condense and freeze moisture present in the air entering the carburetor. Normal fuel vaporization within the carburetor can cause the temperature of the metal parts of the carburetor to decrease as much as 50° F. below that of the entering air. Consequently, prior to the time of complete engine and radiator warm-up, this drop in temperature may cause formation of ice in the carburetor. Ice formation probably occurs most readily under conditions of light load operation. The result is that after a period of light load operation, when the throttle is closed to the idle position, ice already formed on the throttle plate and adjacent walls, plus ice which then forms, restricts the narrow air openings to cause engine stalling. This problem of ice formation is also encountered in aggravated form in the case of those engines employing carburetors which have small Venturi diameters, especially when the Venturi tube is insulated from the casting of the body of the carburetor. It has been found that such carburetors having a Venturi diameter of 21 millimeters or less are particularly subject to ice formation, causing severe throttling of the fuel flow in the Venturi itself.

To define more clearly the problem of engine stalling due to carburetor icing, data were tabulated based on customer reaction surveys, carefully controlled road tests, and laboratory cold room engine performance tests. These tests showed that carburetor icing depends primarily upon atmospheric temperature and humidity conditions. Stalling difficulties due to ice formation in the carburetor were not encountered below about 30° F., nor above about 60° F., when employing fuels having conventional volatility characteristics. The results also show that stalling is only encountered when the humidity is in excess of about 65%.

The other controlling factor for the formation of ice in the carburetor, besides the condition of the atmosphere, is the volatility of the fuel employed. To determine this effect, cold room tests were conducted to evaluate the stalling characteristics during warm-up of a car with a number of fuels varying in volatility. In these tests, a 1947 Chrysler car was installed in a room equipped with temperature and humidity controls. While the temperature and humidity were maintained at particular levels, the stalling characteristics of the car were determined during the warm-up period. The procedure employed was to start the car and immediately to raise the engine speed to 1500 r.p.m. This speed was maintained for 30 seconds, after which the engine was allowed to idle for 15 seconds. If the engine stalled before 15 seconds had passed, the car was again started and raised to a speed of 1500 r.p.m. for 30 seconds; while if stalling did not occur, the speed was immediately increased to 1500 r.p.m. after the 15 second idling time. The alternate cycles of 30 seconds at 1500 r.p.m. followed by 15 seconds at idling were repeated until the engine was completely warmed up. The number of stalls encountered during this procedure, and up to the time of complete engine warm-up were then recorded. Tests were conducted at 40° F. and at a relative humidity of 100% employing three fuels of varying volatilities. The three fuels were motor gasolines of the sort used in modern high-compression auto-

motive engines. They had ASTM motor octane numbers above 80, which were attained by including 1.5 to 3.0 cc. of tetraethyl lead in the form of Ethyl Fluid per gallon. They had less than 0.1% of sulfur by ultimate analysis, and, of course, this small trace of sulfur was in non-reactive combined form free of elemental uncombined sulfur, as is essential for attaining high octane number in a leaded gasoline. The first fuel was a volatile, premium grade, commercial gasoline having a 10% ASTM distillation point of 110° F., a 50% point of 190° F., and a 90% point of 294° F. It was found that this fuel resulted in about 14 or 15 stalls during warm-up. The second fuel had a medium volatility. It was a regular grade commercial gasoline having ASTM distillation characteristics such that 10% distilled at 121° F., 50% distilled at 220° F., and 90% distilled at 342° F. The number of stalls encountered with this fuel was 11. Finally, a low volatility gasoline was subjected to the same test procedure. The gasoline had ASTM distillation 10, 50, and 90% points, at 126° F., 270° F. and 387° F. Five stalls occurred with this fuel.

As indicated by these data, carburetor icing is related to the volatility of the fuel employed. Thus, the least volatile fuel tested above, having a 50% distillation point of 270°, resulted in only 5 stalls, while the highest volatility fuel, having a 50% distillation point of 190° F., resulted in 15 stalls. Extrapolating these data as to the volatility of the fuel, it appears that a fuel having a volatility such that the ASTM 50% distillation point is 310° F., or higher would not be subject to stalling difficulties during warm-up. It must be appreciated, however, that a fuel having ASTM distillation characteristics of this nature would not be desirable as regards warm-up time, cold engine acceleration, economy of fuel consumption and crank case dilution of the lubricating oil. Also, it should be appreciated that even when complete stalling does not occur there may be a marked loss of power output due to icing. This is particularly serious in the case of aviation engines. For example, 30% of the light plane mishaps occurring in the United States in 1947 and 1948 were attributed to the formation of ice in the carburetor or intake manifold, which reduced power output by restricting the flow of combustible mixture to the cylinders.

It has now been discovered that distinctly improved operating conditions are secured with respect to icing and stalling provided that a relatively small critical amount of a material of appropriate volatility, molecular weight and balance of hydrophilic and lyophilic properties, selected from a small class of mono-ethers of an alkylene glycol be incorporated in the fuel.

These ethers are the C_1 to C_4 alkyl mono-ethers of mono- and di-ethylene glycols. For example, the following ethers may be employed: ethylene glycol monobutyl ether, ethylene glycol monopropyl ether, and ethylene glycol monoethyl ether; also diethylene glycol monobutyl ether, diethylene glycol monopropyl ether, diethylene glycol monoethyl ether, and diethylene glycol monomethyl ether. Isomeric alkyl groups, such as isopropyl, isobutyl, secondary butyl and tertiary butyl, as well as n-propyl and n-butyl are suitable for the mono-alkyl ethers of mono- or di-ethylene glycol in this class of C_1 to C_4 alkyl ethers of glycols. Of these compounds, it has been found that diethylene glycol monoethyl ether, and diethylene glycol monobutyl ether are particularly suitable for the purposes of this invention. Furthermore, it has been determined that of this entire class of compounds, diethylene glycol monoethyl ether provides the greatest anti-stalling effect in a gasoline when employed in the smallest amounts as compared to the other compounds named.

Table II shows some physical properties of the most and the least volatile of this class of mono-ethers as listed above.

TABLE II

Mono-Alkyl ether Group	Type of Ethylene glycol	Molecular weight	Boiling Point °C.	Vapor Press mm. Hg @20° C.	Poise @25° C.	Surf. tension, dynes @25° C.
Methyl	mono	76.06	124.3	9.50	0.016	35.0
Ethyl	mono	90.08	135.1	3.70	0.019	32.0
Butyl	mono	118.11	170.7	0.12	0.033	31.5
Methyl	di	120.10	193.2	0.19	0.051	41.3
Ethyl	di	134.10	201.9	0.13	0.038	35.5
Butyl	di	162.14	231.2	0.06	0.045	33.6

For use in accordance with the present invention, the mono-ether should have a molecular weight between 90 and 170 and boiling point between 135° C. and 235° C. Its vapor pressure should be between 0.05 and 5.00 mm. of Hg at 20° C., and its surface tension should be between 31 and 41 dynes per cm. at 25° C.

While the mechanism whereby these materials prevent carburetor ice is not completely understood, it is considered desirable that the boiling point of the additive should be near the end-point of the gasoline, e.g. between 170° C. and 232° C. The surface tension should be at least 30 dynes per cm. at 25° C. The molecular weight should not exceed 170 in order to get a substantial lowering of the freezing point of water.

The partition coefficient of the mono-ethers between gasoline and water is also important. Some of the mono-ether must enter the water-phase in order to prevent ice formation. Yet the mono-ether must not be so soluble in water as to be completely extracted from the gasoline upon first contact with water. The ratios of solubility in petroleum ether to solubility in water are between 9 and 30 times greater for the preferred mono-ethers than for the glycols from which they are formed.

	Ratio of solubility
Ethylene glycol	0.005
Mono-ethyl-ether of ethylene glycol	0.15
Diethylene glycol	0.004
Mono-ethyl-ether of diethylene glycol	0.037

In order to secure the benefits of this invention, critical amounts of the ethers identified must be employed. As will be shown by the data which follows, it is necessary to employ these compounds in amounts greater than about 0.12% by volume in order to secure appreciable anti-stalling results. While amounts of these additives greater than 0.12% ranging upwardly to about 1% by volume may be employed, it is particularly preferred to employ no more than about 0.45% by volume. In this connection, it is the particular feature of this invention to employ these additives in concentrations above 0.12%, but no more than about 0.45% in order to enable the maintenance of anti-stalling results which are only obtained by many times this concentration of those additives now used commercially. Since, as stated, the problems of engine stalling caused by ice formation, are a function of the volatility of the fuel used, the precise amount of additive to be used, chosen from the range stated, will be made with regard to the volatility of the particular fuel involved and of the mono-ether used.

The present invention is particularly directed to the improvement of modern high quality gasoline fuels. Thus, the invention is applied to gasolines having an octane number above about 80, having a volatility such that the ASTM 50% distillation point is 270° F., or lower, and with gasolines of this character which are stable and non-corrosive, passing the conventional inspection tests such as the copper strip corrosion test.

The present invention may be more fully appreciated by the following examples of specific embodiments of the invention.

EXAMPLE 1

A continental light aircraft engine was operated on an aviation grade 80 fuel, and on a blend of the fuel and 0.5 volume percent of the monobutyl ether of diethylene glycol. The base fuel had the following distillation characteristics:

ASTM DISTILLATION

Initial	° F.	100
50%	° F.	200
Final	° F.	325
Reid vapor pressure, p.s.i.		7

The intake air had a temperature of 50° F. and a relative humidity of 97±3%. The temperature of the air surrounding the carburetor was 50° F. The throttle was fixed to give an initial engine speed of 1750 r.p.m. and the loss in speed after operation for 3 minutes and for 10 minutes was determined. The results secured are as follows:

Carburetor Icing in Light Aircraft Engine

[Amount of carburetor ice accumulated is reflected in magnitude of speed loss]

Additive	Concentration Fuel, Vol. percent	Loss in Speed Due to Icing, Δ r.p.m.	
		After 3 Min.	After 10 Min.
None		425	425
Monobutyl ether of diethylene glycol	0.5	0	0

EXAMPLE 2

Tests were conducted in an automobile with carburetors having different Venturi diameters, by substituting carburetors having progressively smaller "choke" or "vena contracta" sizes. Alterations were made to the main jet of the carburetor so as to correct air fuel ratios. The automobile was tested on a chassis-dynamometer in a "cold-room" and the engine-throttle opening was varied to maintain a constant speed of 40 m.p.h. The different choke sizes were 21, 18 and 17 millimeters. A transparent plate on the carburetor permitted visual observation of ice formation and the occurrence of ice and the time required for this ice to disappear as the engine heated up was noted.

TABLE II

Choke Size, mm.	Icing	Time to Disappearance of Ice (min.)	Remarks
21	Slight		No loss in speed.
18	Severe	5.8	Speed fell from 40 to 35 m.p.h.
17	Severe	8.2	Speed fell from 40 to 30 m.p.h.

As indicated by the results above, the choke diameter employed in a carburetor can be responsible for aggravating ice formation. Also, as indicated by the remarks of Table II, ice formation can cause a severe loss in power which can result in actual engine stoppage, as has been found in road tests.

EXAMPLE 3

The location and the volume of ice in the carburetor having been observed in the cold-room tests of Example 2, the effect of the ice was simulated by inserting plastic plugs of the same volume in the same location. In road tests conducted at 40 miles per hour with the car having these partial plugs in the carburetor, it was found that this blockage of the carburetor caused great increase in the fuel consumption of the engine. The increase in fuel consumption was about 50 to 80% above normal operation.

EXAMPLE 4

In order to obtain rapid comparisons of various fuel blends, a test procedure was developed in which a carburetor was fitted to a CFR engine through a 3-foot long pre-heater tube. Inlet air was cooled by passage through an ice tower to a temperature of about 40° F., at a relative humidity of about 70% to 80%. In these tests, a carburetor was employed having a 14 millimeter Venturi tube. A transparent window was fitted to the carburetor to allow visual inspection of the Venturi and spraying well during the tests.

In operating this test, the engine was first run at about 900 r.p.m. After about 30 seconds of smooth running, the engine speed was then adjusted to standard test conditions of steady running at 1330 r.p.m. Providing no stalling occurs, the test run is maintained under these conditions for 30 minutes.

In these tests, it was found that icing which occurs in the carburetor as visually observed causes a change in engine speed which can be used as a criterion of the severity of icing. Consequently, in evaluating the results of these tests, the engine speed is plotted against time and a numerical demerit assigned by measuring the area bounded by the horizontal lines at ordinates of 1330 and 1100 r.p.m. and the experimental r.p.m.-time curve up to the time limit of 30 minutes. Regular runs on the base fuel employed without additive are carried out as a reference and the ratio of demerits (for the experimental test fuel and for the base fuel) multiplied by 100 is taken as the percentage demerit of the experimental fuel containing the additive. In these tests, the base fuel employed had the following inspections.

TABLE III

Inspection of Reference Fuel[1]

Reid vapor pressure, p.s.i.	9.9
ASTM distillation:	
Percent evaporated at 158° F.	28
Percent evaporated at 212° F.	56
Percent evaporated at 257° F.	74.5
Percent evaporated at 302° F.	89
End-point, ° F.	362

[1] Premium-type gasoline containing tetraethyl lead but no solvent oil.

Results of the tests conducted are shown in the following table:

TABLE IV

Carburetor Icing Tests; CRF Engine Test

Additive	Conc., Vol. percent	Percent Demerit
Diethylene glycol monoethyl ether	0.05	54.
Do	0.1	13 (ave. of 4).
Do	0.2	0.
Do	0.3	0.
Ethylene glycol monoethyl ether	0.1	100.
Do	0.15	97.
Do	0.2	51 (ave. of 2).
Do	0.3	0.

These results show that a proportion of 0.1 volume percent of diethylene glycol monoethyl ether is effective in substantially decreasing icing occurrence in a carburetor. However, when percent demerit is plotted against percent additive, it is evident that to eliminate the difficulty and to attain zero percent demerit, at least 0.12% and preferably 0.15% by volume of additive must be used. In the case of ethylene glycol monoethyl ether, the data shows that almost 0.3 volume percent of this additive is required to insure elimination of icing problems. The data therefore shows the marked superiority of diethylene glycol monoethyl ether in small amounts as an anti-icing gasoline additive.

EXAMPLE 5

Road tests were conducted to verify the results indicated by the preceding data under actual road conditions. In these tests, it was found that an amount of diethylene glycol monoethyl ether of 0.12 volume percent or somewhat greater was effective to eliminate problems of choke icing. Similarly, it was found that 0.25 volume percent, or somewhat greater, of ethylene glycol monoethyl ether could be employed to eliminate choke icing.

In the conduct of other tests it was found that the additives of this invention had no adverse effects on the properties of the gasoline compositions in which the additives were employed. In this connection these tests establish that diethylene glycol monoethyl ether in a gasoline of 362° F., end-point had the particular benefit of acting as a solvent oil so as to improve the condition of the induction system and valves of the engine, possibly by virtue of the fact that this additive, boiling at about 395° F., had the proper volatility to evaporate together with the least volatile portion of the gasoline near its end-point.

The gasoline to be used in accordance with this invention is the modern fuel for high compression automotive and aviation engines operating with carburetors in which the fuel is mixed with aspirated air in a Venturi-tube. The composition of the present invention prevents the accumulation of ice, which might be formed from the chilling of moist air by the vaporization of the fuel, in the Venturi tube and on the throttle plate.

The characteristics of modern automotive gasoline are set forth in ASTM specifications for gasoline, D439–52T, and also in semi-annual Reports of Investigation (e.g. RI–4901), entitled "National Motor Gasoline Survey" by the United States Bureau of Mines. The maximum temperature permitted for the 50% point of the gasoline distillation in ASTM D439–52T is 284° F. The values for the temperature at the 50% point shown in the reports of the Bureau of Mines are considerably lower than the permissible maximum and have trended lower, year by year, for many years.

The minimum octane number permitted in ASTM D439–52T is 78, and the actual octane numbers of commercial gasolines exceed that minimum. The actual octane numbers are generally higher than 80 and are sometimes as high as 98 research octane number.

The high values of octane number are required because modern engines have high compression ratios of at least 7. To attain high octane numbers, tetraethyl lead is used as an anti-knock agent. It is used in concentrations up to 3 cc. per gallon. The presence of sulfur in the gasoline, and particularly of elemental sulfur, is

antagonistic to the anti-knock effect of tetraethyl lead. This antagonism of reactive or corrosive forms of sulfur was fully described in 1949 in Industrial and Engineering Chemistry, vol. 41, pages 888 to 893 and 2722 to 2726. The ASTM specifications recognize the harm of corrosive sulfur by requiring that gasoline must pass a corrosion test with a rating no worse than No. 1 on the ASTM copper strip corrosion scale. By actual test it has been determined that in order to have a rating no worse than No. 1, the gasoline must contain less than one part of elemental sulfur per million parts of gasoline by weight; that is, less than 0.0001%.

The characteristics of modern aviation gasoline are set forth in ASTM specification D910–52T. The maximum temperature permitted for the 50% point of the gasoline distillation is 221° F., and the temperature for the 90% point must be between 257° F., and 275° F. The sum of the 10% and 50% points must be at least 307° F.; and since the R.V.P. must be below 7 p.s.i., and 10% point must be at most 158° F., the minimum temperature permitted for the 50% point by these indirect limitations is about 180° F. The minimum octane number permitted by these specifications is 80 by the aviation method. The content of tetraethyl lead specified is between 0.5 and 4.6 ml. per gallon; and, as in the case of the motor gasoline specifications, ASTM D910–52T also requires the aviation gasoline to pass the corrosion test with a rating no worse than No. 1 comparison standard.

What is claimed is:

A gasoline composition comprising a high quality gasoline base having an octane number greater than about 80, a Reid vapor pressure of at least about 7 p.s.i., and ASTM distillation 50% point below about 310° F., and containing less than 0.0001% of elemental sulfur to which has been added as an anti-icing agent 0.12% to 0.45% by volume of diethylene glycol monoethyl ether.

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