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MOTOR GASOLINE

This letter circular has been prepared to facilitate the handling of inquiries to the National Bureau of Standards about motor gasoline. It is based on the experience gained in the development of standard testing techniques for gasoline and summarizes information not generally available in a single source.

Gasoline is composed essentially of a class of compounds known as hydrocarbons. 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. Because crude petroleums vary considerably in composition, it may be seen that gasolines 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 final products are still more complex. 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. 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. The spread between the two ratings measures the sensitivity of the fuel to the severity of test conditions. The relative severity of the operating conditions of an automobile engine determines whether the higher research octane number of the more sensitive fuels will indicate improved antiknock performance.

The most important of the engine design factors influencing the tendency of gasoline to knock during combustion is the compression ratio of the engine. Increasing the compression ratio improves engine efficiency but also subjects the charge to higher temperatures and pressures, requiring fuel or higher octane number for knockfree performance. The average ratings of gasolines have increased about 15 octane numbers since 1930. This has permitted the average compression ratios of automobile engines to be increased from 5.15:1 to 7.87:1. This corresponds to an increase in efficiency of about 35%.

Many of the cars now in service will give adequate antiknock 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 that, 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 intake 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 heat transfer. 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.

The volatility of the gasoline is an important factor in satisfactory engine performance. Enough of the lower-boiling components of a fuel must vaporize to form an explosive mixture in the cylinder before a cold engine can be started. However, if there are too many low-boiling components in a gasoline, there will be a tendency for the fuel to 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 be started again. 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 1954, and winter of 1953-1954.

Table I

Boiling Ranges of Average Gasolines

Percent Evaporated	Temperatures, °F Summer 1954 Regular	Summer 1954 Premium	Winter 1953-1954 Regular	Winter 1953-1954 Premium
Initial	99	100	91	91
10	133	130	120	119
50	230	221	223	211
90	342	339	336	333
95	370	367	365	362
End Point	407	406	405	402

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 distillation temperatures for summer gasolines are somewhat higher than those for winter gasolines, and that the differences between regular and premium gasolines are largest 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. 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 pounds air per pound 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 requied to furnish a readily ignitable mixture of air and fuel vapor when the engine is cold. 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 10-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. Gasoline with a 10-percent point of 104°F will start at temperatures of about -22°F; if the 10-percent point is 176°F, the minimum starting temperature approximately +23°F.

(b) Effect of Fuel Volatility on Vapor Lock: Experience has made it possible for oil refiners to supply gasoline that will not vapor lock in the average automobile except under extreme and unexpected conditions. It has been found that there is a definite relation between the vapor pressure of the fuel and the atmospheric temperature at which vapor lock will occur. 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 the summer averages about 8 lb/in.^{2}, whereas in winter the average is about 10.5 lb/in.^{2}. It is apparent that if there is very warm weather during the winter months, cars supplied with highly volatile gasoline may tend to vapor lock. The tendency to vapor lock may be 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.

(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 not evenly distributed to the cylinders so that some of the cylinders receive a mixture that is too lean. As a result a misfiring will occur, or combustion may take place so slowly 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.

(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 becoming excessive. However, a substantial amount of dilution may accumulate during city driving especially in cool weather. Then, if the car is operated under conditions that raise the oil temperature, this accumulation may be evaporated, with the consequence that the oil level may be lowered. The property of the gasoline that 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. To retard gum formation from these compounds, inhibitors are added at the refinery.

Sulfur is almost always present in crude oil and in gasoline, and may occur as elemental sulfur, as hydrogen sulfide or as sulfur-containing organic compounds. Combustion of sulfur compounds gives oxides of sulfur which 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, and 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 accumulation of water, and aid in expelling water already collected. Under many operating conditions fuels relatively high in sulfur may be satisfactory but there are types of service in which such fuels may seriously damage an engine. 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 other important properties of motor gasoline are the heat of combustion (Btu per gallon) of the liquid fuel and the heat of combustion per 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 gasolines 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 its quality as 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 and at that time, volatility was considered the most important property of gasoline. 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 overall 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 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 is dangerous to use it to start fires, 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. Other solvents, such as dry cleaners' naphtha, although combustible, offer a much lower hazard from fire or explosion.

Most gasolines contain tetraethyl lead, which is added to improve the knock rating. Prolonged or repeated exposure to leaded gasoline may lead to lead poisoning.

Many brands of gasoline contain other additives besides tetraethyl lead and gum inhibitors. These materials may be effective to varying degrees in accomplishing specific purposes, such as prevention of stalling under certain conditions, decreasing spark-plug fouling, prevention of rusting of fuel systems, decreasing the catalytic effects of metal surfaces in formation of gum, and others.

More complete information concerning tests on petroleum products may be found in "Compilation of Standards on Petroleum Products and Lubricants" and "Significance of Tests of Petroleum Products", which are for sale (at $6.00 and $1.25, respectively) by the American Society for Testing Materials, 1916 Race Street, Philadelphia 3, Pa.. All technical phases of the petroleum industry are briefly described in "Fundamentals of Petroleum", for sale at $1.25 by the Superintendent of Documents, Government Printing Office, Washington 25, D. C..