FLH:AM
3.5

U. S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS
Washington 25, D. C.

July 10, 1950

Letter Circular
LC-991
Supersedes LC-551
and LC-281

MOTOR GASOLINE

This letter circular is intended to furnish basic information about gasoline that will assist the average motorist in selecting the proper fuel for his automobile.

Gasoline is composed essentially of a class of compounds known as hydrocarbons, which, as the name implies, are made up of carbon and hydrogen. These compounds differ not only in volatility, or the ease of evaporation, but also in other properties, notably in their tendency to cause combustion knock. The properties of the gasoline are therefore dependent on which of the various hydrocarbons are present, and in what proportions. Since crude petroleums vary considerably in composition, it may be seen that gasoline derived from these crudes may also be quite different. In addition, modern refining processes change the structures of some of the hydrocarbons to more desirable types, so that the products are still more complex.

There are certain minimum requirements that should be - and generally <u>are</u> - met by all gasolines. Gasoline should not contain more than a very small amount of gum, and if gum-forming constituents are present, the gasoline should also contain an inhibitor which is effective in preventing the formation of objectionable amounts of gum. The amount of materials tending to corrode or otherwise damage the engine should be below a satisfactory limit. The antiknock quality should be adequate for the engines in which it is to be used. The volatility range of the fuel should be suited to the season with respect to ease of starting, engine warmup, and vapor lock. The principal difference between gasolines currently marketed is in the octane number which is a measure of the resistance of a fuel to combustion knock. The octane number of a fuel has no relation to its starting and warmup characteristics, or to its tendency to cause vapor lock.

Many properties of gasoline are subject to some degree of refinery control. The more important of these are discussed in the following paragraphs.

1. Antiknock Quality of Gasoline

The resistance of a gasoline to combustion knock is usually expressed as an octane number, a high octane number indicating a good resistance to combustion knock and vice versa. The octane number is the percentage of isooctane in a mixture of isooctane and normal heptane which has the same resistance to combustion knock as that of the gasoline when tested under specified conditions. When a gasoline has an octane number of say 75 its antiknock quality is equal to that of a mixture of 75 percent isooctane and 25 percent normal heptane. Octane numbers are determined on special test engines where the speed, operating temperatures, and other important factors can be precisely controlled.

Fuels for automobile engines are rated according to two methods standardized by the American Society for Testing Materials. One of these (D-357) is known as the Motor Method, the other (D-908) as the Research Method. The Research Method test conditions are less severe and give higher ratings than the Motor Method. For example, two fuels having Motor Method ratings of 75 octane number may have Research Method ratings of 77 and 81 octane number respectively. The spread between the two ratings measures the sensitivity of the fuel to the severity of test conditions. Thus the first fuel is comparatively insensitive, while the second is a typical sensitive fuel. The relative severity of automobile engine operating conditions determines whether the higher Research octane number of the more sensitive fuels will give improved antikock performance in any particular car.

The average knock rating of regular grade gasoline, as marketed in different sections of the country, ranges at present from 75 to 80 Motor octane number and from 80 to 85 Research octane number. Some of the brands of regular gasoline available in a given area may differ in rating by several octane units. However, the fact that one gasoline has a somewhat lower Motor or Research octane number than another does not necessarily mean that it will have a greater tendency to knock in a given car. If the car knocks on a regular gasoline one should make sure that the ignition timing is not unduly advanced and then try other brands of regular gasoline before assuming that premium grade fuel is required. The average knock rating of premium grade gasoline ranges from 80 to 83 Motor octane number and from 87 to 91 Research octane number.

The most important of the engine design factors influencing the tendency of gasoline to knock during combustion is the compression ratio of the engine (ratio of the volume filled by the charge at end of the intake stroke to the volume at end of compression). Increasing the compression ratio improves engine efficiency but also subjects the charge to higher temperatures and pressures, requiring fuel of higher octance number for knockfree performance. The average Motor Method rating of regular gasoline increased from below 63 octane number in 1930 to about 75 octane number in 1941 and the average rating of premium grade gasoline increased from 70 to 80 octane number in the same period. This has permitted the average compression ration of automobile engines to be increased from 5.15:1 to 7.00:1 since 1930. During the past twenty years, the specific output (horsepower per cubic inch) of the average automobile engine has increased nearly 40 percent.

About three quarters of the cars now in service will give adequate anti-knock performance on regular grade gasoline. Some of these cars may knock lightly at low speeds while accelerating or hill climbing, but the knock usually occurs only during a very small part of the total operating time and is not severe enough to affect engine power. In those cars which, due to engine design or condition, knock severely on regular gasoline, the knock can be moderated or eliminated either by retarding the spark or by using premium grade gasoline. Since knock and a retarded spark both tend to reduce engine power, the use of premium gasoline may be advantageous in this case. However, premium grade gasoline will not improve the power and economy of any car which operates without objectionable knock on regular grade gasoline at the normal spark setting.

2. Volatility of Gasoline

Under operating conditions air and gasoline spray enter the manifold of an automobile engine. Here they are intimately mixed by turbulence of the air stream, heated to some extent by contact with the walls of the manifold and enter the cylinders. Entrance through the intake valve still further increases the turbulence and consequent mixing of the charge. Generally, the liquid is not all evaporated at this stage; probably some of it is in the form of small droplets which are further vaporized by mixing with the residual hot exhaust gases in the cylinder and by heat generated during compression of the charge before ignition. Hence under ordinary running conditions little of the liquid should remain at the time of ignition. It can therefore be seen that the volatility of the gasoline is an important factor in satisfactory engine performance. Enough of the lower-boiling components of a fuel must vaporize in the cylinder to form an explosive mixture before a cold engine can be started. However, if there are too many low-boiling components in a gasoline, the fuel may boil and form vapor in the fuel lines, pump, or carburetor. When this occurs the engine may begin to misfire or may stop altogether. This failure of the fuel system due to accumulation of vapor is known as "vapor lock". When an engine vapor locks it is usually necessary to wait for the engine to cool before it can again be started. Volatility also affects the ability of the engine to warm up properly.

The volatility of a gasoline is measured in two ways. First, a measurement of its vapor pressure will give an indication of its vapor-locking tendency. Second, a more complete analysis of its volatility may be made from its distillation curve. The table below shows the average distillation data on regular and premium gasolines as reported in the Bureau of Mines surveys made in the summer of 1949, and winter of 1949-1950.

Table I

Boiling Ranges of Average Gasolines

Percent Evaporated	Temperatures, °F			
	Summer 1949		Winter 1949-1950	
	Regular	Premium	Regular	Premium
IBP	100	101	90	91
5	120	120	105	105
10	137	135	122	120
20	165	159	150	144
30	191	182	177	168
50	237	227	226	216
70	283	273	272	265
90	345	338	336	331
95	371	365	363	358
End Point	404	397	398	394

The data in table 1 are averages for the entire United States; departures from these averages may be large in those areas where climatic conditions require more or less volatile fuel. It will be noted that the average temperatures for summer gasolines are somewhat higher than those for winter gasolines, and that the differences between regular and premium gasolines are quite small, the largest difference being at or near the 50 percent point.

(a) Effect of Volatility on Starting: The starting ability of a gasoline depends on the percentage of its components vaporizing at atmospheric temperature. It has been found that gasoline-air mixtures containing less than about 5 percent by weight of <u>vaporized</u> gasoline are not fired by a spark plug.

A carburetor is designed to furnish air and fuel in varying proportions according to the conditions under which the engine is operating. For road load operation at normal speeds (20 to 60 mph) the air-fuel ratio is usually about 14 to 16 pounds of air per pound of gasoline. For full throttle operation the mixture is enriched for increased power to about 12 lb air per lb fuel. When the choke is fully closed gasoline and air are supplied in about equal proportions. While this is very much too rich for normal operation, it is required temporarily to furnish a readily ignited mixture of air and fuel vapor. For example, when the fuel is only 10 percent vaporized a 1:1 mixture supplied yields a 10:1 mixture of air and fuel vapor which is in the range that will burn in an automotive engine. If less than 5 percent of the fuel normally vaporizes even the choke will not furnish a mixture rich enough to start the engine.

Engine starting temperatures can be estimated from the temperature at which the first ten percent of a gasoline has evaporated. The "10-percent evaporated point" is generally accepted as a reliable index of the starting ability of gasolines provided that the engine is in good mechanical condition. The best 10-percent temperature naturally varies with the season. The relation of the minimum starting temperature to evaporation temperature of gasoline is shown in the table below.

Table 2

Relation of 10-Percent Point to Starting Ability

ASTM 10-Percent Point, °F	Minimum Atmospheric Temperature for Starting, °F
104	-22
122	- 9
140	1
158	12
176	23

(b) Effect of Fuel Volatility on Vapor Lock: Knowledge gained from tests and experience has made it possible for oil refineries to supply gasoline that will not vapor lock in the average automobile except under extreme conditions. It has been found that there is a definite relation of the vapor pressure of the fuel to the atmospheric temperature at which vapor lock will occur in operation. The vapor pressure is usually determined by a standardized procedure and is expressed as "Reid vapor pressure". The Reid vapor pressure of fuel supplied in summer averages 8 $lb/in.^2$, while in winter it may exceed 12 $lb/in.^2$. It is apparent that if there is very warm weather during the winter months many cars supplied with highly volatile gasoline may tend to vapor lock. Some cars are less likely than others to vapor lock because of better design of the fuel system. The tendency to vapor lock is reduced by shielding the fuel lines, fuel pump, or carburetor from the hot parts of the engine so as to lower the temperature of the fuel. In some cars it is possible to move the fuel lines to more favorable locations.

(c) Effect of Volatility on Engine Warmup: The length of time required for the engine to warm up has been found to be closely related to the overall volatility of the fuel. Slow warmup is characterized by irregular engine performance and poor acceleration. On cold days, even with a well balanced gasoline, it is necessary to operate a car for several minutes before it is warmed up enough to give satisfactory performance. Until the manifold and cylinders become warm the gasoline is insufficiently vaporized so that a large proportion of it reaches the cylinders in liquid form. The liquid fuel is unevenly distributed to the cylinders so that some of the cylinders have too lean a mixture. Also some of the fuel may not vaporize in time to become effectively mixed with the air before ignition. As a result the mixture in a cylinder may be so lean that misfiring will occur, or some combustion may take place so late that it is not effective in producing power. Consequently some fuel is wasted during warmup. The temperature at which 50 percent has evaporated is a good indication of the average warmup characteristics of a gasoline. A gasoline with a mid-boiling point above 260°F will not give satisfactory cold weather warmup. Some engineers believe that the 50-percent point of a gasoline should not exceed 240°F.

(d) Volatility in Relation to Crankcase Dilution and Engine Deposits: A fuel that has satisfactory starting and warmup characteristics may be of poor quality with respect to formation of engine deposits and dilution of crankcase oil by high-boiling components. Especially when the cylinder walls and manifold are cold the fractions of a gasoline that boil at a high temperature may become vaporized so late that they do not burn completely. Incomplete combustion tends to increase the deposits of carbon and varnish on the pistons, cylinder heads, etc. Some of the liquid fuel dissolves in the oil film on the cylinder wall, and the diluted lubricant is then carried into the crankcase. Modern cars have provision for ventilation of the crankcase, which tends to prevent this dilution from reaching the point where the viscosity of the lubricant is dangerously lowered. However, a substantial amount of dilution may accumulate during city driving especially in cool weather. Then, if the car is operated under conditions which raise the oil temperature, this accumulation may be evaporated, with the consequence that the oil level may be lowered to a dangerous extent.

The property of the gasoline which gives an indication of its content of high-boiling components is the 90-percent point. While petroleum engineers are not in general agreement as to the maximum satisfactory 90-percent distillation temperature for gasoline, the limit set by current Federal specifications is 365°F.

3. Undesirable Constituents of Gasoline

The most important of the harmful constituents that may be found in gasoline are gum and sulfur. Gum may cause valves and piston rings to stick and become inoperative. Gasolines ordinarily available at filling stations do not contain objectionable amounts of gum, but they may contain some constituents which change to gum if the gasoline is stored for an extended period of time. It is usually possible to retard gum formation from these compounds by use of inhibitors. However, when a car is to be out of service for a period of several months the fuel system and tank should be completely drained, because the inhibitors lose their effectiveness after a time.

Sulfur is almost always present in crude oil and in gasoline. It may occur as elemental sulfur, as hydrogen sulfide or as sulfur-containing organic compounds. Oxides formed by combustion of sulfur compounds combine with water to form corrosive acids. Since water makes up a considerable part of the combustion products, these acids of sulfur are readily formed, particularly when the water condenses in a cold engine. These acids may attack exposed bearing surfaces, rings, pistons, and cylinder walls.

When there is no condensation of water on the cylinder walls or in the crankcase, corrosion is not serious; while with water present some corrosion takes place even without sulfur in the fuel. Water collects normally in cold weather and particularly when an engine is often stopped and started. Crankcase ventilators reduce or prevent collection of water, and aid in expelling water already collected.

It is clear therefore that under many operating conditions fuels relatively high in sulfur might be used with impunity but there are types of service in which such fuels may seriously damage an engine in a short time. An engine kept in a heated garage during cold weather requires less time to warm up and hence is exposed for a shorter time to condensation of water and acid formation. Federal specifications limit the amount of sulfur in gasoline to 0.25 percent, and most gasolines sold to the public contain considerably less than that amount.

4. Other Characteristics of Gasoline

Two of the important properties of motor gasoline are the heat of combustion (Btu per gallon) of the liquid fuel and the heat of combustion per unit volume of the explosive mixture. The former is proportional to the total amount of work which can be obtained from a gallon of fuel, the latter to the motive power which can be produced by a given engine. However, these factors can usually be neglected in comparing motor gasolines for the reason that the heats of combustion per gallon of hydrocarbons in the gasoline range are substantially alike, and the heats of combustion of the air-fuel mixtures, formed from them, are even more nearly the same.

Other properties of gasoline, such as color, odor, and staining on evaporation have little or no bearing on the quality of the fuel.

Half a century ago, when gasoline and other petroleum products were produced mainly by fractionation from a single type of crude, the gravity of a gasoline served as a suitable index of its volatility. With the use of crudes of different types and the introduction of cracking and other refining processes, the chemical composition of gasolines became more diverse and gravity now affords little if any information concerning the quality of gasoline.

At all ordinary atmospheric temperatures (including outdoor temperatures in winter) an exposed surface of gasoline will give off sufficient vapor to form an explosive mixture with air. The vapor mixed with air may spread out along the floor or ground or be carried by a draft for a considerable distance to a source of ignition. The vapor or vapor-air mixture may be easily ignited by a static or frictional spark or a small flame. For these reasons gasoline is potentially a very hazardous material. It should not be used as a dry cleaning solvent or for cleaning floors, woodwork, machine parts, or motors because in such applications relatively large surfaces of gasoline are exposed and large quantities of vapor are given off, thus causing a high degree of hazard from fire or explosion. Other solvents, such as dry cleaners' naphtha, although combustible, offer much less hazard from fire or explosion unless the solvent or parts being cleaned are heated above ordinary atmospheric temperatures. Gasoline should not be used to start fires because the vapor given off may spread the fire to undesired locations or form an explosive mixture with the air.