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DIALKYL ALKANOL AMINES AS ANTI-STALLING ADDITIVES

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The present invention relates to a motor fuel composition adapted to provide distinctly improved motor operation under cool, moist operating conditions. The motor fuel composition of the present invention comprises a hydrocarbon mixture boiling in the gasoline boiling range which contains as an ingredient a very small but critical percentage of a dialkyl monoalkanol tertiary amine. 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, and the like. The present application is a continuation-in-part of Serial No. 170,944 filed June 28, 1950, now Patent No. 2,706,677, issued April 9, 1955.

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 frequent stalling of the engines under idling conditions. This stalling may be encountered whenever the weather conditions in which an engine is used are such as to provide a relatively high humidity and a temperature below about 60° F.

It is significant to note that the stalling problem has of late become of increased importance due to certain specific factors. First, most cars are now provided without 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 the warm-up and the fastest idle which may be used to avoid creeping of the vehicle, is rather low thereby 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 gear—magnifying 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. Fuels of high volatility give rise to more stalling difficulties than fuels of low volatility, 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. Gasoline evaporating in the carburetor exerts sufficient refrigerating effect to condense and freeze moisture present in the air entering the carburetor on a cool, moist day. Normal fuel vaporization within the carburetor can cause a temperature reduction of the metal parts of the carburetor up to 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

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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.

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

Another factor having a bearing on the formation of ice in the carburetor is the volatility of the fuel employed. To determine this effect, laboratory cold room tests were conducted to evaluate the stalling characteristics during warm-up of 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 to then immediately 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 expired, the engine was again started and immediately raised to a speed of 1500 R. P. M. for 30 seconds. If stalling did not occur, the speed was 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 a relative humidity of 100% employing three fuels of varying volatilities. The most volatile fuel was a premium grade of 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. A medium volatility fuel was also tested, consisting of 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 were 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. It was found that five stalls were encountered 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°, only resulted in five 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 and crankcase dilution. However, in appreciating the scope of the present invention, it is important to note that this invention is only of application to gasoline fuels having an ASTM 50% distillation point below about 310° F. At the same time, as will be brought out, it is possible to correlate the quantity of additives required to overcome icing problems with the volatility of the fuel to be improved. In other words, smaller proportions of additives may be employed with fuels of relatively low volatility, while higher proportions of additives may be required with fuels of higher volatility. 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 distinct improvements in the operation of gasoline engines with respect to stalling can be obtained by incorporating relatively small critical amounts of a dialkyl mono alkanol tertiary amine in the fuel. The amine should have from 1-4 carbon atoms in each alkyl group and 2 to 3 carbon atoms in the alkanol group. The substituent groups may have the same or a different number of carbon atoms.

The amount of dialkyl mono alkanol tertiary amine employed should be at least 1/10% by volume based upon the volume of gasoline present and preferably from 0.2 to 0.5 volume percent of the gasoline.

Specific examples of tertiary amines that are suitable for the purposes of the present invention include dimethyl ethanol amine, ethyl methyl ethanol amine, methyl n-propyl ethanol amine, methyl i-propyl ethanol amine, methyl n-butyl ethanol amine, ethyl i-butyl propanol amine, ethyl t-butyl i-propanol amine, n-propyl n-butyl ethanol amine, etc. These compounds, in other words, may be represented by the formula



wherein R_1 and R_2 represent alkyl radicals that possess from 1-4 carbon atoms and wherein R_3 represents an alkanol radical containing from 2 to 3 carbon atoms. It is apparent that the compounds may contain as few as 4 carbon atoms and as many as 11 carbon atoms.

A tertiary amine of the class defined above that has been proven to be particularly effective and is especially preferred for the purposes of the present invention is diethyl ethanol amine. A concentration of 0.2 to 0.5% by volume of this amine in gasoline has afforded excellent carburetor anti-icing results.

The present invention may be more fully understood by the following examples illustrating the same.

Example 1

In this test a motor fuel of the premium grade motor gasoline type was used. Such gasoline normally contains "Ethyl Fluid" corresponding to between 1 and 3 cc. of tetraethyl lead per gallon of gasoline and normally has an octane number of at least 80.

Samples of the gasoline possessing an initial boiling point of about 100° F., a final boiling point of about 350° F., and about 50% distilled at 200° F. by ASTM method D-86 were mixed with various percentages of diethyl ethanol tertiary amine and the carburetor icing characteristics of the resulting fuel blends determined. The fuel blend samples were carbureted by air saturated with water at about 40° F., employing an air-fuel ratio of about 12:1 by weight. The minutes of elapsed time prior to the first indication of ice formation on the car-

buretor throttle plate were noted. The results of these operations are as follows:

Sample	Minutes Elapsed to First Indication of Ice Formation
1. Gasoline, no amine added.....	0.6
2. Gasoline +0.05 vol. % diethyl ethanol t-amine.....	0.8
3. Gasoline +0.1 vol. % diethyl ethanol t-amine.....	7.15
4. Gasoline +0.5 vol. % diethyl ethanol t-amine.....	12+

It is apparent from the above data that di-ethyl ethanol tertiary amine (or diethyl amino ethanol) must be present in a concentration greater than 0.05% by volume and preferably at least 0.1 volume percent in order to prevent ice formation within a carburetor during the critical starting and warm-up period. A concentration of as little as 0.05 volume percent is slightly effective in increasing the time required for the icing of a carburetor, but it is readily apparent that the degree of improvement is insufficient for a worth-while effect in the particular fuel tested.

The above data very clearly demonstrate the effectiveness of concentrations of 0.1 and 0.5 volume percent of diethyl ethanol tertiary amine in preventing carburetor icing. This observation is based on the finding that during a test period of 7 to 12 minutes no icing had occurred.

Example 2

In a second series of tests, samples of another motor fuel also of the premium grade were evaluated in the same apparatus as was employed in obtaining the results of Example 1. The gasoline in Example 2 had an initial boiling point of about 99° F., a final boiling point of about 405° F., and a 50% point of about 205° F., as determined by ASTM method D-86. As with Example 1, each sample of the fuel tested was blended with diethyl ethanol tertiary amine (di-ethyl amino ethanol) in various concentrations. Also, as in Example 1, the fuel was carbureted by air saturated with water vapor at about 40° F., employing an air/fuel ratio of about 12:1 by weight. In this example, the minutes of elapsed time prior to the first indication of ice formation on the carburetor throttle plate were again noted. The results of these operations are as follows:

Sample	Minutes elapsed for First Indication of ice formation
1. Gasoline—no amine added.....	about 1.
2. Gasoline +0.05 vol.% diethyl amino ethanol.....	about 1.
3. Gasoline +0.2 vol.% diethyl amino ethanol.....	over 7.5.

The data in this table completely substantiate the results that are presented in the table of Example 1. Thus, the data in this table clearly show that diethyl amino ethanol in 0.05 vol. percent concentration is not effective in a slightly less volatile fuel in preventing ice formation within a carburetor. Furthermore, the data in table 2 clearly demonstrate the ability of this additive in a concentration of 0.2 vol. percent to effectively prevent such ice formation.

Gasoline is a liquid fuel suitable for carburation in an engine operating on the Otto cycle. For use according to the present invention, gasoline has a volatility such that 50% of it by volume is distilled below 310° F. and preferably below 270° F. by ASTM method D-86. Gasoline is ordinarily a mixture of hydrocarbons of petroleum origin, but it may also be made synthetically from carbon monoxide and hydrogen and it can also contain hydrocarbons of coal origin, as well as oxygenated blending agents like ethers. The vapor pressure

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of gasoline may be varied seasonally; but it usually lies between 7 lbs. per sq. in. and 13 lbs. per sq. in. at 100° F. The end point of gasoline by ASTM method D-86 varies according to grade, but it usually lies between 300° F., and 450° F. For the purpose of this invention, gasolines having end points below 350° F. are particularly adaptable. Commercial gasoline is usually a composite of straight run gasoline or virgin naphtha, cracked or reformed naphtha, and casinghead naphtha or the liquid hydrocarbons carried as vapor in natural gas. Instead of casinghead naphtha, butane, isobutane, butenes, isopentane, pentane and pentenes from petroleum refining operations are frequently used.

What is claimed is:

1. A gasoline having an ASTM 50% distillation point below about 310° F. containing from 0.1 to 0.5 vol. percent of a dialkyl alkanol tertiary amine in which each

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of the alkyl groups contains from 1 to 4 carbon atoms and the alkanol group contains from 2 to 3 carbon atoms.

2. A gasoline as defined in claim 1 containing from about 0.2 to 0.5 vol. percent of the tertiary amine.

3. A gasoline as defined in claim 2 in which the tertiary amine is diethyl amino ethanol.

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