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No. 940

THE LEAD SUSCEPTIBILITY OF FUELS
AND ITS DEPENDENCE ON THE CHEMICAL COMPOSITION

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THE LEAD SUSCEPTIBILITY OF FUELS AND ITS DEPENDENCE ON THE CHEMICAL COMPOSITION*

By O. Widmaier

SUMMARY

The introduction of leaded fuels in vehicle operation in the spring of 1939 has aroused considerable misgivings. Above all, there was some doubt about the toxic effect of tetraethyl lead and possible corrosion phenomena. The fact that by the use of this agent a number of otherwise unsuitable fuels could be made to meet the engine requirements was not sufficiently appreciated. However, while the amount of tetraethyl lead is limited for various reasons, the addition of a special leaded fuel that increases the octane number of the blend is nevertheless imperative for high requirements on many fuels. Among such blending agents, benzol, alcohol, isoparaffin, and isopropyl ether are practical.

In this connection, the extent to which the action of tetraethyl lead through the addition of knock-resistant hydrocarbons to the base gasoline is influenced, is quite important. To the elucidation of this problem and of the storage stability of leaded fuels, the present report is dedicated.

I. USE OF LEADED FUELS IN VEHICLE ENGINES

While in the past the use of ethyl fluid had been confined to aircraft-engine fuels, it is now being employed - in South Germany - also in other vehicles (reference 1), although in very small quantities: up to 0.4 cubic centimeter per liter ethyl fluid compared to about 1 cubic centimeter per liter in aviation gasolines.

*"Die Bleiempfindlichkeit von Kraftstoffen und ihre Abhängigkeit von dem chemischen Aufbau." Automobiltechnische Zeitschrift, vol. 43, no. 3, February 10, 1940, pp. 63-68.

The usual 80-octane gasoline-benzol blend contains at least 30 parts by weight of benzol. This blend has now been supplemented, by the law of May 1, 1939, by the so-called "super gasoline" which may not contain more than 15 parts of benzol by weight, to meet the octane number of 80 with an addition of up to 0.4 cm³/liter ethyl fluid. The tetraethyl lead is blended with ethylene dibromide and other compounds rather than being used in its pure state. For this blend, the U.S. term "ethyl fluid" has become general.

The old 74-octane gasoline-alcohol blend now also contains, according to the new ruling effective in South Germany, 0.4 cm³/liter ethyl fluid instead of alcohol. To meet the octane number of 74, up to 10 parts of benzol by weight is permissible.

II. INCREASING THE KNOCK CHARACTERISTICS THROUGH ANTIKNOCK AGENTS

Of the compounds used to enhance the knock characteristics of Otto-engine fuels, tetraethyl lead [Pb(C₂H₅)₄], commercially known as "ethyl fluid" (references 2, 3, and 4) is the best known and most effective.

Its exact composition and characteristics as prescribed for vehicles is as follows:

TABLE I

Tetraethyl lead (pure) parts by weight	63.30
Ethylene dibromide (pure) " " "	25.75
Ethylene dichloride " " " "	8.72
Coloring matter, petroleum, and other admixtures (pure) parts by weight	2.23
Density at 20° C	1.671
Ratio by volume of ethyl fluid to tetraethyl lead	1.561
Freezing point °C	-23
Flash point °C	110

The knock-inhibiting effect is solely attributable to the tetraethyl lead present in the ethyl fluid. This compound and its action on engine knock was originally established by T. Midgley and T. A. Boyd (reference 5). But in prolonged engine operation with leaded fuels a fine deposit of lead on the cylinder bottom and walls became noticeable, which lead to corrosion of these engine parts. The addition of ethylene dibromide - that is, of an organic halogen compound - eliminated these objectionable features to some extent, since it forms with tetraethyl lead a volatile lead halogen compound at combustion temperature, which escapes with the exhaust gases.

The amount of ethyl fluid that is added to the fuel is limited, first, because of the danger of corrosion; second, the efficiency of tetraethyl lead decreases again in increasing concentration.

The superiority of tetraethyl lead over other anti-knocks is seen from the following:

TABLE II

Relative Efficiency of Different Antiknocks
according to Midgley and Boyd

Benzol	1	Ethyl iodide	13.9
Toluene	1.1	Tetraethyl tin	20.4
Xylene	1.2	Diethyl selenide	62.5
Ethanol	1.9	Diethyl telluride	250
Aniline	11.5	Iron carbonyl	250
Toluidine	11.9	Nickel carbonyl	277
Xylidine	12.0	Tetraethyl lead	528

The knock-reducing efficiency of tetraethyl lead is so explained that the knock-producing chain reactions are interrupted by the metal atoms released at its decomposition in the engine cylinder (reference 6).

The effect of tetraethyl lead on the octane number of a fuel can be computed approximately from (reference 7):

$$N - N_0 = \frac{x}{a + bx}$$

where N is the octane number of an x -percent leaded fuel, N_0 the octane number of the base fuel, and a and b are the chemical values of the gasoline in question. The highest octane number can be computed if x is assumed infinite. But the actual octane number frequently varies from the computed number, the cause lying with the dissimilar composition of the fuels. The divergence is called the blending index of the octane number. If this value is positive, it means that the actual octane number of the fuel is higher than the computed.

In its pure state, tetraethyl lead is extremely toxic, but, mixed with gasoline in proportion of 1,000 cubic centimeters of gasoline to 0.4 - 1 cubic centimeter of ethyl fluid with 60 to 65 parts of tetraethyl lead by weight, its effect is harmless.

Nickel and iron carbonyl and diethyl telluride come closest to tetraethyl lead in efficiency, but even they are only about 50 percent as effective. Another series of proposed antiknocks included iron-acetylacetonate, copper-acetylacetonate, organic ferrous ferricyanide, and iron compounds of β diketones.

Other than these organic metal compounds, there is anilol, a compound of aniline, butyl, and ethyl or methyl alcohol (reference 8), but its effect (about 1:30) is considerably less than that of tetraethyl lead.

III. ACTION OF TETRAETHYL LEAD IN RELATION TO FUEL COMPOSITION

a) Gasolines from Different Sources

The effect of tetraethyl lead on the various fuels is, as previously stated, largely controlled by its chemical composition. The dissimilar behavior of gasolines of different octane numbers and sources is seen from the appended table (reference 9).

TABLE III

Lead Susceptibility of Gasolines of Different Sources

Identi- fication	Base	Octane rating	Octane rating after adding 0.8 cm ³ /l ethyl fluid	Increase of octane rating
X 1	Paraffinic	56	76	20
X 2	"	62	77	15
X 3	Mixed base	69	85	16
X 4	Naphthenic	72	88	16
X 1a	By fragmenta- tion from X 1	67	80	13

This fact corroborates closely with the findings of R. Kobayasi and S. Kajimoto (reference 10) about the lead response of pure hydrocarbons.

In accord with that, the order for lead susceptibility is as follows:

- 1) Paraffins
- 2) Naphthene
- 3) Unsaturated hydrocarbons
- 4) Aromatics

The strongly unsaturated and aromatic gasolines have therefore a lower lead susceptibility than straight-run gasolines, of which again those with paraffin base are most responsive. Aromatics with long side chains are also susceptible, while aromatics with short side chains, such as benzol and olefins (fig. 3), are almost non-responsive.

b) Alcoholic Fuels

Methyl alcohol and especially ethyl alcohol are common aids for raising the knock characteristics of gasolines

and their use for automotive gasoline is in many cases satisfactory. Obviously, the consumption is greater because of the lower heat value. Alcohol, being hydrophilic, removes the icing hazards at low temperatures, but, since it is also easily separated, this tendency must be encountered with higher molecular alcohols or aromatic hydrocarbons.

Then, too, the high heat of vaporization introduces difficulties in engine starting. On the other hand, alcohols show knock-reducing qualities, and, when blended with gasoline, high octane numbers.

In blends with tetraethyl lead, the antiknock characteristics manifest great fluctuations. In most cases, the addition of alcohol causes a reduction in the lead susceptibility of fuels (reference 11). The longer the alcohol chain, the less the efficiency of tetraethyl lead.

The effect of ethyl alcohol and ethyl fluid on leuna gasoline, as illustrated in figure 1, discloses an almost complete absence of increase in octane number by greater alcohol additions, despite the fact that 1.5 cm³/liter of ethyl fluid had been added. For instance, 82.8 octane was reached by adding 1.5 cm³/liter ethyl fluid to leuna gasoline. With the same amount of leading, together with 20 parts of ethyl alcohol by volume, 87.1 octane was reached as against 84.4 with 60 parts by volume.

The use of the higher molecular amyl alcohol in a blend with leuna gasoline reduces the lead susceptibility even more (fig. 2). Here 1.5 cm³/liter ethyl fluid gives a higher octane number, 82.8, as, for instance, a blend of leuna gasoline and 1.5 cm³/liter ethyl fluid with 60 parts of amyl alcohol (77.6) by volume. A slight increase in antiknock characteristics through amyl alcohol is obtained only with blends containing up to about 0.5 cm³/liter ethyl fluid.

c) Gasoline-Benzol Mixtures

The use of benzol as a supplementary agent to gasoline is universally known. Blended with gasoline, it assures a good combustion and increases the antiknock characteristics. The lead susceptibility of gasoline-benzol mixtures, while slightly superior to gasoline-alcohol mixtures, is not so good as that of pure gasoline.

TABLE IV

Physical-Chemical Characteristics of Pure Benzol
(C_6H_6) (reference 12)

Boiling point at 760 mm Hg	79° C
Density at 20° C	0.878 g/cm ³
Refractive index at 20° C	1.5014
Freezing point	5.6° C
Dynamic viscosity centipoise at 20° C	0.647
Heat of vaporization	95 kcal/kg
Upper heat value	9800 kcal/kg
Lower heat value	9450 kcal/kg

The lead susceptibility decreases with the amount of benzol that is added to a straight-run gasoline (reference 4, p. 720). For instance, whereas the addition of 0.26 cm³/liter of tetraethyl lead to a blend with 20 parts of benzol by volume, increases the octane number by seven units, a blend with 80 parts of benzol by volume with the same amount of tetraethyl lead increases the octane number only two units.

The benzol serving to raise the antiknock characteristics without the ethyl fluid blending agent can be manufactured by secondary dealcalization and reduction of the phenols or through decomposition of aliphatic hydrocarbons in coal gas (reference 13). The benzol is obtained from the coal gas by absorption in washing oil or absorption in active coal plants (Benzorbon method) (reference 14).

For engine benzol, a refined fraction of crude benzol with a boiling point of between 80° and 140° C is used.

d) Isoparaaffins

Isopentane (2-methyl butane), a highly knock-resistant hydrocarbon, is obtained by fractionation, absorption, and adsorption, or by low cooling from natural gas or petroleum, and is well suited as a blending agent. Its only drawback is its high vapor pressure and concomitant steam bubbles, which, however, can be countered by adding isopentane of higher boiling fuel components. For illustration, the change in vapor pressure in the blend with isooctane is given in the following table (reference 15):

TABLE V

Vapor Pressure of Isopentane and Isooctane Blends,
According to Reid

Isopentane volume- percent	Isooctane volume- percent	kg/cm ²
100	-	1.434
85	15	.855
70	30	.580
50	50	.366
-	100	.155

In comparison with isooctane, isopentane has a lower octane number: 90; but its lead susceptibility is very good. According to figure 4, where the octane number of a 70-octane benzene is plotted against the isopentane and tetraethyl lead content, discloses that the lead susceptibility grows with the isopentane content in the benzene. According to Neptune, Trimble, and Alden (reference 16), only 1/10000-percent volume of tetraethyl lead is sufficient to return antiknock value of a blend of equal parts of isopentane and a 100-octane fuel to the 100-octane number. Thus, three fuels of 100, 105, and 110 octane, respectively, supplemented by 50-percent-volume isopentane,

can be returned to the original octane number, by merely adding 0.0001, 0.0005, and 0.0014 percent by volume of tetraethyl lead.

Isopentane is therefore an excellent blending agent for raising the antiknock value, the lead susceptibility, and the vapor pressure. Its use at present is largely confined to the United States, where it is found in great quantities in the oil wells.

A further isoparaffin is isooctane (2-2-4) trimethyl pentane (reference 17). Pure isooctane is used in the CFR engine and in the I-G test engine (reference 18) along with normal heptane for the knock rating of fuels. Whereas normal heptane is a violent knock inducer with a zero octane number, isooctane has a very high antiknock value and with its 100-octane number serves as reference fuel. It has, in addition, a high heating value (10,580 kcal/kg), a low freezing point (-108° C) and a low gum content.

Figures 5 and 6 show the blend octane values of a 70-octane fuel with up to 1.05 cm³/liter tetraethyl lead content plotted against the added isooctane quantity. Pure isooctane appears more lead-responsive (fig. 6) than the 95-octane commercial isooctane (fig. 5). While, for instance, the addition of 0.26 cm³/liter tetraethyl lead to pure isooctane in a blend with 30 parts by volume of 70-octane gasoline, gives an octane number of 98, the same blend, for the commercial 95-octane isooctane, is only 95 octane.

Isooctane, with its physical characteristics, as shown in table VI is manufactured by several technical processes (reference 19).

TABLE VI

Physical Characteristics of Pure Isooctane	
Boiling point at 760 mm, Hg pressure	99° C
Density at 20° C	0.691 g/cm ³
Refractive index at 20° C	1.3921
Freezing point	-108° C
Viscosity, centipoise, at 18.3° C	0.543
Heat of vaporization	72 kcal/kg
High heating value	11,440 kcal/kg
Low heating value	10,680 kcal/kg

e) Isopropyl Ether

Isopropyl ether can be produced from the propylene contained in cracked gases (reference 12).

TABLE VII

Physical Characteristics of Isopropyl Ether	
Boiling point at 760 mm Hg pressure	68° C (67°-70° C)
Density at 20° C	0.725 g/cm ³
Refractive index at 20° C	1.3680
Freezing point	-87° C
Viscosity, centipoise, at 20° C	0.322
Heat of vaporization	68 kcal/kg
Upper heat value	9,400 kcal/kg
Lower heat value	8,670 kcal/kg

Although a low-boiling-point material, its vapor pressure is below the maximum allowed for aviation gasolines and, when blended therewith, vapor pressures will be entirely suitable. The freezing point is much lower than for benzol or benzol-blend fuels and comparable with that for isooctane. The heating value is lower than for either isooctane or benzol, but this disadvantage may be wiped out by permitting of leaner fuel-air ratios without excessive cylinder head temperatures.

The water tolerance of isopropyl ether is slightly greater than for normal fuels, but of no measurable amount. The possibility of the absorbed water separating as ice in the winter time is ruled out because of the low freezing temperature of isopropyl ether. Its storage stability is good.

Another characteristic of major importance is its exceptionally good antiknock value. In its pure state its octane value is above 100. The blending value of iso-

propyl ether is even higher and the lead susceptibility substantially greater than for any blending agent considered. Figure 7 shows that isopropyl ether, without tetraethyl lead added, raises the octane number of leuna benzene from 63 to 87.4 with a 60-percent-volume isopropyl ether blend. An addition of ethyl fluid of from 0.5 to 1.5 cm³/liter raises the antiknock value very considerably. The blends with higher isopropyl ether content become so much more lead-responsive as the amount of added ethyl fluid is increased. Octane numbers of around 99 and 114 (by I.G. engine method) are obtained for blends with 40 percent and 60 percent isopropyl ether and 1.5 and 1.0 cm³/liter ethyl fluid, respectively. For 60 percent isopropyl ether and 1.5 cm³/liter ethyl fluid, the octane number is even higher, according to figure 7, although no longer measurable by test engine.

Admittedly, blends with much isopropyl ether cause the engine to run somewhat irregularly and rough.

IV. RESIDUE IN LEADED FUELS

The advantage of increased octane number accruing with tetraethyl lead is endangered by the deposits forming on piston, cylinder head, and valves after some period of operation.

In time, stored leaded fuels also disclose a deposit whose formation is enhanced by light rays and may lead to the stopping up of small nozzle orifices.

a) Effect of Light Rays on the Residue Formation of Leaded Fuels

Different fuels blended with ethyl fluid were exposed to the actions of light rays. The results were, briefly, as follows:

1. The formation of residue increases with the period of exposure.
2. The amount of residue under the effects of light rays increases with the amount of ethyl fluid.

3. The formation of residue, after prolonged exposure, is so great that all samples reached the octane number of the base fuel.

In order to obtain comparable residue values under the exposure of light rays, two commercially available leaded fuels were exposed to mercury vapor light. According to figure 8, the deposits were dissimilar for the same periods of exposure. Leaded gasoline 1 reached its maximum after 180 hours, gasoline 2 at 140 hours. The comparison of the slope of the curves gives the indication of the extent of residue formation. Gasoline 2 manifests a much steeper residue curve than gasoline 1, i.e., forms a certain amount of deposit in less time. Paraffins have a much greater tendency to form deposits than aromatics, according to experiments on pure hydrocarbons.

It is therefore recommended to keep leaded fuels away from the light as much as possible.

b) Reduction in Lead Deposits by Blending Agents

It has been possible to establish in experiments that alcohol acts as a deterrent for deposits in lead-blend fuels; as little as 5 percent suffices, in some cases, to reduce the deposit-forming to a minimum. For instance, whereas leaded gasoline without blending agent gives after a certain period of exposure a residue of 93 ng/400 cm², a 5-percent addition of ethyl alcohol reduces the deposit to 47 ng/400 cm². A high percentage of alcohol has, in general, very little effect on the amount of deposit formation.

In connection herewith the I.G.F. (reference 20) has patented a process according to which a 1-percent solution of alkali fluoride in methanol blended in the tetraethyl lead prevents the formation of lead residue.

V. EFFECT OF LEAD-BLEND ON PERFORMANCE AND CONSUMPTION

The increased antiknock value of fuels with tetraethyl lead makes a higher compression ratio possible, hence a lower specific consumption and increased engine performance. The performance can also be increased with leaded fuels by supercharging, that is, by increasing the break mean effec-

tive pressure, a more economical consumption through leaner fuel-air ratios.

Illustrative of the change in the power and the combustion of an aircraft engine are figures 9 and 10 (reference 21) which are similar to the results by Klein (reference 22) with 100- and 92-octane fuels. The improvements in power ranged from 12 to 30 percent, depending upon the type of engine used and operating condition.

The apparent improvement in antiknock value obtainable by blends containing oxygen, must be reduced relative to pure hydrocarbons in correspondence with the lower heat value, which reduces the apparent improvement per 1-percent lower heat value by about two units of octane number (reference 23).

Translation by J. Vanier,
National Advisory Committee
for Aeronautics.

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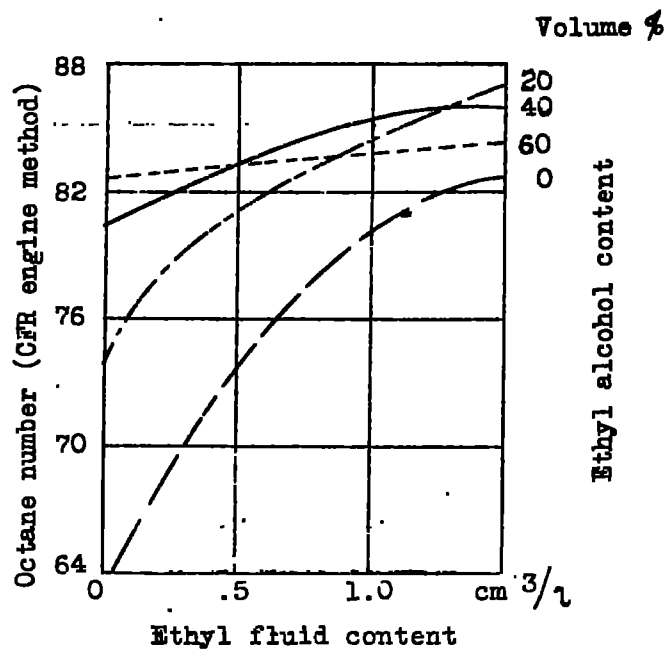


Figure 1.- Effect of ethyl alcohol and ethyl fluid on leuna benzene.

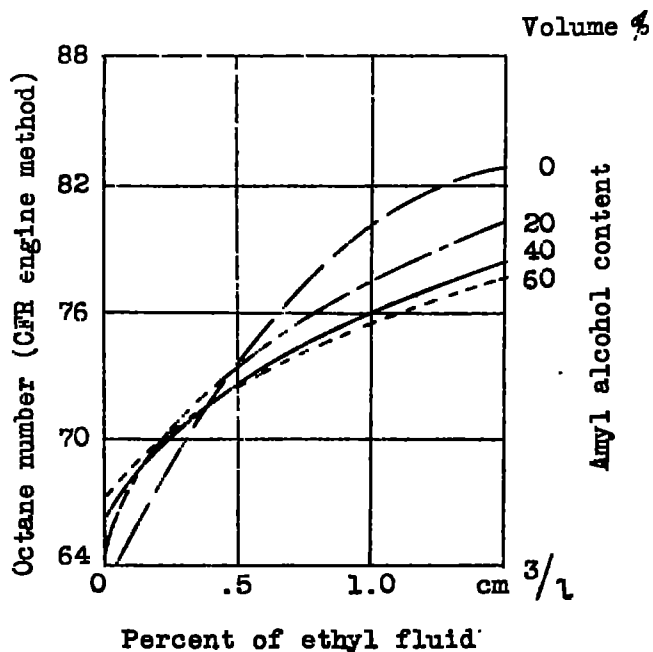


Figure 2.- Effect of amyl alcohol and ethyl fluid on leuna benzene.

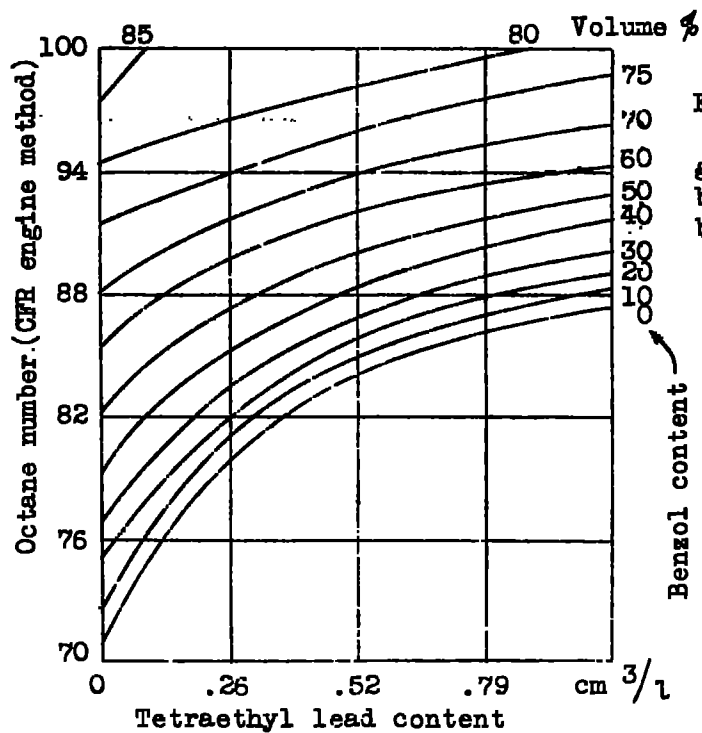


Figure 3.- Octane numbers of straight-run gasoline in relation to benzol and tetraethyl lead blend.

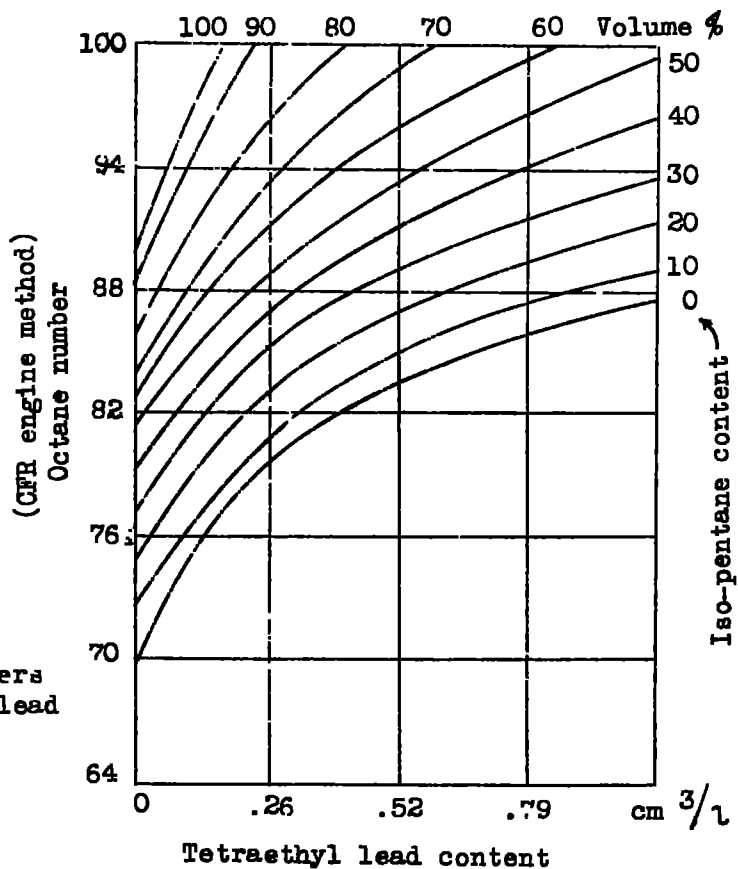


Figure 4.- Relation of octane numbers of fuel to tetraethyl lead and iso-pentane.

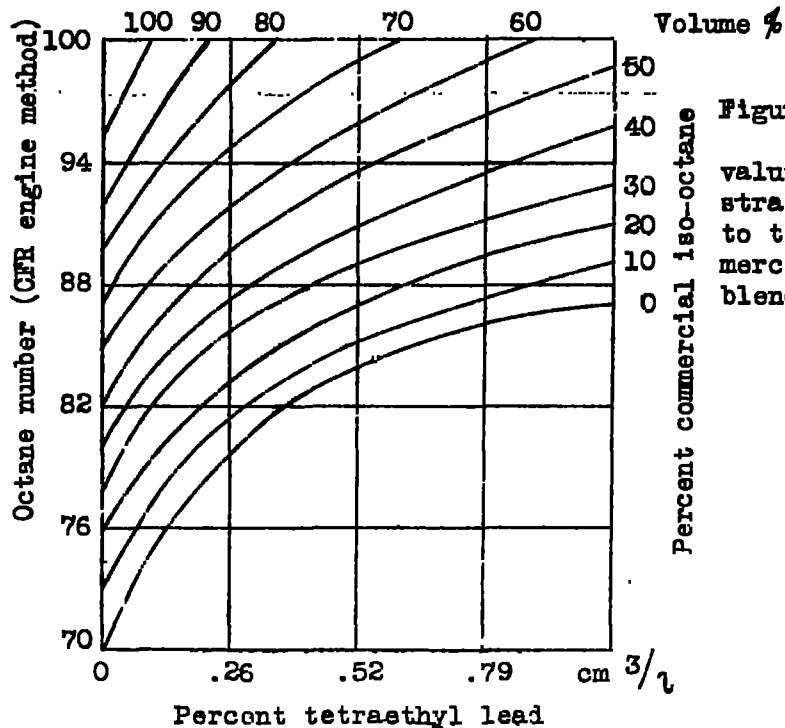


Figure 5.- Relation of anti-knock value of 70 octane straight run gasoline to tetraethyl and commercial iso-octane blend.

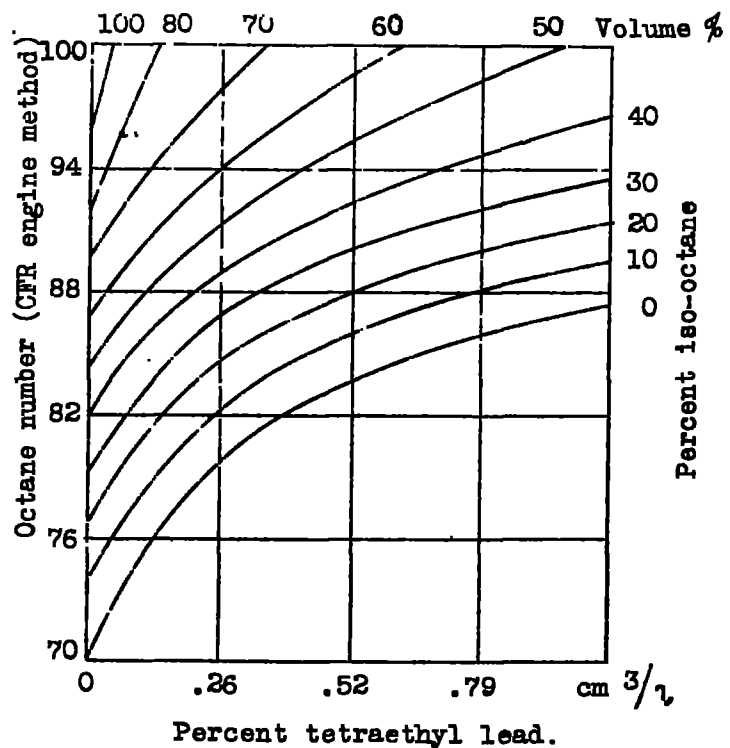


Figure 6.- Relation of anti-knock value of 70 octane straight run gasoline to tetraethyl and pure iso-octane.

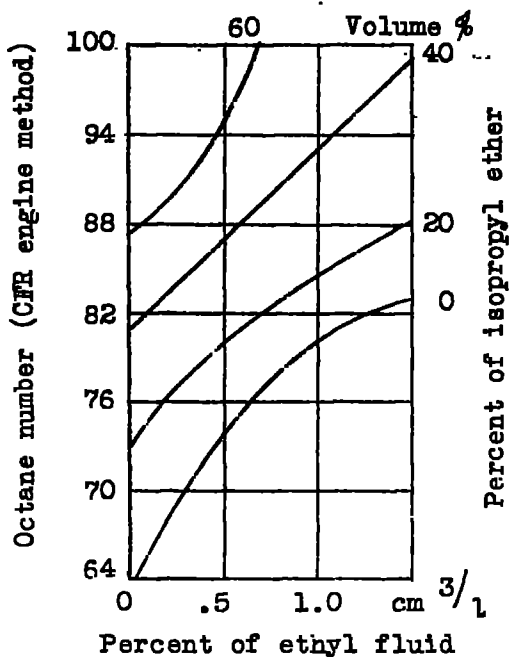


Figure 7.- Effect of isopropyl ether and ethyl fluid on leuna benzine.

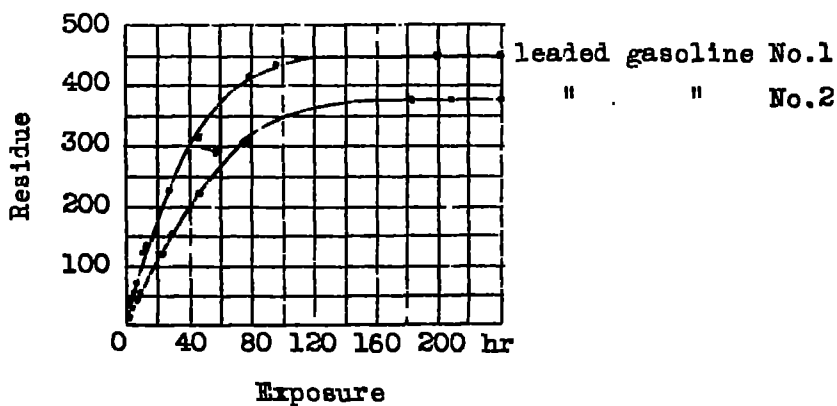


Figure 8.- Deposit of leaded gasolines 1 and 2 against time of exposure to light.

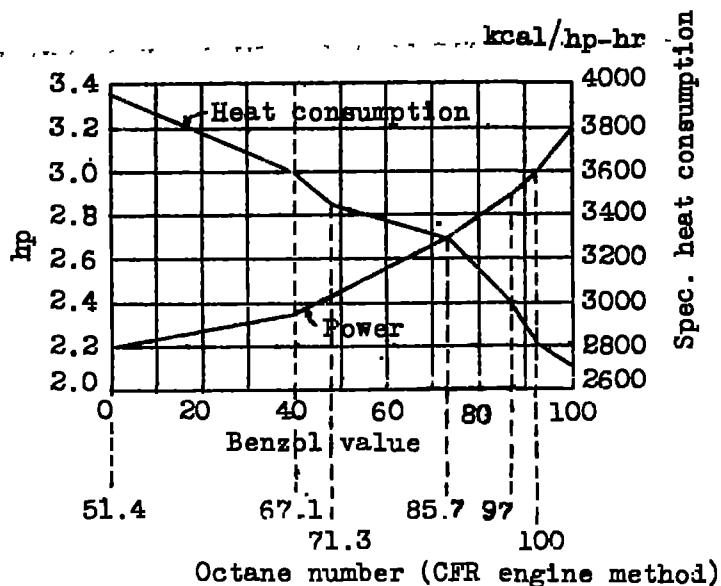


Figure 9.- Change in power and consumption of CFR engine with the anti-knock value.

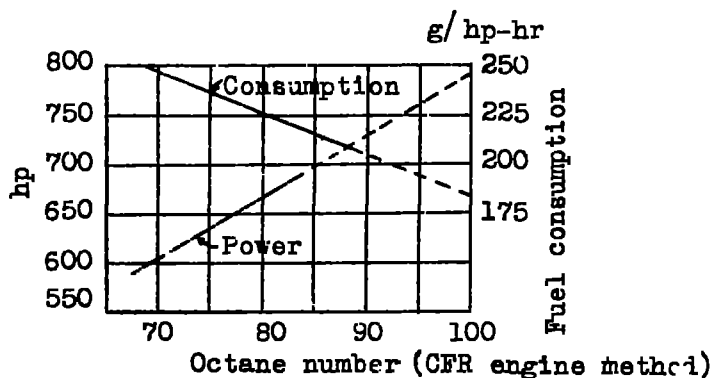


Figure 10.- Change of hp and consumption of aircraft engine with the anti-knock value.

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