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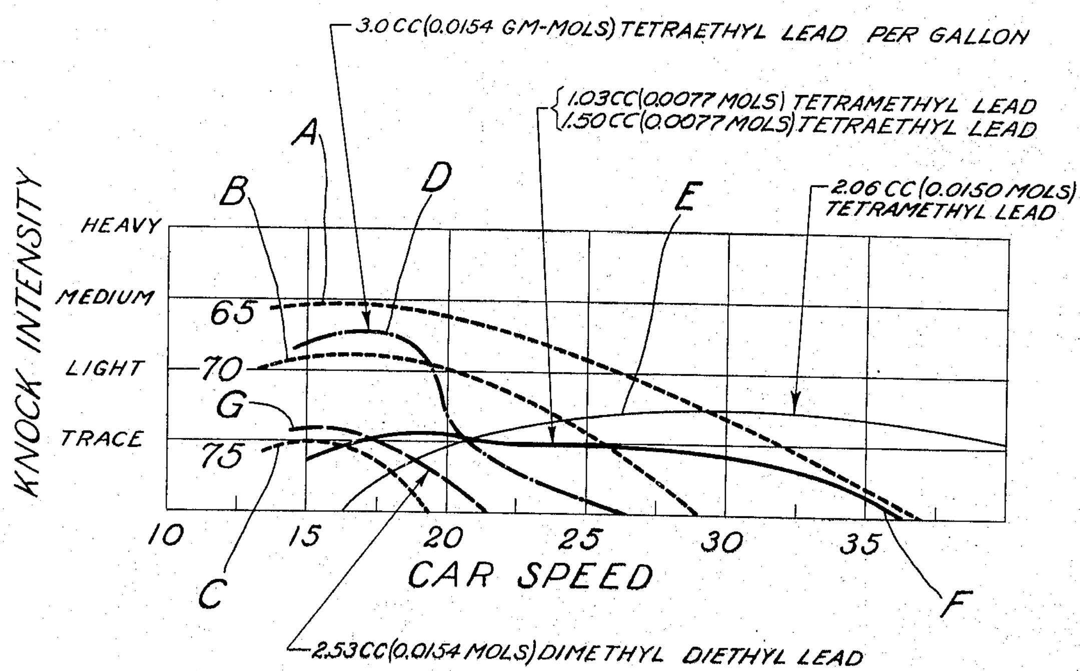
Filed Aug. 24, 1936

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**Patented Dec. 15, 1942** **2,304,883**

# UNITED STATES PATENT OFFICE

2,304,883

## PREVENTION OF KNOCK IN INTERNAL COMBUSTION ENGINES

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Application August 24, 1936, Serial No. 97,525

10 Claims. (Cl. 44—9)

The invention relates to fuel mixtures and their use in internal combustion engines, more particularly engines of the "high-compression" type, i. e., those in which the usual commercial petroleum hydrocarbon fuels, without admixture of special antiknock agents, will produce fuel knock.

The object of the invention is to overcome some disadvantages that have been found in the use of tetraethyl lead as an antiknock agent and in general to improve the operation of multicylinder engines using "low-compression" fuels, i. e., fuels that require additions of antiknock agents.

It has been found that the effectiveness of antiknock agents of the lead alkyl type varies considerably not only with the molecular constitution of the compounds but also with conditions of fuel, of fuel-air mixture, and of engine operation.

I have ascertained, by road tests on standard multicylinder automobile engines, including popular cars of the six-cylinder and eight-cylinder types, that at relatively low speeds and/or low temperatures certain gasolines containing lead alkyls show peculiar eccentricities in their knocking characteristics with different antiknock compounds as compared with their behavior in single cylinder engines. The tests show, for example, using a straight run gasoline, that with a commonly used addition of lead tetraethyl (3 c. c. per gallon) the fuel would rate as much as six octane numbers below what it should show by the usual A. S. T. M. rating, based upon the operation in a single cylinder engine. Similar apparent depreciation, but to an even greater extent, was found with addition of lead tetrapropyl. Additions of lead tetramethyl, on the other hand, resulted in an improvement in antiknock effect to the extent of four or five octane numbers above the A. S. T. M. rating. These variations were especially marked during acceleration from low speeds.

I found also that with relatively volatile fuels, particularly gasolines containing a considerable proportion of highly volatile hydrocarbons, as pentane and hexane, these differences were accentuated, the higher alkyls being even less effective and the lower alkyls more effective than in less volatile fuels. Further trials showed variations in the effectiveness of different lead alkyls with changes in the engine speed, viz., that the higher alkyls, as lead tetraethyl and lead dimethyl diethyl, improved in effectiveness with increase in speed, whereas lead tetramethyl became less effective, for the same lead content, as the engine speed increased. Other tests indicated that increase in mixture temperature tended to lessen the apparent deviations from results that would be expected from determinations made with single cylinder engines.

In the accompanying drawing is shown in graphic form the relative effectiveness at varying engine speeds of equal quantities of lead supplied respectively in 3 c. c. per gallon of tetraethyl lead, 2.53 c. c. dimethyl diethyl lead, 2.06 c. c. tetramethyl lead, and equimolecular amounts of tetramethyl and tetraethyl lead mixed. These data show results of road tests on a straight eight cylinder automobile.

In the tabular presentation of these data the car speed is represented by abscissas and the knock intensity by ordinates. The dotted lines A, B, C, represent the knocking effect in the engine of three reference fuels containing no added antiknock agent and whose octane ratings were respectively 65, 70, and 75. These three fuels were tested merely to determine reference lines for comparison with the several additions to the fuel under investigation. It will be noted that the knock curves of the reference fuels drop off gradually as the speed increases so that the knock substantially disappears with the 65 octane fuel at about 37 M. P. H., with the 70 octane fuel at about 29 M. P. H. and with the 75 octane fuel at about 19 M. P. H.

The fuel under investigation, a gasoline containing considerable amounts of highly volatile hydrocarbons and having a relatively wide range of volatility, was tested with four different antiknock agents as specified. The curve D (dot and dash line) represents the effect of tetraethyl lead, the curve E, (light full line) the effect of tetramethyl lead, the curve F (heavy full line) the effect of the mixture of tetramethyl and tetraethyl lead and the curve G (broken line) the effect of dimethyl diethyl lead.

As indicated by these curves, the tetraethyl lead is the least effective of the four antiknock agents at engine speeds up to about twenty miles per hour of car speed (about 1,000 R. P. M. of engine speed), tetramethyl lead is much more effective at speeds up to twenty miles per hour but increasingly less effective at higher speeds, and the mixture of the tetramethyl and tetraethyl lead averages to a large extent the effect of the two constituents. Dimethyl diethyl lead, however, is not subject to the defects of either of the other alkyls but parallels very closely the normal octane curves of the untreated reference fuels.

Since the antiknock effect of tetraethyl lead is higher than that of tetramethyl lead, based upon the same lead content, when determined in a single cylinder engine, it was my conclusion that the unexpected sensitiveness to knock in the standard multicylinder engines of fuels treated with tetraethyl lead and the improvement noted at low speeds and during acceleration from such speeds with the use of a normally (in a single cylinder engine) less effective lower alkyl such as tetramethyl lead, or with the use of mixed alkyls, were due, at least in part, to lack of uniformity in the distribution of the fuel constituents and antiknock agents. This conclusion is reinforced further by the fact, which I have also observed, that the departures noted in multicylinder engines from the estimated effect based upon single cylinder tests largely disappear at higher speeds and to a considerable extent at higher mixture or engine temperatures.

It is well known that the distribution of gasoline to the cylinders of a multicylinder engine varies considerably both as to quantity and quality, particularly at lower speeds and temperatures. At high engine speeds the liquid gasoline carried into the intake system is more uniformly distributed to the cylinders due to the increased turbulence and the higher carrying capacity of the swiftly moving air stream. Higher temperatures of mixture or engine parts with which the fuel contacts such as "hot spots," or of the air constituent of the fuel also reduce the proportion of fuel that remains in liquid form. However, the present trend of engine design is generally to reduce the application of heat to the fuel. This trend naturally results from the general availability of engine fuels of greater volatility and the effort to increase volumetric efficiency by reducing mixture temperatures.

As to the quality of the fuel charges delivered to the various cylinders, the more volatile fuel constituents will, of course, be more readily vaporized. Hence the charges will vary in proportions of unequally volatile constituents of the fuel when the portion remaining liquid is not uniformly distributed. That is, some cylinders, receiving less of the liquid portions of the fuel, will receive a higher proportion of the more volatile fractions while the cylinders into which more of the liquid portions of the fuel is carried will receive a larger proportion of the less volatile fractions. This applies, as my tests have indicated, to the antiknock agents as well as to the hydrocarbons present in the fuel.

Another effect of low fuel vaporization is that, since the gaseous constituents are substantially uniformly distributed as to quantity, the cylinders receiving less liquid receive leaner charges and the fuel-air ratio in some of these cylinders would then be expected to approach more closely the leanness that is conducive to knocking. Thus the leaner cylinders, although receiving fuel fractions of higher antiknock value, may actually have the greater tendency to knock when the fuel is only partially vaporized in the intake system.

This refers particularly, of course, to the desirable ranges of power output since it is known that mixtures may be made so lean as to reduce knock intensity by mere leanness but with serious loss of power.

During rapid acceleration the sudden introduction of additional fuel and the rush of air over liquid-laden parts of the intake system still further complicate the situation since it is practically impossible to distribute liquid fractions uniformly to multiple cylinders once the liquid is deposited upon the walls of the intake passages. When the throttle is suddenly opened the higher lead alkyls also seem to lag behind the lighter fuel constituents and cling to the walls of the intake passages since, as I have observed, their antiknock effect gradually increases after acceleration when the speed is kept constant for a time and the lead alkyls, which are at first deposited on the manifold walls, are finally swept into the cylinders.

It will be appreciated that, from the standpoint of the driver, knocking in any cylinder is disagreeable, and is also detrimental from the viewpoint of operative efficiency. In accordance with the present invention, therefore, it is proposed to correct or reduce the erratic knocking tendency in multi-cylinder engines by use of an antiknock agent of the lead alkyl type falling between lead tetramethyl and lead tetraethyl whose effectiveness under certain conditions is superior to that of either. Such conditions occur ordinarily at low speeds and temperatures and particularly during acceleration from low speeds. The exact limits within which the superiority of the mixed alkyls is most marked will vary, of course, with engine type and design, but may be generally found in multicylinder engines at engine speeds of 500 to 1500 R. P. M. under open throttle operation or during acceleration. The duration of the period of imperfect distribution and deposition of the antiknock material on the walls of the induction system, and resultant accentuated tendency to knock in some cylinders naturally may vary with the seasonal conditions in any given engine. In my experiments the reduced efficiency of tetraethyl lead has been noted particularly at mixture temperatures below about 110° F.

The advantage, from the viewpoint of volatility, of the use of mixtures of lead alkyls or of the mixed alkyls per se will be appreciated from a comparison of the vapor pressures of the respective alkyls. According to the latest determinations for which data are available the vapor pressures of the respective alkyls, expressed in millimeters of mercury, range as follows: the first figure representing the vapor pressure at 30° C. (86° F.) and the second at 50° C. (122° F.)

| | |
|---|---|
| $PbEt_4$ | 0.6–2.5 |
| $PbMeEt_3$ | 1.5–5 |
| $PbMe_2Et_2$ | 4–12 |
| $PbMe_3Et$ | 15–38 |
| $PbMe_4$ | 45–100 |

The two temperatures mentioned are significant since they represent approximately the mixture temperature range typical of a present automobile engine in normal operation. Still lower temperatures, of course, may prevail during the "warming up" period and in cold weather.

With respect to inherent antiknock effect of the lead alkyls, tetramethyl lead is distinctly less efficient, for the same lead content than tetraethyl lead, trimethyl ethyl lead is about half way between tetramethyl and tetraethyl lead, and the other two methyl-ethyl compounds are of approximately the same value as tetraethyl lead. These values are based upon complete vaporization conditions which probably seldom exist in present engines with ordinary commercial gasolines and my experience indicates that, under the conditions under which knocking most frequently occurs in normal operation, the mixed alkyls are distinctly superior to tetraethyl lead.

Considering only the volatility factor, the use of an antiknock agent comprising a mixture of lead alkyls having tetramethyl lead as a constituent would be advantageous since it would enable the leaner cylinders which tend to knock to receive a mixture rich in antiknock agent. I have found, however, that the desirable properties of the lower and higher alkyls are better combined when both the methyl and ethyl radicals are present in the molecular structure. For example, as shown on the drawing, dimethyl diethyl lead was superior, in the engine tested, to a mixture of tetramethyl and tetraethyl lead at all speeds observed.

While I prefer the dimethyl diethyl lead as best combining the desirable effects of the higher and lower alkyls in the methyl-ethyl lead group, it will be understood that the other members of the group also realize to some degree the respective advantages of the combined radicals.

Reference is made to U. S. Patents 1,592,954 and 1,668,022 for disclosures of the manner of utilizing the lead alkyls in commercial practice.

I claim:

1. A fuel for high-compression multicylinder internal combustion engines comprising a mixture of hydrocarbons of such varying volatility as to cause material variation in the knocking tendency in different cylinders and a relatively small amount of dimethyl diethyl lead.

2. A fuel for high-compression multicylinder internal combustion engines comprising a mixture of hydrocarbons of such varying volatility as to cause material variation in the knocking tendency in different cylinders and a small quantity of dimethyl diethyl lead sufficient to substantially correct the variation in knocking tendency.

3. Method of preventing fuel knock in a multicylinder internal combustion engine comprising supplying thereto a gasoline whose volatility is such as to result in some cylinders receiving an air-fuel mixture tending to knock and other cylinders an air-fuel mixture having less tendency to knock and supplying with such gasoline a relatively small quantity of dimethyl diethyl lead sufficient to substantially correct the difference in tendencies to knock.

4. The process of operating a multicylinder internal combustion engine during acceleration from low speeds comprising supplying to said engine a mixture of air and fuel, the conditions being such that a material portion of the fuel is in liquid form in the intake passages of the engine and is unequally distributed to the cylinders, and supplying with the fuel mixture a relatively small amount of dimethyl diethyl lead.

5. 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 the knocking tendency of the several cylinders in operation and containing a small quantity of a mixture comprising tetraethyl lead and a more volatile lead alkyl than tetra ethyl lead sufficient to substantially correct the variation in separate cylinder knocking tendency.

6. 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 the knocking tendency of the several cylinders in operation and containing a small amount of a mixture comprising amounts of tetraethyl lead and of tetramethyl lead sufficient to substantially correct the variation in separate cylinder knocking tendency.

7. A fuel for high-compression multicylinder internal combustion engines comprising a mixture of hydrocarbons of such varying volatility as to cause material variation in the knocking tendency in different cylinders and a relatively small amount of at least one of the following lead alkyls; triethyl methyl lead, diethyl dimethyl lead, and ethyl trimethyl lead.

8. The method of operating a multicylinder internal combustion engine during acceleration from low speeds including supplying to said engine a mixture of air and fuel, the conditions being such that a material portion of the fuel is in liquid form and is unequally distributed to the cylinders, and supplying with the fuel mixture a relatively small amount of a mixture of tetraethyl lead and a more volatile lead alkyl than tetraethyl lead.

9. The method of operating a multicylinder engine of the type operating on the Otto cycle which includes supplying to the cylinders a fuel comprising a mixture of hydrocarbons of the gasoline boiling range and supplying with the fuel mixture relatively small amounts of tetraethyl lead and tetramethyl lead.

10. The method of operating a multicylinder internal combustion engine during acceleration from low speeds including supplying to said engine a mixture of air and fuel, the conditions being such that a material portion of the fuel is in liquid form in the intake passages of the engine and is unequally distributed to the cylinders, and supplying with the fuel mixture a relatively small amount of at least one of the following lead alkyls: triethyl methyl lead, diethyl dimethyl lead and ethyl trimethyl lead.

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