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.

ACKNOWLEDGMENT

The authors gratefully acknowledge the contributions of D.R. Olson in connection with this study.

LITERATURE CITED

(1) Campbell, J.M. (to General Motors Corp.), U.S. Patent **2,304,883** (December 1942).
(2) Livengood, J.C., Leary, W.A., *Ind. Eng. Chem.* **43**, 2797 (1951).
(3) Nickerson, S.P., *J. Chem. Educ.* **31**, 560 (1954).
(4) Rifkin, E.B., *Proc. Am. Petrol. Inst.* **38**, III, 60 (1958).
(5) Smyers, W.H., Cross, T., Jr. (to Standard Oil Development Co.), U.S. Patent **2,310,376** (February 1943).

RECEIVED for review May 12, 1960. Accepted October 10, 1960. Division of Petroleum Chemistry, 138th Meeting, ACS, New York, N. Y., September 1960.

Carboxylic Acids Extend the Antiknock Effectiveness of Tetraethyllead

W.L. RICHARDSON, M.R. BARUSCH, W.T. STEWART, G.J. KAUTSKY, and R.K. STONE
California Research Corp., Richmond, Calif.

A condensed version of this article appears in *Industrial and Engineering Chemistry,* April 1961, page 306

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

3 ml. in the absence of extenders is characteristic of modern, highly aromatic gasolines.

To demonstrate that extenders become even more attractive with increasing octane number, the responses of two fuels of similar composition but different octane levels of TEL per gallon. The optimum concentration of acetic acid in the 104 octane fuel affords an improvement of 0.3 of an octane number over the 100 octane fuel.

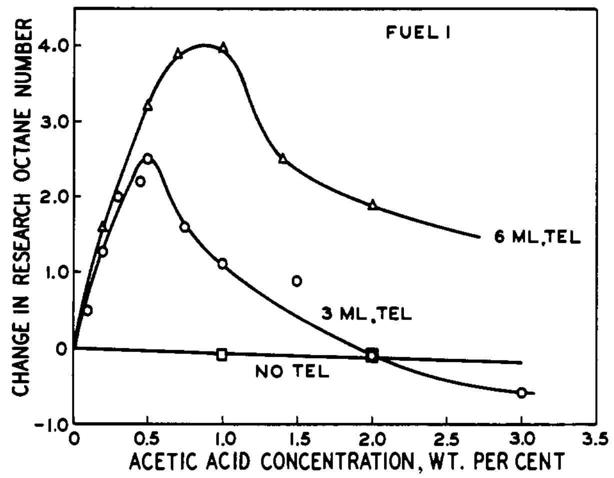


Figure 1. Effect of acetic acid on research octane number

The influence of gasoline composition on the effectiveness of extenders is exemplified in Figure 4. Here, three fuels of varying aromatic hydrocarbon content and nominal research octane ratings of 100 (with 3 ml. of TEL per gallon) are compared. Acetic acid enhances the octane quality of the most aromatic fuel 2.5 numbers, while the least aromatic fuel is improved by 1.2 numbers.

DERIVATIVES OF CARBOXYLIC ACIDS AS TEL EXTENDERS

Other compounds acted as extenders by decomposing thermally in the operating engine to yield a monocarboxylic acid, prior to the antiknock reaction.

Esters of Tertiary Alcohols. Most promising among these were esters of tertiary alcohols, such as *tert*-butyl acetate. These compounds are known to decompose thermally to yield the corresponding acids and olefins. The effectiveness of *tert*-butyl acetate and acetic acid is compared in Figure 5. Generally, compounds which must first decompose to give extender properties were considerably less effective than the parent acid, at optimum concentration. However, the concentration range for maximum effect is greatly broadened.

The effectiveness of *tert*-butyl acetate as an extender in

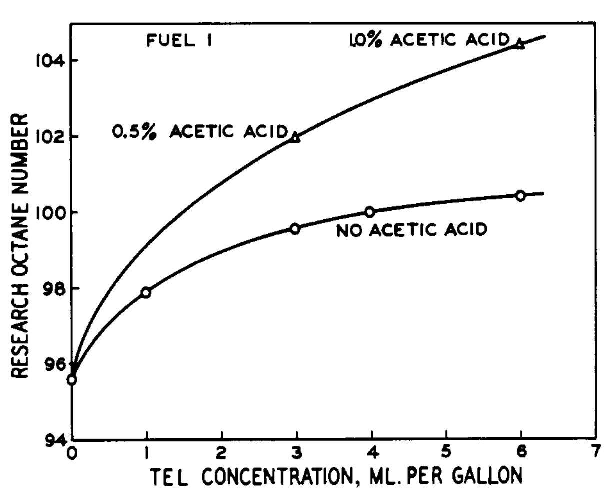


Figure 2. Optimum octane improvement

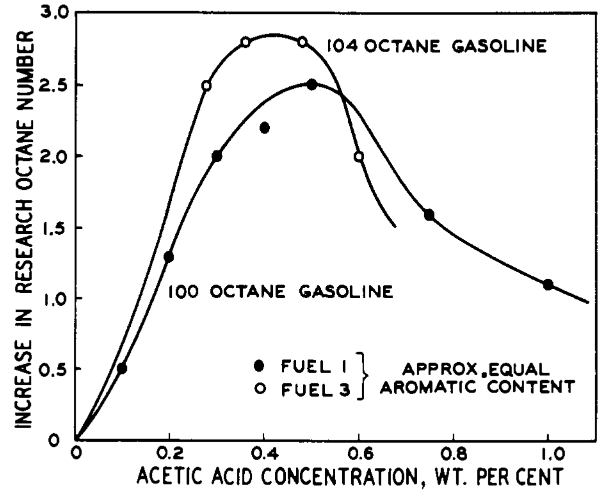


Figure 3. Influence of octane level

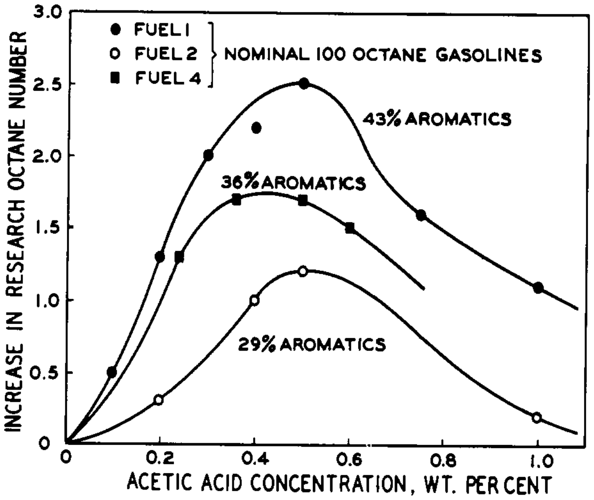


Figure 4. Influence of aromatic content

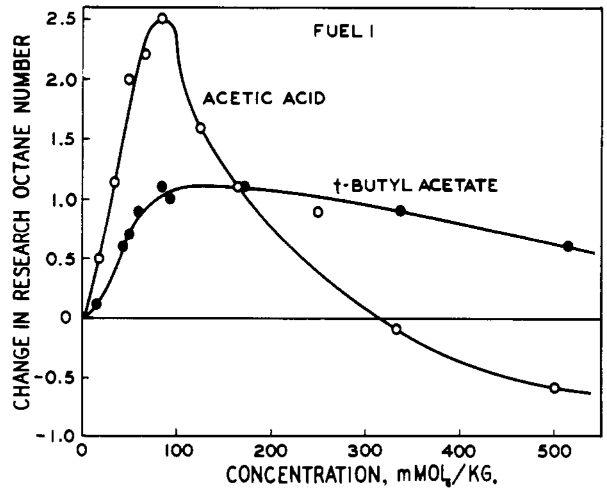


Figure 5. Comparison of *tert*-butyl acetate and acetic acid

laboratory engines and automobiles (three engine test procedures) is shown in Figure 6. The road octane data are averages of results from five test cars. In general, tests in a wide variety of gasolines containing 3 ml. TEL per gallon, show that the optimum concentration of *tert*-butyl acetate in single-cylinder engines is between 75 and 100 mmole per kg. (0.75 to 1.0 volume %), while in automobiles, the optimum response is obtained at between 50 and 75 mmole per kg. (0.5 to 0.75 volume %).

Structural Requirements for Extenders. Research octane number improvement data for some of the hundreds of compounds which were investigated are presented in Table II. Certain requirements for an effective extender become apparent on inspection of these data. A variety of monocarboxylic acids are effective. To be an effective extender an acid must possess a certain minimum thermal stability. Formic acid, being relatively unstable, is ineffective. Dicarboxylic acids, such as dioleic acid, are proknock. A number of *tert*-butyl esters of dicarboxylic acids are also proknock as shown in Table II. *tert*-Butyl malonate is an effective extender because, although malonic acid is a dicarboxylic acid, it can readily decompose to carbon dioxide and acetic acid.

Carboxylic acids and their derivatives which possess functional groupings, known to be proknock in leaded gasolines, are themselves proknock, as are nitroacetic acid and chloroacetic acid. Still another class of carboxylic acids possesses proknock tendencies: compounds known to form chelates with various metals, such as α-keto acids, α-hydroxy acids, and α-cyano acids.

Table II. Effectiveness of TEL Extenders

Compound	Concn. Mmole/Kg.	Change in Research Octane No.[a]
Carboxylic Acids		
Acetic	50	2.0
Acetic	67	2.2
Acetic	83	2.5
Acetic	125	1.6
Propionic	50	2.3
Butyric	44	2.3
Oleic	80	1.4
Trimethylacetic	50	1.7
Cyclohexane carboxylic	80	2.2
Acrylic	80	2.6
Crotonic	46	2.0
β,β-Dimethylacrylic	80	1.2
Benzoic	50	2.1
o-Toluic	40	1.6
m-Toluic	40	1.6
Phenylacetic	43	0.9
Methoxyacetic	44	1.4
Acetylglycolic	57	0.7
Acetyllactic	95	1.7
Ethyl acid adipate	80	2.0
Formic	43	0.2
α-Hydroxydecanoic	80	0.0
Pyruvic	80	−0.6
Salicylic	24	−1.6
Nitroacetic	48	−0.1
Chloroacetic	42	−3.3
β-Chloropropionic	80	−0.9
Dioleic	80	−1.0
Esters of *tert*-Butyl Alcohol		
tert-Butyl acetate	60	0.9
tert-Butyl acetate	86	1.1
tert-Butyl acetate	103	1.2
tert-Butyl propionate	77	0.9
tert-Butyl octanoate	50	0.9
tert-Butyl trimethylacetate	63	1.0
tert-Butyl methacrylate	84	1.2
tert-Butyl benzoate	56	1.4
tert-Butyl *o*-methoxybenzoate	106	1.0
tert-Butyl *p*-nitrobenzoate	80	0.6
tert-Butyl furoate	95	1.3
tert-Butyl methoxyacetate	80	0.6
tert-Butyl phenoxyacetate	80	0.7
tert-Butyl acetylglycolate	55	1.1
Di-*tert*-butyl malonate	80	0.5
tert-Butyl formate	40	−0.1
tert-Butyl formate	80	0.0
tert-Butyl formate	120	0.1
Di-*tert*-butyl oxalate	40	−0.3
Esters of *tert*-Butyl Alcohol (*Continued*)		
Di-*tert*-butyl succinate	40	−0.1
Di-*tert*-butyl adipate	40	−0.5
Di-*tert*-butyl azelate	30	−2.0
tert-Butyl cyanoacetate	106	−0.9
tert-Butyl nitroacetate	50	−3.2
tert-Butyl *o*-chlorobenzoate	80	−1.1
Esters of Alcohols Other Than *tert*-Butyl Alcohol		
tert-Amyl acetate	80	0.9
Terpinyl acetate	83	1.2
1,1-Dimethylpropynyl acetate	80	1.3
α,α-Dimethylphenylethyl acetate	61	1.1
Propenylidene diacetate	75	0.7
Pinacol diacetate	25	0.4
Methyl acetate	81	−0.6
Isopropyl acetate	49	0.2
Isobutyl acetate	43	0.1
sec-Butyl acetate	69	0.1
Vinyl acetate	80	−0.3
Isopropenyl acetate	80	0.0
Phenyl acetate	37	−0.1
Benzyl benzoate	65	−0.2
Furfuryl acetate	43	−0.1
Glyceryl diacetate	28	−0.4
Butyrolactone	80	0.0
Isovalerolactone	80	−0.1
Phthalide	75	−0.3
Other Derivatives of Carboxylic Acids		
Acetic anhydride	80	1.9
Butyric anhydride	80	1.6
Hexanoic anhydride	100	1.8
Mixed formic-acetic anhydride	85	2.4
Mixed acetic-octanoic anhydride	108	1.6
Mixed acetic-benzoic anhydride	110	2.3
n-Hexylammonium octanoate	40	1.6
Di-*n*-butylammonium octanoate	40	1.4
Triethylammonium octanoate	40	1.7
Aniline propionate	60	2.5
N-methylaniline acetate	90	3.3
N,*N*-dimethylaniline acetate	40	1.8
Pyridine acetate	80	2.6
Benzoic anhydride	50	0.0
Ketene	115	0.0
Benzaldehyde	94	0.0
Butyraldehyde	56	−0.1
Propionaldehyde	93	0.0

[a] Base Fuel 1 with 3 ml. TEL per gallon. All octane number data in this paper are based on averages of at least four determinations. For comparisons of quadruplicate determinations, by the Research method, the 90% confidence interval is ± 0.4 number.

Table II contains representative examples of esters of alcohols other than *tert*-butyl alcohol, which were evaluated for extender activity. The effective compounds were all esters of tertiary alcohols which could form olefins on pyrolysis. This agrees with the known ease of pyrolysis of esters of tertiary alcohols relative to secondary and primary alcohols.

Other derivatives of carboxylic acids are compared in Table II. Since most anhydrides can decompose thermally to yield a molecule of carboxylic acid and a molecule of a ketene, they are effective extenders. Benzoic anhydride, which cannot decompose by this route, is ineffective.

Similarly, various ammonium salts and aniline dervatives are effective, since they can revert to the parent amines and carboxylic acids on heating. Aniline and *N*-methylaniline carry an added effect due to the inherent antiknock properties of such aromatic amines.

A number of aldehydes which might have been expected to be oxidized to the corresponding carboxylic acids during the engine cycle were ineffective as extenders.

Because of its physical and chemical properties, *tert*-butyl acetate is a desirable compound from the commercial standpoint. Preliminary work has shown it to be easy to manufacture and relatively inexpensive. Its response, like that of acetic acid, varies with individual gasolines. It should become more attractive commercially as the TEL content, octane level, and aromatic hydrocarbon content of future gasolines are increased. Our findings on the performance of *tert*-butyl acetate are in general agreement with those recently announced by Texaco (*1*).

MECHANISM OF ANTIKNOCK REACTION

The experimental facts which must be explained by any hypothesis concerning the part played by extenders in the antiknock reaction are the following:

Extenders function only in the presence of a primary antiknock agent, such as TEL.

The degree of extender effectiveness is a function of the TEL concentration.

Extender effectiveness for a given TEL concentration shows a distinct maximum at a ratio of about 15 moles of extender per mole of TEL.

Extender effectiveness increases with increasing aromatic hydrocarbon content.

Only carboxylic acid derivatives which thermally decompose to yield an intact carboxylic acid are effective extenders. Fragments of carboxylic acids are ineffective. Formic acid, which decarboxylates at relatively low temperatures, is ineffective.

Dicarboxylic acids and substituted carboxylic acids capable of chelation are proknock in the presence of TEL.

TEL is rapidly decomposed at the temperatures obtained in high compression ratio engines well before it is consumed by the advancing flame front (2); therefore it is generally agreed that not TEL but some product of its decomposition (probably an oxide) is responsible for the antiknock reaction. To explain the role of extenders, we postulate that concurrent with the release of the antiknock species from TEL, a reaction takes place which rapidly drains off the antiknock species. This reaction is probably an agglomeration of the lead oxide species from the finely dispersed state with the accompanying rapid loss of surface and degree of dispersion. The decomposition of TEL will take place earlier in the engine cycle with increasing compression ratio, while the reactions which lead to knock will occur at a more or less fixed time in the cycle. This is so because the oxidative stability of gasoline (its resistance to knock) is of necessity increased with increasing compression ratio for knock-free performance. Therefore, above some octane level, the decomposition of TEL no longer coincides with a critical stage in the reactions which lead to knock; there is a delay between TEL decomposition and the time the antiknock species is needed. During this period the effectiveness of the antiknock species is drastically curtailed, presumably by agglomeration.

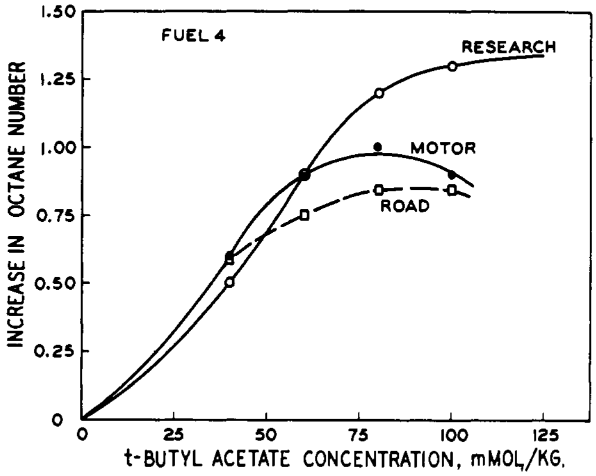


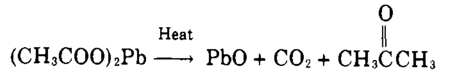
Figure 6. Effectiveness of *tert*-butyl acetate in three rating procedures

Since highly aromatic fuels undergo relatively little preflame oxidation compared to aliphatic fuels, it is likely that the reactions which cause knock start later in the cycle with aromatic fuels. This, as did the effect of octane level, increases the time interval between TEL decomposition and the antiknock reaction.

An explanation of the action of TEL extenders is that they interfere with agglomeration and thus prolong the life of the effective antiknock species until a critical time in the engine cycle. This action is equivalent to increasing the concentration of the antiknock species at the time that it is needed.

A possible reaction sequence whereby carboxylic acids could preserve the degree of dispersion of lead oxide particles is the well-known method for preparing ketones by pyrolysis of their salts.

$$PbO + 2CH_3COOH \rightarrow (CH_3COO)_2Pb + H_2O$$



$$(CH_3COO)_2Pb \xrightarrow{\text{Heat}} PbO + CO_2 + CH_3\overset{\overset{\displaystyle O}{\|}}{C}CH_3$$

The involvement of lead oxide in such a cycle could be expected to retard its agglomeration and, thus, enhance the antiknock activity.

The adverse effect of excessive concentrations of monocarboxylic acids or of dicarboxylic acids and multifunctional acids in tying up the lead oxide so that it cannot take part in the antiknock reaction can also be inferred.

Whether or not this particular reaction sequence is responsible for the extender effect, it appears that such an explanation based on a reduction in the rate of agglomeration of the active antiknock species is consistent with the experimental facts at hand.

ACKNOWLEDGMENT

The authors gratefully acknowledge the assistance of D.R. Olson and R.E. Noble in this work.

LITERATURE CITED

(1) Newman, S.R., Dille, K.L., Heisler, R.Y., Fontaine, M.F., Paper **127U**, S.A.E. National Fuels and Lubricants Meeting, Chicago, Ill., October 1959.

(2) Rifkin, E.B., *Proc. Am. Petrol. Inst.* **38**, III, 60 (1958).

RECEIVED for review June 8, 1960. Accepted December 7, 1960. Division of Petroleum Chemistry, 138th Meeting, ACS, New York, N. Y., September 1960.