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GOOD GASOLINE

When gasoline was a by-product mainly from Appalachian crude oils it was tested and sold on a basis of density or Baume gravity. When a wider variety of crudes became available and it became profitable to put into gasoline for motor car fuel as wide a range of volatilities as the trade would accept, the Engler distillation test was generally adopted and standardized by the American Society for Testing Materials. This has largely displaced the gravity test as an index of gasoline quality although "gravity" is still occasionally used and usually misinterpreted.

It was not until about 1920 that any serious and systematic effort was made to determine what gasoline for use as a commercial automobile fuel ought to be. It is sometimes a long step, from a knowledge of what a product ought to be, to a specification including instructions as to how it shall be tested.

Gasoline is a complex, not a simple material. It is made up of an indefinite number of compounds known as hydrocarbons derived from petroleum. These compounds differ not only in volatility, or the ease of evaporation, but in other properties as well, notably in their tendency to knock when used in high compression engines or when too much carbon is present. The final product, gasoline, has different properties depending upon which of the various compounds are present and in what proportions. And this again is affected by the nature of the crude oil from which the gasoline is refined. Moreover, at present the crude sources of gasoline include not only the natural crude oils but crudes produced by any one of several cracking processes, which produce oils differing from any of the natural petroleums and from each other. It is obvious therefore that gasolines which can be produced and marketed on a commercial basis will differ radically in composition in different parts of the country and at different times.

Specifications are often so drawn as merely to identify some particular product known to be good rather than to define all and only such products as will give good service. However, if cost is to be kept down, one must leave all possible leeway for the use of different products, in specifying the qualities of gasoline. Therefore only those tests should be included in the specifications which relate directly to the behavior of the gasoline in service. The early gasoline specifications were not so drawn. They contained some tests which did not relate at all to use, and others whose relation to behavior in service was not well known. For the past fifteen years the National Bureau of Standards in cooperation with the automotive and petroleum industries has been studying the behavior of gasolines of all sorts in engines of different kinds, in the laboratory and on the road and has found out much about what is required of a good gasoline.

Of these requirements the most obvious is volatility or the ease with which the fuel is evaporated. Volatility is usually tested by distillation of the fuel under standard conditions which are fully described by the American Society for Testing Materials. After several years' work on the subject, this test has been so well related to performance of the fuel in the engine that, given the requirements of the engine, the desired volatility can be determined by the laboratory test. The next question therefore is, what does the engine require of a fuel in order that it may perform properly under all sorts of conditions?

The main items in this catalogue of requirements are somewhat as follows:

(1) The engine must start. To be sure, the oil and the battery and the starting motor have much to do with this, but we are discussing fuel and must assume that these other elements are in order. To start an engine requires that enough of the fuel vaporize at the existing temperature to form an explosive mixture. Since only the lighter fractions of the gasoline will vaporize at starting temperature, and since the lower the temperature, the less will vaporize, excess fuel must be added to supply enough of the lighter portions to produce an explosion.

It has been found that a well designed choke mechanism will enable the carburetor to supply for starting a mixture of about 1 pound of fuel per pound of air, i.e. from 12 to 15 times the normal amount of fuel. A long series of careful tests has shown how to determine with some accuracy the temperature at which any given fuel will start, assuming a 1 to 1 mixture ratio as noted above.

Incidentally the method of measuring the starting ability of a gasoline, as well as its temperature of complete evaporation which will be discussed next, is the standard A.S.T.M. distillation test referred to above which is almost universally used in this country for measuring the volatility of gasoline. (See 1938 Supplement to Book of A.S.T.M. Standards, or Federal Specification VV-L-791a).

When the test is applied to a gasoline and the temperature at which 10% is distilled, together with the percentage distillation loss, is determined as explained in the test procedure, the starting temperature can be computed with sufficient accuracy from this 10% temperature corrected for loss.

Table 1 gives the practical starting temperature for a series of gasolines determined in this way. From this it is shown that different grades of gasoline well may be used at different seasons of the year. In January or February a gasoline with 10% off at 104° or 122°F might be desirable whereas in July one with 10% off at 176° might be preferable. The latter might be cheaper and certainly would be less liable to vapor lock, which we will discuss later. Losses in storage would also be much less for the 176° gasoline.

Table I

10% A.S.T.M.		Starting Temp.
°C	°F	°F
40	104	-22
50	122	- 9
60	140	1
70	158	12
80	176	23

(2) 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 in about the correct proportions. 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 contact with the hot cylinder wall during compression of the charge before ignition. Hence under ordinary running conditions little if any liquid should remain at the time of ignition.

What little gasoline may remain in the form of droplets suspended in the air at the end of the compression stroke is probably vaporized and burned during the power stroke. However, if the cylinder walls, with their film of lubricant, are too low a temperature, liquid particles striking them will be dissolved in the oil film, or, under extreme conditions, fuel vapor may be condensed on the walls. The oil thus diluted in the cylinder is interchanged with oil in the crankcase by the reciprocating action of the piston and thus dilutes the crankcase oil.

A good gasoline must vaporize in the manifold sufficiently to avoid too much crankcase dilution and to give good distribution of the fuel to the different cylinders. Before crankcase ventilators and other devices for removing fuel from the oil in the crankcase became common, the limit in use of heavier or less volatile fuels was set by crankcase dilution. This may not be so at present but, in any case, experience has shown that for practical purposes a fuel is not satisfactory if too much of it remains unvaporized, nor is it entirely satisfactory if too volatile and therefore vaporized too readily.

For a long time the usual gage of volatility in respect to the completeness of evaporation was the "end point" of the distillation. It was shown, however, some years ago that this is not at all a good measure of volatility, but that the temperature of the 90% point of the distillation is a much better and more satisfactory measure. In fact it would be better to omit the end point entirely from specifications as it is both inaccurate and misleading.

Table II gives the dew points, which are the same as the temperatures at which all of the fuel would evaporate, in a mixture of 16 pounds of air per pound of fuel. This is a somewhat leaner mixture than is commonly used in an engine, but the temperature given would permit almost complete vaporization of the fuel in the usual mixture.

Table II

90% A.S.T.M.		16-1 Dew Point	
°C	°F	°C	°F
120	248	3	37
140	284	17	53
160	320	31	88
180	356	45	113
200	392	59	138
220	428	73	163

The sample marked 200°C (392°F) represents the current Federal specification limit for United States Government motor gasoline. This gasoline would vaporize completely at 138°F in a 16 to 1 air fuel ratio. Experience in service has shown this to be a fairly satisfactory motor fuel. Almost all gasolines throughout the country meet this requirement, and it appears to be a good limit to set for ordinary motor fuel which is not intended for use under specially adverse conditions.

(3) A gasoline should not be too volatile, since it may cause vapor lock. Vapor lock is caused by the boiling of the fuel in the gasoline line or the carburetor and often results in stopping the engine, after which one must wait for the fuel to cool down before starting. Vapor pressure is the property of a gasoline which determines its tendency to boil in the fuel line or carburetor and hence cause engine stoppage due to vapor lock. The higher the vapor pressure, the greater is the possibility that vapor look will occur.

Vapor pressure is measured by the Reid method developed by the American Society for Testing Materials (ASTM method D323-38T), and extensive investigations have shown that vapor lock difficulties will not usually occur if the Reid vapor pressure of the gasoline is kept below the values shown in Table III.

Table III

Atmospheric Temperature, °F	Reid Vapor Pressure, lb/in.^{2}
100	8
85	10
75	12

In the early days, trouble from vapor lock did not often happen, since there was a dearth of volatile fractions in most gasolines. Within recent years, however, cracking processes and recovery of natural gas gasoline has changed the situation and precautions are needed to avoid having too large a percentage of volatile fractions in the gasoline. Specifications on vapor pressure are used as a means of avoiding vapor lock and the limits are varied from place to place and from time to time, in accordance with climatic conditions. Thus in many of the Northern states a vapor pressure of 12 pounds is permissible in winter, but the mid-summer limit may be 8 pounds. In the Canal Zone, however, an 8 pound limit applies the year around. For high altitudes, the vapor pressures given in Table III should be decreased approximately one pound per three thousand feet, since the gasoline boils more readily at altitude than at sea level.

(4) The air-fuel mixture in the cylinders should burn smoothly without objectionable knocking or detonation, even when the vehicle is accelerating or climbing a hill.

The relative tendency of gasolines to knock in internal combustion engines is evaluated by comparing them in a standard test engine with blends of two pure hydrocarbons: normal heptane, which knocks more readily than any gasoline, and iso-octane, which has less tendency to knock than any commercial gasoline. The percentage of iso-octane which must be blended with normal heptane to match a given gasoline in the knock-test engine is known as the octane number of the gasoline.

Fuels for automobile engines are rated according to the current revision of ASTM method D357-33T. (See Method 600.11 in Federal Specification VV-L-791a). Blends of secondary reference fuels, which have been calibrated in terms of the octane-number scale, are generally used in place of the primary reference fuels (normal heptane and iso-octane). The test engine and procedure specified were developed over a period of years by the CFR Sub-Committee on Methods of Measuring Detonation(now called the CFR Motor Fuels Division), which comprises representatives of leading automotive and petroleum laboratories and of the National Bureau of Standards.

Most regular (i.e. competitive-price) gasolines today have knock ratings between 70 and 72 octane number. Gasolines of higher knock rating usually command a premium, while the cheaper third-grade gasolines may have ratings above 65 or below 50 octane number in some localities. For most Government purchases of motor fuel a minimum knock rating of 68 octane number is specified, but for some purposes the minimum is raised to 75 octane number. The Federal specifications for United States Government motor gasoline (VV-G-101a) contaian no octane-number requirement.

The octane-number requirement of any particular automobile depends on engine condition and type of service as well as on engine design. The requirement is highest at sea level and decreases with altitude at the rate of three to four octane units per thousand feet. Retarding the spark decreases octane requirement on the average about two units per degree. The octane requirement of a new car may increase with mileage fifteen units or more, due chiefly to the accumulation of carbon.

If an automobile engine knocks on regular gasoline, the knock can be eliminated either by retarding the spark or by using fuel of higher octane number. Since knock and a retarded spark both tend to reduce engine power, the use of premium-price gasoline in such an engine may show a slight gain in power and in miles per gallon of fuel. In the case of automobile engines which do not knock objectionably on regular gasoline at the normal spark setting, no improvement in vehicle performance can be expected from the use of premium-price gasoline due to its higher octane number.

Since the adoption of the present method of knock rating in 1932, the average rating of regular gasoline has increased only from 65 to 71 octane number but the average compression ratio of automobile engines has increased from 5.3 to 6.3. This represents a very significant increase in the power and economy of automobile engines, made possible in large measure by the control of the knock characteristics of the gasolines marketed by the various oil companies.

(5) One other purely physical property of fuels is included in most specifications, viz., the 50 percent point of the distillation curve. Careful tests have shown that this point is of much less importance than the 10 percent and the 90 percent point, but being of some value as an index to the general behavior of a gasoline in the warming up period it may well be included in any general specification for gasoline.

(6) Occasionally a sample of gasoline is found to leave a deposit of gum on intake valve stems and in the intake manifold. Avoidance of this within recent years has required special refining processes and the use of inhibitors to prevent gum formation in the gasoline between the time it is refined and the time it is used in the engine. These precautions are necessary due to the large use of cracked gasolines which are more liable to form gum unless specially treated when refined.

The test employed for the gum content of gasoline has been developed by the American Society for Testing Materials, and many specifications for gasoline place limits on the gum content as determined by this method. (ASTM method D381-36).

(7) One foreign element almost always present in crude oil and in gasoline is sulphur. This may occur as sulphur in solution or as any one of several sulphur compounds. Two sorts of damage are chargeable to sulphur, (a) corrosion of fuel lines and fittings and (b) corrosion in the crankcase.

Corrosion of fuel lines (a) is not common as nearly all gasoline is refined to meet the copper strip corrosion test. Like the other tests mentioned above this has been standardized and is described in the U. S. Government specifications as well as by the American Society for Testing Materials. It is a part of the Federal specifications and should be included in any other specification for motor gasoline.

Corrosion in the crankcase (b) is a much more insidious and serious fault when it occurs. When sulphur is burned along with the fuel it forms SO_2 some of which leaks past the piston rings and, combining with water when present in the crankcase, forms corrosive acids. The acid attacks any exposed surfaces, particularly bearing surfaces, in the colder parts of the crankcase where moisture condenses.

When there is no condensation of water in the crankcase corrosion is not serious while with water present probably some corrosion takes place even without sulphur in the fuel. Water collects normally in cold weather and particularly when an engine is often stopped and started. A four cylinder engine is less subject to water in the crankcase than a six or an eight cylinder engine because with four cylinders the air in the crankcase is partly displaced at each stroke, which is not the case with the other designs. Crankcase ventilators and other devices reduce or prevent collection of water.

It is clear therefore that during most of the time fuels high in sulphur might be used with impunity but there are times when such fuels may practically destroy an engine in a few weeks.

Federal specifications require that total sulphur be not more than 0.10 percent which seems to be a safe limit. This limit probably should be retained in any specifications applying to gasoline for cold weather use, and may be desirable for all gasolines, at least until reliable data are obtained showing that the limit can be safely raised.

Other tests such as color, odor, gravity, staining on evaporation, etc., which have been used, appear to bear no direct relationship to engine requirements, other than as possible indices of qualities already discussed.

Two of the most important characteristics of motor fuels have been omitted entirely from the foregoing discussion as they are omitted from usual specifications. These are the heat of combustion in Btu per gallon or calories per liter 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 per gallon of fuel, the latter to the motive power which can be produced by a given engine.

The reasons that these two important factors can be neglected in specifications are that the heats of combustion per gallon of hydrocarbon in the gasoline range are substantially alike, and that the heats of combustion of the air-fuel mixtures, formed from them, are even more nearly the same. If alcohols or blends containing them were to be considered the heat of combustion of the liquid would need to be specified, but even here the heats of combustion of the air-fuel mixtures are substantially the same.

Present government specifications which are met by the average motor gasoline on sale embody the principles discussed above in so far as the necessary tests have been developed and generally accepted. Accepted test methods have been the result of long continued development, and modifications of them or the substitution for them of other and better methods must necessarily also be gradual. Much is being done by the research laboratories of the Government, as well as by those of the petroleum and automotive industries toward the better realization of the ideal specification for motor fuel.

The following specifications are at present used by the Federal government for the purchase of gasoline:

Federal Specification VV-G-101a for United States Government Motor Gasoline.

Federal Specification VV-M-571a for Motor Fuel V.

The methods of test for gasoline, as well as for other petroleum products, may be found in Federal Specification VV-L-791a. Most of these test methods are identical with those developed by the American Society for Testing Materials and published periodically in the Book of A.S.T.M. Standards. Recently the A.S.T.M. has also developed specifications for gasoline, as a guide to municipalities in the purchase of suitable motor fuel.