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GASOLINE FUEL

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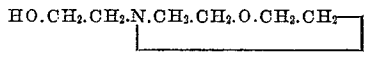
This invention relates to gasoline compositions adapted to provide improved engine operation under cool, moist operating conditions. The invention is applicable to automotive and aviation gasoline compositions. In accordance with this invention, a small amount of N-(methylene-carbinol) tetrahydro para oxazine is employed in these gasoline compositions in proportions generally selected from the range of about 0.1 to 0.5 volume percent. N-(methylene-carbinol) tetrahydro para oxazine is a heterocyclic compound, having the following formula in which the nitrogen atom is connected to ethylol and to two ethylene groups which form a link through an oxygen linkage:



Use of this additive in gasolines is particularly attractive in eliminating stalling commonly encountered when operating a gasoline engine under idling conditions at moist, cool weather conditions. The additive of this invention is compatible with other conventional gasoline additives such as lead alkyl anti-detonants, dyes, gum inhibitors, oxidation inhibitors, and the like, and the compositions of this invention may include such additives. In order to fully indicate the nature and utility of this invention, reference will be made to the problems solved by use of the novel gasoline compositions disclosed herein.

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 engine under idling conditions. This 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.

While this problem has actually been existent for many years, attention has been focused on it particularly in the past ten years, and particularly in the northern portion of the United States. During cool wet weather, cars give poor idling performance, characterized by a high number of engine stalls. The difficulty is 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 three hundred cars of twenty different models, showing the substantial number of stalls encountered in the operation of the cars under the indicated conditions in fall and winter:

Table I

	Number of Complaints of Two Stalls or More (Per 100 Cars)				
Temperature, ° F	32	35	37	52	56.
Relative Humidity, Percent	52	70	96	100	96.
Weather	Clear	Overcast.	Light Rain.	Heavy Rain.	Rain.
Winter Regular Users	5	15	20	21	7.
Winter Premium Users	6	38	40	42	2.

The foregoing information indicates the magnitude of the problem of engine stalling encountered under cool, humid temperature conditions. It is significant to note that this problem has of late become of increased importance due to certain specific factors. First, most post-war 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 the inconvenience of frequent stalls. A fourth factor affecting the magnitude of stalling difficulties relates to the volatility of the fuels now provided for automative use. The volatility of commercial fuels over a period of years has been increased sufficiently 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 lower the temperature of the metal parts of the carburetor 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 in 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 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 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 seconds 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 5 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° F., only resulted in 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 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 having an ASTM 50% distillation point below about 310° F., and particularly of application to gasoline having an ASTM 50% distillation point no higher than 220° 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.

The present invention is based on the discovery that N-(methylene-carbinol) tetrahydro para oxazine is particularly effective for eliminating the problems of ice formation referred to. While other additives have now been disclosed in the art which are capable of eliminating icing, N-(methylene-carbinol) tetrahydro para oxazine is effective in solving the icing problem when used in relatively smaller amounts than other additives. In particular, it is practical to employ N-(methylene-carbinol) tetrahydro para oxazine in an amount of about 0.15% by weight in gasoline so as to minimize or eliminate ice formation under operational conditions as efficiently as with the use of 2% by volume of isopropanol in the same gasoline. When used in modern automotive gasolines having relatively high volatility approaching that of aviation gasolines and when used in aviation gasolines themselves, it is particularly preferred to employ about 0.45% by weight of N-(methylene-carbinol) tetrahydro para oxazine.

The present invention may be appreciated by reference to the following data setting forth a specific embodiment of this invention.

In this example, a winter grade of commercial automotive gasoline of premium quality was employed. This gasoline contained conventional ethyl fluid in a concentration giving about 1.9 cc. per gallon of tetra-ethyl-lead, together with 1.5 theories of ethylene bromide and ethylene chloride, scavenging agents. The gasoline contained 0.5% of solvent oil also and had the following inspections:

API gravity	67.0
Reid vapor pressure	11.4
ASTM distillation:	
Initial, ° F	87
10% evaporated at ° F	112
50% evaporated at ° F	184
90% evaporated at ° F	296
End-point, ° F	371

Employing this gasoline as the base fuel, compositions of this invention were prepared containing 0.1 and 0.5 weight percent of N-(methylene-carbinol) tetrahydro para oxazine. In addition, for comparative purposes, a composition consisting of the base fuel plus 2 volume percent of isopropanol was prepared. These gasoline compositions were then tested in a laboratory icing test which has been established to correlate with stalling problems encountered during operation of gasoline engines.

The laboratory test employed a Zenith carburetor to which the fuel compositions were supplied in 12/1 ratio with air at 45° F., and 100% relative humidity so as to fully simulate conditions of carburetion under cool, moist conditions. The throttle plate of the carburetor was relocated in a glass section so that the ice formation could be seen. When ice crystals formed around the throttle plate, there was an observed pressure drop of 0.1 inch of water in the draft gauge for measuring air flow and the time elapsed from the start of the test to the occurrence of that pressure drop was taken as a measure of the relative effectiveness of the anti-stalling compositions. Data obtained for the fuel compositions tested are summarized in Table II.

Table II

Additive employed:	Minutes for ice formation
None	0.6
2.0% [1] isopropanol	3.6
0.5% [2] N-(methylene-carbinol) tetrahydro para oxazine	8.2
0.1% [2] N-(methylene-carbinol) tetrahydro para oxazine	2.1

[1] Volume percentage basis.
[2] Weight percentage basis.

By straight-line interpolation, it will be observed that only 0.2% of N-(methylene-carbinol) tetrahydro para oxazine by weight was needed to be as effective as 2% of isopropanol by volume in eliminating ice formation in the carburetor. Again, it will be noted that 0.5% of N-(methylene-carbinol) tetrahydro para oxazine by weight was more than twice as effective in eliminating ice formation as isopropanol, although the concentration of the latter was nearly four times as much. These data therefore establish the substantial and unexpected efficiency of N-(methylene-carbinol) tetrahydro para oxazine when used in small amounts for preventing ice formation when operating gasoline engines.

The gasolines in which this additive is particularly effective are those defined in specifications MIL–F–5572 of United States Armed Forces for aviation use, and MIL–G–3056 for automotive use; but the same additive is also effective in the gasolines defined as Fuel M in United States Federal Specification VV–M–561a for regular and premium grades of classes A, B and C.

These gasolines are substantially gum free, having less

than 10 milligrams of gum per 100 ccs., and are non-corrosive to copper.

What is claimed is:

1. A gasoline having an ASTM 50% distillation point below about 310° F. containing about 0.1 to 0.5% by weight of N-(methylene-carbinol) tetrahydro para oxazine.

2. A gasoline composition essentially comprising a major proportion of an automotive grade gasoline having an ASTM 50% distillation point below about 310° F. and containing about 0.2 to 0.5% by weight of N-(methylene-carbinol) tetrahydro para oxazine.

3. A gasoline composition essentially comprising at

least a major proportion of an aviation grade gasoline having an ASTM 50% distillation point below about 310° F. and containing about 0.15 to 0.45% by weight of N-(methylene-carbinol) tetrahydro para oxazine.

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