Tetramethyllead—An Improved Antidetonant

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THE LIMITATIONS placed on the performance of spark ignition engines by "knock" led near the end of World War I to an extensive search for an effective chemical agent to alleviate this troublesome and, in extreme cases, damaging result of uncontrolled combustion (*3*). In 1921 a practical solution was found. Tetraalkyllead compounds other than tetraethyllead (TEL) were evaluated during this period; but TEL was chosen for commercialization because of its superior effectiveness and desirable physical properties.

In the mid-1930's, it was demonstrated (*1, 5*) that in certain gasolines tetralkyllead compounds more volatile than TEL could provide better octane performance than TEL in some multicylinder engines in which the gasoline components were unevenly segregated among the cylinders. However, the principal benefits gained from replacement of TEL with tetramethyllead (TML) in American production automobiles are due to the greater thermal stability of TML.

CHANGES IN GASOLINE COMPOSITION

Over the last 40 years, cracking and refining operations have changed gasoline composition from a mixture of naturally occurring hydrocarbons, chiefly paraffinic and naphthenic in structure, to gasolines composed largely of aromatic and highly branched aliphatic hydrocarbons. The hydrocarbons in today's premium gasolines are largely synthetic, being manufactured during refinery processing.

Gasoline compositions from a typical west coast refinery plotted as a function of octane level are shown in Figure 1.

TETRAMETHYLLEAD IN MODERN GASOLINES

TML was found to be markedly superior to TEL in modern premium grade gasolines which contain more than about 20% of aromatic hydrocarbons. The principal benefit is a gain of 1 to 2 Road octane numbers, with a similar but somewhat smaller increase in octane number as determined by the Motor method. Replacement of TEL by TML has very little effect on the Research octane number.

Effectiveness in Premium Gasolines. The benefit in octane quality gained by replacing TEL with TML in ten experimental gasolines, selected to represent extremes of composition which would result from various refining techniques, is shown in Table I. Compositions and some physical properties of these gasolines appear in Table II. The first three gasolines are "superpremium" grades. The rest are "premium" grade, arranged in order of decreasing aromatic hydrocarbon content. The octane increase upon replacement of 3 ml. of TEL per gallon with the equivalent molar quantity of TML is given for three engine test procedures. The greater octane increase by the Motor method than by the Research method is a characteristic feature of TML. The spread of octane improvement by the Motor method is 0.2 to 1.4 numbers, with an average improvement of 0.8; by the Research method, −0.1 to 0.6 number, with an average improvement of 0.3.

Table I. Effectiveness of Tetramethyllead in Gasolines

No.	Octane Rating with TEL[a]: Research Method	Octane Rating with TEL[a]: Motor method	Aromatic Content, %	Octane Improvement[a] (TML Minus TEL): Research method	Octane Improvement[a] (TML Minus TEL): Motor method	Road[c]	No. of Cars Rated	No. of Road Ratings
			Selected Experimental Gasolines					
1	105.3	97.0	52.5	0.0	1.2	1.5	3	3
2	104.7	96.3	48.1	0.3	1.4	2.1	5	16
3	105.0	100.1	25.8	−0.1	0.2	0.5	3	3
4	99.0	87.8	49.0	0.4	1.1	1.0	9	15
5	101.0	87.2	44.0	0.5	1.2	0.7	9	22
6	100.5	88.2	43.0	0.3	0.8	1.0	6	10
7	100.6	90.7	37.0	0.6	0.6	1.0	6	10
8	99.5	88.3	36.0	0.2	0.2	0.8	9	22
9	99.4	88.1	33.0	0.1	0.1	0.7	6	25
10	98.8	86.6	28.0	0.5	0.5	0.5	7	10
			Full-boiling-range Gasolines					
11	100.4	90.9	44.0	0.8	0.6	1.9	9	39
12	100.3	90.5	39.0	0.5	0.6	1.6	10	45
13	101.1	89.1	33.0	0.3	1.1	1.3	10	42
14	99.8	89.2	32.0	0.9	1.2	1.5	9	39
15	99.3	87.8	32.0	−0.1	0.7	0.8	10	42
16	99.2	87.4	16.0	−1.6	0.1	0.6	10	42

[a] 3 ml. TEL per gallon. [b] Laboratory engine data for selected experimental gasolines based on quadruplicate determinations. 90% confidence interval is 0.4 number by Research method, 0.5 by Motor method. [c] Modified Uniontown procedure. 90% confidence interval is 0.2 number for averages of triplicate determinations in 10 cars.

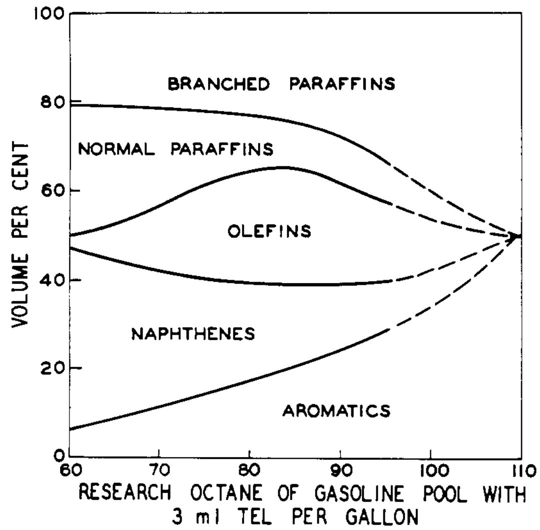

Figure 1. Trends in gasoline composition
---Anticipated, on basis of known processes

The octane increase as determined in automobiles using the modified Uniontown technique averages 1.0 number with a spread of from 0.5 to 2.1 numbers. The advantage of TML is most pronounced in gasolines containing relatively high proportions of aromatic hydrocarbons (clearly demonstrated in Motor and Road octane procedures).

The effectiveness of tetramethyllead in six full-boiling-range gasolines, typical of west coast production, arranged in order of aromatic content, is also shown in Table I. With the Motor method, the benefit of TML disappears below about 20% aromatics in the premium grades of gasoline.

TML exhibits a greater benefit when tested in automobiles and averages 1.3 Road octane number gain in these gasolines.

Response in Test Automobiles. All test automobiles were equipped with automatic transmissions. The Road evaluations were performed on a chassis dynamometer. Typical results with a single test gasoline are presented in Table III.

Table III. Road Results in Individual Test Cars

(Fuel 6)

Car	Improvement in Road Octane Number on Replacing 3 ml. TEL/Gallon with Equivalent Molar Amount of TML
1958 Mercury (10.5:1)	0.7
1958 Oldsmobile (10:1)	1.1
1956 Chevrolet (9.3:1)	1.4
1957 Buick (11.1)[a]	0.7
1956 Chrysler (12:1)[a]	1.4
1956 Pontiac (12:1)[a]	0.8
	Av. 1.0

[a] Engines modified to obtain higher compression ratio.

The response of cars varied from one fuel to another—no car gave consistently the highest or lowest octane improvement.

The improvement in Road octane rating on replacing TEL with the more volatile TML is largely distinct from any special advantage due to improved manifold distribution characteristics. Table IV compares the Road octane gain observed in a 1957 Chevrolet equipped with fuel injection with a number of other cars. Since the injection system is mechanically designed to provide uniform manifold distribution, improved distribution of the lead compound does not account for a major part of the observed effect. The larger octane improvement due to TML than would be predicted by laboratory single-cylinder engines appears to be due to the increasing superiority of TML relative to TEL as temperatures and pressures of modern engines are increased.

Influence of Gasoline Composition and Octane Level. The influence of gasoline composition and octane level on the relative effectiveness of TML is shown in Figure 2. Three types of hydrocarbons were blended with varying proportions of n-heptane and evaluated in laboratory engines. Aromatic hydrocarbons as represented by a mixture of trimethylbenzene isomers exhibit a steep response slope

Table II. Identification of Test Gasolines

No.	Description	Hydrocarbon Composition, %				Distillation[a], B. P., ° F.		
		Paraffins	Olefins	Naphthenes	Aromatics	10%	50%	90%
1	Enriched in C_7 and C_8 aromatic hydrocarbons	36.7	0.0	10.8	52.5	123	227	297
2	Enriched in C_8 and C_9 aromatic hydrocarbons	42.4	0.0	9.5	48.1	118	226	332
3	Enriched in branched aliphatic hydrocarbons	68.3	0.0	5.9	25.8	125	212	310
4	High 90% ASTM boiling point	29.7	14.0	7.3	49.0	123	240	372
5	Enriched in aromatic hydrocarbons	25.7	28.0	2.3	44.0	139	236	315
6	Enriched in aromatic and branched aliphatic hydrocarbons	26.0	21.0	10.0	43.0	124	215	324
7	Enriched in branched aliphatic hydrocarbons	44.7	10.0	8.3	37.0	117	204	323
8	Enriched in branched aliphatic hydrocarbons	38.7	18.0	7.3	36.0	127	212	324
9	Average 1957 commercial	34.4	25.0	7.6	33.0	130	240	340
10	Low 90% ASTM boiling point	31.9	30.0	10.1	28.0	128	192	309
11	Full-boiling-range gasoline	41.0	4.0	11.0	44.0	142	222	327
12	Full-boiling-range gasoline	50.2	7.0	3.8	39.0	134	220	340
13	Full-boiling-range gasoline	36.1	26.0	4.9	33.0	130	215	318
14	Full-boiling-range gasoline	37.8	25.0	5.2	32.0	132	212	304
15	Full-boiling-range gasoline	38.8	21.0	8.2	32.0	124	215	324
16	Full-boiling-range gasoline	38.4	36.0	9.6	16.0	142	217	337

[a] ASTM Procedure D 86.

Table IV. Comparison of Fuel Injection with Standard Carburetion

Car	Fuel 15	Fuel 13	Fuel 12	Average
	Octane Improvement[a] (TML Minus TEL)[b]			
1958 Mercury	1.3	0.9	1.5	1.2
1958 Oldsmobile	1.6	1.2	1.3	1.4
1956 Chevrolet	1.0	1.8	1.7	1.5
1959 Ford (9.6:1)	1.3	0.1	0.8	0.7
1959 Plymouth (10:1)	0.5	0.9	1.4	0.9
1957 Buick	1.1	1.1	1.1	1.1
Av.	1.1	1.0	1.3	1.1
Fuel Injection Chevrolet (9.5:1)	1.1	1.5	0.4	1.0

[a] Modified Uniontown procedure.
[b] Lead concentration equivalent to 3 ml. TEL per gallon.

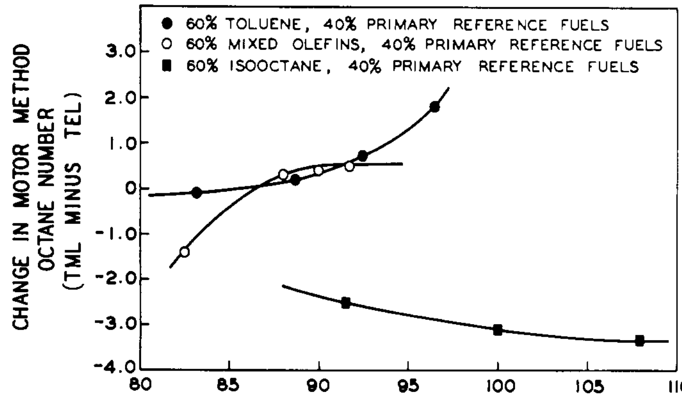

Figure 3. Influence of octane level

with increasing concentration. The n-heptane, used to achieve a reasonable octane level, clearly exerts a deleterious influence. The complete octane data for both the Research and Motor methods are presented in Table V The slope of the diisobutylene-n-heptane curve, representing the olefin family, is less steep but implies that large concentrations of high octane olefins enhance the effectiveness of TML. Branched aliphatics, characterized by the leaded primary reference fuels, respond poorly to TML. The relative effectiveness of TML in the hydrocarbons tested illustrates general trends, but the magnitude of the effects varies considerably from one mixture of hydrocarbons to another. The response of complex mixtures, such as gasolines, to TML is not yet accurately predictable.

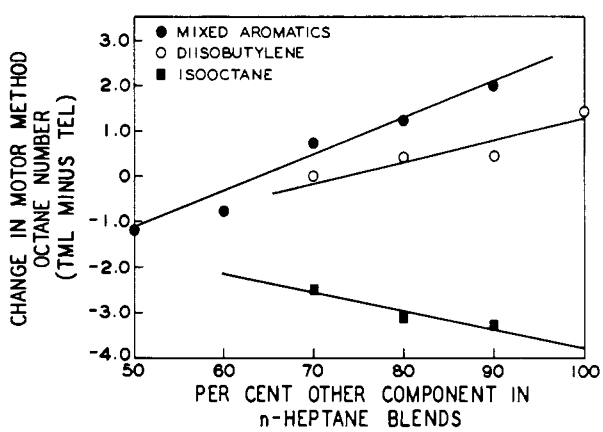

Figure 2. Influence of fuel composition and octane level on effectiveness of TML

The influence of octane level on TML effectiveness is shown in Figure 3 and Table VI. To hold the type of hydrocarbon relatively constant while varying octane level, mixtures of 60 volume % of toluene, commercial olefins, and iso-octane were blended with 40% of various primary reference fuels. With the toluene blends, TML and TEL are about equivalent in the region of 80 to 90 Motor octane. Above 90 octane, TML shows a pronounced upward swing and is 1.8 numbers better than TEL at 96 Motor octane. The olefinic blends exhibit a crossover at 87 Motor octane, going from a differential of −1.4 to +0.5 number in a span of nine Motor octane numbers. The iso-octane fuels in this octane range show a decreasing response to TML relative to TEL with increasing octane number.

Influence of Lead Concentration. The molar concentration of TML has a pronounced influence on its effectiveness relative to TEL. In Figure 4, averages of the Research, Motor, and Road octane values for five west coast premium gasolines are compared at five lead levels. The gasolines containing 3 ml. of TEL per gallon all have a nominal Research octane number of 100. By all three methods, TML is inferior to TEL at a molar lead level equivalent to 0.5 ml. of TEL per gallon. TML becomes equivalent to TEL by the Research method when a molar concentration equivalent to 2.6 ml. of TEL per gallon is reached, and by the Motor method, at a molar concentration equivalent to about 0.9 ml. of TEL per gallon. The Road ratings are equal at 1.0 ml. of TEL per gallon. There appears to be an optimum effectiveness by both the Motor and Road methods at the 3-ml. level in these gasolines.

ECONOMIC IMPORTANCE OF TETRAMETHYLLEAD

At present, it will cost the refiner a premium to replace TEL with an equivalent amount of TML because of initial low volume production and development costs. Upon establishment of a large-volume market, the cost of lead as TML is expected to approach the cost per mole of TEL. Most refiners assign a value of 0.2 to 0.5 cent per gallon for an octane number. The Road octane improvement gained by the substitution of TML for TEL makes TML the additive of choice even at the current price of TML.

MECHANISM OF ANTIKNOCK REACTION

Since the discovery that TML is more effective than TEL in high octane gasolines, the mechanism by which this unexpected result was obtained has been studied. It is concluded that the greater stability of TML is the most

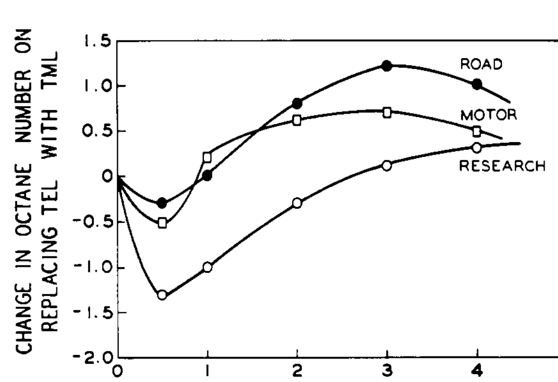

Figure 4. Influence of lead concentration
Average of five west coast refineries

Table V. Influence of Fuel Composition

Fuel Composition, %				Octane Rating with 3 Ml. TEL per Gallon		Octane Improvement (TML Minus TEL)	
				Research method	Motor method	Research method	Motor method
90	mixed aromatics[a]	10	*n*-heptane	104.4	96.6	0.3	2.0
80	mixed aromatics	20	*n*-heptane	100.6	90.2	0.1	1.2
70	mixed aromatics	30	*n*-heptane	96.5	85.6	0.1	0.7
60	mixed aromatics	40	*n*-heptane	92.0	82.1	-1.4	-0.8
50	mixed aromatics	50	*n*-heptane	86.0	78.4	-2.1	-1.2
100	diisobutylene	0	*n*-heptane	104.7	87.1	0.6	1.4
90	diisobutylene	10	*n*-heptane	104.2	86.5	-0.1	0.4
80	diisobutylene	20	*n*-heptane	103.8	85.9	-1.0	0.4
70	diisobutylene	30	*n*-heptane	101.6	85.3	-2.8	0.0
90	iso-octane	10	*n*-heptane	101.7	107.8	-0.6	-3.3
80	iso-octane	20	*n*-heptane	96.2	99.9	-0.3	-3.1
70	iso-octane	30	*n*-heptane	90.9	91.5	-0.3	-2.5

[a] Mixed C_9 aromatic hydrocarbons.

important property influencing its activity as an antiknock agent. That TML is more resistant to decomposition in a motored engine than is TEL was shown by Rifkin (*4*), who confirms earlier findings that TEL must be decomposed (probably to an oxide) in order to exhibit antiknock activity. On the surface, this appears to be a contradiction. How can TML be more resistant to decomposition and show superior antiknock effectiveness when it must be decomposed in order to exhibit these antiknock properties? Anattractive hypothesis is that, following the decomposition of TEL, a rapid reduction in activity of the antiknock species occurs. This reduction, which could curtail the antiknock reaction, might be due to agglomeration of the active antiknock species. With increasing engine severity—i.e., increasing compression pressures and higher temperatures—TEL will decompose earlier and earlier in the engine cycle. If the rapid chain branching reactions which lead to knock become critical at a relatively fixed time in the engine cycle, regardless of the knock-limited compression ratio, then increasing the octane level and compression ratio will eventually cause TEL to decompose prematurely. The effective concentration of antiknock species will be markedly curtailed by the agglomeration process before the critical time for the antiknock reaction to occur. The result is a loss in inherent antiknock effectiveness with increasing octane level and engine severity. The greater stability of TML permits it to survive until later in the engine cycle, suffer less loss in effectiveness due to agglomeration, and thus possess greater antiknock effectiveness at the critical time.

The role played by hydrocarbon composition follows logically from this argument. All that is required to explain the observed differences—i.e., that aromatics are more responsive to the substitution of TML for TEL than aliphatics, with olefins intermediate—is the assumption that the reactions leading to knock are most effectively inhibited late in the engine cycle with aromatics, earlier with olefins, and still earlier with aliphatics. The correlation of this assumption with the tendency of aromatics to undergo relatively little preflame reactions relative to aliphatics is striking and also fits well with previous work (*2*) showing that TEL does not affect induction time for cool flame reactions but prolongs induction time for spontaneous ignition by some process which occurs during the cool flame reaction or later. The fact that TEL is inherently superior to TML in aliphatic fuels implies that TML decomposes too late in the engine cycle when the reactions which lead to knock are already well under way.

The lower effectiveness of TML at low concentration, as shown in Figure 4, may be partially due to octane level but also suggests that the concentration dependence of the agglomeration process may limit the particle growth to an effective size in the case of TEL.

The proposed mechanism thus explains the major overt phenomena of antiknock activity. It relates the relative stabilities of TEL and TML to their effectiveness in fuels

Table VI. Influence of Octane Level

Fuel Composition		Octane Rating with 3 Ml. TEL Per Gallon		Octane Improvement (TML Minus TEL)	
60%	40%	Research method	Motor method	Research method	Motor method
Toluene	PRF[a] 70	107.9	96.4	- 0.4	1.8
Toluene	PRF 50	103.1	92.3	- 0.5	0.7
Toluene	PRF 30	99.0	88.6	- 0.1	0.2
Toluene	*n*-Heptane	93.2	83.1	+0.1	-0.1
Mixed olefins[b]	PRF 100	104.1	91.9	- 0.2	0.5
Mixed olefins	PRF 80	101.8	90.1	- 0.5	0.4
Mixed olefins	PRF 50	97.2	88.1	- 0.9	0.3
Mixed olefins	*n*-Heptane	87.3	82.5	- 2.3	-1.4
Iso-octane[c]	PRF 75	101.7	107.8	- 0.6	-3.3
Iso-octane	PRF 50	96.2	99.9	- 0.3	-3.1
Iso-octane	PRF 25	90.9	91.5	- 0.3	-2.5

[a] Primary reference fuels.
[b] Known commercially as "motor polymer".
[c] Data presented in Table V.

of various compositions and octane levels. The decrease in the relative effectiveness of TML at high concentrations, as shown in Figure 4, requires another explanation and possibly involves the reactivity of the ethyl and methyl radicals toward inducing preflame reactions.

TOXICITY EVALUATION

As demonstrated by careful study through years of commercial use, the vapors of TEL present no public health problem. A program initiated in conjunction with the TEL industry has demonstrated that there is no health hazard associated with the replacement of TEL with TML. R.A. Kehoe, a noted authority on industrial toxicology, served as a consultant.

Studies since the introduction of TEL have demonstrated that persons, such as garage workers, who are in contact with leaded gasolines more than the general urban population exhibit only a barely significant increase in the amount of lead absorbed associated with the use of TEL. Our studies have shown no increase in the amount of lead absorbed when TEL is replaced with TML.

On the basis of these studies, it was concluded that there is no hygienic reason why TML should not be used commercially as a replacement for TEL. These test data were presented to the Surgeon General of the United States to demonstrate that no public health problem is to be anticipated from the marketing of gasolines containing TML.

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Carboxylic Acids Extend the Antiknock Effectiveness of Tetraethyllead

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IN RECENT YEARS, research in these laboratories has been directed toward finding new compounds to enhance the octane quality of modern gasolines. This program stemmed from recognition of two important facts. First, as the octane number of automotive fuels increases, the cost of additional refining facilities increases. An additional octane number in today's premium gasolines costs between 0.2 and 0.5 cent per gallon. Addition of tetraethyllead (TEL) in amounts above 3 ml. per gallon is often unattractive because the cost is not compensated for by sufficient octane increase. Second, major changes have occurred in gasoline composition and engine design since the discovery of TEL almost 40 years ago. These facts made a re-evaluation of the field of antiknock compounds under modern engine conditions very desirable.

By the study of various additives in modern high octane gasolines, we hoped to find compounds which would provide one or two valuable octane numbers by a mechanism that is specific to the modern situation and could have been absent or overlooked in work with lower octane gasolines.

A variety of compounds possessing "labile" hydrogen atoms were investigated, including amines, phenols, and alcohols. Carboxylic acids were tested as a part of this work. Many such acids caused improvements of about 2.5 research octane numbers in 100-octane leaded gasoline.

A NEW CLASS OF ANTIKNOCK COMPOUNDS

It was the finding that the increased octane performance attributed to acetic acid was directly related to TEL concentration which signaled the discovery of a previously unknown class of antiknock agents—the "TEL extenders." The synergistic effect of acetic acid with TEL is shown in Figure 1. There is a narrow range of acetic acid concentration for maxium response; thus, at 0.5 weight %, there is an octane gain of 2.5 numbers with 3 ml. of TEL per gallon. At 1.0 weight % acetic acid and 6 ml. of TEL the gain is 4.0 numbers. The optimum mole ratio of acetic acid to TEL is roughly 15 to 1. The curves in Figure 1 are general for monocarboxylic acids with similar dissociation constants. Descriptive data for the test gasoline are given in Table I.

The optimum octane improvement to be gained from such extenders at various TEL concentrations is shown in Figure 2. The nearly flat response curve for TEL above

Table I. Description of Test Gasolines

Fuel No.	Octane Rating with 3 Ml. TEL/Gal.		Hydrocarbon Composition, Vol. %			Distillation[a] °F., at % Evaporated			Sulfur, Wt. %
	Research	Motor	Aromatics	Olefins	Paraffins and naphthenes	10%	50%	90%	
1	99.5	87.6	43	16	41	123	240	372	0.05
2	98.0	86.2	29	22	49	119	215	341	0.08
3	103.7	92.1	48	11	41	123	242	318	0.06
4	99.9	87.8	36	23	41	118	223	328	0.07

[a] ASTM Procedure D 86