5154 *Organometallics* **2003,** *22,* 5154−5178

Cover Essay

The Rise and Fall of Tetraethyllead. 2.

I. Tetraethyllead Solves the "Knock" Problem: Its Discovery and Early Developments—Thomas Midgley, Jr., and Charles F. Kettering.[1]

As noted in part 1,[2] up to 1920 all investigations of tetraethyllead, starting with its discovery in 1853, had taken place in European university laboratories. In part 2, it has crossed the Atlantic Ocean to the USA and it is American industry which has taken up the further study and exploitation of our cover molecule.

It was the phenomenon of "knock" that occurred during the operation of the gasoline engine of the automobiles in the early 20th century that raised tetraethyllead out of the "noise" of the many known organometallic compounds of the day to its stellar prominence as the most commercially important member of this class. To understand tetraethyllead's importance as a knock inhibitor, it is useful to consider the example of a simple four-stroke cycle internal combustion engine (Figure 1).[3] Pictured are the four strokes of such a cycle. On the intake stroke (a) the intake valve has opened and the piston is moving downward, drawing a homogeneous air and gasoline vapor mixture into the cylinder. The compression stroke (b) follows; the intake valve has closed and the piston is moving upward, compressing the fuel/air mixture. On the power stroke (c) which follows, the ignition system produces a spark that ignites the mixture. High pressure is created as it burns which pushes the piston downward. Then comes the exhaust stroke (d) in which the exhaust valve has opened and the piston is moving upward, forcing the combustion gases out of the cylinder. After most of the fuel/air mixture has burned, detonation of a small part of the less volatile, unburned mixture that remains in the cylinder often occurs, caused by the high temperature and pressure; this is what is called "knock". The consequences of knock, besides the irritating noise, are overheating, loss of power output, waste of gasoline, and, when extreme, damage to the engine.

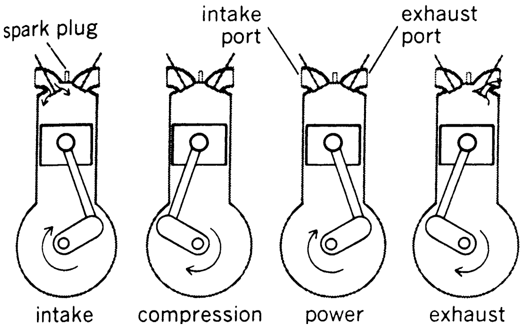

Figure 1. The four strokes of a four stroke engine cycle (reproduced by permission from *The McGraw Hill Encyclopedia of Science and Technology*,[3a] copyright by the McGraw-Hill Companies, Inc.).

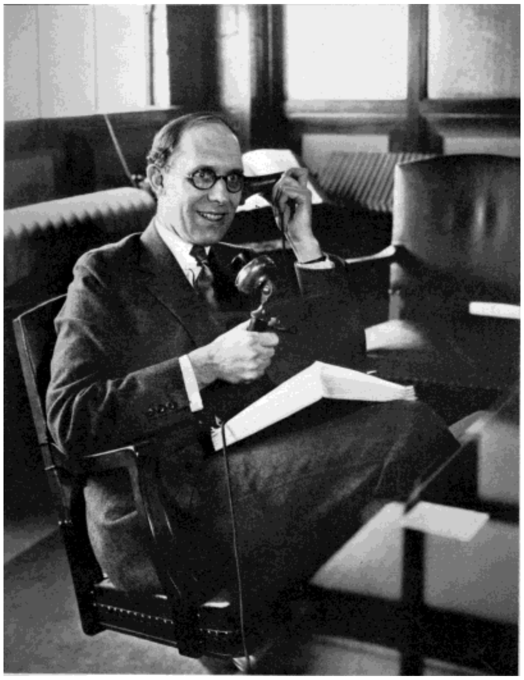

Figure 2. Charles F. Kettering in his office at the General Motors Research Corporation (from *Professional Amateur*, by T. A. Boyd, copyright 1957, renewed 1989; used by permission of Dutton, a division of Penguin Group (USA) Inc.).

It was Charles F. Kettering (1876−1958) (Figure 2)[4] who confronted this problem while he was with the

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[1] There are many sources which give useful, often more detailed overviews of the history of tetraethyllead and tetramethyllead. Some just give the chemistry, and others provide historical accounts with a pro-industry or an anti-industry bias: (a) Kovarik, W. Charles F. Kettering and the 1921 Discovery of Tetraethyl Lead in the Context of Technological Alternatives (talk presented to the Society of Automotive Engineers Fuels and Lubricants Conference, Baltimore, MD, 1994; revised in 1999; available at http://www. Radford.edu/~wkovarik/papers/kettering.html). (b) Robert, J. C. *Ethyl. A History of the Corporation and the People Who Made It*; University Press of Virginia: Charlottesville, VA, 1983 (the tetraethyllead story from the point of view of industry). (c) Nickerson, S. P. *J. Chem. Educ.* **1954**, *31*, 560. (d) Edgar, G. *Ind. Eng. Chem.* **1939**, *31*, 1439. (e) Frey, F. W.; Shapiro, H. *Top. Curr. Chem.* **1971**, *16*, 243−297. (f) Shapiro, H.; Frey, F. W. *The Organic Compounds of Lead*; Wiley-Interscience: New York, 1968. (g) McCormack, W. B.; Moore, R.; Sandy, C. A. *Kirk-Othmer Encycl. Chem. Technol.* **1981**, *14*, 180−196. (h) Nriagu, J. O. *Sci. Total Environ.* **1990**, *92*, 13. (i) Kauffman, G. B. *CHEMTECH* **1989**, 717. (j) Kitman, J. L., The Secret History of Lead. *The Nation* **2000**, March 20 issue (http//www.thenation.com/doc.mhtml?i=20000320&s=kitman) (a lengthy review with a strong anti-industry bias). (k) Leslie, S. W. *Boss Kettering*; Columbia University Press: New York, 1983; Chapter 7, pp 149−180 (references pp 357−359).

[2] Seyferth, D. *Organometallics* **2003**, *22*, 2346. A correction is needed: C. J. Löwig was a professor at the University of Zürich, which was founded in 1833 (not the ETH in Zürich, which was founded in 1854). My thanks to Prof. Albrecht Salzer for pointing this out.

[3] (a) MacCoull, N.; Anglin, D. L. *Internal Combustion Engine* in *Encyclopedia of Science and Technology*, 8th ed.; McGraw-Hill: New York, 1997; Vol. 9, pp. 342−349. (b) Hochhauser, A. M. Gasoline and Other Motor Fuels. *Kirk-Othmer Encycl. Chem. Technol.* **1992**, *12*, p 341. (c) Lewis, B.; von Elbe, G. *Combustion, Flames and Explosions of Gases*, 2nd ed.; Academic Press: New York, 1961.

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Figure 3. Thomas Midgley, Jr., in the 1920s (from ref 5a, by permission of Thomas Midgley IV).

Dayton Engineering Laboratories Company (DELCO) in Dayton, OH, which he had founded in 1909. In 1916, Thomas Midgley, Jr., then 27 years old, joined the DELCO research staff.

Midgley (1889–1944) (Figure 3)[5] had studied engineering at Cornell University, graduating in 1911. Employment at the National Cash Register Company in Dayton followed. After a year, Midgley left NCR to join his father, an independent inventor active in the fields of bicycles, woven wire, and detachable tires, in Columbus, OH, who was trying on his own to develop better cord tires for automobiles. Here Midgley worked to improve cord tires and tire design. He joined the small company, the Midgley Tire and Rubber Company, that his father founded, becoming chief engineer and, later, superintendent. However, the company eventually failed. It was then that Midgley joined DELCO. There he first worked on an ongoing project. Having completed it, he asked Kettering what he should do next. It was then that he learned about knock. As Kettering explained it, although knock was not a serious problem in the low-compression automobile engine of that day, it prevented the development of more efficient and powerful high-compression automobile engines. The problem was that knock increased with increasing compression ratio and this precluded the use of higher compression ratios which, if realizable, would lead to greater fuel economy and greater power output. An automobile engine operating at a higher compression ratio was Kettering's cherished goal; thus, a solution of the knock problem was essential. At the time it was believed that the knock was a result of preignition, but Midgley's initial work showed that knock was caused by a sudden pressure increase *after* ignition.

As Kettering told it,[5b]

> "In talking over the problem we thought maybe if the fuel were colored red it would absorb more radiant heat and evaporate more completely, thus preventing the rough combustion. This theory came to us then because we both happened to know that the leaves of the trailing arbutus are red on the back and that they grow and bloom under the snow."

On the Saturday afternoon in December 1916 that this discussion took place, Midgley found no gasoline-soluble red aniline dye in the stockroom to test this idea. However, the stockroom man offered him a deeply colored substance: iodine. This dissolved in kerosene to give a brownish black solution which was examined in a test engine. To Midgley and Kettering's surprise and delight, there was no knock. However, as Midgley recounted,[6] they soon found out that

> "... iodine had a few slight drawbacks. It added over a dollar to the cost of a gallon of fuel and we were afraid that would be considered a trifle excessive by most motorists. Then too, it had the delightful habit of making iodides out of the car metals with which it came into contact. Carburator and gasoline piping gradually changed into copper and zinc iodides, the cylinders were transformed to iron iodide."

The discovery that iodine was an effective, though impractical, antiknock agent was important, in that it encouraged Midgley to search for others. The red color theory quickly fell by the wayside when it was found that kerosene-soluble red dyes had no antiknock effect. However, colorless ethyl iodide, like iodine, was an effective knock inhibitor; thus, it appeared that iodine was the species responsible for the antiknock action.

The search for an antiknock agent that was both effective and practical was interrupted by World War I, during which Midgley devoted his efforts toward the development of a useful synthetic aviation fuel. He developed, with some difficulty, a catalytic process for the hydrogenation of benzene which gave a 70:30 cyclohexane–benzene mixture. This was tested successfully, but the war ended before it could be put to its intended use.

In 1916 Kettering sold DELCO and founded Dayton Metal Products Co. The Research Division of this new

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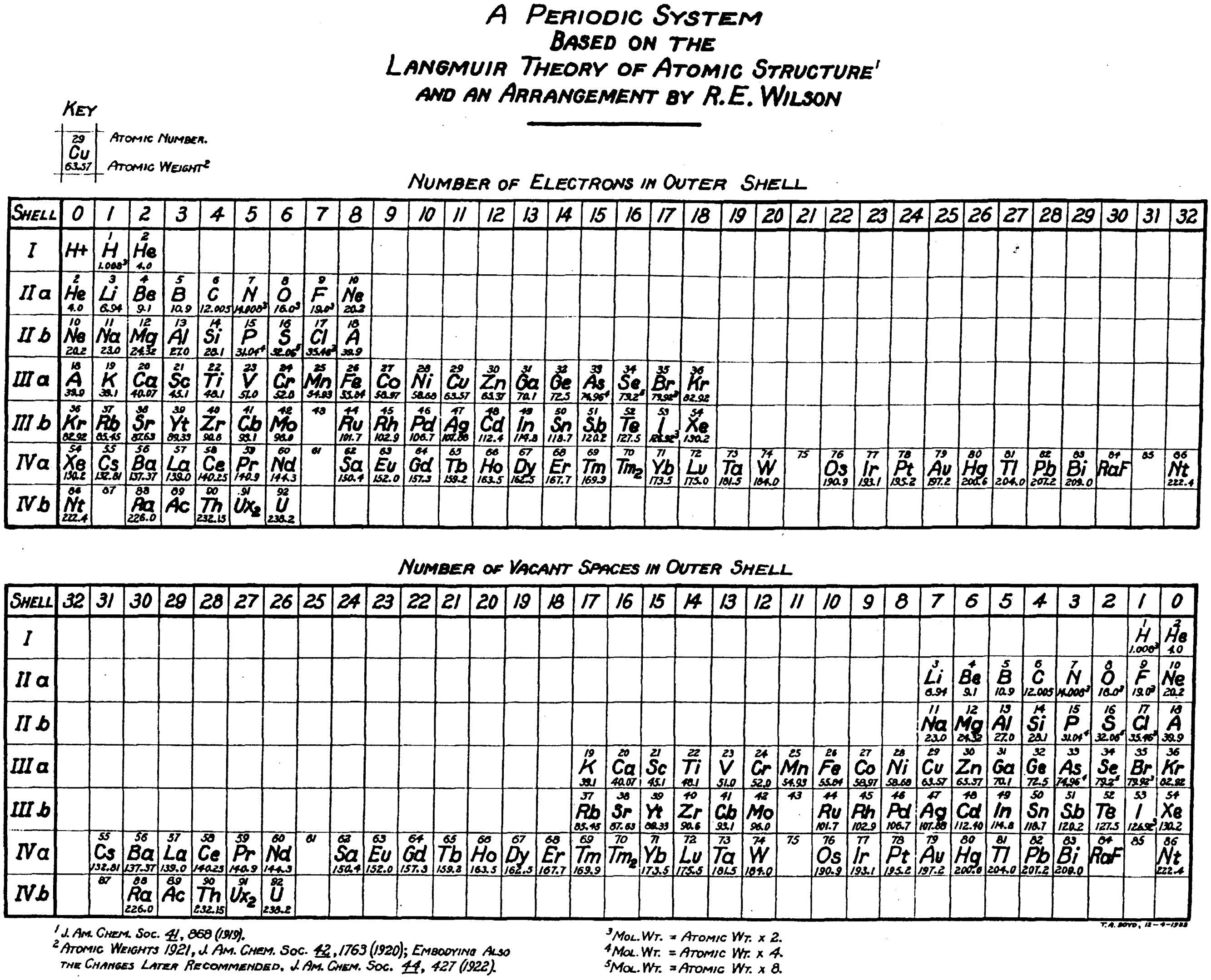
(4) (a) Jeffries, Z. *Biographical Memoirs*, Scientific Memoirs series, National Academy of Sciences, National Academy Press: Washington, DC, 1960, XXXIV, p 106. (b) Boyd, T. A. *Professional Amateur: The Biography of Charles Franklin Kettering*; E. P. Dutton: New York, 1957. (c) Reference 1k.

(5) (a) Midgley, T., IV. *From the Periodic Table to Production: The Life of Thomas Midgley, Jr., the Inventor of Ethyl Gasoline and Freon Refrigerants*; Stargazer Publishing: Corona, CA, 2002. (b) Kettering, C. F. *Biographical Memoirs*; Scientific Memoirs series; National Academy of Sciences, National Academy Press: Washington, DC, 1947; Vol. XXIV, p 361. (c) Kettering, C. F. *Science* **1944**, *100*, 562. (d) Boyd, T. A. *J. Am. Chem. Soc.* **1953**, *75*, 2791. (e) Bernstein, M. *Invention and Technology (American Heritage)* **2002**, Spring issue, 38.

(6) Midgley, T., Jr. *MoToR*, **1925**, *43*, 92.



A PERIODIC SYSTEM
BASED ON THE
LANGMUIR THEORY OF ATOMIC STRUCTURE[1]
AND AN ARRANGEMENT BY R.E. WILSON

KEY

29 — ATOMIC NUMBER.
Cu
63.57 — ATOMIC WEIGHT[2]

NUMBER OF ELECTRONS IN OUTER SHELL

SHELL	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32
I	H+	1 H 1.008[3]	2 He 4.0																														
II a	2 He 4.0	3 Li 6.94	4 Be 9.1	5 B 10.9	6 C 12.005	7 N 14.008[3]	8 O 16.0[3]	9 F 19.0[3]	10 Ne 20.2																								
II b	10 Ne 20.2	11 Na 23.0	12 Mg 24.32	13 Al 27.0	14 Si 28.1	15 P 31.04[4]	16 S 32.06[5]	17 Cl 35.46[3]	18 A 39.9																								
III a	18 A 39.9	19 K 39.1	20 Ca 40.07	21 Sc 45.1	22 Ti 48.1	23 V 51.0	24 Cr 52.0	25 Mn 54.93	26 Fe 55.84	27 Co 58.97	28 Ni 58.68	29 Cu 63.57	30 Zn 65.37	31 Ga 70.1	32 Ge 72.5	33 As 74.96[4]	34 Se 79.2[5]	35 Br 79.92[3]	36 Kr 82.92														
III b	36 Kr 82.92	37 Rb 85.45	38 Sr 87.63	39 Yt 89.33	40 Zr 90.6	41 Cb 93.1	42 Mo 96.0	43	44 Ru 101.7	45 Rh 102.9	46 Pd 106.7	47 Ag 107.88	48 Cd 112.4	49 In 114.8	50 Sn 118.7	51 Sb 120.2	52 Te 127.5	53 I 126.92[3]	54 Xe 130.2														
IV a	54 Xe 130.2	55 Cs 132.81	56 Ba 137.37	57 La 139.0	58 Ce 140.25	59 Pr 140.9	60 Nd 144.3	61	62 Sa 150.4	63 Eu 152.0	64 Gd 157.3	65 Tb 159.2	66 Ho 163.5	67 Dy 162.5	68 Er 167.7	69 Tm 169.9	70 Tm$_2$	71 Yb 173.5	72 Lu 175.0	73 Ta 181.5	74 W 184.0	75	76 Os 190.9	77 Ir 193.1	78 Pt 195.2	79 Au 197.2	80 Hg 200.6	81 Tl 204.0	82 Pb 207.2	83 Bi 209.0	84 RaF	85	86 Nt 222.4
IV b	86 Nt 222.4	87	88 Ra 226.0	89 Ac	90 Th 232.15	91 Ux$_2$	92 U 238.2																										

NUMBER OF VACANT SPACES IN OUTER SHELL

SHELL	32	31	30	29	28	27	26	25	24	23	22	21	20	19	18	17	16	15	14	13	12	11	10	9	8	7	6	5	4	3	2	1	0
I																																1 H 1.008[3]	2 He 4.0
II a																										3 Li 6.94	4 Be 9.1	5 B 10.9	6 C 12.005	7 N 14.008[3]	8 O 16.0[3]	9 F 19.0[3]	10 Ne 20.2
II b																										11 Na 23.0	12 Mg 24.32	13 Al 27.0	14 Si 28.1	15 P 31.04[4]	16 S 32.06[5]	17 Cl 35.46[3]	18 A 39.9
III a																19 K 39.1	20 Ca 40.07	21 Sc 45.1	22 Ti 48.1	23 V 51.0	24 Cr 52.0	25 Mn 54.93	26 Fe 55.84	27 Co 58.97	28 Ni 58.68	29 Cu 63.57	30 Zn 65.37	31 Ga 70.1	32 Ge 72.5	33 As 74.96[4]	34 Se 79.2[5]	35 Br 79.92[3]	36 Kr 82.92
III b																37 Rb 85.45	38 Sr 87.63	39 Yt 88.33	40 Zr 90.6	41 Cb 93.1	42 Mo 96.0	43	44 Ru 101.7	45 Rh 102.9	46 Pd 106.7	47 Ag 107.88	48 Cd 112.40	49 In 114.8	50 Sn 118.7	51 Sb 120.2	52 Te 127.5	53 I 126.92[3]	54 Xe 130.2
IV a		55 Cs 132.81	56 Ba 137.37	57 La 139.0	58 Ce 140.25	59 Pr 140.9	60 Nd 144.3	61	62 Sa 150.4	63 Eu 152.0	64 Gd 157.3	65 Tb 159.2	66 Ho 163.5	67 Dy 162.5	68 Er 167.7	69 Tm 169.9	70 Tm$_2$	71 Yb 173.5	72 Lu 175.5	73 Ta 181.5	74 W 184.0	75	76 Os 190.9	77 Ir 193.1	78 Pt 195.2	79 Au 197.2	80 Hg 200.6	81 Tl 204.0	82 Pb 207.2	83 Bi 209.0	84 RaF	85	86 Nt 222.4
IV b		87	88 Ra 226.0	89 Ac	90 Th 232.15	91 Ux$_2$	92 U 238.2																										

T.A. BOYD, 12-4-1922

[1] J. Am. Chem. Soc. 41, 868 (1919).
[2] Atomic Weights 1921, J. Am. Chem. Soc. 42, 1763 (1920); Embodying also the Changes Later Recommended. J. Am. Chem. Soc. 44, 427 (1922).
[3] Mol. Wt. = Atomic Wt. x 2.
[4] Mol. Wt. = Atomic Wt. x 4.
[5] Mol. Wt. = Atomic Wt. x 8.

Figure 4. Robert E. Wilson's version of the periodic table (from ref 8).

company was merged into the General Motors Company (GM) in 1919, becoming the GM Research Division with Kettering as GM vice president for research in charge of this laboratory.

After his wartime activities, Midgley had returned to his search for a practical antiknock compound, helped by Thomas A. Boyd, Carroll A. Hochwalt, and others, trying all chemicals that became available to him without success. After the merger had become effective, he was given 2 weeks to find a new knock inhibitor so that this research would be funded by GM. Just in the nick of time, on January 30, 1919, Boyd found that aniline was an effective antiknock agent.

The development of better fuels and better engines was a matter not only of engineering but also of petroleum and chemical research and development. This realization led Kettering to establish contacts with Standard Oil of New Jersey and the E. I. du Pont de Nemours Company. Both companies, for obvious reasons, were interested in the development of a practical antiknock agent.

Aniline was not the answer. Although it had useful antiknock activity, it had a very bad odor (which exited the exhaust), it oxidized in air, and there were concerns about toxicity and its corrosive effects on metals. Therefore, aniline fell out of contention and the search continued. By the spring of 1921, nothing had been found by Midgley and co-workers, and it looked as though the effort would not be continued. But then Kettering learned of Victor Lenher's synthesis of selenium oxychloride at the University of Wisconsin. A sample was obtained and found to be a very effective antiknock compound. However, it was, as might have been expected, highly corrosive and, hence, not practical. However, this finding led Midgley and co-workers to the alkyl compounds of the heavier group 16 elements. Diethyl selenide was found to inhibit knock effectively, but diethyl telluride was even better. The latter, however, had a serious drawback: when only minute quantities were inhaled or absorbed through the skin, "tellurium poisoning" resulted, the most notable manifestation of which was the strong garlic-like odor given off apparently from every pore in the body − a most objectionable odor to anyone coming in contact with the offending person. This "satanified garlic odor", as Midgley called it, "was so powerful that a change of clothing and a bath at the end of the day did not reduce your ability as a tellurium broadcasting station. Nor did the odor grow much weaker when several days were passed in absence from the laboratory."[6]

A less Edisonian, more scientific approach then was brought to bear on the problem. Robert E. Wilson, then

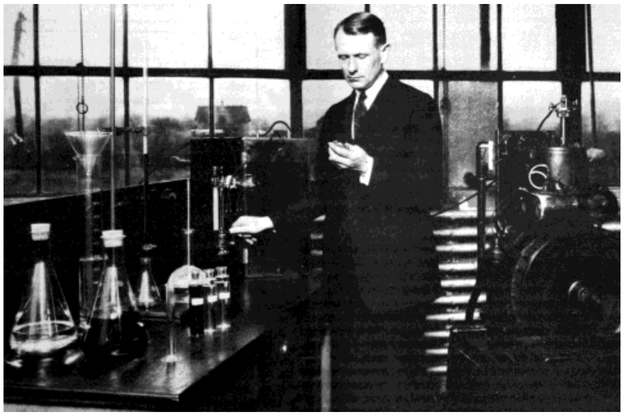


Figure 5. Thomas A. Boyd and the Delco-Light engine in which tetraethyllead was first tested (from *Ethyl. A History of the Corporation and the People Who Made It*, by J. C. Robert, copyright 1983; used by permission of Ethyl Corporation).

Director of the Research Laboratory of Applied Chemistry at the Massachusetts Institute of Technology (later chairman of the board of Standard Oil Company of Indiana), who was working on some projects with GM, discussed with Midgley his search for the magic antiknock agent and suggested using as a guide a version of the periodic table that he had devised (Figure 4). The search, having found positive results with the heaviest group 17 and 16 elements, now focused on the lower right side of the bottom table in Figure 4. What Midgley described as a “scientific fox hunt” now was on. Tetraethyltin was found to have modestly effective antiknock properties, and this suggested that tetraethyllead should give good results. A sample of tetraethyllead was not available or procurable; therefore, a small amount was prepared by Hochwalt by the reaction of diethylzinc with $PbCl_2$. The sample was tested in a one-cylinder engine on December 9, 1921 (Figure 5). Boyd fed a 1% solution of tetraethyllead in kerosene into the test engine: no knock! Further studies with more dilute solutions showed that a one-fortieth of one percent solution of tetraethyllead was equivalent in knock inhibition to 1.3% aniline in kerosene. With the discovery of an extremely effective, apparently practical antiknock agent, the modern high-compression, high power output internal combustion engine could now become a reality. That tetraethyllead was far superior to any other organometallic or organic compound that had been tested for antiknock action is shown in Tables 1[1f] and 2[7] and Figure 6.[8]

However, the discovery of the efficacy of tetraethyllead as an antiknock agent was only the beginning of a long and expensive program of research whose goal was the development of a *commercially practical* antiknock system. As Midgley said some years later:[9]

Table 1. Relative Antiknock Effectiveness of Various Compounds[a]

tetraethyllead	118	tetraethyltin	4
tetraphenyllead	73	triphenylarsine	1.6
iron pentacarbonyl	50	xylidine	1.6
nickel carbonyl	35	diphenylamine	1.5
diethyl telluride	27	*N*-methylaniline	1.4
triethylbismuth	24	dimethylcadmium	1.2
diethyl selenide	7	aniline	1.0
stannic chloride	4.1	ethanol	0.1

[a] Vs aniline = 1 on a mole basis. From ref 1e, by permission of Springer-Verlag and Ethyl Corp.

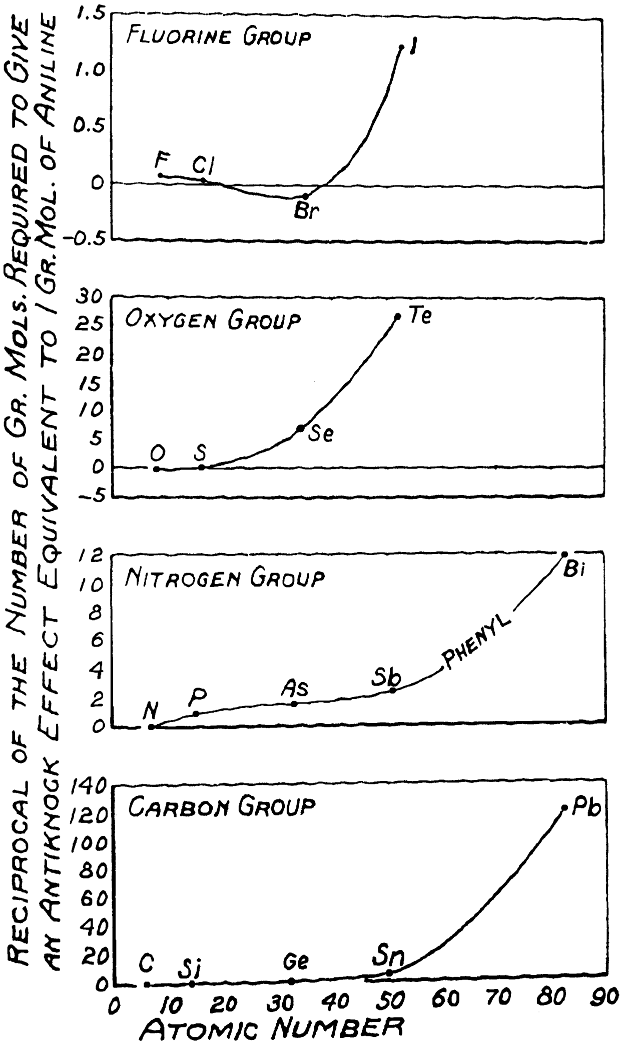


Figure 6. Comparison of antiknock activity within periodic groups 14, 15, 16, and 17 as a function of atomic number (from ref 8).

“The popular idea might be that when we found tetraethyllead we shouted hosannas for it, and all marched in to ask the boss for a raise. Actually, there was not a pause in the program. We started spending more money, doing more research, and looking for other ingredients to go with tetraethyllead, to make up a commercially practical compound that could transfer the antiknock qualities of tetraethyllead to a gallon of gasoline. Thousands of miles were run in various types of automobile tests, hundreds of hours of operation were put in by engines on dynamometer blocks, running day and night. We thought we knew what we had, but we knew we knew very little about it. We had to find the answers, the right answers, to many questions.”

Further work showed that tetraethyllead was not without its problems. When used as a knock inhibitor

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(7) (a) Midgley, T., Jr.; Boyd, T. A. *Ind. Eng. Chem.* **1922**, *14*, 897 (first scientific publication on the antiknock effect of tetraethyllead). (b) U.S. Patent 1,573,846 (Feb. 23, 1926) (Figure 7), application Apr. 15, 1922, was awarded to Midgley. A Midgley patent, U.S. 1,592,954 (July 20, 1926), disclosing the use of an organohalogen scavenger in leaded gasoline followed soon after.

(8) Midgley, T., Jr. *Ind. Eng. Chem.* **1937**, *29*, 241.

(9) Midlgey, T., Jr. *Ind. Eng. Chem.* **1939**, *31*, 504.

Table 2. Compilation of the Relative Effects of a Number of Compounds for Suppressing Detonation as Compared with Benzene[a]

element	compd	% by vol in kerosene required to effect a given suppression of detonation	no. of g molecules in resulting 355 mL mixture with kerosene to give equal suppression of detonation	approx no. of mol of theor fuel−air mixture in which 1 mol exerts an effect on detonation of a given magnitude[b]
	benzene	25.0	1.0[c]	150
iodine	C_2H_5I	1.6	0.07	2150
nitrogen	xylidine	2.0	0.059	2600
tin	$(C_2H_5)_4Sn$	1.2	0.021	7100
selenium	$(C_2H_5)_2Se$	0.4	0.013	11750
tellurium	$(C_2H_5)_2Te$	0.1	0.003	50000
lead	$(C_2H_5)_4Pb$	0.04	0.0007	215000

[a] From ref 7a. [b] The computations of these values have been made on the basis of a kerosene having $C_{18}H_{28}$ as its average molecule. [c] 25% by volume.

in gasoline, it left a grayish yellow residue of lead oxide deposited on the exhaust valves, spark plugs, and combustion chamber, thus negatively affecting engine performance and shortening engine life. It took some time and many engine tests to find a solution to this problem. Finally it was found by Boyd that 1,2-dibromoethane, when added to the tetraethyllead-containing fuel, prevented the formation of lead-containing deposits. Reaction with the dibromide converted the inorganic lead products formed in the engine to $PbBr_2$, which at the temperature of the operating engine was volatile and was expelled from the engine into the exhaust system and from there into the air.

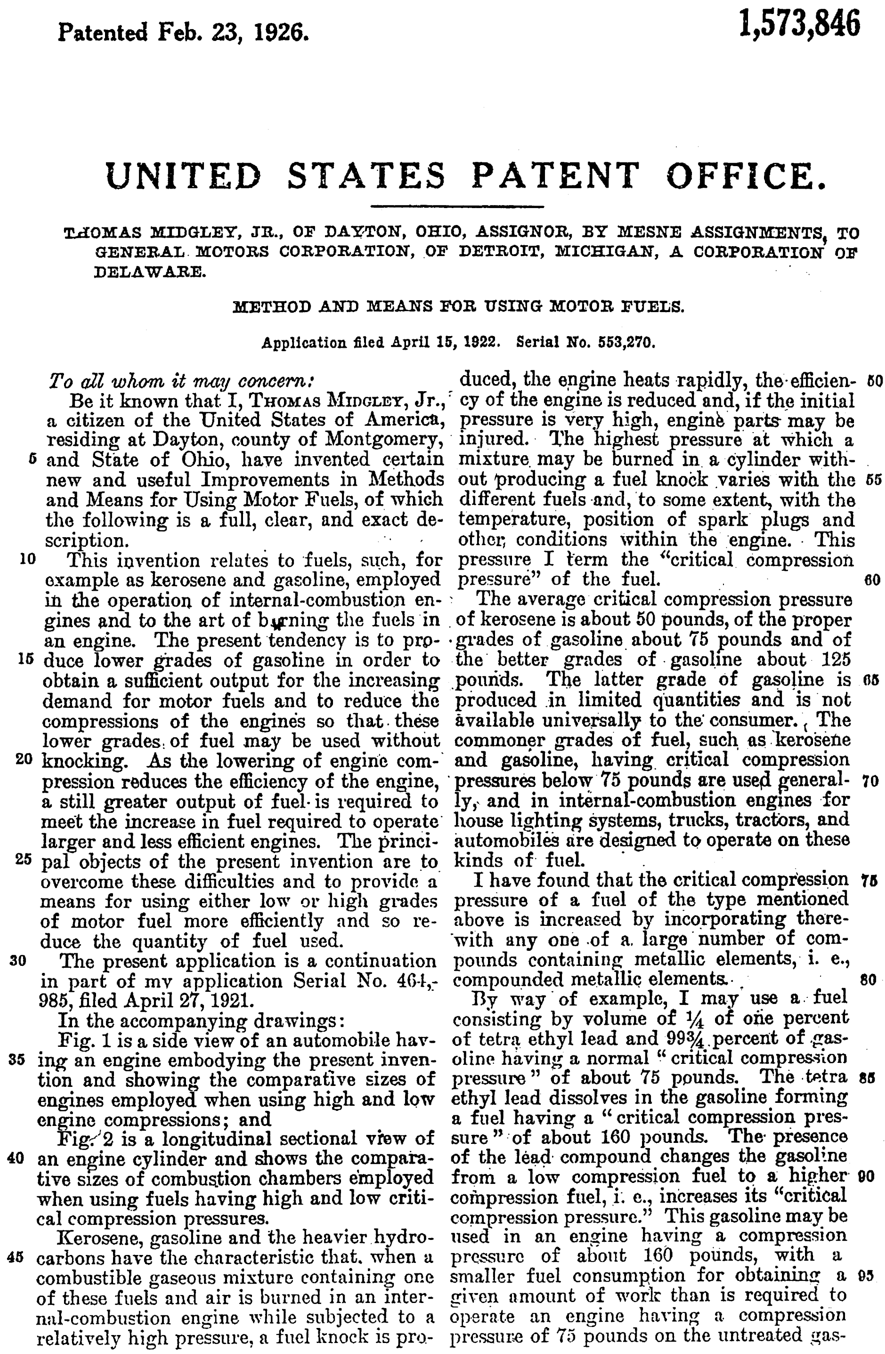
Large quantities of 1,2-dibromoethane would be required, but at that time supplies of bromine were limited and expensive. In the United States, the Dow Chemical Company was by far the major supplier. Its wells in Michigan were the source of a brine rich in alkali bromides, whose oxidation with chlorine gave elemental bromine. Confronted with this problem, Kettering, Midgley, and colleagues developed a process for the extraction of bromine from seawater (whose bromide content is only ∼67 ppm). A pilot plant study in Ocean City, MD, was followed by a test of the process in April 1925, at sea in a converted freighter rechristened the S.S. Ethyl. The effectiveness of the chemists on board was compromised by their seasickness, but about 100 pounds of bromine was produced. Ultimately Ethyl and Dow collaborated in continued work on the bromine process, and this resulted in formation of the Ethyl-Dow Chemical Company to commercialize the process. The first full-scale bromine extraction plant was built in Kure Beach, NC, and the bromine problem was solved. A larger plant was built during World War II in Freeport, TX, which can process up to 550 million gallons of seawater per day.

It is a curious fact of history that *both* of the components of the antiknock additive mix, tetraethyllead and 1,2-dibromoethane (the large-scale availability of the latter resulting from the extraction of bromine from seawater), hark back to Carl Löwig, a protagonist of part 1 of this essay.[2] It was Löwig who was an independent discoverer of bromine (obtained by oxidation with chlorine of the bromide in water from a mineral spring in 1825), and it was Löwig who first prepared tetraethyllead by reaction of ethyl iodide with a sodium−lead alloy in 1853 (although he missed identifying it as a product in his reaction mixture).

Another major problem that remained was the need for a practical synthesis of tetraethyllead. The diethylzinc route was not considered to be a useful large-scale synthesis, and the Midgley group turned to the original synthesis of Löwig, the reaction of ethyl iodide with a sodium−lead alloy. In 1922 GM contracted with DuPont to manufacture tetraethyllead. DuPont was a leader in synthetic organic chemical manufacture; furthermore, it owned a block of 38% of GM stock and two du Pont brothers at the time were presidents of the two companies involved: Pierre S. du Pont of GM and Irénée du Pont of the DuPont Company.[10] Pierre made the initial contact to his brother at DuPont, pointing out the potentially large and profitable market for tetraethyllead but also warning of its known toxicity.

The use of ethyl iodide as the ethyl source was prohibitively expensive, and further research by Midgley and his colleagues at the GM Dayton laboratory in April 1922 showed that the cheaper ethyl bromide could be used in place of the iodide. The successful reaction with ethyl bromide was described by George Calingaert as follows:[11]

> “In a reacting vessel equipped with a suitable stirring device and reflux condenser, one molecule of ground lead sodium alloy $PbNa_4$, is poured into four molecules of ethyl bromide to which 0.4 mole of pyridine has been added. Water is then added slowly, under constant stirring. Some hydrogen is evolved, together with butane, the sodium is converted into sodium bromide and most of the ethyl groups go to form tetraethyl lead. The reaction is controlled by the rate of addition of the water and the rate of cooling of the reaction mass. Much heat is evolved in the process and the temperature must be kept around the boiling point of the alkyl halide in order to avoid excessive evaporation losses.
>
> When all the sodium is used up, as indicated by the fact that no reaction takes place on addition of water, enough water is added to render the mass fluid, and it is subjected to steam distillation. The alkyl halide, if present in excess, distills first, and then the lead tetraethyl, the condensate being tetraethyl lead and water in the ratio of 1 to 4 by volume. The product is then washed free from pyridine and filtered or settled to separate a small amount of water kept in suspension.
>
> The pyridine, which can be replaced by an amine, triethylamine or diethylamine for instance, plays an important, though little understood, part in the mechanism of the reaction. It probably



Patented Feb. 23, 1926. **1,573,846**

UNITED STATES PATENT OFFICE.

THOMAS MIDGLEY, JR., OF DAYTON, OHIO, ASSIGNOR, BY MESNE ASSIGNMENTS, TO GENERAL MOTORS CORPORATION, OF DETROIT, MICHIGAN, A CORPORATION OF DELAWARE.

METHOD AND MEANS FOR USING MOTOR FUELS.

Application filed April 15, 1922. Serial No. 553,270.

To all whom it may concern:

Be it known that I, THOMAS MIDGLEY, Jr., a citizen of the United States of America, residing at Dayton, county of Montgomery, and State of Ohio, have invented certain new and useful Improvements in Methods and Means for Using Motor Fuels, of which the following is a full, clear, and exact description.

This invention relates to fuels, such, for example as kerosene and gasoline, employed in the operation of internal-combustion engines and to the art of burning the fuels in an engine. The present tendency is to produce lower grades of gasoline in order to obtain a sufficient output for the increasing demand for motor fuels and to reduce the compressions of the engines so that these lower grades of fuel may be used without knocking. As the lowering of engine compression reduces the efficiency of the engine, a still greater output of fuel is required to meet the increase in fuel required to operate larger and less efficient engines. The principal objects of the present invention are to overcome these difficulties and to provide a means for using either low or high grades of motor fuel more efficiently and so reduce the quantity of fuel used.

The present application is a continuation in part of my application Serial No. 464,985, filed April 27, 1921.

In the accompanying drawings:

Fig. 1 is a side view of an automobile having an engine embodying the present invention and showing the comparative sizes of engines employed when using high and low engine compressions; and

Fig. 2 is a longitudinal sectional view of an engine cylinder and shows the comparative sizes of combustion chambers employed when using fuels having high and low critical compression pressures.

Kerosene, gasoline and the heavier hydrocarbons have the characteristic that. when a combustible gaseous mixture containing one of these fuels and air is burned in an internal-combustion engine while subjected to a relatively high pressure, a fuel knock is produced, the engine heats rapidly, the efficiency of the engine is reduced and, if the initial pressure is very high, engine parts may be injured. The highest pressure at which a mixture may be burned in a cylinder without producing a fuel knock varies with the different fuels and, to some extent, with the temperature, position of spark plugs and other conditions within the engine. This pressure I term the "critical compression pressure" of the fuel.

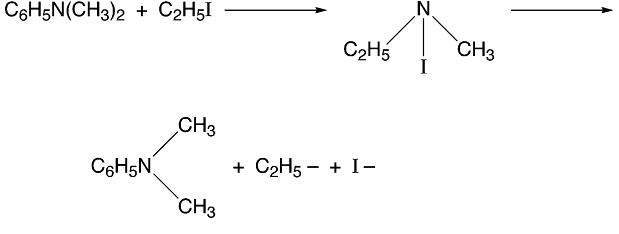
The average critical compression pressure of kerosene is about 50 pounds, of the proper grades of gasoline about 75 pounds and of the better grades of gasoline about 125 pounds. The latter grade of gasoline is produced in limited quantities and is not available universally to the consumer. The commoner grades of fuel, such as kerosene and gasoline, having critical compression pressures below 75 pounds are used generally, and in internal-combustion engines for house lighting systems, trucks, tractors, and automobiles are designed to operate on these kinds of fuel.

I have found that the critical compression pressure of a fuel of the type mentioned above is increased by incorporating therewith any one of a large number of compounds containing metallic elements, i. e., compounded metallic elements.

By way of example, I may use a fuel consisting by volume of ¼ of one percent of tetra ethyl lead and 99¾ percent of gasoline having a normal "critical compression pressure" of about 75 pounds. The tetra ethyl lead dissolves in the gasoline forming a fuel having a "critical compression pressure" of about 160 pounds. The presence of the lead compound changes the gasoline from a low compression fuel to a higher compression fuel, i. e., increases its "critical compression pressure." This gasoline may be used in an engine having a compression pressure of about 160 pounds, with a smaller fuel consumption for obtaining a given amount of work than is required to operate an engine having a compression pressure of 75 pounds on the untreated gas-

Figure 7. Midgley's 1926 patent in which the use of organolead antiknock agents is disclosed.

promotes the reactivity of the alkyl halide molecule by the intermediate formation of an addition compound:



In all cases, the catalyst is recovered unchanged at the end of the reaction."

As far as the addition of water to the C_2H_5Br/sodium−lead alloy mixture is concerned, it would seem that Ghira[12] indeed was right. A sodium−lead alloy of stoichiometry Na_2Pb_4 also worked, but with ethyl chloride these alloys gave only poor results. Not all experiments were that successful. As Leslie relates in

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(10) An account of the manufacture of tetraethyllead by DuPont is given in: Hounshell, D. A.; Smith, J. K., Jr., *Science and Corporate Strategy. DuPont R&D.; 1902−1980*; Cambridge University Press: Cambridge, U.K., 1988; pp 150−155, 557−558, 584.

(11) (a) Calingaert, G. *Chem. Rev.* **1925**, *2*, 43. This was written when Calingaert, a Belgian, was a member of the Research Laboratory of Applied Chemistry at M.I.T. He later joined Ethyl Gasoline Corp., ultimately becoming Director of Chemical Research. (b) See also: Midgley, T., Jr. U.S. Patent 1,622,228 (March 22, 1927).

(12) Ghira, A. *Gazz. Chim. Ital.* **1894**, *24*(I), 42. See discussion in part 1.[2]

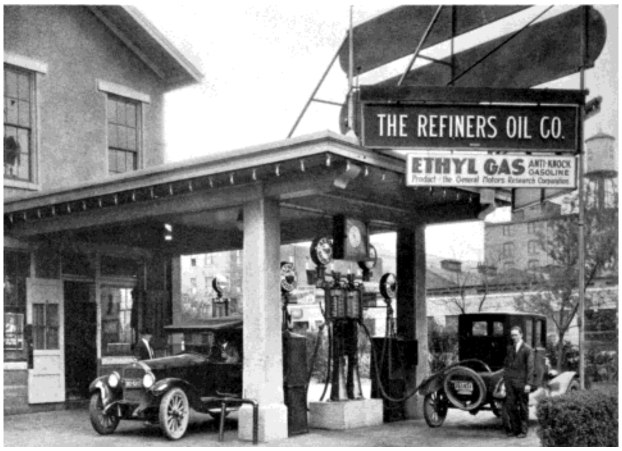

Figure 8. The Refiners Oil Co. gasoline station in Dayton, OH, in which the first gasoline containing tetraethyllead was sold on Feb 1, 1923 (from *Professional Amateur*, by T. A. Boyd, copyright 1957, renewed 1989; used by permission of Dutton, a division of Penguin Group (USA) Inc., and Ethyl Corporation).

his book *Boss Kettering*,[1k] in a misguided attempt to develop a faster tetraethyllead synthesis, a reaction of ethyl nitrate with sodium−lead alloy was tried in an autoclave. After an initially slow reaction, there was a rapid pressure rise and the autoclave exploded before the safety valve could be released. Much laboratory glassware was shattered and some 50 windows were smashed, but nobody was seriously injured.

At this point DuPont took over the preparation of tetraethyllead by the ethyl bromide process, first with a unit that produced 1 gal/day. This effort was led by William S. Calcott, a chemical engineer. By September 1922 the DuPont chemists had obtained tetraethyllead yields of 85% and DuPont began construction of a 1300 lb/day plant. Since GM wanted to bring tetraethyllead-containing gasoline to market as soon as possible, there was great pressure on Calcott to begin production. This was done in September 1923, before proper ventilation had been installed and before safe operating procedures had been developed. A DuPont worker recalled that tetraethyllead at these beginnings was handled in open buckets and that operators dipped their fingers into it in order to test its clarity. Also, controlling the reaction initially was difficult and this led to exposure of the workers to the toxic tetraethyllead. During the first month of the plant's operation a worker died from tetraethyllead poisoning and others had minor cases of poisoning, manifested mostly by neurological disorders.

However, it appeared that tetraethyllead was relatively safe in dilute gasoline solution. The first public sale of Ethyl gasoline (the name given it by Kettering) occurred on February 1, 1923 in Dayton, OH at 25 cents per gallon (regular gas cost 21 cents per gallon) (Figure 8) before large-scale production had started. To distinguish Ethyl gasoline from unleaded fuel, a red dye was added (shades of the first Midgley/Kettering experiment!). How to add tetraethyllead to the gasoline was another problem. Midgley's first idea was to sell it as a pill in which the tetraethyllead was contained in a *p*-toluidine wax. The pills then could be added to the gasoline at the gas station. This method was patented by Midgley, but in practice tetraethyllead in the early days was added as concentrated “Ethyl fluid”, which was poured by hand into the glass container of the gasoline pump. Later the concentrated “Ethyl fluid” was blended into the gasoline by the respective oil company. In September 1922 Standard Oil of Indiana was granted the first major sales contract by GM, giving it an exclusive right to sell Ethyl gasoline in its area.

Ethyl gasoline, which produced no knock, was well received by scientists and by the motoring public. Midgley received immediate recognition, being awarded the William H. Nichols medal by the New York Section of the American Chemical Society in March 1923.[13]

The manufacture of tetraethyllead by the C_2H_5Br + Na/Pb alloy reaction was not the optimum one possible, since bromine was in limited supply; hence, ethyl bromide was expensive. Ethyl chloride was readily available and much cheaper, but for some reason DuPont chemists had not investigated this possibility.

II. The Ethyl Chloride Based Synthesis of Tetraethyllead Permits Large-Scale Commercialization. Toxicity Problems in Its Manufacture

The Standard Oil Company of New Jersey had been interested in the work reported by Kettering, Midgley, and their colleagues since 1919 on their search for an effective and practical antiknock agent, and chemists in their Bayway, NJ, laboratory, working toward this goal, also found aniline to have useful antiknock properties at low, but not at high, speeds.[14] Midgley's discovery of tetraethyllead's outstanding knock-inhibiting properties stopped further efforts by Standard Oil of New Jersey to find a new antiknock agent. GM was interested in having Standard Oil of New Jersey distribute “Ethyl fluid”, but the terms offered were not to Standard's liking.

The advent of tetraethyllead had not stopped Standard's research on antiknock agents, but it was refocused. Realizing that the GM/DuPont ethyl bromide-based synthesis was overly expensive and that ethyl bromide was corrosive, they pursued an alternative preparation based on the cheap ethyl chloride. This project was contracted out to Professor Charles A. Kraus (1875−1967) (Figure 9)[15] of Clark University in Worcester, MA. Kraus had carried out his undergraduate studies at the University of Kansas, majoring in electrical engineering to start but becoming pulled more in the direction of physics through an interest in the electrical conductance of metals. As an undergraduate he carried out research with E. C. Franklin on the properties of liquid ammonia solutions, studying liquid ammonia's solvent properties and later the conductivity of acids, bases, and salts in that solvent. Kraus stayed with Franklin for another year after graduation. He continued his work on conductance in liquid ammonia

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[13] Midgley, T., Jr. *Ind. Eng. Chem* **1923**, *15*, 421 (Nichols Award address).

[14] An account of the work by Standard Oil of New Jersey on tetraethyllead and on its relations with GM is given in: Gibb, G. S.; Knowlton, E. H. *History of Standard Oil Company (New Jersey). The Resurgent Years 1911−1927*; Harper and Brothers: New York, 1956; pp 539−549, 495.

[15] (a) Fuoss, R. A. *Biographical Memoirs*; Scientific Memoirs series; National Academy of Sciences, National Academy Press: Washington, DC, 1971; Vol. 42, p 119. (b) Gordon, N. E. *J. Chem. Educ.* **1929**, *6*, 4. (c) Reference 1c.

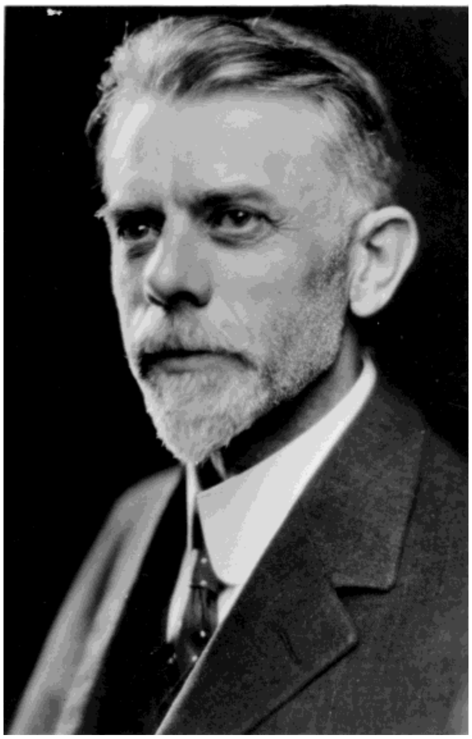

Figure 9. Charles A. Kraus, 1939 (American Chemical Society photo archives).

at Johns Hopkins University during 1899−1900 and then returned to Kansas for a year. Kraus subsequently joined the University of California as an instructor in physics and continued his pioneering research on the conductance of diverse inorganic and organic compounds in liquid ammonia. In 1904 Kraus went to the Massachusetts Institute of Technology to join the Research Laboratory of Physical Chemistry (which Albert A. Noyes had founded in 1903) as a research assistant. He was awarded the Ph.D. degree by M.I.T. in 1908, stayed on as a research associate, and was promoted to assistant professor of physical chemistry in 1912. Kraus' 10 years at M.I.T. were very productive, with classical studies on solutions of metals and of amines in liquid ammonia published during this time. In 1914 came an appointment at Clark University in Worcester, MA, as Professor of Chemistry and Director of the Chemical Laboratory. It was at M.I.T. that Kraus first carried out research on organometallic chemistry. The electrolysis of liquid ammonia solutions of methylmercuric halides was found to result in a deposit at the cathode of a species of stoichiometry CH_3Hg. Up to 1914 Kraus had planned and carried out his experimental work by himself. At Clark he initiated a graduate program and with time was assisted by graduate students, continuing his studies of liquid ammonia solutions and making notable contributions to the understanding of the nature of the solutions of the alkali metals in liquid ammonia.

Kraus began a program of investigations on organotin chemistry at Clark, publishing nine papers in this area in the period 1922−1924, studies of synthesis and reactivity, including reactions in liquid ammonia. In 1924 Kraus moved to Brown University as Professor of Chemistry and Director of Chemical Research. He stayed at Brown until his retirement in 1946 at age 71 but remained active in research until his mid-eighties. At Brown he pursued three research directions: the physical chemistry of liquid ammonia systems, electrolytic conductance in nonaqueous systems, and organometallic chemistry. In the last area he was mainly concerned with the organometallic chemistry and the hydride compounds of silicon, germanium, and tin but also carried out some studies on organoboron, -aluminum, and -gallium compounds. To obtain the needed starting materials for his study of organogermanium compounds, Kraus devised a procedure for extracting germanium from germanite, an ore which occurred in South West Africa. A bonus was that germanite also contained appreciable quantities of gallium, allowing Kraus to study its organometallic chemistry. Kraus was President of the American Chemical Society in 1939.

Kraus' studies on organotin compounds noted above seemed a good qualification for research on organolead chemistry in the eyes of Standard Oil of New Jersey management. One of his students, Conrad C. Callis, had in fact prepared methyltin compounds by the reaction of methyl chloride with a sodium−tin alloy. Of interest is the quotation from an account by Kraus on this work, as given in Nickerson's article on tetraethyllead in the *Journal of Chemical Education*.[1c]

> "...after World War I, I decided to make a more thorough investigation of organo tin compounds, particularly methyl derivatives. I turned the job over to Callis, and he carried out the investigation for his Ph.D. degree.
>
> Our results with the new Grignard reaction were not very promising, and so we decided to begin by preparing trimethyl tin iodide by the reaction of sodium−tin alloy and methyl iodide, a process which I had used successfully many years earlier. This reaction proceeded satisfactorily after we learned that zinc acted as a catalyst when added to the alloy.
>
> We were confronted with a practical difficulty, because I had in mind carrying out rather extensive investigations with the methyl tin derivatives, and iodine at that time was a very expensive element. Even bromine was not too plentiful and was rather costly. Accordingly, I decided to carry out the reaction of the alloy with methyl chloride, which at that time was available on the market in cylinder form. We built an autoclave having a capacity of about three liters, charged it with alloy and methyl chloride, and allowed it to react.
>
> We found that we had to control the reaction by keeping it going for some time, about 24 h, at 0° and then allowing the reaction to come up gradually to 100°. On allowing the reaction to stand for some time at any one temperature, the pressure fell as the methyl chloride was consumed, and so the temperature was raised to keep the pressure substantially constant. On heating to 100° for a period of time, virtually all the methyl chloride was used up and practically quantitative yields of tetramethyl tin were obtained"

Kraus, with the assistance of Callis (who returned to Clark after having left with his Ph.D.), W. N. Greer, and R. Rosen, began the investigation aimed at a more practical tetraethyllead synthesis. Kraus' own words tell us how this work proceeded.[1c]

> "When Callis came back to the laboratory at Clark in the fall of 1922, we decided to proceed on the basis of our experience with tin compounds. It seemed logical to us that if alkyl halides such as methyl iodide and methyl chloride in reaction with sodium–tin alloy would produce satisfactory yields of tin halides, we would do well to attempt to make tetraethyl lead with some suitable member of the alkyl halide family.
>
> Inasmuch as bromine and iodine were both expensive, and my job was to find a process which would be commercially practical, it seemed to us that the reaction of sodium–lead alloy and ethyl chloride represented the only practical solution.
>
> Neither one of us was familiar with tetraethyl lead. We made it in experimental quantities by the established method of reacting sodium–lead alloy and ethyl iodide while we were getting together the necessary apparatus and materials. I might say that we had little to go on. We designed and built all our equipment ourselves. The first thing we made was an autoclave of about three liter capacity from a section of heavy steel tubing, about 15 in. long and four inches in diameter, as I remember it. I did the welding myself.
>
> We attached a motor with a chain drive to the autoclave in order to revolve it while the reaction was taking place. Inside the autoclave we had steel balls about the size of large marbles so that the mixture could be agitated. The reaction was allowed to proceed to completion under pressure, which required about 6 h. Tetraethyl lead was then separated from this reaction by steam distillation."

Thus, the much cheaper ethyl chloride gave good results and it was a 1:1 Na/Pb alloy which was the most effective. The process was improved with further effort, giving yields of tetraethyllead of 70–75% and, occasionally, up to 85%. It took only 6 months to have the process ready for further development in a small pilot plant of the Standard Oil of New Jersey Bayway plant.

The development of a really practical process for the large-scale manufacture of tetraethyllead was a tremendous achievement, and Kraus was awarded the Nichols medal in the year following Midgley's award. Kraus and Callis never published this work in a scientific journal, but patents were applied for and awarded which covered this discovery. These were assigned to Standard Oil Development Company (a subsidiary of Standard Oil Company of New Jersey).[16] Thus, Standard Oil Company of New Jersey had a superior process for the manufacture of tetraethyllead (with patents applied for), but GM had the basic patents for the application of tetraethyllead as an antiknock agent. What the two companies then did made good sense: they joined forces, forming the Ethyl Gasoline Corporation in August 1924. (In 1942 there was a name change to Ethyl Corporation.) Kettering was named president, Frank A. Howard of Standard Oil, first vice president, and Midgley, second vice president and general manager.

DuPont continued to be involved as the main source of tetraethyllead, but Standard Oil was allowed to produce small amounts of the antiknock in its Bayway semi-works plant using its ethyl chloride process.

DuPont began operation of a 1000 gal/day tetraethyllead unit in which Standard Oil's ethyl chloride based process was used in Deepwater, NJ, in January of 1925.[10] At the beginning the reaction was difficult to control. Pressure surges burst the reactor safety disks, discharging tetraethyllead into the air.

The toxicity of tetraethyllead was noted already in part 1.[2] It is more dangerous than inorganic lead compounds since it is volatile and can be inhaled. Also, it is lipid soluble and is rapidly absorbed through the skin. Its toxic effects caused major problems almost right from the start. Midgley himself and three coworkers suffered digestive problems, subnormal body temperature, and reduced blood pressure, presumably the result of their work on synthesis routes to tetraethyllead during the latter part of 1922. Midgley went to Florida for a month in February 1923 to recuperate. Warnings about the toxicity of tetraethyllead came to Midgley from various sources. The letter of Erich Krause concerning its toxic effects, quoted in part in part 1,[2] written on November 30, 1922, to George Calingaert (then at M.I.T.) was forwarded to Midgley in December 1922 by W. G. Whitman, Assistant Director of the M.I.T. Research Laboratory of Applied Chemistry. However, despite his own health problems and these early warnings, Midgley did not appear to be overly concerned about the health issues associated with the handling and use of tetraethyllead. U. S. Surgeon General Hugh Cumming, however, was concerned about the lead-containing automobile exhaust as a health hazard and, as a result of his urging, the Bureau of Mines in Pittsburgh, in collaboration with GM, undertook some tests in the fall of 1923. Various animals were exposed to the exhaust from a small Delco motor in which Ethyl gasoline was used as fuel. In a report issued in October 1924 the Bureau of Mines concluded on the basis of its animal tests that the danger to the public of breathing lead in automobile exhaust was negligible.

It was during the early years of its commercial production that the dangerous toxic effects of tetraethyllead itself reached alarming proportions. At the small Bayway semi-works unit of Standard Oil of New Jersey, which began operating in September 1924, five workers died and 44 were hospitalized. This was no wonder, considering the equipment and procedures used and the lack of safety precautions in the Bayway plant. Kovarik's review[1a] describes the manufacturing process at the Bayway plant as summarized in a 1936 DuPont report by N. P. Westcott on the origin and early history of the tetraethyllead business as follows:

> On "a large open factory floor" stood "a large iron vessel shaped like two ice cream cones stuck top to top" which "was rotating on its side. From within the vessel came the muffled sound of heavy explosions as sodium reacted violently with ethyl chloride and lead. As the double cone rotated, steel agitation balls churned through the boiling sodium to ensure proper mixing. When the reaction calmed down, a crane moved the double cone to the second work area, where workers unbolted the hatches

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[16] Kraus, C. A.; Callis, C. C. U.S. Patents 1,612,131 (Dec 28, 1926), 1,690,075 (Oct 30, 1928), 1,697,245 (Jan 1, 1929), and 1,694,268 (Dec 4, 1928).

> over the narrow ends, releasing concentrated fumes from inside. They attached steam lines and condensers and tetraethyllead was distilled....”
>
> “When the distillation was over, workers opened the iron vessel once again and scraped the steaming leftover lead mush through a grate in the floor with shovels, gloves and boots. As the mush went through the grate, the workers recovered the steel balls that would be used to agitate the next batch.”

The unit was shut down in October, and Standard Oil terminated its tetraethyllead manufacturing operations in November.

In the DuPont plants there also were deaths: one in September 1923, three in 1924, and four in 1925 (when the ethyl chloride process started up), and also many illnesses. In the Dayton laboratory of GM there were several deaths at the time when the ethyl bromide process was being used to produce 7 gal of tetraethyllead/day. These deaths were due to inadequate safety precautions, poor ventilation, and carelessness. Midgley, in a 1925 article entitled “Tetraethyl Lead Poison Hazards”[17] concluded “the actual hazard involved in the general program of treating gasolin with tetraethyl lead has been found to exist only in the manufacturing and handling of the concentrated material.” The symptoms of tetraethyllead poisoning he listed as, in order of their appearance, “drop of blood pressure, drop of body temperature, reduced pulse, sleeplessness (at which point the person is in danger), loss of weight, sometimes nausea, sometimes tremor, and, in the most serious cases, delirium tremens.” After the Ethyl concentrate has been mixed with gasoline (1 part of tetraethyllead to 1300 of gasoline) Midgley said there is no health hazard, provided that it is not misused; nor, he claimed, was there any evidence that the exhaust of a motor using leaded gasoline as fuel was dangerous.

A furor erupted following the deaths at Standard Oil and DuPont, with much negative press comment, which led to the belief that tetraethyllead-containing gasoline itself was a health hazard. The state of New Jersey and New York City and Philadelphia suspended the sale of leaded gasoline. As ref 1j relates, the New York City Board of Health said, when they banned the use of leaded gasoline, “such mixtures of gasoline, containing lead or other deleterious substances, may be liable to prove detrimental and dangerous to the health and lives of the community, particularly when released as exhaust from motor vehicles.” In view of all these difficulties that confronted the Ethyl Gasoline Company, Alfred P. Sloan, the new CEO of GM, in April 1925 replaced Kettering and Midgley by new management with some experience and aptitude in law and business. (Kettering and Midgley returned to research, which was their strength.) The new president of the Ethyl Gasoline Corporation, Earle W. Webb, on May 1 suspended the sale of leaded gasoline until its potential public health hazards could be assessed. An investigating committee was appointed by the Surgeon General to do this. The committee, composed of authorities in the areas of industrial hygiene, clinical medicine, and physiology, concluded that leaded gasoline was not a health hazard to the public, saying that “there are at present no good grounds for prohibiting the use of Ethyl gasoline with a composition specified as a motor fuel, provided that its distribution and use are controlled by proper regulation.”[18] However, in view of the great increase in the number of automobiles, the committee recommended that these studies be continued under the supervision of the Surgeon General. This was not done. On May 16, 1926, after a 1 year hiatus, leaded gasoline was back on the market. The Ethyl Gasoline Corporation and DuPont now worked under stringent regulations applicable to the manufacture of tetraethyllead, its blending into the gasoline, and its distribution. It appeared that leaded gasoline was here to stay.

It should be mentioned, if only briefly, that tetraethyllead was not the only solution to the knock problem that had been considered. Tetraethyllead and the compounds in Tables 1 and 2 are “low percentage” antiknock agents, i.e., only small concentrations of these sufficed to deal with knock. However, “high percentage” gasoline additives also were a possibility: benzene and ethyl alcohol blended to the extent of 20−30% with gasoline. Midgley and Boyd in 1920−1921 carried out extensive research in this area and favored ethanol, since its use brought the significant advantages of clean burning, no carbon deposits, increase in power, and no knock and only minor disadvantages. Nevertheless, in the early 1920s at least, there were major problems: the problem of ethyl alcohol supply and also the problem of producing and using ethyl alcohol on an industrial scale during the prohibition era. In any case, when the antiknock action of tetraethyllead was discovered, ethyl alcohol, which would displace 20−30% of the gasoline, no longer found favor. It was used for a time as a “high percentage” additive in Europe. Now, following the demise of tetraethyllead in the USA and in most of Europe, and after the present phasing out of methyl *tert*-butyl ether which succeeded tetraethyllead as a gasoline additive, ethanol has found its way into gasoline again. More information concerning the consideration of ethyl alcohol as a gasoline additive in those early days can be found in refs 1a,j.

Research on the commercial preparation of tetraethyllead and on its optimization as an antiknock additive in gasoline continued.[19] The use of 1,2-dibromoethane as a lead “scavenger”, an action which made the practical use of tetraethyllead as a gasoline additive in the automobile engine possible, has already been noted. Later research showed that a mixture of 1,2-dibromo- and 1,2-dichloroethane provided an even more effective scavenging action. In succeeding years there was much research at Ethyl, DuPont, and other companies on the ethyl chloride/sodium−lead alloy reaction. This resulted

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(17) Midgley, T., Jr. *Ind. Eng. Chem.* **1925**, *17*, 827.

(18) (a) *The Use of Tetraethyl Lead Gasoline in its Relation to Public Health*; Public Health Bulletin No. 163; U.S. Public Health Service, Treasury Department: Washington, DC, 1926. (b) For an account of the first industrial experiences with tetraethyllead toxicity and the reactions of industry, the government, and public health advocates, see: Needleman, H. L. *Environ. Res.* **1997**, *74*, 95. Rosner, D.; Markowitz, G. *Am. J. Public Health* **1985**, *75*, 344. See also ref 1b.

(19) For more detailed discussions of the commercial practice of the $C_2H_5Cl/NaPb$ reaction see: (a) References 1e−g. (b) Shapiro, H. In *Metal-Organic Compounds*; Advances in Chemistry Series 23; American Chemical Society: Washington, DC, 1959; pp 290−298. (c) Vogel, C. C. *J. Chem. Educ.* **1948**, *25*, 55. (d) Sittig, M. *Organometallics*; Chemical Process Monograph No. 20; Noyes Development Corp.: Park Ridge, NJ, 1966; pp 67−104 (details gleaned from the patent literature). The discussion in the text which follows is based mostly on the information provided by Shapiro and Frey in refs 1e and 19b.

in a great number of patents covering all possible modifications, some of which brought appreciable improvements. Of chemical interest is the use of organic catalysts and accelerators such as ketones, aldehydes, acetals, esters, anhydrides, and amides. However, the basic reaction (eq 1)

$$4NaPb + 4C_2H_5Cl \rightarrow (C_2H_5)_4Pb + 3Pb + 4NaCl \quad (1)$$

remained unchanged. Gaseous byproducts include ethylene, ethane, and *n*-butane, which suggests (but does not require) that a free radical pathway is involved. As a heterogeneous reaction carried out in an autoclave under autogenous pressure, the process is difficult to study. The most reactive alloy is 1:1 NaPb (10% Na, 90% Pb by weight), and it reacts rapidly only with ethyl chloride; thus, Kraus and Callis had it right at the start. Other ethyl and methyl halides inhibit the reaction. Other substances are known inhibitors, in particular an acetylene impurity in the ethyl chloride of only 0.0025%. The reaction is characterized by an induction period, which is shortened by the catalysts and accelerators noted above. A more rapid initiation of the reaction also can be achieved by substituting a small amount of potassium for sodium in the NaPb alloy. It follows from eq 1 that 75% of the lead charge of the alloy is converted to metallic lead. This is recycled. The yields of tetraethyllead in the commercial process are around 85−90% based on eq 1. Only negligible amounts of hexaethyldilead are produced.

The batch manufacturing process for tetraethyllead and Ethyl gasoline concentrate is shown in Figure 10. This is a fully integrated process: the sodium required for the alloy is prepared by electrolysis of dry NaCl in a modified Downs cell. Molten sodium and molten lead are mixed to make the NaPb alloy, which is cast, broken up, ground, and stored under nitrogen. Ethyl chloride is prepared by the catalytic hydrochlorination of ethylene. The required anhydrous HCl is prepared by the reaction of hydrogen with chlorine from the NaCl electrolysis.

For the tetraethyllead synthesis, the NaPb alloy is charged into a horizontal mild steel autoclave equipped with plow-type agitators. The ethyl chloride and the catalyst, usually acetone, are added during a period of several hours. The reaction temperature is maintained at 70−75 °C by the refluxing ethyl chloride and external cooling, and the reaction mixture is maintained at this temperature for another 30−60 min. The gases formed as byproducts are vented as the reaction proceeds.

After the reaction is completed, the autoclave is vented and the residue is charged into water-containing steam stills. Steam distillation in which steam is passed through the still in which the reaction mass is being agitated follows. Some dissolved ethyl chloride is removed first, and then the tetraethyllead is steam-distilled. Anticoagulants (sodium thiosulfate, ferrous and ferric salts) usually serve to prevent the finely divided lead from forming balls. Purification of the crude tetraethyllead by mild oxidation (treatment with dilute aqueous H_2O_2 or $Na_2Cr_2O_7$ or by air blowing) follows. This procedure is needed to remove organobismuth compounds derived from the bismuth impurity in the lead metal. Finally, the tetraethyllead is washed with water and, now about 99% pure, is blended with the required quantities of 1,2-bromo- and 1,2-dichloroethane scavengers, red dye, antioxidant, and other additives to give the final Ethyl antiknock fluid.

DuPont developed a continuous process which began to be used in Deepwater, NJ, in 1953. A second plant was built in California in 1957. The chemistry is basically the same. The reactants are fed continuously into an agitated cascade reactor, where their residence time is several minutes at 230−300 psi and 110−150 °C. A stripper then serves, through injection of steam and water, to separate unreacted ethyl chloride and the tetraethyllead from the lead and sodium chloride. The sodium chloride is dissolved in water, and the lead is recycled. Tetramethyllead[20] was introduced by Ethyl and DuPont as a commercial antiknock agent in 1960. Its manufacture is quite similar to that of tetraethyllead, i.e., the reaction of methyl chloride with NaPb alloy, except for the following differences: (1) the use of a catalyst (an aluminum halide or alkylaluminum compound) is required since in its absence the CH_3Cl/NaPb reaction is very slow; (2) higher reaction temperatures and pressures are used with the lower boiling methyl chloride; (3) for safety's sake a small amount of toluene or other hydrocarbon with a vapor pressure similar to that of tetramethyllead is added to reduce the methyl chloride vapor pressure and to stabilize the tetramethyllead. (The hydrocarbon is not removed from the tetramethyllead and remains as a component of the final antiknock fluid.) Tetramethyllead is a less effective antiknock agent than tetraethyllead, but it finds special utility in gasolines that contain large concentrations of aromatic compounds.

Antiknock fluids containing mixtures of tetraethyl- and tetramethyllead as well as mixtures of $(C_2H_5)_n(CH_3)_{4-n}$ ($n = 0-4$) compounds resulting from Lewis acid catalyzed redistribution of tetraethyl- and tetramethyllead mixtures also have been produced and used.

At the beginning, tetraethyllead was used in a concentration of 3 mL/gal of gasoline. In 1959 the Surgeon General approved an increase to 4 mL/gal. The use of organolead antiknock agents did indeed lead to Kettering's cherished goal, an automobile engine which operated at higher compression ratios and which was more fuel efficient and more powerful. Midgley's discovery made possible the great surge in the Automobile Age. For a time, most gasolines were “leaded” and the manufacture of tetraethyl- and tetramethyllead became “big business” indeed. Tetraethyllead was being transported throughout the country as “Ethyl concentrate” from the manufacturing site in tank trucks and in 6000 gal railway cars. Figure 11 shows the annual consumption of lead in the USA in gasoline in metric tons per year from 1925 to 1985.[1h] It peaked at 279 000 metric tons in the USA in 1970. To this should be added another 326 000 metric tons of lead consumption in 1970 in the manufacture of organolead antiknock agents worldwide.[21] By 1936 90% of the gasoline sold in the

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(20) All the reader might want to know about tetramethyllead, with an abundance of references, is given in: Huber, F. *Gmelin Handbook of Inorganic Chemistry*, 8th ed.; *Pb. Organolead Compounds. Part 1. Tetramethyllead*; Petz, W., Vol. Ed.; Gmelin Institut für Anorganische Chemie der Max-Planck-Gesellschaft zur Förderung der Wissenschaften and Springer-Verlag: Berlin, 1987; xii + 194 pages. Unfortunately, a similar volume devoted to tetraethyllead will not be published, since the Gmelin Institute has been discontinued.

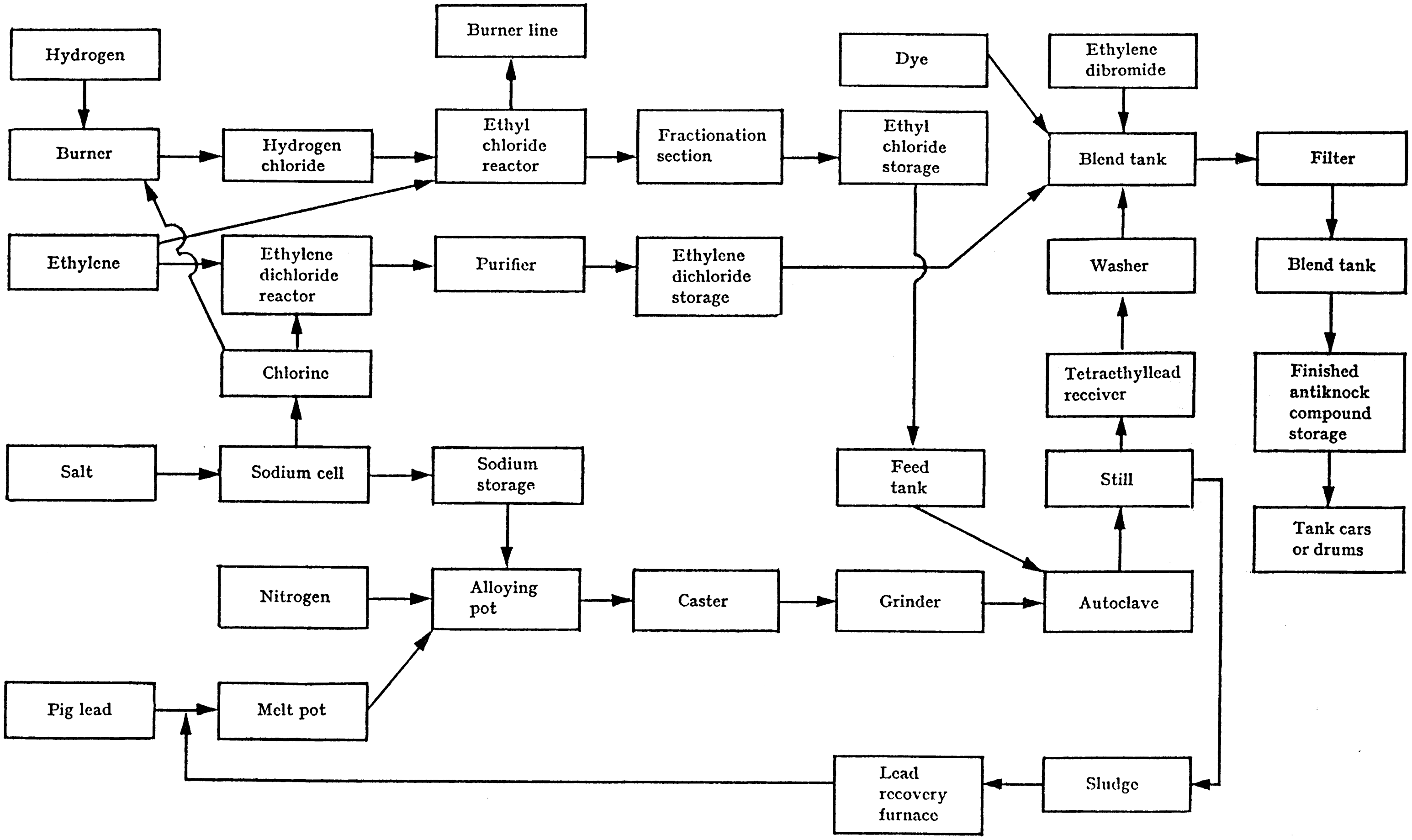

Fig. 1. Tetraethyllead manufacture flow sheet

Figure 10. Flowsheet showing the commercial C_2H_5Cl + NaPb tetraethyllead process (from ref 1e by permission of Springer-Verlag and Ethyl Corporation).

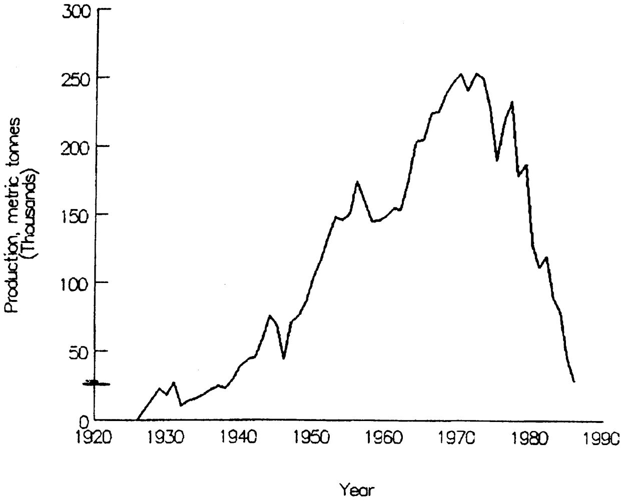

Figure 11. Consumption of lead in gasoline in the USA, in thousands of metric tons (from ref 1h, reproduced by permission of Elsevier).

USA contained tetraethyllead; by 1963 this figure had risen to greater than 98%. The dramatic fall in lead antiknock production starting in the late 1970s will be discussed later.

DuPont was the sole producer of tetraethyllead after Standard Oil of New Jersey dropped out. By 1937 DuPont's annual production of tetraethyllead had reached 65 million pounds, and it was clear that still more capacity was needed. DuPont built a new plant for Ethyl in Baton Rouge, LA; thus, in 1938 Ethyl also became a manufacturer. However, it was DuPont that operated the plant for the next 10 years. As of 1948 Ethyl and DuPont manufactured tetraethyllead separately. Ethyl expanded the Baton Rouge plant in 1949 and built new plants in Pasadena, TX, in 1952 and in Pittsburgh, CA, in 1958. Tetraethyllead also was manufactured outside of the United States, principally in Europe.

At this point, when tetraethyllead has become a major industrial product, it is appropriate to devote a few words to the nature of its antiknock action. Excellent, well-referenced discussions of this topic are given in refs 1e,f. For the purpose of this essay it will suffice to say that, in order to be effective, tetraethyllead must undergo thermal decomposition in the automobile engine to give ultimately ethyl radicals and gaseous lead atoms. The latter, in the presence of air, are oxidized to lead monoxide. This, either in gaseous form or as a fog of fine particles, is believed to inactivate intermediates of the hydrocarbon oxidation, perhaps alkyl hydroperoxides, thus inhibiting the chain-branching reactions that would result in detonation (i.e., knock). Thus, tetraethyllead is a gasoline-soluble and volatile source of lead atoms at the operating temperature of the engine. It is not the intact molecule which is the effective antiknock agent; it is merely a lead carrier.

III. Return to Midgley

Thomas Midgley's further career at GM, in which he continued to show outstanding inventiveness, deserves a short section in this essay, although it did not involve organometallic chemistry. Midgley was outstandingly effective in industrial research. As Kettering said:[5b] "Midgley demonstrated unusual talents in all three of the important phases of industrial research: first, in original investigation; second, in development or in conversion to the stage of practical usefulness; and, third, in selling the new thing to the public – or in some instances to the management first." Midgley had done just this with tetraethyllead, and he did this again in the case of the Freons. A new refrigerant which is nonflammable and nontoxic was badly needed, in particular for use in air conditioning systems. Again, using the periodic table as a guide, Midgley decided that organofluorine compounds might be the answer to the problem. Midgley and his colleagues A. L. Henne and R. MacNary solved the problem quickly, finding $CHFCl_2$ to be just such a compound. (The story of this discovery is told very entertainingly in ref 8). This led to the development of other Freons, CCl_2F_2, CCl_3F, and various ethane chloro fluoro derivatives. These found many other uses (e.g., as propellants in aerosol sprays), but like tetraethyllead, their dramatic rise was followed by an equally dramatic fall because those compounds that contain chlorine were shown to form chlorine atoms by photodissociation in the upper atmosphere. These, by reaction with ozone molecules present in the upper atmosphere, deplete the essential protective ozone layer. However, it appears that similar compounds that do not contain chlorine are safe to use. In its time, Midgley's discovery of $CHFCl_2$ was greeted with great acclaim, since the refrigerants then in use, NH_3, CH_3Cl, and SO_2, all are toxic and ammonia and methyl chloride are inflammable.

To really appreciate Midgley's accomplishments, one must recall that he was trained as a mechanical engineer and that he learned chemistry as he went along. Perusal of his publications list in ref 5b is all the more remarkable in that, of the 57 items listed, 18 were part of a series entitled "Natural and Synthetic Rubber", in which he reported, inter alia, studies of the composition of natural and synthetic rubber, the structure of polystyrene, and the reversible vulcanization of rubber by organometallic derivatives. Although this work did not result in anything of commercial utility, Kettering noted that "Midgley considered the work he did on rubber as the most scientific of all his endeavors." Midgley received many awards for his achievements in chemistry; notable are the Priestley Medal of the ACS, the Perkin Medal, the Willard Gibbs Medal, and, as already noted, the Nichols Medal. He was a Director of the ACS for 14 years, chairman of the Board of Directors for 10 years, and President of the ACS in 1944 (Figure 12). In May 2003 he was inducted (posthumously) into the National Inventors Hall of Fame for his inventions of Ethyl gasoline and the Freons, a notable honor since this organization has only 201 elected members to date.

Midgley died at age 55 on November 2, 1944. He had contracted polio in 1940, resulting in paralysis of his legs. He nevertheless continued his professional activities. Ever the inventor, he devised a harness with pulleys with which he could raise himself from bed. He accidentally became entangled in the device one day and strangled.

Midgley was a truly remarkable man—remarkably creative but always focused on practical problems,

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(21) Grandjean, P.; Nielsen, T. *Residue Res.* **1979**, *72*, 97.

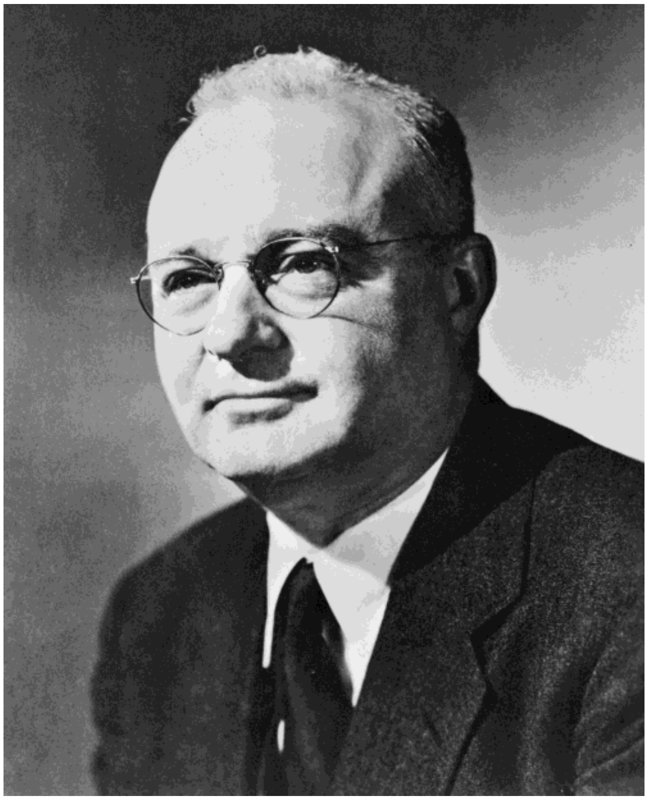

Figure 12. Thomas Midgley, Jr., as President of the American Chemical Society (American Chemical Society photo archives).

extremely persistent in his search for a solution. His two great discoveries, the tetraethyllead antiknock agent and the chlorofluoromethane refrigerants, had short half-lives, but they were important in their time, permitting important technological advances: the modern automobile and air conditioning and safe refrigeration. That the use of these compounds was dangerous to the environment was not generally appreciated until some years after their discovery. It is notable that Midgley's early work on the use of ethyl alcohol as a "high percentage" antiknock additive for gasoline was prophetic: ethyl alcohol is now present in some gasolines on the market.

IV. Defensive Research in the Ethyl Laboratories

With tetraethyllead manufacture well in hand, research and development never stopped at Ethyl. With every new development in the processing of petroleum into gasoline, with every change in the design of automobile engines, changes in the composition of the blended antiknock fluid might be needed, and this required a continuous research effort. Some of these research activities were devoted to obtaining a better understanding of tetraethyllead's antiknock effect. This involved efforts to understand the fundamentals of the combustion process which occurred in the automobile engine, to determine the mechanism of the knock reaction that occurred in the absence of an antiknock agent, and to achieve an understanding of how tetraethyllead suppressed knock. Such understanding, it was hoped, would assist Ethyl chemists in their search for other antiknock agents.

Ethyl began its existence as a one-product company, and despite several attempts to develop other businesses,[1b] it remained a one-product company until the 1960s. Because of this, Ethyl's research was largely defensive in nature. There always was the danger that another company might develop a better, more economical process for the manufacture of tetraethyllead and tetramethyllead or might find another organolead compound that was a more effective or cheaper antiknock agent. However, such a new competitive antiknock agent need not be a lead compound. Although tetraethyllead was far superior to all of the other organometallic, organometalloidal, and organic compounds that had been tested as antiknock agents, there always was the possibility that a new compound that was not a lead derivative might outperform tetraethyllead. Thus, the Ethyl Corporation was obliged to maintain active research programs in its Baton Rouge and Detroit laboratories. Not surprisingly, much of this research focused on lead chemistry.

(a) Reactions of Lead and Its Alloys with Alkylating Agents. A hint that lead metal itself reacts with ethyl iodide was given in 1853 by Cahours, who reported the formation of a small amount of a lead-containing product, which, however, he did not identify.[22] The cost of sodium added significantly to the cost of the NaPb/C_2H_5Cl process for tetraethyllead; thus, there was some incentive to explore this idea. An excellent summary of this work, carried out for the most part in the Ethyl laboratories, but with some work also at DuPont, and reported almost exclusively in patents (which are referenced), has been given by Hymin Shapiro of Ethyl.[19b] Equation 2 summarizes the RX/Pb reaction; only one-third of the charged lead is converted to tetraalkyllead.

$$4RX + 3Pb \rightarrow R_4Pb + 2PbX_2 \qquad (2)$$

Examination of this reaction showed that it works reasonably well at 100−130 °C, provided the lead is finely divided (powder or flakes) and is not surface-contaminated with air or moisture. Good yields were obtained when RX = C_2H_5I, CH_3I, CH_3Br. With C_2H_5Cl, C_2H_5Br, and CH_3Cl the reaction proceeded only in the presence of iodine or an iodine-containing catalyst. The lead metal formed in the NaPb/C_2H_5Cl reaction is especially reactive, and it was possible to combine both reactions (eqs 1 and 2) by carrying out the NaPb/C_2H_5Cl reaction in the presence of an excess of ethyl chloride (eq 3).

$$2NaPb + 4C_2H_5Cl \rightarrow (C_2H_5)_4Pb + PbCl_2 + 2NaCl \qquad (3)$$

This process was carried out in a one-pot, consecutive, two-step manner: first eq 1 and then eq 2 at higher temperature.

Other alkylating agents such as diethyl sulfate and triethyl phosphate could be used in place of ethyl chloride (eqs 4 and 5), but they offered no advantage.

$$2(C_2H_5O)_2SO_2 + 3Pb \rightarrow (C_2H_5)_4Pb + 2PbSO_4 \qquad (4)$$

$$4(C_2H_5O)_3PO + 9Pb \rightarrow 3(C_2H_5)_4Pb + 2Pb_3(PO_4)_2 \qquad (5)$$

Of interest, but not of commercial utility, are the combined reactions of lead metal, an alkyl halide, and an organometallic compound (as such or generated in situ). Thus, reaction of ethyl chloride and lead and magnesium chips at 70 °C in the presence of diethyl ether (10−20% based on C_2H_5Cl), in which C_2H_5MgCl was formed in situ, gave tetraethyllead in 75% yield (eq 6).

$$4C_2H_5Cl + Pb + 2Mg \xrightarrow{Et_2O} (C_2H_5)_4Pb + 2MgCl_2 \quad (6)$$

A similar result was obtained when preformed C_2H_5MgCl in diethyl ether was used in place of the magnesium. Best results (90% yield) were obtained when ethyllithium was the organometallic reagent used (eq 7).

$$2C_2H_5Li + 2C_2H_5Cl + Pb \rightarrow (C_2H_5)_4Pb + 2LiCl \quad (7)$$

In that case an ether catalyst was not required. Other organometallic reagents such as $(C_2H_5)_2Zn$, $(C_2H_5)_2Cd$, and C_2H_5CdI also were effective, but these required the use of ethyl iodide rather than ethyl chloride. Frey et al.[23] carried out a detailed study of the reaction of sodium tetraethylaluminate and other sodium "ate" complexes with lead metal and ethyl chloride (eq 8).

$$2NaAl(C_2H_5)_4 + 2C_2H_5Cl + Pb \rightarrow (C_2H_5)_4Pb + 2NaCl + 2(C_2H_5)_3Al \quad (8)$$

Several variables (type of lead metal, reaction temperature, and solvent) were examined. Best results, yields of 85%, were obtained when the highly reactive (sometimes pyrophoric) lead obtained in the $NaPb/C_2H_5Cl$ reaction (eq 1) was used and the reaction was carried out in diethyl ether at 90−95 °C in an autoclave at autogenous pressure. Other "ate" complexes that were examined, $NaB(C_2H_5)_4$, $NaAl(C_2H_5)_3F$, $NaAl(C_2H_5)_3OCH_3$, and $NaZn(C_2H_5)_3$, were less effective. Drawbacks in the use of $NaAl(C_2H_5)_4$ are that only one of its four ethyl groups is utilized and that in ethereal solvents hexaethyldilead is formed as a byproduct. The latter, when heated, decomposes as shown in eq 9;

$$2(C_2H_5)_3PbPb(C_2H_5)_3 \xrightarrow{\Delta} 3(C_2H_5)_4Pb + Pb \quad (9)$$

the 85% tetraethyllead yield noted above includes product from this source. The reaction in which $NaAl(C_2H_5)_3OCH_3$ was used gave a 47% yield of tetraethyllead. When a reaction of $NaAl(C_2H_5)_4$ with ethyl chloride and lead metal (300% excess) in diethyl ether was carried out in the presence of 3.7 molar equiv of CH_3ONa, the yield of tetraethyllead was 132%. Obviously, the triethylaluminum released reacted with sodium methoxide to form $NaAl(C_2H_5)_3OCH_3$, which reacted with lead and ethyl chloride to form additional product.

The sodium−lead alloy/alkyl halide reaction was the subject of continuing research after the commercialization of the $NaPb/C_2H_5Cl$ reaction. Many different reaction conditions were examined. Catalysts that would accelerate the reaction were sought; inhibitors were identified. The preparation, the gross structure, the surface of the alloy, and how best to grind it to fine particle size were all considerations. With time, significant improvement of the basic $NaPb/C_2H_5Cl$ process resulted.

However, other alloys of lead and sodium and of lead with magnesium and calcium and ternary alloys such as NaMgPb also were examined. None showed superior performance. As Shapiro concluded,[19b] "The reaction of monosodium−lead alloy with ethyl chloride as it is carried out today is unique in its combination of favorable characteristics." This was true in 1959 when ref 19b was written; it still was true during all the time that Ethyl manufactured tetraethyllead.

(b) Reactions of Organometallic Compounds with Inorganic Compounds of Di- and Tetravalent Lead. The first pure samples of tetraethyllead were prepared by Buckton in 1859 by the reaction of diethylzinc with $PbCl_2$,[2] and the first sample of tetraethyllead that Midgley had available for his engine test was prepared by the same method. Also, the ethyl Grignard reagent had been used to prepare tetraethyl- and tetramethyllead. In their search for new, proprietary routes to tetraethyllead the Ethyl chemists investigated the other available inorganic lead starting materials for such organometallic-based syntheses. Also, since the advent of the organomagnesium and organo alkali-metal reagents, other nucleophilic organometallic reagents had been discovered and/or developed and their potential application to the synthesis of tetraethyllead also was examined.

In previous studies of the preparation of tetraethyllead by the ethylation of a Pb(II) derivative by an organometallic compound, it was $PbCl_2$ which usually was used as a starting material. In a broad investigation, Ethyl chemists studied the reactions of various ethylmetal reagents with lead(II) sulfide, oxide, and acetate, as well as with lead(IV) oxide.[24] The results are summarized in Tables 3−5. As might have been expected, the fastest rates of reaction and highest tetraethyllead yields were obtained when lead carboxylates that are soluble or at least partially soluble in the reaction medium were used. It is surprising that the very insoluble PbS, PbO, and PbO_2 reacted at all to give tetraethyllead under such relatively mild conditions. Yields reported are based on 50% conversion of the charged lead to tetraethyllead (eq 10).

$$4C_2H_5Li + 2PbO \rightarrow (C_2H_5)_4Pb + Pb + 2Li_2O \quad (10)$$

In the reactions of ethylmetal reagents with PbO and PbS it was found that the mode of addition is important. When the organometallic reagent was added slowly to a suspension of the lead chalcogenide, the tetraethyllead yields were significantly higher than in a reaction in which solid PbO or PbS was added to a solution of the organometallic reagent.[24c]

An interesting finding was that triethylborane reacts with lead(II) oxide in aqueous NaOH medium to give

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(22) Cahours, A. *C. R. Acad. Sci.* **1853**, *36*, 1001

(23) Frey, F. W., Jr.; Kobetz, P.; Robinson, G. C.; Sistrunk, T. O. *J. Org. Chem* **1961**, *26*, 2950.

(24) (a) Pearson, T. H.; Blitzer, S. M.; Carley, D. R.; McKay, T. W.; Ray, R. L.; Sims, L. L.; Zietz, J. R. In *Metal-Organic Compounds*; Advances in Chemistry Series 23; American Chemical Society: Washington, DC, 1959; pp 299−305. (b) Details are given in: Blitzer, S. M.; Pearson, T. H. U.S. Patents 2,859,225−2,859,232 (Nov 4, 1958); *Chem. Abstr.* **1959**, *53*, 9149−9151. (c) Blitzer, S. M.; Pearson, T. H. U.S. Patent 2,989,558 (June 20, 1961).

Table 3. Tetraethyllead Yields from Reactions with Oxides of Lead[24]

					reacn conditions		
oxide of Pb	EtM[a]	mole ratio EtM[a]/oxide	solvent	EtM[a] concn, mol/L	time, h	temp, °C	yield, %[b]
PbO	C_2H_5Li	3.0	diethyl ether	0.19	3.0	125[c]	64
	C_2H_5MgBr	2.4	hexane	0.28	3.0	120[c]	13
	$(C_2H_5)_2Mg$	2.0	diethyl ether	0.15	6.0	35	18
	$(C_2H_5)_2Zn$	0.5	toluene	0.19	4.5	110	47
	$(C_2H_5)_3Al$	0.7		0.70	2.5	110	63
	$LiAl(C_2H_5)_4$	1.8	hexane	0.16	2.0	130[c]	64
	$NaAl(C_2H_5)_4$	0.5	toluene	0.70	1.0	110	3
PbO_2	$(C_2H_5)_3Al$	1.3	none		2.0	105	19[d]

[a] EtM = organometallic compound. [b] Based on 50% theoretical conversion of lead to $(C_2H_5)_4Pb$. [c] Conducted under pressure. [d] Based on 100% theoretical conversion of lead in PbO_2 to $(C_2H_5)_4Pb$.

Table 4. Tetraethyllead Yields from Reactions with Lead Sulfide[24]

				reacn conditions		
EtM[a]	mol ratio EtM[a]/PbS	solvent	EtM[a] concn, mol/L	time, h	temp, °C	yield, %[b]
C_2H_5Li	4.9	diethyl ether	0.43	2.5	35	15
C_2H_5Li + C_2H_5Na	1.1		0.10	4.5	25	81
C_2H_5MgBr	3.4	toluene	0.87	3.5	110	6
$(C_2H_5)_2Mg$	1.0	diethyl ether	0.15	3.0	35	42
$(C_2H_5)_2Zn$	4.0	toluene	7.7	3.5	110	53
$NaZn(C_2H_5)_3$	3.0	dimethyl ether	0.97	9.0	−24	30
$(C_2H_5)_3Al$	3.1	toluene	0.37	1.5	110	65
$LiAl(C_2H_5)_4$	1.0	hexane	0.09	4.2	120[c]	38
$NaAl(C_2H_5)_4$	3.3	toluene	0.70	1.0	110	66

[a] EtM = organometallic compound. [b] Based on 50% theoretical conversion of lead in sulfide to $(C_2H_5)_4Pb$.

Table 5. Tetraethyllead Yields from Reactions with Lead(II) Acetate[24]

				reacn conditions		
EtM[a]	mol ratio EtM[a]/Pb(OAc)$_2$	solvent	EtM[a] concn, mol/L	time, h	temp, °C	yield, %[b]
$(C_2H_5)Na$	1.67	heptane	1.0	1.7	60	100
$(C_2H_5)_2Mg$	0.91	ethylene glycol dimethyl ether	0.34	2.0	60−100	76
$(C_2H_5)_2Zn$	1.0	toluene	0.70	1.0	111	93
$(C_2H_5)_3Al$	0.61	ethylene glycol dimethyl ether	0.70	0.5	room temp	97
$(C_2H_5)_3Al$	0.61	tetrahydrofuran	0.73	1.5	66	96
$NaAl(C_2H_5)_4$	0.50	toluene	0.70	3.0	111	73

[a] EtM = organometallic compound. [b] Based on 50% theoretical conversion of lead to tetraethyllead.

tetraethyllead in 42% yield.[25] Lead(II) oxide is partially soluble in water, forming $Pb(OH)_2$, and even more so in aqueous bas, in which the $[Pb(OH)_3]^-$ anion is formed. However, triethylborane is not hydrolyzed by aqueous NaOH; thus. ethyl group transfer via the "ate" complex $[(C_2H_5)_3BOH]^-$ can occur. In neutral water the reaction of $(C_2H_5)_3B$ with PbO gave tetraethyllead in only 19% yield. Sodium tetraethylborate, like its aluminum analogue, reacted readily with lead(II) compounds in aqueous medium to give tetraethyllead in high yield[26] (eq 11). With $PbCl_2$ a 92% product yield was obtained, but

$$4NaB(C_2H_5)_4 + 2PbCl_2 \rightarrow (C_2H_5)_4Pb + 4(C_2H_5)_3B + Pb + 4NaCl \quad (11)$$

good results also were obtained with lead(II) acetate and oxide. Even the use of very insoluble $PbSO_4$ resulted in a 44% tetraethyllead yield. These yields are based on the utilization of only one of the ethyl groups of $NaB(C_2H_5)_4$, but since triethylborane also reacts with Pb(II) compounds in aqueous solution, use of the appropriate reactant stoichiometry would have given higher product yields.

In all of these reactions of organometallic reagents with Pb(II) compounds the formation of metallic lead in addition to the tetraalkyllead product is unavoidable. However, as Gilman and Jones showed, the reaction can be modified so that a larger fraction of the charged lead is converted to R_4Pb.[27] When a solution of methyllithium was added to a mixture of solid PbI_2 and methyl iodide in diethyl ether, the reaction mixture became "quite black" (an indication of Pb metal formation) when about half of the methyllithium had been added. However, as more of the lithium reagent was added, the black color rapidly disappeared. Finally, the solution was clear and

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[25] Honeycutt, J. B., Jr.; Riddle, J. M. *J. Am. Chem. Soc.* **1960**, *82*, 3051.

[26] Honeycutt, J. B., Jr.; Riddle, J. M. *J. Am. Chem. Soc.* **1961**, *83*, 369.

[27] Gilman, H.; Jones, R. G. *J. Am. Chem. Soc.* **1950**, *72*, 1760.

colorless. The hydrolyzed mixture was treated with bromine at −60 °C to give $(CH_3)_2PbBr_2$ in 92% yield, indicating an essentially quantitative yield of $(CH_3)_4Pb$ based on PbI_2 charged. In a $CH_3MgCl/CH_3I/PbCl_2$ reaction, using the same procedure except for a 1 h reflux period, a 70% yield of tetramethyllead was indicated. In a similar reaction of $C_2H_5MgBr/C_2H_5Br/Pb$ an 85% yield of $(C_2H_5)_4Pb$ was proposed on the basis of a 15% recovery of lead metal. Shapiro[19b] repeated one of these reactions and showed that it could be carried out in a two-step procedure: first the reaction shown in eq 12 and then the reaction shown in eq 13, in which

$$4CH_3MgCl + PbCl_2 \rightarrow (CH_3)_4Pb + 4MgCl_2 + Pb \quad (12)$$

$$Pb + 2CH_3Cl + 2CH_3MgCl \rightarrow (CH_3)_4Pb + 2MgCl_2 \quad (13)$$

the lead metal formed in eq 12 reacted. As noted in part 1,[2] Erich Krause had suggested that the course of the $C_2H_5MgBr/PbCl_2$ reaction was as shown in eqs 14−16. The sum total of eqs 14−16 is eq 17. Gilman, Summers,

$$2C_2H_5MgBr + PbCl_2 \rightarrow (C_2H_5)_2Pb + MgBr_2 \quad (14)$$

$$3(C_2H_5)2Pb \rightarrow 2(C_2H_5)_3Pb + Pb \quad (15)$$

$$4(C_2H_5)_3Pb \rightarrow 3(C_2H_5)_4Pb + Pb \quad (16)$$

$$4C_2H_5MgBr + 2PbCl_2 \rightarrow (C_2H_5)_4Pb + 2MgCl_2 + 2MgBr_2 \quad (17)$$

and Leeper[28] had found that in the case of the reaction of phenyllithium with $PbCl_2$ the $(C_6H_5)_2Pb$ intermediate could be intercepted if an excess of phenyllithium was present and the reaction was carried out at low (−10 °C) temperature (eq 18). Addition of benzyl chloride to

$$(C_6H_5)_2Pb + C_6H_5Li \xrightarrow{-10\ ^\circ C} (C_6H_5)_3PbLi \quad (18)$$

a solution of $(C_6H_5)_3PbLi$ thus prepared gave $(C_6H_5)_3PbCH_2C_6H_5$ in 69% yield. This approach was used by K. C. Williams in the Ethyl laboratories at Baton Rouge in a preparation of tetraethyllead from $PbCl_2$ in which no lead metal was formed (eqs 19 and 20).[29] In practice, 1 molar equiv of $PbCl_2$ was added

$$3C_2H_5MgCl + PbCl_2 \rightarrow (C_2H_5)_3PbMgCl + 2MgCl_2 \quad (19)$$

$$(C_2H_5)_3PbMgCl + C_2H_5Cl \rightarrow (C_2H_5)_4Pb + MgCl_2 \quad (20)$$

slowly to 3 molar equiv of ethylmagnesium chloride in THF at 5 °C. The $(C_2H_5)_3PbMgCl$ reagent formed a greenish brown, homogeneous solution. When the reaction of eq 20 was carried out as a separate step, the yield of tetraethyllead was 90%. Addition of CH_3Cl rather than C_2H_5Cl resulted in the formation of $(C_2H_5)_3PbCH_3$ in 89% yield. The $(CH_3)_3PbMgCl$ reagent was prepared in a similar manner. This procedure seems to be the best laboratory-scale route to symmetrical tetraalkyllead compounds, and it also is applicable in principle to the preparation of unsymmetrical compounds of the types R_3PbR', $R_2PbR'_2$, and $R_2PbR'R''$.

There have been very few studies of the use of Pb(IV) compounds as starting materials in the preparation of organolead compounds. Lead tetrachloride is poorly stable at room temperature, but ionic complexes with alkali-metal chlorides, the hexachloroplumbates $M_2[PbCl_6]$, are stable solids. Lead tetraacetate and lead tetrakis(trifluoroacetate), $Pb(O_2CCH_3)_4$ and $Pb(O_2CCF_3)_4$, also are stable Pb(IV) derivatives. Pearson et al.[24] reported that the reaction of triethylaluminum with PbO_2 at 105 °C gave tetraethyllead in only 19% yield, not surprisingly since the oxide is very stable and very insoluble. A reaction of triethylaluminum with lead tetraacetate fared better; tetraethyllead was produced in 65% yield based on eq 21. A detailed study of the

$$4(C_2H_5)_3Al + Pb(O_2CCH_3)_4 \rightarrow (C_2H_5)_4Pb + 4(C_2H_5)_2AlO_2CCH_3 \quad (21)$$

reactions of various ethylmetal reagents with $K_2[PbCl_6]$ and $(NH_4)_2[PbCl_6]$ and with several lead tetraacylates was undertaken by Frey and Cook.[30] Results are given in Tables 6 and 7. High product yields ($(CH_3)_4Pb$, 89%; $(C_2H_5)_4Pb$, 90%) were obtained when the reaction of the respective Grignard reagent with lead tetraacetate was carried out in THF solution.[31]

Many organolead compounds other than tetraethyl- and tetramethyllead were prepared and tested for antiknock activity. Many were found to be effective antiknock agents, but none could compare economically with tetraethyl- and tetramethyllead. All of this research devoted to the exploration of alternate routes to tetraethyl- and tetramethyllead produced much interesting new chemistry and new syntheses that were useful on the laboratory scale, but none proved to be more economical or better than the RCl/NaPb processes.

(c) Organic Compounds of the Transition Metals as Antiknock Agents. In 1924, right after its founding, Ethyl first looked to the transition metals for a possible alternative antiknock agent.[1b] Having heard that the Badische Anilin-und-Soda-Fabrik (BASF) in Ludwigshafen, Germany, was testing iron pentacarbonyl as a knock inhibitor in gasoline engines, Kettering and J. E. Crane of DuPont visited BASF to find out more details. Iron pentacarbonyl was relatively cheap and soluble in gasoline but had some drawbacks; its oxidation produced iron oxides, and these caused extreme wear in the cylinders and, since they were electrical conductors, fouled the spark plugs. Nevertheless, studies concerning the use and marketing of iron pentacarbonyl were undertaken by Ethyl. Its drawbacks, apparently insoluble, led BASF to discontinue marketing it in Europe, but Midgley was persistent and believed that the magic iron oxide scavenger could be found. He pushed research on this problem because iron pentacarbonyl was cheap and readily available and, also, iron is less toxic than lead. He outsourced this research, first to a small company and then to Richard Scales, a chemistry student at Cornell (who later joined Ethyl).

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[28] Gilman, H.; Summers, L.; Leeper, R. W. *J. Org. Chem.* **1952**, *17*, 630.
[29] Williams, K. C. *J. Organomet. Chem.* **1970**, *22*, 141.
[30] Frey, F. W., Jr.; Cook, S. E. *J. Am. Chem. Soc.* **1960**, *82*, 530.
[31] Williams, K. C. *J. Org. Chem.* **1967**, *32*, 4062.

Table 6. Reactions of Hexachloroplumbates with Ethylmetal Compounds[30]

hexachloroplumbate (amt, mequiv)	ethylmetal compd (amt, mequiv)	solvent	tetraethyllead yield (%)
ammonium (115.2)	Et_3Al (110.4)	toluene	3.6, 4.0
ammonium (115.2)	Et_3Al (110.4)	hexane	3.2
ammonium (115.2)	Et_3Al (110.4)	diglyme	2.3
potassium (55.0)	Et_3Al (110.4)	toluene	48.1, 50.3
potassium (55.0)	Et_3Al (110.4)	diglyme	50.2, 48.0
potassium (64.8)	EtMgBr (65.0)	toluene	0.8
potassium (64.8)	EtMgBr (65.0)	DME	68.3, 68.8
potassium (47.6)	Et_2Zn (95.4)	toluene	56.1, 53.7
potassium (47.6)	Et_2Zn (95.4)	DME	50.0, 49.6
potassium (95.2)	Et_2Zn (95.4)	toluene	47.3
potassium (95.2)	Et_2Zn (95.4)	DME	48.1
potassium (63.6)	EtLi (65.0)	DME	64.2
potassium (48.6)	Et_2Cd (97.4)	DME	45.5
potassium (102.4)	$Et_3Al_2Br_3$ (253.5)	toluene	none
potassium (37.8)	Et_2Hg (37.8)	diglyme	none

Table 7. Reactions of Lead Tetraacylates with Triethylaluminum in Toluene[30]

	normal addn		inverse addn and excess Et_3Al	
lead salt	R:Pb ratio	% yield of R_4Pb	R:Pb ratio	% yield of Et_4Pb
K_2PbCl_6			11.0	64.0, 57.8
$Pb(OAc)_4$	2.5	57.6, 54.6, 55.5	5.0	64.0
$Pb(OBz)_4$	4.4	66.4, 64.6	11.0	90.1, 97.0
$Pb(OBu)_4$	4.4	57.2, 66.1	11.0	93.1, 85.8

Many potential scavengers were tried, but none were effective. Thus, iron pentacarbonyl finally was dropped from further consideration. Iron pentacarbonyl reappeared in a 1959 Ethyl patent,[32] in which it was claimed that minute amounts of $Fe(CO)_5$ cause a small concentration of tetraethyllead in gasoline to have the same antiknock effect as much larger concentrations of tetraethyllead in the absence of $Fe(CO)_5$.

The discovery of ferrocene in 1951 and the subsequent rapid development of transition metal cyclopentadienyl complexes by E. O. Fischer at the Technische Hochschule München and Geoffrey Wilkinson at Harvard and their respective co-workers opened up what promised to be a vast new area of organometallic chemistry and, hence, a vast new source of potential antiknock agents. The chemists in the Ethyl laboratories in Baton Rouge and Detroit jumped into the fray. If there was such a new antiknock agent to be found, one that would compete with tetraethyllead or even surpass it, Ethyl wanted to be the one that found it.

At the beginning, in 1952, the guiding principle of cyclopentadienyl−metal chemistry was the "effective atomic number rule" of Sidgwick: that ligand coordination provided the opportunity for a transition-metal atom or ion to achieve the stable configuration of the next higher noble gas atom. Thus, in iron pentacarbonyl the iron atom (26 electrons), by coordination of 5 CO ligands (10 electrons donated), reaches the krypton (36 electrons) configuration. Thus, those organotransition-metal complexes in which the metal atom through electron donation by ligands reaches a noble gas configuration were the ones that would be expected to be stable. Recognizing this principle, the Ethyl chemists applied it rather broadly to the formulation of new transition-metal and main-group-metal complexes, and this led to a most remarkable patent application on December 10, 1952, entitled "Cyclomatic Compounds". The patent was issued 5 years later.[33] On the basis of the effective atomic number rule, there was claimed: "A compound having a cyclopentadienyl group coordinated with a metal having an atomic number from 6 through 13 less than that of the next higher rare gas, the compound being stabilized by additional coordination with at least one different electron donating group capable of donating from 1 through 4 electrons, the sum of all coordinated electrons and the atomic number of said metal being equal to the atomic number of the next higher rare gas." This would have been fine if it had been restricted to the transition metals using reasonable ligands, but, in the attempt to cover all bases, it was applied also to periodic groups 1 and 2. In illustrative tables can be found such "noble gas achievers" as $(C_5H_5)Na(CO)$, $(C_5H_5)Li(H_2O)$, $(C_5H_5)_2Rb(C_2H_5)_2$, $(C_5H_5)_3Cs(CO)_2(H)_2$, $(C_5H_5)_3Ca(NO)_2$, $(C_5H_5)_2Ca(CH_2{=}CHCH{=}CH_2)(H)_2$, $(C_5H_5)_2Sr(CH_3SH)_2(H)_2$, etc. However, among the transition-metal complexes were ones that were prepared later, such as $(C_5H_5)_2Ti(CO)_2$, $(C_9H_7)_2ReH$, $(C_5H_5)Fe(CO)_2H$, $(C_5H_5)NiNO$, and $(C_9H_7)Mn(CO)_3$. The methylcyclopentadienyl analogue of the latter, $(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_3$, was prepared later by Ethyl chemists and found to be a very effective antiknock agent.[34] Tests showed it to be a synergistic additive in organolead-containing gasolines,[34d] and it has been used as such. However, it is an effective antiknock agent in its own right. (Methylcyclopentadienyl)manganese tricarbonyl was commercialized by Ethyl and is still being produced and used today, since a number of other useful applications have been found.

V. Development of Competitive Processes for the Preparation of Tetraethyllead and Tetramethyllead Antiknock Agents

As Figure 11 shows, the rate of consumption of lead in gasoline was climbing steeply in the early 1950s and

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(32) Brown, J. E. U.S. Patent 2,901,336, 1959.

(33) Brown, J. E.; Shapiro, H.; De Witt, E. G. U.S. Patent 2,818,416 (Dec 31, 1957).

(34) (a) Brown, J. E.; Shapiro, H.; De Witt, E. G., U.S. Patent 2,818,417 (Dec 31, 1957) (application July 11, 1955). (b) Shapiro, H.; De Witt, E. G.; Brown, J. E. U.S. Patent 2,898,354 (Aug 4, 1959). (c) Brown, J. E. U.S. Patent 2,913,413 (Nov 17, 1959). (d) Brown, J. E.; Lovell, W. G. *Ind. Eng. Chem.* **1959**, *50*, 1547. (e) Anon. *Chem. Eng. News* **1957**, *35*(July 15), 20. (f) Sittig, M. *Organometallics*; Chemical Process Monograph No. 20; Noyes Development Corp.: Park Ridge, NJ, 1966; pp 110−112. (g) In the early 1960s Ethyl's TEL Motor 33 Mix for blending with gasoline contained about 57.5% tetraethyllead, 7.0% methylcyclopentadienylmanganese tricarbonyl, 17.6% 1,2-dichloroethane, 16.7% 1,2-dibromoethane, and 1.2% dye: Harwood, J. H. *Industrial Applications of the Organometallic Compounds*; Reinhold: New York, 1963; p 127.

showed promise of continuing to do so in future years (as indeed it did). This attracted other companies into what obviously was a profitable business after Ethyl's controlling patent expired in 1947. One new tetraethyllead process was developed and commercialized by Nalco Chemical Company.

(a) Electrochemical Synthesis of Tetramethyl- and Tetraethyllead.[35] Although the cathodic process in which tetraalkyllead compounds are generated (eq 22) was reported by Tafel in 1911,[36] it was the anodic processes, developed in the mid-1950s and early 1960s, which proved to be effective routes to tetramethyl- and tetraethyllead. This approach dates back to 1922, to the

$$(CH_3)_2C{=}O \xrightarrow[\text{e}^-,\ \text{Pb cathode}]{20\%\ H_2SO_4} [(CH_3)_2CH]_4Pb \tag{22}$$

work of Franz Hein and co-workers at the University of Leipzig on the electrolysis of ethyl alkali-metal compounds in diethylzinc and triethylaluminum solution.[37] These solutions contained ionic species of the types $M[R_3Zn]$ and $M[R_4Al]$ and were electrically conducting. In their electrolysis ethyl radicals were discharged at the anode. When the anode was composed of a reactive metal such as antimony, bismuth, lead, tin, cadmium, or thallium, the respective peralkylmetal compound was produced. In this manner Hein effected the first electrochemical synthesis of tetraethyllead. Some 30 years later, at the Max-Planck-Institut für Kohlenforschung in Mülheim (Ruhr) in Germany, Karl Ziegler and co-workers had been developing the new organoaluminum chemistry.[38] Among the triethylaluminum complexes that they had prepared were those of the types $M[R_4Al]$, $M[R_3AlH]$, and $M[R_3AlOR']$ and the novel $Na[(C_2H_5)_3Al\cdots F\cdots Al(C_2H_5)_3]$, an air-sensitive liquid which conducted an electric current (conductance at 63 °C $0.02\ \Omega^{-1}\ cm^{-1}$). Electrolysis of the last complex using a lead anode resulted in formation of tetraethyllead as a heavier insoluble liquid layer and deposition of aluminum metal on the cathode.[39] Since the Ziegler process for triethylaluminum involves the reaction of ethylene, hydrogen, and metallic aluminum, the synthesis of tetraethyllead can be summarized by the stoichiometric reaction in eq 23. To obtain a practical

$$Pb + 4CH_2{=}CH_2 + 2H_2 \rightarrow (C_2H_5)_4Pb \tag{23}$$

system, a number of more sophisticated, more complicated electrolytic processes based on the electrolysis of solutions of $NaAl(C_2H_5)_4$ using a lead anode were developed by Ziegler and co-workers.[40] None was ever commercialized.

Chemists in the Ethyl laboratories also investigated the electrolytic synthesis of tetraethyllead using organoaluminum electrolytes,[41] and this approach has also been studied by other companies.[42] However, none of these organoaluminum-based electrolytic processes left the research laboratory.

It has been known at least since 1912 that ether solutions of Grignard reagents conduct an electric current.[43] Kondyrew appears to have been the first to study the electrolysis of Grignard reagents using “reactive” anodes.[44] Thus, when a platinum cathode and a zinc anode were used in the electrolysis of C_2H_5MgBr in diethyl ether, a change in conductivity was observed and metallic zinc was deposited on the cathode. An aluminum anode was attacked, but other metal anodes (Pt, Cu, Fe, Pb, Sn, Co, Ni, Ag) were reported to be unreactive. Similar experiments were carried out by French and Drane,[45] who found that anodes of aluminum, zinc, and cadmium were dissolved when an ether solution of isoamylmagnesium chloride was electrolyzed. W. V. Evans and co-workers at Northwestern University studied the electrolysis of Grignard reagents in detail.[46] Of interest is that in an unstirred system in the electrolysis of C_2H_5MgBr using platinum electrodes magnesium migrates to both electrodes, with magnesium plating out on the cathode and $MgBr_2$, ethane, and ethylene forming at the anode. A possible ionization equilibrium (eq 24) could be responsible for this observation.

$$2RMgBr(Et_2O)_2 \rightleftharpoons RMg(Et_2O)_3{}^+ + RMgX_2(Et_2O)^- \tag{24}$$

One of Evans' Ph.D. students, David G. Braithwaite (1913−1981, Figure 13), joined Nalco Chemical Company in Chicago in 1935. In the late 1940s he applied the Grignard reagent ionization equilibrium, with which he had become familiar at Northwestern, to the development of a new electrochemical synthesis of tetramethyl- and tetraethyllead. Braithwaite's initial patents covering this work were issued in 1961.[47] Further patents covered process chemistry,[48] electrolysis cell design,[49] and tetraalkyllead product recovery and purification.[50] Braithwaite's career at Nalco was a very successful one. He became Vice President and General

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[35] For a review see: Marlett, E. M. *Ann. N. Y. Acad. Sci.* **1965**, 25, 12. See also refs 1e,f.

[36] Tafel, J. *Ber. Dtsch. Chem. Ges.* **1911**, *44*, 323. In earlier work Tafel had reported the formation of unidentified, lead-containing red oils in the electrolysis of dialkyl ketones using a lead cathode: Tafel, J. *Ber. Dtsch. Chem. Ges.* **1906**, *39*, 3626; **1909**, *42*, 3146. He thereupon assigned one of his students the task of finding out what these products were: Renger, G. Ph.D. Dissertation, University of Würzburg, 1909.

[37] (a) Hein, F. *Z. Elektrochem.* **1922**, *28*, 469. (b) Hein, F.; Wagler, K.; Segitz, F. A.; Petzschner, E. *Z. Anorg. Allg. Chem.* **1924**, *141*, 161. (c) Hein, F.; Segitz, F. A. *Z. Anorg. Allg. Chem.* **1926**, *158*, 153.

[38] Review: Ziegler, K. In *Organometallic Chemistry*; Zeiss, H., Ed.; Reinhold: New York, 1960; Chapter 5, pp 194−269.

[39] Ziegler, K.; Lehmkuhl, H. *Angew. Chem.* **1955**, *67*, 424.

[40] Lehmkuhl, H. *Ann. N. Y. Acad. Sci.* **1965**, *135*, 124.

[41] Examples from the patent literature are given in refs 1f and 35.

[42] E.g.: Wunderlich, D. K.; Fussell, L. N. U.S. Patent 3,159,557 (Dec 1, 1964) (to Sinclair Research, Inc.)

[43] Jolibois, P. *C. R. Acad. Sci.* **1912**, *155*, 353.

[44] Kondyrew, N. W. *Ber. Dtsch. Chem. Ges.* **1925**, *58*, 459.

[45] French, H. E.; Drane, M. *J. Am. Chem. Soc.* **1930**, *52*, 4904.

[46] (a) Evans, W. V.; Lee, F. H. *J. Am. Chem. Soc.* **1934**, *56*, 654. (b) Evans, W. V.; Field, E. *J. Am. Chem. Soc.* **1936**, *58*, 720, 2284. (c) Evans, W. V.; Braithwaite, D. *J. Am. Chem. Soc.* **1939**, *61*, 898. (d) Evans, W. V.; Braithwaite, D.; Field, E. *J. Am. Chem. Soc.* **1940**, *62*, 534.

[47] (a) Braithwaite, D. G. U.S. Patent 3,007,857 (Nov 7, 1961). (b) Braithwaite, D. G. U.S. Patent 3,007,858 (Nov 7, 1961) (filed July 31, 1957).

[48] (a) Braithwaite, D. G. U.S. Patent 3,312,605 (April 4, 1967). (b) Braithwaite, D. G.; Bott, L. L. U.S. Patent 3,380,899 (April 30, 1968). (c) Braithwaite, D. G.; Bott, L. L.; Phillips, K. G. U.S. Patent 3,380,900 (April 30, 1968). (d) Braithwaite, D. G. U.S. Patent 3,391,066 (July 2, 1968). (e) Braithwaite, D. G. U.S. Patent 3,391,067 (July 2, 1968). (f) Craig, R. L.; Hunter, E. A.; Mayerle, E. A. U.S. Patent 3,497,428 (Feb 24, 1970).

[49] (a) Braithwaite, D. G.; D'Amico, J. S.; Gross, P. L.; Hanzel, W. U.S. Patent 3,141,841 (July 21, 1964). (b) Braithwaite, D. G.; Hanzel, W. U.S. Patent 3,189,534 (June 15, 1965). (c) Braithwaite, D. G.; D'Amico, J. S.; Gross, P. L.; Hanzel, W. U.S. Patent 3,287,249 (Nov 22, 1966).

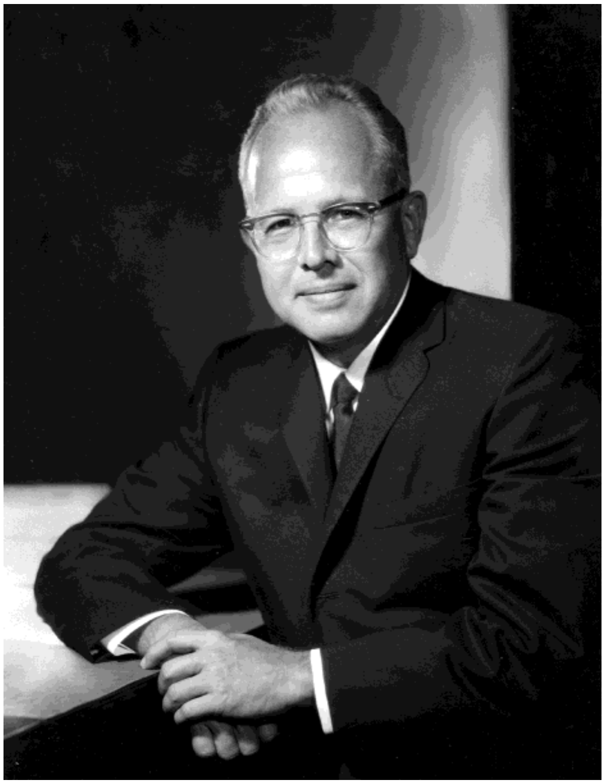


Figure 13. David G. Braithwaite, 1961 (ONDEO Nalco Chemical Company Archives, reproduced by permission of ONDEO Nalco Chemical Company).

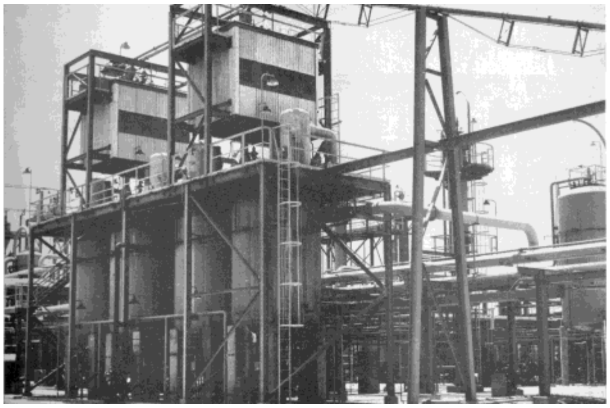
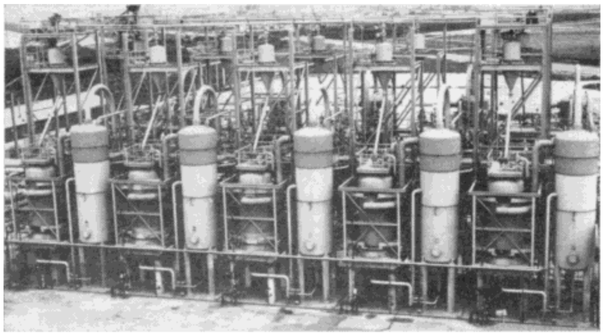


Figure 14. Four agitated, propane-cooled Grignard reactors at the Nalco tetramethyllead plant (from ref 51c, reproduced by permission of Gulf Publications).

Manager of the Catalysis Division in 1954, a Director of Nalco in 1957, Nalco Executive Vice President in 1959, President in 1961, CEO in 1962, and Board Chairman in 1965. He retired in 1971.

Nalco's plant in Freeport, TX, in which tetramethyllead was produced by the electrolysis of methylmagnesium chloride using a lead anode, went on stream in 1964[51] (Figures 14 and 15). In the Nalco process a new cell design was developed in which the anode was composed of lead pellets and the steel walls of the cell were the cathode. Anode and cathode were separated by a suitable membrane. The lead consumed in the electrolysis could be replaced without opening the cells. The methyl chloride was reacted with magnesium curls in a mixed ether solvent (e.g., THF, which increases the conductivity of the Grignard reagent, and a dialkyl ether of diethylene glycol) at 10−20 psig and 100 °F with agitation in a propane-cooled 8000 gal reactor. The CH_3MgCl solution, which contained a large excess of methyl chloride, was pumped into the electrolysis cells. The electrolysis was operated using a low voltage (to minimize power costs) and high amperage current. The methyl radicals which were discharged at the anode reacted with the lead pellets to give tetramethyllead. Metallic magnesium, the reduction product at the cathode, was intercepted by the excess methyl chloride in the solution to form more CH_3MgC and, hence, did not plate out on the cathode. Thus, the total reaction is that shown in eq 25. Figure 16 shows a flow sheet of



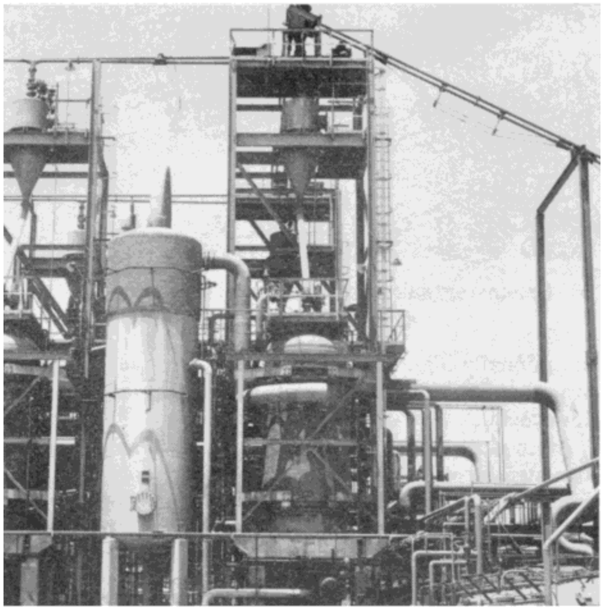


Figure 15. (a, top) Grignard reagent electrolysis cells with separate recirculation drums at the Nalco tetramethyllead plant and (b, bottom) close-up view of an electrolysis cell (from ref 51c, reproduced by permission of Gulf Publications).

$$2CH_3MgCl + 2CH_3Cl + Pb \xrightarrow[\text{DC voltage}]{\text{electrolysis}} (CH_3)_4Pb + 2MgCl_2 \quad (25)$$

the Nalco process, which also was adapted to the

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(50) (a) Braithwaite, D. G.; Bott, L. L. U.S. Patent 3,359,291 (Dec 19, 1967). (b) Braithwaite, D. G.; Bott, L. L.; Gross, P. L.; Laubach, J. E.; Altman, W. L.; Hanzel, W. U.S. Patent 3,408,273 (Oct 29, 1968).

(51) (a) Anon. *Chem. Eng. News* **1964**, *42*(49), 52. (b) Anon. *Chem. Week* **1964**, *95*(24), 77. (c) Bott, L. L. *Hydrocarbon Process. Petrol. Refiner* **1965**, *44*, 115. (d) Guccione, E. *Chem. Eng.* **1965** (June 21), 102.

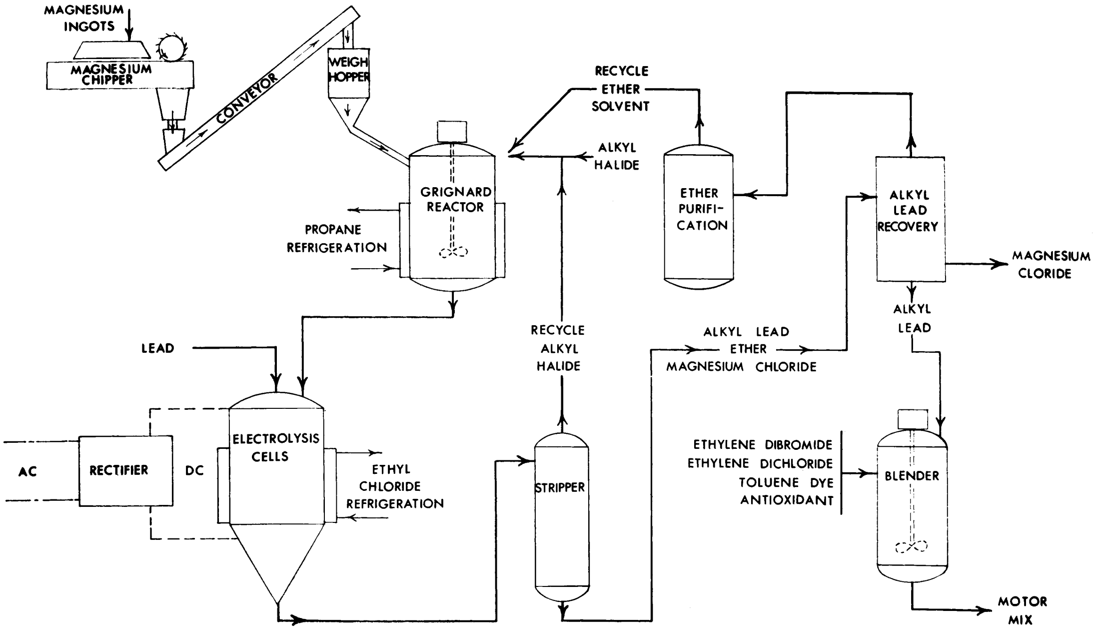

Figure 16. Flowsheet showing the Nalco electrolytic tetramethyllead process (from ref 51c, reproduced by permission of Gulf Publications).

preparation of tetraethyllead and mixed ethylmethyllead compounds, $(CH_3)_nPb(C_2H_5)_{4-n}$ ($n = 0-4$).

Other companies have investigated RMgX or R_2Mg electrolysis using a lead anode as a route to tetraethyllead. Thus, at Ethyl Corp. Giraitis electrolyzed diethylmagnesium while hydrogen and ethylene were led into the cathode chamber to react with magnesium as it was formed to give additional $(C_2H_5)_2Mg$.[52] Linsk and coworkers at the Standard Oil of Indiana laboratories electrolyzed Grignard reagents to prepare tetraethyllead.[53]

Another electrochemical route to tetraethyllead, instead of starting out with an organometallic electrolyte, cathodically generates the reactive organometallic reagents by electrolysis of ethyl iodide or ethyl bromide in dimethylformamide or dimethyl sulfoxide. If a lead anode was used, the organometallic compound then reacted to form tetraethyllead. Cathodes of magnesium,[54] zinc,[55] and cadmium[56] have been used. This approach to tetraethyllead synthesis seems rather roundabout. Furthermore, the yields are modest at best and there is uncertainty about the anode process that is taking place.

(b) Organolead Chemistry at Houston Chemical Corp./PPG Industries, Inc. Houston Chemical Corp., a division of PPG Industries, also was a producer of organolead antiknock agents. The standard NaPb + RCl process was used to prepare tetraethyl- and tetramethyllead, but a new, competitive process based on lithium rather than sodium had been developed (eq 26).[57]

$$Pb + 4Li + 4C_2H_5Cl \rightarrow (C_2H_5)_4Pb + 4LiCl \quad (26)$$

Lithium of 97.5−99.9% purity that contained minor impurities of sodium or potassium (which were essential) and of high surface area with minimal or no oxide or nitride impurities was required. A 10−15% excess of lithium was used. Finely divided lead powder with a particle size of less than 44 μm worked best. A large excess of alkyl chloride was used (25−100% for CH_3Cl; 100−300% for C_2H_5Cl). The presence of ~10 mol % of an ether helped eliminate byproduct formation. The reactions were carried out under argon at reflux (in the case of ethyl chloride) and low pressure. Excellent yields were reported in the examples: $(C_2H_5)_4Pb$, 91%; $(CH_3)_4Pb$, 86%. Procedures for the recycling of LiCl to lithium metal, essential for the economical operation of the process, were devised. An industrial process was developed which, it was believed, would compete favorably with the sodium−lead alloy process, but development of this new process for commercial production came too late. The demise of tetraethyllead was already underway; thus, there was no need for more capacity. A plant was never built.

VI. The Decline and Fall of Organolead Antiknock Agents

As Figure 11[1h] shows, the production and consumption of tetraethyl- and tetramethyllead underwent a steep decline around the middle 1970s. Tetraethyllead had nearly been taken off the market permanently in

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(52) Giraitis, A. P. Ger. Patent 1,046,617, 1958; *Chem. Abstr.* **1961**, *55*, 383.

(53) (a) Linsk, J. U.S. Patent 3,116,308 (Dec 31, 1963). (b) Linsk, J.; Mayerle, E. A. U.S. Patent 3,155,602 (Nov 3, 1964). (c) Pearce, F. G.; Wright, L. T.; Birkness, H. A.; Linsk, J. U.S. Patent 3,180,810 (April 6, 1965). (d) Coopersmith, J. M.; Linsk, J.; Field, E.; Carl, R. W.; Mayerle, E. A. Ger. Patent 1,157,616 (Nov 21, 1963); *Chem. Abstr.* **1964**, *61*, 1892.

(54) (a) Fleischmann, M.; Mengoli, G.; Pletcher, D. *Electrochim. Acta* **1973**, *18*, 231. (b) Tedoradze, G. A. *J. Organomet. Chem.* **1975**, *88*, 1

(55) (a) Mengoli, G.; Daolio, S. *J. Appl. Electrochem.* **1976**, *6*, 521. (b) *Electrochim. Acta* **1976**, *21*, 889.

(56) Mengoli, G.; Daolio, S. *J. Organomet. Chem.* **1977**, *131*, 409.

(57) Cortez, H. (a) French Patent 1,544,454 (Oct 31, 1968) (to Houston Chemical Corp.); *Chem. Abstr.* **1969**, *71*, 91657. (b) French Patent 1,544,455 (Oct. 31, 1968); *Chem. Abstr.* **1969**, *71*, 113089.

the mid-1920s, but it survived the scare occasioned by the fatal poisoning of a number of workers in the GM, DuPont, and Standard Oil of New Jersey production facilities. Appropriate changes in the procedures used in the manufacture and blending plants to ensure the safety of the personnel were developed and instituted, and no major problems were encountered in future operations. However, right from the start, there were serious concerns about the environmental and public health impact of tetraethyllead when it was used as an additive in gasoline.[1j,k] The Bureau of Mines tests and the Surgeon General's Committee report mentioned earlier gave tetraethyllead a clean bill of health. The sale of leaded gasoline resumed in 1926, and tetraethyllead flourished for another 50 years. However, some environmental and public health advocates were not convinced that tetraethyllead, when used as a gasoline additive in the ever-growing number of automobiles and trucks, was harmless (as its supporters claimed). It was pointed out that not only was tetraethyllead highly toxic but also toxic inorganic lead compounds were formed in the engine and that a large percentage of these exited into the environment through the exhaust system.

If one looks at Figure 11, which shows the consumption of lead in the production of organolead antiknock compounds over the years, one can just as well consider this figure as showing how much lead entered the environment, one way or another, during these years. About three-fourths of the lead burned in the engine is emitted from the tailpipe in the form of inorganic lead compounds.[58] Most of the remainder is retained in the automobile: in deposits in the exhaust system, in the motor oil, and in the oil filter. This also ultimately ends up in the environment when the oil and oil filter are discarded or when the exhaust system deposits are lost mechanically during driving. A small amount of the organolead additives never get into the automobile but also enter the environment, through spillage at the gas pump and during transport from the blending plant to the gasoline station, through leakage into the soil and groundwater from underground gasoline storage tanks, and by evaporation from the gas tank and carburetor. Another small amount, 0.3−3% of the lead emitted, leaves the tailpipe as undecomposed tetraethyllead and triethyl- and diethyllead compounds[58a] (which also are toxic).

However, it is the inorganic lead compounds that make up the bulk of the lead that is emitted from the exhaust system, and inorganic lead compounds have long been known to be toxic.[59] The scavengers present in the lead antiknock mix, 1,2-dichloro- and 1,2-dibromoethane, react with the inorganic lead species formed in the engine; thus, the primary inorganic lead compounds that leave the engine are $PbCl_2$ and $PbBr_2$. These lead halides are volatile as formed in the hot engine (boiling points: $PbCl_2$, 954 °C; $PbBr_2$, 916 °C).[60] In the gas phase a mixture of $PbCl_2$ and $PbBr_2$ is in equilibrium with lead chlorobromide (eq 27).[61a] However, PbO may be present in the combustion gases; therefore, basic lead halides also may be formed in the engine.

$$PbCl_2(g) + PbBr_2(g) \rightleftharpoons 2\ PbClBr(g) \qquad K = 0.38\ (700\ °C) \quad (27)$$

This mixture of lead compounds will leave the exhaust system with the hot combustion gases as an aerosol and will form a fine airborne dust. Ultimately, most will come to earth as finely divided, solid lead compounds. However, airborne lead compounds, 5 μm or less in size, will remain a continual problem, especially in urban areas and along freeways, since they are being continually replenished by the many automobiles on the road. (In the early 1960s airborne lead compound concentrations of 1−3 $\mu g/m^3$ were being measured in urban areas.) Electron microprobe examination of airborne lead samples taken near and at a distance from a busy highway showed the following zero time composition (in percent of the lead particles counted): $PbCl_2$, 10.4; $PbBr_2$, 5.5; PbClBr, 32.0; Pb(OH)Cl, 7.7; Pb(OH)Br, 2.2; $(PbO)_2PbCl_2$, 5.2; $(PbO)_2PbBr_2$, 1.1; $(PbO)_2PbClBr$, 31.4; $PbCO_3$, 1.2; PbO_x, 2.2; $(PbO)_2PbCO_3$, 1.0; $PbSO_4$, 0.1.[62] These lead compounds, when they come to earth, will contaminate the roadway and vicinity and the roadside ecosystem.[63]

Even in the early days of tetraethyllead usage such dispersal of lead in the environment was viewed with concern by some, but the controversy between the environmental and public health advocates and industry did not really flare up until 1962, when Rachel Carson published "The Silent Spring" and the environmental movement began in earnest. What followed with regard to organolead antiknock agents is told in reviews written from the environmental/public health point of view by Nriagu[1h], Kitman,[1j] and Needleman[64] and in the book by Robert[1b] from Ethyl's point of view. The renewed concerns about the automobile that used leaded gasoline as a source of toxic lead compounds in the environment led to many clinical and laboratory studies in the 1960s and 1970s and, ultimately, as many of these studies provided support for these concerns, to legislation, first by the state of California, which had bad smog problems in Los Angeles, and then by the Federal Government. The Clean Air Act was passed by Congress in 1970. In 1982 the Environmental Protection Agency (EPA) mandated a decrease of the average lead content of gasoline sold in the USA from 0.52 to 0.28 g/L and, in 1986, to 0.026 g/L. Challenges in hearings and in the courts by organolead producers were of no avail. However, another major blow to organolead antiknock additives came in January 1970, when the president of GM announced that GM planned to install catalytic converters in its new automobiles in order to meet the Federal Government's air quality require-

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[58] (a) Hirschler, D. A.; Gilbert, F. *Arch. Environ. Health* **1964,** *8*, 297. (b) Hewitt, C. N.; Rashed, M. B. *Appl. Organomet. Chem.* **1988**, *2*, 95.

[59] Hernberg, S. *Am. J. Ind. Med.* **2000**, *38*, 244−254 and references therein (a useful introductory review).

[60] Sidgwick, N. V. *The Chemical Elements and Their Compounds*; University Press: Oxford, U.K., 1950; Vol. I, p 625.

[61] (a) Bloom, H.; Hastie, J. W. *J. Phys. Chem.* **1967**, *71*, 2360. (b) $PbCl_2$ and $PbBr_2$ form a complete series of solid solutions in which the 1:1 compound PbClBr is highly favored: Calingaert, G.; Lamb, F. W.; Meyer, F. *J. Am. Chem. Soc.* **1949**, *71*, 3709. For the crystal structure of PbClBr, which is isomorphous with $PbCl_2$, see: Goodyear, J.; Ali, S. A. D.; Duffin, W. J. *Acta Crystallogr.* **1969**, *B25*, 796.

[62] Ter Haar, G. L.; Bayard, M. A. *Nature* **1971**, *232*, 553.

[63] Smith, W. H. *J. Air Pollution Control Assoc.* **1976**, *26*, 753.

[64] Needleman, H. L. *Environ. Res. A* **2000**, *84*, 20.

ments of the automobile engine exhaust. The purpose of the catalytic converter was to destroy nitrogen oxides, carbon monoxide, and hydrocarbons in the exhaust gas. It used noble metal oxidation catalysts to do this, and studies showed[65] that 1,2-dibromethane (one of the lead scavengers) decreases catalyst activity, especially of catalysts containing palladium. In pure isooctane (the fuel used in this study) catalyst activity was restored completely. However, it was found that tetraethyllead causes permanent destruction of the catalyst, shrinking the Pt/Pd surface area. In the 1970s an ever-increasing number of automobiles were built that had catalytic converters and thus could not tolerate leaded gasoline. These two factors, the government-mandated reduction in the lead content of leaded gasoline and the introduction of the catalytic converter, were responsible for the drastic decline in organolead consumption shown in Figure 11.

VII. Reactions and Other Uses of Tetraethyllead

Now that the application of tetraethyllead as an antiknock agent in gasoline has declined so drastically, what other uses are left? The answer: not many. The applications of the organic derivatives of all heavy metals, especially those of mercury, lead, and thallium but also, to a lesser extent, of tin, have declined greatly in the last 30 years. Their organic derivatives generally are toxic and for this reason are avoided wherever possible.

One former application of tetraethyllead was based on the facile electrophilic cleavage of its Pb−C bond. Reaction of tetraethyllead with mercuric acetate resulted in the formation of ethylmercuric acetate (eq 28),

$$(C_2H_5)_4Pb + 3Hg(OAc)_2 \rightarrow 3C_2H_5HgOAc + C_2H_5Pb(OAc)_3 \quad (28)$$

which is a water-soluble fungicide[66] but is no longer used as such. Ethylation of group 15 trihalides occurs readily (eq 29).[67]

$$(C_2H_5)_4Pb + 3MCl_3 \rightarrow 3C_2H_5MCl_2 + C_2H_5Cl + PbCl_2 \quad (29)$$

$$M = P, As, Sb$$

The use of tetraethyllead as a cocatalyst in systems such as $AlCl_3 + (C_2H_5)_4Pb$ and $AlX_3 + VCl_3$ (or $TiCl_4$) $+ (C_2H_5)_4Pb$ for olefin polymerization also is based on its reactivity with metal halides as an ethyl group source. A three-component reaction of tetraethyllead, $TiCl_4$, and an aldehyde (eq 30) gave high yields of secondary alcohols, both aromatic (R = Ph) and aliphatic ($R = C_7H_{15}$).[68]

$$(C_2H_5)_4Pb + TiCl_4 + RCH{=}O \xrightarrow[-78\text{ to }-30\,^\circ C]{CH_2Cl_2} \xrightarrow[MeOH]{H_2O} R-C(OH)HC_2H_5 \quad (30)$$

Other tetraalkyllead compounds, R_4Pb ($R = n\text{-}C_4H_9$, $i\text{-}C_3H_7$, cyclohexyl), reacted similarly, but the secondary alkyl compounds gave only moderate yields. The mechanism of this reaction is not clear. The authors favored a process in which the $(C_2H_5)_4Pb$ attacks an $RC^+H-O\rightarrow Ti^-Cl_4$ complex which contains an activated C−O bond, rather than a transmetalation reaction in which $C_2H_5TiCl_3$ is the reactive intermediate. Tetraethyllead also alkylates acid chlorides (eq 31).[69] A Pd(0) catalyst, $Pd(PPh_3)_4$, was required.

$$(C_2H_5)_4Pb + C_6H_5C(O)Cl \xrightarrow{\Delta} C_6H_5C(O)C_2H_5 + (C_2H_5)_3PbCl \quad (31)$$

Tetra-*n*-butyllead reacted similarly. However, using organolead compounds in organic synthesis today is swimming against the tide. Heavy-metal compounds have become reagents non grata in organic synthesis.

A review reports the reactions of tetraethyllead with a variety of reactants: hydrogen, oxidizing agents, halogens, inorganic and organic acids, phenols, thiols, metal and metalloid halides and salts, and metals.[70]

The volatility of tetraethyllead and its ready thermal decomposition to lead and organic products, factors important in its use as an antiknock agent in the gasoline engine, have also been useful in its application as a lead source in chemical vapor deposition of lead-containing solid films for ferroelectric applications. Thus, films of lead titanate, $PbTiO_3$, were prepared using a vapor reactant system of $(C_2H_5)_4Pb/Ti(OC_3H_7\text{-}i)_4/O_2$.[71] Similarly prepared were thin films of lead zirconate titanate, $Pb(Zr_xTi_{1-x})O_3$,[72] and of other lead-containing solid materials such as $Pb(Mg_{0.33}Nb_{0.67})O_3$[73] and lead lanthanum zirconate titanate.[74]

And now, toward the end, we come full circle and return to the beginning: to the discovery of the first organolead compounds by Carl Löwig in 1853.[2] In one of the first experiments that he described an ether solution of the liquid product of his reaction of ethyl iodide with sodium−lead alloy was allowed to evaporate partially in air, leaving an insoluble white precipitate. This was bis(triethyllead) carbonate, derived by air oxidation of the hexaethyldilead byproduct and subsequent reaction of the latter with CO_2 in the air. The major product, tetraethyllead, was not isolated. To obtain more information, the product of another C_2H_5I

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[65] Otto, K.; Montreuil, C. N. *Environ. Sci. Technol.* **1976**, *10*, 154. This is just one of many such studies carried out around this time.

[66] Whelen, M. S. In *Metal-Organic Compounds*; Advances in Chemistry Series 23, American Chemical Society: Washington, DC, 1959; pp 82−86 (review).

[67] Kharasch, M. S.; Jensen, E. V.; Weinhouse, S. *J. Org. Chem.* **1949**, *14*, 429.

[68] Yamamoto, Y.; Yamada, J.; Asano, T. *Tetrahedron* **1992**, *48*, 5587.

[69] Yamada, J.; Yamamoto, Y. *J. Chem. Soc., Chem. Commun.* **1987**, 1302.

[70] Milde, R. L.; Beatty, H. A. In *Metal-Organic Compounds*; Advances in Chemistry Series 23; American Chemical Society: Washington, DC, 1959; pp 306−318. See also refs 1e,f.

[71] For instance: (a) Hong, L. S.; Wei, C. C. *Mater. Lett.* **2000**, *46*, 149. (b) Tong, M.; Dai, G.; Gao, D. *Mater. Lett.* **2000**, *46*, 60. (c) Dormans, G. J. M.; De Keijser, M.; Larsen, P. K. *Integr. Ferroelectr.* **1992**, *2*, 297. (d) Lee, W. G.; Woo, S. I. *Integr. Ferroelectr.* **1994**, *5*, 107 (using glow discharge). (e) Pan, C.-Y.; Tsai, D.-S.; Hong, L.-S. *Mater. Chem. Phys.* **2001**, *70*, 223. (f) Hong, L.-S.; Wei, C.-C. *Jpn. J. Appl. Phys., Part 1* **2000**, *39*, 4964.

[72] (a) Cheng, W. Y.; Hong, L.-S. *Thin Solid Films* **2002**, *415*, 94. (b) De Keijser, M.; Dormans, G. J. M.; Van Veldhoven, P. J.; Larsen, P. K. *Integr. Ferroelectr.* **1993**, *3*, 131.

[73] Bai, G. R.; Streiffer, S. K.; Baumann, P. K.; Auciello, O.; Ghosh, K.; Stemmer, S.; Munkholm, A.; Thompson, C.; Rao, R. A.; Eom, C. B. *Appl. Phys. Lett.* **2000**, *76*, 3106.

[74] Tominaga, K.; Shirayanagi, A.; Takagi, T.; Okada, M. *Jpn. J. Appl. Phys., Part 1* **1993**, *32*, 4082.

+ Pb/Na reaction was treated with $AgNO_3$ in ethyl acetate. Metallic silver was formed. Treatment of the solution after filtration of the silver with aqueous KOH resulted in the formation of $[(C_2H_5)_3Pb]_2O$. Again, tetraethyllead was not isolated. Löwig, who was the first to prepare tetraethyllead, never did isolate it as a pure compound. Tafel in 1911 found that the action of $AgNO_3$ on tetraethyllead resulted in reductive cleavage of one ethyl group, giving $(C_2H_5)_3PbNO_3$,[36] which explains Löwig's finding. The system $(C_2H_5)_4Pb/AgNO_3$ showed up again in 1960 when it was found to initiate the polymerization of methyl methacrylate,[75] vinyl fluoride,[76] and other monomers.[77] A mechanism was suggested in which tetraethyllead reacts with silver nitrate at −78 °C to give C_2H_5Ag, which decomposes at higher temperature to produce metallic silver (as Löwig had reported) and ethyl radicals. The latter then initiate free radical polymerization of the monomer. Old chemistry put to new uses!

Miscellaneous uses of tetraethyllead, none of which appear to have been commercialized, are discussed in ref 34g and in a review by Marshall and Wirth.[78] Of more recent interest is that tetraethyllead is an effective coal liquefaction promoter.[79]

Outlook

Considering Figure 11, the outlook for tetraethyllead is not at all good. One might think, that in view of its now recognized environmental problems, the health hazards associated with its use as a gasoline additive, and its detrimental effect on the noble-metal catalytic converter in today's automobiles, that its commercial production would have dropped to zero. But such is not the case. Organolead antiknock agents are still being manufactured in the U.K. by Associated Octel (which was once Ethyl's subsidiary in the U.K.) and is still being marketed in some "developing" countries. It has not been possible to obtain specific information about the annual production of tetraethyl- and tetramethyllead or about the countries in which it is still being marketed.

The use of tetraethyllead as an antiknock agent in gasoline has been prohibited in the USA. The 1970 Clean Air Act had required that leaded gasoline be phased out by the mid-1980s. A 1977 amendment to this act mandated the prohibition of leaded gasoline in on-road motor vehicles by the end of 1995. From 1975 to 1979 the permissible lead levels decreased from 1.7 to 0.5 g/gal and to 0.1 g/gal by 1986. The EPA (at least in 1996) still permits the sale of leaded gasoline for off-road uses: in propeller aircraft, in racing cars, and in marine engines. Gasoline that contains organolead antiknock agents has by now been banned for on-road use in many other countries: in Canada and Mexico, in the European Union, in Switzerland, in Brazil and Argentina, in Australia and New Zealand, in Russia, in Japan, China, Taiwan, Korea, Singapore, and India. In some of the countries of "New Europe"—Poland and Hungary—it is banned already, but, in any case, all of the countries that will join the European Union in May 2004 will have to conform to EU standards. Those countries in which leaded gasoline still is being sold will have to prohibit its use. In some countries (Sweden and the Czech Republic) an organolead compound concentrate can be purchased at the present time. This may be added to the lead-free gasoline for use in older automobiles. Leaded gasoline is still in use in Norway and South Africa but is being phased out. It is still used in Venezuela.

I have been unable to obtain information as far as the rest of the world is concerned, but ref 1j mentions that "as of 1996, 93% of all gasoline sold in Africa contained lead, 94% in the Middle East, 30% in Asia, and 35% in Latin America." Now, 7 years later, these percentages will have decreased, especially those in Asia and Latin America.[80]

Some concluding remarks are in order. This account has focused on the *chemistry* of tetraethyl- and tetramethyllead—their synthesis, their reactions, and their commercial applications. In view of their past importance, extensive work has been carried out on the physical, spectroscopic, and thermodynamic properties of tetraethyl- and tetramethyllead. These are discussed in detail, with many references, in refs 1f and 20.

Tetraethyl- and tetramethyllead have been controversial molecules ever since they became commercial products. These controversies, which pitted public health and environmental advocates against the manufacturers of organolead antiknock agents and the producers of leaded gasoline and have involved also the U.S. Federal Government and some state governments, have been covered only superficially in this account. They are, however, a very important part of the history of our cover molecule. The interested reader should consult ref 1b for an industry view of this controversy and refs 1h,k and 64 for accounts written from the public health/environmental point of view. Business aspects, such as the purchase of the Ethyl Corporation by the Albemarle Paper Company in 1962, are beyond the scope of this essay. They are covered in great detail by Robert in his history of the Ethyl Corporation.[1b]

The "war" over tetraethyllead is essentially over in most parts of the world, except for some current and future minor conflicts which may be expected in some "Third World" countries. However, there is no peace as

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(75) (a) Bawn, C. E. H.; Janes, W. H.; North, A. M. *J. Polym. Sci.* **1962**, *58*, 335. (b) Bawn, C. E. H.; Johnson, R. *J. Chem. Soc.* **1960**, 3923.

(76) (a) Demiel, A.; Levy, M.; Vofsi, D. Israeli Patent 37,150, 1974. (b) Raucher, D.; Demiel, A.; Levy, M.; Vofsi, D. *J. Polym. Sci., Polym. Chem. Ed.* **1979**, *17*, 2825

(77) Furukawa, J.; Tsuruta, T.; Takeda, Y. *Kogyo Kagazu Zasshi* **1961**, *64*, 1307.

(78) Marshall, E. F.; Wirth, R. A. *Ann. N. Y. Acad. Sci.* **1965,** *125*, 198.

(79) Attala, M. I.; Quezada, R. A.; Vassallo, A. M.; Wilson, M. A. *Fuel* **1992,** *71*, 401.

(80) Apropos these data, it is of interest to read what the Octel website (http://www.octel-corp.com/products/leadalkyls/leadalkyls.htm) says: "As the world's leading producer of tetraethyl lead (TEL), Octel recognises that reductions in the amount of lead present in the man-made environment, from which few overall benefits result, represent a prudent step forward in terms of environmental management. The transition by refineries to unleaded gasoline due to environmental concerns and its incompatibility with the catalyst in catalytic converters will inevitably take some time. During this period, the economies of some countries will continue to depend on leaded gasoline and TEL. Octel remains committed to maintaining a professional working partnership with these customers to ensure the continuity of its supply during the phase-out period."

yet between the two opposing sides, whose differences seem to be irreconcilable. Tetraethyllead has not yet disappeared into its original place as a molecule lost within the “noise” of the many known main-group organometallic compounds.

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