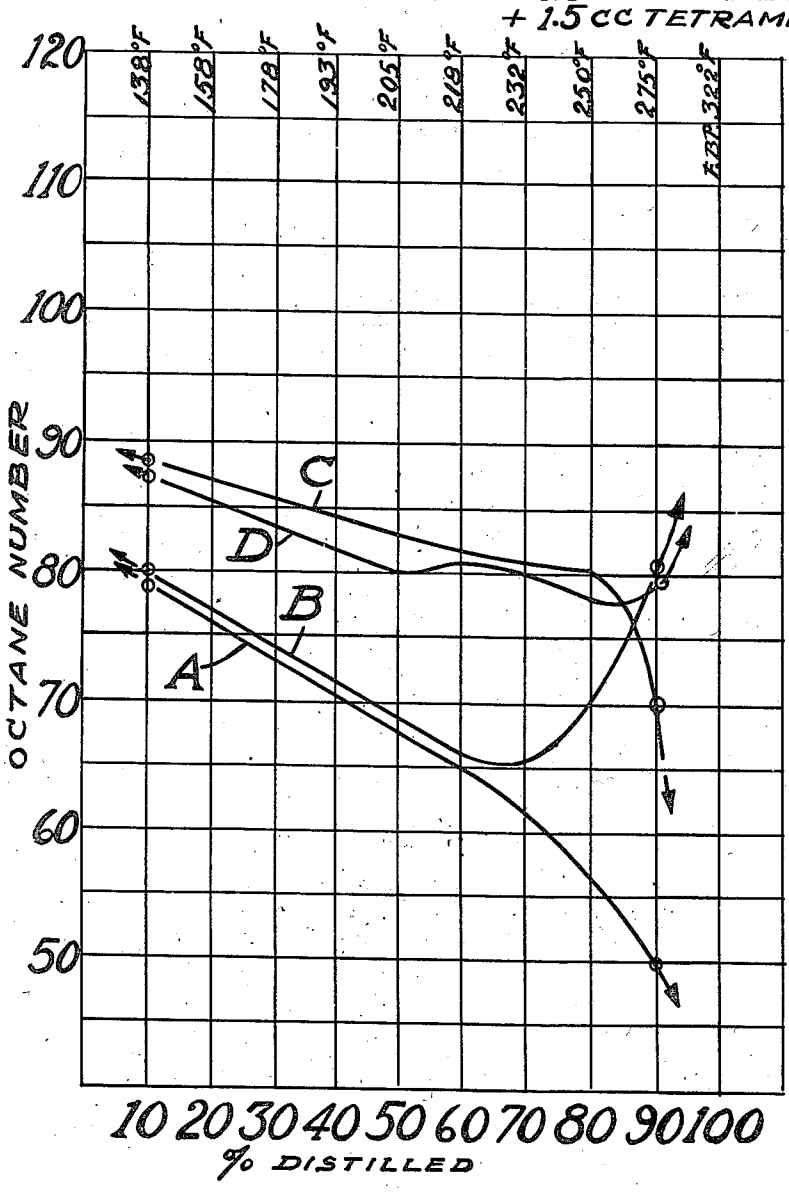
Feb. 9, 1943. W. H. SMYERS ET AL 2,310,376

MOTOR FUEL

Filed Aug. 15, 1936

A GASOLINE BASE-INITIAL BP-99°F; 95%-302°F; FBP-322°F
B " " + 3 CC TETRAETHYL LEAD
C " " + 3 CC TETRAMETHYL LEAD
D GASOLINE BASE + 1.5 CC TETRAETHYL LEAD
+ 1.5 CC TETRAMETHYL LEAD



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MOTOR FUEL

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2 Claims. (Cl. 44—69)

The present invention relates to improvements in motor fuels and more specifically to motor fuels of higher and more uniform anti-detonation qualities. The invention will be fully understood from the following descriptions:

The drawing is a diagram showing the octane numbers of different fractions of fuels free of and containing certain anti-knock agents.

For many years it has been understood that various low boiling hydrocarbons, for example, the aromatic, naphthenic and paraffinic hydrocarbons, are characterized by different anti-detonation qualities when used as fuel in internal combustion engines, particularly those using high compression ratios, and at the same time there has been a considerable use of anti-detonation agents to increase the inherent anti-detonation quality of the particular hydrocarbons used. Among such materials the best known are the metal alkyls, in particular tetraethyl lead, but others are also known. These materials are added to the motor fuel in relatively small amounts, but they produce a powerful influence on the anti-detonation properties.

It has been observed that anti-detonation agents exert their effects to a greater or less extent depending on the nature of the fuel constituents to which they are added, but aside from this it has also been found that the same fuel frequently operates quite differently in different types of engines; furthermore, that the fuels have different qualities depending on the atmospheric temperature and other conditions. For example, blends containing lead tetraethyl do not show, or show only to a small degree, the qualities at low temperatures in multi-cylinder engines but the anti-detonation effect is much greater at more elevated temperatures. For testing such fuels there is a widely accepted method known as the Cooperative Fuel Research (C. F. R.) test described in the A. S. T. M. bulletin, Committee D–2, September 1934, designation D357–34T. In this test the fuel is used to operate a single cylinder engine under prescribed conditions and it has been found by experience that this test is sufficiently accurate for practical purposes and that various laboratories are able to check each other's results quite closely. It has been found, however, that fuels giving substantially the same rating or octane number according to the C. F. R. method, frequently give quite different results when used in multi-cylinder engines and under actual driving conditions on the road. Present specifications and tests take no account of this anomalous behavior and consequently the automobile driver may find certain gasolines which are alleged to have the same anti-detonation value, and in fact do so according to the C. F. R. test, which however operate quite differently in his car. The one, for example, may knock decidedly, particularly on starting in the cold, whereas another will not knock under these conditions.

After prolonged study it has been found that these anomolies described above are largely due to improper distribution of the fuel among the cylinders of the engine. This is to some extent a matter of carburetor or engine design, but the manufacturer of motor fuel has no control over engine design and is forced to provide a fuel which will operate at its best under the most diverse conditions of design, and one object of the present invention is to adapt a fuel so that it will possess its maximum anti-detonation properties irrespective of the design of the particular car in which it is used, and also under the most diverse operating conditions.

Motor fuels are mixtures mostly of hydrocarbons of widely varying boiling range; for example, they range from about 100° F. to 400° F., containing butane as the lightest and decane or dodecane as the heaviest constituent. In airplane and premium fuels the end point may be as low as 350° F., but in any case there is a wide range in the volatility of the various fuel constituents. In cold weather and on starting, the motor fuel is not vaporized completely and it has been found that the fractions vaporized may, and frequently do vary in anti-detonation quality to a large extent from the unvaporized fractions; for example, in one case a gasoline having an octane number of 66.5 C. F. R. on fractionation gave cuts differing as widely as 47–75 O. N. by the same test.

In multicylinder engines the liquid constituents are not equally distributed among the cylinders and if the anti-detonation quality differs from that of the vaporized portion, it can be readily seen why there is a wide diversity in detonation among the cylinders of a single car or in different cars. Thus, often though the anti-detonation quality of the total fuel may be satisfactory, some of the cylinders may be supplied with fuel which is far below standard and therefore will knock, whereas others may be supplied with fuel of anti-detonation quality far greater than would actually be necessary to prevent knocking under the particular conditions of compression and temperature. Thus the inherent properties of the fuel are often wasted.

The hydrocarbon fractions making up a normal gasoline are derived mainly from the lighter fractions of petroleum and they may be either straight run or cracked or made by polymerization or hydrogenation and the like. In any case, ordinary gasolines are characterized by the fact that the "inherent anti-detonation quality" of the particular fraction varies according to the boiling range, the higher boiling fractions having a greater tendency to cause knock than the lower. It is highly desirable to produce a fuel in which all of the various fractions have substantially the same anti-detonation quality, or at least in which all fractions exceed a specified minimum value which shall be set for particular conditions, principally compression ratios required to operate properly in the engine. It is now the practice to provide two grades of gasoline of higher and lower quality respectively for cars of higher and lower compression ratio, but examination has shown that certain fractions of the low compression fuel have higher O. N. than other fractions of the high compression fuel. It is desired to provide each fuel with a more nearly uniform O. N. throughout all of the fractions of each. While it will be desirable to have exactly the same anti-detonation quality throughout, this is not entirely practical, but at the same time it has been found possible to prepare fuels such that the anti-detonation qualities of the various fractions will be much closer to the average in C. F. R. value than is now the case with fuels containing only one anti-detonation compound.

According to the present invention with the ordinary motor fuel, gasoline in which cracked and uncracked fractions are used, it is desirable to employ a plurality of anti-detonation agents of different volatility. In such a gasoline the total amount of the anti-detonation material need not be more than is customarily used at the present time and the amount of the several separate anti-detonants may vary in proportion to the knocking tendencies of or inversely proportional to the anti-detonation qualities of the hydrocarbon fraction with which they vaporize; that is to say, if, for example, the light fraction has the least tendency to knock, there will be used the lowest amount of the more volatile anti-detonant and increasing amounts of the less volatile anti-detonants. In this way the anti-detonation quality of the fractions actually vaporized can be made much more uniform than where a single anti-detonation agent is used. While it would be theoretically desirable to use a relatively large number of different anti-detonation agents, it has been found for practical purposes that two or three may be used with good results such that no fractions, between the 10 and 95% fractions, will have an octane number more than 10 or even 5 points below the C. F. R. octane number of the total fuel. If two such compounds are to be used in the ordinary type of gasoline, it is found that the more volatile should have a boiling point within the range from 100 to 275° F. under normal pressure and the less volatile one should boil from 120 to 250° F. at 13 m.m. of Hg or approximately 275 to 400 or 425° F. at atmospheric pressure. As stated above, with the usual type of gasoline, the heavier one will ordinarily be used in excess of the lighter, for example, it will comprise three-quarters to one-half of the total anti-detonation agent. The compounds used should differ in boiling points (at atmospheric pressure) by from 75° to 250° F., and this ensures that there will be a substantially uniform distribution of the anti-detonation agents so as to produce a desired result in which the amount of the lead compounds in the vapor are sufficient to maintain a good octane number of these fractions and at the same time to provide enough in the unvaporized residue to produce satisfactory value for these fractions. The total amount of the anti-detonating agent used will depend on the improvement desired and the susceptibility of the fuel to improvements by such anti-detonation agents. Ordinarily from 1 to 3.0 cc. of the metallo alkyls per gallon of fuel are sufficient, but may be increased as circumstances demand, more may be required of less potent anti-knock agents.

The following table gives the names and boiling points of certain lead compounds which may be used in the present fuel composition, but it will be understood that other compounds can be employed, including compounds containing other metals, particularly those mentioned in the paragraph below:

Compound	Boiling point at 13 mm. pressure
	° F.
Tetramethyl lead	45
Trimethyl ethyl lead	84
Dimethyl diethyl lead	124
Methyl triethyl lead	156
Dimethyl di-isopropyl lead	153
Tetraethyl lead	180
Diethyl di-isopropyl lead	203
Tetra isopropyl lead	246

It will be understood that a wide variety of anti-detonation agents may be used, among which may be mentioned the metallo-alkyls and aryl compounds. Among these compounds, the particular hydrocarbon radicals may be varied to change the boiling point of the compound through a wide range. Ordinarily the ethyl compounds will boil from 80 to 140° F. above the methyl compounds of the same metal. Intermediate boiling compounds can be readily produced by using mixed alkyl groups, methyl, ethyl, propyl compounds, and the like. A suitable selection of the alkyl groups can be made to give any desired boiling point throughout the gasoline range. Among the metals that may be mentioned are lead, tin, bismuth, antimony, arsenic, thallium, selenium and tellurium. While simple metallo-alkyls are usually preferred, halo or hydroxy alkyls can also be used.

In the above description the various metal alkyls which can be used have been specified generally, and it will be understood that a judicious selection of these is to be made in producing the combined fuel blending agent. While it is quite desirable to use a mixture of equal parts of tetramethyl and tetraethyl lead, it is usually preferable to substitute somewhat higher boiling compounds for the methyl compound. The following mixtures have been found to be particularly desirable: Equal parts of trimethyl ethyl lead, dimethyl diethyl lead, and tetraethyl lead, particularly for use in the ordinary type of gasoline having an end point of 400° F. or above. For a lower boiling stock for aviation purposes, it is desirable to retain the methyl compound and to substitute a somewhat lower boiling material for the tetraethyl lead, for example, equal parts of the following compounds may be used: Tetramethyl lead, dimethyl diethyl lead, monomethyl triethyl lead. It is found that a somewhat better arrangement may be obtained with even

larger numbers of compounds. In any case where several compounds are to be used, it has been found desirable to adjust their proportions for the particular stock used and it will be different depending on whether the stock is cracked or uncracked and what the lead response of the various fractions happens to be.

Example I

An aviation fuel having an octane number of 66.5 C. F. R. and a boiling range from approximately 100 to 400° F. is carefully distilled so as to collect a large number of separate fractions. The octane numbers of the separate fractions are then determined by the C. F. R. method.

These octane numbers were then plotted on ordinary coordinate paper against the percentage number of the cut. Temperatures in Fahrenheit degrees are plotted along the upper edge of the diagrams. Each of the narrow cuts is represented by its midpoint; for example, a cut consisting of the 25 to 35% cut is plotted on the curve as 30%. A smooth line is then drawn through the points and represents the curve marked "A" on the drawing. There is, of course, uncertainty as to the ends of the curve and the directions are indicated by arrows beyond the 10 and 95% points.

In examining this curve, it will be seen that the octane numbers of the fractions gradually decrease from about 79 O. N. at 10% to about 62 O. N. at 65%, and thereafter rapidly fall off to about 49.5 O. N. at 90%. In the operation of an engine with such a fuel throughout the range of temperature at which there is an incomplete vaporization, some of the cylinders will be furnished with the vaporized material, while others will be supplied with the unvaporized. From the curve it can clearly be seen that the vaporized fractions represent a much higher octane number than the unvaporized fractions. For example, the first 50% of the fuel shows an octane number of 72 as against 57 for the last 50%. From this it can be clearly seen that imperfect distribution among the cylinders can result in the irregular operation which a test in multicylinder engine actually shows. Those furnished with the low grade fuels knock while those of the higher do not. This would be especially noted at low temperatures where a large portion of heavy fractions would not be vaporized but the knocking would disappear where the temperature rose to the point where the fuel is completely vaporized.

In order to determine the effect of tetraethyl lead on such a fuel, 3 cc. were added to a gallon of the same base, and a similar distillation process was carried on just as before, resulting in a large number of separate cuts. The octane numbers in these cuts were separately determined and the results, being plotted on the same diagram, gave the curve marked "B." An inspection of this curve shows that the effect of the tetraethyl lead is almost exclusively shown in the higher boiling fractions. The effect of this material is very pronounced indeed, but in actual engine operation the result is even more marked than would be supposed from the octane numbers alone. The vaporized low boiling fractions will be fed to certain cylinders, and will be in relatively low concentrations, that is, in a lower fuel-air ratio. On the other hand the heavier unvaporized fractions containing the bulk of the lead will be fed to the other cylinders in a relatively rich condition; that is to say, a rich air fuel ratio which is favorable to suppression of knocking. For these reasons the actual performance of the heavier fractions is much superior to that of the lighter ones, even more so than would be accounted for by the presence of the anti-knock agent, and a similar erratic behavior is found in the operation of the engine.

The total fuel will, of course, be much better than the original containing no lead, but at the same time there is a marked difference in the performance of the light and heavy ends, which produces the erratic behavior.

In a third experiment, tetramethyl lead is added to the fuel base to compare with the results of tetraethyl lead. The distillation and determination of the octane number of the separate cuts followed and this data is plotted just as before, giving the curve marked "C" on the diagram. The octane number of the total fuel C is substantially the same as that of the fuel B when tested in the ordinary C. F. R. engine, but the performance is quite different in a multicylinder engine. The lower boiling fractions this time contained almost all of the lead, while the heavier boiling fractions from 80% upward contained a minimum or no lead. While the fuel, as a whole, is a great deal better than the original fuel A, still if there is an incomplete vaporization, as on cold days, and at starting, the unvaporized fuel is much poorer in respect to anti-detonation than the vaporized portion.

In the fourth and last experiment, 1½ cc. of tetraethyl lead and 1½ cc. of tetramethyl lead are added to the fuel base and the distillation and measurement of octane number of the separate fractions are carried on as before. The results are shown in the curve D. It will be noted from the curves that this fuel has a much closer uniformity in respect to octane number of the fractions than any of the others mentioned. The total variation throughout the entire range is less than 15 O. N. and in operation the fuel is markedly superior to the others shown on the diagram. In cold weather, where there is partial vaporization, the octane numbers of the vaporized and unvaporized fractions are both sufficiently high and sufficiently uniform so that no cylinder is supplied with a fuel markedly superior or inferior to the others, and this same condition is maintained as the engine heats up and until complete vaporization is reached. The dip of the curve between 80 and 90% can be corrected, if desired, by supplying instead of tetraethyl lead a compound such as dimethyl diethyl lead or monomethyl triethyl lead which have boiling points that would supply the intermediate fractions from 60 to 90% with a sufficient quantity of lead to offset the depression at that point.

The data of the charts are summarized in the following table:

Fuel	O. N. of the fuel fractions—Different per cent off								
	10	20	30	40	50	60	70	80	90
A	79	76	73	70.5	67.5	65	62	56	49
B	80	77	74	72	68	66	65.5	70	80
C	88	85.5	86	84.5	83.5	82	81	80	70
D	87	85.5	84	82	80.5	81	80	78	79

Studying these curves from another point of view, it will be noted that curve B shows a pronounced dip in the middle. Actually 80% of this fuel falls (10–90%) below the C. F. R. value of 80 O. N. Of these fractions the average is about 9.5 points below 80.

Curve C shows its dip at the heaviest end and about 20% (80–100%) is below the approximate C. F. R. value of 80. The average of these fractions is 16.5 points below.

Curve D shows but a very little below the C. F. R. of 80. These fractions (70–91%) are actually quite close to the 80 value; however being on the average of 1.6 points below.

These experiments show clearly why the latter fuel is superior to the other two, but such comparisons are only qualitative. It is just as important to know what fractions are below average as how much of the total fuel these fractions comprise. It is found, for example, that it is important that the fractions below average be included within the heaviest one-third of the fuel. This indicates a superiority of fuel C over fuel B. In comparing C and D, however, D is much superior because although it contains as great a proportion under average as C it will be noted that such fractions of D are only 1.6 points below the average, while the fractions of C are 16.5 points below C. F. R. average.

Example II

In the following test the gasoline base stock was a premium grade gasoline ordinarily sold and employed for aviation use. To the first sample was added 2.4 cc. of tetraethyl lead; to the second sample was added 2.4 cc. of tetramethyl lead; to the third sample was added 1.2 cc. of tetraethyl lead and 1.2 cc. of tetramethyl lead. The C. F. R. octane numbers were determined on each of these blends and road octane numbers were then obtained in the same cars, under conditions as closely comparable as possible. The data are included in the following table:

Fuel	Road O. N. determined on Buick		C. F. R. Octane No.
	Cold	Hot	
(1) Naphtha+2.4 cc./gal. of tetraethyl lead	72.1	63.8	69.8
(2) Naphtha+2.4 c.c/gal. of tetramethyl lead	70.7	64.4	68.1
(3) Naphtha+1.2 cc./gal. of each	73.3	64.9	67.8

The above mentioned tests, it will be seen, indicate that the C. F. R. octane number of the first fuel is slightly higher than the remaining. This appears to be due to the inherent superiority of tetraethyl lead over tetramethyl lead in respect to the particular gasoline. The road octane numbers show that the first sample containing tetraethyl lead operates quite satisfactorily in the cold. Indeed, it is somewhat better than the second sample containing tetramethyl lead in the cold. This seems to be due to the fact that under these conditions in which air is fed to the carburetor at 20° F., the vaporized portion is endowed with a satisfactory octane number even without the addition of lead. Most of the tetramethyl lead in the second sample is vaporized, and therefore adds its advantage to the vaporized fractions which do not actually require this help. The tetraethyl lead is not substantially vaporized under these conditions and remains, therefore, in the unvaporized fractions where it raises the octane number of the heavy fractions of the first sample noticeably. The second sample is somewhat deficient in this point because of the fact that the tetramethyl lead is almost completely vaporized and the heavy ends do not get the lead that they require.

The third sample containing equal quantities of tetramethyl and tetraethyl lead is more satisfactory than either of the previous samples because a sufficient amount of tetramethyl lead is vaporized to assist the vaporized fractions, and the tetraethyl lead remaining unvaporized is sufficient to improve the octane number of the unvaporized fractions.

Considering the tests under hot conditions, in which air fed to the carburetor is at 100° F., it should be understood that a fairly large portion of the fuel is vaporized. In this case the vaporized fractions include not only the low boiling high octane number fractions, but also a substantial part of the middle fractions which are not endowed with a sufficient octane number to be useful alone. This results in the fact that the second sample shows up considerably better than the first.

Considering these results in detail, it will be apparent that under the hot conditions, sample No. 1 is not totally satisfactory because some portions of the vaporized fractions do not contain a sufficient amount of lead, and they therefore cause knocking when there is improper distribution. The unvaporized fractions however contain a much larger concentration of lead than is required, and a considerable part of this is wasted. In the second test, the vaporized fractions contain a large portion of tetramethyl lead and are quite satisfactory. The heavier fractions in this case do not cause as much trouble as might be expected because of the fact that they cause an over-rich condition in the cylinders to which they are fed, which condition is known to be favorable toward suppression of knock. However, at the same time it will be seen that the third sample shows improvement under hot conditions. In this case tetramethyl lead is vaporized with the lighter fractions, improving their results, just as in the previous sample, while at the same time a sufficient amount of tetraethyl lead remains unvaporized so as to improve the O. N. rating of the unvaporized fractions making them superior to those of sample 2. It will therefore be seen that the third sample is superior to either of the two previous samples.

The operation of the fuel containing the mixed anti-knock agents would be superior to either of the other fuels even if it did not produce a better octane number under hot and cold conditions as it does in these tests; in other words, even if it merely increased the road octane number of the blend so as to equal sample No. 1 cold and sample No. 2 hot. From the C. F. R. values it will be seen that the actual octane number of the third sample is actually lower than either of the previous samples. It is possible to produce a more satisfactory fuel by blending the anti-knock agents, and actually superior operation may be obtained using less lead than would be used where a single compound is employed.

The present invention is not to be limited by any theories of the operation of the fuel, nor to any particular anti-knock agents, or combination thereof, nor to the use of compounds containing any particular metallic elements, nor to any particular type of gasoline, but only to the following claims in which it is desired to claim all novelty.

We claim:

1. Liquid fuel for internal combustion engines of the Otto cycle multicylinder type comprising a mixture of hydrocarbons of such varying volatility and forming such varying air-fuel ratios as to cause material variation in knocking tendency of the several cylinders in operation and

containing a small quantity of a mixture of volatile lead alkyls consisting of tetra ethyl lead, tri ethyl methyl lead, diethyl di methyl lead, ethyl tri methyl lead, and tetra methyl lead, whereby variation in separate cylinder knocking tendency is eliminated and the antiknock value of the fuel is raised.

2. Liquid fuel for internal combustion engines of the Otto cycle multicylinder type comprising a mixture of hydrocarbons of such varying volatility and forming such varying air-fuel ratios as to cause material variation in knocking tendency of the several cylinders in operation and containing a small quantity of a mixture of volatile lead alkyls consisting of tetra ethyl lead, tri ethyl methyl lead, di ethyl di methyl lead, ethyl tri methyl lead, and tetra methyl lead, whereby variation in separate cylinder knocking tendency is substantially reduced and the anti-knock value of said mixture of hydrocarbons is raised.

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