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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, as you know, 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 six years the Bureau of Standards 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 those 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 in an engine 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 vaporized 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 A.S.T.M. Book of Standards, 1927, or Bureau of Mines Technical Paper 323B, or current revision thereof.

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 at 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 entirel 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 measure, in fact a very satisfactory one. This is the point therefore which is stressed in the Federal Specification and should be so in any specification. In fact it would be better to omit the end point entirely 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. 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. The average gasoline throughout the country meets 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 gaseline 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 lock will occur.

Table 3 gives the gas-free vapor pressures in pounds per square inch for a series of gasolines when heated to a temperature of 100°F. The lightest of these gasolines will almost boil at this temperature.

Table III.

| 10% A.S.T.M. | | Vapor Pressure 100°F | |
|---|---|---|---|
| °C | °F | mm | lb./sq.in. |
| 40 | 104 | 720 | 13.9 |
| 50 | 122 | 545 | 10.5 |
| 60 | 140 | 415 | 8.0 |
| 70 | 158 | 310 | 6.0 |
| 80 | 176 | 235 | 4.5 |

The vapor pressures of gasolines, excluding those undesirable fuels which are not properly stabilized, is related to the 10% point in the distillation test. In fact, trouble from vapor lock will almost certainly occur if the temperature of the gasoline in the fuel lines exceeds the 10% point temperature.

Formerly this trouble did not often happen, since there was a dearth of volatile fractions in most gasolines. Of late cracking processes and increased recovery of natural gas gasoline have changed this. At present volatile fractions are plentiful and gasolines are often too "good" at the 10% point. To avoid trouble from vapor lock the Federal Specifications Board has included a lower as well as an upper limit to the 10% point of Government gasoline. This appears to be the best solution of the difficulty. It is not wise to make the lower limit too high as this would limit competition and raise the price. There is hardly any need of a lower limit in winter unless one forgets to open the radiator shutters.

In specifications like those of the U. S. Government which apply to Government purchases throughout the country at all times, these limits must be as wide as possible to meet all conditions without limiting competition. Some discretion is left to the purchasing officer as will appear when the detailed U. S. specifications are considered. Where purchases are made locally under specifications which can be modified at will to meet local or temporary conditions it may be desirable to require different limits for the 10% point under different climatic or operating conditions.

(4) But for the tendency of fuels to knock or detonate when the compression ratio is raised, much more power and better economy could be had in automotive engines.

It is only within the past 4 or 5 years that this subject has been given much attention and even yet we have no uniform and generally accepted test for the rating of fuels in this regard, as we have for volatility. As a result there is much confusion in the industry and among users of fuels as to relative qualities of different fuels on the market.

Broadly speaking there are four classes of fuels on the market which are better than straight distillate gasoline from Appalachian crude oils in knock rating; these are (a) California and west coast oils which are high in aromatic compounds, (b) cracked gasolines, particularly vapor phase cracked products, (c) blends of gasoline with benzol and other coal tar derivatives and (d) blends with tetraethyl-lead. Classes (a) and (b), particularly the latter, may rate anywhere between wide limits. Classes (c) and (d) on the other hand can be accurately controlled by the producers and in general are kept to a rather definite standard; this is particularly true of class (d).

While the knock characteristics of fuels are perhaps as important as any of the other items noted, there is at present no accepted means of defining or specifying the knock rating. However a group of interested parties is very actively studying the problem and experiments are being made jointly in a dozen different laboratories from which it is hoped that a rating system soon will be decided upon.

The only means so far found of measuring fuel knock is to test it in an engine, and the plan of the group working on the problem is to devise a standard engine and a standard test procedure for this purpose. An experimental engine has been designed and supplied to all the laboratories concerned.

Until an acceptable standard method of knock rating is found it is best to postpone any specifications for the knock characteristics of fuels.

(5) One other purely physical property of fuels is included in the Federal 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) Rarely a sample of gasoline is found to leave a deposit of gum on intake valve stems and in the intake manifold. This fault has become somewhat more common of late since cracked gasolines, which are more liable to form gums, have been increasing in amount. This is a fault which should be avoided. The "copper dish" test, described in Bureau of Mines Technical Paper 323B is commonly used to measure gum-forming tendencies of gasoline. This test is not very satisfactory. Some gasolines which deposit gum in the test give no trouble in the engine. It is a fairly safe test, however, in that gasoline which passes is not likely to give trouble. This test is not included in the Federal Specification for motor gasolines, but is included in those for aviation gasolines. Much work is being done by several laboratories toward devising a better test for gum formation and more satisfactory test methods are under development.

If trouble is experienced from gum formation the copper dish test may be adopted until a better test is developed.

(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. 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. The cause was definitely discovered only a few years ago. 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.

The Government requires that total sulphur be not more than 0.10 percent which seems to be a safe limit. This limit certainly should be retained in any specifications applying to gasoline for cold weather use, and probably is best for all gasolines, at least until reliable data are at hand to show 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.

If gasoline is to be purchased on specification it is believed that the present Federal specifications adopted last September are a reasonably satisfactory basis for such purchase. Copies of these specifications can be secured from the Federal Specifications Board, Washington, D. C.

Figure 1 gives the distillation limits for U. S. Motor gasoline when the temperatures are plotted against the per cent evaporated, assuming an average distillation loss. The upper full line and the lower full line at the 10 per cent point represent maximum and minimum limits. Between these, as indicated by the dotted lines, a certain amount of discretion is allowed to the purchaser to meet climatic conditions.

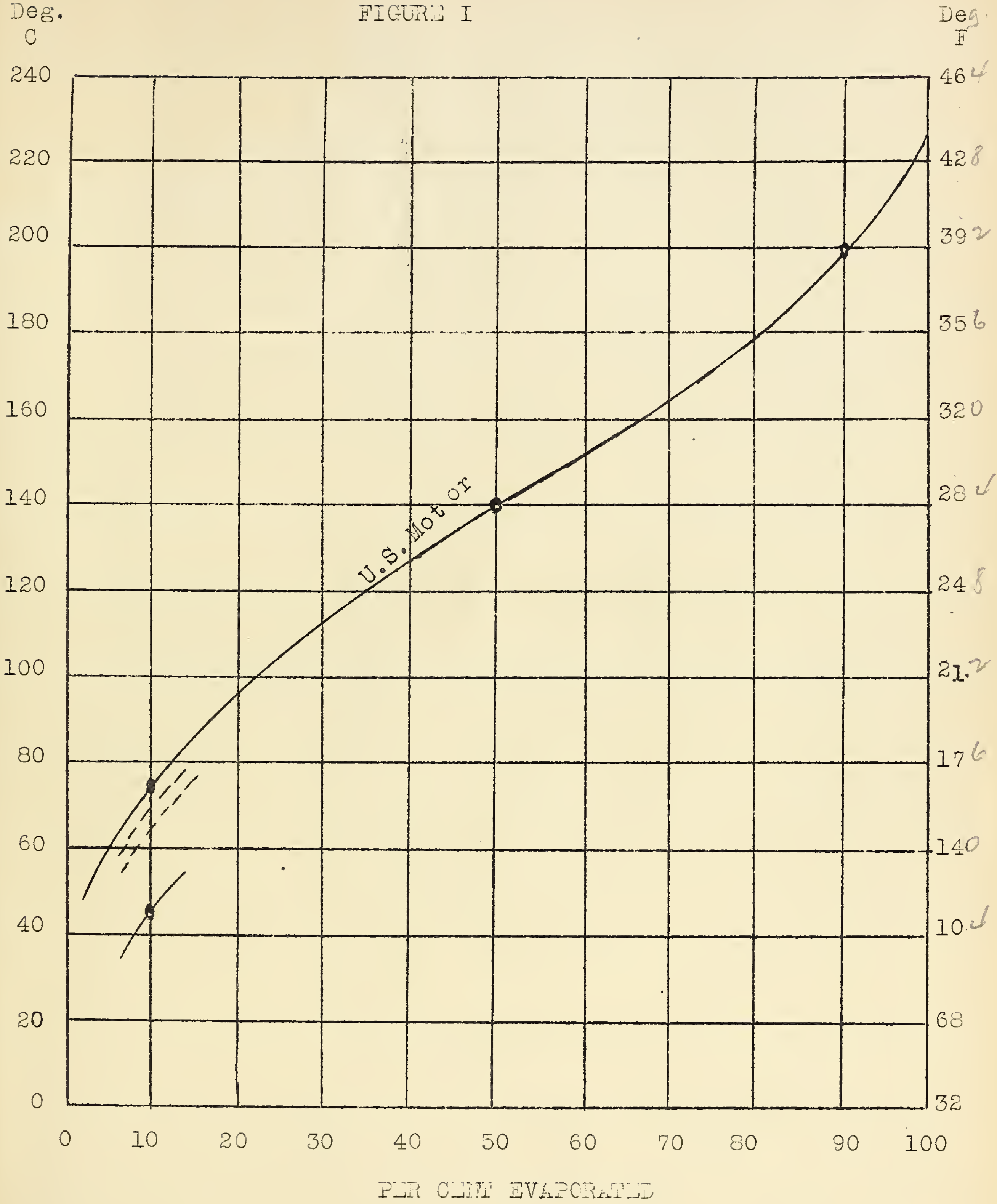
It may be well to take account of atmospheric temperature when making purchases locally for immediate use. Thus when freezing temperatures or lower are to be expected the upper limit at 10 per cent evaporated well may be fixed at 149°F, although it is not desirable to reduce the upper limit for fuels to be used in summer weather.

On the other hand, for fuels subject to long storage at high temperatures, the lower limit at 10 per cent evaporated may well be raised to 131°. This limit, however, should not be set unless conditions require it, because gasoline purchased on this basis may not start as readily as would otherwise be the case.

If a special high test gasoline is to be purchased on specification for such purposes as operation of fire apparatus, ambulances and emergency vehicles in cold weather, a special grade of gasoline, Motor Fuel V, is provided for in the Federal specifications.

As for the anti-knock characteristics of gasolines, as noted above, no satisfactory basis for specification exists at present. If the grade of straight gasoline procured does not knock, no improvement in operation of the vehicle is to be expected from the use of special anti-knock gasolines of like volatility, although there may be increased satisfaction in the use of the latter. On the other hand, if serious knocking occurs with ordinary gasoline, there should be a gain in mileage and in horsepower and a saving in up-keep cost by the use of fuels having better anti-knock qualities. Since the need for anti-knock gasolines varies widely with the type of equipment and the conditions of operation the user must determine whether the added advantages justify the increased cost under any particular set of circumstances.

FIGURE I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