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THE EARLY HISTORY OF FINE GARDENS

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RESEARCH LABORATORIES DIVISION
GENERAL MOTORS CORPORATION

Detroit, Michigan

THE EARLY HISTORY OF ETHYL GASOLINE

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FOREWORD

This history of the development of Ethyl Gasoline and of the early years of its commercialization is based mostly upon records, reports, and correspondence in the files of the Research Laboratories Division, General Motors Corporation. It represents a revision and extension of matter first prepared in 1938 and 1939 from a search made for another purpose. The object has been to write a comprehensive account for the record, not a popular story. However, this matter might well serve as source material for such a story, if one should be written later on.

The order of sequence is roughly chronological, and the text is divided into chapters. But the purpose of this division is chiefly to break up a long story into parts. An outline of CONTENTS, which can serve as a guide in finding items of interest, begins on page 379, and a list of ILLUSTRATIONS on page 397.

CHAPTER I

THE BEGINNING

In 1916, Charles F. Kettering set up an institution called the Dayton Research Laboratories Company. And, at Mr. Kettering's invitation, Dr. F. O. Clements, who fifteen years before had been his instructor in chemistry at the Ohio State University, resigned his job as chief chemist of the National Cash Register Company to become the technical director of the new organization. This institution was organized to undertake the kind of pioneering research that Mr. Kettering had found it difficult to get done at the Dayton Engineering Laboratories Company (Delco). That organization had become a manufacturing company with the usual host of commercial problems to solve. It was thus to get the isolation needed for pioneering research that Mr. Kettering founded the new organization completely removed from manufacturing problems.

The subject of fuel was the one in which Mr. Kettering's interest primarily lay. Before the New York Section of the S.A.E. in February, 1919, he spoke as follows about the founding of the new laboratory: "Some three or four years ago, we started a little laboratory over home, just a sort of playhouse in which to study, from various angles, the application of fuel to an engine. We intended to do this studying in about the same spirit as a man plays golf, but I don't think we used the same proportion of profanity as is used in that game."

Thomas Midgley, Jr., was employed as the first member of the technical staff of the new laboratory. Prior to this, on a trip which Dr. Clements had made to Cornell University in search of personnel for the National Cash Register Company, he had chosen Midgley from the men graduating that year as a suitable man for a place on the staff at "The Cash," and Midgley had later been given a job there by general manager E. A. Deeds.

However, just before he was assigned to the Dayton Research Laboratories as the first member of its staff, Midgley had been working on mercury-cooled exhaust valves for Mr. Kettering at the Domestic Engineering Company (later the Delco-Light Company). It was there also that he first began to investigate the bugbear of fuel knock in engines; and it was partly as a result of early events in this study that Mr. Kettering decided to found the new research laboratory. Midgley's first work in the study of knock was done with the aid of a Dobbie-McInnes engine indicator made in England, which Mr. Kettering had bought earlier and stored away against the time when it could be put to just that use.

For the problem of knock in engines was one which had first troubled Mr. Kettering about 1911 in connection with his work on battery ignition for cars. Because of the rapid increase just then in number of cars in use and the consequent need to make more gasoline out of each barrel of crude oil refined, gasoline became less volatile and at the same time worse in degree of freedom from knock. So the magneto makers, with whom Mr. Kettering was competing, made the claim that the cause of the knock was his new battery ignition.

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And now again, 5 years later, in the effort that he was then making to develop a farm-power engine to run on kerosine, knock was troubling Mr. Kettering once more, and to an even greater degree. This came about because, in order to comply with the requirement of the fire underwriters that no more than one gallon of gasoline be kept at a private residence, he had to run an engine on kerosine that originally had been intended to burn gasoline. This meant that, if knock was to be avoided, the compression of the engine would have to be reduced, with corresponding loss in power and efficiency.

And so, with the newly developed Delco-Light engine and an indicator, Midgley began to study the knock. The object was of course to find out how to eliminate it. With his indicator—he soon made a modified one after some of his own ideas—Midgley got his first indicator card, a pressure-volume one, on November 16, 1916. The first such card showing knock he got the next day, on November 17. This card demonstrated that knock was not due to, or was not accompanied by, preignition, as had been generally supposed, but that the disturbance of knock came several degrees later than the ignition spark. This observation is well illustrated by the indicator cards, Figure 1, page 4, but taken at a later date. Compare the pressure-time record of knock (middle card at the left) with that of preignition (bottom card at the left).

In speculating about why kerosine knocked so much worse than gasoline as it was observed to do, Kettering and Midgley reasoned as follows: The chief difference between a kerosine and

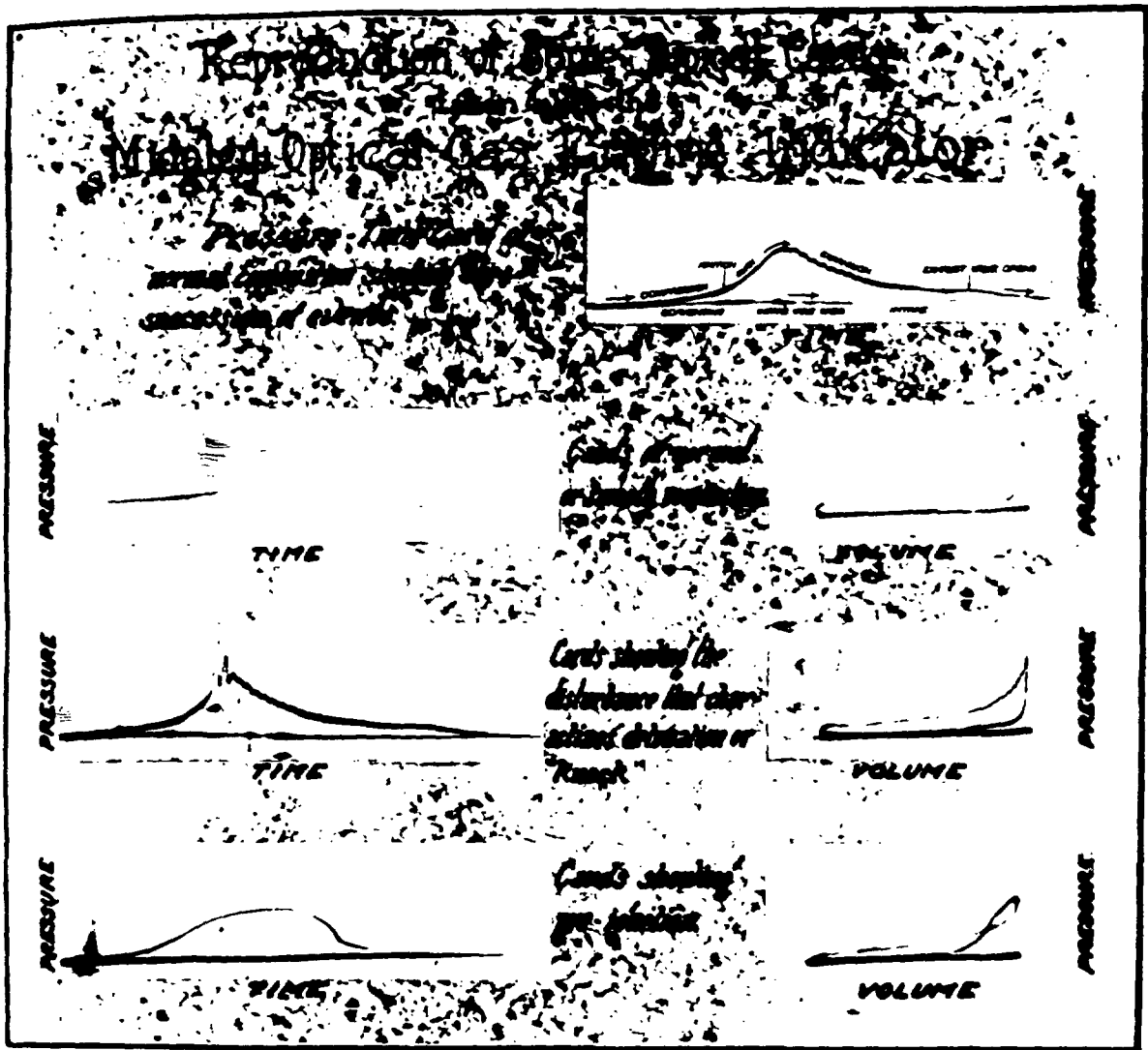


FIGURE 1

SOME TYPICAL CARDS TAKEN WITH THE MIDGLEY OPTICAL GAS ENGINE INDICATOR, AND SHOWING DIFFERENCES BETWEEN NONKNOCKING COMBUSTION, KNOCKING COMBUSTION, AND COMBUSTION IN WHICH PREIGNITION IS PRESENT.

a gasoline, so long as both were made from the same crude oil, was in respect to readiness to vaporize. They supposed that gasoline evaporated easily and completely as it entered the combustion chamber, forming there a homogenous mixture with air, which accordingly burned smoothly and uniformly. But kerosine, being less volatile than gasoline, they supposed to persist in part as minute droplets, even during a portion of the combustion period. They then imagined that at the point where the piston began to recede on the expansion stroke, and so to relieve the pressure somewhat, all the minute globules of kerosine vaporized rapidly or all at once under the high temperature present at that time, and thus burned at the same instant. It was that instantaneous combustion, they thought, which produced the knock. On this basis they reasoned that if the droplets were to be dyed some dark color--like the rusty leaves of the trailing arbutus, which blooms in the spring even before the snow has gone--the fuel fog would then absorb more radiant energy, and so should be vaporized soon enough to prevent the trouble of knock.

Iodine, the First Antiknock Agent

It so happened--and fortunately, as will later appear--that when Midgley attempted to test out this theory no oil-soluble dyes were to be had. He went over to H. R. Wolf's chemical laboratory at Delco to try to get such a dye, and told his problem to Fred L. Chase, who happened to be the only one there just then. Fred could find no oil-soluble dyes, but he reached up on the shelf, took down a bottle of iodine, and made the suggestion that iodine would probably color kerosine red. So iodine was tried and found to work

well as a dye. And when kerosine that had been made red with iodine was run in the engine the knock did die out completely, and the first antiknock compound had been discovered.

The date of this discovery is said to have been December 2, 1916. This date is taken from the chronology in Figure 2, page 7, which is a copy of a large chart prepared by Midgley about 1922 for use in a discussion of developments in the research on antiknock agents up to that time. Some of the later dates given on this chart are not in precise agreement with records kept at the time. So all the dates given there are presumed to be merely approximately chronological.

Wiping out knock by the simple expedient of dyeing the fuel red seemed so simple as to be hardly credible. So to make sure Midgley next got from H. C. Mougey at the Lowe Brothers Paint Company some true dyes that were soluble in kerosine. None of these, he found, reduced the knock to any degree whatsoever, no matter how deeply the kerosine was dyed. The fine theory about the value of a dye for absorbing radiation, and so preventing the knock, was thus demolished. But there remained the important discovery that iodine did stop the knock.

127 North Ludlow Street

The new research institution had for some time no place of its own in which to carry on its endeavors. The discovery of iodine as the first antiknock compound was made in the early engine laboratory located at the Domestic Engineering Company on the second floor of an

DEVELOPMENT OF FUEL RESEARCH WORK

Oct. 1, 1916 Started work on indicator
 Nov. 16, 1916 First Press-Vol. card taken
 Nov. 17, 1916 First Press-Vol card showing knock
 This established that the knock was not preignition as
 commonly supposed
 Dec. 2, 1916 Elemental iodine was discovered to be an antiknock
 compound
 This established that a small amount of material could
 be added to a fuel and prevent knocking
 July 15, 1917 New indicator built to facilitate work
 Oct. 1, 1917 Co-operation started with Bureau of Mines on aviation
 fuel for war work
 Oct. 22, 1917 Cyclo-hexane was being prepared
 Cyclo-hexane run in a motor and found to be a perfect
 high compression fuel.
 Nov. 19, 1917 Larger production of cyclo-hexane started
 Discovery that Ethyl iodide was an antiknock
 June 21, 1918 First dynamometer test with cyclo-hexane at
 Mc Cook field. 200° compression.
 June 26, 1918 First flights with cyclo-hexane at 200° compression
 Aug. 1, 1918 Flights with cyclo-hexane at South Field
 Sept. 1, 1918 Flight with cyclo-hexane at Wilbur Wright Field
 Discovery that anilin was an antiknock
 Discovery that ortho-toluidine and xylene were antiknocks
 Feb. to June Spent trying to get cheap, soluble antiknocking
 nitrogenous compounds
 July 1, 1919 Co-operation of DuPont Co. asked to secure cheap
 source of antiknock
 Jan. 15, 1920 DuPont Co. started research on flame propagation
 Ran Buick car on fuel oil distillate and antiknock
 Conception of injector method
 July 15, 1920 Injector development satisfactory for installation on several cars
 Aug. 15, 1920 Injection method generally unsatisfactory to most users
 Selenium oxychloride discovered to be powerful antiknock
 Di-ethyl-telluride discovered to be powerful antiknock
 May 1, 1921 Production of di-ethyl-telluride started
 Periodic function of antiknock materials conceived
 Systematic investigation of periodic function started
 May 19, 1921 7 to 1 compression ratio Chevrolet completed
 Tin-tetra-ethyl discovered to be an antiknock contrary
 to expectations
 Oct. 30, 1921 Tests of Chevrolet 7:1 compression ratio completed and
 prove 100 % increase of mileage
 Oct. 20, 1921 DuPont's flame propagation results analyzed and dis-
 closed the cause of the knock.
 Lead-tetra-ethyl discovery
 Study of production of lead-tetra-ethyl started

FIGURE 2

APPROXIMATE CHRONOLOGY OF EVENTS IN THE
SEARCH FOR A PRACTICAL ANTIKNOCK AGENT

old building in Dayton across Second Street from the main factory of Delco. Figure 3, page 9, is a picture, taken in 1939, of the building in which the iodine discovery was made. In the first half of 1917 a new plant, built at Moraine City as a home for the Domestic Engineering Company, became available and it was intended to establish the laboratory in a corner of that building. But just then the United States entered the War in Europe and the new building had to be devoted to the making of airplanes by the Dayton-Wright Airplane Company. And so a large old residence at 127 North Ludlow Street in Dayton was rented and converted into a laboratory. A building to house a machine shop was then constructed at the rear of the laboratory. Figure 4, page 10, is the only known contemporary picture of the laboratory at 127 North Ludlow Street.

The name of the institution was changed at that time from the Dayton Research Laboratories Company to the Research Division of the Dayton Metal Products Company. One reason for the change was the difficulty, amounting almost to an impossibility, experienced in securing the things necessary to outfit and operate the laboratory in the days at the outset of our participation in the World War. The Dayton Metal Products Company, which was manufacturing military supplies exclusively, had the priority classification necessary to command what was needed.

The second member of the laboratory staff was H. C. Mougey, who had been for several years at the Lowe Brothers Paint Company, and who it was that gave Midgley the dyes to test after the discovery of iodine as an antiknock agent, as already related. It was on

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FIGURE 3

IODINE, AS THE FIRST ANTINKNOCK COMPOUND, WAS DISCOVERED IN THIS BUILDING ON EAST SECOND STREET, DAYTON, OHIO.

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FIGURE 4

THE FIRST LABORATORY AT 127 NORTH LUDLOW STREET, DAYTON, OHIO

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August 1, 1917, that Mougey joined the staff, and when he arrived at 127 N. Ludlow Street he found the new laboratory just in the process of being fitted out. There the fuel research was done for the most part in what had been the kitchen and the dining room of the main residence, the engines having been located in the kitchen, Figure 5, p. 12, and the dining room and butler's pantry having been the chemical laboratory.

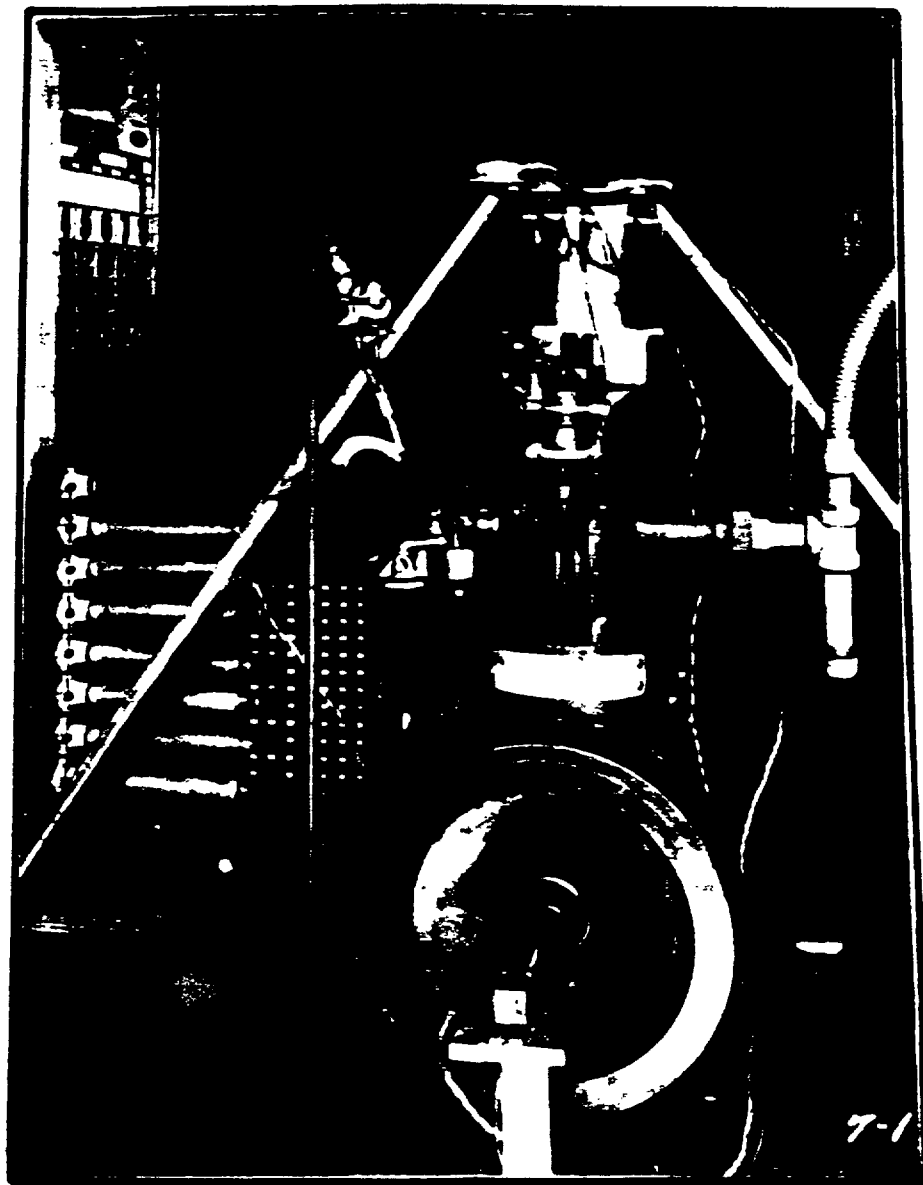


FIGURE 5

DELCO-LIGHT TEST ENGINE IN THE KITCHEN ENGINE ROOM AT 127 NORTH LUDLOW STREET. MOUNTED ON THE ENGINE IS AN EARLY MODEL OF THE MIDGLEY OPTICAL INDICATOR, THE PRESSURE ELEMENT OF WHICH WAS ADAPTED FROM THE DOBBIE-MCINNES INDICATOR.

CHAPTER II

THE WORLD WAR—AND "HECTER"

The United States being then in the World War, there was an insistent demand for a better fuel for our fighting planes. Enough reputation from their researches on fuel and knock had already come to Messrs. Kettering and Midgley to cause the Bureau of Mines, with the backing of the War Department, to enlist their aid in searching for a more nearly knock-free airplane fuel. Messrs. E. W. Dean and Clarence Netzen of the Bureau of Mines, in their paper, "An Investigation of Airplane Fuels" (S.A.E. Jour., 5, 126, August, 1919), published about two years later, said this:

"The work of the Dayton Research Laboratory had shown the necessary characteristics of fuels capable of standing higher compressions . . . and it seemed that this investigation could be applied with great advantage to the aviation fuel problem. It was arranged that the Bureau of Mines and the research division of the Dayton Metal Products Co. should cooperate in ascertaining what fuels capable of standing high compressions were most desirable and most practical."

And so, with the moral and financial support of the War Department, the Research Division of the Dayton Metal Products Company began a cooperative endeavor with men from the U. S. Bureau of Mines (Messrs. E. W. Dean, Chester Naramore, Clarence Netzen, and John P. Smootz) in the search for a better airplane fuel than the straight-run Pennsylvania-base gasoline of about 55 octane number then used. This arrangement is understood to have become effective on October 1, 1917.

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Just prior to this date, Dr. A. R. Albright, an organic chemist, had been added to the staff of the Research Division to help Midgley in his endeavors. The first entry in Dr. Albright's record (Record 1)* is headed "Preliminary Work" and relates to a test, made in a one-cylinder Liberty engine at the Dayton Engineering Laboratories Company, of TNT added to gasoline as a possible means of boosting power.

The TNT experiment did not yield any useful result. But many other fuels and combinations of fuels collected from a variety of sources were tested both in the Delco-Light engine at 127 N. Ludlow Street and in the one-cylinder Liberty engine at Delco supplied by the War Department and operated by Netzen and Smootz of the Bureau of Mines. This engine is pictured in Figure 6, page 15. The many fuels tested in this survey included gasolines from several types of crude, both domestic and foreign; gasolines made by different cracking processes; blends of alcohol in gasoline, of benzene in gasoline, and of alcohol, benzene, and gasoline; as well as different alcohols, ethers, and aromatic hydrocarbons without admixture. Among the many fuels tested was one from Henry Ford called "H. Ford's Knocknocker." Where Mr. Ford got such a fuel is not known, but being highly unsaturated—it was yellow in color and had a highly cracked odor—it was fairly free from knock.

From this survey it was found, in brief, that of fuels which could be had commercially at the time some California gasolines would have permitted a boost in engine compression of over

* The records referred to by number in parenthetical references are the correspondingly numbered record

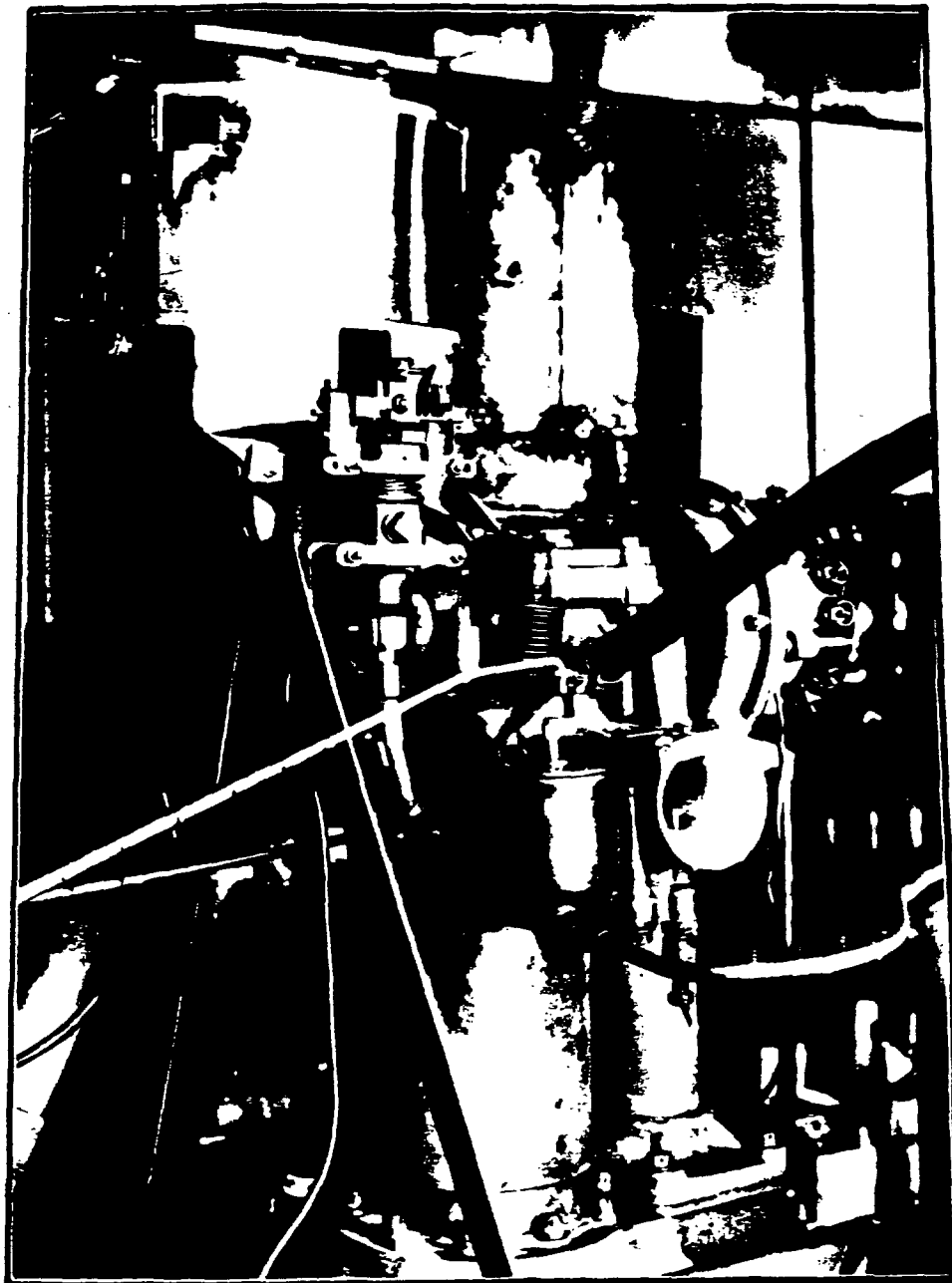


FIGURE 6

ONE-CYLINDER LIBERTY ENGINE AT DELCO, USED BY BUREAU OF MINES
MEN FOR TESTING AVIATION ENGINE FUELS DURING THE WORLD WAR,
1917-18. THE ENGINE IS FITTED WITH THE EARLY MODEL OF THE
MIDGLEY OPTICAL INDICATOR, AS PICTURED IN FIGURE 5.

one ratio, as would also some cracked gasolines. Blends of benzene or alcohol with aviation gasoline would have permitted larger boosts still. For use in airplane engines, however, each of these more nearly knock-free fuels, except the California gasoline, had certain drawbacks. Thus benzene freezes at about 40 deg. F., and it is so high in carbon content that by itself it did not always burn clean; and so there was fear that it might cause spark plugs to short out from deposits of fluff carbon. Alcohol was too low in B.t.u. per pound. The cracked gasolines of the time were thought too liable to oxidation and gumming. It was accordingly recommended that California gasoline be used for fighting grade airplane fuel. But for some reason, not easy to understand, that recommendation was not acted upon.

Just after the joint investigation had been begun, gasoline from a German airplane captured by the French was examined on the other side and reported to contain cyclohexane. This information was cabled across the Atlantic; and, because German airplane engines were known to have higher compressions than ours, an effort to make some cyclohexane for test by hydrogenating benzene was begun immediately. It was later found that, although the German gasoline did apparently contain some naphthene hydrocarbons, very little cyclohexane was included. In the Bureau of Mines paper mentioned above (S.A.E. Jour., 5, 128, August, 1919), the following is said:

"A review of the properties of this hydrocarbon (cyclohexane) indicated that it might be exactly the fuel that was required for high compression engines. It was believed that in spite of their reputed efficiency the German engineers had 'missed a bet.' Experimental work on the hydrogenation of benzol . . . developed shortly into an activity that proved highly interesting and important."

It was at 5 P.M. on October 22, 1917, that work was begun in an effort to make cyclohexane by hydrogenating benzene (Record 1). Nickel oxide was used as catalyst, and ordinary commercial benzene was the raw material. But the record was "No result," although Midgley, Netzen, Smootz, and Albright worked all night. This failure appeared to bear out a prediction made by Dr. Leo H. Baekeland, who, as a member of the Naval Consulting Board along with Mr. Kettering, had contact with the endeavor. Dr. Baekeland had advised against the attempt and offered to give the group a wooden medal if they could make a pint of cyclohexane.

But on October 25 Dr. Albright went to The Ohio State University to look up methods of hydrogenation in the library there. And on October 26 a second trial was made. This time the benzene used had been carefully purified by washing in acid and alkali, and the catalyst used was nickel oxide spread on pumice. A yield of "about 23%" cyclohexane was obtained. Then on November 7 some of the cyclohexane produced was run in the Delco-light engine and gave "no knock." On November 8 a freezing curve of cyclohexane and of its mixtures with benzene was determined. Cyclohexane by itself was found to freeze at about the same temperature as benzene, 40° F.; but at 80% cyclohexane and 20% benzene an eutectic of freezing point 40° below zero was found. This eutectic mixture was given the name "Hecter." A larger hydrogenating tube was built and on December 4 the "10th gallon of 80% cyclohexane (was) finished about 10 P.M."

Incidentally, from the first cyclohexane made, a liter bottle of it was presented to Dr. Baekeland in a plush lined mahog-

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Incidentally, from the first cyclohexane made, a liter bottle of it was presented to Dr. Baekeland in a plush lined mahog-

any box, which is still one of his prized possessions. At the same time he was given a suggested design for the wooden medal he had promised to present to the group. This design is copied as Figure 7, page 19.

On January 7 it was decided to build a still larger hydrogenation furnace, and on February 18 hydrogenation work was begun again. The new furnace was located in the northwest room downstairs at 127 N. Ludlow St.,--in the room which had been the kitchen of the north apartment of the old residence. Figure 8, page 20, is a picture of the hydrogenation furnace and controls taken at a later time. Russell Wells was the operator. But Midgley and the men from the Bureau of Mines were busy with many things, and the effort to hydrogenate benzene did not go at all well, the amount of cyclohexane made having been far below that expected.

So, on June 6, 1918, T. A. Boyd, who six weeks before had been added to the staff of the Research Division, was taken off the physical testing of airplane parts and put to work on fuel problems. He was asked to make the hydrogenation of benzene to cyclohexane work successfully on the 5-gallon-per-day scale then being attempted. (Just prior to this Dr. A. R. Albright had left to go to the Du Pont Company.)

The reasons why very little output was being obtained were that the two difficulties, (1) that of purifying the benzene and (2) that of preparing a suitable catalyst and keeping it active, had not been overcome. However, it proved possible to solve both of these problems rather well in about six weeks. The problem of purification

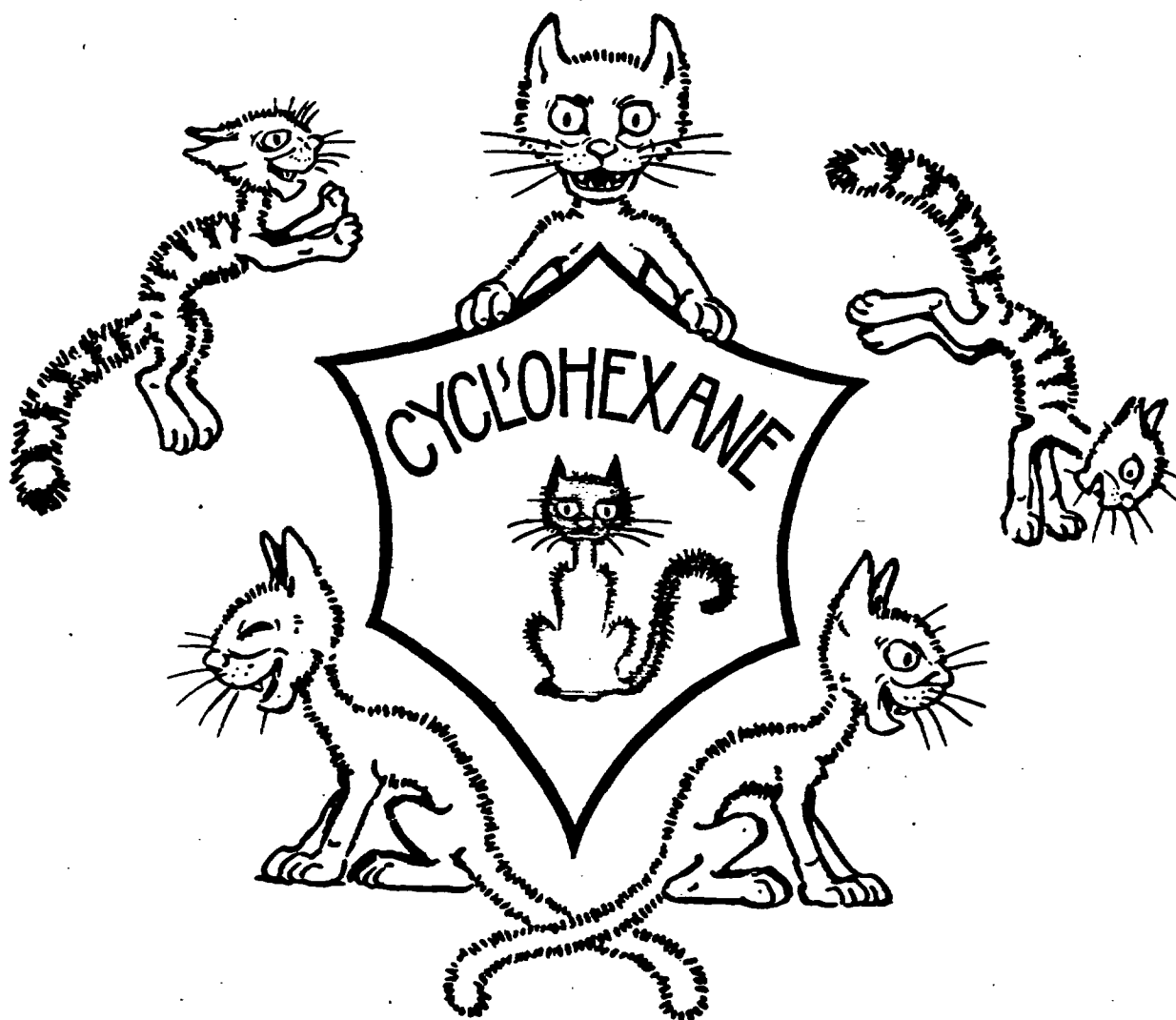


FIGURE 7

DESIGN SUGGESTED TO DR. LEO H. BAEKELAND FOR THE WOODEN MEDAL HE PROMISED TO GIVE MR. KETTERING IF HIS MEN COULD MAKE A PINT OF CYCLOHEXANE. IT WAS HANDED TO HIM ALONG WITH A LITER BOTTLE OF CYCLOHEXANE IN A PLUSH-LINED MAHOGANY BOX, AND IS INTENDED TO SUGGEST THE PLACE OF CATALYSIS IN THE HYDROGENATION OF BENZENE.

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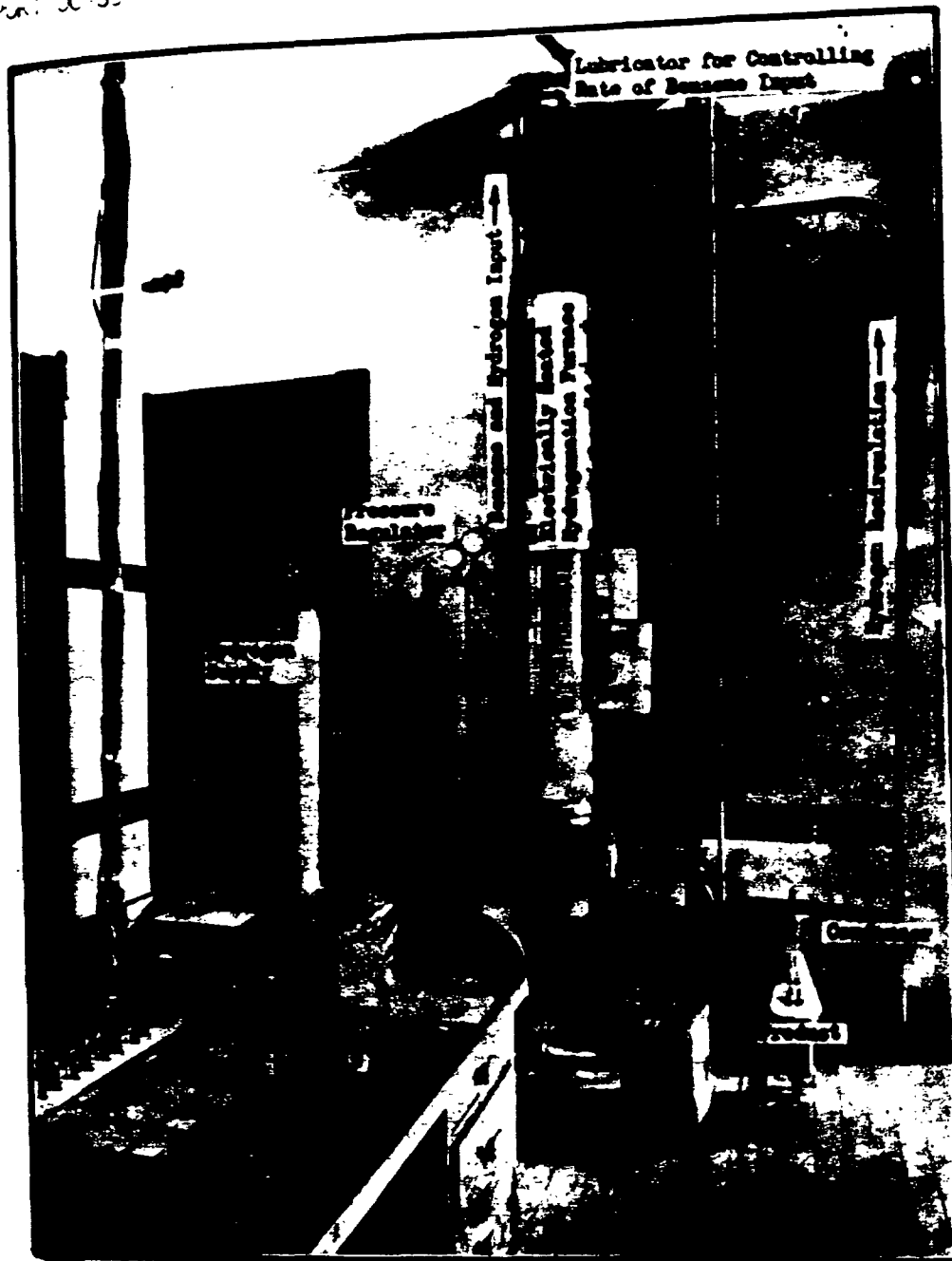


FIGURE 3

SMALL-SCALE PLANT FOR HYDROGENATING BENZENE
AS OPERATED DURING 1918 IN MAKING THE SYNTHETIC
AIRPLANE FUEL CALLED "HECET".

was solved by passing benzene through spent catalyst--called a "dead cat"--under hydrogenating conditions but without any hydrogenation of benzene occurring (Record 4, p. 15, July 9, 1918), followed by washing with sulphuric acid and alkali. Later on, temperatures somewhat higher than that used for hydrogenation were found to give more perfect purification. New tests to determine the freedom of the treated benzene from sulphur were sought out and used also.

The problem of catalyst was solved by the painstaking preparation of nickel oxide by persistently heating nickel nitrate until completely free of nitric oxide. Nickel silicate was being used at the start of Boyd's work, although nickel oxide had been used earlier. Experiments were made also with palladium, iron oxide, nickel oxide+cobalt oxide, nickel oxide+cerium oxide, and nickel oxide+copper oxide. But the most effective catalyst found was made from Mallinckrodt's commercial nickel nitrate. Catalysts prepared from Baker's c. p. nickel nitrate had, by comparison with those made from the commercial nickel nitrate, very low degrees of activity. The commercial nickel nitrate contained copper, iron, and cobalt as impurities. The percentages of cobalt and copper present were experimentally increased at different times, but however with no apparent improvement in the effectiveness of the catalyst.

On July 9, 1918, 50 gallons of Hecter (80 parts cyclohexane and 20 parts benzene) was shipped to the Bureau of Standards for use in engine tests in their altitude chamber, leaving 30 gallons still on hand. Later, larger amounts were sent o.f to various places: over 200 gallons to McCook Field, 100 gallons to South Field, and 100 gallons to Wilbur Wright Field. During the latter part of the endeavor

Hecter contained only 70 per cent cyclohexane, the change in composition having been made because of preignition difficulties experienced in full-scale engine tests at McCook Field with the 80 per cent mixture of cyclohexane (S.A.E. Jour., 5, 129, August, 1919). The total amount of Hecter produced and used in airplane engine tests was around 650 to 700 gallons of 70 per cent cyclohexane (Record 4, pp. 15 and 41). The best yield of Hecter (70% cyclohexane) obtained in any one 24-hour run was about 28 gallons (Record 7, Nov. 7, 1918). This production was obtained in a furnace designed originally to produce 5 gallons per day.

The Hecter thus made was subjected to a variety of tests in airplane engines; to dynamometer tests at McCook Field and at the U. S. Bureau of Standards; to flight tests at McCook Field, Wilbur Wright Field, and South Field; and later on to altitude chamber tests at the U. S. Bureau of Standards (Report No. 90, N.A.C.A.). It was found that the use of Hecter would allow a boost in the compression of airplane engines from 5.5:1, then generally used, to about 8:1. From the results of all these tests, Hecter was judged to be so far superior to the conventional aviation gasoline of the time that in early November, 1918, plans were completed for building a plant large enough to produce 300 gallons of Hecter per day, and capable of extension to any amount desired. But the Armistice, which came just at that time, caused the plan to be dropped. It was estimated that the cost of producing Hecter would not be above 50 cents per gallon, and that it would probably be around 40 cents per gallon. Incidentally, it was in connection with the tests of Hecter at McCook

field that the high-compression engine was run on gasoline, thereby producing the historic damaged pistons and connecting rod, Figure 9, page 24.

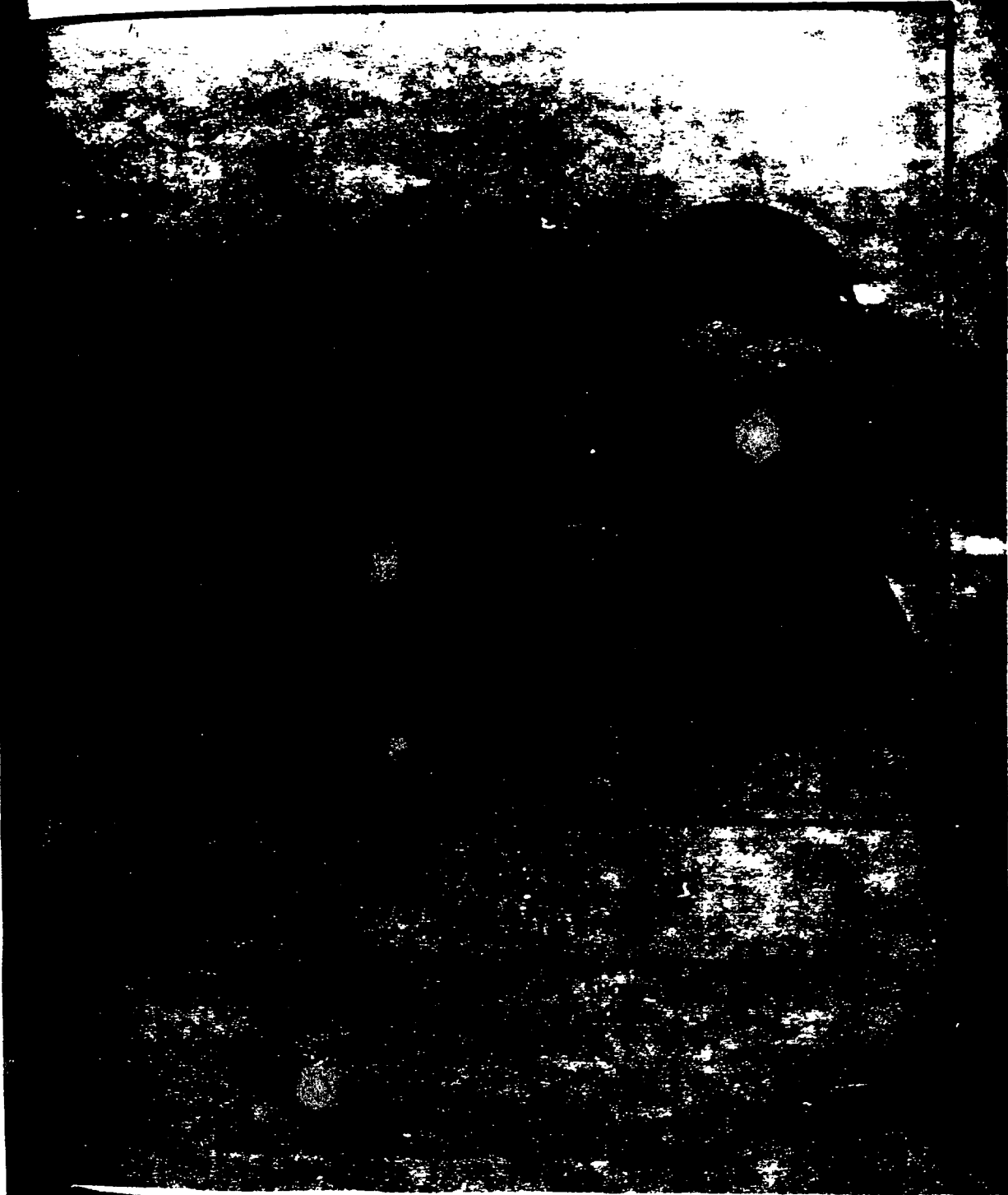
On Nov. 7, 1918, the following entry was made in the cyclohexane log book: "Cyclohexane will never win this war." Also in the log for November 11, 1918 (Armistice Day), is carefully printed the following entry: "Shut down 10 P.M., November 11, to 8:30 A. M., November 12, acc. holiday." And jotted just above this was the following: "Some holiday—Russ Welis."

Following the Armistice in November, 1918, the work on cyclohexane was continued for a while, chiefly in the making of pure cyclohexane (about 70 gallons of substantially 100 per cent cyclohexane was prepared), and in the fractionation of 100 per cent cyclohexane to find what other hydrocarbons might be present.

Of the various items of written matter relating to the fuel work during the War, including the cyclohexane endeavor, the most comprehensive was the unpublished treatise: "A Report of Fuel Research Work by the Research Division of the Dayton Metal Products Company and the U. S. Bureau of Mines, Dayton, Ohio, July 27, 1918." Among the important items of information included in this report was the classical observation that ethyl ether and normal butyl alcohol, which have precisely the same ultimate chemical composition, $C_4H_{10}O$, but distinctly different chemical constitutions, differ widely in degree of freedom from knock. Ether knocks badly, whereas butyl alcohol is very good in respect to freedom from knock. These same compounds illustrated the important fact that a very volatile fuel (ether)

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may knock more than one not so volatile (butyl alcohol). Some of the results of these fuel studies and the cyclohexane endeavor were later published.*

The unpublished treatise, "A Report of Fuel Research Work by the Research Division of the Dayton Metal Products Company and the U. S. Bureau of Mines," July 27, 1918, contained a section entitled "General Description of Fuel Research Work." From that section it may be worth while to quote the following, because it shows that the problem of eliminating knock, and the advantages of improved power and economy to be gained by doing so, were pretty clearly understood at the outset:

"Engineers have heretofore believed knocking to be the unavoidable result of too high a compression, and while the fact that alcohol did not knock at extremely high compressions was well known, it was attributed to its extremely high ignition point. That higher compressions are desirable from the standpoint of output and economy has been universally recognized by engineers. It was also believed that compressions higher than those now in use on airplane motors could not be used with fuels of high heating value, because of violent knocking. From the results of our investigation we seriously doubted the truth of the above accepted belief. Attention was then turned to the effect of various hydrocarbons and other compounds on the knock, and it was soon discovered that the chemical structure of the fuel played a much more important part on the knock than the volatility, although the latter exerts a very large influence on fuels belonging to the same series of hydrocarbons."

*"More Efficient Utilization of Fuel," Charles F. Kettering, S.A.E. Jour., 4, 263 (April, 1919); Statement of Mr. Kettering, S.A.E. Jour., 5, 197 (September, 1919); and "The Combustion of Fuels in the Internal-Combustion Engine," Thomas Midgley, Jr., S.A.E. Jour., 7, 189 (December, 1920). Also the following U. S. patents relate to the cyclohexane endeavor: 1,446,984, February 27, 1923, Thomas Midgley, Jr., Method of Revivifying Spent Catalysts and Apparatus Therefor; 1,467,905, September 11, 1923, Thomas Midgley, Jr., Hydrogenation Furnace; 1,491,998, April 29, 1924, Thomas Midgley, Jr., Motor Fuel.

From this quotation it is apparent that the objective of the research on the elimination of knock was considered to be a general one. From the start of the research on knock initiated by Mr. Kettering, the interest was not limited to solving the then immediate problem of knocking in the Delco-Light engine. It was recognized that the problem applied to automobile engines and airplane engines as well. For, as before said, it was in the automobile that Mr. Kettering first experienced the bugbear of knock. That was around 1911 during his introduction of battery ignition and the electric self-starter. But, just at the time when the above was written in the World War year 1918, the research was, of course, aimed primarily at eliminating knock from airplane engines.

There was an interesting sequence to the preparation of the before-mentioned treatise dated July 27, "A Report of Fuel Research Work by the Research Division of the Dayton Metal Products Company and the U. S. Bureau of Mines." As before said, this report was not published, it having been prepared during the War for the information of the aviation branch of the Army. Of the several copies made, two were however sent to the aircraft authorities in England. One went to the Aeronautical Inspection Dept. Laboratories in London, and one to the Chief Chemist, Department "H", Royal Aircraft Establishment, South Fairborough, Hants, England. Aside from the description of the research on cyclohexane, this report had in it a great deal of intimate information on the relationship of fuel composition or structure to freedom from knock. It was surmised that the report was seen by Harry R. Ricardo, who was attached to the Air

Ministry, and that he used it as a guide or inspiration for the work which he did later with the support of the Asiatic Petroleum Company and published in the Automobile Engineer (London) as a series of 7 papers beginning early in 1921 (11, 51), entitled "The Influence of Various Fuels on the Performance of Internal Combustion Engines." This work of Ricardo's purported to be an altogether original and pioneer endeavor, and thus caused some resentment on the part of some of the men who participated in the early fuel studies mentioned above.

Of the men who worked on the cyclohexane endeavor, John P. Smootz is now with the Standard Oil Company of Ohio, Clarence Netzen died of flu in December, 1918, and Russ Wells died about 1934. A. R. Albright is now with the Hecker Products Corporation in Indianapolis. Another man who operated the hydrogenation furnace a short time on one of the shifts was W. A. Goechal, whose present whereabouts is not known.

Still another man who worked on the hydrogenation furnace during the summer and fall of 1918, when it was being run 24 hours a day was W. K. Gilkey. One night, when Gilkey was there alone, he spilled concentrated sulphuric acid on his trouser legs due to the breaking of a 5-pint bottle of the acid. Instead of stripping the trousers off and wiping off the acid first, as he should have known to do, he ran water on the trouser leg right away in the effort to wash the acid off. The result was that the acid, heated by the water, burned his legs so badly that he was laid up for some considerable time.

There was another man too, mention of whom should not fail to be made, Carroll A. (Ted) Hochwalt. Hochwalt worked in the laboratory and on the cyclohexane endeavor during his summer vacation in 1918. He was back again at the Christmas vacation, and also during the summer of 1919. Then in June, 1920, when he graduated from college, Hochwalt joined the Fuel Department staff as a regular member and made important contributions to be mentioned later on.

It was also on this job that Midgley met with an accident that had an interesting outcome. One of the fusible plugs in a hydrogen tank (bismuth, tin, and lead) accidentally blew out, sputtering 40 or 50 particles of the finely divided metal into the cornea of one of his eyes. He went to the eye doctor, who told him that the metal was too widely scattered and that it was located in positions too delicate to be picked out. The doctor tried treatments to soften the cornea, but with little benefit, "and," quoting from a letter of June 26, 1919, which Midgley wrote to E. J. Crane, a boyhood friend of his and now editor of Chemical Abstracts, "after about three weeks of nuisance, I decided that there were two possible ways to get them out quickly: one of which was to heat them up until they melted out; the other was to use mercury and dissolve them out. Upon consulting with my doctor in the matter, he felt sure that the temperature needed to melt them out would destroy the cornea; so this experiment was never attempted. He gave his consent to the use of mercury, which I used in an eye cup, redistilling and cleansing the mercury in the ordinary way with dilute nitric acid and using fresh

mercury at each application. This procedure gave immediate relief from irritation and, inside of two weeks, every piece was out and my eye was restored to normal condition." This story impressed E. J. Crane so much that he wrote an account of the accident and its interesting outcome and published it in Industrial and Engineering Chemistry (11, 892, September, 1919).

The making of cyclohexane by hydrogenating benzene was discontinued on November 18, 1918, one week after the Armistice and somewhat over a year after it had been begun. But, as before said, the work on preparing a quantity of pure cyclohexane and on determining by means of fractional distillation what other hydrocarbons were present in the product of hydrogenating benzol was continued on into January, 1919, and even later. As supplementing fractionation in the effort to determine what other hydrocarbons were present in cyclohexane, the method of T.C.D's, or temperatures of critical dissolution with aniline, was used. This method, which was intended to distinguish among paraffin, olefin, naphthene, and aromatic hydrocarbons was based on the War work of Chavanne, Simon, and Dort, as published in Comptes rendus, 168, 1111 (1919), but was given to us prior to publication by Mr. Robert G. Dort, who by that time had returned from France and was located at McCook Field.

All the work on cyclohexane soon came to an end, however, and meanwhile other lines of endeavor were gradually taken up. Thus at the end of December, 1918, work was begun in the search for flux and for a core sand binder which would permit the casting of engine cylinders with copper fins. However, these experiments,

which were thus begun as a side-issue at the outset of the extensive work in the development of a copper-cooled engine, were not pursued very long in the Fuel Section. The problem of making copper-finned cylinders was given to another group, which solved it successfully.

In the period, November, 1918, to January, 1919, practical tests were made of a 50-50 mixture of kerosine and benzol as an automobile fuel. The car tests were run by John Sheats in his 1917 model Dodge and later laboratory tests were made by Boyd. In the report of these tests, January 10, 1919, it was said that the performance of the engine was the same as it was on the gasoline of the time, but with two exceptions, viz, that at 0°F. the benzene froze and separated from the mixture and that the engine did not idle so well on the blend as on gasoline. A patent on the use of mixtures of kerosine and benzol as a fuel for internal-combustion engines had been applied for on January 7, 1918, by Thomas Midgley, Jr. It was issued on March 11, 1919, No. 1,296,832. Incidentally, the "Liberty Fuel" proposed by the Bureau of Standards in 1918 is believed to have been a mixture of kerosine, about 65 parts, and benzol, about 35 parts (Record 9, page 65).

Other Events of the War Period

During the period of research on cyclohexane some work was done also in searching for an antiknock agent similar to iodine but not suffering from the defects of iodine. On December 29, 1917, (Record 1), Dr. Albright tried iodoform, but made no record of its effect except this: "something wrong with intake." Then on April 9, 1918, sixteen months after the discovery of the antiknock effect of

iodine, Dr. Albright recorded: "Mixture of small percentage of ethyl iodide in kerosine found to depress greatly fuel knock in 75 lb. compression head engine" (Record 4). Within the period after October 1, 1917, when, as before said, Record 1 of the Fuel Section begins and before the record about the effect of ethyl iodide just mentioned, Dr. Albright's records show that he tried the effect upon knock of camphor, ethyl acetate, nitrobenzene, halowax oil, cresol, aluminum chloride, ethyl chloride, and diphenylamine. He recorded that camphor seemed to help knock slightly. How he missed finding the considerable antiknock effect of diphenylamine, which was later found to be an effective antiknock agent, is not known. But in his record of the testing of diphenylamine on January 23, 1918, he did not mention it as having antiknock effect, and he apparently did not report it otherwise.

Dr. Albright tried also the effect upon knock of plating cylinder heads with copper and with nickel. According to his entries in Record 1, he tested also the following "colloidal" metals made by arcing between poles of the metal immersed in kerosine: copper, nickel, cadmium, and tin. Of copper and nickel he recorded once (March 7, 1918) that knock was decreased. He there indicated that this test was observed also by Messrs. Thomas Midgley, Jr., F. O. Clements, and J. H. Hunt. But later, April 8, 1918, with "concentrated" solutions of copper, cadmium, nickel, and tin he recorded: "knock not appreciably affected."

However, Dr. Albright seems to have concluded that the colloidal metals were effective antiknock agents. On June 30, 1926,

he wrote a letter to the editor of Industrial and Engineering Chemistry, (18, 985, September, 1926), in comment upon a paper about spectroscopic work by Clark and Thee in which he said: "The principal fact here to be recorded is the discovery by the writer that finely divided metals do exert a positive repressing action upon detonation of gaseous mixtures in gasoline engines." There he says also that "A large number of metals were tried; all the common ones, and several of the rarer." He says, further, that "colloidal" copper gave the most promising results,

There were two other events that occurred during the period when Dr. Albright was on the staff that are perhaps worthy of mention. One was his making for Orville Wright a manometer 12 feet in length. It was Orville's intention to use in this manometer two liquids differing in specific gravity by only 0.1. And one of the early jobs given to Boyd after he joined the Fuel Department in June, 1918, was to search for suitable liquids to use in this manometer. Several were tried, and the two settled upon were water for one side and a mixture of halowax oil and kerosine of sp. gr. 1.100 for the other. These liquids were partially successful, but the problem not solved was how to keep the manometer tube in such condition that the dissimilar liquids would not begin to stick to it in parts touched alternately by one and the other.

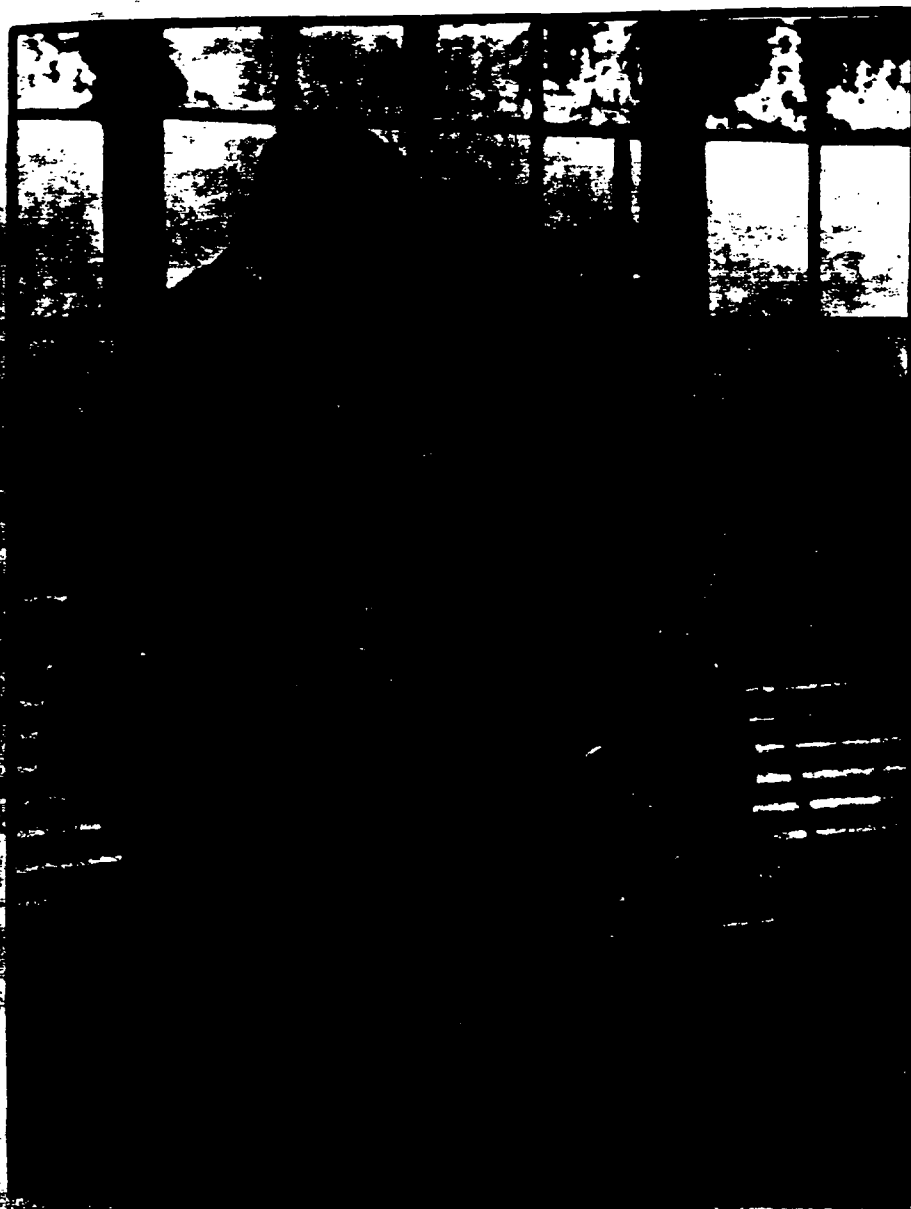
The other event was the trip of Midgley and Netzen to Terre Haute, Indiana, on November 2, 1917, to investigate the process of some alleged inventor there who said he was making gasoline

out of kerosine. His process was apparently nothing more than to pass natural gas through kerosine. The investigators suspected the common deception of a secret valve and hidden source of gasoline, of course, and so they stayed by the process continuously day and night, only one of them going away at a time for meals. Finally the "inventor" broke down and said: "I can't make this process work if you fellows are going to stick around here all the time." And so Midgley and Netzen went back to Dayton to make Hec-ter instead.

Midgley Indicator Improved and Manufactured for Sale

In the summer of 1917 an improved form of the indicator on which Midgley had done his early work was constructed. It was an optical indicator so made as to project pressure-time cards on a glass screen at the front by means of a beam of light. This is presumably the indicator shown in Figure 5, page 12, mounted on a Delco-Light engine in the kitchen engine room at 127 N. Ludlow Street, and also mounted on the one-cylinder Liberty engine at Delco, Figure 6, page 15, used in the war work of Netzen and Smootz, ("A Report on Fuel Research Work," etc., July 27, 1918). Some of the cards taken with this indicator are contained in the report just cited and in the paper, "More Efficient Utilization of Fuel," by Charles F. Kettering, S.A.E. Jour., 4, 263 (April, 1919).

While this indicator was very useful, it suffered considerably from inertia effects, and so gave rough, jagged cards. Later, during 1918 and 1919, a further improvement was made in it which was worked out through the help of John Sheats. Figure 10, page 34, is a picture of the indicator as finally developed, mounted



THOMAS BRIDGLEY, ENGINEER, MIDGLEY OPTICAL
GAS ENGINE RESEARCH, ONE OF THE SINGLE-CYLINDER, AIR-
COOLED ENGINE RESEARCH, AND IN THE SEARCH FOR A PRAC-
TICAL ENGINE.

on a one-cylinder engine. This new indicator was much freer from inertia effects than any made up to that time. It gave the kind of cards, both pressure-time and pressure-volume, shown in Figure 1, page 4, and was used extensively in the studies of knock for a period of several years. It was named the Midgley Optical Gas Engine Indicator.

A fine leather-covered descriptive booklet, "The Midgley Gas Engine Indicator," was prepared and printed during the latter part of 1919. The preparation of this booklet took some night work on the part of the Fuel Department staff, and it also interfered somewhat with the search for an improved fuel. The Midgley Indicator was later manufactured for sale at a price of \$750.00. A considerable number of them were sold, a special group in charge of W. S. Whittaker, who is now general manager of the Inland Manufacturing Company, having handled the distribution and servicing of them. The Midgley Indicator was described too in a published paper, "High Speed Indicators," Thomas Midgley, Jr., S.A.E. Jour., 15, 317 (April, 1920). The indicator was patented: 1,490,223, April 15, 1924, Thomas Midgley, Jr., Indicator. Also in December, 1925, the Franklin Institute awarded to Midgley for this development the Edward Longstreth Medal (Jour. Franklin Institute, 201, 123, January, 1926).

CHAPTER III

SEARCH FOR AN ANTIKNOCK AGENT RESUMED

The search for effective knock suppressors, an endeavor on which nothing had been done for the several months during which the work on production of cyclohexane and Hecter was so intensively pursued, was taken up again at the middle of December, 1918. The first compounds tested were a mixture of rosin and one of oleic acid in kerosine. Neither of these proved to be antiknock compounds. A large number of tests on various concentrations of methyl iodide and of ethyl iodide in kerosine were then made, partly for Boyd to gain experience in running the Delco-Light test engine and in observing degree of knock.

At this stage in the search for an antiknock compound, degree of knock was judged by ear for the most part, although in special cases the Midgley optical indicator was used as an aid. The tests were made by the "Edisorian" method of "cut and try," as there was as yet no information upon which to base any other system of search. In selecting substances to try, oil soluble compounds were preferred. Solubility in kerosine was in fact an essential requirement for such tests, unless the material was a liquid that could be fed to the engine independent of the fuel. A great many solid compounds were tried, however. But tests of solid materials were never very satisfactory, because of the clogging of inlet passages and of the depositing of solids on the valves; and so compounds that were soluble in kerosine or that were themselves liquid were employed wherever possible.

On December 20, 1918, water admitted as a liquid independent of the gasoline was found to be a fairly effective knock suppressor. On December 31 liver of antimony dissolved in kerosine was found to be a very mild suppressor of knock. On January 29, 1919, the first metallic alkyl was run. It was zinc ethyl, made synthetically by Boyd, and was found to have no knock-suppressing effect. At the same time another alkyl compound, also prepared synthetically and thought to be antimony methyl or trimethyl stibine, was tested and recorded as having had no antiknock effect. But this failure to find that antimony was an effective antiknock agent was an error, for antimony alkyls were later found to be more effective than aniline. Only 1.5 cc of the supposed trimethyl stibine was available, however, and it may not have been the compound it was thought to be, or else the observation itself was wrong. At any rate, triphenyl stibine was later found to be an antiknock more effective than aniline on a molecular basis (Record 13, page 170), and it was patented, U. S. 1,575,439, Thomas Midgley, Jr., March 2, 1926.

One of the compounds tested early, on December 20, 1918, was hydrogen peroxide. The record made of the test of hydrogen peroxide in kerosine was that the engine knocked at every stroke (Record 8, page 6). So this was apparently the first instance of a knock inducer, of which several were later discovered; although, perhaps due to low solubility of hydrogen peroxide in kerosine, it was not then recognized as a knock inducer.

The Aniline Discovery

On January 30, 1919, a very important observation or discovery was made, namely, that aniline is an effective knock suppressor. The observation was first made by Boyd working alone and then checked in the presence of Messrs. Sheats, Gilkey, and Goechal. In tests of aniline run the next day, Midgley also was an observer of its effectiveness as an antiknock agent. (Record 8, page 17.) A copy of the original laboratory record of these tests is included as Figure 11, page 39.

Aniline was thus the second real antiknock compound to be discovered, iodine—or iodine and its compounds—having been the first, as already related. In a later comparison of the antiknock effectiveness of aniline by comparison with that of iodine, it was found that 2 cc of aniline was equivalent in effectiveness to 1 gram of iodine (Record 13, page 24).

It is perhaps peculiar that the discovery of aniline as an antiknock compound was not made earlier, or right away at the middle of December, 1918, when the search for an antiknock compound was resumed. This seems to be strange because during the five or six weeks intervening, in which many compounds were run in the engine in the search for an effective knock suppressor, aniline had often been used in the T.C.D. method of examining hydrocarbons. In this method, as related earlier, aniline was employed as a means of studying the composition of the hydrocarbons other than cyclohexane present in completely hydrogenated benzene. Aniline was therefore available and it was known to be soluble in kerosine to some degree. But for some reason it did not get included among the

Tests of Elements As Knock Preventers						
Belco-Light Motor. 75° Compression Head						
Element	Combination	Solvent	Solution	Result	1919 Date - Test	Observer
Br	Br	Ker	5%	No effect	Jan. 20, 1919	Boyd
	T. Benz acid	"	5% almost same	" "	" " "	"
Ca	Ca Ac	"	color - blue	" "	" " "	"
Ag	AgNO ₃	"	Yes - HCl	" "	" " "	"
Hy	Hg Cl ₂	"	Yes color - 1% KO ₂	" "	" " "	"
	oil	"	About 5%	apparently very slight knock	" " "	"
K	KBr	"	Yes - AgNO ₃	No effect	" " "	"
	unknown oil	"	10%	No knock	" " "	"
	"	"	5%	" "	" " "	Boyd
	"	"	8%	" "	" " "	Boyd
	"	"	5%	" "	" " "	Boyd
	"	"	3%	very slight if any knock	" " "	Gilbey
	aniline oil	Ker	100% Compression head			
	"	"	20%	apparently very little knock if any	Jan. 21, 1919	Muggley
	"	"	10%	Some knock	"	Boyd
	"	Gas.	5%	Some knock	"	Boyd
	"	"	10%	Little or no knock	"	Boyd
	"	"	8%	very little knock	"	Boyd
						JA Boyd

FIGURE 11

COPY OF PAGE 17 OF LABORATORY RECORD NO. 8 ON WHICH
THE DISCOVERY OF ANILINE AS AN ANTICKNOCK AGENT WAS
RECORDED.

many compounds tested until the date given above.

Mention may also be made again of the fact that, according to his record, A. R. Albright tested diphenylamine on January 23, 1918, just about a year before the discovery of aniline as an effective antiknock agent. But for some unexplained reason, Dr. Albright missed finding the considerable antiknock effect of diphenylamine, which as found later is about one and one-half times that of aniline.

There is an impression that the discovery of aniline as an antiknock compound, although it did not itself ultimately turn out to be a thoroughly practical solution of the knock problem, did save the search for such an agent from being abandoned prematurely. It was understood that, since there were other things that needed badly to be done and since the search for an antiknock compound better and more practical than iodine had so far shown no encouraging signs of success and might after all be merely a "wild goose chase," Midgley had been given instructions to the effect that the search for an antiknock compound might continue only for a short time more. Two weeks is understood to have been the period of grace set. If nothing promising were to be discovered within that time, the decision was that the search would have to be abandoned.

It is interesting to note here also that for one reason or another, as Records 8 and 9 show, no engine tests in the search for an antiknock compound had been made within the period from January 1 to January 29, 1919. One reason for this condition, as well

as for the two-weeks limit on further search, is perhaps implied in the following quotation from the monthly report of Dr. Clements to Mr. H. E. Talbott, Sr., of February 4, 1919: "Mr. Midgley has tenaciously adhered to the opinion that it was possible to secure a so-called 'pill' to overcome motor knocks. The balance of the organization has given him very little encouragement."

The various endeavors which interfered with engine tests during January, 1919, were those already mentioned: the search for a flux and core sand binder to permit casting copper-finned cylinders; the purification and analysis of cyclohexane; the tests of mixtures of kerosine and benzol as a motor fuel; and in addition a preliminary effort to make alcohols out of olefins in gasoline and kerosine by treatment with sulphuric acid and subsequent hydrolysis, as well as an effort to synthesize zinc ethyl and trimethyl antimony as possible antiknock compounds. But, in view of the verdict setting a time limit upon how much further the search for an antiknock compound might continue, work was resumed at once in making engine tests of whatever further compounds happened to be available on the shelves of the laboratory, downstairs and up, or which could be gotten readily. It was on the second day of this "must" search that the antiknock effect of aniline was discovered. The event thus marks one of the several occasions on which the element of luck has appeared to enter largely into the history of Ethyl gasoline.

Following the important discovery of the antiknock effect of aniline, an immediate effort to get a semi-quantitative measure of its effectiveness was made, and it was concluded (Record 8, page 21) that 3.5 per cent of aniline added to kerosine made a fuel

equivalent in degree of freedom from knock to the regular automobile gasoline of the time (Ohio Red Crown). And, because the solubility of aniline in kerosine was so low that a 3.5 per cent mixture of aniline in kerosine began to separate around 35 deg. F., a search was made for a suitable solvent to hold it in solution down to lower temperatures. Of the many materials tried for this purpose, amyl alcohol and amyl acetate were found to be best (Record A, pages 101 and 102). Also the amine of toluene, toluidine, was prepared and found, as expected, to be somewhat more soluble in kerosine. Toluidine was also found to have an antiknock effectiveness about equal to that of aniline.

Attempts to prepare other nitrogen compounds were made, some successful and some not. Phenyl hydrazine was prepared and found to be an antiknock compound, and an attempt—unsuccessful—was made to add amino groups to the unsaturated constituents of cracked gasoline by passing vapor-phase cracked gasoline (Ramage) and ammonia through a copper tube heated in an electric furnace, with and without catalysts. It is perhaps of interest to record, in passing, that the Ramage gasoline used in this attempt, which was a sample sent to Mr. Kettering for test, was some of the early output of the process that later on became the basis of the "Gyro" cracking process operated by the Pure Oil Company and others.

Bad Luck on Lead in 1919

And then on February 13 and 14, 1919, only two weeks after the discovery of aniline as an antiknock agent, occurred what was perhaps one of the most unlucky events of the whole research that resulted finally in Ethyl. This was the complete failure of the

attempt made at that time to prepare an alkyl compound of lead in order to get an oil-soluble compound to test the antiknock effectiveness of lead. A small amount of lead-sodium alloy was first made by fusing the two metals together in a metallurgical muffle furnace. The product was then heated for a time in a flask with ethyl bromide. Next, the ethyl bromide was distilled off, and the residue was extracted with ether. But no ethyl lead was obtained. It is now known that if ethyl iodide had been used instead of ethyl bromide, which latter needs a catalyst to make it react, and if the product had been extracted with wet ether or if water had been added and the product then distilled out in the presence of steam, some lead ethyl would almost certainly have been obtained. There would then have been a chance to observe the marvelously effective antiknock action of tetraethyl lead almost three years before the discovery was actually made in December, 1921.

A further attempt to prepare tetraethyl lead was not made at that time, partly because there was then no particular reason to think that lead might be a good knock suppressor, but mostly for another reason. The other reason was that the man who made the alloy of sodium and lead did so in the muffle furnace upstairs in the center room at 127 N. Ludlow Street. This furnace was a part of the equipment used by H. C. Mougey's department in making receiving inspections on the materials purchased by the several companies which they were serving, including the Dayton-Wright Airplane Company. And, during the work on the preparation of the active alloy of sodium and lead, the operator had let the thermocouple in the furnace get into the sodium-lead melt and had ruined

it, thereby rendering the furnace inoperative for a time, as there was no other thermocouple available. This, as he soon found out, was an error utterly inexcusable to the men who had the furnace in charge. So inexcusable was it that he was not at all welcome to use the furnace any further. And so, since no particular brief could then be held for lead compounds as antiknock agents anyway, the investigation passed on to the testing of other materials, and the chance to discover the effectiveness as an antiknock agent of the essential ingredient of Ethyl gasoline almost three years before it was made was thereby missed.

It is perhaps worth noting here that at least as early as January, 1919, when the record shown in Figure 11, page 39, was made, it was the intention to test suitable compounds of the various elements. This may be seen from the heading, TESTS OF ELEMENTS AS KNOCK SUPPRESSORS. It explains why the effort to get an oil-soluble compound of lead, as just related, was made so early in the search.

For a while after the discovery of the antiknock effectiveness of aniline a considerable amount of work was done in the effort to make amines by some cheap method. A few of the ideas experimented with, none of which produced useful results, were these (Record 9): Attempts to react anhydrous ammonia with olefins, with alcohols, with brominated and chlorinated hydrocarbons under pressure, with the sludge obtained by treating olefins with sulphuric acid, and with kerosene in the presence of aluminum chloride.

Experiments on Cracking

Although not related to the search for an antiknock compound, a great deal of work on cracking kerosene and gas oils was

done during the same period also, it having been begun in March, 1919, and pursued at various times. These cracking experiments were carried out for the most part in electrically-heated tube furnaces of special design, and almost altogether in the vapor phase. In the fall of 1919 a large amount of experimentation was done on the cracking of kerosine, in which possible cracking catalysts or "pills" were added to the kerosine before subjecting it to the cracking treatment (Report, week October 20, 1919, et seq). *where is it?*

The materials whose possible effects as catalysts were tried consisted of known antiknock agents, as well as many other compounds. Many different schemes were tried, including a plan to hydrogenate the olefins formed in the cracking process by means of hydrogen produced by passing water over hot carbon in a water-gas reaction. In the latter phases of this work (November, 1919), the du Pont Company sent one of their men, Mr. H. A. Lewis, to the laboratory to carry out a series of experiments of this kind on their behalf. *Guery did this?*

An extensive literature study of cracking was made also which included abstracts of all the literature, both patents and scientific papers, from 1907 up to October, 1919.

No practical result came of all this work, except a useful knowledge of cracking problems and some understanding of the effects of heat upon hydrocarbons. The cracking furnace was used also in preparing diphenyl by cracking benzene at very high temperatures. Later on, around 1923, after the antiknock properties of selenium had been discovered, Midgley and Hochwalt experimented with the effects of some compounds of selenium as cracking catalysts,

notably ferrous selenide, and they found such compounds to have a definite catalytic effect upon cracking, particularly in producing a high content of aromatic hydrocarbons. The results of this work were published as a paper, Ind. Eng. Chem., 16, 365 (1924), and also patented, U. S. 1,721,523, Thomas Midgley, Jr., July 23, 1929.

Antiknock Agents Furnished to Others for the First Time

It was apparently during the week following March 17, 1919, that aniline was first given to persons outside the laboratory for use as an antiknock agent. A mixture of 3.5 per cent aniline in gasoline was put into Mr. W. A. Chryst's Essex car, in which he was having trouble from knocking. Knocking was a trouble that was characteristic of the Essex car which first came out that year, the engine having had higher compression than was usual for the time. Because of the good results in Mr. Chryst's car, there was then a further request to send some of the knock suppressing mixture to the Hudson Motor Car Company, makers of the Essex car. And so a gallon of mixture containing the following ingredients was prepared for the Hudson people:

Aniline	1325 cc.
Amyl alcohol	380
Camphor	80
Benzol	1 gallon

The materials other than aniline were added to increase the solubility of the mixture in gasoline, and perhaps also to disguise the composition somewhat. The low solubility of aniline in gasoline is illustrated by the fact that, in spite of all these added solution agents, the mixture as prepared was completely soluble in gasoline at a concentration of 3.5 per cent aniline down only to 9 deg. F.

On March 24, 1919, enough aniline mixture to treat 5 gallons of fuel was also sent over to the Domestic Engineering Company, makers of Delco-Light engines.

As a matter of interest, record should be made of the fact that men at McCook Field and others were supplied with considerable amounts of a fluid to be used as an aid in starting cold engines, which was a very real problem around 1919 when the volatility of gasoline was the lowest it has ever been. This mixture, suggested by Mr. Kettering, was called Kettering's Priming Fluid. It had the following approximate composition, and under proper conditions was quite an effective aid in starting cold engines:

Petroleum ether	1335 cc.
Benzol	<u>2450</u>
Total	1 gallon

Later the composition was changed to the following: petroleum ether, 50%; sulphuric ether, 20%; benzol, 30% (Record 10, page 274).

Beginning in April, 1919, and continuing for some time, a large amount of work was done in an effort to prepare cyanamide, $CN.NH_2$, or other nitrogen compound soluble in kerosine, from calcium cyanamide. Calcium cyanamide was a nitrogen compound commercially available at comparatively low cost, being manufactured at Niagara Falls for use as an ingredient of fertilizers. It was thought likely that if cyanamide could be obtained from calcium cyanamide it would be an effective antiknock agent and one that might be made cheaply. But, although a great deal of ingenuity and effort were applied to the problem over a period of several weeks, at times to the exclusion of all other work, no useful result was obtained. The reason why so much work was done on calcium

cyanamide in the search for a cheap source of a nitrogen-containing antiknock compound was that at the then current price for aniline, 15 to 20 cents per pound, the direct material cost of adding 3.5 per cent of aniline to gasoline would have been of the order of 3.5 to 4.5 cents per gallon of treated gasoline.

Dr. W. C. Ebaugh, professor of chemistry at Dennison University, Granville, Ohio, joined the Fuel Section staff for the summer months of 1919. He engaged himself busily at work relating to the search for antiknock compounds, his various endeavors having included the following: assembling theoretical thermochemical data on the addition products of benzene; joining in the experiments on calcium cyanamid by making a careful quantitative analysis of the raw material, by treating calcium cyanamid with benzene sulphonic acid, and by electrolysis of calcium cyanamid in water solution; and making a study of shale oil as a possible source of nitrogen compounds for use as antiknock agents. Dr. Ebaugh also brought from the stock of chemicals at Dennison a group of compounds to be tested as possible antiknock agents, among them diphenylamine which was found to be quite an effective antiknock agent. This is the compound among those tested by Dr. A. R. Albright during the winter of 1917-18 which should have shown antiknock effect, but which effect—as mentioned earlier—he failed to find for some reason.

The organization of the whole Research Division of the Dayton Metal Products Company at about this time, the middle of 1919, is shown in Figure 12, page 49, which is a copy of a contemporary organization chart.

THE D.M.P. CO. RESEARCH DIVISION F. C. CLEMENTS --DIRECTOR				
CHIM. & PHYS. LABORATORIES	MECHANICAL LABORATORIES		OVERHEAD	
H. C. MUSEY Lead Chemist	THOMAS HINGLEY, JR., Mechanical Engineer In charge of Drafting Rooms, Machine Shop, Fuel Research, Refrigerator Research, and General Mechanical Problems.		Greer H. Marcha Patent Att'y	
In charge of General Chemi- cal work and the routine Testing Labora- tories	SHOP HEADQUARTERS	REFRIGERATION RESEARCH	HERCENE RESEARCH	
CHEMICAL TESTING LABORATORY	C. F. Geatty --In Charge	J. G. King Research Engineer	Object: To de- termine the principles un- derlying satis- factory utili- zation of Heavy Fuels in the Internal- Combustion Motor.	
C. L. Petty Prin. Labora- tory Ass't	G. W. Leach Ass't Foreman	E. George Refrigeration Design	To collect data pertaining to "The Ultimate Fuel of the Future"	
R. J. Wirsching Ass't Chemist	C. P. Harding Mechanic	MOTOR RESEARCH		Dr. W. C. Ebaugh Industrial Chem
E. C. Crome Ass't Chemist Co-op. Student	C. R. Pope Mechanic	Charles Lee Superintendent Plant Three.		Thomas A. Boyd Organic Chem.
Fred Thaman Ass't Chemist Co-op. Student	Herman Basse Mechanic	W. B. Earshaw Ass't Mechan- ical Engineer --In charge of all motor test- ing.		R. D. Wells Helper
Franklin Stephens Helper	Luther Doren Apprentice	J. P. Andrew Research Engi- neer on Solder		W. E. Gilkey Helper
	R. E. Annis	D.P. Alexander Research Engi- neer on Solder ing Methods		C. A. Hochwalt Helper
	DRAFTING ROOM			
	R. V. Hutchinson Engineer in Charge of Design			
	H. E. Kershhouse Motor Design			
	R. J. Thompson Phone Graph Design			
PHYSICAL TEST- ING LABORATORY	Florence Burns Detailer	DISTRIBUTION		OF EMPLOYEES
R. A. Weaver -In Charge	Glennard Fry Detailer	Laboratories-----		5
		Overhead-----		12
		Fuel-----		5
		Motor Research-----		4
		Drafting-----		2
		Refrigeration-----		1
		Shop-----		6
		Patent Attorneys-----		1
		Total-----		56

FIGURE 12

ORGANIZATION CHART, RESEARCH DIVISION, DAYTON METAL PROD-
UCTS COMPANY, SUMMER 1919.

On June 20, 1919, Dr. William E. McPherson of The Ohio State University made a visit to the laboratory and he was retained as a consultant to give whatever help he could in the search for a practical knock suppressor. He in turn enlisted the aid of Prof. C. E. Boord, a colleague of his at the University. On July 23, Dr. Boord came to the laboratory with about 50 compounds and mixtures to be tested for possible antiknock effects. Some of these had been tested before and some had not. They consisted of aromatic amines, aliphatic and aromatic alcohols, esters, chlorine and bromine derivatives of benzene, various homologues of benzene, and unsaturated derivatives of petroleum. No new or unknown types of antiknock agents were found among these compounds. Again on September 13, 1919, Drs. McPherson and Boord came to the laboratory with more than 20 further compounds for similar test. These included additional esters, various azo derivatives, terpenes, and further homologues of aniline. Only the latter compounds showed any considerable effect as knock suppressors.

In the search for effective knock suppressors, it was of course natural that the alkyl amines should be tested for effect by comparison with the aromatic amines, such as aniline. And so as soon as suitable alkyl amines could be had they were run; but in every case they were found to be inferior in antiknock effect to compounds of the aniline type (Reports, weeks of May 20, and July 28, 1919, and Record 10, page 243). Thus it was found that 10% ethylamine by volume in kerosine did not give as much suppression of knock as did 3.5% aniline.

First Work on Decarbonizers

It was early in the effort to eliminate knock that the idea of removing carbon by some means, such as by the action of powerful solvents, was given consideration. And some work was done on the idea in the spring of 1919. The first thing done, though, was to filter some dark fuel oil through Fuller's earth until it was nearly water-white and to run the clean oil in a Delco-Light engine by comparison with the original oil. No lessening in carbon deposited was observed. Carbon deposit from an engine was then extracted in a soxhlet tube with a series of solvents. Among the most effective of the carbon solvents found in this way were diphenyl and aniline (Record 12, pages 24 and 25). Next a considerable amount of work was done (by D. F. Alexander) on the ultimate analysis of carbon deposit. In these analyses it was very difficult to get check results. So that composition was not established with any precision. However, it was established that engine carbon is not really carbon at all, but is a complex mixture of tars, carbon or coke, and ash-giving solids (Record 12, page 27).

Some experiments were made too on adding various materials to the fuel as a "pill" to see whether they would reduce carbon formation (Record 12, page 41). This work was inconclusive, but shortly the important discovery was made that if a piston coated with hard carbon and with rings cemented tight in the grooves were soaked for a short time in hot aniline, the carbon was so softened and loosened that it could be wiped off easily and the rings were entirely freed.

It was found also that aniline placed directly in the cylinder of an engine had a marked effect in softening and loosening the carbon deposited there (Report, week July 28, 1919). This discovery, after further experimentation was patented—U. S. 1,787,419, Thomas Midgley, Jr., and Carroll A. Hochwalt, filed April 15, 1922, issued December 30, 1930.

In the summer of 1919 a comprehensive list of ring compounds containing nitrogen in the forms of NH_2 and NH was prepared to be used as a list of possible antiknock agents.

Then, as a means of extending further the information about the antiknock qualities of homologues of aniline, Boyd embarked on a program of collecting and testing the various alkyl and other derivatives of aniline in a systematic manner. Some of these compounds were synthesized by heating aniline hydrochloride with less than the theoretical amount of each of a number of alcohols in a sealed glass tube at 150 deg. C. for about 15 hours. (Report, week Aug. 18, 1919). Several explosions of these tubes occurred. But the heating was done in an electric furnace especially fitted for such work, and so no harm was done. The results of this study in respect to antiknock effect arranged themselves with a curious consistency, as may be seen from the chart, Figure 13, page 53. It is there seen that aniline—plotted at the extreme left—is one of the better of the antiknock compounds of nitrogen, but not the best. A paper based upon this work was published later on, "Relative Effects of Some Nitrogen Compounds upon Detonation in Engines" by T. A. Boyd (Ind. Eng. Chem., 16, 893, September, 1924).

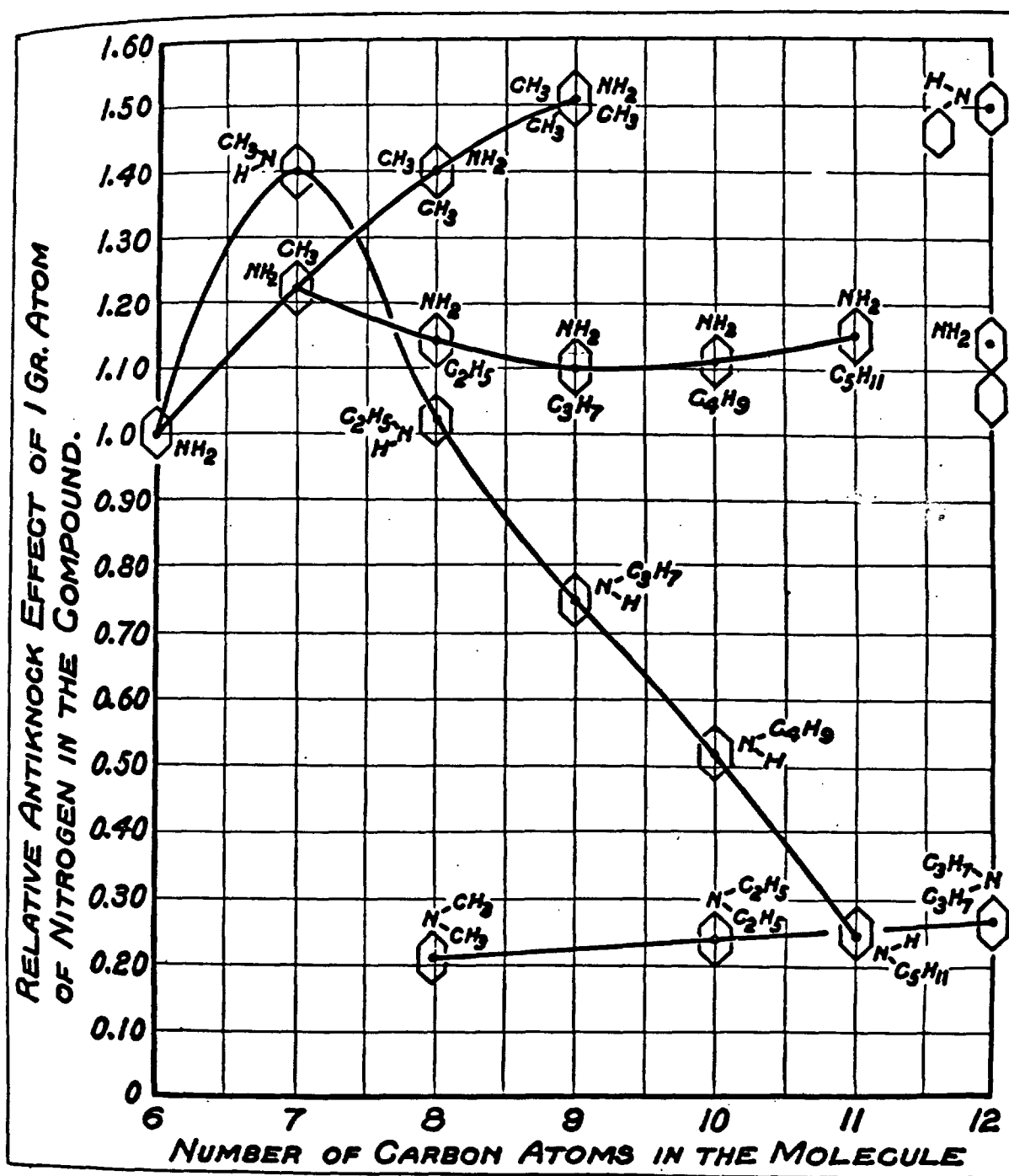


FIGURE 13

CHART SHOWING THE INFLUENCE ON THE ANTIKNOCK EFFECT OF ANILINE OF SUBSTITUTING VARIOUS ORGANIC RADICALS FOR HYDROGEN IN THE RING AND IN THE AMINE GROUP.

First Cooperation with Du Pont

It was on August 13, 1919 that cooperation with the Du Pont Company, or their participation in the program which led finally to Ethyl gasoline, began. On that day, Dr. C.M.A. Stine, at that time Asst. Chemical Director of Du Pont (Dr. C. L. Reese was still chemical director then), and John Marshall, Manager of the Miscellaneous Division of the Eastern Laboratory, first visited the laboratory. They were then made familiar with the work done up to that time toward the solution of the problem of knock. A complete list of compounds tried as possible antiknock agents was later sent to Mr. Marshall, and he was requested to send us certain of the homologues of aniline. H. A. Lewis came to the laboratory to participate in some of the experiments on cracking, as previously mentioned. And Midgley visited the Du Pont Company in November for a conference on the antiknock program, at which on the basis of Du Pont price quotations it was estimated that for each per cent of aniline added to gasoline the material cost would be 1.25 cents per gallon and for each per cent of xylidine added to gasoline the cost would be 2.75 cents per gallon. Later on (December, 1919) the men at Du Pont made a study and submitted a report on the possibility of producing enough alcohol to serve as automobile fuel. One of the conclusions of that report was that it would take about 55-60 per cent of the combined sugar and grain crop of the country to make enough alcohol to replace the gasoline consumption of that time.

In 1920 a formal or written contract was entered into with the Du Pont Company under which they were to study combustion and

detonation in a closed bomb fitted with a window and a camera with moving film for recording the explosions. This work, which was done at the Eastern Laboratory by Messrs. Woodbury, Lewis, and Canby, was actively pursued for a time but was discontinued in the early fall of 1920 due to the financial stringency which developed that year. The work was done on a cost-plus basis, and the cost of it turned out to be something over thirty thousand dollars. The results obtained were presented in a report submitted by the Eastern Laboratory on October, 1920, "Motor Fuels, Rate of Flame Propagation." These results also formed the basis of a paper presented to the S.A.E., "The Nature of Flame Movement in a Closed Cylinder," by C. A. Woodbury, H. A. Lewis, and A. T. Canby (S.A.E. Jour., 8,209, March, 1921). The work was incomplete, but photographs were obtained which showed the rate of flame travel with a few fuels, and which furthermore showed that sulphuric ether gave a characteristic self-ignition during the latter part of the combustion of the charge in the bomb, whereas under the same conditions petroleum ether was free from such a disturbance.

The Detonation-Wave Theory of Knock

The Du Pont work just reported formed the basis of an analytical paper published later by Midgley, "Molecular Movements During Combustion in Closed Systems," (S.A.E. Jour., 10, 357, May, 1922). It is interesting to note that it was from the 1920 Winter Meeting of the S.A.E. at which the paper of Woodbury, Lewis, and Canby had been presented that Midgley returned with the detonation-wave theory of knock. This theory was to the effect that a

detonation wave, which is known to accelerate to a maximum, is originated and supported by a decomposition of the fuel molecules which release an amount of energy that varies from one type of fuel compound to another. It was thought that the magnitude of this released energy determined the tendency of a fuel to knock. A great deal of work was then done in computing the relationships among different types of fuels in terms of heating value. That is to say, the changes in heating value as molecular size in the paraffin series increases were compared, and the values of paraffins versus olefins, etc., were compared in the light of known differences in degree of freedom from knock.

But the results of all these computations were not thoroughly conclusive. And so a series of paraffin hydrocarbons, pentane, hexane, heptane, octane, and nonane were prepared in as pure condition as practicable by fractionation from high-test gasoline, and these—along with benzene, toluene, and xylene and a number of alcohols--were rated relatively in terms of tendency to knock by finding how much of each had to be mixed with kerosine to make a mixture as free from knock as gasoline. It was thus found, by the rough means of test available, that the paraffins increased uniformly in tendency to knock from pentane to nonane (impure though the samples were), that toluene is freer from knock than benzene and xylene than toluene, and that cyclohexane was better than pentane under the conditions of test.

It is interesting to note in this connection that the observation mentioned just above that toluene was freer from knock

than benzene and xylene than toluene gave Midgley the idea that iso-paraffins, or paraffin hydrocarbons having methyl groups as side chains might be freer from knock than normal or straight-chain paraffins. To check this point work was started in the attempt to fractionate out of casinghead gasoline iso-pentane and possibly other hydrocarbons having methyl groups as side chains (Record 10, page 249). Some attempt was made also to synthesize such hydrocarbons by chemical means (Record 10, page 251). But this investigation was not at that time pursued far enough to establish the validity of the idea. One reason why that investigation was dropped so prematurely was perhaps because a cut from gasoline, boiling from 63 to 65 deg. C. and thought to contain considerable amounts of iso-hexane, did not prove to be freer from knock than another cut thought to be normal hexane. But the 63-65 cut was probably largely normal hexane, for it was noted that its sp. gr. did not agree with the value given in the literature for iso-hexane. And so it was not until the work of Graham Edgar and of Wheeler G. Lovell and John M. Campbell several years later that the great superiority in respect to freedom from knock of paraffin hydrocarbons closely compacted in space arrangement over paraffin hydrocarbons of the same molecular size but having extended or straight-chain structure was established (Edgar, Ind. Eng. Chem., 19, 145, 1927; Lovell, Campbell, and Boyd, ibid, 23, 26, 1931, and later papers).

The various items of work mentioned above did not fully explain the mechanism of knock. However, Midgley continued to

adhere to and to develop further the detonation-wave theory of knock. This theory appears in a number of the papers published later, but has in recent years had to be modified in view of the observation from photographic studies of engine combustion that knock arises from a self-ignition of a portion of the charge (Ind. Eng. Chem., 23, 539, May, 1931). However, in the light of this later information obtained directly in engines, it is seen that the inference that knock is due to, or is accompanied by, self-ignition of a portion of the charge might have been made from the records obtained in the bomb experiments at du Pont. Further contacts with the Du Pont people will be mentioned later on.

It should be mentioned in passing, that during the fall of 1919 a considerable amount of effort was put into the development of improved laboratory-size fractionating columns, and into an attempt to devise a special means of measuring the specific gravities of liquids. Neither of these endeavors, however, were pursued beyond the experimental stage. Among other miscellaneous endeavors engaged in at the close of 1919 and the beginning of 1920 were a study of the viscosities of fuels and of the surface tension of fuels and possible means of controlling it. The chart, Figure 14, page 59, is of interest in this connection, since it shows for the fore-part of November, 1919, both the personnel of the Fuel Section and a list of the various endeavors which were then being pursued or were in mind for the immediate future.

A Temporary Change in Objective

However, in the early part of December, 1919, the emphasis in respect to the research of the Fuel Section was changed somewhat

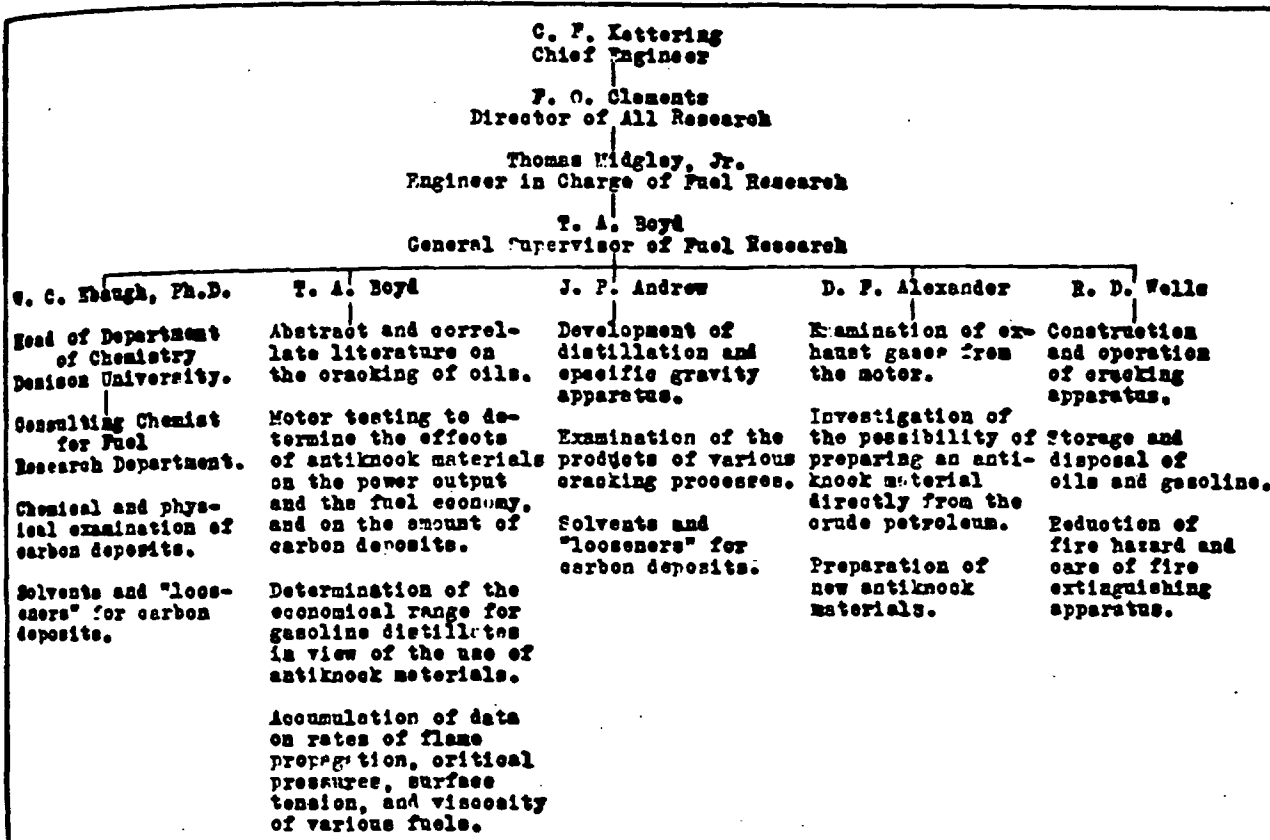


FIGURE 14

PERSONNEL OF FUEL DEPARTMENT WITH PROVISIONAL WORK ASSIGNMENTS, NOVEMBER, 1919.

in that it was decided to divert the main trend of the fuel work from the search for a practicable antiknock compound into an effort to improve the possible fineness of atomization of heavy fuels, hoping thus to be able to burn heavy fuels satisfactorily and with comparative freedom from carbon and crankcase dilution. It was hoped then that the knocking difficulty might be taken care of by means of decomposition products of water in a suction burner or by introducing a percentage of exhaust gas (Record 10, p. 213). This change was brought about by the following events:

1. T. A. Boyd with John Marshall of Du Pont visited E. W. Dean at the Bureau of Mines, Pittsburgh Station, to ask for his opinion about what changes in the distillation curve of gasoline would represent unit increases in the amount of gasoline produced. Dr. Dean's opinion was that each degree Centigrade of rise in the temperature at which the gasoline cut was made would represent an increased production of gasoline of about one per cent (Record 10, page 211).
2. It was found by test that, on the basis of the figure given by Dr. Dean, a comparison of the gasolines then being sold with the average on the basis of which he spoke indicated that a considerable increase of production over the then current 25% average from the crude was already being put into effect by refiners, and that at the same time gasoline storage was full. It thus appeared that there was little likelihood of an

immediate shortage of light fuel, and that refiners were being able to sell lower grades of gasoline than the average of that time without serious trouble from knocking. And so it was decided "that work on antiknock materials done with a view toward making possible the use of low-grade fuels in internal-combustion engines is not very urgent at the present time."

Thus it is seen that the primary idea back of the search for an antiknock compound had up to that time been that the gasoline supply was in danger of being inadequate and that to use a heavier fuel, such as kerosine, an antiknock agent was needed to keep down its tendency to knock. But, of course, antiknock agents had already been added to automobile gasoline, and it was known that in some cars, notably in the Essex, knock was greater than some drivers wanted to tolerate. And so with this start the ideas apparently came around gradually, first to the use of an antiknock agent to make it possible to put a larger percentage of the crude into the motor fuel fraction, and then to the need for an antiknock agent, even though gasoline did not include a deeper cut into the crude.

The first of these stages in the evolution of ideas about the place of this research in respect to the fuel situation is shown by the discussion of "The Motor Fuel Problem," Appendix 1. The matter in Appendix 1, prepared in May, 1920, is a part of the first of four quarterly reports on the fuel situation mentioned later on in this history. It is there concluded that the best solution of the motor fuel problem would be to make available for use in gasoline engines a larger percentage of the crude oil, and a plan of research

p. 301

directed toward that end is presented in which the use of antiknock compounds has again a prominent place.

But for a time beginning in December, 1919, the search for an antiknock agent was discontinued for the most part, and work was concentrated instead upon the effort to atomize and distribute heavy or non-volatile fuels. A great deal of work was done on this project over a period of months. Many schemes of atomization were tried, with and without heat. Engine runs were made, including the operation of Midgley's car for a time, and the effect of degree of atomization upon the amount of carbon deposited in a given time was determined. But since nothing directly useful came out of the endeavor, it will not be reported further here.

Water as an Antiknock Agent

The supplementary idea of using water as a knock suppressor had already been experimented with to some considerable degree. Beginning in October, 1919, an extensive series of engine tests of the effect of water as an antiknock agent were run. The observation was that it required the admission of about one-third as much water as kerosine to a Delco-Light engine to be equivalent to 3.5 per cent aniline in decreasing knock, and that if the water were admitted as steam it was less effective than as a liquid (Report, week October 20). A study of the possibility of emulsifying water with kerosine was then made also (Record 10, page 231 et seq.). It was found possible to make fairly stable emulsions by suitable means, but emulsions did not meter at all well through carburetor jets, although the Delco-light mixing valve would handle them to good advantage. The ul-

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timate result of the work on water as a possible knock suppressor was to abandon it altogether, both because of the difficulties mentioned, because water would freeze in winter, and because there is no supply of pure water available to engine operators—all they have usually is hard water, which is a solution of various salts in water.

Mention should be made of the fact that it was during the work on the atomization of non-volatile fuels that Charles P. (Charlie) Harding began to work in the Fuel Section. He had been working at the laboratory for several months preceding, having been located in the shop at the rear of 127 N. Ludlow Street.

First Use of an Antiknock Agent in the Army Air Service

In February, 1920, 3.5 gallons of xylidine was supplied to Maj. G.E.A. Hallett of McCook Field for use in a high altitude flight by Maj. R. W. Schroeder. Maj. Schroeder used this material as an antiknock agent in his flight of February 27, 1920, during which he reached the then very high record altitude of 36,020 feet. The xylidine was added to his fuel to overcome an apparent condition of preignition previously encountered with gasoline alone when attempting to supercharge at high altitudes. Maj. Schroeder reported to Midgley that in the flight test made after the xylidine had been added that he could not make the motor preignite and that it "ran like a sewing machine." It was in this flight that Maj. Schroeder became unconscious from lack of oxygen and fell with his plane for some miles before he revived, righted the plane, and landed safely. Tests had previously been made on the Delco-Light engine, from the results of which it was estimated that the xylidine should be used

in a concentration of 3.5 per cent in the 68-degree aviation gasoline employed.

In early March, 1920, the first work was done in developing a system of demonstrating and studying detonation in a glass tube. By experiment an arrangement consisting of a glass tube closed at one end and open at the other, with a means of charging the tube from the closed end with a suitable mixture of gas and air, and a spark for igniting it, was worked out which either would or would not develop the detonating type of combustion with a sharp crack and shattering effect upon the end of the glass tube, depending upon the fuel supplied to it. A mixture of acetylene, oxygen, and air was developed by trial which of itself would give detonation but which in the presence of ethyl iodide vapor would burn quietly. This was first developed for use by Midgley in a lecture given at the Dayton Engineers' Club on March 16, 1920, and later on in Buffalo. The demonstration worked well—except at the lecture at the Engineers' Club, where for some reason it failed completely, to the great embarrassment of those trying to make the demonstration. This same experiment, with subsequent refinements, was used later on also, as will appear.

CHAPTER IV

AFFILIATION WITH GENERAL MOTORS AND MOVE TO MORaine CITY

In the early part of 1920, an important change occurred in the status of the Research Division of the Dayton Metal Products Company. This was its absorption by General Motors Corporation in accordance with an arrangement by which the Corporation purchased and assumed control of the various Dayton interests of Charles F. Kettering and those associated with him. An important part of this arrangement was an agreement that Mr. Kettering would organize around the existing nucleus, called the Research Division of the Dayton Metal Products Company, a pioneering research laboratory for General Motors, and that he would become the director of it. Under this plan, the laboratory became for a time a part of the Dayton-Wright Division of General Motors Corporation. This arrangement was a temporary one which began about March, 1920, and which lasted only until the research laboratory was given separate status as the General Motors Research Corporation, incorporated on June 12, 1920.

*Site 25/1919
approved with
D. & P. Co.
S. units*

In the short period within which the research laboratory was a part of the Dayton-Wright Division of General Motors Corporation it was moved from 127 N. Ludlow Street, and from the site on West Third Street (Plant 3) where the Inland Manufacturing Company is now located into which the mechanical portion of the laboratory had been expanded following the close of war activities, to the large building at Moraine City which during the War had been occupied by the Dayton-Wright Airplane Company. Figure 15, page 66, is

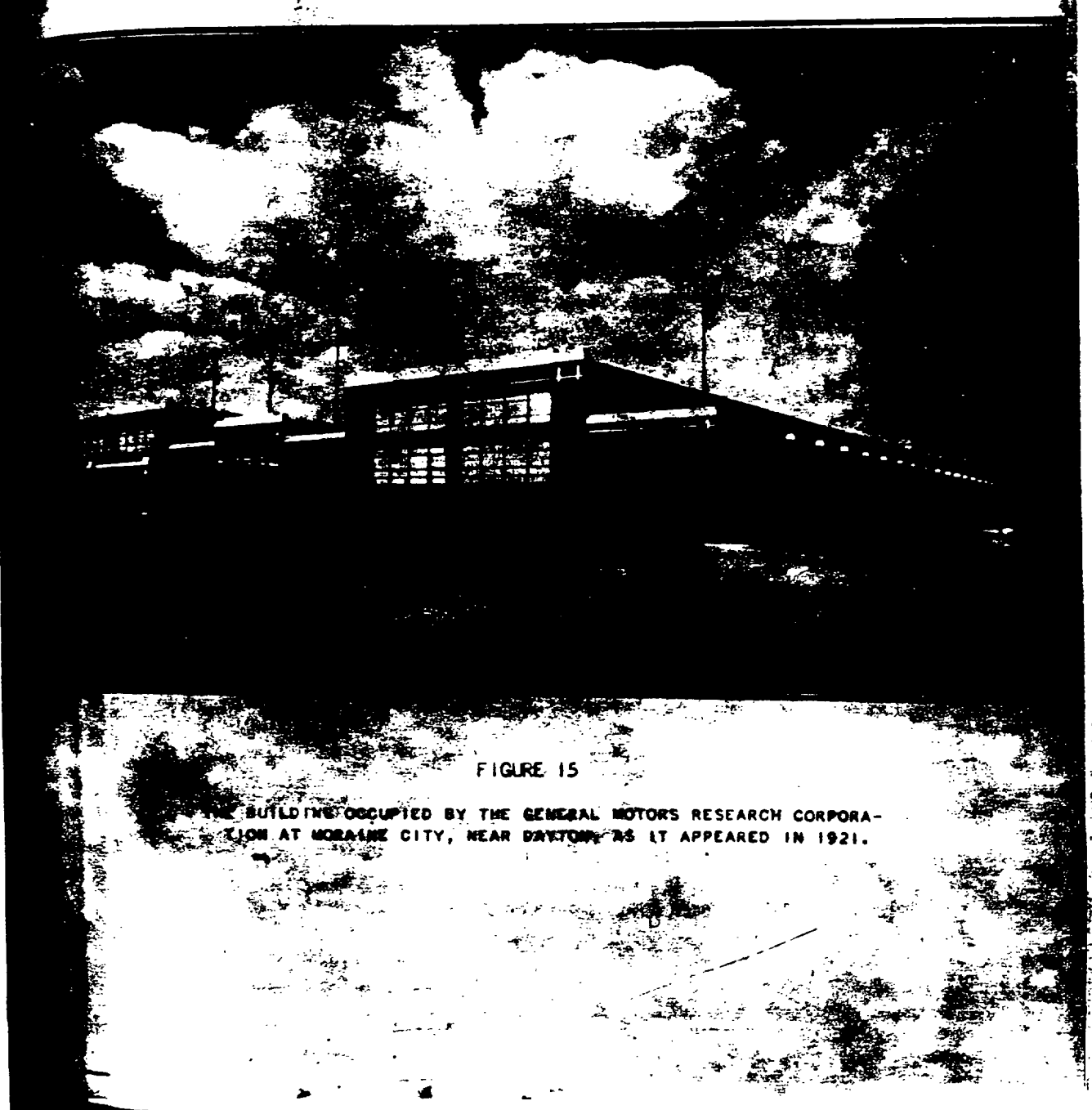


FIGURE 15

THE BUILDING OCCUPIED BY THE GENERAL MOTORS RESEARCH CORPORATION AT MORAINES CITY, NEAR DAYTON, AS IT APPEARED IN 1921.

a contemporary picture of the new laboratory building. This building, it is interesting to note, was the same one in a corner of which Mr. Kettering had originally intended to locate his new research laboratory in 1917 when, as already related, the necessities of the War prevented the plan from being carried out. But this enlarged research institution of General Motors could not now be housed in a corner of the building, large though it was. The new laboratory occupied about two-thirds of the floor space of the building, which was nearly 300 feet wide and 1000 feet long. A lay-out of the laboratory of the Fuel Section as it was first constructed in the new location is shown as Figure 16, page 68. It was in February, 1920, that these new laboratory plans first began to be drawn, and the actual move to the new laboratory was made in April or May of that year.

It was originally intended to construct also in the new location, as an adjunct to the research facilities of the Fuel Section, a small or semi-works refinery, similar to those which some petroleum refineries had at the time. Boyd made a trip to the Sinclair Refinery in East Chicago, and to the refinery of the Standard Oil Company of Indiana at Whiting, to inspect two such semi-works refineries. Suitable plans for a small refining unit were drawn up, and equipment consisting of stills--the largest 100 gallons, the smallest 5 gallons--condensers, pumps, and agitator were designed and ordered. But other things intervened, and the small refinery was not actually built.

A record of the cost of the work on fuels and on the search for a practical antiknock compound during the period from July 1, 1917,

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to the end of February, 1920, which latter date marked the end of the Research Division of the Dayton Metal Products Company, is contained in Appendix II. The total cost of salaries, supplies, and overhead for that period relating directly to the research on fuels, as given there, was about forty-two thousand dollars.

Beginning in May, 1920, and continuing to June, 1921, a series of five quarterly reports on the motor fuel situation were prepared and circulated to all those men in General Motors to whom it was thought that they might be useful. The discussion which is presented as Appendix I, and which gives an outline of the motor fuel problem as it was thought to be in 1920, is a portion of the first one of this series of reports and gives a general idea of the character of most of them. "The problem," as stated there, "is to increase the available supply of fuels suitable for use in motor vehicles and, at the same time, to conserve the fuel resources of the country, in order to insure the present and future usefulness of motor-driven vehicles." Through these bulletins an attempt was made to establish what was called the "General Motors Fuel Service," to give information, and practical assistance where possible, to General Motors engineers and others interested.

The final bulletin of this series (which was really the fifth bulletin, but was designated Bulletin No. 4) was a comprehensive treatise on the testing of gasoline and on how to interpret the results in terms of service. This bulletin was based both upon experience accumulated up to that time, and upon an extensive investigation conducted during the spring and early summer of 1921 to refine

some of the methods so as to make them usable by others and practically useful to them. This final bulletin of the series was perhaps the most practical and the most useful of all of them. At the request of the editors of Automotive Industries, it was later published in a somewhat modified form (Automotive Industries, October 13 and 20, 1921).

Vegetation Investigated as Possible Source of Motor Fuel

During the summer and early fall of 1920, there was again interest in, and some investigation was made of, the possibility of getting motor fuels from vegetation. This activity was, of course, occasioned by the fear, which still persisted, that the supply of gasoline from petroleum might soon become inadequate. It consisted chiefly of these two items: First, was the work that Hochwalt did on the preparation of furfuraldehyde from corn stalks, straw, and corn cobs, and in the attempt to hydrogenate it to the furfuryl alcohol, and also on the hydrolysis of wood to produce sugars which might be converted to alcohol by fermentation. As a motor fuel, furfuraldehyde was found to suffer from the difficulty of preignition. Second, was the library study of cellulose conducted by Boyd at Yale University, consisting of daily conferences with Dr. Harold Hibbert and of a study of the literature in the University library relating to cellulose, which was as extensive as could be made within the few weeks devoted to it. Dr. Hibbert, who is now professor of industrial and cellulose chemistry at McGill University, was retained after a survey had been made of the various men in the country who were active in the field of cellulose

chemistry had suggested him as best fitted for the purpose. He gave a series of lecture-conferences designed to cover in so far as possible the existing knowledge on the subject of cellulose chemistry, particularly in respect to the basis of the effort he was then making to synthesize cellulose.

On July 20, 1920, Boyd wrote to Midgley from New Haven: "I find that it will be impossible to cover the literature of the subject of cellulose in such a way as to gather the previously obtained information on the subject in four weeks, even counting ten hours a day. In fact, I believe that it would take from four to six months to do the job thoroughly. But I am trying to cover as much of the territory as is at all possible while I am here. If you are up this way, I hope you will arrange to spend a day or two here seeing what Dr. Hibbert and I are doing." Midgley did pay a visit there within a week after that letter was written. Incidentally, he had previously asked Boyd to make some search of the literature for further information on cyanamide. This he did because at Moraine City additional investigation of this compound, which had been studied so extensively the previous year, was then in progress.

After the discontinuance of the paper studies of cellulose at Yale, not a great deal further of that kind was done in the effort to make motor fuel out of cellulose. Midgley was anxious for Boyd to get back to the laboratory, because his help was thought to be needed on the other endeavors then under way, one of these having been the effort, now to be described, to develop an injector for.

feeding aniline or other antiknock compound to the engine as needed. Interest in the subject of getting gasoline out of plants continued, however, and Hochwalt carried on an investigation of the hydrolysis of cellulose and wood which lasted until March, 1921 (Record 14). Also some economic studies were made and a paper entitled "Motor Fuel from Vegetation" was published later on (Ind. Eng. Chem., 13, 636, September, 1921).

The Aniline Injector

Because of the high cost of antiknock agents of the aniline type—which, as has already been indicated, was of the order 3 to 4 cents per gallon of gasoline for 3.5 per cent aniline and about twice that much for an equivalent concentration of xylydine—and also because of the belief that not enough aniline to treat all gasoline could be had at any price, work was begun in the early summer of 1920 in an effort to develop a device to inject aniline in just the amount needed to eliminate knock, and not to consume any aniline at all when none was needed. It was believed, on the basis of experiments made then that injecting aniline only as required would reduce the amount consumed to about one-tenth that used when the aniline was put directly into the gasoline so that it would be consumed at part throttle as well as at full. The background of this endeavor was explained in some detail in a letter which Midgley wrote to Dr. Charles L. Reese of the du Pont Company on June 9, 1920, and which is included as Appendix III.

In connection with this letter and with the work on the development of an aniline injector, it is interesting to note here

three items of information: first, that the decision to discontinue research on antiknock compounds, which had been reached six months before, had now been abandoned; second, that it was then thought unlikely that a better antiknock agent than aniline would be found; and, third, that it was then believed that the supply of petroleum was so limited that, as Midgley said in his letter to Dr. Reese, "This year will see the maximum production of petroleum that this country will ever know."

A large amount of work on the development of an aniline injector was done throughout the rest of 1920 and the early part of 1921. This work consisted not only of the effort to develop a practical mechanical injector, but also of determining the relationship between knock and degree of vacuum in the intake systems of engines, of making viscosity studies on aniline and its homologues at various temperatures, of making studies of the solubility of aniline in solvents such as benzene at low temperatures, and of trying to prevent the gumming of aniline which developed in injectors after continued use. An effort was made also to find some means of destroying the unpleasant odor of aniline, which asserted itself both before entering the engine and in the exhaust gas. There was so much of the peculiar stuffy odor from aniline in the exhaust of an engine using it that the presence of a car using aniline or one of its homologues was sometimes unpleasantly apparent. A large number of perfumes and aromatic oils—such as camphor, pennyroyal, citronella, and the like—were added to aniline in an effort to disguise these odors, but without appreciable benefit. A great deal of

trouble was experienced in making a valve for the injector that would remain tight and which would function properly otherwise. Leather was about the most satisfactory valve material found, but there was trouble from the aniline gumming in injectors after they had been in service for a time. Some of the injectors were put into operation on cars and it was planned to build a combined carburetor, suction burner (for warm-up), and aniline injector.

First Plan to Market an Antiknock Agent

In spite of the difficulties met with, Midgley held a conference with men at the Du Pont Company in August, 1920, at which the following rather definite plans were made (as quoted from letter of August 5, 1920, Midgley to Dr. Reese):

"I understand that the Du Pont Company will co-operate with our company in placing aniline on the market for use as an anti-knock material, in connection with the aniline injector which we are developing. The first phase of this program would consist in one of the General Motors Companies marketing an aniline injector through the ordinary channels of accessory dealers. The Du Pont Company would simultaneously put aniline in small quantities, such as pints, or quarts, or perhaps, gallons, which could be sold in conjunction with the injector. A further working out of this program would comprise the sale of aniline in bulk by the Du Pont Company through some satisfactory distributing agency, such as has been suggested by the Standard Oil Company, who could give aniline national distribution, similar to lubricating oil, selling same in bulk at the filling stations."

This plan was not put into effect, however.

In December, 1920, an extension of the injector idea was made in the initiation of an effort to develop such a device for use on airplane engines. The incentive for this endeavor came from

the men at McCook Field, chiefly Maj. G. E. A. Hallett, who had shown a great interest in the possibilities of using antiknock agents as a means of eliminating knock, which was a barrier alike to higher compressions and to greater degrees of supercharging. The development of an injector for airplane engines involved an aneroid for controlling the flow of aniline with altitude as well as the customary means for varying the amount injected with manifold vacuum. The same problems were encountered in the effort to make an injector for airplane engines as were being encountered in the work on an injector for automobile engines, and some additional ones as well. The plan to inject an antiknock agent into airplane engines met with some measure of success, however. And in March, 1921, 500 gallons of a mixture of 70 parts ortho-toluidine and 30 parts benzol, called Antiknock No. 1, was sold to McCook Field for use there. This material had been purchased from the Du Pont Company. Four hundred gallons of Antiknock No. 1 were sold also to the Navy Department at about the same time.

During the year 1921, a considerable amount of antiknock agent consisting of the mixture of ortho-toluidine and benzol was in fact either sold, or given in small amounts, to a good many different people. No attempt will be made to give a list of these. But mention may be made of one of them, Edsel Ford, who on December 1, 1921, wrote to Mr. Kettering as follows:

"In conversation with Colonel Hall day before yesterday, he mentioned the fact that you were selling your anti-knock solution, and if this is true we would like to have you send a few gallons for trial in our experimental engine shop."

To this letter Midgley responded on December 3, saying that at Mr. Kettering's request he was sending Edsel 5 gallons of the antiknock compound.

The work on an aniline injector for automobile engines was continued on into 1921. These devices were successful enough to be used to some degree and to be patented. Two U. S. patents on aniline injectors were issued, as follows: 1,501,568, July 15, 1924, Thomas Midgley, Jr., Aniline Injector; 1,467,222, September 4, 1923, Fred E. Aseltine, Method and Means for Incorporating an Antiknock Substance with a Motor Fuel Mixture.

Dark Hour Before a Break in the Clouds

But by the spring of 1921 the problems of using aniline as an antiknock agent, either added directly to the fuel or separately injected as needed, began to make it appear that the use of compounds of the aniline type might not be practicable. In a letter of April 2, 1921, to Dr. C. M. A. Stine of the Du Pont Company, Midgley said:

"There are one or two problems connected with the use of antiknock that, while they have been mentioned in the past, are now assuming very serious proportions and unless they can be overcome, our engineering results may never be realized in practice. The outstanding problem which faces us at the present time is the odor of unburned aniline, or partially burned aniline, coming out of the exhaust. I doubt if humanity, even to doubling their fuel economy, will put up with this smell."

There was also the danger arising from the toxicity of aniline, and the difficulty of the action of the alkaline compounds of the aniline type on metals with which the fuel came into contact.

This latter was a factor that had caused trouble in the work on injectors, the gumming difficulty having already been mentioned. The airplane people at McCook Field made a series of tests to measure the effect of such antiknock agents on metals. Their findings were published in Automotive Industries, March 23, 1922. They found that "aluminum and zinc are very slightly affected, if at all, by the doped fuels, but copper, brass,terne plate and iron are badly affected."

So the first of April, 1921, came—more than two years after the discovery of the antiknock effect of aniline. And, although some small success had been had in using aniline compounds as antiknock agents, the accumulation of difficulties which appeared to be insurmountable made it appear that there was very little prospect of commercializing such compounds successfully. Enthusiasm of those working on the antiknock endeavor was accordingly at a low ebb, some even thinking that the antiknock endeavor might have to be abandoned. Mr. Kettering has related that Midgley came to him about this time and suggested that possibly it might not be worth while to pursue the antiknock endeavor much further. No better antiknock agent than aniline had been found, it did not then seem likely that any better one would be found (see Midgley's letter to Dr. Reese, Appendix III) and the use of aniline-type compounds had met with difficulties that seemed insurmountable.

CHAPTER V

SELENIUM DISCOVERY OPENS NEW FIELD

On April 6, 1921, a very important discovery was made-- the discovery that a compound of selenium, selenium oxychloride, was a great deal more effective as an antiknock agent than anything tested up to that time. This amazing result (Record 13, page 25; Record 20, page 2) seemed all the more remarkable since it was known that, in general, compounds containing oxygen or chlorine--and selenium oxychloride contains both--are knock inducers. Sulphur oxychloride, as a similar compound, was in fact tested at the same time as selenium oxychloride and found to be an inducer of knock. So it is easy to understand that the discovery of the remarkable antiknock effect of selenium oxychloride was an exciting event.

Selenium oxychloride had first come to attention in May, 1920, the year prior to the discovery just mentioned. There had been newspaper stories about it then, these having been based upon the work of Prof. Victor Lenher at the University of Wisconsin. He was investigating selenium and tellurium under the sponsorship of the National Research Council, and at the instigation of copper, lead, and silver producers. These producers had selenium and tellurium as by-products of their smelters, without having found much use for them. In one phase of Dr. Lenher's work he had made some selenium oxychloride, and in the early summer of 1920 had described its effectiveness as a solvent.

As the tests on carbon solvents previously mentioned were then in progress, Midgley wrote to Dr. Lenher on May 15, 1920, asking how some of this new compound might be obtained. One of the purposes in trying to get a compound called a "universal solvent" was of course to test it as a carbon solvent. The other was to try it as a possible antiknock agent, in accordance with the custom of testing every available compound in the engine. But Dr. Lenher replied that selenium oxychloride was not yet on the market. Interest in the compound was not then sufficient to cause us to try to prepare it ourselves, especially so since that was a very busy time just after the removal of the laboratory from 127 N. Ludlow Street to Moraine City.

And thus nothing further in respect to selenium happened until the early part of 1921, when, following further publications relating to Dr. Lenher's work on selenium oxychloride (Jour. Am. Chem. Soc. 43, 29, 1921), a letter was written to Dr. Lenher on March 14, 1921, asking again where some of the compound might be obtained. The reply said that it could then be purchased from Baker and Adamson and from Eimer and Amend. And so a small amount was bought from Eimer and Amend; and on April 6, 1921, it was tested for possible effect as a knock suppressor, with the surprising results already reported, namely, that it was a much more effective antiknock agent than any discovered up to that time.

The following interesting story about selenium oxychloride, related to Boyd by Mr. Kettering, January 17, 1929, may be inserted here. About the time when the search for a practical antiknock agent reached its lowest ebb in the spring of 1921, as already

recounted, Mr. Kettering went on a trip to New York. All the while he was gone the question of what should be done about the search for an antiknock agent was on his mind. Because so much effort and expense had been put into it already, and because he did not want, therefore, to drop the work unwisely, he was greatly concerned about what decision should be reached in regard to it.

Coming back to Dayton from New York, he was thinking about this problem; and in the evening when the porter came to make up the berths in his drawing room, he and Mrs. Kettering went out of the room and sat in one of the seats at the end of the car. As Mr. Kettering sat down he picked up a paper that was lying there, and his eye happened to fall on a news item in it, which was to the effect that Dr. Victor Lenher of the University of Wisconsin had discovered what was termed a "universal solvent" in the compound called selenium oxychloride. Because Mr. Kettering just happened to know a funny story about a universal solvent, he was interested enough to read the item; and, as he did so, it occurred to him that here was a compound that had not, so far as he knew, been tried for effect on knock, in spite of the fact that a very large number had been investigated. Figure 17, page 81, is a copy of a newspaper item about selenium oxychloride which appeared around that time, but it is probably not the particular one which Mr. Kettering saw on the train that night.

The story about the universal solvent that was in Mr. Kettering's mind was to the effect that a man who had car trouble on the road one day went to a small building near by in search of a telephone. There he found two men busily engaged in making chemical

NEW CHEMICAL SOLVENT.**Waste By-Product of Copper Refining is a Remarkable Reagent.**

A new chemical reagent which has proven to be one of the most striking solvents discovered in recent years and contains possibilities of extensive industrial use has recently been worked out in the chemical laboratories of the University of Wisconsin. The discovery was announced at the meeting of the American Chemical Society in St. Louis recently by Professor Victor Lenher, the chemist who discovered it.

The new solvent is technically known as selenium oxychloride, and it is made of a commercial by-product of which hundreds of tons go to waste. As a chemical reagent, this new substance possesses the property of acting as an excellent solvent for some of the most insoluble substances, such as rubber, asphalt, and the bituminous material in soft coal.

The reagent is an excellent solvent for unsaturated organic substances. The unsaturated hydrocarbons, such as acetylene, benzene, toluene, etc., dissolve readily in it, while the paraffin hydrocarbons, such as gasoline, kerosene, and the so-called mineral waxes, vaseline and paraffin, are unaffected. The soluble oils are acted upon, many with violence, and linseed oil forms a thick exceedingly mucilaginous and rubber-like mass.

Lakeite, reditanol, the waterproof insoluble casein glue used in a ship construction, pure rubber, vulcanized rubber, asphalt and bitumen all dissolve with ease. The bituminous material in soft coal can be dissolved out leaving a carbonaceous residue, and in all probability some information as to the character of the naturally occurring asphalt and bitumens can be obtained by the use of this new solvent.

The selenium from which the solvent is made is a by-product in the electrolytic refining of copper, a substance for which there is now no market, although hundreds of thousands of pounds of it are annually going to waste. During the late war, when manganese was not obtainable for the purpose, selenium was used for the decolorization of glass, and a very considerable quantity was produced for this purpose. But now that manganese is again obtainable, practically no selenium is being put on the market. A small amount is used for the preparation of light sensitive cells, but the amount used is infinitesimal from the production standpoint.

A committee of the National Research Council, of which Professor Lenher of the University of Wisconsin chemistry department is a member, has been working for more than a year on the question of finding a market for the enormous amount of this element now going to waste, but nothing remarkable has developed until this very recent discovery by Dr. Lenher. The method of preparation of the new compound is simple, according to the discoverer.

This work has developed a remarkable degree of interest among chemists, and, by request, Dr. Lenher presented the results of this research.

FIGURE 17

ONE OF THE NEWSPAPER ITEMS ABOUT SELENIUM OXYCHLORIDE AS A "UNIVERSAL SOLVENT" WHICH, AS RELATED IN THE TEXT, PLAYED A PART IN THE DISCOVERY OF SELENIUM AS AN ANTI-KNOCK AGENT HAVING A NEW AND HIGHER ORDER OF EFFECTIVENESS. IT WAS THIS DISCOVERY THAT SET THE SEARCH FOR A PRACTICAL ANTIKNOCK AGENT OFF ON ITS FINAL, AND MORE

experiments. While he waited around, he learned that they were trying to discover a universal solvent—something that would dissolve everything it touched. After pondering the matter a little while, the stranded traveler said to the two experimenters, "Of course it's none of my business, but I have just been wondering what you are going to keep that stuff in when you get it."

It was just about the time that Mr. Kettering got back to Dayton, or shortly thereafter, that the sample of selenium oxychloride was obtained, as previously related, and tested with the remarkable results mentioned.

But selenium oxychloride is a compound highly corrosive to metals, one that fumes when exposed to the air. In its disintegrating effect upon engines, it would be almost as bad as the universal solvent mentioned in the press at the time in connection with it. This, coupled with the fact that its content of oxygen and chlorine would seem to keep it from being the most effective compound of selenium, caused an immediate search to be begun for a better and more effective compound of selenium. It was, however, found possible at the time to make first an alkyl compound of the similar element tellurium, diethyl telluride (Record 14, page 75). This happened because, following the letter which Midgley wrote Dr. Lenher in May, 1920, some tellurium had been sent to us from Omaha by the American Smelting and Refining Company, and so was readily at hand to work with. Using this tellurium as starting material, Hochwalt made some diethyl telluride by preparing an alloy of tellurium and potassium and then reacting it with ethyl chloride under pressure.

The diethyl telluride thus made was first tested by Boyd for effect as an antiknock agent on April 8, 1921, and found to be several times more effective still than the selenium oxychloride which two days before had been found to have what was then thought to be such a remarkable effect (Record 13, page 26; Record 20, page 4). Later diethyl selenide was prepared and found to be considerably more effective than selenium oxychloride, but not so effective as diethyl telluride (Record 13, page 27). It finally turned out that on a volume basis diethyl selenide was about five times as effective an antiknock agent as compounds of the aniline type and that diethyl telluride was about twenty times as effective as aniline. These discoveries naturally put an entirely different aspect on the antiknock endeavor, and gave a new lease of life to the investigation.

On April 15, 1921, Midgley wrote to Dr. C.M.A. Stine of the du Pont Company a letter the tone of which was quite different from that of his letter of April 2, quoted on page 76. "I know you will be interested," he wrote, "in hearing that we have recently discovered an antiknock material which is twenty-four times as strong as aniline, volumetrically. The material looks very, very practical and I feel sure that this is going to radically change our previous plans, obsoleting the injector; in fact obsoleting the use of aniline or coal tar products in any way, shape, or form, except, possibly as carbon removers."

Miscellaneous Events of 1920 and 1921

Before proceeding to recount the events which followed these important new discoveries, it seems desirable to digress long enough to tell about some earlier events, which were passed over in order to tell the story of the development of the aniline injector in continuous fashion.

In December, 1920, and January, 1921, work was done on a project which is of interest because it formed at least a part of the development of the crankcase ventilators now used almost universally on American cars. This work consisted of experiments on the removal of low-boiling materials from the oil in the crankcase by means of a stream of exhaust gas (Record 13, page 5 et seq.). The experiments consisted both of bench tests of various kinds and of tests directly in engines, and they showed that it was possible to remove considerable amounts of volatile material from crankcase oil containing such material.

During the first half of 1921 the hydrogenation furnace and other equipment in the semi-works laboratory—called "Refinery" in Figure 16, page 68—were used in preparing a series of compounds on a small scale for the Eastman Kodak Company. This work was done at the request of Eastman, and the furnaces were operated by Russ Wells. The following is a list of these compounds and how each was made:

- Sec-butyl alcohol, by hydrogenating methyl ethyl ketone
- Heptyl alcohol, by hydrogenating heptaldehyde
- Cyclohexanol, by hydrogenating phenol
- Hexahydrocresol, by hydrogenating cresol
- Hexahydrotoluene, by hydrogenating toluene
- Hexahydrocymene, by hydrogenating p-cymene
- Amylene, by dehydrating amyl alcohol

It was in January, 1921, that the members of the Fuel Section had their first practical contact with the sticking of engine parts from gummy gasoline (Record 13, page 7). Mr. Charles H. Fox of the Ahrens-Fox Fire Engine Company and Mr. Campbell of the Cincinnati Fire Department enlisted the aid of Mr. Kettering to help solve the problem of the sticking of carburetors on some of their fire engines, which trouble in some instances got so bad that engines could not be started due to the freezing of throttle valves. They brought to the laboratory samples of the gasolines being used. They brought along also a carburetor having a considerable amount of the characteristic brown varnish-like gum in its passages. They feared that the troubles had been occasioned by some malicious person having put acid in their gasoline storage tanks. By examination of the samples of gasoline and by quizzing Messrs. Fox and Campbell, together with a representative of the gasoline supplier, Mr. L. S. Bale, it was possible to clear up the mystery by finding that the gumming of the gasoline and consequent sticking of engine parts was caused by using a cracked gasoline in too adverse a manner. The fuel tanks on infrequently used fire equipment were kept full and the equipment stood nearly all the time in a heated engine house. Some pieces of equipment used so little gasoline that the supply in the fuel tank sometimes did not get changed completely for a very long time—for a time long enough to allow harmful amounts of gum to form in the gasoline. So their trouble was easily cured, and the men in the Fuel Section

were glad to have had a hand in finding the cause of it and how to cure it.

In January, 1921, Mr. Kettering assigned to the Fuel Section the job of investigating three devices which had been proposed to him by P. G. Tismer of Tompkinsville, New York. Tismer, who was a most peculiar character, spent a great deal of time around the laboratory advising how to design and build his devices for application to a Delco-Light engine. His three devices consisted of a ringless piston, clearance 0.001" to 0.002", a lubricator for the piston, and an igniter to facilitate starting from the cold on kerosine. Broad claims were made for these devices, of course. But, after building samples with Tismer's advice and giving them suitable tests, it was concluded that, in view of the difficulties experienced with them and the lack of benefits from their use, Tismer's devices were at least of no interest to General Motors. The program covered a period of about two months, and the results as well as drawings of the apparatus were presented in a formal report dated March 12, 1921, a copy of which is still in the Fuel Section files.

It seems appropriate to mention here, as the one who made the drawings for the Tismer devices, another of the men who participated in the early activities of the Fuel Department, R. J. (Tim) Thompson. The drawings, and some of the designs, for other mechanical elements which entered into the early research on fuels were made by Thompson also, such as the Midgley Optical Gas Engine Indicator, the aniline injectors, and the like.

Thompson was for some time a member of the Fuel Section staff directly. Since 1925 he has been with Frigidaire and Kinetic Chemicals, Inc.

Further Work on Selenium and Tellurium

Now that these miscellaneous happenings have been mentioned, it is possible to return to the events which followed the important discovery of the remarkable antiknock effects of compounds of selenium and tellurium, as made in early April, 1921. This discovery naturally resulted in an intensive effort to investigate similar compounds, and consequently in the substantial abandonment of further research on compounds of the aniline type. (In respect to aniline compounds, however, see the discussion of the high-compression Chevrolet which follows below. Gasoline treated with ortho-toluidine was used as fuel in this car during the summer of 1921.)

Other oil-soluble compounds of both selenium and tellurium were made and tested just as rapidly as possible. These included the methyl, the ethyl, the propyl, and the phenyl compounds. All were found to be quite effective as knock suppressors (Rec. 20, pp. 2-10); and, by the approximate methods of test then available, tellurium compounds appeared to be about four times as effective as equivalent compounds of selenium (Rec. 13, p. 30).

An immediate effort was made to find out also whether, in case the use of selenium and tellurium as antiknock agents should prove to be practical, the supply would be adequate to permit any considerable proportion of the gasoline used to be treated. For

this purpose Midgley and Boyd attended the spring meeting of the American Chemical Society in Rochester, N. Y., about April 25, 1921, at which a conference on the subject was held with Dr. Victor Lenher. This survey of resources showed that the largest estimated production of tellurium from any one producer was 30 tons per year by the Raritan Copper Works, whereas to add even one one-hundredth of one per cent to the gasoline consumed then would have required 1,500 tons per year. And so the potential supply of tellurium was judged to be inadequate (letter, August 4, 1921, Boyd to Dr. Victor Lenher). The cost of the compound was low enough, however, and its effectiveness as a knock suppressor was high enough that, if it had not been for the problem of availability and one other mentioned in the next paragraph, tellurium as an antiknock agent might have become commercial.

It was at the Rochester meeting of the Chemical Society that knowledge of the discovery of the remarkable effects of selenium and tellurium began to be spread around. This resulted, first, from conversations about the discovery with men at Rochester, and, second, from the impression left on those with whom we came in contact there by an unusual and disagreeable property of selenium and tellurium, and particularly of tellurium, which was apparent wherever we went. Any one who worked with volatile compounds of tellurium got an affliction called tellurium poisoning. This is not conventional poisoning, but just a bad odor imparted to the victim. Some one spoke of the odor as a satanic garlic smell, and that is what we carried to Rochester with us. "There was no getting rid of it (Midgley, Motor, January, 1925, p. 92).

It was so powerful that a change of clothes 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." Incidentally, this quotation from Midgley may be broken here to insert the observation that when these notes were prepared in September, 1938, 17 years after the work on tellurium, the familiar odor of tellurium was apparent on the hands of the writer from having handled the records of the time. This odor was the more pronounced on that particular day because it was a humid one, and the tellurium odor is greatly accentuated by dampness.

"However," Midgley's story about the tellurium odor continued, "my family quickly became accustomed to it. and those at the laboratory were likewise immune. Going out at night, however, was a problem, although I found one neat solution. When we went to the movies, I would look around until I found a man of Mediterranean extraction, and we would sit down beside him. Presently people would scowl at him from all directions as they got my perfume, but we were secure and comfortable." After returning from a visit to the laboratory one day in May, 1921, Harry L. Horning of the Waukesha Motor Company wrote to Midgley: "This is to let you know that I reached home safely and that every one is greeting me with gas masks on."

At the outset of our work on selenium and tellurium there was, however, concern about whether the compounds might produce poisoning of a more harmful nature. In the laboratory care was accordingly taken to work in the hood. Later on, in the fall of

1921 when a quantity of diethyl selenide was to be made up for the Air Service to use in experiments at McCook Field, Dr. Victor Lenher and some of the producers of selenium and tellurium were asked about possible dangers from poisoning. All the reports were that no trouble from the poisoning of workers had ever been experienced. Dr. Lenher wrote (letter of November 3, 1921): "We have had a large force of men working with selenium on rather a large scale for a university for the past few years and we have had no symptoms whatever of selenium poisoning of any kind." Nevertheless, when some years later Doctor Lenher died from an undiagnosed ailment, it was commonly supposed that selenium, with which he had worked for many years, might well have had something to do with it. But we had no poisoning, aside from the bad odor, which to some degree afflicted every one who worked in the laboratory, regardless of whether they came into direct contact with any of the compounds.

First High-Compression Car--"The Goat"

During that summer of 1921 the compression of an FB Chevrolet engine with a displacement of 223 cu. in. was boosted to 7:1 from the normal value of 4.1:1. The car which contained this engine, a Chevrolet "Baby Grand," driven on gasoline alone before the boost in compression and on gasoline containing 9 per cent of ortho-toluidine by volume after the boost, gave the relative results summarized in the following tabulation (Report for July, 1921, August 3, 1921):

	<u>Standard Compression</u>	<u>High Compression</u>
Compression ratio	4.1:1	7.0:1
Acceleration, 5 to 30 miles per hr.	13 seconds	9 seconds
Miles per gallon		
Maximum	24	34
Touring :	16	25
Town driving :	12	20
Knock suppressor	none	9% ortho- toluidine

A picture of the "Baby Grand" Chevrolet car used in the tests just reported is included as Figure 18, page 92. It was dubbed "The Goat." This name was given the car, and it appeared appropriate, first, because of its mountain-climbing ability (its high horsepower), and, second, because of the musty smell of orthotoluidine which always hovered around it and which issued from the exhaust pipe whenever the car was driven.

At the summer meeting of the S.A.E. at White Sulphur Springs in June, 1921, Midgley presented comment on "Mileage Increase and Antiknock Materials" as discussion of a formal paper by Fred C. Ziesenheim on "Developing a High-Compression Engine" (S.A.E. Jour., 9, 270, October, 1921). In this discussion Midgley gave comparative fuel economies based on the data in the above tabulation. He also reported approximate figures on the relative degrees of effectiveness for a number of antiknock compounds, including diethyl selenide and diethyl telluride.

The Periodic System Becomes the Guide

The discovery of the remarkable knock suppressing effects of compounds of selenium and tellurium inaugurated an important new stage in the search for a practical antiknock agent. This

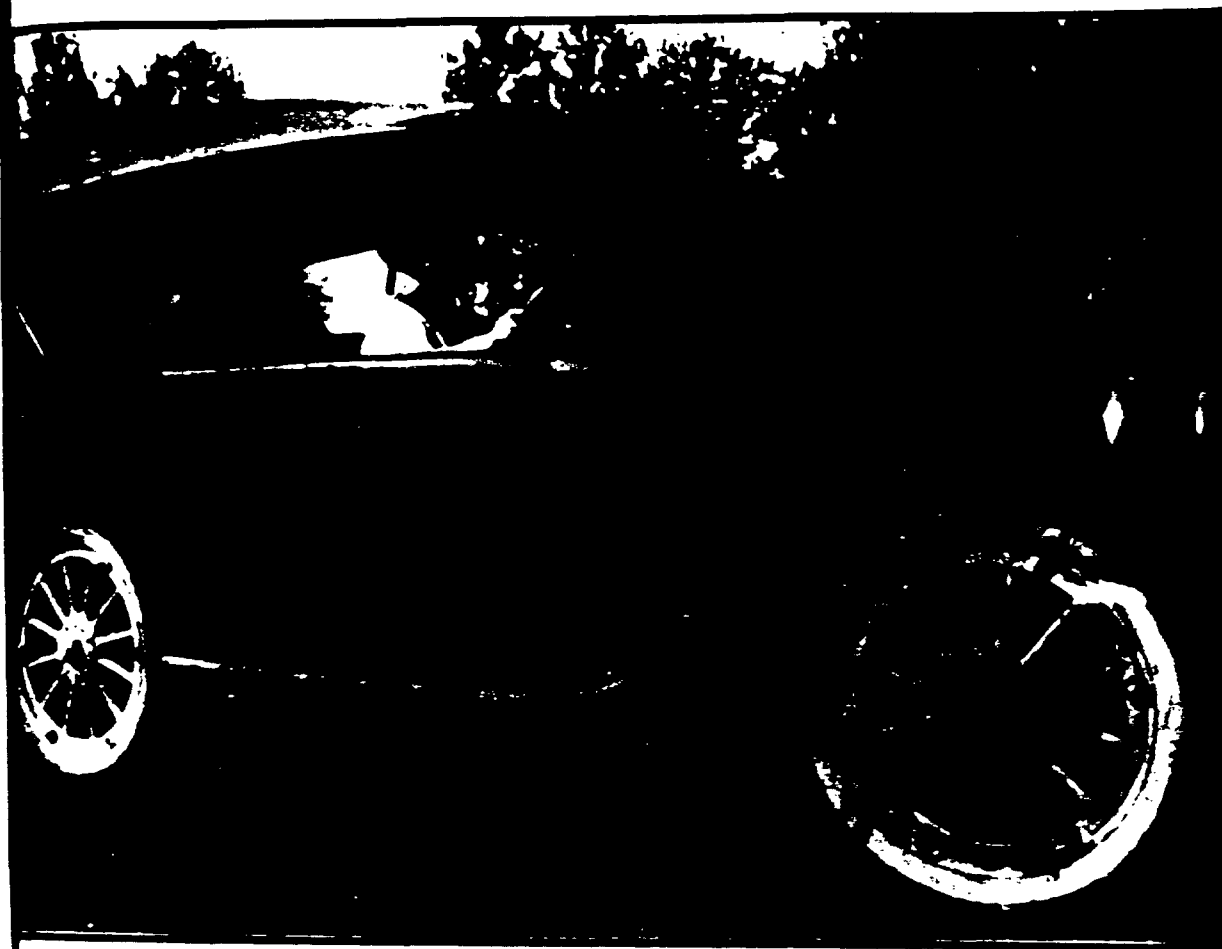


FIGURE 18

CHEVROLET CAR USED IN FIRST HIGH-COMPRESSION TESTS. IT WAS
DUBBED "THE GOAT," AND HAD AN ENGINE WITH COMPRESSION RATIO
BOOSTED FROM 4.1 UP TO 7.

was a systemization of the search in terms of the periodic grouping of the elements. Up to that time the selection of compounds to test had been made altogether by the Edisonian method of "cut and try." But the discovery of the effects of selenium and tellurium, when taken together with the information already obtained on compounds of iodine and nitrogen, and then viewed in the light of a special periodic arrangement of the elements to which we had access, suggested that the antiknock property might be a periodic function. The arrangement of the periodic system referred to was one made by R. E. Wilson based upon the Langmuir-Lewis Theory of Atomic Structure.

The type of chart used in this phase of the research is shown in Figure 19, page 94. There the elements are arranged not alone in terms of number of electrons in the outer shell, as grouped by Langmuir, but also in terms of number of vacant spaces in the outer shell. And, from the knowledge obtained in the search up to that time, it was noted, first, that all the elements yet found effective as knock suppressors were located at the far right in the lower group. It was observed, second, that the valence of the element in the compounds which were effective corresponded to the number of vacant spaces in the outer shell: viz, iodine, one; selenium and tellurium, two; and nitrogen, three. From the knowledge that bromine increased knock while iodine reduced it, and that tellurium was much more powerful than selenium as a knock suppressor, it was surmised also that antiknock effect increased toward the bottom of each column. The search was thus turned into a systematic "fox hunt" (Midgley's term).

**NEW PERIODIC SYSTEM
BASED ON THE
LANGMUIR THEORY OF ATOMIC STRUCTURE**

ELECTROPOSITIVE PROPERTIES																		ELECTRONEGATIVE PROPERTIES																	
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	Li	Na																															H	He
II a																																			
II b																																			
III a																																			
III b																																			
IV a																																			
IV b																																			
V a																																			
V b																																			
VI a																																			
VI b																																			
VII a																																			
VII b																																			
VIII a																																			
VIII b																																			
IX a																																			
IX b																																			
X a																																			
X b																																			
XI a																																			
XI b																																			
XII a																																			
XII b																																			

RES. LAB. APP. CHEN.
MASS. INST. TECH.
REIN

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

KEY AND AN ARRANGEMENT BY R. E. WILSON

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
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

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	Li	Na																														
II a																																	
II b																																	
III a																																	
III b																																	
IV a																																	
IV b																																	

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																																	
II a																																	
II b																																	
III a																																	
III b																																	
IV a																																	
IV b																																	

FIGURE 19

SPECIAL ARRANGEMENT OF THE PERIODIC SYSTEM OF THE ELEMENTS WHICH WAS USED AS A GUIDE IN THE FINAL "FOX HUNT" THAT LED TO THE DISCOVERY OF THE REMARKABLE EFFECTIVENESS OF LEAD AS AN ANTIKNOCK AGENT. IN THE BOX AT THE TOP OF THE PAGE IS THE ORIGINAL GROUPING AS MADE BY R. E. WILSON. THE MODIFIED ARRANGEMENT IN THE LOWER BOX IS THAT USED IN THIS SEARCH, AND THE MOST SIGNIFICANT PART OF IT IS ENCLOSED BY THE DASHED LINES AT THE LOWER RIGHT.

Work was begun at once on the synthesis of the ethyl and phenyl derivatives of other elements at the right in the lower grouping of Figure 19, such as phosphorus, arsenic, and antimony. A special project entitled "Periodic function of elements with respect to antiknock quality" was set up to cover this new phase of the investigation (Monthly report, August 3, 1921).

The first of the compounds made were tested as soon as obtained. These tests were made by the customary procedure used up to that time, which was to run in the Delco-Light engine a solution of the compound in kerosine and to note either by ear alone or by observing the pressure-time card of the Midgley indicator whether the knock was reduced by comparison with kerosine alone. If it was reduced, some quantitative idea of the relative effectiveness of the compound was then obtained by comparing its antiknock effect with that of aniline or ortho-toluidine—the latter more easily soluble in kerosine than the former—by the same listening or looking process.

Bouncing-Pin Indicator Developed

But these procedures, although they had served the purpose very well up to that time, were not very precise. And, now that small differences in effect upon knock needed to be measured if the periodic function was to be evaluated properly, some more precise and reproducible procedure for making measurements of knock was needed. The effort to solve this problem began in the early summer of 1921. The experimental work was done by Boyd with the active collaboration of Midgley. On June 2, 1921, (Rec. 13, p. 48) a search for a fuel that could be used as a scale of refer-

ence in knock measurements was begun. Experiments were made with various mixtures of benzol, petroleum ether, sulfuric ether, pentane, hexane, acetone, ethyl and methyl alcohols, various anti-knock agents of the aniline type, and knock inducers such as methyl nitrate. The Midgley indicator was used in these tests, Volatility effects and varying effects with changes in mixture ratio caused results to be erratic, however, and the use of the Midgley optical indicator was open to too much error in observation to be good enough for the purpose (Rec. 13, p. 55).

Next, a temperature method then in use by the Standard Oil Company of New Jersey was investigated (Rec. 13, p. 55). In this method a thermocouple inserted in a plug screwed into an opening in the cylinder head was used to register the rise in temperature. An attempt was made first to measure the variations in temperature with a potentiometer. But, when this method of measurement did not prove to be very successful, the potentiometer was replaced by a sensitive galvanometer borrowed from J. H. Hunt. It was found, though, that this method of measurement was erratic and could not be relied upon to indicate reliably even fairly large differences in knocking tendency.

And then began what turned out to be one of the important developments in the series of discoveries which led up to Ethyl gasoline. At a meeting of the S.A.E. which Midgley had attended, Dr. H. C. Dickinson of the Bureau of Standards had described a device which he had used to detect whether or not an airplane engine was knocking, such engines being usually so noisy

that the sound of knock was too obscure to be observed by ear. This device, which Dr. Dickinson called a "diddle pin," consisted simply of a free pin held loosely in a guide with its lower end resting on the cylinder head of the engine, as illustrated in the top sketch, Figure 20, page 98. When knock was present the violence of the explosion was such that it made the pin jump off the cylinder head momentarily. But, when knock was absent, the pin did not jump but rested continuously on the cylinder head.

This pin in the hands of Doctor Dickinson had been only a qualitative device which had been employed merely for detecting the presence of knock. In an effort to utilize the idea embodied in Doctor Dickinson's pin in developing a quantitative instrument for measuring knock, it was incorporated with the pressure element of the Midgley optical gas engine indicator by removing the shaft which ran from the piston to the mirror arm and putting in its place a free pin held in guides top and bottom. The pin was connected in an electric circuit, and, using the lower end of the pin and the piston on which it rested as contact points, an attempt was made to measure degree of knock by means of a galvanometer in the circuit. But that did not work, partly because of the fouling of the contact points. Various changes were then made in the arrangement to give at last the circuit illustrated at the bottom in Figure 20, page 98, which is a copy of page 57 and a part of page 56 of Laboratory Record 13. It is worth noting that at this time the contact points were continuously in contact, except as they were separated

3. Use of Scott's Dickinson's (Conn. of Sts.)
"Piddle Pin". This is a pin which when
held against the head of a knocking glider
is bounced up and down from the impact
of the knock.



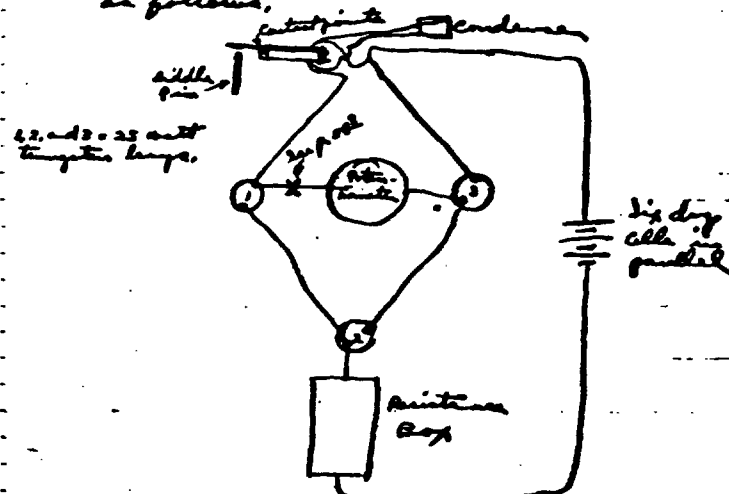
9. on one work an indicator pressure clamped with the light shaft connecting the piston with the arm on the main shaft removed and a pin held in a top and bottom guide post in its place
T.H. Bost

Т.А. Роза

57

was used. Measurement was made by means of a galvanometer, the D.P. being connected in an electric circuit with contact points on the piston and lower end of the D.P. This was found to be unsatisfactory, due to rapid fouling of the contact points; so an external make and break was used, which worked satisfactorily from this standpoint.

Various changes were made in the apparatus, the thermometer being replaced by a potentiometer, and the apparatus in use on July 18, 1901, was substantially as follows.



So long as no knock occurred, the "diddle put" simply followed the resignation of one indicator, pressure element plunger.

Tia. Bond

FIGURE 20

COPIES OF THE ORIGINAL NOTES IN LABORATORY RECORD 13 RELATING TO THE DEVELOPMENT OF THE BOUNCING-BIN INDICATOR.

ETC 36896

by the motion of the pin resulting from knock.

From this point on the apparatus and technique were consistently improved as experimentation continued. On July 22, 1921, the elaborate wheatstone bridge circuit shown at the bottom of page 98 was abandoned and replaced by a simple direct-current circuit embodying a resistance, and an electrolytic cell instead of a potentiometer (Record 13, page 60). Then on August 4 the contacting mechanism was changed in such a way that the points were normally separated, instead of being in contact as before, and they were closed only momentarily when the pin was propelled upwards during knock (Record 13, page 79). The circuit, contacting mechanism, and pin arrangement thus arrived at are shown in the drawing, Figure 21, page 100. This drawing was made after the system had been developed into a thoroughly usable one and after it had proved extremely useful in pursuing the periodic antiknock function of the elements, as related below.

As a description of the development of this new instrument, a paper on "Methods of Measuring Detonation in Engines" by Thomas Midgley, Jr., and T. A. Boyd was prepared and presented at the Winter Meeting of the S.A.E. in January, 1922 (S.A.E. Jour., 10, 7, January, 1922). It was in connection with the preparation of this paper that Boyd suggested that the instrument be called the bouncing-pin indicator, by which name it has been known ever since.

The bouncing-pin indicator as thus developed is substantially the same instrument which is now used universally in making knock ratings. About 1926, at the suggestion of Robert Janeway, now of the Chrysler Corporation, the piston of the pressure element

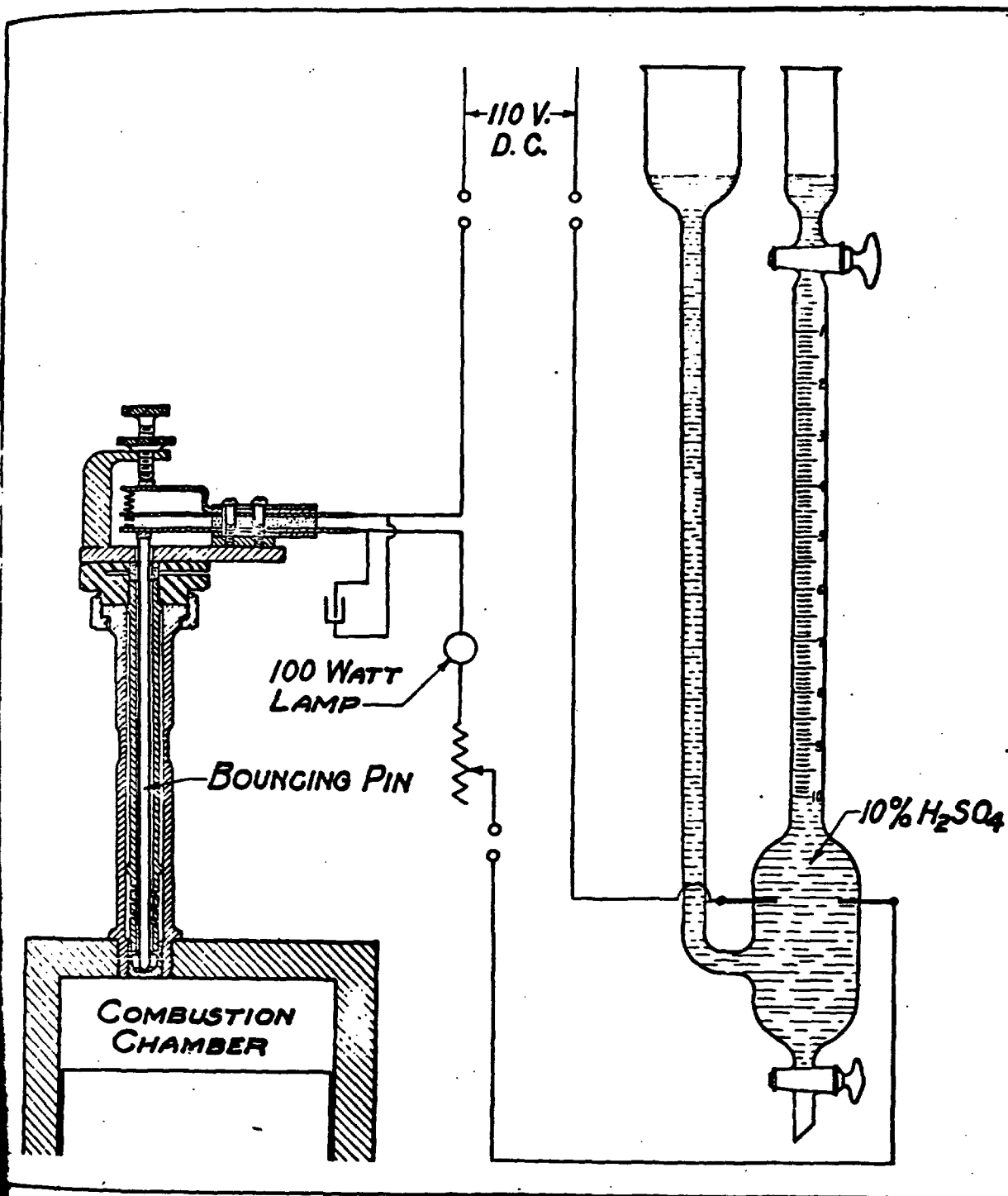


FIGURE 21

THE BOUNCING-PIN INDICATOR AS DEVELOPED IN 1921, SHOWING THE CIRCUIT, THE PIN ARRANGEMENT, THE CONTACTING MECHANISM, AND THE ELECTROLYTIC CELL.

was changed to a diaphragm, which further improved the consistency of the instrument. A picture of the first cabinet form of the instrument with the element mounted on a Delco-Light engine, and taken in 1923, is shown as Figure 22, page 102. The later development, in which the bouncing-pin indicator was applied to a variable-compression engine with a double-float device for regulating mixture ratio by adjusting the flow of fuel to the engine by hydrostatic level is pictured in Figure 23, page 103. This picture, taken in 1927, just a year before the organization of the Detonation Subcommittee of the Cooperative Fuel Research Committee which developed the present official knock-testing method, thus shows several of the features which were finally incorporated in the official method: the bouncing-pin indicator, a variable-compression engine, and a double-bowl hydrostatic-level carburetor for making measurements by the method of matching fuels, as had been done in this work from the first. Others of the features incorporated in the official method, such as the knockmeter which was substituted for the electrolytic cell and the synchronous motor for absorbing engine output and holding the speed constant, were first used by the Ethyl Gasoline Corporation, in the course of the large amount of work which they did on problems relating to the precise knock-rating of fuels.

Still another important item in respect to knock testing, which came out of the later work of the Ethyl Gasoline Corporation and which may be mentioned here in passing, was the suggestion to use heptane and iso-octane as a basic scale of antiknock quality (Graham Edgar, "Measurement of Knock Characteristics of Gasoline in Terms of a Standard Fuel," Ind. Eng. Chem., 19, 145 January, 1927).

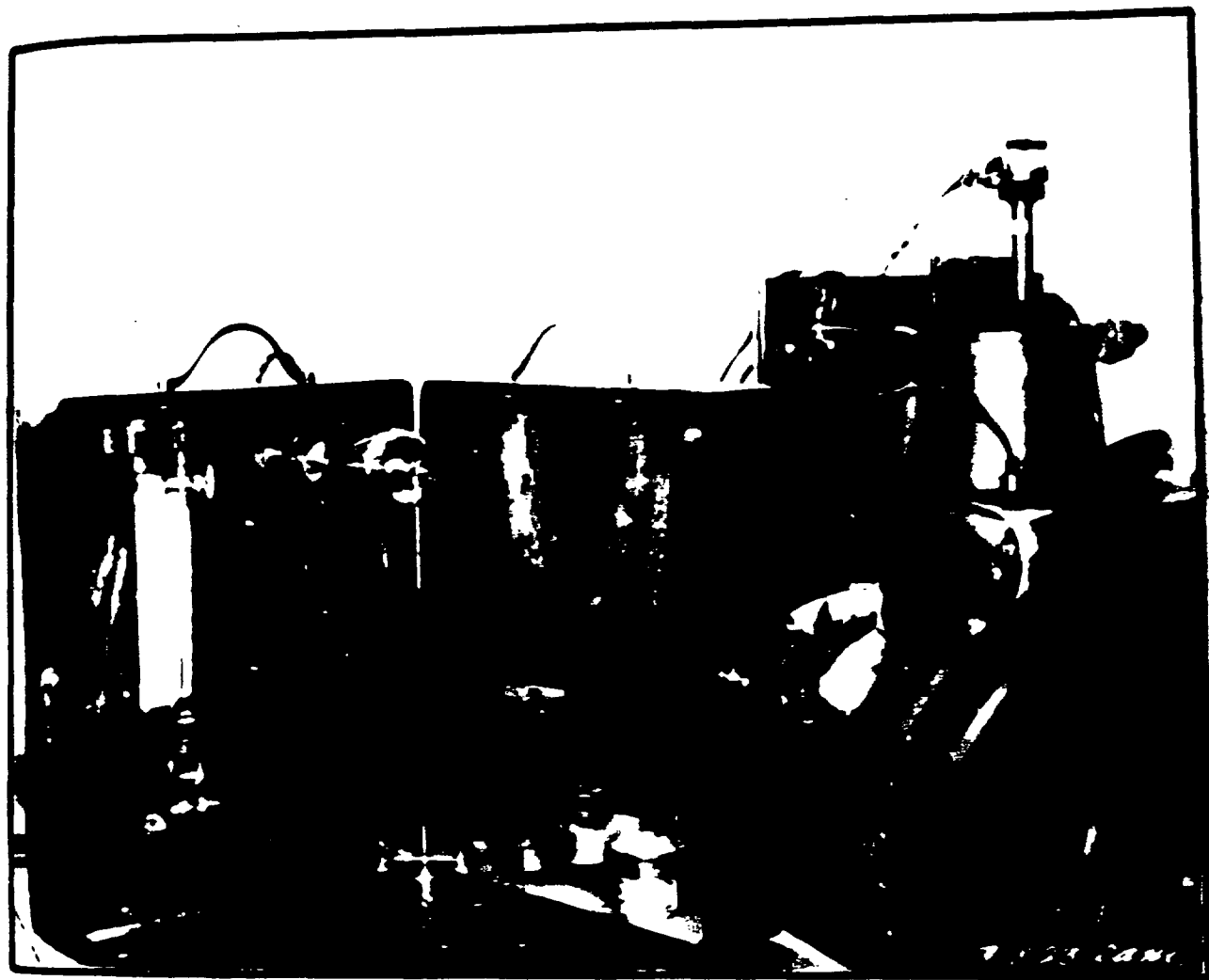


FIGURE 22

THE FIRST CABINET FORM OF THE BOUNCING-PIN INDICATOR.

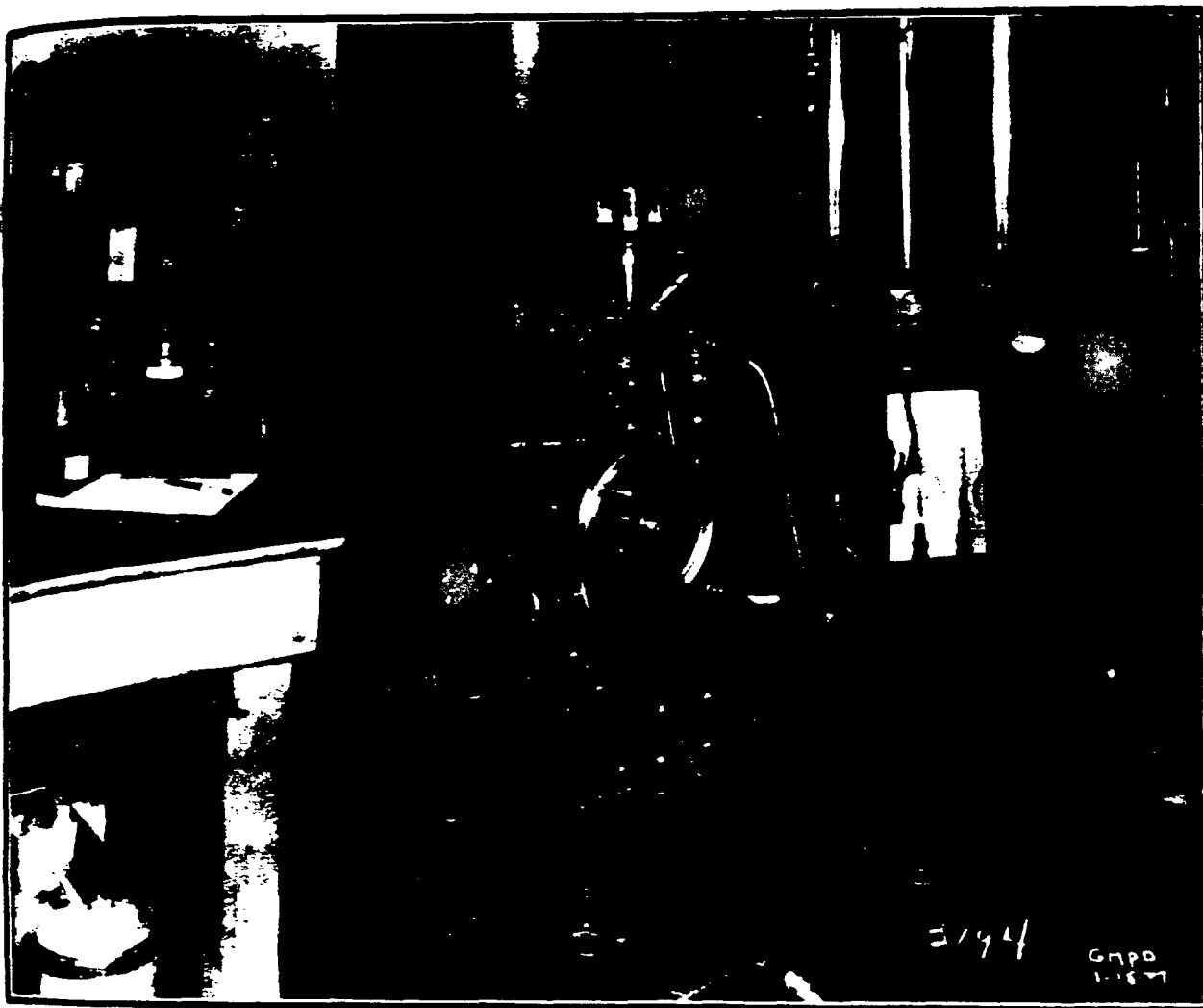


FIGURE 23

PICTURE TAKEN IN 1927 SHOWING THE BOUNCING-PIN INDICATOR APPLIED TO A VARIABLE-COMPRESSION ENGINE WITH DOUBLE-FLOAT HYDROSTATIC-LEVEL FUEL-METERING DEVICE.

This suggestion was adopted by the Cooperative Fuel Research Committee in 1930, came into general use in 1931, and has been used universally ever since, altogether supplanting the arbitrary standards necessarily employed prior to that time.

Finding the Periodic Function of Antiknock Effect

By the latter part of August, 1921, the bouncing-pin indicator and the method of making knock ratings by its aid had reached a stage of development at which it was thought suitable to begin rating the several compounds prepared during the summer to be used in investigating the periodic function of the elements in respect to effect upon the fuel knock. The plan, as before said, was to test in a systematic manner suitable compounds of all the elements at the extreme right in the lower grouping of the special arrangement of the periodic system shown as Figure 19, page 94. The investigation was centered in the first four groups, which, lifted from the arrangement, Figure 19, and expanded with explanatory matter, are as follows:

4	3	2	1
<u>Carbon</u> <u>Group</u>	<u>Nitrogen</u> <u>Group</u>	<u>Oxygen</u> <u>Group</u>	<u>Fluorine</u> <u>Group</u>
C	N	O	F
Carbon	Nitrogen	Oxygen	Fluorine
Si	P	S	Cl
Silicon	Phosphorus	Sulphur	Chlorine
Ge	As	Se	Br
Germanium	Arsenic	Selenium	Bromine
Sn	Sb	Te	I
Tin	Antimony	Tellurium	Iodine
Pb	Bi		
Lead	Bismuth		

The compounds which had already been prepared for test, or which were prepared as the tests proceeded, were rated in the order given immediately below. All were ethyl, amyl, or phenyl compounds of the respective elements. The primary period of these tests extended from August 25, 1921, to December 7, 1921, although extensions and refinements in the ratings were made later, as will subsequently appear.

<u>Element</u>	<u>Compound Tested</u>	<u>Page Recorded in Record No. 13</u>
Oxygen	phenyl ether	125
Bromine	phenyl bromide amyl bromide	126 and 150 129
Iodine	amyl iodide	129
Chlorine	phenyl chloride amyl chloride	131 133
Tellurium	diethyl telluride diphenyl telluride	135 137
Selenium	diethyl selenide diphenyl selenide	138 141
Fluorine	phenyl fluoride	142
Sulphur	diethyl sulphide	145
Oxygen	diethyl ether	149
Nitrogen	triethyl amine triphenyl amine	155 157
Phosphorus	triethyl phosphine triphenyl phosphine	159 161
Antimony	triphenyl stibine triethyl stibine	171 172 (takes fire spontaneously in air)
Arsenic	triphenyl arsine triethyl arsine	173 175
Tin	tetraethyl tin	177 Induced persistent preignition

Some of these compounds--such as those of chlorine, bromine, iodine, selenium, and tellurium--had of course been tested before. But they were included in the present program anyway, because now the object was to get really accurate ratings of equivalent compounds of the various elements under comparable conditions. As each rating was obtained it was plotted on a 3-dimensional graph called "The Peg-Board." This consisted of a square board in which a peg was set at the point corresponding to the location of each element as arranged in Figure 19, page 94, or more elaborately in the text above, the height of each peg being made to conform with the degree of effectiveness as a knock suppressor of the element for which it stood. On this graph it soon became apparent that, as suspected from prior results, there is a periodic function of the elements with respect to effect upon knock, in that degree of effectiveness increased as the bottom of each column was approached. Interest in the results was accordingly so intense that the ratings for arsenic, antimony, and tin were telegraphed to Midgley who happened to be visiting at the time at his father's home in Massachusetts. It was on October 28 and 29, 1921, that the ratings of tetraethyl tin were made. These showed that tin, the first element in the 4-column or the Carbon Group to be tested, was an effective antiknock-agent. This was so in spite of the fact that the presence of the tin compound induced preignition in the engine, and thus made ratings difficult and results a little uncertain in a quantitative sense. The discovery, based on ratings made on successive days, that tin is an effective antiknock element was considered to be extremely important. This was so because it pointed to lead, the ele-

ment immediately below tin in the Carbon Group, as very likely to be
a powerful knock suppressor.

CHAPTER VI

THEN CAME LEAD

And so the effort to make tetraethyl lead as a possible antiknock agent, which as already related had been abandoned nearly three years before when Gilkey damaged the thermocouple of the muffle furnace in Mougey's laboratory, was soon taken up again. This time another method of synthesis was tried. This method was old also, having been used by Buckton in 1859 and by Frankland and Lawrence in 1879. The procedure was to prepare zinc ethyl and then to drop it on lead chloride. It was by this procedure--the same as had been used previously in making some of the alkyl compounds already tested--that C. A. Hochwalt prepared on December 8 and 9, 1921, the first tetraethyl lead obtained, just a few cubic centimeters.

Then on December 9, 1921, in the presence of Midgley and Hochwalt, Boyd made the first engine test of this historic product (Record 13, p. 200). For the first exploratory test, a solution of 1 per cent tetraethyl lead by volume in kerosine was prepared.* The intention was to compare this solution with 2 per cent aniline in kerosine and 1 per cent aniline in kerosine as bracketing reference fuels. But right away it was seen that the tetraethyl lead mixture was much too free from knock to be tested by comparison with these fuels. Successively weaker solutions of

*Kerosine rather than gasoline was used as fuel in most of the early work on testing antiknock agents, chiefly because it was more prone to knock than gasoline, but also because in the mixing valve with which the Delco-Light engines used for testing were fitted kerosine gave more uniform and consistent operation than did some gasolines.

tetraethyl lead in kerosine were accordingly made by diluting the original mixture, until at last it was decided from the results that a solution containing one-fortieth of one per cent tetraethyl lead in kerosine could be compared with the reference fuels—that is to say, this mixture lay in degree of freedom from knock somewhere between the two aniline mixtures. The customary quantitative rating by means of the recently developed procedure employing the bouncing-pin indicator was then run, and showed that one-fortieth of one per cent tetraethyl lead in kerosine was equivalent to 1.3 per cent aniline in kerosine. A copy of the page from Record 13 on which the original data of this test were recorded is included as Figure 24, page 110. Figure 24-A, page 111, is a copy of the plot of these data made at the time, which shows that one-fortieth of one per cent of tetraethyl lead in kerosine turned out to be equivalent in knock-suppressing effect to 1.3 per cent aniline in kerosine.

This amazing and exciting result was then checked by another and still more careful determination, using both one-eighth and one-fortieth per cent tetraethyl lead in kerosine (Rec. 13, p. 202), and these ratings agreed well with the first. Thus the astounding result obtained was that on the volume basis tetraethyl lead was about 50 times as powerful as aniline for suppressing knock, and that on the molecular basis one mol of tetraethyl lead was equivalent in antiknock effect to about 120 mols of aniline.

It is easy to understand that the excitement produced by this discovery was great. At the first opportunity, the result was

200

December 9, 1921

Lead Tetraethyl

Sp. gr. greater than that of water. Prepared by C.A. Harkness
and represents steam distilled and exsiccated product

Fuel	Run	Main Side			Run	Fan Side		
		Volts	Amperes	cc Gas/min		Volts	Amperes	cc Gas/min
2 an 98 Ker	1	38.8	26	0.55				
		38.8	26.2	0.65				
1 an 99 Ker					2	38.7	25.5	1.03
						36.5	27	1.00
1% Pb. tetraethyl in Ker (Vol)	3	no gas to gas determiner						
After experimenting, prepared solution of 10 cc 1% Lead tetraethyl in 400 cc total benzene. = 40% Lead tetraethyl								
40% ind. tetraethyl in ben. by vol. (0.48)	4	39.3	25.3	0.78	11	37.3	27.7	(5 min) 0.50
		39.3	25.3	0.79				
2 an 98 Ker (0.14)	10	37	28.4	0	5	37.2	27.7	(2 min) 0.56
		37	28.5					
1 an 99 Ker (0.63)	6	37.2	27.3	0.79	9	35.5	28.7	0.60
		37.2	27.4	0.77		35.5	29	0.35 Lat
Kerosene (1.20)	8	37	26.4	1.22	7	37.1	26.8	1.07
		37	26.4	1.27		37	26.5	1.23
					T.A. 120 ja			

FIGURE 24

COPY OF ORIGINAL LABORATORY RECORD OF THE FIRST TEST OF TETRAETHYL
LEAD IN AN ENGINE IN WHICH THE DISCOVERY OF THE REMARKABLE EFFECTIVE-
NESS OF LEAD AS AN ANTIKNOCK AGENT WAS MADE.

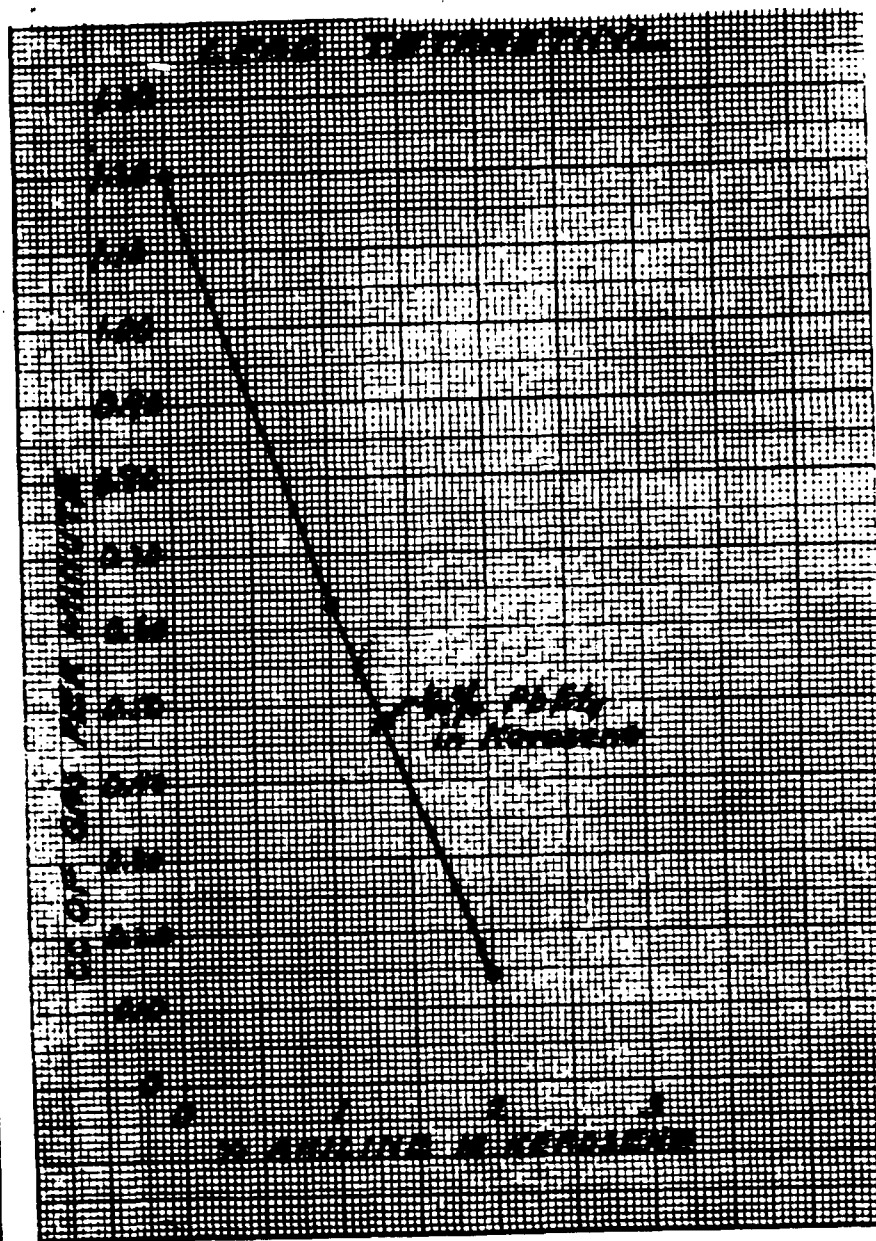


FIGURE 24-A

COPY OF THE ORIGINAL PLOT OF THE RESULTS OF THE FIRST TEST OF TETRAETHYL LEAD AS AN ANTICKNOCK AGENT, SHOWING THAT ONE-FORTIETH OF ONE PER CENT TETRAETHYL LEAD WAS AS EFFECTIVE AS 1.3 PER CENT ANILINE

demonstrated to Mr. Kettering and to Dr. Clements, of course. From the time of the first discovery of an antiknock agent, it had been the practice of Mr. Kettering to demonstrate for the benefit of visitors the striking effect of eliminating knock in a running engine by the simple means of adding a little of the antiknock agent to the knocking fuel. The demonstration was usually made by running the Delco-Light engine on kerosine fed from a supply in a 4-ounce sample bottle; and, when the engine was knocking loudly, some easily soluble antiknock agent such as toluidine was added in small amount to the kerosine in the bottle, thus stopping the knock completely. Now that in tetraethyl lead an eliminator of knock which was so extremely powerful that only a drop or two of it need be added to the bottle to quiet a knocking engine, the demonstration became much more striking; and Mr. Kettering accordingly showed it to his visitors all the more frequently. Incidentally, the practice of showing the discovery to so many people had long been deplored by the men in the patent department. But Mr. Kettering went ahead with the demonstrations anyway, and no bad results ever came of them.

It may be of interest to note here also a feature of the bouncing-pin indicator which was very useful in such demonstrations, as well as in making approximate measurements of antiknock quality, but which was not mentioned in the account of the bouncing-pin indicator given earlier. Employed then as a resistance in the electrical circuit was a mazda lamp. This lamp is indicated in the drawing, Figure 21, page 100, and it may be seen in the cabinets, Figures 22 and 23, pages 102 and 103. Whenever knock occurred, this lamp would light up intermittently from the current then flowing in the circuit,

and the intensity with which it glowed was an excellent visual indicator of the degree of knock occurring. In demonstrations of knock and of the effect of antiknock agents, it thus served so effectively as an aid to the ear as to make such a demonstration quite impressive.

The discovery of the marvelous effectiveness of lead compounds as antiknock agents thus further established the validity of the periodic function of the elements, so far as those in the section of the arrangement represented by the fluorine, oxygen, nitrogen, and carbon groups were concerned (Figure 19, page 94). The three-dimensional peg board plot, previously mentioned, is no longer in existence, but would not lend itself well to representation in a photograph anyway. And so the effect is shown as well as may be in the two graphs, Figure 25, page 114, and Figure 26, page 115. These graphs, which were prepared at a little later time, have had an interesting history, as will be related further on in this story. In Figure 25 the antiknock effects of the elements in each of the four groups are shown, each to a different scale. There the increase in antiknock effect toward the right, which is toward the bottom of the corresponding column in the periodic arrangement, Figure 19, page 94, is apparent. Then in Figure 26 the antiknock effects for three of the four groups are plotted all to the same scale. There the great height to which lead towers above all the other elements considered is readily seen. Another picture of some of these relative effects is shown in Figure 27, page 116.

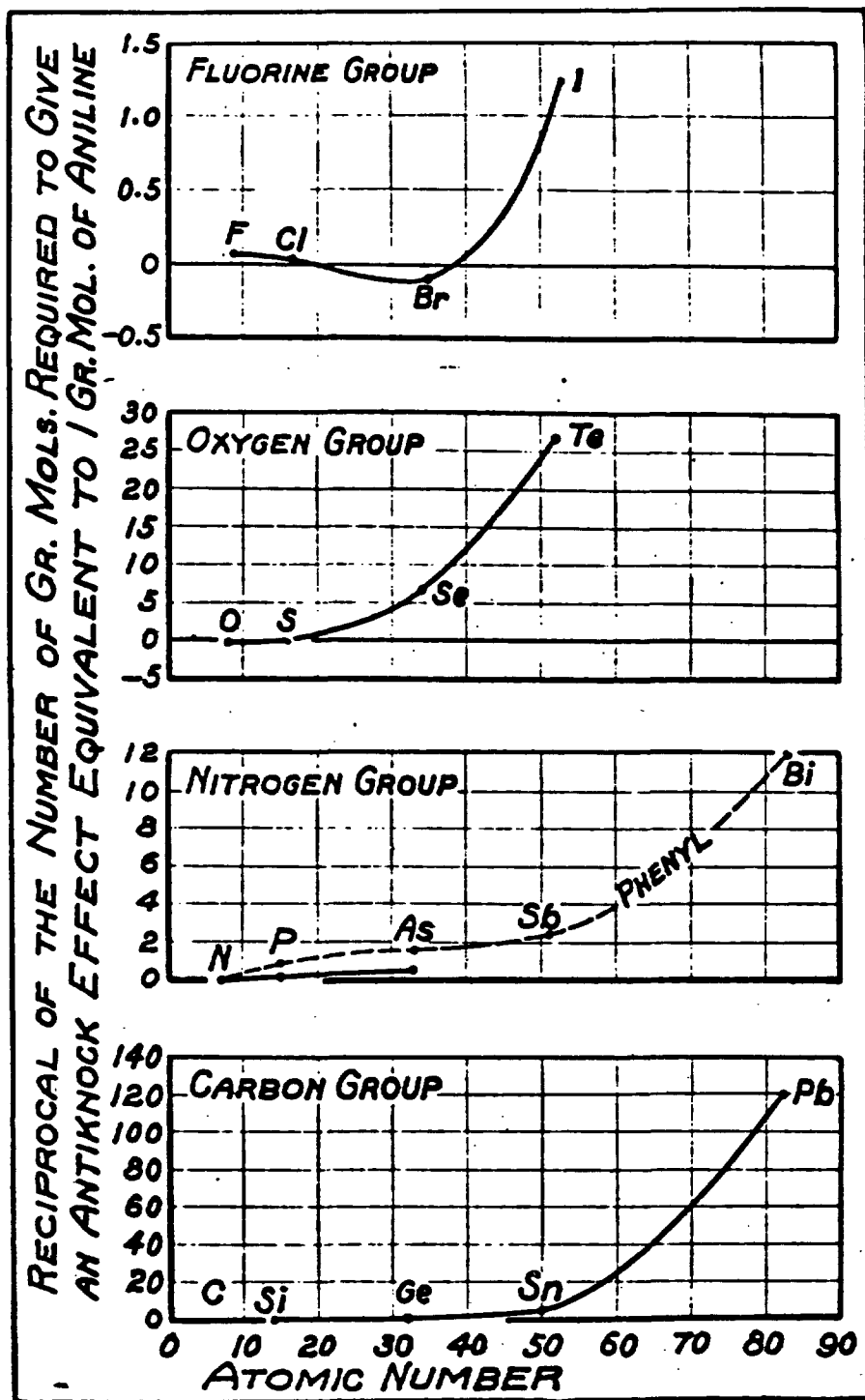


FIGURE 25

PLOT OF THE ANTIKNOCK EFFECTS OF THE ELEMENTS IN FOUR GROUPS OF THE SPECIAL PERIODIC SYSTEM USED AS A GUIDE IN THIS SEARCH. THE VERTICAL SCALES ARE DIFFERENT, BUT THE RISING ANTIKNOCK EFFECT TOWARD THE RIGHT IN EACH GROUP IS APPARENT.

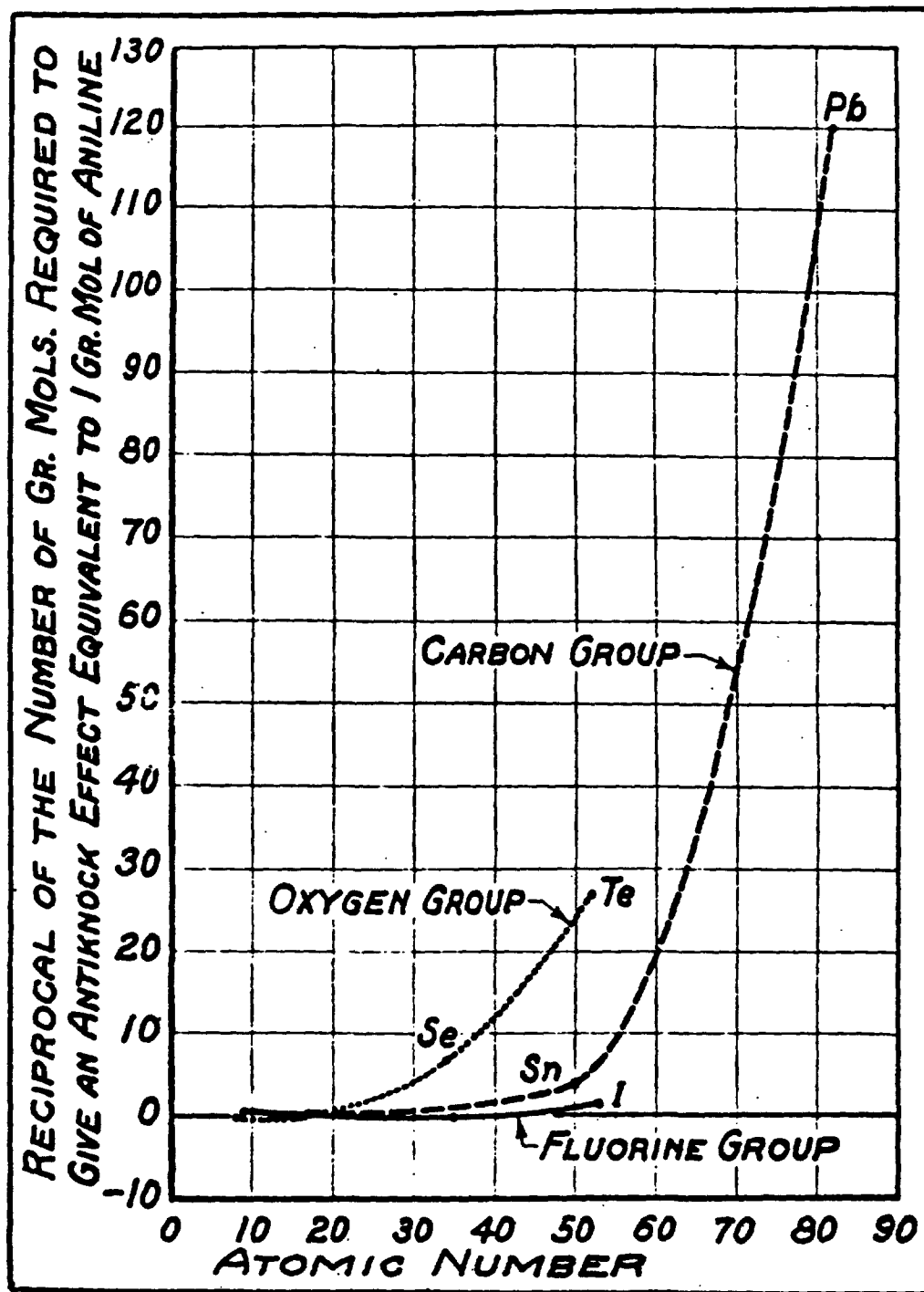


FIGURE 26

THE OUTSTANDING ANTIKNOCK EFFECT OF LEAD IS APPARENT HERE, WHERE THE RELATIVE EFFECTS OF THE ELEMENTS IN THREE OF THE GROUPS SHOWN IN FIGURE 25 ARE PLOTTED TO THE SAME SCALE

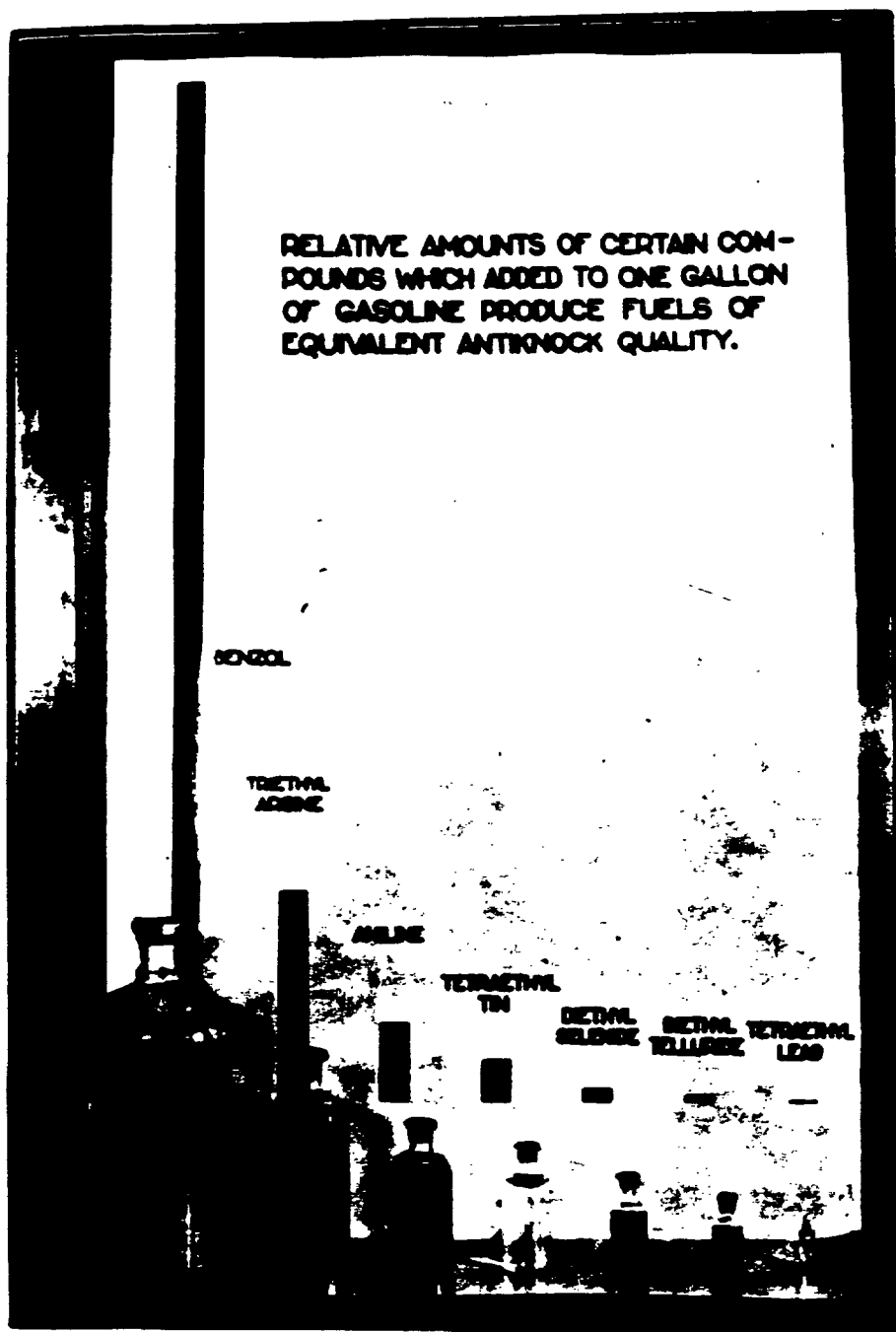


FIGURE 27

HERE THE MINUTE AMOUNT OF TETRAETHYL LEAD NEEDED FOR A
GIVEN ANTIKNOCK EFFECT BY COMPARISON WITH SOME OTHER
COMPOUNDS IS PICTURED IN ANOTHER WAY.

Of the many materials tested in the search for an anti-knock agent, which led finally to the discoveries just described, only a few have thus far been mentioned. Appendix IV is accordingly included to give some idea of the extent of the testing that was done during the course of the endeavor. The several-page list, Appendix IV, was prepared in 1925, and thus contains a few compounds tested after the time of the discoveries described above.

Early Contacts with the Standard Oil Development Company

Another interruption in the main thread of the story may be made at this point to tell about some supplementary events of the year 1921. The first of these relates to a further effort made during the summer of 1921 to produce antiknock agents directly in the gasoline. This was an idea upon which experiments were made at different times in the course of this research. The present attempt was commented upon on June 10, 1921, in a letter from Midgley to Frank A. Howard of the Standard Oil Development Company, as follows: "I am planning to be east the week after next . . . and I am hoping at that time that I may have some of the fundamental chemistry towards producing our antiknock material in gasoline at the refinery. I feel that our greatest hope for commercialization now lies in this direction. Diethyl telluride is a wonderful antiknock material, but the tellurium poisoning, which is nothing more than a very obnoxious odor, makes diethyl telluride a highly disagreeable material and there are really but very small quantities of tellurium available. These two factors apparently knock tellurium out as a possibility, and we are going ahead attempting to eventually

nitrate and reduce natural compounds to make antiknock materials therefrom." Such compounds, if obtained by the process of nitration and reduction, would of course be of the amine or aniline type; and, as has already been said, these are not free from difficulties either (bad odor, attack on metals, toxicity).

But the work was not confined to the nitration and reduction of compounds in gasoline. Attempts were made also to produce compounds of selenium directly in gasoline. No such compounds were obtained in a practical way, but the investigation did lead to the discovery, mentioned earlier in this account, that iron selenide is a catalyst for the cracking of oils (monthly report, September 30, 1921), and particularly for aiding the formation of hydrocarbons of the aromatic type. Some of the results of this particular discovery were published in a paper by Midgley and Hochwalt (Ind. Eng. Chem., 16, 365, 1924), and also patented by Midgley (U. S. 1,721,523, July 23, 1929).

The letter of June 10, 1921, from Midgley to Frank A. Howard of the Standard Oil Company of New Jersey Development Department, quoted above in part, shows that in the summer of 1921 there was contact with men in that company on matters relating to knock suppressors, and specifically in respect to the possibility of making such compounds in the refinery. This contact was continued and later resulted in a plan for a definite written agreement relating to collaboration on making antiknock compounds in the refinery, as well as on other matters relating to antiknock compounds. The state of affairs in this regard in the early part of 1922 is suggested in Figure 28, page 119, which is a copy of a letter

STANDARD OIL COMPANY

DEVELOPMENT DEPARTMENT

25 Broadway

FRANK A. HOWARD

NEW YORK March 14, 1932.

Mr. Thomas Midgley, Jr.,
General Motors Research Corp.,
Dayton, O.

My dear Mr. Midgley:

Wilson of "Tech" spent Saturday with me in Elizabeth and told me that you and I seem to have gotten our wires crossed on the "knock" proposition which we discussed in Chicago. I am sure that I am to blame for this. I had expected to see you and have you meet our people on the last day of the meeting but when I went to look you up I found you had already left. I talked to some of our officers and directors who were in Chicago at the time and they could see no possible objection to the arrangement which we had discussed.

I had the impression that it was agreed between us that you would advise me to a definite line of development work which we were to undertake with the idea of working out a method and costs of producing an anti-knock motor fuel according to your plan in the refinery. We were then to either accept or reject this specific proposal. If accepted it was to be on the basis that this Company would secure a license for itself as compensation for developing the refinery or production end. If we declined the specific proposition, you were to be free to deal with it in any way you thought fit. Wilson tells me that it was his impression from his talks with both of us that I was going to prepare a general contract and then only after this contract was executed were you to submit a definite proposal. If this is the understanding of the matter which you had, please accept my apologies for delaying so long. As you know, I had already secured approval of two propositions from our people along this line and after our talk in Chicago, I am sure that there will be no difficulty in getting through anything of this sort which you and I agree upon. As I got it from you, the important thing at the present time was to have us get busy on a definite line which you believe justifies the immediate attention of a refiner.

I have been out in California since the latter part of January and have just returned. I am threatened with some rather prolonged absences during the coming four months. I am very anxious to get this thing cleaned up and the work which you had in mind

started at the earliest moment. If you will advise what would be necessary for us to do down here, I will undertake to get it accomplished promptly and if you think it would expedite the final arrangements, I can come out to Dayton with any proposition along the lines which we discussed which you want to have in formal shape from us and try to settle it on with your people at once so I can be sure that any future absences of mine will not delay the working out of this most important problem.

Wilson has just started his work with us in co-operation with your people and I find it is certainly a joy to have him co-operating. Do you not think we could both use him to advantage in this anti-knock work? Except for yourself, Wilson is the first man I have met whose mind worked with absolute clarity on this problem. We have had some little success with some laboratory work in modifying the properties of oils during the past few months and I hope that we will be able to make some experiments on a large scale on this soon. It would be a great advantage if we could get our arrangement with you completed so that we could open up in full on both sides on this matter and perhaps have the benefit of Wilson's view as well.

With best regards,

Very truly yours,

F. C. Howard

FIGURE 28

LETTER FROM FRANK A. HOWARD TO MIDGLEY RELATING TO DISCUSSIONS OF POSSIBLE COOPERATION BETWEEN THE GENERAL MOTORS RESEARCH CORPORATION AND THE STANDARD OIL DEVELOPMENT COMPANY.

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of March 14, 1922, from F. A. Howard to Midgley.

It was between the time of the conversations in Chicago mentioned in Mr. Howard's letter (presumably at the time of the 1921 Annual Meeting of the American Petroleum Institute) and the writing of his letter in March, 1922, that the discovery of the remarkable antiknock effect of lead was made. This discovery changed matters so profoundly that on March 16, 1922, Midgley wrote to Howard as follows (in part): "Very shortly after seeing you in Chicago, our research work took a very sudden turn in a direction that would indicate that it would be a mistake both on your part and on ours to enter into an agreement such as we discussed at that time" (Letters, page 41)* Thus it was not until more than two years later, after the lead discovery had been put on the market, that an agreement was entered into between General Motors Corporation and the Standard Oil Company of New Jersey.

However, it may be worth while to go still further back and to include here also a brief outline of the earlier contacts between the Standard Oil Company of New Jersey and Mr. Kettering's group. Contact began first in 1919 right after the publication of Mr. Kettering's paper, "More Efficient Utilization of Fuel" (S.A.E. Journal, 4, 263, April, 1919). Frank A. Howard, who was then a patent attorney in Chicago, having read Mr. Kettering's paper, wrote E. M. Clark of the Standard Oil Company of New Jersey telling him how important he thought the paper and the disclosures made in it were from the viewpoint of the oil industry. In May, 1919, Mr. Howard visited Mr. Kettering at his laboratory in Dayton

*This and subsequent similar references in this report refer to a group of photostats in the records of the Fuel Department, "Copies of Matter Selected from Correspondence Files."

and was much impressed. He wrote a long report to Mr. Clark about his visit, and suggested that a research laboratory similar to Mr. Kettering's be established by Mr. Clark's company. Mr. Clark then sent two of his own men, Dr. Marle Meacham and F. C. Fyke, to visit Mr. Kettering's laboratory. They likewise were impressed with the great pioneering importance of Mr. Kettering's endeavors and recommended the establishment of such a research laboratory by the Standard Oil Company of New Jersey. Right away, in June, 1919, as a step in that direction, the Standard Oil Company of New Jersey ordered a Midgley indicator.

The result of the events mentioned in the preceding paragraph was that in the fall of 1919 Mr. Clark employed Mr. Howard and assigned him the job of organizing a research laboratory for the Standard Oil Company of New Jersey. The following paragraph from a letter, written April 27, 1927, by Frank A. Howard to William Benham of the Department of Justice, gives in Mr. Howard's own words an account of events following his new connection:

"In the fall of 1919, I entered the service of the Standard Oil Co. of New Jersey as Manager of Development for them, and was assigned the task of building up the research laboratories of the Company. One of my first steps in this work was to again get in touch with Mr. Kettering and Mr. Midgley and ask their advice on how best to proceed along the line of research in the field in which Mr. Kettering had pioneered. These gentlemen very generously gave me the benefit of much of their experience in this connection and actually supplied for the Standard Oil Co. of New Jersey, at cost to them, three experimental engines especially adapted for this work and some additional scientific equipment which they had devised. From this time on, the personnel of our laboratory, which was located at Bayway, N. J., kept in general touch with the personnel of Mr. Kettering's laboratory and exchanged views and information which it was thought would be mutually helpful."

The Spectroscope Applied to Studies of Combustion

The second of the supplementary events of the year 1921 to be mentioned was the work done by Midgley with the aid of W. K. Gilkey on the use of the spectroscope to observe combustion in an engine, and especially knocking combustion. The object was to get what information was possible by such means on the temperatures and the pressures within the combustion chamber and on the chemical reactions occurring there. Observation was through a small glass window placed in the shell of a spark plug which was screwed into the combustion chamber opposite the spark plug. A special spectroscope was built for this investigation with the aid of Henry C. Lord, professor of astronomy at the Ohio State University. This instrument had a particularly wide dispersion due to the fact that it combined the effects of a prism and a grating for dispersion. The course of this spectographic research need not be reported here, as it did not enter in an important way into the search for an antiknock agent. But a paper by Thomas Midgley, Jr., and W. K. Gilkey relating to this investigation and entitled "Spectroscopic Investigation of Internal Combustion" was presented before the S.A.E. at the Annual Meeting in 1922 and was published later in the S.A.E. Journal, 10, 218 (March, 1922).

Further Aid to the Army

The third supplementary event of the year 1921 relates to the continued effort of the men in the Army Air Service at McCook Field to get an antiknock agent that would be usable in airplane fuels. As related earlier, they had not found the soluble compounds

of the aniline type (toluidines and xylydines) and their use in injectors to be very practical. One reason for this was the attack which such compounds made on metals, as was mentioned earlier in this story. Another was the probability that in time of war such compounds could not be had, because the toluene and the xylene from which they are made have to be had for explosives. On the evening of October 25, 1921, Captain G.E.A. Hallett visited Midgley at his home and, quoting from the notes made later by Captain Hallett (Letters, page 46), "It was agreed that the General Motors Corporation would make up samples of three anti-knocks in sufficient quantities to mix with three hundred gallons of gasoline in each case." The antiknock compounds to be supplied were diethyl selenide, ethyl aniline, and some of the naphthylamines, the latter only if they could be made soluble enough. A considerable amount of work was accordingly done during November, 1921, chiefly by Hochwalt, in preparing diethyl selenide to meet this demand. The ethyl aniline was purchased from du Pont. As further indicated in Captain Hallett's notes, it was his intention to incorporate the most promising of the antiknock agents in all the Army Air Service fuel specifications. But of course the problem was not really solved until the discovery of the effect of tetraethyl lead shortly thereafter.

Intensive Research on How to Make Tetraethyl Lead

Returning now to the important discovery of the antiknock effectiveness of tetraethyl lead, as made on December 9, 1921, it may be of interest to quote what was said about it in the regular monthly progress report dated December 29, 1921:

"The outstanding development of the past month was the discovery of the remarkable effectiveness of organic compounds of lead for the suppression of detonation in the combustion of highly compressed mixtures of gasoline and air. This discovery was made as a result of the systematic investigation of compounds of the chemical elements which we have been conducting for some time. Preliminary measurements of the effectiveness of tetraethyl lead indicate that it is roughly 50 times as effective as aniline for the suppression of detonation. This material (tetraethyl lead) has only a faint but rather pleasant odor; it imparts no noticeable odor to the exhaust when run in sufficient concentration to permit a compression ratio of 7:1 to be used; it is very soluble in gasoline; it is colorless; and, while there has not yet been sufficient time to thoroughly test the stability of the material in gasoline solution, references to the compound in the literature indicate that it is very stable in air, and even in pure oxygen. The raw materials for the preparation of the material are cheap and plentiful. It is necessary to develop a satisfactory process for making the proper organic compounds of lead, and intensive work is now being done with this end in view."

In the intensive research on methods of making tetraethyl lead, as just mentioned, several methods were soon tried. In addition to the reaction between zinc ethyl and lead chloride by which the tetraethyl lead first tested had been made, these included the following:

1. Refluxing various alloys of sodium and lead and of magnesium and lead with ethyl sulphate, with ethyl carbonate, and with ethyl benzoate.
2. Treating zinc-copper couple with ethyl iodide and lead chloride directly, that is, without making zinc ethyl as an intermediate.
3. Electrolysis of acetone in 20 per cent sulphuric acid solution, using lead electrodes. (This method was later studied at Massachusetts Institute of Technology.)

4. Grignard reaction, trying both methyl chloride and ethyl chloride with magnesium and with ether as solvent (pentane tried as solvent also), and then adding lead chloride in theoretical amount.
5. Reformatsky's synthesis, a one-stage reaction in which ethyl chloride was treated with lead chloride, using zinc as a condensing agent.
6. Refluxing various alkylating agents--ethyl sulphate, ethyl benzoate, ethyl acetate, and ethyl alcohol--with magnesium and lead chloride.
7. Heating lead with ethyl iodide in the presence of aluminum chloride (Friedel and Crafts' reaction), and heating lead chloride and ethyl iodide with sodium metal (Fittig's reaction).

Some of these several trials met with fair success, but none seemed to offer more promise than the method of preparing zinc ethyl and reacting it with lead chloride, as employed in preparing the tetraethyl lead on which the tests reported above were made. So, during the week of January 1, 1922, the effort to make tetraethyl lead began to be concentrated on this method. In brief, the process (Lead Diary, page 7)* consisted in making a zinc-copper couple (10% copper, later reduced to 1%) by heating a mixture of 30 mesh zinc and

*Beginning in February, 1922, with a summary of the work done up to that time on lead as an antiknock agent, a daily record of all the work done on lead in the Fuel Department was written by Boyd. This special record is No. 13 in the Fuel Department files and it was called the "Lead Diary." It is in three volumes and extends to May 1, 1923.

copper powder, the latter prepared by reducing copper oxide; in reacting the resulting couple with ethyl iodide; in distilling out the zinc ethyl formed, and collecting it in an inactive atmosphere of carbon dioxide; and then in slowly adding to the zinc ethyl under a reflux condenser lead chloride in theoretical amount. After having allowed the mixture to stand for several hours, water was added slowly with cooling to the mud-like product at that stage, and the tetraethyl lead formed in the reaction was then distilled out.

As a result of many experiments, the technique of the method was rapidly improved, and in early February, 1922, a larger apparatus—one intended to yield about one gallon of tetraethyl lead per day—was constructed. The two pieces of equipment built especially for the synthesis of zinc ethyl on this scale are pictured in Figure 29, page 127 and Figure 30, page 128. Then in early March, 1922, after much experimentation in glass apparatus as well as in the larger metal apparatus, a second semi-works outfit for making zinc ethyl was built. This was called the "pan apparatus", and as later modified is pictured in Figure 31, page 129. In this apparatus each batch was on the basis of about 5 pounds ethyl iodide, and the yields of zinc ethyl were up to 82 per cent on the basis of the ethyl iodide used and not recovered, although the average yield was not nearly so high.

Then on April 3, 1922, a plan was made for a plant to produce 100 gallons of tetraethyl lead per day by the zinc ethyl method. This lay-out, as later put into definite form is shown as in Figure 32, page 130. The processes indicated there for recovering iodine and for

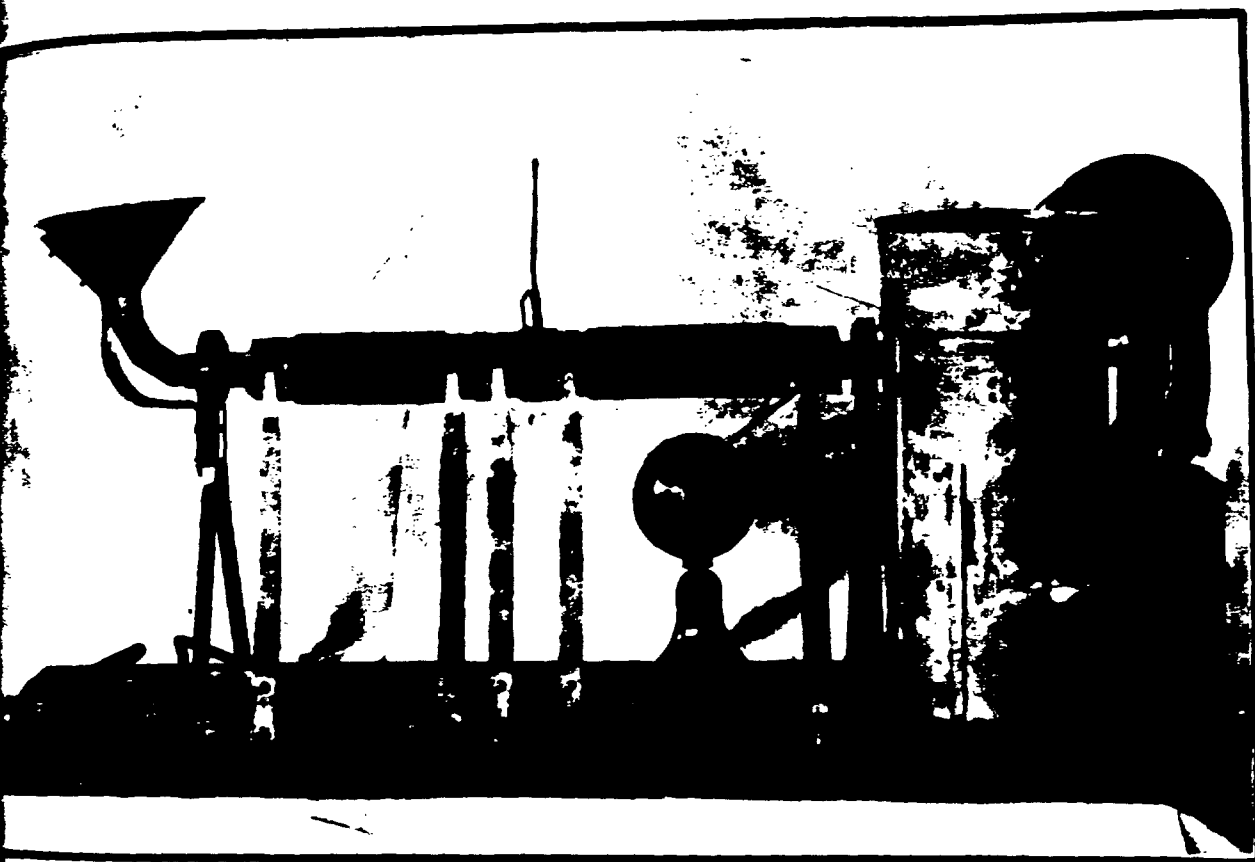


FIGURE 29

APPARATUS FOR MAKING THE COUPLE OF COPPER AND
ZINC USED IN PREPARING ZINC ETHYL IN THE EARLY
METHOD OF MAKING TETRAETHYL LEAD



FIGURE 30

VESSEL FOR MAKING THE ZINC ETHYL USED IN THE EARLY
METHOD OF SYNTHESIZING TETRAETHYL LEAD

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FIGURE 31

THIRD FORM OF APPARATUS USED IN PREPARING ZINC
ETHYL, AN INTERMEDIATE FOR MAKING TETRAETHYL LEAD

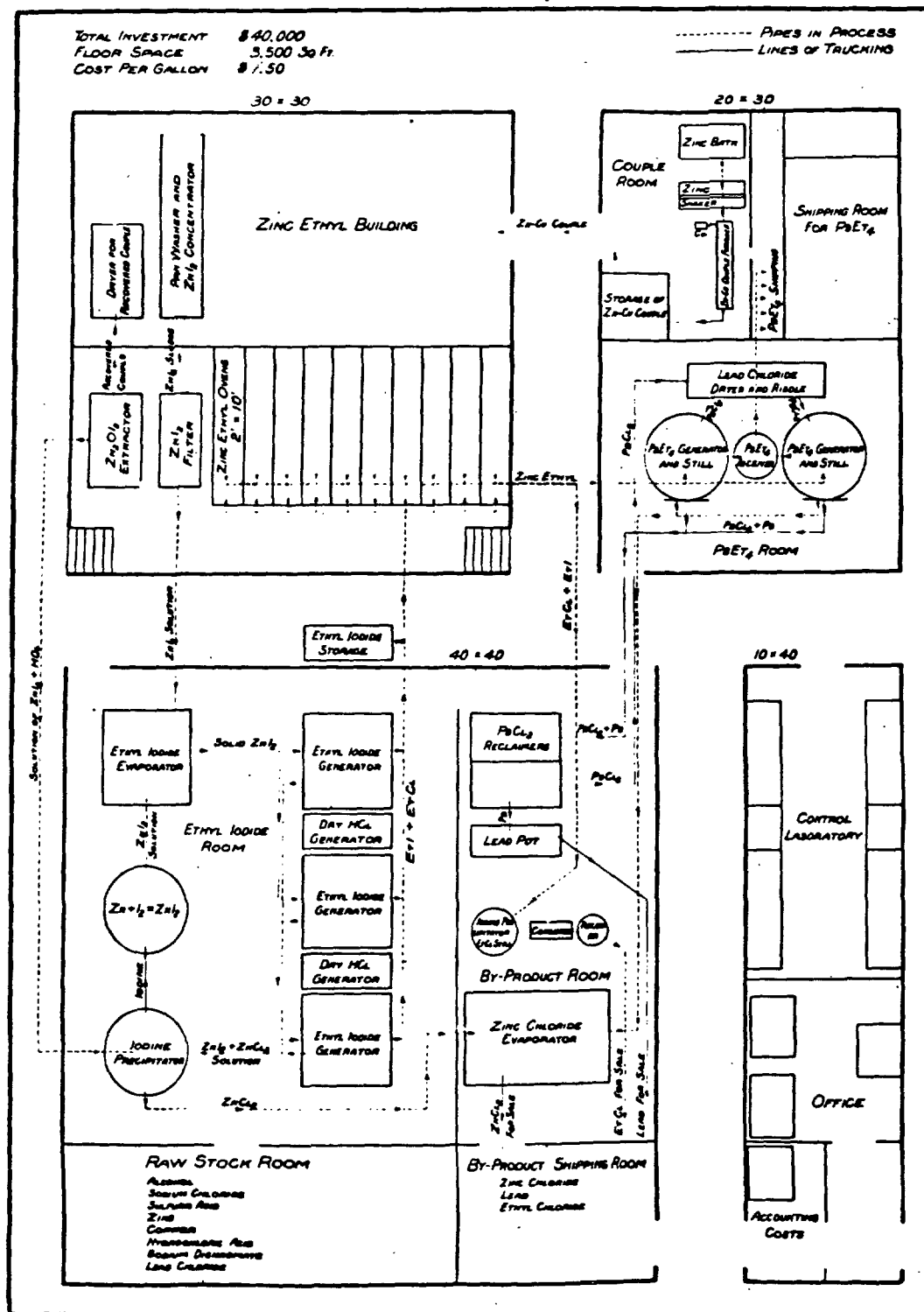


FIGURE 32

LAYOUT OF PROPOSED PLANT FOR MAKING 100 GALLONS OF TETRAETHYL
LEAD PER DAY BY THE ZINC ETHYL ROUTE, THE METHOD UNDER CON-

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converting it again into ethyl iodide had been developed, chiefly by James P. Andrew, simultaneously with the work on the making of zinc ethyl done by C. A. Hochwalt and described above. By the zinc ethyl process, it was then expected to make tetraethyl lead at a cost of about \$7.50 per gallon.

But on April 4, 1922, Midgley and Hochwalt left for Birmingham, Alabama, to attend the spring meeting of the American Chemical Society. Events which happened there, to be related presently, changed the course of the research on making tetraethyl lead. But, before telling of these events, a digression will be made to tell about the beginning of research on lead problems in the Research Laboratory of Applied Chemistry at Massachusetts Institute of Technology.

The Participation of M.I.T. Begins

R. E. Wilson and C. S. Venable, respectively director and assistant director of the Research Laboratory of Applied Chemistry at M.I.T., spent February 8 and 9, 1922, at the laboratory at Dayton. The visit was made for the purpose of becoming familiar with the work that had been done up to that time on the problem of making a liquid compound of lead suitable for use as an antiknock agent. The laboratory at M.I.T. had for some time previous been conducting a research on lubrication which had been supported in part by the General Motors Research Corporation. Now, in view of the apparent magnitude of the problem of making lead compounds for use as antiknock agents, it was thought that the group at M.I.T. might be of assistance in solving it in a thoroughly commercial manner. So an initial expenditure of \$2400 was authorized by the

General Motors Research Corporation to cover five months of research at M.I.T. on the preparation of lead compounds.

R. E. Wilson was destined to play an important part in the later developments relating to tetraethyl lead as an antiknock agent, which will appear as this account proceeds. C. S. Venable did not have such an important part in the endeavor, however, for a few months after his visit to the laboratory at Dayton he left M.I.T. to become director of research for The Viscose Company.

After going over various ideas on possible methods of making lead alkyls during the visit of Wilson and Venable, it was agreed that it would be best for them to investigate the possibility of making a suitable compound by the electrolysis of acetone in sulphuric acid solution using lead electrodes, a method described in the chemical literature and already mentioned. The product so obtained was tetraisopropyl lead. Although a great deal of fine work on this method was done at M.I.T., and although the endeavor, which was continued to the end of April, 1922, progressed past the stage at which preliminary estimates were made for a full-scale plant (Lead Diary, page 88), that particular phase of the work did not come to any practical conclusion. Among the reasons for this were that the tetraisopropyl lead produced was found to be highly unstable, that its effectiveness as an antiknock agent by comparison with tetraethyl lead was low, and that the work at Dayton soon yielded what appeared to be a thoroughly practical method of making tetraethyl lead. Besides Wilson and Venable, one other man worked on the electrolytic research at M.I.T. in 1922. This was Dr. William G. Horsch, who for several years

has been a research chemist in the research laboratory of the Socony-Vacuum Oil Company at Paulsboro, New Jersey.

The Executive Committee Asks for Some Information

In late January, 1922, the President of General Motors Corporation, Mr. P. S. du Pont, sent Mr. Kettering an "Advice of Action" of the Executive Committee to the effect that, \$120,000 having been expended in fuel research since the laboratory had become a part of the Corporation, the President had been requested to ask for several items of information on progress in the development of an antiknock agent. These related to probable cost, expected beneficial effects, steps taken toward commercialization, and the like. In answer, Midgley prepared a report under date of February 2, 1922, in which he outlined the expected usefulness of an effective antiknock agent in giving more miles per gallon and so conserving fuel supplies, gave a resume of progress up to that time in the search for a practical antiknock agent, and included specific answers to each of the questions asked in the "Advice of Action."

In his answers, Midgley estimated that tetraethyl lead could probably be made for less than \$20 per gallon and that on the basis of its value it could be sold for \$30. He told what progress had been made up to that time on methods of making tetraethyl lead, and estimated that to satisfy the existing potential market for such an antiknock agent a total investment of \$2,000,000 would be needed. It was just one year after this report was written at the request of the Executive Committee that the sale of tetraethyl lead to the public as an antiknock agent began; but, as will subsequently appear, it was more than 5 years later before any profit was realized from the en-

CHAPTER VII

THE SODIUM-LEAD METHOD OF MAKING TETRAETHYL LEAD

Returning now to the events which caused the research at Dayton on the making of tetraethyl lead to be diverted from the zinc ethyl method, the turning point was a conversation between Midgley and Dr. Charles H. Milligan (now manager of research and development, American Agricultural Chemical Company). This conversation occurred on the train returning from the Birmingham meeting of the American Chemical Society. The essential item was a remark by Dr. Milligan that he had found isopropyl compounds unstable and very difficult to make by comparison with the corresponding normal propyl compounds. Midgley had tried a month earlier to get isopropyl iodide to react with sodium-lead alloy; but with very little success, although he had used ethyl acetate as a catalyst. He had also tried to combine ethyl iodide with sodium-lead alloy, apparently without any success whatever (letter Midgley to R. E. Wilson, March 2, 1922; Lead Diary, pages 48 and 49). The method of making lead alkyls by the use of sodium-lead alloys was an old one, having first been used by Löwig and described in the literature about 1853 (Lead Diary, page 167). It was this method which W. K. Gilkey had followed in his historic but unsuccessful attempt to prepare lead ethyl in February, 1919, as already related.

The result of Dr. Milligan's hint that normal propyl compounds formed more readily than isopropyl compounds was that the day after Midgley and Hochwalt returned from Birmingham on Friday, April 7,

Hochwalt began the preparation of some normal propyl iodide. Then on Monday, April 10, 1922, the propyl iodide so obtained was treated with the alloy of lead and sodium, Na_4Pb . "A violent reaction ensued, in which much gas was evolved" (Lead Diary, page 125). Some tetra-normal-propyl lead was obtained in this reaction, which in the engine test made immediately proved to be of about the same effectiveness as tetraethyl lead for suppressing knock. Reasoning that methyl iodide would probably behave more like the normal propyl iodide than would ethyl iodide, which as related above had already been tried without success, methyl iodide was tried but showed no activity. However, it was then found that ethyl acetate would catalyze the reaction to some degree and that aniline was still more effective as a catalyst (Letter Midgley to Wilson, April 12, 1922). And so aniline was next tried as a means of making ethyl iodide react with sodium-lead to form tetraethyl lead.

This last was on April 11, and the next day Midgley wrote R. E. Wilson as follows: "We are contemplating very seriously abandoning the zinc ethyl method of making the lead compound, the reason being that we have been able to make the sodium-lead reaction go. . . By using the sodium-lead method we reduce our material cost on the basis of equal yields from \$10.20 to \$2.60 per gallon." (The \$10.20 mentioned here is more, of course, than the \$7.50 previously mentioned on the basis of a 100 gallon per day basis, but considerably less than the estimate of \$20 included in Midgley's report to Mr. P. S. du Pont.) Within a few days after Midgley wrote to Wilson as just quoted, the zinc ethyl method was discontinued.

Many substances were tried as catalysts for bringing about the union between ethyl iodide and sodium-lead to form tetraethyl lead. A number of these—including aniline, ethyl acetate, diethyl aniline, and later pyridine—proved to be effective. As the research proceeded, the ability to control the process and the yields of tetraethyl lead obtained were consistently improved. James P. Andrew and W. K. Gilkey worked on the preparation of the sodium-lead alloy—which at the time was confined to the Na₄Pb alloy. This, as was discovered later, did not happen to be the best alloy to use, for it was so highly reactive that under some conditions it took fire in air and had to be prepared and handled in an atmosphere of carbon dioxide or nitrogen. Also, it left too much unreacted sodium in the reactor which had to be combined with water afterwards. Hochwalt and Midgley conducted the experiments on treating the sodium-lead alloy with ethyl iodide to form tetraethyl lead.

In general the procedure was to prepare the mixture of ethyl iodide and sodium-lead alloy, together with the catalyst, and to apply heat to it for a time. Then, either immediately afterwards, or after having allowed the mixture to stand for some time, water was added slowly with cooling to decompose the mixture and to combine with the unreacted sodium. Afterwards any unused ethyl iodide was distilled out in the presence of steam formed by the water present, followed by the tetraethyl lead produced. The tetraethyl lead had to be distilled out with steam to keep the distillation temperature low enough to prevent it from decomposing. A

chart showing the process in outline, as taken from a report prepared for J. W. Morrison by Boyd on April 26, 1922, is included as Figure 33, page 138.

Sometimes at the outset, or before proper control was developed, a rapid decomposition or "deflagration" occurred during the addition of the water or during the subsequent period of distillation, in which the batch was lost. Through suitable control, the deflagration trouble was overcome, but the cause of it was not understood. Later the theory was proposed by the men at M.I.T. that the violent reaction called deflagration was the result of the formation first in the reaction of diethyl lead, which subsequently decomposed with the evolution of heat to give tetraethyl lead and some free lead (Lead Diary, page 374). If the conditions under which the diethyl lead was formed were such that a considerable amount of it could accumulate before the breaking down to tetraethyl lead occurred, the decomposition reaction would run away, the theory said. This seems to be a likely explanation. but it is understood of course to consist at least in large part of speculation.

On April 18, 1922, less than two weeks after the work on the sodium-lead process had been begun, an experiment was made in which ethyl bromide was substituted for ethyl iodide, with dimethyl aniline as catalyst. In still another experiment ethyl chloride was substituted. The ethyl bromide experiment was successful, but the yield of tetraethyl lead was small, and it was more than two months after this before a shift was made to ethyl bromide as the agent for ethylating lead. The experiment with ethyl chloride was altogether

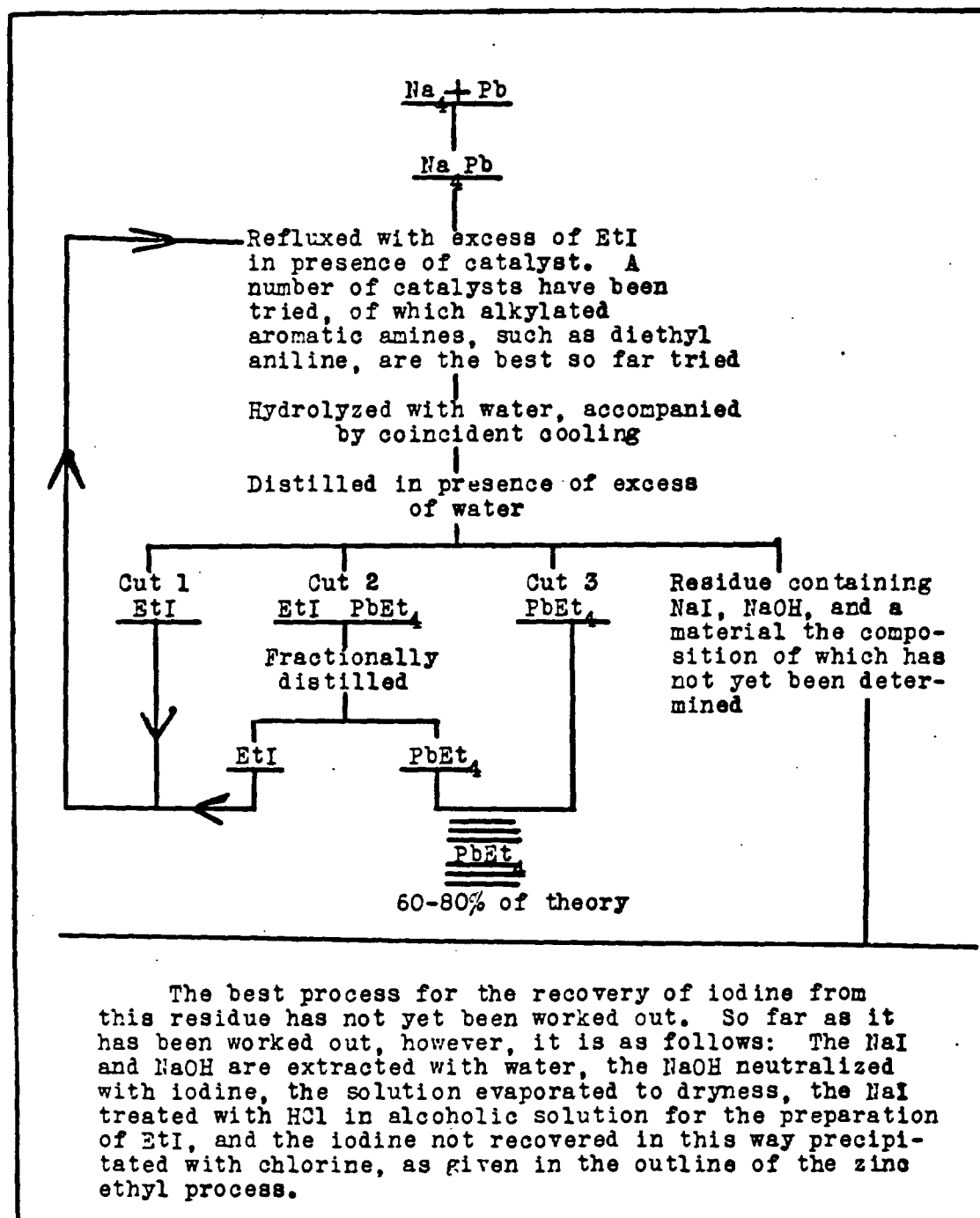


FIGURE 33

OUTLINE OF PROCEDURE FOR MAKING TETRAETHYL LEAD BY MEANS OF THE SODIUM-LEAD PROCESS, AS IT EXISTED IN APRIL, 1922.

unsuccessful as to any yield of tetraethyl lead. This is now understandable in the light of the work of Dr. Charles A. Kraus at Clark University, on the basis of which ethyl chloride is now being used in the manufacture of tetraethyl lead. Dr. Kraus found that, to get ethyl chloride to combine with lead, the sodium-lead alloy used must not be the Na4Pb employed in these experiments, but an alloy of only 10% Na and 90% Pb.

Contact with Dr. E. E. Reid

When Midgley and Hochwalt returned on April 7 from the Birmingham meeting of the American Chemical Society, they were accompanied by Dr. E. E. Reid, professor of organic chemistry at Johns Hopkins University. Dr. Reid, who came to the laboratory on Midgley's invitation, spent the better part of the day looking over the progress that had been made in investigating lead as an antiknock agent, and was given as complete a picture of the work as possible. At Midgley's suggestion that he help in the synthesis program in an advisory capacity, he promised to think about whether he could properly do so in view of his duties at Johns Hopkins and of his contract with the du Pont Company, for whom he was already acting in a consulting capacity. Because of his du Pont contract, Doctor Reid did not enter into an agreement with us, but he did later help with the endeavor to the extent of making a critical examination of the chemical literature on the subject of organic compounds of lead and of reporting his results, and also in advising that after studying the problem he considered that, for making tetraethyl lead "the lead-sodium method or some modification of it is the most promising." (Lead Diary, page 193).

Incidentally, it is understood that one reason why Dr. Reid consented to return to Baltimore from Birmingham via Dayton and to spend the day in consultation there was because Midgley had promised to have him taken up at Dayton for his first ride in an airplane. From the flying field beside the laboratory "Bernie" Whalen took Doctor Reid up in the enclosed cabin plane called the "Honeymoon Express." Much against his will, Midgley went up with them. It was just before a thunder storm and the ride was very bumpy. Midgley said afterwards that he was mighty glad to get down; but Dr. Reid, he said, enjoyed the ride thoroughly and showed no concern whatever. Later Dr. Reid wrote Midgley: "Thank you and Mr. Kettering for a most pleasant day in and above your plant." (Lead Diary, page 252). The high place assigned to Dr. Reid in Midgley's estimation is suggested by the wire he sent to Boyd from Birmingham asking that the laboratories be spruced up in advance, especially Russ Wells' room, which was perpetually in need of straightening and cleaning.

The research on making tetraethyl lead by the action of ethyl iodide on sodium-lead alloy was continued by using larger and larger amounts in each charge. In one of these experiments, begun on April 28, 1922, Na_2Pb was used as the alloy, instead of the Na_4Pb usually employed. The alloy lower in sodium gave a good yield of tetraethyl lead, but in this first run with Na_2Pb not quite as high a yield as was by that time being obtained with the Na_4Pb (Lead Diary, pages 190 and 200). And so the use of Na_4Pb was continued for some time.

The First One-Gallon Lead Plant

On May 5 and 6, 1922, the first run was made in an apparatus which had been designed to produce a gallon of tetraethyl lead in one batch (Lead Diary, page 210). This apparatus in its first form is shown in the photograph, Figure 34, page 142, the man in the picture being Russell Wells. The cooker, shown sitting in the frame on the scales, had inside it a coil of pipe for heating with steam or for cooling with water as needed and a motor-driven stirring device. (This cooker was later modified in some respects, one of the changes providing for charging the alloy of sodium and lead to the cooker in the ingot form and so making grinding outside unnecessary, Lead Diary, pages 299 and 300). The charge was about 30 pounds pulverized Na_4Pb , nearly 47 pounds ethyl iodide, and 2.5 pounds diethyl aniline. The heating of the batch was begun at 7:30 P. M. on Friday, May 5. The temperature was maintained at 155-160 deg. F. and meanwhile the batch was stirred continuously until 2:30 the next afternoon, Saturday. The excess sodium in the alloy was then removed by the gradual addition of water over a period of 3 hours. At 5:30 P.M. on Saturday, May 6, the distillation of the product was begun. It was finished about midnight, and the yield of technical grade tetraethyl lead was 3200 cc., or just about a pint less than a gallon.

So important was this first large-scale trial thought to be that almost every member of the group working on the job of making tetraethyl lead was present during a large part of the 30-hour trial. This group consisted of Midgley, Hochwalt, Andrew, and Boyd, together



FIGURE 34

IN THIS QUICKLY-CONSTRUCTED APPARATUS, THE MAKING OF TETRAETHYL
LEAD BY THE SODIUM-LEAD METHOD WAS BOOSTED FROM A LABORATORY
SCALE TO A ONE-GALLON BASIS. ACTUAL YIELD IN THE FIRST RUN,
0.96 GAL. V. RUSSELL WELLS IS THE OPERATOR.

with C. P. Harding and James Taylor, who had done the work on preparing and pulverizing the alloy of sodium and lead. Mr. Kettering also spent a large part of Saturday evening on the scene during the final distillation. At midnight on Saturday everyone went home from the long stand pretty well encouraged with the success of the initial large-scale trial.

Then on May 11, James P. Andrew was asked to begin work on the design of a plant to make 100 gallons of tetraethyl lead per day by the sodium-lead method. Ethyl iodide was to have been used as the ethylating agent, and the iodine was to be recovered afterwards, converted into ethyl iodide, and used over again, according to the general scheme outlined in Figure 33, page 138, and more completely in Figure 35, page 144, prepared a little later.

Iodine being so expensive and so scarce, the recovery of the iodine--the almost complete recovery of it--was of course necessary to the success of the process. But 8 pounds of iodine was lost in the first large-scale trial just described (Lead Diary, page 222). So an intensive investigation of means of conserving and recovering iodine was undertaken, and an improved scheme for the recovery of iodine over that given in Figure 33, page 138, was later worked out (Lead Diary, page 262).

The effects of time and temperature, as well as of other variables, upon the making of tetraethyl lead by the reaction of ethyl iodide with sodium-lead alloy were investigated also in a series of small-scale experiments. Meanwhile the costliness of iodine, and the difficulties involved in recovering it completely, caused some

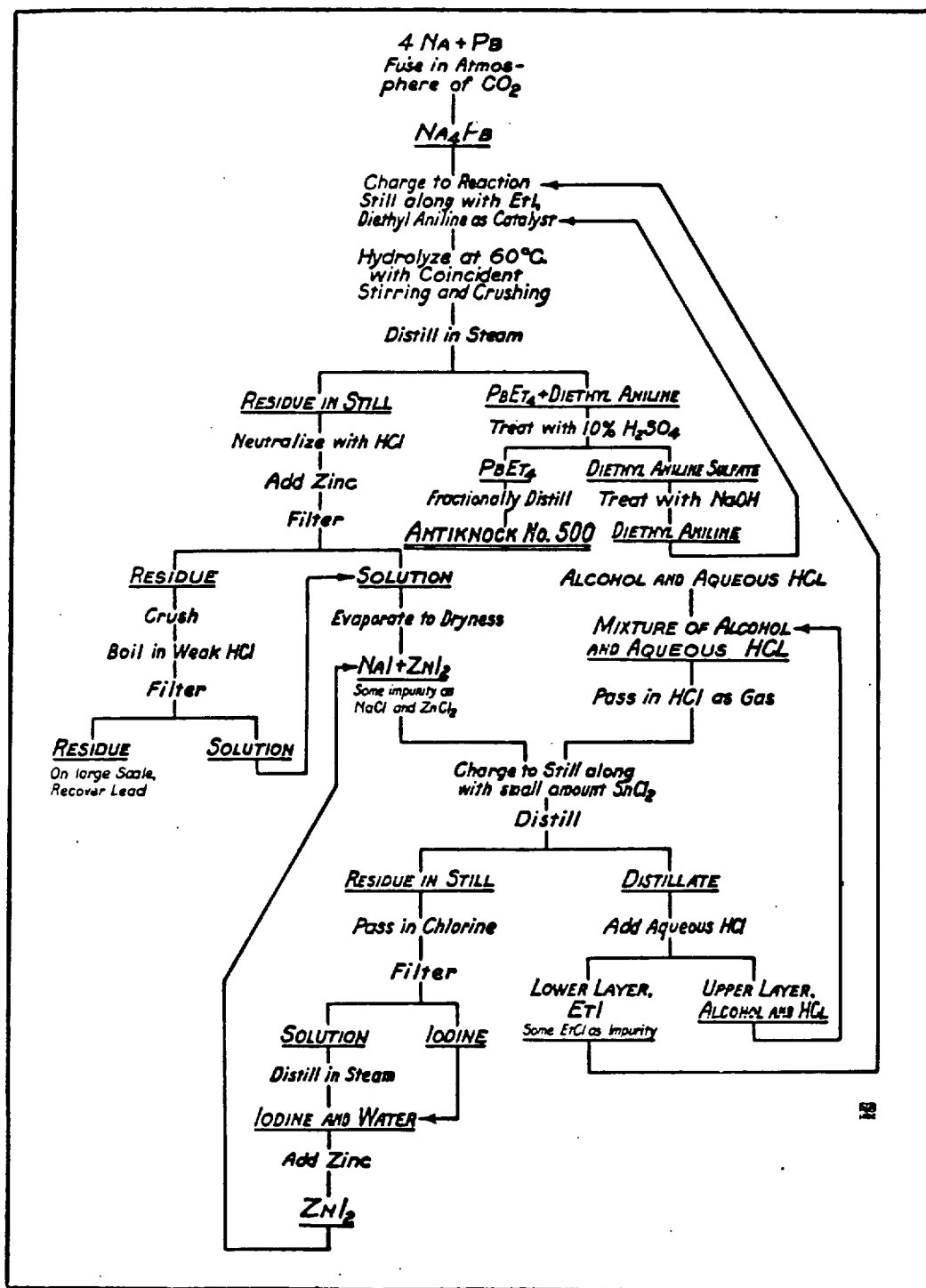


FIGURE 35

FLOW DIAGRAM OF PROCESSES IN PROPOSED METHOD OF MANUFACTURING TETRAETHYL LEAD BY REACTION BETWEEN ETHYL IODIDE AND SODIUM-LEAD ALLOY, MAY, 1922.

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effort to be directed toward finding other means of getting ethyl radicals to join with lead to make tetraethyl lead.

One of these attempts, in particular, should not fail to be mentioned. This was the effort to get ethyl nitrite to combine with sodium-lead alloy. A test-tube experiment had been made (Lead Diary, page 238) which seemed to show that iso-propyl nitrite would combine with sodium-lead alloy to give tetra-isopropyl lead, the same compound as was being made in the electrolytic experiments at M.I.T. And so some ethyl nitrite was prepared for use in an effort to make tetraethyl lead in the same way. A preliminary test-tube experiment with ethyl nitrite was not successful, but the failure was thought to be due to the low boiling point of the ethyl compound, by comparison with the isopropyl used before. About 50 cc of ethyl nitrite was accordingly mixed with Na₄Pb in a small autoclave or pressure vessel made out of a short piece of 1-1/2" iron pipe. The autoclave was fitted with a pressure gauge, and, for supposed safety, with a convenient hand-operated relief valve.

The reaction in this vessel had proceeded for a short time with the pressure rising slowly and then being maintained uniformly at about 10 pounds. Then all at once the pressure began to rise rapidly. The operator reached for the relief valve to open it; but, before he could even get his hand to the valve, there was a terrific explosion which blew the lower end out of the autoclave and the pressure gauge off the upper end. So violent was the concussion that about 50 panes of glass in the windows and partitions of the room were shattered, as well as some of the glass apparatus inside the work benches. This large breakage of glass occurred in spite of the

fact that the windows were open, it having been summer, May 25, 1922. The lucky thing—a very lucky thing—about it all was that, although three of the men were standing immediately in front of the apparatus at the time of the explosion, all escaped with nothing more than minor scratches.

Conclusion of Effort at M.I.T. to Make Tetraethyl Lead by Electrolysis of Acetone

The investigation going on at M.I.T., which when it was left, several pages back, in the early part of April, 1922, was being concentrated on the making of tetra-isopropyl lead by the electrolysis of acetone in dilute sulphuric acid solution, went forward on that line until the end of April. At that time R. E. Wilson wrote to Midgley: "I am inclined to agree with you that we should stop work on this process for the present, in view of the much greater promise of your new process" (Lead Diary, p. 196). He was referring, of course, to the sodium-lead and ethyl iodide process of making tetraethyllead.

For a time there was uncertainty about what ought to be done at M.I.T. But on May 18 and 19, 1922, Dr. Venable visited the laboratory in Dayton and was given a complete account of the progress made there up to that time. It was agreed then that at M.I.T. they should prepare a report on the electrolytic experiments, and among other things try to find a method of making tetraethyl lead without using the alkyl halides, and also try to determine under what conditions ethyl chloride or ethyl bromide could be substituted for ethyl iodide in making tetraethyl lead. The final report on the electrolytic preparation of lead alkyls at M.I.T. was submitted on June 22, 1922.

Attempt to Substitute Ethyl Bromide for Ethyl Iodide

Returning to the research at Dayton on making tetraethyl lead, an important move was made on June 29, 1922. This was a systematic attempt to substitute ethyl bromide for ethyl iodide, the first trial of which had been made in April, as previously related. Work was now begun not on a laboratory scale, but in the apparatus intended to produce 1 gallon of tetraethyl lead at a time, diethyl aniline having been used as catalyst (Lead Diary, page 311). The reaction went to a considerable degree, but the yield of tetraethyl lead was definitely lower than that then being obtained with ethyl iodide. Following this, the large-scale apparatus was run from time to time using ethyl iodide and sodium-lead alloy, and the possibility of substituting ethyl bromide for ethyl iodide was actively investigated in small batches in the laboratory. After this program had gone on for two weeks, or until June 13, 1922, the men who had been working on the project—Hochwalt, Andrew, Gilkey, and W. H. Charch, the latter doing summer work at the laboratory—all concentrated their endeavors upon finding catalysts or conditions which would make the use of ethyl bromide as efficient as ethyl iodide. A great many such experiments were run, and, of all the materials tested as catalysts, pyridine proved to be the best. Pyridine was effective enough, in fact, to bring the yields of tetraethyl lead when using ethyl bromide up to, or nearly up to, those obtained when ethyl iodide was used.

Du Pont Comes in On the Manufacturing Problem

The time was now toward the end of July, 1922. And another important event in the history of this endeavor then occurred. On July 22, Messrs. W. F. Harrington, E. K. Bolton, and W. S. Calcott of the du Pont Company visited the laboratory. They came at the invitation of Mr. Kettering to study the process of making tetraethyl lead and to see whether the manufacture of the compound could be carried out in the dye plant of the du Pont Company. Mr. Kettering had visited the du Pont Company a week before, and had taken with him the diagram reproduced as Figure 35, page 144. This diagram was the result of consideration given by our whole group since July 8 to the possibility of building a plant to produce 100 gallons of tetraethyl lead per day by the sodium-lead and ethyl iodide process (Lead Diary, page 329).

As a part of this analysis, a memorandum also had been prepared for Mr. Kettering on the cost and availability of chemicals for producing tetraethyl lead, in which it was estimated that by this process tetraethyl lead could be made at a cost for materials of about \$5.25 per gallon (Lead Diary, page 333). But in this same report the fact was recognized that ethyl bromide might later be substituted for ethyl iodide; and it was estimated that such a substitution, if it could be made, would reduce the cost of materials per gallon of tetraethyl lead from \$5.25 to about \$4.

By the time the du Pont men made their visit to the laboratory on July 22, the use of ethyl bromide instead of ethyl iodide had begun to look so promising that the process detailed to them was that using ethyl bromide. Just as much information as

possible was given the du Pont men during their stay.

A digression should perhaps be made here to explain the meaning of the term in Figure 35, "Antiknock No. 500." This term stood for tetraethyl lead in a decimal system devised on June 6, 1922, (being a revision of an earlier one given in Lead Diary, page 159), to designate the various known antiknock agents without actually naming them in such a way as to disclose their compositions.

In about a week after the visit of the men from the du Pont Company, a letter was received from Doctor Bolton, saying, among other things, the following: "During the past week we have carried out laboratory experiments on tetraethyl lead by the ethyl bromide method, according to the recipe which you gave us, and have not found any difficulty in duplicating your results of 60%. We are assembling equipment at the present time to carry out semi-works operations in order to have actual experience with the mechanical difficulties of this process before attempting to go to a larger scale. . . . We are carrying out the manufacture of the sodium lead alloy under a very thin film of molten caustic and find that when the material is ladled out for casting into molds there is not any great danger in firing when the surface of the liquid is broken." (Lead Diary, page 378).

Changes in the Research at M.I.T.

Returning again briefly to the work at M.I.T., the investigation there had been actively prosecuted since the visit of Venable to Dayton in May, when the course of their endeavor had

been changed. With the discontinuance of the electrolysis work, Dr. Horsch dropped out of the investigation. On July 8, 1922, George Calingaert and Brian Mead began to work on lead problems, the supervision remaining with Venable and Wilson. However, in August Walter G. Whitman took over Venable's part, and shortly thereafter Venable went to the Viscose Company, as previously mentioned. The new activities at M.I.T. included the effort to substitute ethyl chloride for ethyl iodide in making tetraethyl lead, the making of tetrabutyl and tetra-phenyl lead for test, some experiments on the use of alcohol instead of water for hydrolysis, and the investigation of the course of the reactions in the making of tetraethyl lead and of the composition of the intermediate lead compound formed during the process. As already said, this latter study led to the belief that diethyl lead was the intermediate compound, and that it was the decomposition of this diethyl lead to tetraethyl lead which accounted for the deflagration troubles experienced in the early experiments at Dayton (Lead Diary, page 374).

A Conference Brings Some Changes

In the laboratory at Dayton there was during August, 1922, active investigation of still another method of making tetraethyl lead. It consisted in reacting ethyl iodide with powdered lead in the presence of granular zinc, all under a layer of a solution of sodium hydroxide (caustic soda). The first trial by this method had been made on July 3, 1922, by J. P. Andrew (Lead Diary, page 321). The method was now being actively experimented with (Lead Diary, page 382 et seq). By the end of August ethyl bromide was being substituted

for ethyl iodide, and the granulated zinc was being coated with lead by precipitation from a lead salt. Midgley became so enthusiastic about this modified method that he arranged for the men at du Pont and at M.I.T. to come to Dayton for a conference about it. On August 28 Midgley wrote R. E. Wilson: "This reaction sounds so good that we believe it will be the opinion of the conference with you and du Pont that we should abandon the sodium method and concentrate on this new reaction."

The conference as called was held at the laboratory in Dayton, or Moraine City, on August 29, 1922 (Lead Diary, page 406). Calcott from du Pont and Whitman and Calingaert from M.I.T. attended it. Out of this conference came a very important decision, but as it finally turned out it did not involve a change from the sodium-lead to the zinc-lead method of making tetraethyl lead. The decision reached was that research on the making of tetraethyl lead in our laboratory should be dropped at that point, and that all our efforts should be concentrated on the problems of utilization. The investigation of utilization problems, not yet reported but to be described below, had already been going on for some months, conducted chiefly by Boyd. Further work on the making of tetraethyl lead, it was decided, should be carried out at the du Pont Company, with the men at M.I.T. continuing to investigate some of the more important problems incident to such production. The work at du Pont on making tetraethyl lead had already by this time progressed to the stage at which they had begun to ship tetraethyl lead to Dayton, seventy pounds at one time and forty-six at another (Lead Diary, page 400). Calcott went back home that night to continue research on

CHAPTER VIII

PROBLEMS OF USING TETRAETHYL LEAD INVESTIGATED

Simultaneously with the extensive research on means of making tetraethyl lead, described in the several pages just preceding, matters relating to utilizing it as a practical antiknock agent had been under active investigation also. These endeavors were chiefly four in number, as follows:

1. Measuring the antiknock effectiveness of tetraethyl lead and other lead compounds in various concentrations in different fuels, and finding the influence of added agents upon it.
2. Studying the stability of tetraethyl lead in storage, both by itself and when mixed with gasoline, and trying to improve the resistance of the compound to the decomposing action of light.
3. Making an intensive effort to find a way to correct the spark plug corrosion and exhaust valve deposition difficulties soon seen to be connected with the burning of tetraethyl lead in engines.
4. Taking the first steps toward investigating possible toxic hazards in the use of tetraethyl lead as an antiknock agent.

Also, one of the first tests to which tetraethyl lead was subjected after the lead discovery was for its degree of solubility in kerosene and gasoline. It was found, in short, that tetraethyl

lead was extremely soluble in these fuels. Thus in kerosene tetraethyl lead was so soluble that a 1 per cent solution of it had not begun to separate at 40 degrees below zero F. (Record 13, page 204).

Following the discovery of the remarkable effectiveness of tetraethyl lead in December, 1921, other lead compounds were naturally tested for antiknock effect. In the several ratings of tetramethyl lead that were made (Record 13, page 207, et seq.), that compound also was found to be a very effective antiknock agent; but lead oleate, a different kind of lead compound, was found to have no antiknock effect whatever, even in a concentration as large as 1 per cent (Record 13, page 204). The tetraisopropyl lead made at M.I.T. was found to be only about one-half as effective as tetraethyl lead, but tetra-normal-propyl lead proved to have about the same effectiveness as tetraethyl lead. Also the samples of tetrabutyl and the tetraphenyl lead made at M.I.T. were rated and found in each instance to be about one-half as effective as tetraethyl lead (Record 13, pages 110 and 207). The first tests were made, too, in which the degree of effectiveness of tetraethyl lead as antiknock agent was found to change with mixture ratio (Lead Diary, page 13).

It was in January, 1922, that the first tests were made in determining how much tetraethyl lead need be added to one gasoline to make it match another in degree of freedom from knock. The object was to find how much tetraethyl lead to add, first, to the export grade naphtha of the Vacuum Oil Company, and, second, to the 66-68 degree naphtha of the same company, to make each equal in degree of freedom from knock to the Shell spirit with which they had to compete abroad.

After a number of the most careful determinations that could then be made, it was concluded that to equal Shell spirit, the export naphtha needed 1/20 per cent tetraethyl lead and the 66-68 naphtha 1/30 per cent. Three gallons of the former fuel and about four gallons of the latter were treated accordingly and shipped to the Vacuum Oil Company on January 30, 1922. The men in the Vacuum Oil Company with whom we were in contact with regard to these tests were Messrs. F. B. Killian and G. A. Round, both of whom are still active in what is now the Socony-Vacuum Oil Company.

A particularly important one of the early jobs of rating was done as a result of experience with the various cars run on gasoline containing tetraethyl lead, some of which had compression ratios boosted as high as 7.5:1. It was observed that apparently the amount of tetraethyl lead needed to prevent knock did not increase directly with compression ratio (Monthly Report for April, 1922). On this account, careful measurements of the effectiveness of tetraethyl lead in kerosene were made by comparison with xylydine in kerosene over a wide range of concentration. The results of these measurements are shown in Figure 36, page 155 (Lead Diary, page 206). There the continual decrease in increment of antiknock effectiveness as the concentration of tetraethyl lead was increased, particularly above one-tenth of one per cent by volume, is apparent. This is a characteristic that was to have an important effect upon the future usefulness of the compound.

It was in the series of tests just described that another important observation was made, namely, that the degree of effectiveness of tetraethyl lead is greater in some fuels than in others.

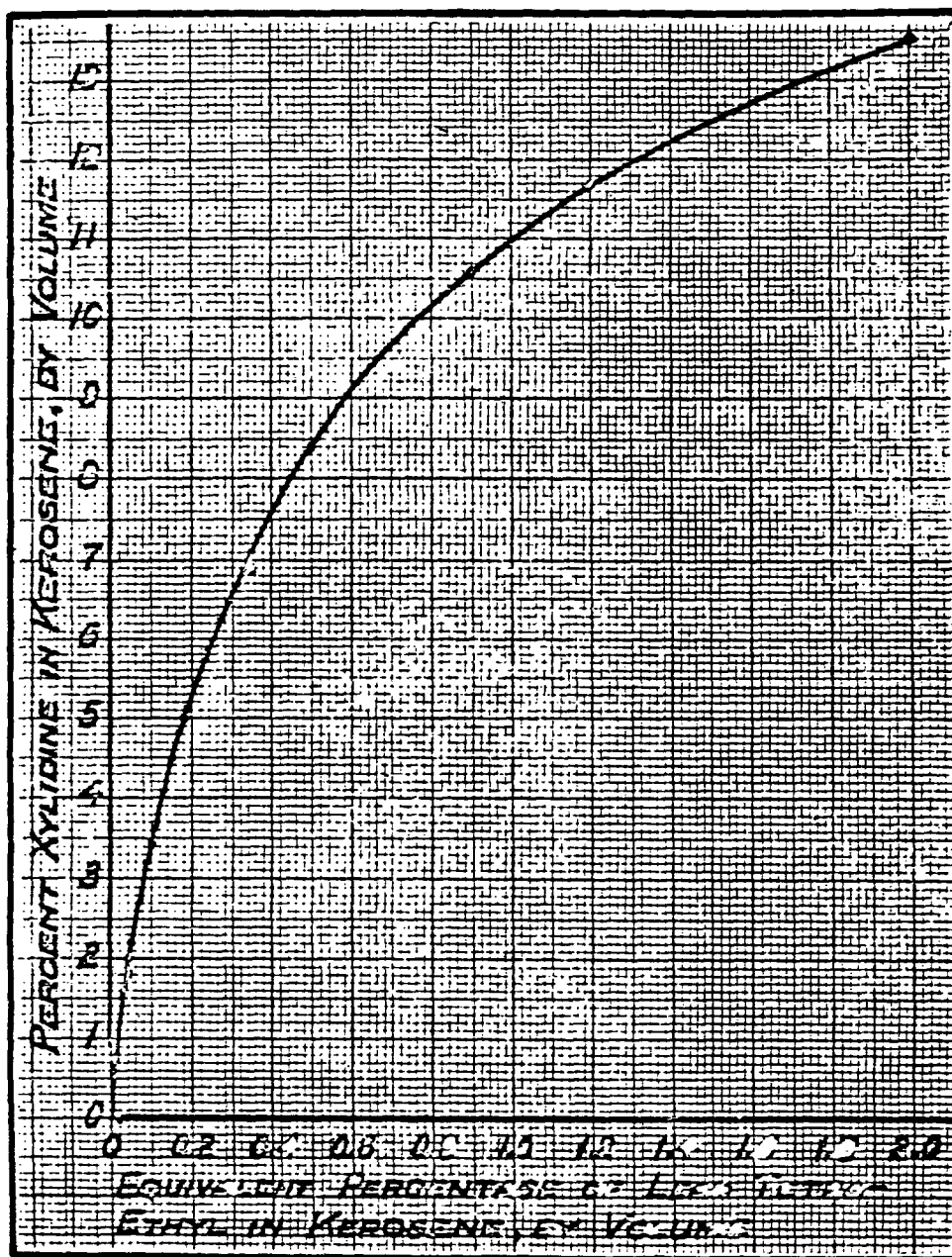


FIGURE 36

PLOT OF EARLY MEASUREMENTS WHICH SHOWED THAT THE EFFECTIVENESS OF EACH UNIT OF TETRAETHYL LEAD AS AN ANTIKNOCK AGENT DECREASES AS CONCENTRATION RISES. THUS, FROM THE ABOVE CURVE, THE FIRST 0.1 PER CENT OF TETRAETHYL LEAD IS EQUIVALENT IN ANTIKNOCK EFFECT TO 3.5 PER CENT XYLIDINE, BUT THE SECOND 0.1 PER CENT TO ONLY HALF AS MUCH XYLIDINE.

Thus tetraethyl lead was found then to be 20 per cent more effective in the gasoline used than in the kerosine (Lead Diary, page 207). This was the first observation of a characteristic which, as is now known, can vary in the case of tetraethyl lead from an antiknock effect in some fuels of 10 times the usual magnitude to a large negative or knock-inducing effect in other fuels, the different degrees of effectiveness depending only upon the composition of the fuels to which the tetraethyl lead is added (Antiknock Effect of Tetraethyl Lead, Campbell, Signaigo, Lovell, and Boyd, Ind. Eng. Chem., 27, 593, May, 1935).

Another considerable job of knock rating done during this period was the extensive measurements made on mixtures with kerosene and gasoline of benzene, toluene, xylene, and ethyl alcohol by comparison with mixtures of xylinene in kerosene as reference fuels (Record 13, pages 246-285). In a series of about 65 ratings the knocking characteristics of these fuels were established extensively enough to form the basis of two published papers, as follows:

1. Detonation Characteristics of Blends of Aromatic and Paraffin Hydrocarbons
Thomas Midgley, Jr., and T. A. Boyd
Ind. Eng. Chem., 14, 589 (July, 1922).
2. Detonation Characteristics of Some Blended Motor Fuels
Thomas Midgley, Jr., and T. A. Boyd
S.A.E. Jour., 10, 451 (June, 1922).

These two papers were based on the same data, and were therefore similar in content, except that the second contained the data on ethyl alcohol, none of which was included in the first. The former

paper was presented at the meeting of the American Chemical Society in Birmingham, which Midgley and Hochwalt attended, as previously recorded. The latter was presented at the summer meeting of the S.A.E. at White Sulphur Springs in June, 1922. Among the items of information contained in these papers was the observation that toluene is more effective as a knock suppressor than benzene, and that xylene in turn is more effective than toluene.

First Studies on the Stability of Tetraethyl Lead in Storage

It was only a few days after the effectiveness of tetraethyl lead as an antiknock agent was discovered, in December, 1921, that Boyd began tests to see whether tetraethyl lead was stable in storage. The first tests were made on the same kerosine solution as was used for the first measurements of antiknock quality on December 9, 1921. That solution was filtered clear and set on the shelf above a laboratory work table in an Erlenmeyer flask. Shortly thereafter, similar tests were begun on tetraethyl lead by itself (Record 13, page 220). It was soon found that if tetraethyl lead, either alone or in solution in kerosine or gasoline, were kept away from the light, in a dark glass bottle or in a can, no break-down in it occurred. But the compound is light-sensitive, and if any white light can get to it a slow decomposition occurs with the depositing of lead oxide on the bottom of the vessel. This decomposition in light appeared to be somewhat faster in tetraethyl lead by itself than in the dilute solution of the compound in a fuel such as gasoline or kerosine.

Because Mr. P. S. du Pont had expressed the fear that tetraethyl lead might possibly not be stable enough, even when stored away from the light in metal containers, to permit the compound to be packaged and shipped successfully, a special series of tests were undertaken to find out about that. Samples were put into containers, each with a connected manometer to record pressure changes. It was found that, when tetraethyl lead was stored in metal containers that protected it from all light, it underwent so little change that no measurable rise or fall in pressure had recorded on the manometer after a year of storage (Record 13, page 287 and Record 19, page 80).

If not protected from the light, however, tetraethyl lead did decompose slowly with the depositing of a solid and the evolution of a hydrocarbon gas. Because it was then thought desirable to make the compound stable in white light if possible, a long search was conducted for some material that could be added to it to make it resist light. In this work, which extended over many weeks, the effect of more than 150 addition agents to tetraethyl lead was tried (Lead Diary, page 184). The tests were conducted by exposing the samples to light, and sometimes to direct sunlight, in clear glass containers. A few of the compounds tried did exert a stabilizing effect, but this was apparently due in some instances to the effect of color imparted to the mixture by the compound in reducing light penetration. In the case of one of the compounds which appeared to be most effective as a stabilizer, cresol, it was found that the effect was only apparent.

Although even in direct sunlight the mixture of tetraethyl lead and cresol would remain clear for several days, it was later found that meanwhile a gas was being given off. The evolution of gas was so slow as not to be perceptible in an open vessel, but it was found that if, after standing for some time in light, the mixture were poured into gasoline it was no longer completely soluble, but threw down a voluminous precipitate of solid matter not miscible with the gasoline. A quantity of the gas given off by the mixture of tetraethyl lead and cresol, even though the solution remained clear, was collected and found to be mainly a saturated hydrocarbon, either ethane or butane or a mixture of the two.

Thus the long search for a means of stabilizing tetraethyl lead against slow decomposition in light did not prove to be very successful, except to the small extent that the following compounds, best of those found, served: turpentine, terebene, allyl alcohol, and dimethyl aniline (Lead Diary, page 398). However, colored substances did protect tetraethyl lead and its mixtures to a considerable degree, for they filtered out much of the white light. And, as later experience showed, no more protection than that was really needed in practice.

First Work on Spark Plug Corrosion and Exhaust Valve Deposit Problems

The third and perhaps the most important of the supplementary items of investigation carried along during the first eight months of 1922, simultaneously with the research on how to make tetraethyl lead, was the effort to find a way to correct the spark

plug and exhaust valve troubles seen to be connected with running engines on gasoline containing tetraethyl lead. The spark plug troubles—erosion of electrode wires and melting in blobs on the porcelain causing the porcelain to crack and pieces of it to split out—were first observed on April 1, 1922 (Lead Diary, page 107). The observation was made in the high-compression "FB" Chevrolet, called "The Goat" and mentioned earlier, which had then been run for some time on gasoline treated with 10 cc. tetraethyl lead per gallon. This car was put back into condition and continued to be run on the same lead-treated fuel. It was not until later on that trouble from the depositing of lead oxide on exhaust valves was experienced (Lead Diary, page 284). But by the middle of April, 1922, at least three other cars were being run on gasoline containing tetraethyl lead, as follows (Lead Diary, page 149; Letters, page 35):

A company Cadillac, 7:1 compression ratio, 15 cc. tetraethyl lead per gal,

Harold Talbott's Packard, 5.8:1 compression ratio, 5 cc. tetraethyl lead per gal.

Midgley's Buick, 8:1 compression ratio, 30 cc. tetraethyl lead per gal.

In the light of present knowledge, it is not surprising that, with such large concentrations of tetraethyl lead as 30 cc. per gallon, spark plug and exhaust valve troubles in the engines should develop in a short time. And so they did. By the time a month more had passed, it was quite apparent that here was a problem that would have to be solved if lead-treated gasolines were ever to be used in automobile engines.

In the latter part of May, 1922, Boyd was therefore assigned the still further job of trying to find a means of correcting these spark plug and exhaust valve troubles. It was thought at first that the difficulties might be caused by an impurity of ethyl iodide in the tetraethyl lead. Ethyl iodide was then being used in making tetraethyl lead, and the product did therefore contain a minute amount of ethyl iodide. (As it later turned out, however, ethyl iodide proved not to be a harmful material but a mild corrective agent.) A quantity of tetraethyl lead was accordingly purified by various means and a number of runs were made in engines using gasoline treated with the carefully purified tetraethyl lead. These tests were made in one-cylinder "copper cooled" engines in the dynamometer room of the research laboratories, which was under the supervision of William B. Earnshaw. But the man who actually operated the engines for the most part was E. E. Gold, an ex-member of the U. S. Coast Guard and of the crew of the famous revenue cutter "Bear". Gold ran engines for these tests throughout the more than two years over which the investigation extended, after a while devoting his entire time to it.

The engine tests using tetraethyl lead purified to any content of ethyl iodide turned out to be just as bad in respect to effects on spark plugs and exhaust valves as had those in which the original tetraethyl lead was used. Work was then begun on adding different compounds to the gasoline along with tetraethyl lead in the hope that during the combustion the lead would be converted to a compound other than lead oxide—to a compound which would not have

bad effects on spark plugs and exhaust valves. There was no basis for selecting compounds to try other than the old one of "cut and try." Hence that method was followed. By this means it was found on June 16, 1922, that the presence of the chlorine compound, chlorobenzene, improved the condition of the spark plug to a marked degree, but the exhaust valve was damaged some possibly because too much chlorine had been used for the tetraethyl lead present (Lead Diary, page 295; Record 19, page 95). And thus, just a few days after the tests began, one compound had been found which effected a considerable improvement.

As rapidly as could be, other compounds were tried for effects as possible corrective agents. And meanwhile a careful literature study of lead oxide was made (Lead Diary, page 295), and some laboratory experiments were conducted on the effects of sulphur dioxide and chlorine upon lead oxide (Lead Diary, page 298). Sulphur compounds and other chlorine compounds were among the several materials tested as rapidly as possible, two one-cylinder engines being used for the tests. Some of the tests on chlorine showed excellent results (Lead Diary, page 304-5, 318). Also a run was soon made with bromine as bromobenzene. But for some reason this first run on bromine, which element later proved to be the best corrective agent of all, did not turn out as well as it should (Record 19, page 97). Later, however, on July 11, 1922, bromine as ethylene dibromide was added to the lead-treated gasoline and showed excellent results as a corrective agent (Record 19, page 101; Lead Diary, page 333).

This hunt for a corrective agent could not go faster than the engine tests gave results. But it was pursued intensively, and a third engine was soon put into service. Most of the engine tests were made with a concentration of 10cc tetraethyl lead per gallon of gasoline. By the end of August, 1922, when, as before said, it was decided that the laboratory at Dayton should stop experiments on methods of making tetraethyl lead and that everyone should concentrate his endeavor on the solution of the problems of running engines on gasoline containing tetraethyl lead, the status of matters was as follows:

1. It had been found on the basis of a great many tests that chlorine compounds corrected the spark plug troubles rather well, but were apparently not effective in removing completely the deposit that formed on exhaust valves.
2. It had been found that bromine compounds were quite effective for correcting the spark plug troubles (Record 19, page 101), but specific information about effect for keeping exhaust valves clean had not yet been gotten at that time.
3. It had been found that the presence of chloroform or carbon tetrachloride in amount sufficient to contain theoretical amounts of chlorine for the tetraethyl lead present reduced somewhat the effectiveness of tetraethyl lead as a knock suppressor (Lead Diary, page 328).

4. It had been found that tetraethyl lead was light sensitive, but that when protected from the light it was quite stable. Some preliminary tests on the stability of mixtures of tetraethyl lead and carbon tetrachloride had been made also (Lead Diary, page 358).
5. Some tests to find whether lead oxide formed by burning tetraethyl lead in engines increased the wear on piston rings had shown, in a preliminary way at least, that it did not (Record 19, page 134).

First Attention to Possible Health Hazards

The fourth one of the utilization problems mentioned, namely, the possibility that putting lead into gasoline might introduce hazards to health, was also given consideration early. One of the first things done by R. E. Wilson after the arrangement with M.I.T. in early February, 1922 (Lead Diary, page 19), was to consult Dr. Reid Hunt of the Harvard Medical School to get his opinion about any possible poisonous effects of tetraethyl lead in dilute solution in gasoline, and to ask whether he would be willing to undertake an investigation of the subject. This was done with Midgley's approval, of course. The result, as extracted from R. E. Wilson's letter of February 20, 1922, to Midgley (Lead Diary, page 38) was as follows:

1. Dr. Hunt "has very grave fears as to the toxicity of the lead alkyl compounds, even in the very dilute solutions with which we would ordinarily deal."
2. "He was quite skeptical as to the effectiveness of any antidote."

3. "He thinks it quite possible that the lead alkyl compounds could be assimilated through the skin."
4. "He feels that the best men to undertake a study of the compounds and get quick results would be Henderson and Haggard of Yale."
5. In a later letter, Wilson to Midgley (Lead Diary, page 53): "Dr. Hunt was concerned with the building up of the lead content of the dust in our city streets by the material coming from the exhaust."

Midgley next asked Wilson to inquire of Dr. Yandell Henderson at Yale University whether he would be willing to investigate tetraethyl lead from the viewpoint of possible health hazards. In reply, Dr. Henderson wrote Wilson on March 16, 1922, (Lead Diary, page 75), in part as follows:

"As a preliminary opinion I would say that I should expect the exhaust gas under the conditions you mention to constitute an extremely serious health hazard. . . . It appears to me that the risk of poisoning would amount almost to a certainty for every one around garages and for the part of the public which will use vehicular tunnels. There will be a distinct risk even for people living and working around such congested streets as Fifth Avenue, New York City. Of course these statements are provisional. . . . My associate, Dr. H. W. Haggard, and I will undertake the investigation for you. I believe that we could get it done in about two and a half months. If so our charge would be \$5,000. If, because of the raising of additional points for investigation, the work was continued thereafter, the rate of our charge would be \$2,000 per month. This would cover all expenses."

On this letter from Dr. Henderson, Wilson in a letter to Midgley, March 18, 1922, (Lead Diary, page 77), commented as follows, in part:

"The price mentioned seems somewhat high, but it undoubtedly covers the work of a considerable number of men. . . . As to his excessive fear of injury by the exhaust gases, I think part of this may be based on the assumption that some of the undecomposed lead alkyls will pass out through the exhaust."

Midgley then wrote Wilson, March 24, 1922, (Letters, page 34), in part:

"Have talked over the proposition of Dr. Henderson with Mr. Kettering. I am inclined to agree with you that his price seems high. However, if we could arrange with him that he would agree to being called upon at a later date, free of any other charge than his expenses, to refute any false propaganda which might be started against the use of lead compounds that it might be possible to get together."

There was apparently one further letter from Dr. Henderson to Wilson at this time, written in the latter part of March, 1922. In it he said, among other things, the following (Lead Diary, page 89):

"The more I think on the topic of introducing lead alkyls into automobile fuel, the more seriously I am concerned regarding the situation which will arise. . . . The use of lead in this way would, I believe, result in wide-spread lead poisoning among chauffeurs and garage workers. . . . Chronic lead . . . is one of the worst diseases known. Indeed, if one had his choice between (1) partial asphyxiation, (2) syphilis, (3) tuberculosis, and (4) chronic lead, he would be well advised to choose in this order."

But Dr. Yondell Henderson was not retained to investigate the problem of possible toxicity. And nothing more on the subject happened during the extremely busy summer of 1922. However, the suggestion made in Midgley's letter quoted above about the part which Dr. Henderson might later play in refuting propaganda about the hazards of putting lead compounds into gasoline is particularly interesting in the light of subsequent events, to be recounted when the time comes; for, as it turned out, Dr. Henderson became not the refuter of such propaganda but the active disseminator of it.

Other Events During 1922

Except for a number of miscellaneous events, this brings the story of the lead research up to the end of August, 1922. One of the incidental events was that in June, 1922, Midgley conducted experiments on making "solid" tetraethyl lead and on making a lead "pill" by coating a quantity of this "solid" tetraethyl lead with a protective layer of paraffin (Lead Diary, page 290). It was found that, if tetraethyl lead was mixed with melted para-toluidine, a solid containing as much as 50 per cent of tetraethyl lead could be obtained upon cooling to room temperature. This material could then be coated with a protective layer of paraffin--and an apparatus and means for doing this were worked out. In this way a smooth cake of material was obtained containing a large percentage of tetraethyl lead and having all its ingredients soluble in gasoline. The results of these experiments were never applied in a practical way, but they are covered by U. S. Patent 1,592,953, July 20, 1926, Method and Means for Treating Motor Fuels, Thomas Midgley, Jr.

J. W. Morrison, who some time prior to 1922 began to take care of the patent phases of the antiknock research, had formerly been with the B. F. Goodrich Company in Akron. In the summer of 1922 Morrison wrote to H. L. Trumbull at Goodrich and inquired about the experiments that had been made there on tetraethyl lead as a possible vulcanization accelerator. (As later published, in 1925, George Oenslager at Goodrich had tried tetraethyl lead as a possible vulcanization accelerator in 1906, and had found it to have

mild accelerating effect. Ind. Eng. Chem., 17, 395, 1925.) As a result of this contact and later ones, four ounces of each of the following lead compounds were prepared and sent to George Oenslager in early November, 1922: tetraethyl lead, lead triethyl sulphide, and lead triethyl hydroxide. These compounds were tested by Oenslager as possible vulcanization accelerators and showed some accelerating effect. But to the vulcanized product they imparted a very disagreeable odor. Oenslager said the vulcanized pieces smelled like garlic; but Midgley said no, they smelled like mercaptans--which compounds have, if possible, a still more disagreeable odor than garlic.

Oenslager, who was the original discoverer of organic vulcanization accelerators for rubber, as well as of the value of high percentages of carbon black for making long-wearing tread stocks, was in 1932 awarded the Perkin Medal by the Society of Chemical Industry for his achievements. And there is an interesting parallelism between his research on vulcanization accelerators conducted around 1906 and the search for an antiknock agent which began 10 years later. The first active accelerator of the vulcanization reaction discovered by Oenslager was an iodine compound, mercuric iodide (Ind. Eng. Chem., 17, 393, 1925). And, as already related, the first antiknock agent was iodine too. The second vulcanization accelerator discovered by Oenslager was aniline. So also the second antiknock compound discovered was aniline. At one stage of the search for an antiknock agent, it was accordingly believed that there was possibly a close relationship between antiknock compounds and vulcanization accelerators. It was partly due

to that surmise that the lead compounds were sent to Oenslager for test, as related above.

In April, 1922, attention was first given to a method of determining the lead content of tetraethyl lead. The method of analysis as then proposed (Lead Diary, page 136) consisted in adding a weighed amount of tetraethyl lead to an alcohol solution of iodine, driving off the alcohol, treating the residue with strong sulphuric acid to convert the lead to lead sulphate, driving off the excess acid, and weighing the lead sulphate present. The methods of analysis for tetraethyl lead and for tetraethyl lead in gasoline as used today were developed later on, however.

In the summer of 1922, W. H. Charch made some nickel carbonyl and attempted to prepare also an oil-soluble compound of bismuth, triphenyl bismuthine. This was done in further pursuance of the program of measuring the antiknock properties of the elements in the periodic system, which, as already related at some length, had led to the discovery of lead as an antiknock compound. The nickel carbonyl was tested on August 15, 1922, (Record 19, page 130) and was found to be a powerful antiknock agent, about one-fourth as effective as tetraethyl lead. This led to the intensive effort to make the carbonyl compound of iron and the important sequence to it, which will be related further on. The triphenyl bismuthine made at this time was impure, but showed nevertheless that bismuth is an effective antiknock agent (Record 19, page 130).

It was in the summer of 1922 that the first known effort was made by an outsider to capitalize on the discovery of antiknock

compounds. The Raritan Aniline Works, New Brunswick, N. J., began then to distribute aniline as an antiknock agent. They tried to sell it to the public through filling stations in New Jersey. Midgley and Sanford Brown of the Condensite Company of America visited one of these stations, located at Mill Street and River Road in Belleville, N. J., and purchased a quart of motor aniline (Letters, page 26). Nothing further was done about it apparently, but the sale of aniline by the Raritan people was soon discontinued anyway.

In the summer of 1922 came also the first one of the complaints from a user of tetraethyl lead that it caused troubles with which it had nothing whatever to do, but for which it got blamed because it happened to be new and perhaps a little mysterious. This is the kind of resistance that any new product has to face, of course, but which persisted longer in the case of tetraethyl lead than is usual with new things. Mr. Kettering had given some tetraethyl lead to Ward Cromer who used it on a long automobile trip that he took. Upon his return, Mr. Cromer reported that the lead compound had eaten the coating of shellac off his carburetor float, and that it would accordingly no longer float in gasoline. So a test was begun to see whether the presence of tetraethyl in Mr. Cromer's gasoline could have had anything to do with the trouble. But after many days no action on shellac coatings could be detected (Lead Diary, page 399).

In view of subsequent events, it is of interest to record here that the first order for any considerable amount of tetraethyl lead—10 gallons of it—came from the Sun Company (now the Sun Oil

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Company) in a letter of July 15, 1922, from A. Ludlow Clayden to Midgley. When Midgley attended the S.A.E. Summer Meeting at White Sulphur Springs in June, 1922, he described and demonstrated the effects of tetraethyl lead to a number of those in attendance. Herbert Chase, in his report of that meeting in Automotive Industries, 46, 1412, June 29, 1922), said: "Among the most interesting things which developed at the Research Session was the statement by Thomas Midgley, Jr., of the General Motors Research Laboratory to the effect that his organization has discovered and developed a process for making an anti-knock substance which can be added to gasoline and will thereby prevent detonation even when an engine of very high compression is employed. . . . The writer was given an opportunity to ride in a car which when pulling knocked badly on ordinary gasoline, but which ceased to knock entirely even on heavy pulls when the new dope was employed."

Included in the story by Mr. Chase was a picture of several men gathered around watching a demonstration—Clayden kneeling directly opposite Midgley—and underneath the picture was this legend: "This is not a crap game, but a group of engineers observing the cremation of tetraethyl lead, the new fuel 'dope' which Midgley exhibited." Clayden was sufficiently impressed by what he saw at White Sulphur Springs that June to give Midgley a verbal order for 10 gallons of "Anti-Knock," which he later confirmed by his letter of July 15, already mentioned. "I would like to get a gallon of it as soon as possible," Clayden wrote, "and as to the rest there is no hurry whatever." Whether Clayden ever got the ten gallons of tetraethyl lead that he ordered then is not now known, but he could have had it many times over, of course.

CHAPTER IX

THE FIRST PAPER ON TETRAETHYL LEAD

While Midgley was at the Birmingham Meeting of the American Chemical Society in April, 1922, he received an invitation to present a paper on the antiknock research before the American Chemical Society at its meeting to be held in Pittsburgh in September. And on April 12 he wrote to Dr. H. E. Howe, editor of Industrial and Engineering Chemistry in part as follows:

"Upon my return to Dayton I took up the matter of presenting our antiknock work before the American Chemical Society meeting in Pittsburgh and found a very enthusiastic attitude toward this on the part of Mr. Kettering, which assures us being able to do the job thoroughly.

"We are making our plans to present this subject. At the present time we would like to suggest the title, 'The Chemical Control of Gaseous Detonation with Particular Reference to the Internal-Combustion Engine,' paper by Thomas Midgley, Jr., and T. A. Boyd.

"We would start the presentation with a demonstration in glass tubes of normal combustion and detonation, showing the removal of the detonation by the addition of a small amount of antiknock material with a few remarks as to the limitation of this method of investigation. We would then use a large sized demonstrating chart of the gaseous movements during enclosed combustion and show how high pressure waves are generated during high velocity combustion. Following this will be a motor demonstration which would evidence detonation both by instrumentation and audibility . . . we would operate this motor on detonating and non-detonating fuels and (on) detonating fuel compared to detonating fuel plus antiknock material.. This is a rather striking demonstration of the antiknock property. . . . We would then close the paper by presenting graphically with slides the periodic variation of the antiknock value among the 18 elements that show this characteristic."

The above quotation is given at such length because the outline of the proposed presentation contained there is just what was actually prepared and presented. Or rather this is true except for the last sentence quoted, which promised a discussion of the systematic variation of the antiknock property with the periodic arrangement of the elements, as based on the research described some time earlier in this account. Because of objections from the patent section, however, this part of the proposed presentation was not included. The objection from Mr. Morrison to publishing any of the antiknock story at that time was in fact so great that it was only after much persuasion by Boyd during the preparation of the paper that the inclusion of any quantitative data whatever on the effects of antiknock agents was allowed to be incorporated in it. But finally the quantitative data forming Table II of the paper and the discussion of it were allowed to go in (Ind. Eng. Chem., 14, 894, October, 1922). This is mentioned as perhaps being of particular importance, because, without such data, the paper would have lost almost altogether its effect as a scientific presentation. And, as it later turned out, this was the paper upon which Midgley was awarded the William H. Nichols Medal by the New York Section of the American Chemical Society.

On May 5, 1922, Dr. A. C. Fieldner, who was chairman of the program committee for the meeting in Pittsburgh, wrote Midgley as follows (in part): "The committee was unanimously in favor of accepting your paper for presentation before the general meeting of the society." (It was a special honor to have the paper scheduled for the general meeting, as most papers are presented at sec-

tional meetings.) "Colonel Church, President of the Carnegie Institute, was a little shocked when I told him we wanted to put a gasoline engine on the stage in connection with one of the papers. I suppose it seemed sacrilegious to him to have a gasoline engine on the boards where Madam Schumann-Heink, Fritz Kreisler, and others usually perform." But the matter was referred to Mr. Cunningham, superintendent of the buildings of the Carnegie Institute, and suitable arrangements were made to use the stage for the presentation. "Our committee was very much impressed," wrote Dr. Fieldner also, "with the publicity value of your paper. Everyone is interested in automobiles and the newspaper men would give this a lot of space which would result in good publicity for the rest of the meeting."

With the plans thus made, it was only necessary to prepare the demonstrations in suitable form and to write the paper in such shape that it could be published later. The difficulty met with in preparing a paper considered as proper for presentation on the occasion has already been mentioned. A request was received from Dr. H. E. Howe, editor of Industrial and Engineering Chemistry, to prepare a supplementary paper to be published ahead of the one to be presented at Pittsburgh and outlining the background of the work on antiknock agents, or suggesting the reasons why the investigation was important. This was done, and a paper, "The Application of Chemistry to the Conservation of Motor Fuels" by Thomas Midgley, Jr., and T. A. Boyd, was prepared and published (Ind. Eng. Chem., 14, 849, September, 1922).

The two most striking demonstrations planned for the presentation at Pittsburgh were the one to show detonation in an open glass tube and the removal of it by means of an added antiknock agent, and the one consisting of the engine tests showing knock and its removal by means of tetraethyl lead. Engine demonstrations had been made so often that little preparation was needed for them. But the tube experiment was completely overhauled to substitute diethyl selenide for the ethyl iodide formerly used as an antidetonant and to make the demonstration more certain to work as intended. The embarrassment when, as related earlier, a similar experiment failed completely during an attempt to present it at the Engineers' Club in Dayton had not been forgotten. So the system illustrated in Figure 37, page 176, which incorporated semi-automatic metering of gases to the explosion tube and automatic ignition when the valve was closed, was developed. To make doubly sure that the presentation would go off as planned and that it was a suitable one, arrangements were made to give a dress rehearsal of it on August 22, 1922, before a special meeting of the Engineers' Club of Dayton to which were invited the members of the Cincinnati Section of the American Chemical Society (which then included the Dayton area). This meeting was well attended and went off in good style.

Then on Monday, September 4, 1922, Midgley, Boyd, Hochwalt, and W. W. (Mac) Welsh (mechanic for the Fuel Department) arrived in Pittsburgh for the meeting of the American Chemical Society. The engine, the explosion tube, and other demonstration

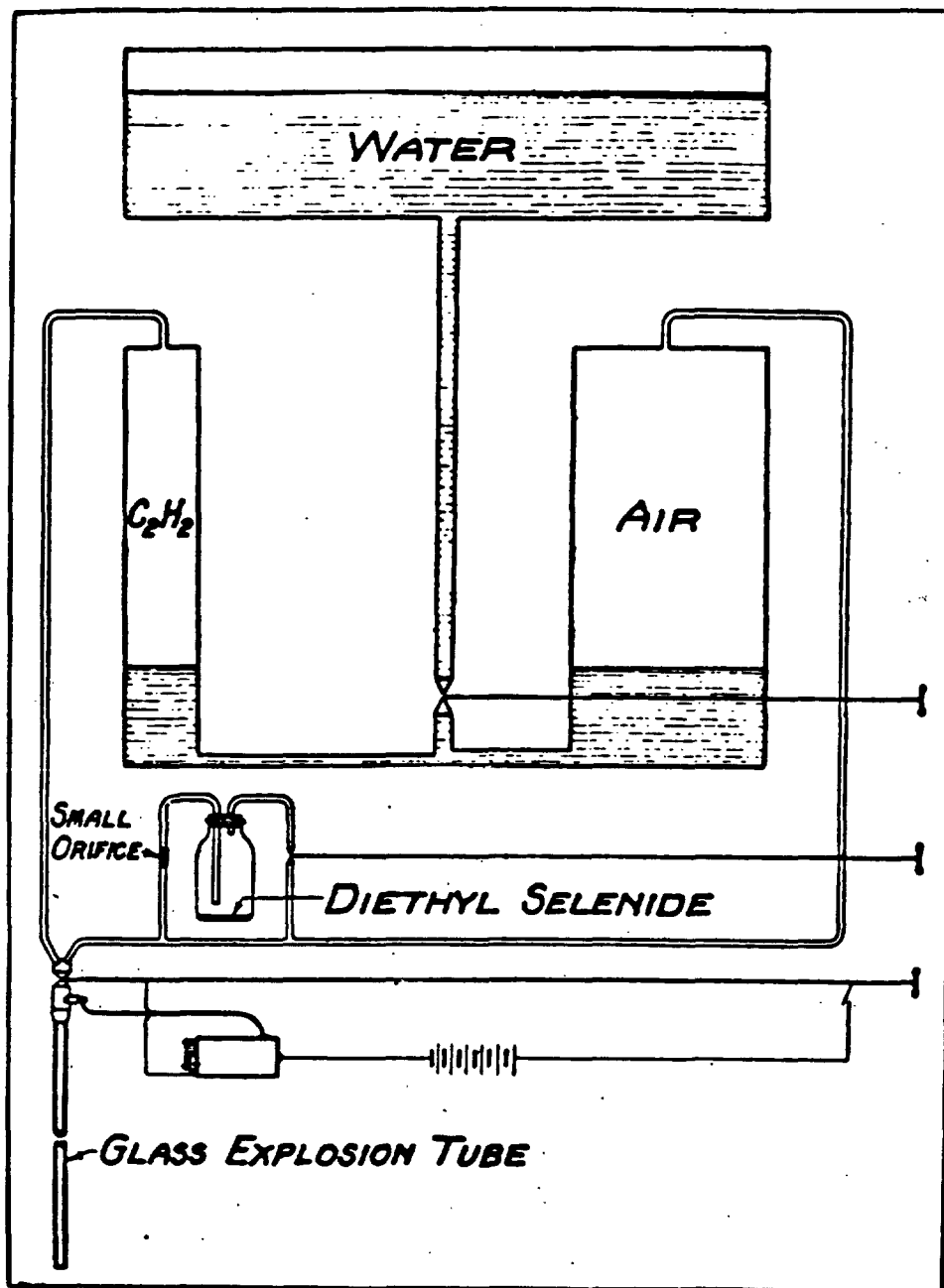


FIGURE 37

DIAGRAMMATIC SKETCH OF APPARATUS USED AT PITTSBURGH MEETING, AMERICAN CHEMICAL SOCIETY, FOR SHOWING DETONATION IN AN OPEN GLASS TUBE AND FOR DEMONSTRATING ITS REMOVAL BY THE ADDITION OF AN ANTIKNOCK AGENT.

equipment had been shipped to the Carnegie Institute in advance. The engine was a Delco-Light equipped with bouncing-pin indicator, having a mazda lamp in the circuit, all as pictured in Figure 22, page 102. The entire day Monday was spent setting up the apparatus and getting it into shape. Or rather it should be said that the latter part of the day was so spent. For, it having been Labor Day, there was no help around the Institute to move the pieces to the stage, nor could a truck be found. So we had to carry each piece, some of them having been very heavy, for the long distance from the place where they were stored, through hallways and doors, and up and down stairways until at last with great relief it could be set down on the stage. But finally, after having solved the transportation problem in this fashion and having repaired such parts as were broken in transit, everything appeared to be in place, and in good order.

The presentation of the paper and the demonstrations which accompanied it were to be made as the first item on the program in the afternoon on Tuesday, September 5. The hall was in use during the forenoon. But during the noon intermission we all went up on the big stage to check everything over again. There was only a little time, for the forenoon session had not adjourned until late. After having adjusted everything else, we came at last to the engine and decided to run it a few minutes to make sure everything was all right and to get it warm, so that it could be warmed up more quickly to the operating temperature during the presentation.

And then happened one of the most unlucky events—or perhaps it was a very lucky one—of the whole endeavor. The engine had only been run a minute or two when out blew a cylinder head gasket, followed by the loud hissing of escaping gas at each stroke. Here was a pretty kettle of fish! Because no such thing had ever happened before in all our experience, we had not thought to bring along a spare gasket. But it was apparent that the crucial engine demonstration of knock and its removal by means of tetraethyl lead or diethyl selenide could not be made without a new gasket. And already it was so near to the time for the program to begin that the audience was gathering. But there was no gasket and we did not know where in Pittsburgh to get such an uncommon article as a cylinder head gasket for a Delco-Light engine.

Then it was that Mac Welsh performed one of the greatest services of his career. He jumped down off the stage, ran up the aisle and out to Forbes Street in front of the Institute. There he spied a car with a sticker on the windshield identifying it as a courtesy car of the Pittsburgh Section of the Chemical Society. He told his problem to the driver of the car. And, as luck would have it, the driver just happened to know about the distributor of Delco-Light engines in that area, and where he was located some distance from there in East Pittsburgh. They drove to his store as fast as possible, were lucky enough to find the proper gasket, and then raced back to the Carnegie Institute. Welsh came running triumphantly down the aisle with the gasket and jumped up on the stage just as fast as he had left it some time before, for by then it was past time for the meeting to begin. But to put the new gasket

in place took only a very few minutes, and the meeting got under way at once with the introduction of Midgley by Dr. Edgar Fahs Smith, then president of the Society.

From that point on, things went off without any further hitch. Midgley's presentation was excellent, the explosion tube demonstration did not fail, and the engine demonstration of knock and its removal with antiknock agents, was enthusiastically received by the audience. In fact the presentation, so elaborate and so striking, was such a great success that in chemical circles Midgley got there the high reputation for showmanship which he still retains. The presentation later received favorable mention in the official Society report of the Pittsburgh meeting (Ind. Eng. Chem., 14, 885, October, 1922). And later still Midgley was awarded for this paper and outstanding presentation the William H. Nichols Medal by the New York Section of the American Chemical Society.

Substantially the same matter as that given at the Pittsburgh meeting of the American Chemical Society was later presented, about October 27, 1922, before the Ohio State University Chapter of Sigma Xi, and on December 7, 1922, before the American Petroleum Institute at the meeting in the Statler Hotel, St. Louis (Bulletin American Petroleum Institute, 5, 84, December 30, 1922).

This paper, with its successful presentation and later publication, had extraordinary importance. This was so, not only on account of the medal awarded for it, but also because of the effect it had a few years afterwards when the addition of tetraethyl lead to gasoline was under attack by those who claimed that it would

poison the whole nation. When that time came, as is brought out later on, those in technical circles, having been informed about the development and sympathetic to it, demanded and got a factual rather than a hysterical consideration of the case.

CHAPTER X

WORK ON EXHAUST VALVE AND SPARK PLUG PROBLEMS RESUMED

As stated some pages previously, the status of the Ethyl gasoline development at the end of August, 1922, was as follows:

1. Research on means of making tetraethyl lead had just been transferred to the du Pont Company, where the sodium-lead method as developed in the work at Dayton and at M.I.T. was to be pursued further and put on a commercial scale.
2. Research on the reactions involved in the synthesis of tetraethyl lead by the sodium-lead route was being continued at M.I.T.
3. The research at Dayton was now to be concentrated altogether upon the solution of the spark plug and exhaust valve deposit and erosion problem.

The considerable work done up to that time on the spark plug and exhaust valve problem had shown that additions of compounds of chlorine or bromine were very beneficial in lessening the erosion and deposit troubles so far as spark plugs were concerned, and of material benefit also in reducing deposits on exhaust valves. It was now thought that maybe if the chlorine or bromine were to be added as an integral part of the tetraethyl lead molecule its effect might be still greater. Hence work was begun to prepare lead triethylchloride and lead triethylbromide (Lead Diary, 409). It was found readily possible to make these compounds. Other compounds of the same type prepared included these: lead triethylhydroxide,

lead triethylacetate, lead triethylsulphate, lead triethyloleate, lead triethylcyanide, and lead triethylsulphide.

In preparing to test lead triethylchloride in the engine, the compound was found to have a very low degree of solubility in gasoline (Lead Diary, 415), and in the engine tests some of it sometimes separated out in the carburetor. Lead triethylbromide seemed to give better results than the corresponding chloride in respect to valve and spark plug condition, and late in September, 1922, (Lead Diary, 436), a 100-hour engine test of the compound was begun in one of the single-cylinder test engines. At the same time another engine was run on untreated gasoline for comparison. The full 100-hour run was completed, but the spark plug electrode in the engine running on the treated gasoline was by that time badly corroded. The exhaust valve, however, was in pretty good condition. A second run was then begun using well purified lead triethylbromide (Lead Diary, 447), and this test was run about 120 hours with somewhat better results, although about midway in the test the spark plug porcelain was broken by a wrench and a new one had to be put in at that point, thus invalidating to some extent the spark plug test. However, at the end of 120 hours, the spark plug in the engine run on the lead-containing fuel was about like that in the engine on straight gasoline (Lead Diary, 451). Another interesting observation from this run was that the engine operated on the lead-containing fuel appeared to contain less carbon than the other (Lead Diary, 451). This same observation was made also on later occasions; but, carbon deposits being usually so erratic, the observation was never

deemed definite enough to justify any conclusion that the presence of lead reduced carbon deposits.

The antiknock effectiveness of lead triethylbromide was measured and found to be only about three-fourths that of tetraethyl lead (Lead Diary, 446 and 486). This observation, coupled with the fact that the presence of the bromine within the molecule materially reduced the solubility in gasoline, caused the men at M.I.T. to be asked to undertake the preparation of a compound in which one ethyl radical of tetraethyl lead would be replaced not by bromine alone but by an organic compound of bromine, such as C_2H_4Br (Monthly Report, November 1, 1922). But this attempt did not prove to be very successful.

Meanwhile, the tests of other possible corrective agents added along with tetraethyl lead were being continued as opportunity offered, and a great many were tested (Rec. 19, p. 145 et seq.). These included carbon tetrachloride and many other compounds of chlorine, as well as chlorinated lubricating oil and chlorinated oleic acid. Ethyl carbonate was another one of the many possible corrective agents tried and one that looked quite promising for a while. So promising did ethyl carbonate look as a corrective agent that car tests of it were begun by Joe Dutz. But in the end these tests did not turn out well. Of all the many addition materials tested, those containing chlorine and bromine were the only ones that showed consistent improvement.

Here it is interesting to note that, in all the tests made during the intensive program pursued during the last four months of 1922, no separate bromine compounds were apparently used

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as addition agents. And this suggests how strong was the belief at that time that bromine was too scarce and costly to be practical, for tests reported earlier had shown bromine to be a powerful corrective agent. So far as bromine was concerned, the tests during the fall of 1922 were confined to lead triethylbromide. But, although bromine in that form showed pronounced corrective effect, the amount of combined bromine present in lead triethylbromide was not sufficient to overcome the spark plug and valve troubles completely enough. This was shown conclusively by car tests (Lead Diary, 490 and 494). Right at the end of 1922, therefore, the amount of corrective compound began to be increased by adding to the gasoline in addition to lead triethylbromide a small amount of chlorinated lubricating oil. But soon carbon tetrachloride was substituted for the chlorinated lubricating oil.

Sale to the Public Decided Upon

The result of the road tests of lead triethylbromide following this addition of chlorine, although not having shown perfect correction of the lead effects in respect to spark plugs and valves, were nevertheless thought to be good enough that in January, 1923, a decision was reached to begin selling the material to the public in a small way. This decision was a cause of considerable concern to some of the men active in the development who were struggling with the shortcomings of the compound, they having felt that the material was not yet ready for the market. But nevertheless the decision to put it out was in accord with Mr. Kettering's philosophy that the commercialization of a product should not wait on

its being altogether perfected. And, as it turned out, the decision to begin selling it then was not a mistake, for the product was rapidly improved further as the investigation proceeded.

Miscellaneous Events During Fall of 1922

Before proceeding to give an account of the first sales of tetraethyl lead to the public, some other events of the five months following August, 1922, will be recounted. A supplementary effort was made to develop a laboratory method as a substitute for the engine test for finding whether a compound would be effective as a corrective agent for the spark plug and exhaust valve troubles resulting from the presence of lead in the gasoline (Lead Diary, 472-4). Many compounds were studied, but the results were not reliable enough to make such tests a suitable substitute for those run directly in the engine.

If lead triethylbromide was to be used as an antiknock agent, it demanded of course that some suitable means of producing the compound be developed. The job of finding such a means was given to J. P. Andrew, and he began work on it in September, 1922 (Lead Diary, 435). After a great deal of experimentation, during which he made the small amounts of lead triethylbromide needed for use in the current test program, he settled on a method of preparation which consisted in passing hydrobromic acid gas into a solution of tetraethyl lead in kerosene (Lead Diary, 490). This method, which worked well, was finally carried out in the apparatus shown in Figure 38, page 186. In this large laboratory-scale apparatus was made later on all the lead triethylbromide used in the first two months of the sale of Ethyl Gasoline to the public.

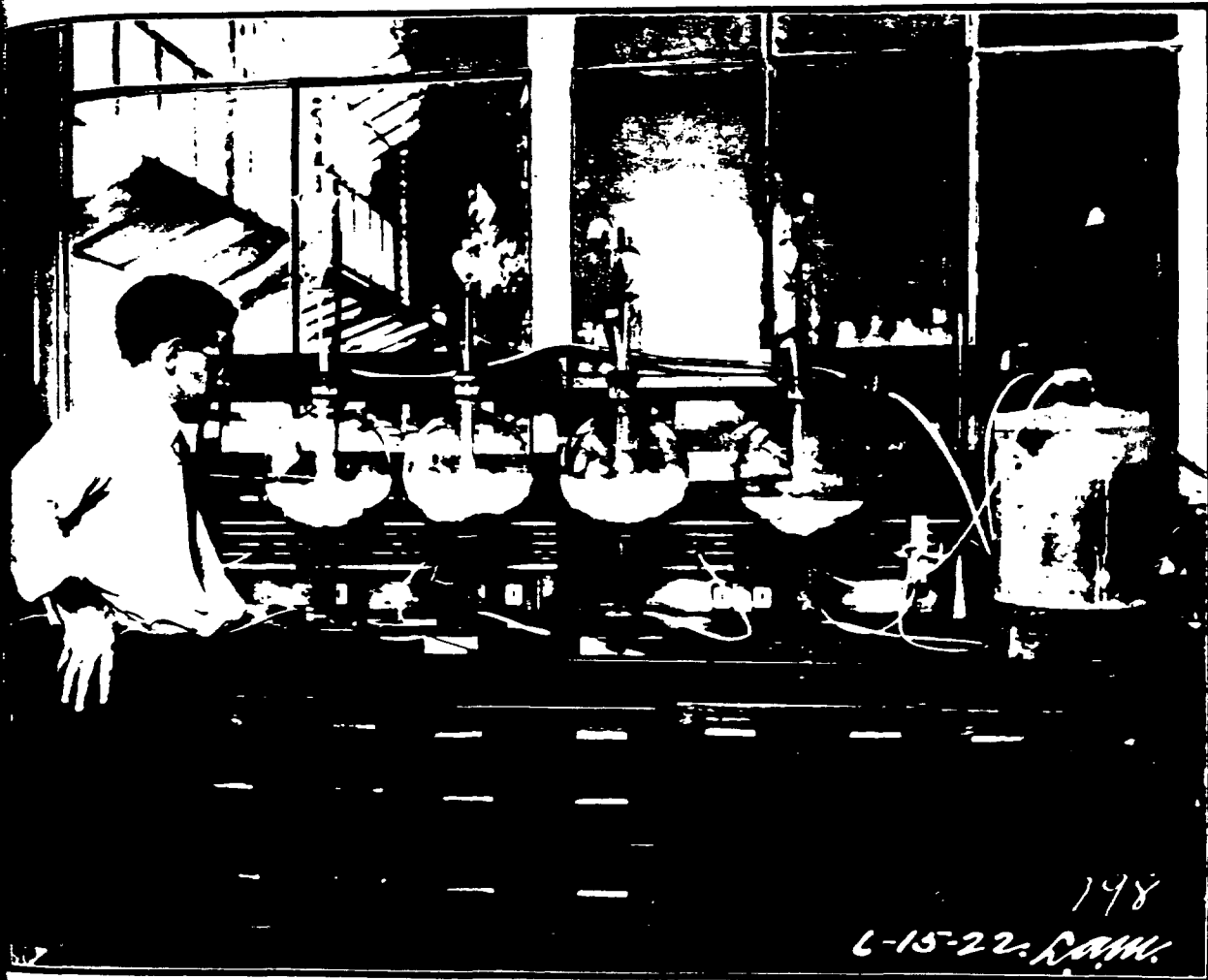


FIGURE 33

APPARATUS FOR CONVERTING TETRAETHYL LEAD INTO LEAD TRIETHYLBROMIDE,
THE COMPOUND USED IN THE FIRST ETHYL GASOLINE SOLD. THE OPERATOR
IS JAMES P. ANDREW.

Tests were made also on the stability of lead triethylbromide in gasoline solution. And again, as in the case of tetraethyl lead reported earlier, a long search was made for a material that could be added to the solution to make it decompose less readily (Record 19, page 142 et seq). But it was found that, after having been purified by fractional crystallization, lead triethylbromide dissolved in gasoline was stable enough of itself in the absence of white light for all practical purposes (Record 19, page 146).

On October 16, 1922, Messrs. A. Felix du Pont, R. G. Woodbridge, and F. W. Brading of the du Pont Company visited the laboratory to inquire whether antiknock compounds such as tetraethyl lead might possibly have any usefulness for controlling the burning rate of gun powder. They were made acquainted with the results obtained by W. H. Charch in which tetraphenyl lead and tetraethyl lead mixed with black powder apparently affected the nature of the resulting explosion in a gun in such a way that the noise was lessened. They were also supplied with a few grams of each of the following compounds (Lead Diary, 455): lead triethylchloride, lead triethylsulphate, and tetraphenyl lead.

W. H. Charch, who had worked at the laboratory during the summer of 1922, returned in October to the Ohio State University to pursue work toward his doctor's degree; and, through the patent department, a contract was made with him by which he was to work on the antiknock problem under a kind of fellowship arrangement. Under this arrangement, he made up a number of special lead compounds for test of knock suppressing effect, and began his studies of the con-

ductivity of the gases in an engine and of the effect upon it of the presence of knock and of antiknock compounds (Lead Diary, 488). He also continued the long effort to make iron carbonyl (Lead Diary, 506 and 550) which turned out finally to be unsuccessful at atmospheric pressure.

A considerable number of new materials were tested for knock suppressing effect (Monthly Report, December 30, 1922). These included several new compounds of lead, and some of tin, titanium, and gold. Several of the compounds proved to have antiknock effect, but none was superior to tetraethyl lead.

Two items of correspondence during the fall of 1922 may be mentioned. First, in early September came a letter from Harry Spears of the Spears and Riddle Company, Wheeling, W. Va., asking that when the new compound about which he had read in the August number of Motor became available his company be allowed a chance to market it. Later Spears and Riddle did become one of the earliest distributors of gasoline treated with tetraethyl lead. And, as it turned out, the sale of Ethyl Gasoline in West Virginia by Spears and Riddle had some influence in getting the Standard Oil Company of New Jersey to decide to sell it also.

Second, was a letter from F. E. Moskovics of the Nordyke and Marmon Company asking for more of the tetraethyl lead of which Mr. Kettering had previously given him a sample. Midgley wrote back telling Mr. Moskovics about the spark plug and exhaust valve problems, and suggesting that he wait for a further supply until the problem had been more nearly solved. But back came a letter from Mr. Moskovics saying, "As bad as it is, I should like to get some more."

At the du Pont Company, development work on the making of tetraethyl lead continued to go forward successfully. Within a few weeks they were getting yields by the sodium-lead process of better than 85 per cent of theory. This was accomplished by virtue of making use of the Na_2Pb_4 alloy which had come out of the work at M.I.T. (Lead Diary, 376 and 381), and of controlling the degree of alkalinity of the reaction mixture. The latter was effected by using calcium chloride to precipitate the excess of hydroxide. By the end of September a stock of 70 gallons of tetraethyl lead had been accumulated at Dayton, and this was gradually increased as the work at du Pont went forward (Monthly Report, October 4, 1922). By the middle of November, Midgley was able to report to Mr. Kettering ("Summary of Present Situation on Antiknock Material," November 20, 1922) that the production "phase of the tetraethyl lead problem seems to be pretty well solved and we have the assurance of the du Pont Company in the form of a contract that they will produce tetraethyl lead at a price that renders it quite commercial."

Further Report of Work at M.I.T.

Meanwhile, at M.I.T. work on various items, chiefly relating to methods of synthesis, was going forward. The methods of making tetraethyl studied included some not previously mentioned, such as the effort to use silicon and phosphorus in the synthesis. Some additional lead compounds were prepared also and sent to Dayton for test of antiknock effect. There was at M.I.T., too, some collaboration with Midgley in the work which he and Hochwalt did in November in the preparation of a special ethyl compound of lead,

Pb_2Et_6 , by the electrolysis of lead triethylhydroxide in alcoholic solution (Lead Diary, 481 and 483). Results of this study were later published ("A New Metallo-Organic Compound: Diplumbic Hexaethyl," Thomas Midgley, Jr., C. A. Hochwalt, and George Calingaert, J. Am. Chem. Soc., 45, 1820, 1923). And later on a great deal of work was done at M.I.T. in examining the deposits on spark plugs and valves. The Dayton laboratory cooperated in this work to the extent of supplying deposits and parts obtained by running engines on tetraethyl lead plus various corrective agents, chiefly chlorine, bromine, and sulphur. The results appeared to show that bromine owed its superiority over chlorine as a corrective agent either to more complete reactivity with lead or to yielding a more volatile compound (Lead Diary, 515, 542, and 544). But bromine was not substituted for chlorine as a corrective agent until quite some time later when it could be bought at a lower price and when events had dispelled somewhat the then current fears about the inadequacy of the supply of bromine.

The Toxicity Problem Again

There were also during the fall of 1922 some further incidents relating to the possible toxic hazards arising from tetraethyl lead. First, was a letter from Dr. Eric Krause of the Institute of Technology, Potsdam, Germany, written at the request of the men at M.I.T. (Lead Diary, 491). This was the Dr. Krause of Grüttner and Krause, who had published several papers jointly and individually on organic compounds of lead, chiefly lead alkyls. In his letter, Dr. Krause expressed the belief that the organic compounds of lead

are exceedingly dangerous. He told of the elaborate precautions which were taken in his work to guard against possible lead poisoning, and said that in spite of this he was at that time being forced to take many vacations from lead work because of damage to his health. He gave it as his opinion that the health of Drs. Grüttner and Tafel, both of whom had died some years before, had been seriously affected by their work with lead compounds.

Second, was a letter of December 20, 1922, from U. S. Surgeon General Hugh S. Cumming to Mr. Pierre S. du Pont (Letters p. 51). A member of the staff of the U. S. Public Health Service, said Dr. Cumming had been detailed to attend a meeting of the New York Section of the American Chemical Society on November 10, 1922, at which the discovery of tetraethyl lead as an antiknock compound was discussed in the lecture of the evening by Midgley. (The member of the Public Health Service staff who attended the meeting was Surgeon Norman Roberts. There is a copy of his report to Doctor Cumming, November 13, 1922, among the letters at the front of Vol. 3 of the Lead Diary.) Doctor Cumming expressed his concern about the possible hazard that would be introduced by finely divided lead in engine exhausts if tetraethyl lead should be put into gasoline.

The letter from Doctor Cumming to Mr. du Pont was sent on to Mr. Kettering, and Midgley responded to it on December 30, 1922. In his reply Midgley expressed confidence that no health hazard to the public would result, but said that the exhaust problem had not yet been investigated, partly because in engine tests made

in the Dayton laboratory up to that time it had not been possible to separate from the exhaust more than a fraction of the lead entering the engine. "We expect in the near future," Midgley concluded, "to place a small quantity of this lead compound on the market in some districts. There will not be enough lead used in the early stages of this development to present any health hazard whatsoever and during this period we propose to investigate the toxicity of these exhaust gases very thoroughly so as to determine just what the ultimate limit to the use of lead compounds actually is. We hope to secure your most hearty cooperation in carrying on this work."

What Midgley referred to in the sentence just quoted was a proposed investigation of the possible toxicity of the engine exhaust by the Bureau of Mines, he having already some time before that been in contact with Dr. A. C. Fieldner about it (Summary of Present Situation on Antiknock Material, November 20, 1922. Also correspondence with A. C. Fieldner, Bureau of Mines, October, 1922.) The possible hazard thought of here was not from tetraethyl lead itself but from finely divided lead compounds in engine exhausts. Relating to the more active tetraethyl lead itself, it may be noted that Midgley and Hochwalt had been having digestive derangements, subnormal body temperature, and reduced blood pressure, which were thought to have been caused by the too intimate contact with lead compounds that they had been having for some months past. Also in a letter of December 22, 1922, (Lead Diary, 497), Calingaert said that he and Mead were taking a little vacation for the rest of the year because they had absorbed somewhat

more lead than they ought. Shortly thereafter the men at M.I.T. were under treatment by Doctor J. C. Aub of the Harvard Medical School, although continuing their work. Also, as is related below, Midgley went to Florida in February for a month of rest.

Nichols Medal Award to Midgley

An outstanding event of December, 1922, was the award to Midgley by the New York Section of the American Chemical Society of the William H. Nichols Medal. This award was for the two years 1921 and 1922 and was made for the work reported in the paper on "The Chemical Control of Gaseous Detonation with Particular Reference to the Internal-Combustion Engine," which had been presented before the American Chemical Society at Pittsburgh in September and published in Industrial and Engineering Chemistry in October. Among the many letters of congratulation on the award that Midgley received was one from R. E. Wilson, then at the Standard Oil Company of Indiana, in which was expressed the belief that the Nichols Medal was just the beginning of the recognition Midgley would receive for this work. And that opinion turned out to be a correct one. Among these later items of recognition was the award of the Perkin Medal to Midgley in 1937 by the American Section of the Society of Chemical Industry; of the Priestley Medal by the American Chemical Society in 1941, highest honor the Society can confer; and of the important Willard Gibbs Medal by the Chicago Section of the Society in 1942. At the presentation of the Perkin Medal in New York on January 8, 1937,

R. E. Wilson, now by that time promoted to President of the Pan American Petroleum and Transport Company, made a fine address about Midgley and his accomplishments and about Wilson's own association with him (Ind. Eng. Chem., 29, 239, February, 1937).

CHAPTER XI

SALE OF ETHYL GASOLINE TO THE PUBLIC BEGINS

In preparation for the sale to the public of gasoline treated with tetraethyl lead, a name for the product was chosen and arrangements were made with a gasoline retailer to sell it. The name selected was "Ethyl Gasoline," the suggestion having been made by Mr. Kettering from the ethyl in tetraethyl lead on which it was based. At the outset the name was however customarily abbreviated to "Ethyl Gas." Arrangements were made with The Refiners Oil Company, an independent gasoline distributor in Dayton of which Willard Talbott was manager, to experiment with selling the product in one of its stations, that located at Sixth and Main Streets. There one dispensing pump and the underground tank with which it connected was set aside for the new product.

At the beginning of February, 1923, the experimental sale was started. The storage tank contained "New Navy" gasoline to which had been added lead triethylbromide and carbon tetrachloride in the amount of 7 grams of the former and 1.5 grams of the latter per gallon. The addition had been made by dissolving in benzol, to a total volume of 4 gallons, enough of the lead triethylbromide and carbon tetrachloride to treat 1,000 gallons of gasoline, and then blending that solution with the gasoline by running it in along with the stream of gasoline as it went into the storage tank from the tank wagon.

The retail prices of the four gasolines sold at the station at the outset of the sale were as follows:

"New Navy" gasoline	20 cents per gallon
Aviation (high test) gasoline , . . .	24
Benzol gas, 40% benzol-60% gasoline .	27
Ethyl Gasoline , ...	24

The prices of all except the Benzol gas were raised 1 cent a gallon each on February 10, and again on February 24.

The product was advertised there by two signs about 5 ft. X 1 ft. in size placed above the driveway as shown in the picture of the station, Figure 39, page 197, and lettered as follows:

"ETHYL GAS Antiknock Gasoline, Product of the General Motors Research Corporation"

There was also an illuminated face at the top of the vending pump bearing the words, "ETHYL GASOLINE" in the center with "The General Motors Research Corporation" arranged in a circle surrounding it.

At 10 o'clock the first morning not a single sale of the new product had been made. Then the research laboratory representative on duty at the station began to approach customers as they came into the station telling them about the new product, without exaggerating its merits. In that way 70 gallons were disposed of during the succeeding three hours. The first customer for the product bought only 2 gallons, saying that he would take a chance on that much (Letters, page 4). After the evening newspapers came out bearing a news item about the new product (copy in Appendix VIII), the sales showed a steady increase. And, by the time the meters were read at the customary time the next morning, 10 A.M., 408 gallons had been sold.

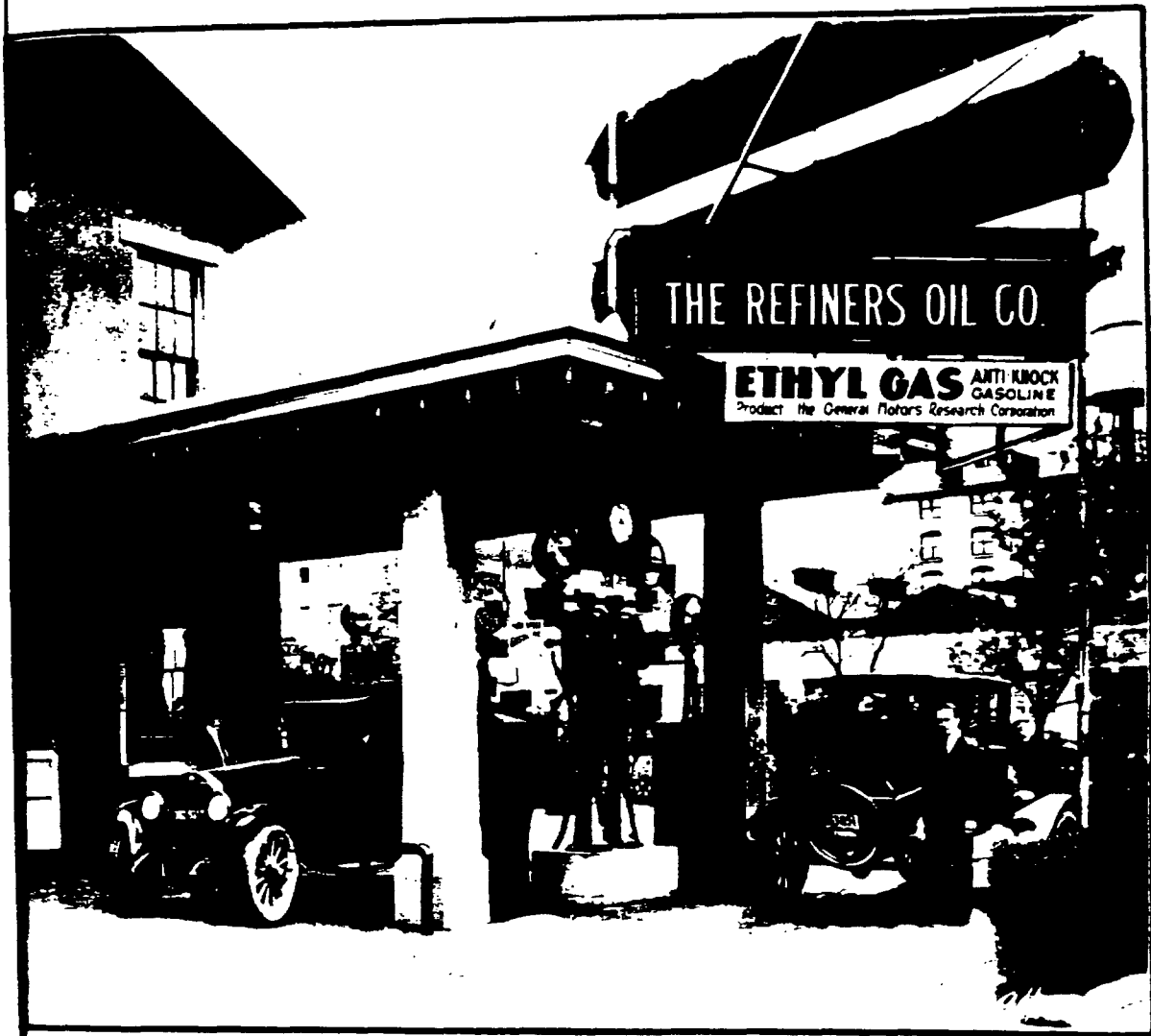


FIGURE 39

CONTEMPORARY PHOTOGRAPH OF THE FIRST STATION IN WHICH
ETHYL GASOLINE WAS SOLD TO THE PUBLIC. IT WAS DIS-
PENSED THROUGH THE SECOND PUMP FROM THE RIGHT.

The representatives of the research laboratory on duty at the station were R. D. Wells and A. R. Brubaker. One or the other of these men was there all the time during the early weeks of the experimental sale. Besides answering questions and talking to customers about the new product when opportunity offered, they kept a record of each sale in such a way as to give the following items of information: date, gallons purchased, license number of car. These records were kept by a special system which enabled them to tell at a glance whether any customer had bought Ethyl Gasoline before. And here it may be noted that the customer to whom the first sale was made, saying that he "would take a chance on 2 gallons," bought Ethyl Gasoline twice again within a week.

On the second day, the sales of Ethyl Gasoline jumped to 838 gallons; and on the next day following, which was Saturday, to 1,057 gallons. From that point on the general trend during February was downward. This may be seen from the graphical sales record for February, Figure 40, page 199, which shows also, for comparison, the sales of the other gasolines distributed at the station. Aside from the customary falling off in the case of a product that was not advertised, there was the factor that on February 4 the weather got extremely cold and stayed cold almost throughout the month. This caused some complaints about hard starting from users of the new gasoline, for the base of New Navy gasoline was of low volatility, even for that time. The total amount of the new product sold in February was 8,375 gallons. March sales were down to 4,175 gallons. In April there was an increase again to 6,187 gallons, although on one day in April, the 13th, only 47 gallons of Ethyl

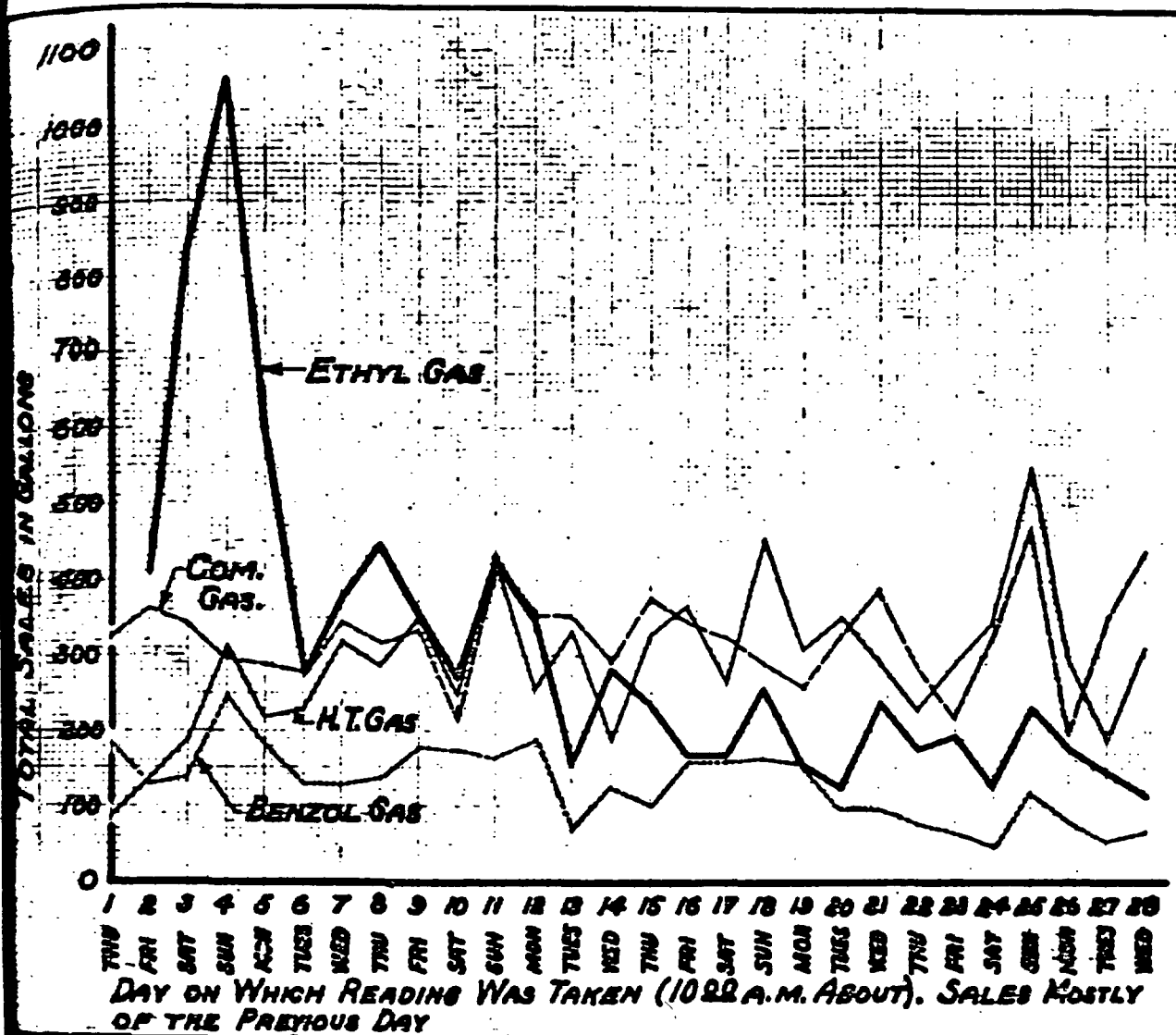


FIGURE 40

DAILY SALES OF ETHYL GASOLINE AT THE PIONEER STATION DURING THE FIRST MONTH, FEBRUARY 1923. SALES OF OTHER GASOLINES AT THE STATION ARE PLOTTED ALSO FOR COMPARISON.

Gasoline were sold.

Starting about February 3, Midgley was absent for more than a month, he having taken a trip to Miami Beach, Florida, for a rest. This he did in an effort to get rid of the lead effects which he had suffered from too intimate contact with the stuff during the experiments of the previous several months, chiefly on methods of making tetraethyl lead. The symptoms of his difficulty were the subnormal temperature and the reduced blood pressure spoken of previously. The outcome of his rest he reported in a letter written to R. E. Wilson on March 15 after his return, as follows: "I had a very fine month in the south. . . . I am much improved in health so far as the way I feel is concerned, but my temperature is not yet back to normal."

On February 7 Midgley wired Boyd from Miami Beach: "Suggest you try three cubic centimeters tetraethyl lead and two cubic centimeters carbon tetrachloride per gallon in the Buick for two thousand miles." The next day he sent a supplementary wire saying: "Reason for wishing to run Buick on tetraethyl lead is to replace the bromide with it if humanly possible to do so and as quickly as possible. This would mean quick production and reduced cost both of which are needed." This suggested car test of tetraethyl lead and carbon tetrachloride was not a "wild stab." It was based upon the results of a recent series of the laboratory engine tests being conducted by Boyd and E. E. Gold (Record 19, 145 et seq.). The Buick car test was run for a distance not of 2,000 miles but of 8,500 miles, at the end of which the spark plugs "were still in

satisfactory operating condition, the electrodes being burned to only a small degree and the porcelains being dark but whole" (Monthly Report, March 31, 1923).

First Change in Formula

The result of the test just mentioned was that during March, 1923, the composition of Ethyl fluid was changed from lead triethyl bromide plus carbon tetrachloride to the following:

Tetraethyl lead 3 parts by volume
Carbon tetrachloride . . 2 parts by volume

It was expected that this mixture would have the following advantages over that in use initially:

1. About 25 per cent increase in antiknock effect
2. Lower cost
3. Greater solubility
4. Lesser tendency to decompose

The use of this composition was continued until about October 1, 1923; but because of the troubles experienced with it, which will be described later, carbon tetrachloride was then replaced with another compound of chlorine.

At the end of February, 1923, Boyd went to Chicago at the request of Mr. Kettering and made arrangements with Mr. Harry Croninger of the Yellow Cab Manufacturing Company to furnish them enough of the antiknock compound or Ethyl fluid to treat 500 gallons of gasoline per day. It was arranged that the compound was to be sent to three of the Yellow Cab Companies: Chicago, Cincinnati, and Buffalo. The use of the compound by the Yellow Cab companies was however discontinued after a short time.

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Nichols Medal Conferred

Another one of the several problems with which Boyd was struggling during Midgley's stay in Florida was the preparation of a paper to serve as Midgley's address on the occasion of his receipt of the Nichols Medal, which was to be presented to him at the Chemists' Club in New York on March 9, 1923. It was intended, of course, that this should be a scientific paper worthy of the occasion. And so the assembling of data for the paper was begun in December right away after word came that the medal had been awarded. The hope was to use some of the scientific data accumulated in the search for a practical antiknock compound, particularly the matter showing the relationship of antiknock effect to position in the periodic system, as already shown in Figures 25, 26, and 27, pages 114, 115, 116. These charts were in fact prepared at that time and for this specific purpose. A strenuous effort was made to get the further experimental data needed to round out the story which Midgley wished to present. On February 5, Boyd wrote to Midgley: "I am devoting my whole time to the paper."

Within a few days a copy of a tentative draft was sent down to Midgley and simultaneously one was dispatched to J. W. Morrison for review from the patent standpoint. Midgley seemed well enough pleased with the product, but Morrison took a different view. All the tables, all the figures, all reference to specific compounds, and much of the text must come out, he said, leaving really nothing in the way of a scientific paper. Upon receipt

of this word, Midgley wired Morrison his contrary view and also wired Boyd, telling him to "take this stand and fight." But after conferences, letters, and more telegrams the upshot of the matter was that for his Nichols Medal address Midgley had to give what was pretty much a repetition of the matter that had been presented in Pittsburgh to the American Chemical Society. The matter published afterwards was consequently quite brief and contained very little that was new (Ind. Eng. Chem., 15, 421, April, 1923). The data so laboriously assembled for the paper was not then published until 14 years later, when it was included in Midgley's Perkin Medal address (Ind. Eng. Chem., 29, 239, February, 1937).

Midgley went directly from Florida to New York for the meeting at the Chemists' Club on March 9 at which the Medal was presented. The various demonstrating equipment needed had been sent on in advance. Everybody was so busy during the day getting it into shape that no one thought to inquire whether a lantern had been provided to show the slides, as had been duly requested in advance. But after the dinner and just before the meeting it became known that there was no lantern. Because a lantern was really quite necessary to the presentation, there was much scurrying around by the men who had the meeting in charge. Finally a lantern with its operator appeared, but not until after Dr. Wilder D. Bancroft, who had been delegated to speak on the medalist and his accomplishments, had talked for a solid hour to fill in the time. From that point on however the meeting went off well. At any rate, Midgley retained the reputation for showmanship which he had acquired in the meeting at Pittsburgh. In the absence of Dr. William H. Nichols on a trip

abroad, the presentation of the medal was made by Dr. Charles H. Herty, former president of the American Chemical Society, and at that time editor of Industrial and Engineering Chemistry.

Personnel of Fuel Section, April, 1923

The personnel of the Fuel Section of the General Motors Research Corporation in April, 1923, was as follows:

Thomas Midgley, Jr.
James P. (Jimmy) Andrew
F. E. (Fred) Aseltine
A. M. Babitch
W. G. (Doc) Berry
T. A. (Tab) Boyd
A. R. (Art) Brubaker
Ruth Dornbusch
H. S. Gerdes
W. K. (Gilk) Gilkey
C. P. (Pat) Harding
C. A. (Ted) Hochwalt
R. N. (Bob) Janeway
R. D. (Russ or Shorty) Wells

Of the above persons not previously accounted for in this history, Fred Aseltine and A. M. Babitch were working on carburetor research and on producing a fuel system for a kerosene-burning tractor.

Aseltine is now at Delco-Remy and Babitch is at the A. C. Spark Plug Company. Ruth Dornbusch was then secretary of the Fuel Section, and is now at the Thomas and Hochwalt Laboratories in Dayton. H. S. Gerdes was working with Harding on the mechanical and the engine-testing endeavors. Bob Janeway was working not on Ethyl Gasoline but on a project called "Theoretical Study of Combustion." He is now at the Chrysler Corporation.

CHAPTER XII

GENERAL MOTORS CHEMICAL COMPANY

In the Monthly Report for March, 1923, occurs the following:

"The arrangements for distributing Ethyl Gas Fluid on a larger scale which are in charge of Messrs. Sloan, Mott, Kettering and Midgley are being rapidly rounded into shape. An apparatus for metering Ethyl Gas Fluid into gasoline in the proper proportion is being developed."

A part of these arrangements was the founding of the General Motors Chemical Company, which was incorporated under the laws of Delaware on April 23, 1923, to take over the manufacture and sale of Ethyl fluid. The total authorized capital stock of this new corporation was \$100,000. The directors were:

Charles F. Kettering
Thomas Midgley, Jr.
Charles S. Mott
Alfred P. Sloan, Jr.
Earle W. Webb

At the first meeting of the directors held in Detroit on May 3, 1923, the following were elected officers of the General Motors Chemical Company:

President	Charles F. Kettering
Vice President	Thomas Midgley, Jr.
Secretary	T. S. Merrill
Asst. Secretary	F. O. Clements
Treasurer	M. L. Prentis
Asst. Treasurer	H. G. Guimaraes
Comptroller	Frank Turner
Asst. Comptroller	H. G. Guimaraes

On March 29, 1923, Midgley sent to W. F. Harrington of the du Pont Company a wire which contained the following:

"It was officially decided this morning to go ahead with the antiknock program as rapidly as possible. Consequently this constitutes official notification that you are to get out one hundred gallons of tetraethyl lead per day as soon as possible."

In the effort to extend the outlets for Ethyl gasoline, Midgley visited on April 3 and 4, 1923, three of the eastern oil companies: the Atlantic Refining Company, the Tide Water Oil Company, and the Standard Oil Company of New Jersey. All showed interest, but none made any definite commitments (Letters, page 33). Atlantic, through Dr. T. G. Delbridge, said that when convinced of the merit of the compound they would like to have Pennsylvania and Delaware as exclusive territory for a period of five years. Tide Water, through Byron Benson, said they would like to have New York City as exclusive territory for a year. But neither company sold Ethyl Gasoline until some years later.

First Knowledge of Research on Lead at Standard of New Jersey

At the Standard Oil Company of New Jersey, Frank Howard was the man seen. His company, he said, would like to treat their entire production of gasoline with an antiknock agent at a cost of not more than one cent a gallon and without telling the public anything about it. Further Mr. Howard informed Midgley that they were making application for a patent on making tetraethyl lead by the sodium-lead method using ethyl chloride under pressure as the alkylating agent, and that they were sure they could make tetraethyl lead for six dollars per gallon--less than one-fourth the price the du Pont Company was then being paid for it at two dollars a pound. The process to which Mr. Howard referred, as became known later, was

developed by Dr. C. A. Kraus at Clark University (Dr. Kraus is now at Brown University) with the assistance of Dr. C. C. Callis. The work of Doctor Kraus was subsidized by Mr. Howard's Company, and was begun after it became known that tetraethyl lead was a practical antiknock agent, although in past years Doctor Kraus had done a great deal of work in investigating the making and properties of alkyl compounds of other metals. (For his extensive work on the alkyl metals, including that on how to make tetraethyl lead by the use of ethyl chloride, Dr. Kraus was awarded the Nichols Medal for 1923, the year following the award to Midgley.)

It was at this time also that a definite suggestion was made that General Motors and Standard of New Jersey join hands to commercialize Ethyl. In a memorandum of April 9, 1923 (Letters, p. 33), Midgley said this about it:

"Mr. Howard suggested that the General Motors and Standard Oil Company of New Jersey pool interests in regard to antiknock gasoline and Mr. Howard felt that his patent for making tetraethyl had opened the door to such negotiations. It cannot be denied that from our standpoint it would be a very desirable thing to have the New Jersey Company lined up with us."

The ideas advanced here were later to result in the formation of the Ethyl Gasoline Corporation. But, although there followed other meetings with men in the Standard Oil Company of New Jersey, this did not come about until several months later (in August, 1924), after Ethyl Gasoline had been on the market for some considerable time. A previous attempt to set up a joint arrangement between the Standard Oil Company of New Jersey and the General Motors Research Corporation has already been mentioned (page 120).

Standard of Indiana Becomes First Large Distributor

In his search for a wider outlet for Ethyl Gasoline it was natural that Midgley should see also R. E. Wilson, who had gone to Whiting as director of research of the Standard Oil Company of Indiana. As a result of these contacts with Wilson, with Dr. William M. Burton, then president of the Standard Oil Company of Indiana, and later on with vice-president Allan Jackson, Wilson was sent to Dayton to observe the sale of Ethyl Gasoline in the single station from which it was then to be had.

After lunch at the Engineers' Club, Midgley and Wilson went over to the filling station and, as luck would have it, they saw there a string of five cars lined up waiting turns at the one Ethyl pump. There was much joking then between Wilson and Midgley about how perfectly Midgley had staged the affair, and they still recall it on occasion. But nevertheless the unusual rush of demand that developed just then, although purely accidental, may well have had an influence on the decision under which in the latter part of 1923 the Standard Oil Company of Indiana became a distributor of Ethyl Gasoline. They did so under an agreement which gave them the exclusive right to sell the product in the eleven states of their territory for a period of eighteen months.

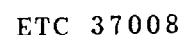
This having been the first one of the major oil companies to take on the sale of Ethyl Gasoline, it was of course a very cheering and an extremely important event. Even the prospect of it called for a conference at the du Pont Company, June 16, 1923, on how to step up the projected production of 100 gallons of tetraethyl lead

per day to the larger amount which it was expected this promising new contract would call for when it went into effect.

The further activities relating to sales in 1923 resulted in extending the distribution of the initial distributor, the Refiners Oil Company, to Cincinnati, where sale of Ethyl Gasoline was begun in the early summer. Spears and Riddle Company, the West Virginia jobbers, already spoken of, also became distributors in 1923, with "Fleet-Wing Ethyl." How the number of distributors then grew in the years following is shown in Figure 41, page 210. That none were added in 1925 was due to the poisoning episode of November, 1924, as related further on. This episode resulted in the product being taken off the market from the summer of 1925 until early 1926, while it was undergoing the searching investigation by the Surgeon General's Committee to be described later. But Ethyl Gasoline came out of that investigation with a clean bill of health. (There is a slight error in the list of distributors of Ethyl gasoline, Figure 41, in that Gulf Refining Company, not mentioned there, was distributing Ethyl gasoline in 1924 in certain states.)

First Efforts to Measure the Lead Requirements of Gasolines

It was for the Standard Oil Company of Indiana that the first regular work was begun on rating gasolines or on measuring the amount of tetraethyl lead needed per gallon to get a given degree of freedom from knock. The first of this work was done in April, 1923 (Record 21, page 2). And on July 10 several samples of gasoline from the Standard Oil Company of Indiana were rated. There



was at that time no definite standard fuel, of course; but the gasolines "were compared with our stock gasoline by determining roughly the amount of PbEt_4 (tetraethyl lead) necessary to add to each sample to make it equivalent in knocking tendency to 3 cc. PbEt_4 per gal. of our gasoline" (Record 21, page 33). The matches were made by comparing the intensity of the light in the lamp in the circuit of the bouncing-pin apparatus. Also 20 per cent of kerosene was added to each gasoline after it had been treated with the given amount of tetraethyl lead. This was done to produce a suitable degree of knock in the engine. The ratings as thus made were as follows:

<u>Source of Sample</u>	<u>cc. Tetraethyl Lead Per Gallon to Make Sample Equivalent to Stock Gasoline plus 3 cc. Tetra- ethyl Lead per Gallon</u>
Whiting	3
Sugar Creek	2.75
Wood River	2.5
Casper, No. 1	3
Graybill	2.5
Casper, No. 3	2.5
Laramie, No. 2	2.5

Thus there was at this time no standard fuel of definite degree of freedom from knock and nothing more than an elementary method for matching it had been developed as yet. But some of the later improvements in respect to knock rating and reference fuels have already been mentioned in the section on "Bouncing-Pin Indicator Developed," beginning on page 95.

Advertising of Ethyl Gasoline Begins

It was in the summer of 1923 that the first advertising of Ethyl Gasoline was done. The initial program was put into the

nands of the Campbell-Ewald Company of Detroit, who assigned Webb Taylor to the job. The Ethyl emblem or trade mark design was suggested and sketched then by Henry Ewald himself. After it had been drawn up and approved, a series of newspaper advertisements were prepared to be used first in Cincinnati and Dayton. A copy of the first one of the advertisements put into the Cincinnati papers is included as Figure 42, page 213. The emblem as designed by Mr. Ewald is reproduced at the top in Figure 42. It was printed in colors, where that was possible, among which yellow was prominent, and was placed on the illuminated face at the top of filling station pump, as may be seen in Figure 48, page 221. When the ads first appeared in Dayton in May, 1923, the sales of Ethyl Gasoline in the one filling station at which it was then being distributed in Dayton rose from 1,796 gallons the week before the advertisements appeared to 2,666 gallons the week they were run first (Monthly Report, May 29, 1923). This later increased to 3,500 gallons per week for the one station (Monthly Report, July 2, 1923).

Mixing Meters or "Ethylizers"

Providing an apparatus for metering the Ethyl fluid into the gasoline, as before mentioned, was one of the important activities begun in the spring of 1923. Development work in this field continued for more than a year, and the progress of the endeavor can be followed to some degree by the series of photographs included as Figures 43 to 48 following. The first model of these devices, called "ethylizers" and later mixing meters, is shown in Figure 43, page 214. The Ethyl fluid was then supplied to the meter in a 5-gallon sheet steel container which was inverted in a chicken-feed

GENERAL MOTORS

introduces

ETHYL GAS

A Better Fuel for Motors

For years, in the great General Motors Laboratories, extensive experiments and exhaustive tests have been carried on to provide a fuel of greater efficiency than ordinary gasoline. And now General Motors is able to offer motorists this fuel whose marked superiority has been tried and proved—Ethyl Gas.

Since the earliest days of the automotive industry, engineers have known that it would be possible to get greater power and economy from the use of petroleum fuels in internal combustion engines. If compression could be increased without a very objectionable fuel knock developing in the engine.

This "knock" is an audible snap of the piston which can be felt and very

often this same inefficiency in fuel combustion is present when no knock is heard.

Ethyl Gas readily eliminates the "knock" from automotive engines and as a result of removing this knock, with its attendant loss of power, waste of gasoline and carbonization of cylinders—Ethyl Gas not only produces greater power from every drop of fuel, but also adds to the economy of maintaining and the pleasure of operating an automobile.

Ethyl Gas is produced by the General Motors Chemical Company of Dayton, Ohio—a subsidiary of the General Motors Corporation. As a product of such a company, and as a product of General Motors—Ethyl Gas can be received by the trade and the public with the utmost confidence.

Ethyl Gas can be obtained at the following filling Stations in Cincinnati

Gas Station Ave. & College Street	Union Ave. & Bridge Street
Madison Road & Cincinnati Street	High & Central Avenue
Wayne & New Street	Clinton & Montgomery Road
Reading Road & Main Street	Winton Road between 4th & 5th

General Motors Chemical Company, Dayton, Ohio
Division of General Motors Corporation

FIGURE 42



FIGURE 43

FIRST OF THE SERIES OF "ETHYLIZERS" OR MEANS FOR
METERING ETHYL FLUID INTO GASOLINE AS IT WAS
BEING PUMPED INTO THE CUSTOMER'S TANK. ONLY A
FEW OF THIS FIRST MODEL WERE BUILT AND THOSE WERE
USED IN CINCINNATI ONLY.

reservoir in the body of the unit. At the top was a gasoline meter and a bucket wheel for putting the fluid into the gasoline at the proper rate as it ran out of the meter into the hose. These first meters were used only in Cincinnati, and they were soon changed to the next model pictured in Figure 44, page 216.

This new device was greatly simplified and cheapened over the first model. It consisted of a graduated sight glass placed above the hose coupling at the top, and a reservoir and manually operated pump below by means of which the desired amount of Ethyl fluid was elevated to the sight glass just before delivery of gasoline to the customer. The Ethyl fluid was now contained in a 5-liter sheet steel can called an "amyliter." From the sight glass the fluid automatically entered the stream of gasoline as it passed through the hose to the customer's fuel tank. The visible feature was thought to be an advantage from the viewpoint of the customer by enabling him to see that he was getting the proper amount of Ethyl fluid and from the viewpoint of the General Motors Chemical Company by making the customer one of its inspectors. This form of mixing meter was patented (U. S. 1,544,922, Thomas Midgley, Jr., July 7, 1925). One of these devices installed in an actual filling station is shown in Figure 45, page 217. This was the station of the Refiners Oil Company at the corner of Far Hills Avenue and the Cincinnati Pike in Oakwood, suburb of Dayton. and was the second station through which Ethyl Gasoline was sold in Dayton. Figure 46, page 218, is a copy of the inside spread of a leaflet prepared by the General Motors Chemical Company for the Standard Oil Company of

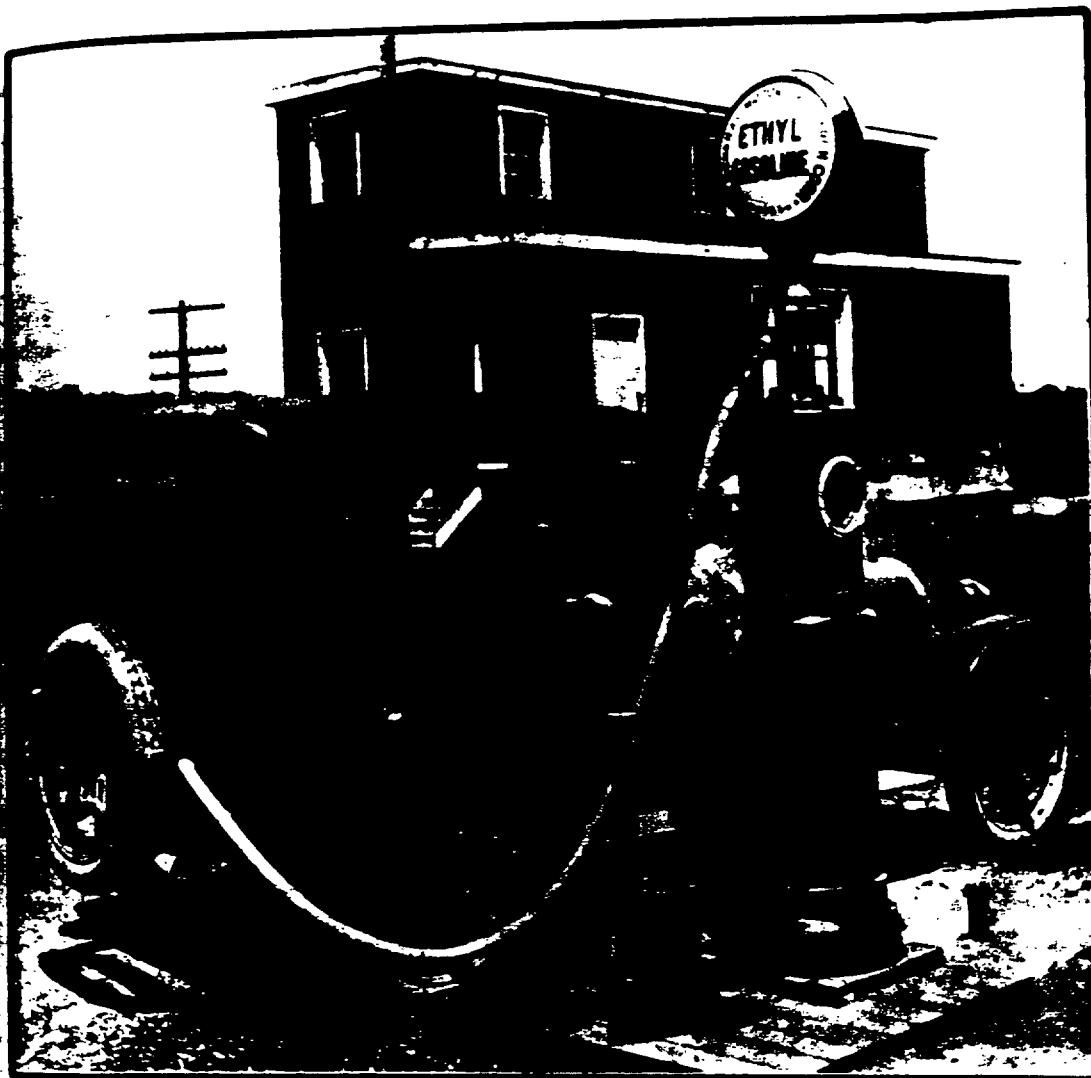


FIGURE 44

SECOND MODEL OF MIXING METER DEVELOPED IN THE SUMMER OF 1923. THIS MODEL WAS SIMPLER THAN THE FIRST, AND IT HAD AS ITS SPECIAL FEATURE A SIGHT GLASS FROM WHICH THE CUSTOMER HIMSELF COULD SEE THE ETHYL FLUID ENTERING THE GASOLINE AS IT WAS BEING PUMPED INTO HIS TANK.



FIGURE 45

A FILLING STATION WITH THE SECOND MODEL OF MIXING METER
INSTALLED IN IT. THIS STATION WAS THE SECOND ONE IN
WHICH ETHYL GASOLINE WAS SOLD IN DAYTON.

How Ethyl Red Crown is sold

Drive your car to a Standard Oil Company (Indiana) service station. Ask the attendant for Ethyl Red Crown. He will serve you from a gasoline pump through the regular hose. This simple method of supplying Ethyl Red Crown is made possible by a device called the Ethylizer.

The Ethylizer

The Ethylizer is a device designed by the General Motors Chemical Company, which automatically mixes the Ethyl Fluid with gasoline to make Ethyl Red Crown. This device, shown in the illustration, is attached to the ordinary gasoline pump. It contains a graduated glass tube, in which the filling station attendant pumps a sufficient quantity of the Ethyl Fluid to mix with the amount of gasoline asked for by the customer. This tube is in plain sight of the customer, so it makes visible the supply of Ethyl Fluid, thus offering protection and a guarantee to the purchaser. The proper quantity of Ethyl Fluid is pumped into this glass tube, then the station attendant pumps the regular quantity of gasoline from the gasoline pump which, as it flows through the hose into your car, is automatically mixed with this Ethyl Fluid so that it is finally deposited into the

tank of your car properly mixed, full-powered Ethyl Red Crown Gasoline.

In some cases where the sales of Ethyl Red Crown are very large, an entire tank and pump are devoted to its use, and it is therefore put into the owner's car from a regular gasoline pump without an Ethylizer attached. In either case the car owner is fully assured that he is purchasing genuine Ethyl Red Crown.

Coloring

Upon observing the Ethyl Fluid flow into this glass tube, you will notice that it has a wine color. This coloring matter is put into the fluid for your protection so that it may be easily recognizable. Of course, when the very small amount of Ethyl Fluid required to mix with gasoline to make Ethyl Red Crown is so mixed, the dilution affects this color so that when Ethyl Red Crown flows into the tank this wine color is very much lighter than it appears when the Ethyl Fluid is standing in the glass tube.

Inspection

The Ethylizing devices that are attached to the gasoline pumps at the service stations are regularly inspected by representatives of the General Motors Chemical Company.

These inspections are to see that the Ethylizer is kept continually in perfect working order. Ethyl Fluid is delivered in special cans to the service stations by the General Motors Chemical Company.

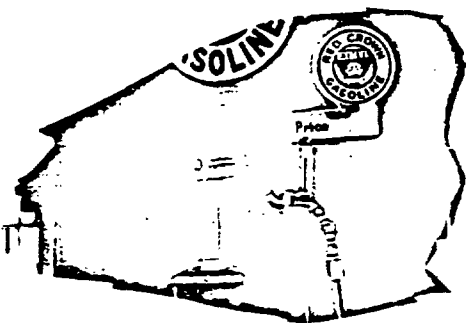


FIGURE 46

CENTER SPREAD OF FOLDER PREPARED BY THE GENERAL MOTORS CHEMICAL COMPANY FOR THE FIRST LARGE DISTRIBUTOR OF ETHYL GASOLINE, THE STANDARD OIL COMPANY OF INDIANA, EXPLAINING HOW ETHYL GASOLINE WAS BEING SOLD IN 1923.

Indiana. The text explains how Ethyl gasoline was then delivered to the customer by means of the sytem pictured in Figure 44.

Soon another change in the ethylizer or mixing meter was made to the device pictured in Figure 47, page 220. A later model of the same meter, designed for production at Delco, is shown in Figure 48, page 221, as it was mounted on the gasoline pump with direct connection to the gasoline hose. In this modification, the Ethyl fluid was contained in a one-liter sheet steel can called a "methylliter" inverted in the top portion of the mixing meter itself. It was then metered into the sight glass in proper amount by turning the crank which is visible in the pictures. There was a counter connected to the crank to serve as a check on the station operator. The steel "methylliter" cans and the method of boxing them for shipment is shown in Figure 49, page 222.

One of the troublesome problems met with in connection with the gravity-feed type of mixing meter, such as is pictured in Figures 47 and 48, was leakage or creeping of the Ethyl fluid through the valves and even through an apparently tight joint made by two metal surfaces in contact, in spite of the fact that a gasket was employed. But, as a result of considerable experimentation, it was discovered that a film of the material called "carbaloid" not only sealed the valves and joints against leaking of the Ethyl fluid, but also served to lubricate the rotary valve in the meter (Monthly Report, November 1, 1923).

The ethylizers or mixing meters were put into the hands of distributors of Ethyl Gasoline under an arrangement by which they

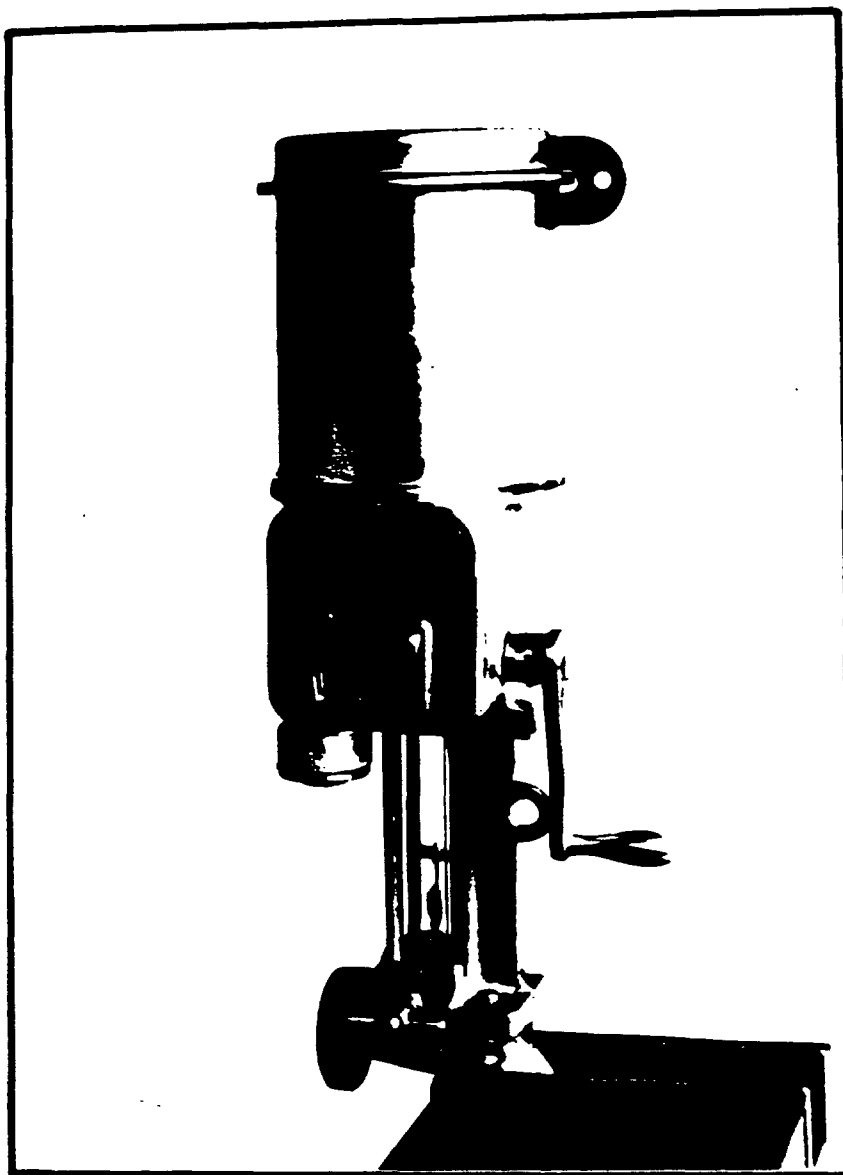


FIGURE 37

THIRD MODEL OF MIXING METER, DEVELOPED IN 1923.
THIS MODEL DID AWAY WITH THE PUMP AND DEPENDED
UPON GRAVITY FEED THROUGH A METER OPERATED BY
THE CRANK SHOWN. THE SIGHT GLASS WAS RETAINED.

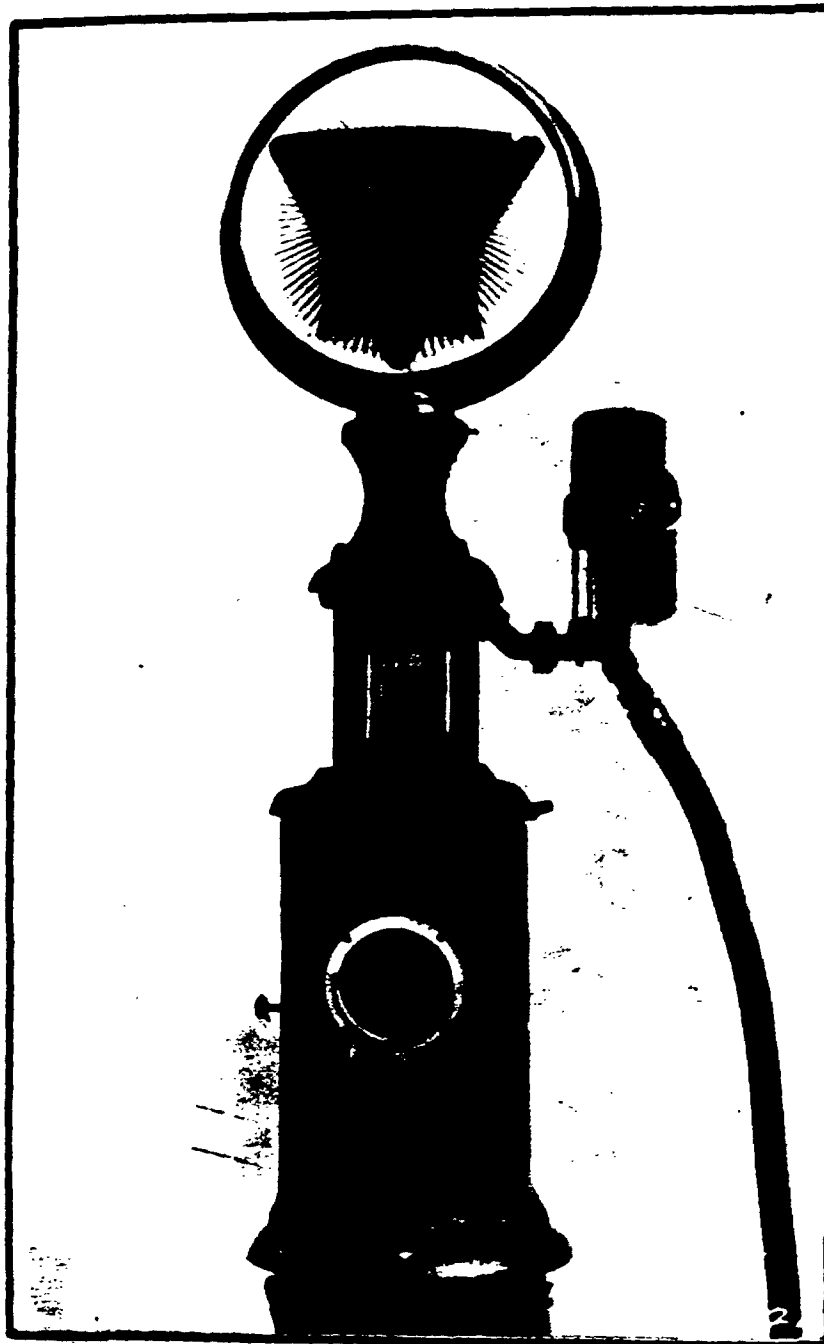


FIGURE 48

MODIFIED FORM OF THE THIRD MODEL OF MIXING
METER, AS DESIGNED FOR QUANTITY PRODUCTION,
SHOWN IN PLACE ON A GASOLINE PUMP.

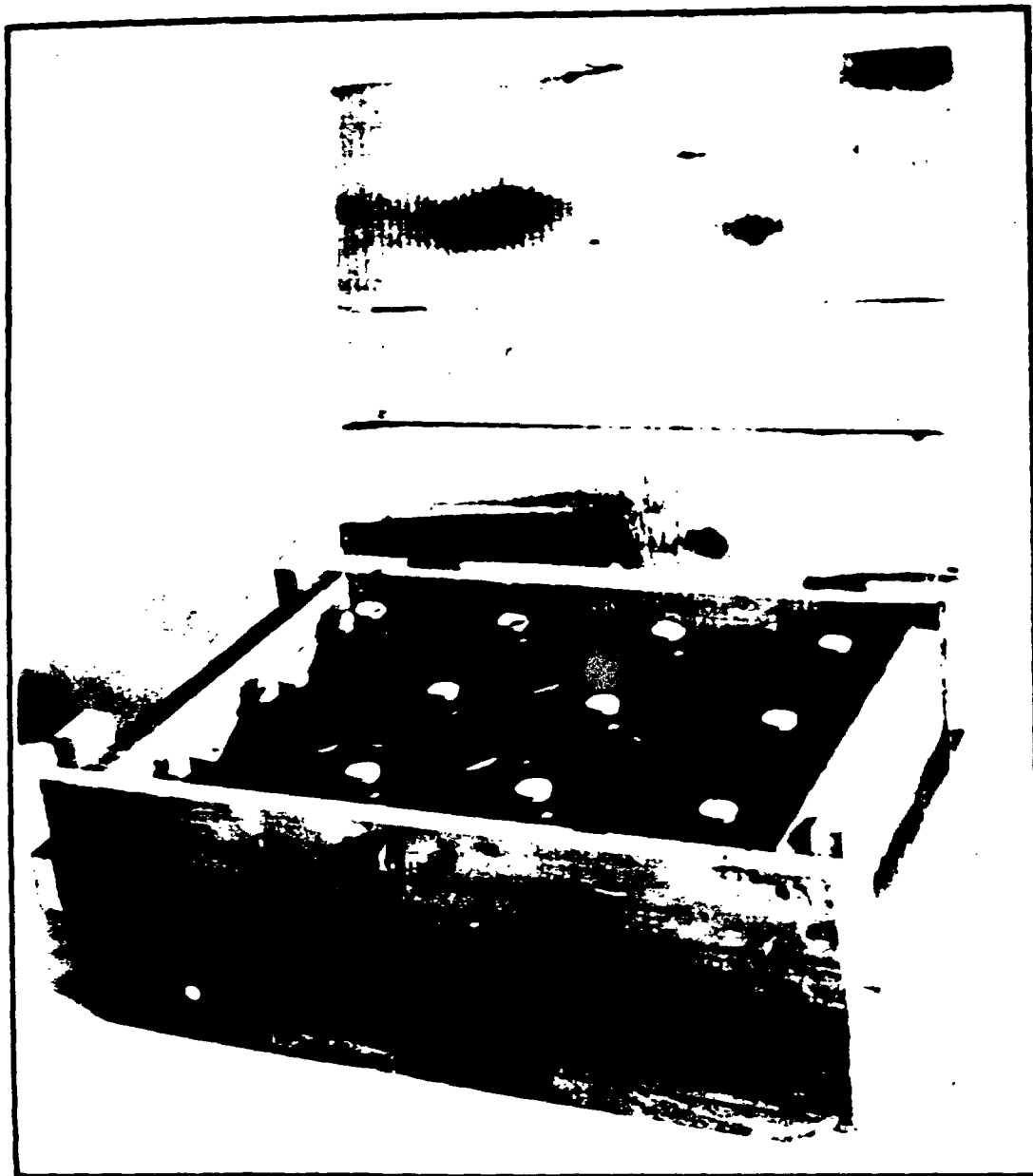


FIGURE 49

ONE-LITER STEEL CONTAINERS FOR ETHYL FLUID, CALLED
"METHYL TERS," SHOWING HOW THEY WERE PACKED FOR
SHIPMENT, 12 IN A CASE.

remained the property of the General Motors Chemical Company. But for each ethylizer received the distributor paid to the Company \$30 in the way of a deposit on, or rental for, the use of the machine.

The problem of blending the Ethyl fluid and packing it in the containers in which it was shipped to the filling stations was another one that had to be met. The first plant for doing this was built in the southwest corner of the room in the laboratory marked "Motor Room" in Figure 16, page 68. The capacity was 160 gallons of Ethyl fluid per day. Elementary precautions in respect to ventilation and handling to prevent poisoning hazard were incorporated, but these were greatly improved in similar plants built later. This first blending and canning plant was put into service about August 1, 1923, and was operated by R. D. Wells,

As illustrations of later developments in the blending and packaging of Ethyl fluid the pictures, Figure 50 and 51, pages 224 and 225, are included. The machine shown in Figure 50 was developed in the laboratory at Dayton as an automatic means of filling the methyliter cans. The enclosure in which it was operated for safety reasons is pictured in Figure 51. This plant was located in the north end of the laboratory building at Moraine City. These elaborate precautions were taken to prevent the poisoning hazard from the handling of Ethyl fluid. Under methods of blending in use before this, several cases of poisoning had occurred among the men who worked at blending the fluid. Some of these proved to be fatal, the men having died under distressing circumstances. It was

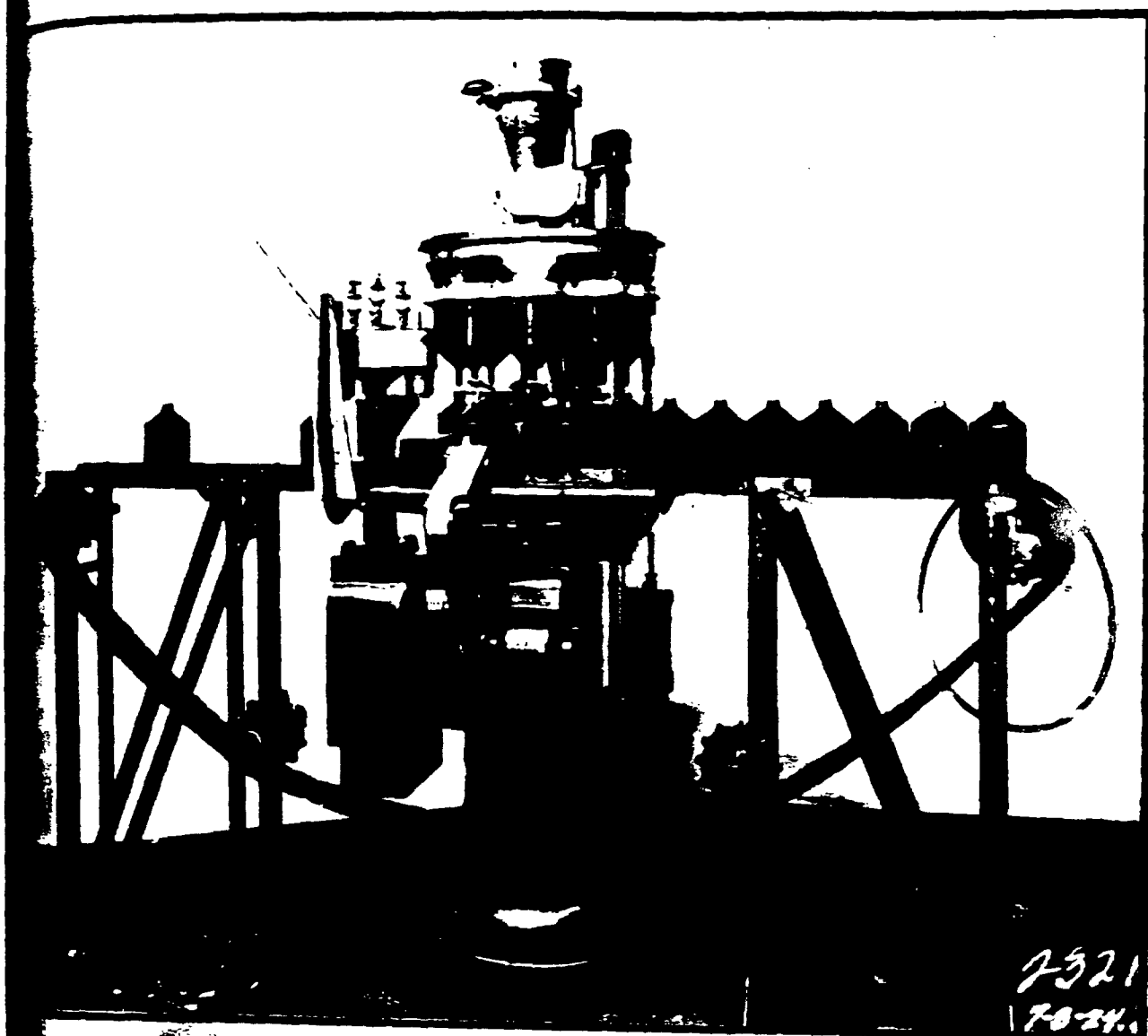


FIGURE 50

AUTOMATIC MACHINE DEVELOPED FOR FILLING THE
ONE-LITER CANS OF ETHYL FLUID.

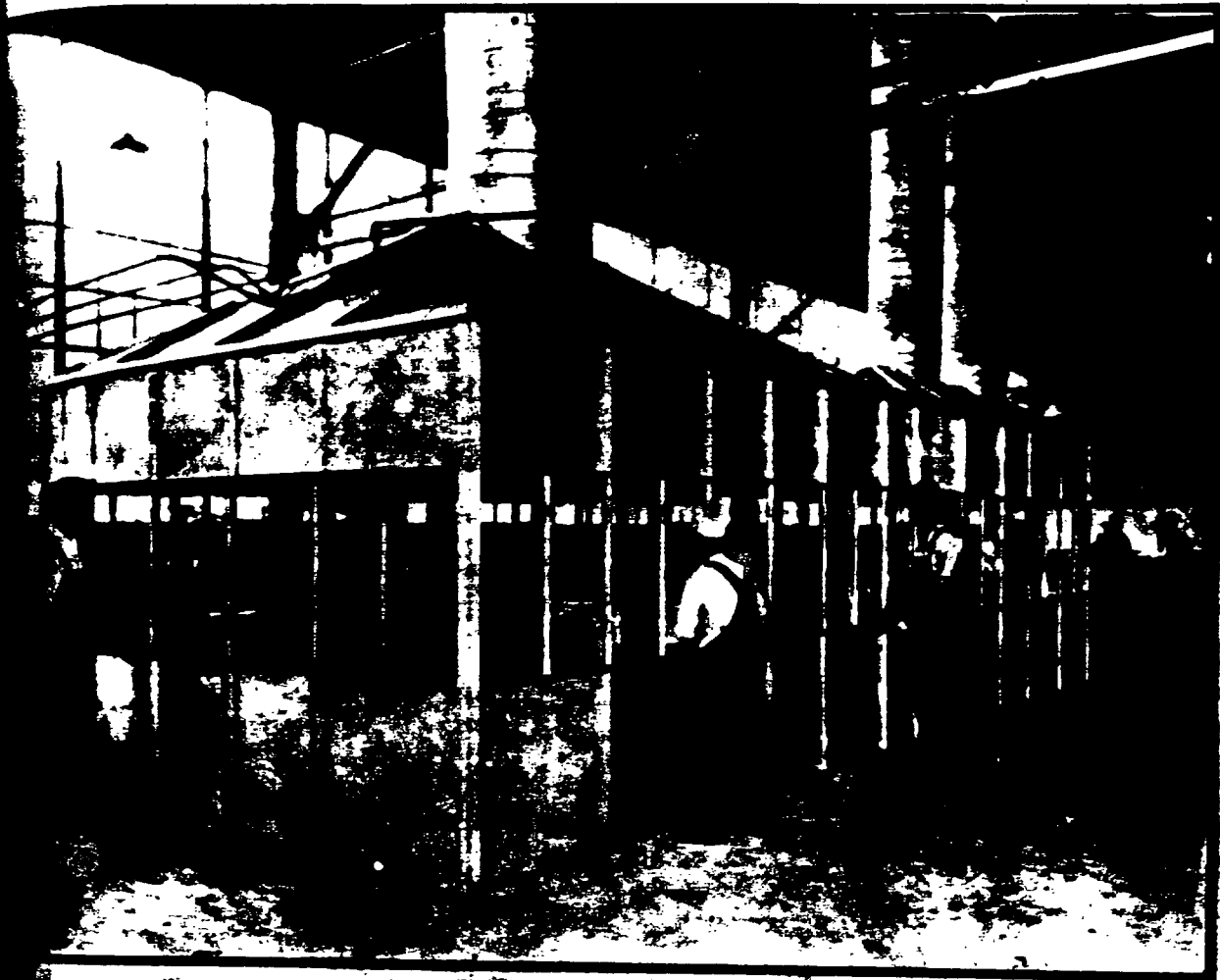


FIGURE 51

HIGHLY VENTILATED ENCLOSURE IN WHICH THE MACHINE FOR FILLING
CARS WITH ETHYL FLUID WERE OPERATED FROM THE OUTSIDE.

at that time, summer of 1924, that Dr. Robert A. Kehoe of the University of Cincinnati was retained to try to find a solution for these problems, and he has served in the cause of Ethyl Gasoline ever since. Later on all the blending and packaging activities were moved to the lead plant of the du Pont Company.

There developed gradually also the blending of Ethyl fluid with gasoline in bulk, or before it was distributed to the filling station. For use in this method of distribution was developed also what was called the "bulk ethylizer," an early model of which is pictured in Figure 52, page 227. For such bulk distribution the Ethyl fluid soon began to be shipped in drums, however, and some years later still in tank cars. The bulk method of ethylizing gradually displaced the small mixing meter method; and, when in 1926 Ethyl Gasoline came back on the market after its year of withdrawal for the Surgeon General's investigation, as will be related further on, the individual mixing meter method was abandoned altogether.

There were made also in 1923 a few strong steel containers with screw caps called a "tourist ethylizer." The aim in the marketing of Ethyl Gasoline was to get national distribution just as quickly as possible, in order that the user who might have his engine fitted with high-compression so as to take full advantage of Ethyl could get the product everywhere. But, because this was of course not possible all at once, the idea of the tourist ethylizer was to take care of the man who had to drive where there was no general distribution of Ethyl. But it was never used.

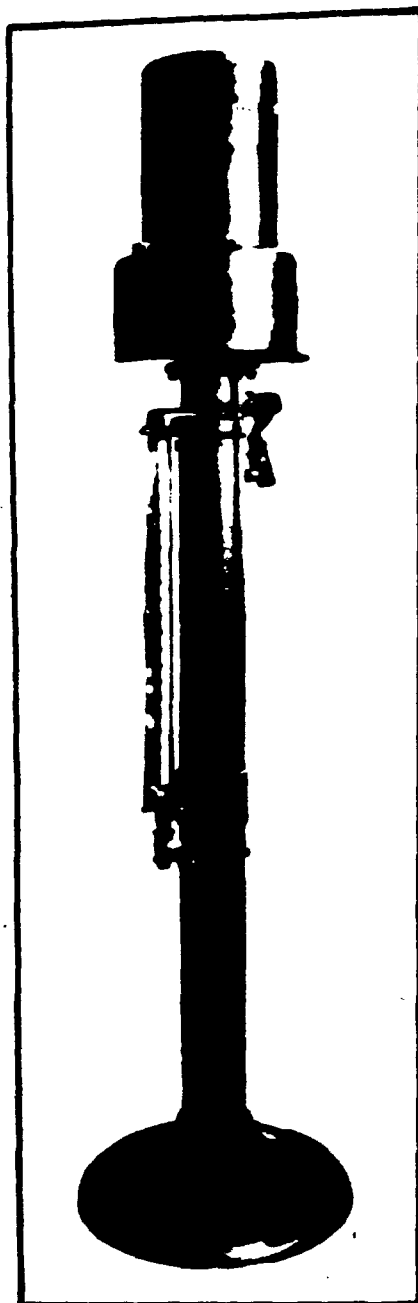


FIGURE 52

EARLY MODEL OF BULK MIXING
METER, USED FOR PUTTING ETHYL FLUID
INTO GASOLINE IN QUANTITY.

Proposal to Dye Ethyl Gasoline

In May, 1923, Boyd made the suggestion that Ethyl Gasoline be dyed (Record 21, page 13). It was thought that this might have the following advantages, as quoted from the Monthly Report for May, 1923:

1. It will permit estimation of the amount of Ethyl Gas Fluid in the fuel by the very simple method of direct color comparison.
2. The psychological effect on the customer will be good, in that the gasoline will be noticeably different after it has been passed through the "Ethylizer."
3. It will improve the stability both of the Ethyl Gas and the Ethyl Gas Fluid against light. This will be especially desirable if Ethyl Gas is allowed to stand in the light, such as in the usual type of vending pump.
4. A distinctive color will simplify the prevention of the use of Ethyl Gas as a dry cleaner or washing medium. The prevention of the use of Ethyl Gas in this way is very essential.
5. An attractive color may act as a stimulus to sales, especially if it is delivered from visible vending pumps.

Some dyes that appeared to be suitable for the purpose were obtained from the du Pont Company; and, after some experimentation, the suggestion was put into effect using the red dye called Sudan IV. No automobile gasoline had yet been dyed at this time, although during the World War fighting grade aviation gasoline had been colored for identification.

Only part of the anticipated advantages of dyeing Ethyl gasoline, as enumerated above, worked out however. Although a method for inspecting the gasoline for content of Ethyl fluid by simple color

observation was developed, it proved to be impractical, and for a reason that was not then anticipated. It was found that the slow decomposition which occurred in the Ethyl fluid of that time gradually carried the dye out of solution, so that the intensity of color was not permanent enough for the observation of color to be useful as a means of inspection.

The Problem of Stability in Storage

This brings up the serious problem of decomposition in the Ethyl fluid which was one of the principal items of investigation during the summer of 1923. It was noted that, with the mixture of tetraethyl lead and carbon tetrachloride then being used, gas was sometimes generated which built up pressure in sealed containers of Ethyl fluid. This was therefore not the same as the decomposition of tetraethyl lead in white light, previously discussed. Taking up the investigation of this problem on May 1, 1923, (Record 21, page 6), Boyd sealed a gallon of Ethyl fluid in a metal can fitted with a pressure gage. Nothing appeared to happen for some time, possibly because the generated gas was meanwhile being dissolved by the fluid. Soon however pressure began to build up in the container. It was thought that the gas which produced the pressure came from a decomposition of tetraethyl lead, brought about in turn perhaps by a hydrolysis of carbon tetrachloride. Such decomposition, in the presence of traces of water, could give hydrochloric acid and thus convert tetraethyl lead to lead triethylchloride, with the simultaneous formation of a hydrocarbon gas. At any rate, the pressure in the can soon built up to more than 5 pounds

on the gage. At that point the seal was broken and a tube was attached to the can in such a way that the generated gas was to have been collected in a 2000-cc graduate serving as a gasometer. But this arrangement, left for the week end, was destroyed by the violent bursting of the container—fortunately at a time when everyone was absent from the laboratory—scattering the contents over the room.

No such serious difficulties from gassing were experienced in the field however, possibly because the fluid was being used up too fast. But that the explosion mentioned above was not simply a freak case is shown by a letter from Guido Behn which O. Lee Harrison received and passed on to Mr. Kettering in August, from which the following is quoted:

Please tell Kettering for me that the anti-knock in addition to being a good remedy for knocks in motors is also very effective as a bomb. The bottle you left with me has been standing on my desk ever since you were here, and yesterday while I was telephoning the bottle blew up. Pieces of the bottle went in all directions. Fortunately not into my eyes and the liquid flooded my desk and everything on it. You cautioned me against getting the stuff on my hands but I not only got it on my hands but on my face and for itching it has poison ivy beat a mile.

Also a can of the unstable Ethyl fluid of that time, sitting in the garage of John J. Raskob, not only burst but also inflamed spontaneously, setting fire to the garage and doing considerable damage.

Again, as reported more than once through the course of this record, an effort was made to find some addition agent that would stabilize the mixture. But, as in the past, this effort did

not prove to be successful. However, extensive tests of organic chlorine compounds other than carbon tetrachloride, which were made also, showed that some of them did give great improvement in the stability matter (Record 21, page 42). This resulted in September, 1923, in a change being made in the chlorine compound used for making Ethyl fluid from carbon tetrachloride to trichlorethylene (Monthly Report, October 1, 1923). And fortunately this change, although adding somewhat to the cost of Ethyl fluid, completely solved the gassing and decomposition problem.

During the spring and summer of 1923 some further work was done at Dayton on methods of making tetraethyl lead, chiefly in studying catalysts for the process. Also, after the report by Frank Howard of their success in making tetraethyl lead by using ethyl chloride instead of ethyl bromide some work was done in investigating the possibilities of an ethyl chloride process. Several other possible antiknock compounds were tested also, but these are included in the list, Appendix IV.

Further Work on Decarbonizers

Some further work was done, too, in the effort to produce an effective liquid decarbonizing agent. This was done under the belief that "the ability to remove carbon easily is quite essential to any program into which high compression engines enter" (Monthly Report, July 2, 1923). Mixtures of alcohol, naphthalene, benzol, and pyridine (also aniline) were found to be fairly effective and resulted in the obtaining of a patent, (U. S. 1,786,860, December 30, 1930, Thomas Midgley, Jr., and Carroll A. Hochwalt).

During the fall of 1923 such carbon remover liquids were given a practical trial by the Chicago Yellow Cab Company, where they were applied with some success to about 200 engines at the Huron Street Garage. These trials were supervised by C. A. Hochwalt. However, the coming of cold weather introduced starting difficulties in some instances (Monthly Reports, November 30 and December 29, 1923). These were overcome to a fairly satisfactory degree, but at the cost of diluting the carbon remover with gasoline and so reducing its effectiveness. Later, when summer came, it was found that the harder coke-like carbon formed then did not yield so readily to the action of the compound as had the softer winter carbon. Due to these difficulties and to the rush of other problems which interfered with the experiments, the use of the decarbonizer was discontinued (Monthly Report, July, 1924) at that time. But later on the research on decarbonizer was taken up again in other quarters, and pursued in a more detailed and extensive manner.

More About the Research at M.I.T.

The work done at M.I.T. during the summer of 1923 and through to the spring of 1924 consisted primarily of the following items: (M.I.T. Reports on the Antiknock Problem):

Study of the reactions involved in the manufacture of tetraethyl lead from ethyl bromide by substitution, that is, without the use of reducing agents.

Study of the possible catalyzers for the reaction between ethyl halides and sodium-lead. Of the 30 compounds studied, alkyl cyanides were found to be best, and better than the pyridine which had been in use at du Pont.

Study of hydrolysis in the sodium-lead process.

Comparative study of the reaction of sodium-lead with ethyl bromide and ethyl chloride. It was not there found possible to get as good yields with ethyl chloride as with ethyl bromide. But it later became known that the secret of the success of Kraus and Callis with ethyl chloride was the use of an alloy containing only 1 part sodium and 9 parts lead.

Laboratory investigation of the spark plug and valve problem. Results were in general agreement with those obtained in the engine tests at Dayton.

The investigation at M.I.T. during this period was under the supervision of W. G. Whitman and R. T. Haslam, and those who worked on the problems at various times that year were the following: George Calingaert, J. C. Pope, Alan C. Johnston, and J. Lurie.

CHAPTER XIII

CONCLUDING WORK ON EXHAUST VALVE AND SPARK PLUG PROBLEMS

By the summer of 1923, some of the problems discussed above having been got out of the way and the use of chlorine compounds as corrective agents not having solved the spark plug and exhaust valve problems as completely as could be desired, the search for a more perfect corrective agent was actively taken up again (Record 21, pages 8 and 27). By the early fall of 1923 the work on this problem had reached an intensive stage. The twelve one-cylinder engines shown in Figure 1 of Appendix 5, had been installed in the room next the Fuel Section office in the Dayton Laboratory, and a program of tests which lasted about a year and which were run 24 hours a day for much of the time was under way. The typical test on a formula was run for 48 hours, and a new exhaust valve and spark plug were used for each test. In the early stages, condition of the exhaust valve and spark plug was noted simply by visual observation. Later the weight of deposit on the valve was determined by removal and weighing, and later still both the weight and composition of the deposit was determined.

It soon became apparent from these tests that bromine was a distinctly superior corrective agent. And so in early November, 1923, Boyd made a trip up to Midland, Michigan, to see the Dow Chemical Company about possible supplies of bromine. There he talked with the late Dr. H. H. Dow, president of the company, as well as to L. C. Camp and E. O. Barstow. They were only mildly interested in the matter and in our request for compounds of bromine, or of

bromine and chlorine combined, which would combine stability from our standpoint with relatively low cost. But they were nevertheless willing to sell bromine. Upon returning to Dayton, a sample of Ethyl fluid was sent to Doctor Dow for him to try in his car.

On November 21, shortly after this trip to Midland, the following telegram was sent to Mr. Camp of the Dow Chemical Company:

How are your facilities for making ethyl bromide by this time? If General Motors Chemical Company should place order for twenty-five thousand pounds at what rate could you make deliveries?

In response came a wire saying that they could begin deliveries in about six weeks at the rate of a thousand pounds per day and at a price of 50 cents per pound.

But the situation as it was seen on November 30, 1923, is outlined in the following, taken from the Monthly Report prepared on that day:

The use of bromine compounds in conjunction with lead tetraethyl appears to solve the depositing trouble. Bromine suffers from some serious defects, though, that will make its use in a large way out of the question. The maximum amount of bromine that could be obtained would be utterly inadequate to take care of the situation, because not over 10,000,000 gallons of gasoline could be ethylized per month. The other major trouble with bromine is its prohibitive cost.

We are therefore concentrating on an effort to influence the behavior of chlorine so that it will give the same effect as bromine.

This effort to enhance the corrective effect of chlorine was pursued in an intensive manner for several months following, and involved thousands of hours of testing in the 12 engines shown in Figure 1 of Appendix V.

But meanwhile, beginning in the late fall of 1923, practical tests of Ethyl Gasoline containing bromine instead of chlorine as a corrective agent were run by the Dayton Power and Light Company in all their cars and trucks. These tests turned out well from the viewpoint of righting the exhaust valve and spark plug difficulties, and they were reported also to have lowered the operating and maintenance cost of their transportation. From this time on for some years, incidentally, the Dayton Power and Light Company served as a kind of proving ground for new developments in Ethyl Gasoline. The fleet there was under the charge of O. B. Remelin, general superintendent, and its direct supervisor was at first William Schreiber and later F. O. (Fred) Lewis.

Dr. Wilder D. Bancroft Retained as Consultant

Early in 1924 Dr. Wilder D. Bancroft of Cornell University was retained as a consultant for any aid that he might give in solving the spark plug and exhaust valve problem. The current effort to enhance the corrective effect of chlorine to make it as effective as bromine was explained to him, and he thought the endeavor might possibly meet with success. He suggested that the effect of copper compounds be tried as an aid to this end, and also that sulphur be tested again, both of which were done, but without success. In the case of sulphur, a road test was run also. This showed some protection of exhaust valves, but none in respect to erosion of spark plug electrodes.

A series of engine tests were made meanwhile to determine by chemical means the actual composition of the products formed when

organic halogen compounds were burned in the engine, both with and without the presence of tetraethyl lead. These tests, which involved careful examination of the exhaust by C. J. Allen, showed that during combustion the halogen compounds were converted in each instance to the corresponding acid, either hydrochloric, or hydrobromic, and that a more perfect union with lead occurred in the case of bromine than in that of chlorine (Monthly Report, April, 1924). This latter was found to be true also in tests conducted in a heated glass tube in the laboratory (Monthly Report, February, 1924). This laboratory and engine work was supplemented also by literature studies, some of which were made by W. H. Charch at the Ohio State University.

Dr. Graham Edgar Arrives

About the first of June, 1924, Dr. Graham Edgar came to Dayton, Midgley having employed him to take the position of research director of the General Motors Chemical Company. He came from the University of Virginia, where for some years he had been professor of physical chemistry. The General Motors Chemical Company had not yet at that time established a separate laboratory. C. A. Hochwalt had however been transferred to the payroll of the Chemical Company, but was still working in the laboratory of the Fuel Section.

Giving his attention to the spark plug and exhaust valve problem, which was being pursued so actively then, Doctor Edgar, using the information obtained in the engine tests described above, computed on theoretical chemical grounds that there was perhaps little chance of chlorine being made as effective as bromine, because lead chloride is too highly dissociated by water vapor which is always

present in engines. This finding was checked also by the men at M.I.T. And, because it agreed with the results of the several months of unsuccessful effort to enhance the effect of chlorine, it was decided to discontinue this phase of the endeavor at that point.

There were, however, two other elements of importance which entered into this decision. The first of these was that a further analysis of bromine resources had been made, which, as will be reported later on, showed that the possible supply of bromine was much greater than had previously been supposed. The second element was that, on the basis of the superior corrective effect of bromine over chlorine which this long series of tests had so clearly demonstrated, the corrective agent in Ethyl Gasoline had already been changed from the all-chlorine compound, trichloroethylene, to the one-half bromine compound, ethylene chlorobromide (Monthly Report, July, 1924). This was Ethyl fluid 3-E.

The further endeavor on the spark plug and exhaust valve problem may now be related rather briefly by means of quotations from succeeding monthly reports as follows:

From the report for August, 1924. ✓

"The most outstanding development of the past month has been the decision . . . to begin the use of bromine compounds for correcting valve trouble as had been recommended. This has meant the termination of research looking to the discovery of other materials to serve this purpose, and the concentration of effort on securing thoroughly reliable data on bromine-chlorine mixtures and on bromine alone. At the beginning of August the road work was turned over to Dr. Edgar."

From the report for September, 1924.

"We have been 'mopping up' on this investigation by collecting data to fill in the gaps in the chemical and physical results of using bromine and chlorine in various amounts."

From the report for October, 1924.

"The laboratory and single-cylinder engine investigation of these problems (exhaust valve and spark plug problems) have been completed and the final report is about ready for submission. The summarized results of the work as quoted from this report are as follows:

"It has been found that bromine compounds are the only materials that prevent the depositing of lead compounds on exhaust valves, and at the same time correct the erosion of spark plugs to a satisfactory degree. Chlorine is fairly effective, but unless used in high concentration relative to the lead present it does not prevent the deposition of lead oxide on exhaust valves, although it seems to protect the spark plug electrodes fairly well."

From the report for November, 1924.

"As a result of the findings of this investigation the decision has definitely been made to abandon the use of chlorine and go over entirely to bromine in the Ethyl Gas program." (Further findings about the bromine supply situation to be discussed in the chapter following were involved in this decision also.)

Because of the importance of the work it covers, the summary report on the investigation of the exhaust valve and spark plug problems is included in full as Appendix V.

The amount of bromine as ethylene bromide used initially was 1.55 times that theoretically required to convert the lead present to lead bromide. This was reduced to 1.25 equivalents for a time, but was soon changed to 1.5 equivalents of bromine plus a small amount of halowax oil (chlorinated naphthalene). The halowax oil was added after car tests made by the Ethyl Gasoline Corporation during late

1924 and early 1925 had appeared to show that it functioned as an exhaust valve lubricant. Later on, about 1928, an extensive series of further car tests was undertaken by the Ethyl Gasoline Corporation. These tests showed that, with the intervening improvements in spark plugs and exhaust valves, it was then possible to reduce the bromine in Ethyl fluid to 1.15 equivalents of the lead present plus a small amount of halowax oil. Later the bromine was reduced to 1.00 equivalent, still retaining the halowax oil. Some time afterwards the halowax oil was discontinued and the corrective agent was changed to 0.85 equivalents of bromine and 0.30 of chlorine, and later still to 0.75 bromine and 0.4 chlorine. In September, 1933, the corrective agent became 0.70 equivalents of bromine and 0.45 of chlorine. Still more recently, in 1942, the composition of the corrective agent was changed once more to 0.5 equivalents of bromine and 1.0 of chlorine. All of these changes were of course based upon extensive car tests by the Ethyl Gasoline Corporation. The Ethyl fluid used in aviation gasoline is, however, a special mixture containing 1.0 equivalent of bromine as ethylene dibromide for the tetraethyl lead present.

CHAPTER XIV

THE FINAL SEARCH FOR BROMINE

The available supply and the cost of bromine were factors that entered into the decision about whether to use it as a corrective agent. And, as already mentioned, it was the belief that bromine was too scarce and therefore fundamentally too costly which delayed for so long the decision to use it as the corrective agent. The story of the first negotiations with the Dow Chemical Company about bromine in the fall of 1923, and the resulting conclusion that not enough bromine could be obtained is given in the preceding chapter. By June of 1924 it became apparent from the long series of tests conducted meanwhile and already reported that not only was bromine the best corrective agent found, but also that there was apparently no other material which could take its place.

Hence, a further analysis of possible bromine supplies was made, including a literature survey of the bromine resources of the world. The literature survey was based chiefly on Bulletin 695 of the U. S. Geological Survey, "Data of Geo-chemistry," by F. W. Clarke. The result of this further analysis, as quoted from the Monthly Report for June, 1924, was this:

"Briefly we find that the supplies of bromine are much greater than we had been led to believe. The Dow Chemical Company is willing to agree to supply the Chemical Company with all the bromine needed if they will contract in advance for four years' supply at present prices. Then, although we are informed that for some reason the du Pont people do not consider it as available, we have computed that there is enough bromine in the water of the Dead Sea to ethylize all the gasoline consumed in the United States (1923 rate of consumption) for over 15,000 years."

Some time in July or early August, 1924, Messrs. Kettering and Midgley accompanied by H.G.M. Fischer of the Standard Oil Company of New Jersey (General Motors and Standard of New Jersey were then in process of joining interests to form the Ethyl Gasoline Corporation, as related further on) went up to Midland to consult further with the Dow people about the problem of assuring an adequate supply of bromine. They took along from the staff of the Standard Oil Company of New Jersey an experienced oil well driller, thinking that possibly the application of the technique of drilling oil wells to the sinking of brine wells might increase the supply of bromine, or reduce its cost. Out of that conference came the opinion that the only source of bromine in really adequate amounts available in this country would be the water of the ocean. But the Dow people said that, without first concentrating sea water--a thing which would be far too costly to think of--they could not possibly extract bromine from it, any more than blood can be got out of a turnip. Why, they said, there is far more bromine in our brine after we get all through processing it for the extraction of bromine than there is in sea water in the first place!

As a means of effecting the concentration considered necessary, Dr. H. H. Dow made the following suggestion. He proposed that a pipe line be built from the Pacific Ocean right up over the mountains and down into one of the deserts on this side, so that sea water pumped over the mountains could evaporate there in the hot sun until the brine got strong enough to be worked for bromine. Since this suggestion did not appear to be at all practical, the meeting broke up with no apparent solution of the bromine problem in view.

Midgley tells that, while sitting in the smoking compartment on the train returning from Midland, he said to Fischer, "I have just had one of the best ideas that ever came to me." This idea as Midgley explained it was that it was not really necessary to get bromine out of sea water as bromine. What was wanted in Ethyl gasoline was not bromine itself but an organic compound of bromine. And he asked whether if sea water were to be treated first with chlorine and then with ethylene the bromine could not be separated and got out as ethylene dibromide. His thought was to build a wall across a bay in the ocean so that it would fill with water when the tide came up. And then at low tide to treat the water with chlorine and ethylene, run the water out and sponge up the ethylene dibromide. But, when upon returning to Dayton he looked up the solubility of ethylene dibromide in water, it was quite apparent that far too much would stay in the sea water for such a process to work, even if the compound formed under such conditions would be ethylene dibromide, about which there is some question.

But nevertheless in August, 1924, all the men in the Fuel Section and those in the newly formed research laboratory of the Ethyl Gasoline Corporation (established August 1, 1924) were set simultaneously to searching for some means of getting bromine out of sea water as an oil-soluble bromide. We did not even wait to have water shipped in from the ocean to work on, but used instead a synthetic sea water made up in the laboratory from the knowledge that ocean water contains about 0.0065 per cent of bromine, or about 65 parts per million. Doctor Edgar, after making a study of the solubilities of organic compounds of bromine in water, suggested

that the bromine might possibly be removed by causing it to react with phenol. This suggestion of phenol was later changed, on the basis of experiments, to aniline. And trial showed that, when the bromine had first been set free in the sea water by chlorine, the addition of aniline (or aniline sulphate) to the solution made it possible to remove about half the bromine as the compound, tribromaniline. And so a great many experiments were made to find the proper degree of acidity and the best means of separating the tribromaniline from the sea water.

But at the outset the difficulty with this process was that no more than half of the very minute amount of bromine in sea water could be got out in one operation. The reason for this was that, when the aniline and bromine reacted, only half of the bromine combined with the aniline. The other half reacted with the hydrogen released in the reaction to form hydrobromic acid, which of course remained in the sea water. Because the concentration of bromine in sea water initially was so minute, the amount recovered was thus too small to make the process practical.

Then one morning James P. Andrew came into the laboratory with the suggestion that, if, in setting the bromine free with chlorine, twice the amount of chlorine theoretically required were used, the hydrogen released from aniline when the bromine reacted with it might possibly satisfy itself with the excess chlorine present, and thus leave all the bromine free to combine with the aniline to form the tribromaniline desired. As luck would have it, this idea did work out, and so gave a process by means of which the tiny trace of

bromine present in sea water could be got out in high percentage yield, at least in the laboratory.

The compound, tribromaniline, was however a solid—not a liquid. But engine tests showed it to be just as effective as a corrective agent as were other bromine compounds. Being a solid, though, it would separate at any points where the gasoline evaporated completely, as at small leaks around the carburetor. Nevertheless, it was concluded that the compound could be made to serve the purpose of a practical corrective agent. The two ideas on which the success of the process mainly hinged were then patented, as follows:

U.S. 1,662, 305, Graham Edgar, March 13, 1928, on the use of aniline as a means of removing bromine.

U.S. 1,662,355, James P. Andrew, March 13, 1928, on the use of twice the theoretical amount of chlorine.

Du Pont Builds Semi-Works Plant to Extract Bromine from Sea Water

The next step was to see whether the new process would work on a larger scale. This being rightfully a problem for experienced chemical manufacturers, the aid of the du Pont Company was enlisted in the endeavor. When in November, 1924, the new method was first explained to the men at du Pont, they were skeptical about whether it would work. And not until they had found from laboratory trials of their own that the reactions did go as represented did they proceed. They were to build first a semi-works plant, which they constructed on the shore at Ocean City, Md. This phase of the work was undertaken by du Pont for a fee from the Ethyl Gasoline Corporation of \$20,000 to cover administration, expense, and necessary experimentation. But, when trouble was ex-

perienced in the semi-works plant with the method of separating the tribromaniline by flotation, which had been successful in the laboratory, another \$20,000 was added to the appropriation.

Meanwhile, in the late fall of 1924, Mr. Kettering was in Europe; and, in company with men from the du Pont Company (P. H. Chase), he went to Tunis in northern Africa to inspect there the war-time bromine plant at Ain-es-Serah, then inoperative, which the French interests controlling it proposed to lease or sell to be operated by du Pont on behalf of the Ethyl Gasoline Corporation, or else to re-open and operate it themselves on a cost-plus basis. But, after a great deal of consideration, conferences, and correspondence, this proposal came to naught. At about the same time also H.G.M. Fischer of the Standard Oil Company of New Jersey made a trip to Palestine to inspect the Dead Sea. Through the office of Mr. W. O. Kennington in London, some steps were taken later to try to get a favorable concession to operate the waters of the Dead Sea for bromine. Among the prominent Britishers who figured in these negotiations were Sir Herbert Samuel and Sir Josiah Stamp. But nothing came of it, partly perhaps because the granting of any such concession was strenuously objected to by Sir Alfred Mond, chairman of the British chemical company, Brunner-Mond.

Also Dr. E. B. Peck and Mr. Adams of the Standard Oil Company of New Jersey were sent to Mexico to inspect the possibilities of getting bromine out of the salt water from oil wells. But it was concluded that the prospects there were not as promising as those in Tunis mentioned above (Annual Report of the Officers, Ethyl Gasoline

Corporation, 1924). One other thing that worked against commitments abroad was a duty of 10 cents per pound on bromine. Accordingly, in the fall of 1924 a contract was made with the Dow Chemical Company to supply ethylene dibromide at the rate of 100,000 pounds monthly for 5 years at a price of 58 cents per pound the first year, and reducing yearly until a price of 49 cents per pound was reached (Annual Report of Officers, Ethyl Gasoline Corporation, 1924).

The semi-works operation by the du Pont Company at Ocean City on the process of extracting bromine from sea water developed by the two laboratories at Dayton proved to be reasonably successful. But it brought up a new set of problems. These were how to keep sand and suspended solids out of the water entering the works, and how to insure a supply of sea water not diluted by surface waters or effluent water from the plant.

The Good Ship Ethyl

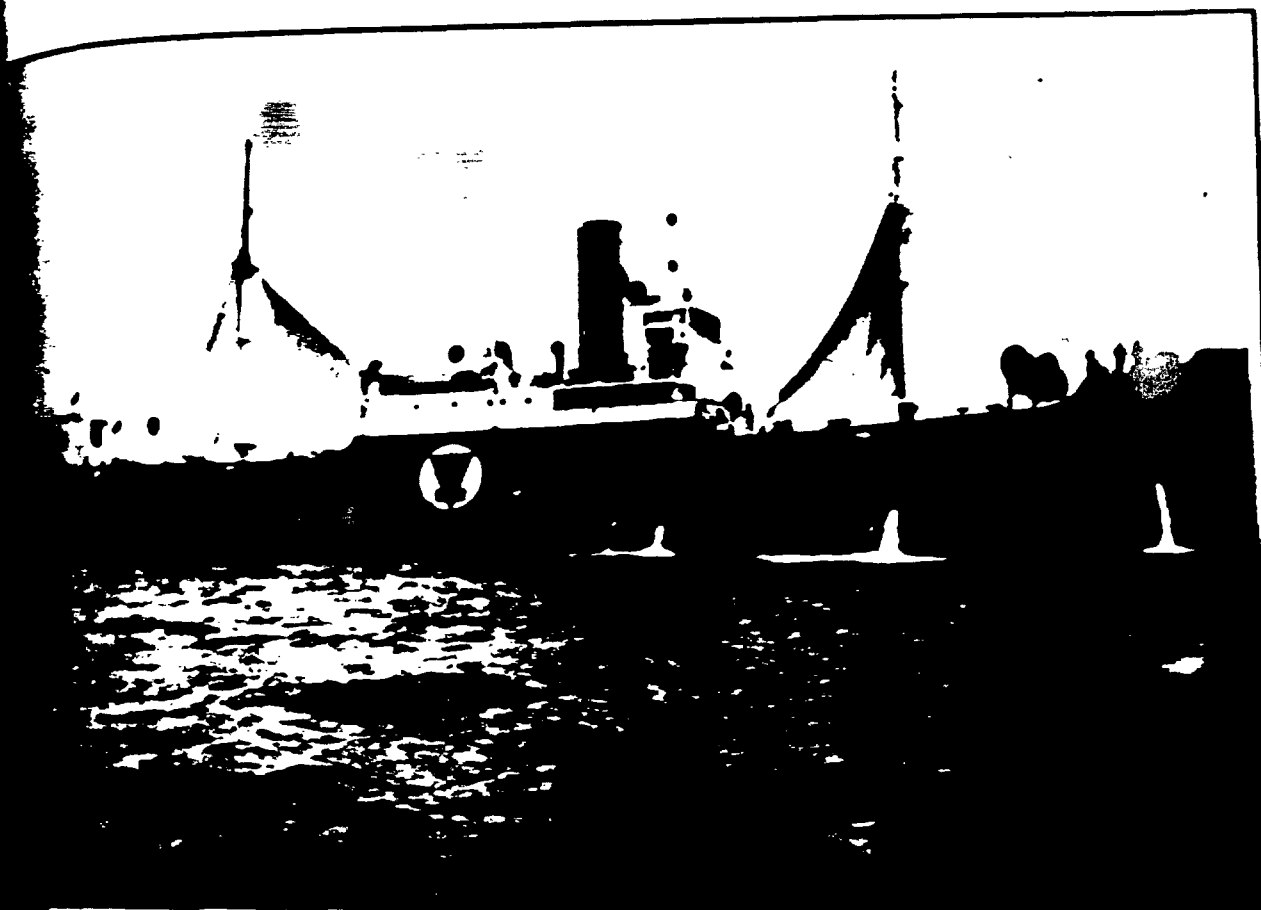
To solve these problems Mr. Irene du Pont suggested that the full-scale plant, for which the directors of the Ethyl Gasoline Corporation appropriated \$150,000 in December, 1924, be put not in a building along the shore, but on a ship which could sail out to sea away from the dirt and other troubles of the shore. And that was done. A cargo ship 254 feet long, one of the many built by the Emergency Fleet Corporation during the World War, was bought from the U. S. Government. It had been built on the Great Lakes and originally christened the Lake Harminia. But it was renamed the Ethyl, and on it the Bethlehem Shipbuilding Corporation installed a full-scale bromine plant designed by du Pont on the basis of the tests

at Ocean City. A photograph of the steamship Ethyl is included as Figure 53, page 249. This ocean-going plant was expected to put sea water through the process at the rate of 8,000 gallons each minute. From the 480,000 gallons of sea water thus treated each hour the plant was expected to produce about 200 pounds of bromine.

Near the end of April, 1925, the good ship Ethyl put to sea to glean bromine out of the water through which she sailed, like a big whale straining her dinner out of the ocean she swims in. She sailed southeast into the Gulf Stream, about 250 miles due east of the Virginia capes, and then southwest along the axis of the Gulf Stream until she got as far south as the latitude of Wilmington, North Carolina. There the ship turned north again and came finally back up the Delaware River to Wilmington and home. The actual cost of the endeavor turned out to be about half a million dollars. But the ship brought back a cargo of bromine, although not quite as large as it might have been. The reason for the deficiency was not so much that the process did not work out as that the landlubbers who were operating it often got too seasick to work. An account of this endeavor, as carried out by the du Pont Company, is given in a published paper by Dr. Charles M. A. Stine, "Recovery of Bromine from Sea Water," Ind. Eng. Chem., 21, 434 (May, 1929).

But when the steamship Ethyl came home she was forgotten for several months, because just then the Ethyl Gasoline Corporation was passing through one of its greatest tribulations, and there was no assurance that there would be any money to pay for

PORT 00-53



BROMINE RECOVERY - S S ETHYL PROCESSING SEA WATER IN GULF STREAM
45 MILES S E OF CAPE HATTERAS, N C

FIGURE 53

THE STEAMSHIP ETHYL ON WHICH WAS BUILT THE FIRST FULL-SCALE
PLANT FOR EXTRACTING BROMINE FROM SEA WATER.

ETC 37047

further work. The trouble referred to was that arising out of the poisoning episode previously mentioned, and to be described in some detail later on.

When some months afterwards, in early 1926, Ethyl gasoline came back on the market after having been given a clean bill of health by the Surgeon General's investigating committee, the demand for bromine was revived. Now Dr. H. H. Dow, who all along had been kept fully informed of progress in the effort to get bromine out of the sea, had continued to insist that it could not be done, that the job was impossible. The success of the cruise of the steamship Ethyl had therefore been a surprise to him. Perhaps with the fear of losing his profitable bromine business through this joint Ethyl Gasoline-du Pont endeavor, Dr. Dow came forward at once with the offer of bromine at a lower price, and with assurances that he would be able to supply the demand from Michigan wells for some time to come. The uncertainty of the times was still such that the Ethyl Gasoline Corporation decided to accept Dr. Dow's offer and to let the steamship Ethyl stay at her pier, particularly so since she was now to be paid for through the lower bromine prices which she had helped to win.

Dr. Dow Overhauls His Bromine Process

But the cruise of the steamship Ethyl had had still another important effect up at Midland. Dr. Dow had called in his chemists and instructed them to find out just how it came that the Dow process would not work on sea water when the General Motors, Ethyl Gasoline, and du Pont people were doing the job so successfully. After a

great deal of effort the men at Dow found out that, if only they would control very precisely the pH or the degree of acidity of the brine, they could extract bromine from sea water by their process after all. And thus it developed that in their case the difference between im-possible and possible was nothing more than a tiny trace of acid.

This was a very important discovery, because the Dow process had the great advantage of getting the bromine out, not as a compound of bromine but as bromine itself. Thus it could then be made into the precise compound best suited to put into gasoline, which would of course be a liquid, not a solid.

Dr. Dow then wired the Ethyl people asking them to come up to Midland. When they got there, he said: "We have it." The outcome was a proposal that the Ethyl Gasoline Corporation and the Dow Chemical Company join forces and use this improved process of Dow's to extract bromine from sea water. The Ethyl Gasoline Corporation was glad enough to do this because they greatly preferred to have the bromine for Ethyl Gasoline in the liquid compound which could be produced by the Dow process, rather than in the solid compound, tribromaniline. Before the event recorded in this paragraph, however, consideration had been given by men within the Ethyl Gasoline Corporation to building a small plant to produce tribromaniline from sea water as a supplementary source of bromine (Minutes Ethyl Gasoline Technical Committee, July 18, 1927).

First Bromine Plant at Kure Beach

Now, just as had been so with the tribromaniline process, it was decided to build first a small plant to try out this new process of Dow's on a semi-works scale. With the difficulties which the du Pont people had experienced from surface water and suspended dirt in mind, and also with a recollection of the helpless crew of seasick chemical workers aboard the steamship Ethyl, a very careful search was made for a suitable shore site.

At one stage of the bromine-from-sea-water endeavor--possibly somewhat earlier than this--Charles A. Thomas, (then with the Ethyl Gasoline Corporation, now with Monsanto Chemical Company) went down along the Carolina coast and collected samples of sea water at several points in the general vicinity of Albemarle Sound. The purpose was to find by analyzing the samples at what location the sea water contained the maximum concentration of bromine. Returning through Norfolk with his samples, Thomas was arrested by prohibition enforcement officers because of the suspicious character of his heavy baggage full of bottles. But of course sea water did not smell or taste enough like alcohol for him to be held for long.

A suitable site for the bromine plant was finally found at Kure Beach on the Carolina coast in a long, narrow peninsula running south from Wilmington, North Carolina, between the Cape Fear River and the ocean. There clean sea water could be pumped in from the ocean on one side and, after treatment, discharged into the river on the other side.

The Ethyl-Dow Chemical Company

The pilot plant was built in 1931 on the site selected, and was then operated successfully for a period of six months. The results were so encouraging that in July, 1933, in the face of mounting demands for bromine, the Ethyl-Dow Chemical Company was incorporated jointly by the Ethyl Gasoline Corporation and the Dow Chemical Company, and construction of a full-scale plant on the same site was decided upon. This plant was intended to produce about 6 million pounds of bromine a year, or about 6.5 million pounds of ethylene dibromide. But in the summer time when the sea water was warmer it was found that the process worked so well that the plant could be operated at a rate corresponding to about 9 million pounds of bromine per year.

In 1933, when this plant was built; was just the time when lead began to be put also into regular-price gasolines, as will be mentioned later. The demand for bromine thus generated mounted so fast that the size of the plant soon had to be doubled. Then in 1938 the plant was enlarged again, until it was three times as big as the original, and could be run at a rate of about 40 million pounds of bromine per year. Furthermore, it is understood that bromine was being extracted from sea water there at lower cost than it can be got out of the strong brine up at Midland. A photograph of the plant is included as Figure 54, page 254. Later still another plant for getting bromine out of the sea was built on the coast of the Gulf of Mexico.



Fairchild Aerial Surveys, Inc.

FIGURE 54

THE PLANT AT KURE BEACH, NEAR WILMINGTON, NORTH CAROLINA, FOR EXTRACTING BROMINE FROM SEA WATER. WATER IS PUMPED IN FROM THE OCEAN AT THE UPPER RIGHT, AND, AFTER REMOVAL OF ITS BROMINE, IT IS DISCHARGED INTO THE RIVER THROUGH A FLUME EMPTYING JUST BELOW THE DOCK AT THE LEFT.

ETC 37052

After the first bromine plant had been built down there on the Carolina coast, it was thought that because the operation of army and navy aircraft depends so vitally nowadays on lead-treated gasolines, it might be well to call the attention of the Army authorities to the location and importance of the plant. They might, it was thought, want to work out some plan of defending it in case of war. Soon came a letter from an important Army official, which said among other things that it was most unfortunate that they had not been advised of this endeavor before the plant was built. If only that had been done, he said, the Army would have recommended that the plant to get bromine out of sea water be located not there beside the sea where sea water could be had, but 200 miles back from the coast.

Brief Description of Process for Extracting Bromine from Sea Water

Without going into detail, the process put into operation at the Ethyl-Dow bromine plant was briefly this. Water from the Atlantic Ocean was pumped into the plant through a settling basin at the rate of about 100,000 gallons or so per minute. As the column of sea water entered the plant through rubber-lined pipes it was treated automatically with the right amount of sulphuric acid and chlorine gas. This set the bromine free in an extremely dilute solution. The bromine was then blown out of the water with counter-current air in tall towers. Next in other towers the bromine was absorbed out of the air by passing it up through a spray of soda ash solution. This solution of washing soda was circulated round and round until a liquor strong in bromine had been obtained. Then,

when this strong liquor was treated with sulphuric acid and blown with steam, it gave up bromine as a red liquid more than 3 times as heavy as water. Next, the separated bromine was reacted with ethylene gas, and so gave ethylene dibromide which is the liquid bromine compound that is put into Ethyl fluid. A technical description of the original plant and process by Leroy C. Stewart of the Dow Chemical Company was published in 1934 (Ind. Eng. Chem., 26, 361, April, 1934).

CHAPTER XV

THE ETHYL GASOLINE CORPORATION

Incidental mention has already been made of the formation of the Ethyl Gasoline Corporation, jointly by General Motors Corporation and Standard Oil Company of New Jersey, as well as of some of the events which led up to the idea of such a joint enterprise. Early in 1924 the Standard Oil Company began to distribute Ethyl Gasoline in Washington and Baltimore under a contract with the General Motors Chemical Company. And this distribution was later extended to other areas. Meanwhile the Standard Oil Company of New Jersey was experimenting further with the Kraus and Callis process of making tetraethyl lead by using ethyl chloride instead of ethyl bromide, as previously mentioned.

Events thus shaped themselves so that the two companies which had discussed some such joint endeavor off and on ever since 1921, got together and on August 18, 1924, the Ethyl Gasoline Corporation (name changed in 1942 to the Ethyl Corporation) was incorporated under the laws of the State of Delaware, with an authorized capitalization of 50,000 shares of common stock, par value \$100. The Standard Oil Company of New Jersey and General Motors Corporation each subscribed initially to 3,750 shares at par. Later—on October 20, 1924—each of the sponsoring companies subscribed to an additional 2,000 shares of common stock at par, thus making the paid-in capital \$1,150,000.

The agreement between General Motors Corporation and Standard Oil Company of New Jersey under which this joint endeavor was undertaken provided among other things for the following: The Ethyl Gasoline Corporation was to be owned one-half by each of the two companies entering into the contract. All the patents on antiknock agents and fuel improvers or methods of making such compounds then held by either, together with any further discoveries of like character made or acquired prior to August 1, 1940, were to become the property of the Ethyl Gasoline Corporation. Profits of the business were to be divided equally. However, because the discovery of the antiknock agent in Ethyl Gasoline upon which the business was founded had been made by General Motors Corporation after long search, it was provided that a sum equal to one-fourth the yearly profits resulting from the distribution and sale of Ethyl fluid should first be paid to General Motors Corporation as a royalty. It was provided also that the newly formed Ethyl Gasoline Corporation should take over the physical assets of the General Motors Chemical Company at their replacement cost. (This figure was later set at \$362,767.19.) The Board of Directors of the new Corporation was to be composed of an even number of men, one-half to be elected by the Standard Oil Company of New Jersey and one-half by General Motors Corporation.

The directors of the Ethyl Gasoline Corporation, as thus elected at the outset, were as follows:

From General Motors

Alfred P. Sloan, Jr.
Donaldson Brown
John Thomas Smith
Charles F. Kettering
Thomas Midgley, Jr.

From Standard Oil

W. C. Teagle
J. A. Moffett, Jr.
E. M. Clark
F. A. Howard
A. M. Maxwell

In December, 1924, John Thomas Smith resigned as director and was replaced by Irene du Pont.

At the first meeting of the Board of Directors on August 28, 1924, the following officers were elected:

President	Charles F. Kettering
1st Vice President	F. A. Howard
2nd Vice President and Gen. Mgr.	Thomas Midgley, Jr.
3rd Vice President and Sales Mgr.	A. M. Maxwell
Sec'y and Treasurer	A.E. Mittnacht
General Counsel	Chester O. Swain

As the presidency of the new corporation demanded more time than Mr. Kettering, with all his manifold activities, was able to give it, Earle W. Webb from the legal department of General Motors Corporation was soon made president. And he has filled that position with distinction ever since.

When the Ethyl Gasoline Corporation was organized there existed a manufacturing contract with the du Pont Company for 1,100,000 pounds of tetraethyl lead at \$2.00 per pound, one-half of which had already been fulfilled. A new contract was drawn then by which the balance due on the \$2.00 contract was to be delivered at that rate, any further amount manufactured prior to April 15, 1925, was to be delivered at \$1.66 a pound, but after April 15 the price was to become \$1.17 per pound. (Later on the price was still further reduced, of course.) These reductions were made possible by

the building of a new lead plant and by the adoption at the du Pont Company of the ethyl chloride modification of the sodium-lead process initiated by Kraus and Callis for the Standard Oil Company of New Jersey, as mentioned elsewhere. Manufacture by du Pont under this modified process was begun early in January, 1925. In the early days of making tetraethyl lead, the cost of plant and equipment were figured on the basis of amortization in one year. !

About August 1, 1924, a separate research laboratory was set up for the Ethyl Gasoline Corporation in the northeast corner of the main laboratory building at Moraine City. This laboratory was in charge of Graham Edgar, whose coming to Dayton in June, 1924, as director of research for the General Motors Chemical Company has already been mentioned. Some of the first men added to the staff were Charles A. Thomas, who had been working in the Fuel Section of the General Motors Research Corporation for more than a year, C. A. Hochwalt, Fred Thamann, and B. B. Owen. Without attempting to give an account of the subsequent history of this laboratory, or of its extensive activities, it may be mentioned that at the end of 1925 it was moved to Yonkers, N. Y. Then in November, 1927, the mechanical department, which Dr. Edgar had established at Yonkers under Earl Bartholomew who came to the job from a teaching position at Harvard University, was moved to Detroit. Again in December, 1932, the chemical department of the research laboratory also was brought to Detroit and was put in charge of Dr. George Calingaert, who, as previously related, had worked on lead problems at M.I.T.

Shortly after the formation of the Ethyl Gasoline Corporation, the Ethyl emblem and trade mark was changed from that shown at the top in Figure 42, page 213, to the emblem shown as Figure 55, page 262. Giving advice in respect to this change was Mr. E. S. Rogers, famous trade mark attorney of Chicago.

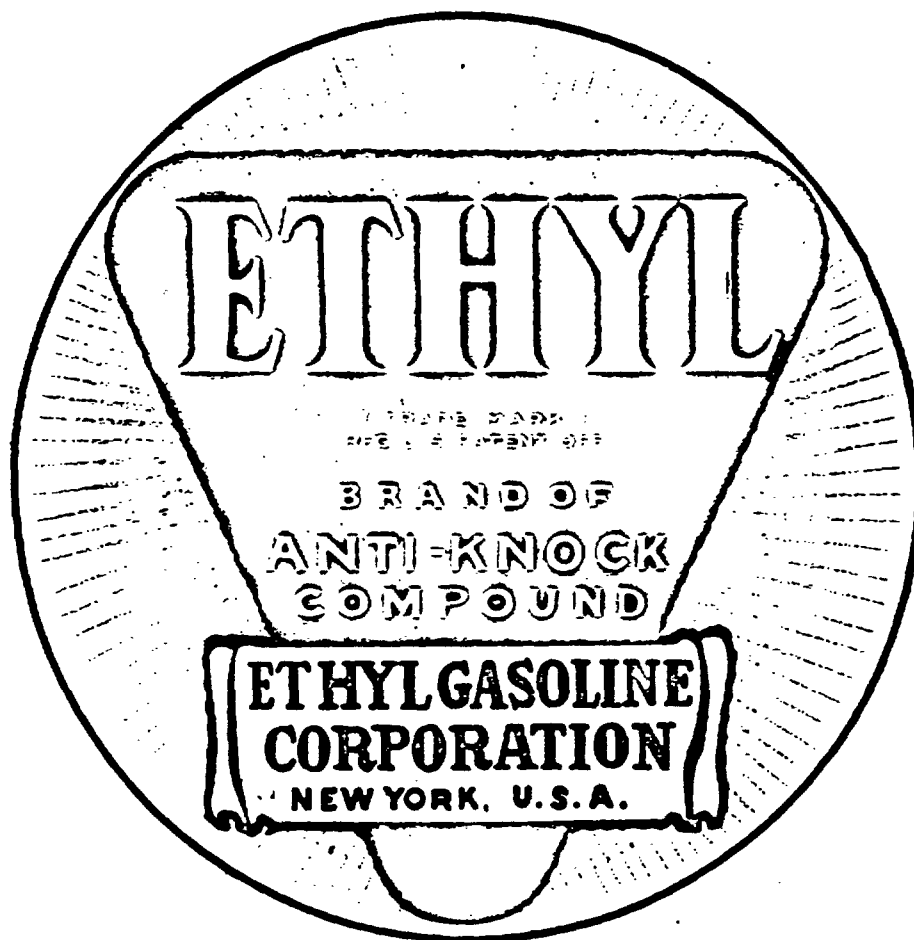


FIGURE 55

THE ETHYL EMBLEM AND TRADE MARK AS IT WAS MODIFIED AFTER THE FORMATION OF THE ETHYL GASOLINE CORPORATION. IN THE ACTUAL EMBLEM THE RAYS ARE BLUE IN COLOR, THE TRIANGLE AND THE LETTERS ON THE PENNANT ARE BLACK, AND THE LETTERS ON THE TRIANGLE AND THE BACKGROUND OF THE PENNANT ARE YELLOW.

CHAPTER XVI

THE HEALTH HAZARD QUESTION

So far the subject of toxicity in respect to Ethyl Gasoline has only been touched upon lightly, such as to relate the contacts with Drs. Reid Hunt of Harvard and Yandell Henderson of Yale, mentioned on pages 165 and 166, and to refer to the fears of Dr. Eric Krause and Surgeon General Cumming on page 191. At the outset the concern about possible poisoning hazards was confined chiefly to the products exhausted by engines burning lead. The exhaust did not, however, prove to be the source of the poisoning difficulties actually experienced, for those came from the handling of the tetraethyl lead itself in concentrated form. But the belief that the hazard, if any, would come from lead compounds blown out in the exhaust explains why the early endeavors related almost altogether to possible hazards arising from exhaust products.

In the summer of 1923 tests on the exhaust of engines running on Ethyl gasoline were begun in the laboratory at Dayton. In the first of these a 4-cylinder engine was run at half load and 1000 r.p.m. for over a hundred hours, during which time the exhaust gas was first cooled and then passed through distilled water in an effort to get a measure of the amount of lead in the exhaust. However, this test did not prove to be very quantitative; for, in spite of the pains taken to recover all the lead, it was possible to account for only about half of it (Monthly Report, August 29, 1923).

A more extensive test was accordingly undertaken, this time to determine how much lead would be deposited as floor dust in the garage of the Research Laboratory when all the cars kept there used Ethyl Gasoline. A request was made that each car using the garage burn Ethyl Gasoline during the period of the test. The company trucks and service cars kept in the garage were run on Ethyl Gasoline too. In addition, a Chevrolet car was placed in the garage, the engine of which was kept running on Ethyl Gasoline throughout the working day. This test was conducted for 30 working days. The garage floor was swept just before the test began. And, although it was not swept again during the entire 30-day period, the amount of lead found in the sweepings collected at the end of the test was so small that a person would have had to absorb each day all the lead from about 4.5 grams of floor dirt in order to be in danger of developing lead poisoning according to the tolerance of 6 milligrams per day as given by Dr. J. C. Aub of Harvard Medical School (Report, "Accumulation of Lead in Garages Where Ethyl Gas is Used," September 30, 1923).

The Bureau of Mines Investigations

Meanwhile the previously mentioned arrangements were being made under which the U. S. Bureau of Mines conducted a comprehensive investigation of the possible hazards from the exhaust of engines running on Ethyl Gasoline. In these tests, which were begun in the fall of 1923, the Bureau utilized the large chamber that had been employed in the studies they had previously made to determine the ventilation required for the Holland Vehicular Tunnel at New York City. A copy of the agreement signed on October 19.

1923, under which this work was undertaken is included as Figure 56, page 266 (from Bur. Mines report to the General Motors Research Corporation and the Ethyl Gasoline Corporation, "Experimental Studies on the Effect of Ethyl Gasoline and Its Combustion Products," 1927).

The then superintendent of the Pittsburgh Station of the Bureau of Mines, with whom the arrangements were made and under whose supervision the investigation was conducted, was Dr. A. C. Fieldner, now chief of the Technological Branch of the Bureau. As before said, it was Doctor Fieldner who arranged for the presentation of the paper at the Pittsburgh meeting of the American Chemical Society on the basis of which Midgley was later awarded the Nichols Medal. Here it may be mentioned also that during a visit which he made to the Research Laboratories of General Motors in December, 1938, Doctor Fieldner said that he considered the work which he did in investigating Ethyl Gasoline as the high spot of his whole career.

In direct charge of the investigation at the Bureau was W. P. Yant, now director of research of the Mines Safety Appliances Company. The medical aspects of the tests were under the supervision of Dr. R. R. Sayers, who was then chief surgeon of the U.S. Bureau of Mines and also surgeon of the U.S. Public Health Service and who is now Director of the Bureau of Mines. Dr. Sayers was assisted by Dr. W. J. McConnell, assistant surgeon of the U. S. Public Health Service. Pathological studies were made by B.G.H. Thomas. Other men taking part in the endeavor were G. W. Jones, R. D. Leitch, D. W. Meyers, J. F. Farren, and L. B. Berger.

COPY OF AGREEMENT.

BETWEEN THE DEPARTMENT OF THE INTERIOR
AND
GENERAL MOTORS RESEARCH CORPORATION*
DAYTON, OHIO.

WHEREAS, The Department of the Interior, acting through the Bureau of Mines (hereinafter referred to as the Bureau), is conducting investigations on the more efficient utilization of fuels and in determining the amount of air required to ventilate mines and tunnels contaminated with motor exhaust gases, and

WHEREAS, The General Motors Research Corporation (hereinafter referred to as the Corporation), is also interested in the same subjects, and in particular in whether there is any increase in the toxicity of motor exhaust gases due to the addition to the fuel of certain special chemical substances known as "anti-knock" compounds which enable the use of higher compression engines, thus increasing the mileage from a gallon of gasoline and conserving the liquid fuel resources of the country, and desires to cooperate with the Bureau in this research,

NOW THEREFORE, it is agreed:

(1) That the Bureau and the Corporation will cooperate in planning and directing an investigation on the toxicity of exhaust gas from motors using tetraethyl lead and certain halogen compounds as anti-knock materials in the fuel according to the general plan outlined in appendix A [not included in this report] of this agreement. It is understood that this plan may be modified during the progress of the work as mutually agreed upon.

(2) The Bureau will furnish such laboratory facilities and apparatus as are at hand, heat, light, power, technical supervision of chemists, physiologists and physicists, including actual assistance of pathologist.

(3) The Corporation shall pay the salary of an assistant chemist to carry on the analytical work incident to this research for a period estimated at six months and shall provide additional assistance as needed and mutually agreed upon by the contracting parties.

(4) The Corporation shall pay all expenses incurred in the purchase of supplies, repairs, and special equipment not available at the Bureau or provided by the Corporation. These expenses are to be paid direct by the Corporation on vouchers approved by the Director of the Bureau or his authorized agent; likewise the salary of the assistant chemist shall be paid in a similar manner.

(5) The investigation shall be carried on under the direction of the Superintendent of the Pittsburgh Experiment Station in a manner satisfactory to both parties of the agreement.

(6) Publication of the results of this investigation shall be under the control of the Director of the Bureau. All manuscripts, before publication, will be submitted to the Corporation for comment and criticism. Due acknowledgment will be made in the publications to the cooperation of the Corporation. No progress reports will be given out for publication before the investigation is completed without mutual consent of both parties of this agreement.

Upon the approval of the Secretary of the Interior, this agreement shall remain in force until June 30, 1924. The actual experimental work is estimated to cover a period of six months.

IN WITNESS WHEREOF, the parties have hereunto set their hands by their duly authorized officers.

WITNESSES:

(Signed) J. A. HUFF
(Signed) W. F. WHELAN

BUREAU OF MINES

(Signed) H. FOSTER BAIN,
Director.

GENERAL MOTORS RESEARCH CORPORATION.

(Signed) THOMAS MIDDLEY, JR. (Signed) C. F. KETTERING,
(Signed) T. A. BOYA. President.

DEPARTMENT OF THE INTERIOR.

Approved Oct. 19, 1923.

(Signed) E. C. FINNEY,
First Assistant Secretary.

FIGURE 56

COPY OF FIRST AGREEMENT WITH THE BUREAU OF MINES UNDER WHICH THE BUREAU INVESTIGATED THE QUESTION OF WHETHER THE EXHAUST FROM ENGINES RUNNING ON ETHYL GASOLINE MIGHT CONSTITUTE A HEALTH HAZARD.

For the General Motors Research Corporation the tests were followed by Boyd and Dr. E. R. Hayhurst. Frequent trips to Pittsburgh were made for this purpose. Dr. Hayhurst was a professor in the Medical College of the Ohio State University and a member of the Ohio State Department of Health concerned with industrial diseases. He was retained on the recommendation of Dr. J. C. Aub of the Harvard Medical School, who himself visited the Bureau and inspected the endeavor on at least one occasion.

For these tests a Delco-Light engine, sent to the Bureau from Dayton, and run on Ethyl Gasoline, was arranged to pour all its exhaust into the 1000-cu. ft. chamber, previously mentioned. The plan of the investigation, as quoted from the official report of this phase of the endeavor by the Bureau of Mines (R.I., Serial No. 2661, "Exhaust Gases from Engines Using Ethyl Gasoline," December, 1924), was as follows:

"Various types of animals were exposed for certain periods of each day to a definite concentration of exhaust gas from an engine using ethyl gasoline. These exposures were made to simulate the worst conditions, as to time of exposure and concentration of gas in the air, to which people could be exposed without being poisoned by the carbon monoxide in the exhaust gases. The tests were continued over a period of 8 months in order to bring out cumulative effects. Animals of several species, sizes, and ages were used to take care of a possible tolerance or susceptibility."

Among the animals thus exposed to the exhaust from the engine running on Ethyl Gasoline were a number of dogs. During the period of the test, five puppies were actually born in the chamber. These the men dubbed "The Ethyl Gas Hounds," and they went back into the chamber with their mother each day during the remaining period

of the test, without harm of any kind. A photograph of these puppies is included as Figure 57, page 269. The man at the center in the picture is W. P. Yant, who was in direct charge of the tests.

At the end of this investigation, during which the most careful and elaborate medical, pathological, and chemical tests were made on the animals exposed to the engine exhaust, the conclusion reached was as follows (R.I. 2661, December, 1924):

"In summing up the investigation it can be stated that there has been no indication of plumbism in any of the animals used, though they were exposed for 188 days during a period of approximately 3 months to exhaust gases from ethyl gasoline in concentrations with respect to lead content that are several times that allowable from the standpoint of the carbon monoxide."

As there was no evidence of lead poisoning in any of the animals at the end of the period reported, a second campaign of the same kind was begun in July, 1924, using now 5 times the commercial concentration of tetraethyl lead in the gasoline. This program was continued until August, 1925, a period of 12 months. It was found that the 5-fold concentration used was close to the maximum permissible for monkeys, dogs, rabbits and guinea pigs, in that some of the animals began to show lead storage "though not a comparatively large amount." (Experimental Studies on the Effect of Ethyl Gasoline and Its Combustion Products, U. S. Bureau of Mines, 1927, p. 16).

After the expiration of the original contract between the General Motors Research Corporation and the Bureau of Mines, a new contract was made with the Bureau by the Ethyl Gasoline Corporation.

200-55



FIGURE 57

PUPPIES BORN IN THE EXPOSURE CHAMBER AT THE BUREAU OF MINES DURING THE TESTS OF THE QUESTION OF WHETHER THE EXHAUST FROM AN ENGINE RUNNING ON ETHYL GASOLINE CONSTITUTED A HEALTH HAZARD. THESE PUPS WERE DUBBED "THE ETHYL GAS HOUNDS," AND THEY STAYED IN THE CHAMBER WITH THEIR MOTHER EACH DAY DURING THE REMAINING PERIOD OF THE TESTS, ALTOGETHER WITHOUT HARM.

ETC 37067

This arrangement, which extended from September 15, 1924, to June 30, 1925, called also for the investigation of possible hazards from breathing the vapors of Ethyl Gasoline and from exposing the skin to Ethyl Gasoline under conditions similar to those that might occur in its distribution and use. The tests were not confined to Ethyl Gasoline, however, but other motor fuels were included as well, including white (unleaded) gasolines and benzol blends.

Those who followed these later tests for the General Motors Chemical Company and the Ethyl Gasoline Corporation were, first, Dr. Graham Edgar, whose first actual endeavor in his position as director of research of the General Motors Chemical Company was on June 2, 1924, when on his way to Dayton he stopped in Pittsburgh and attended a conference at the Bureau of Mines. Second, was Dr. Robert A. Kehoe, Department of Physiology, University of Cincinnati, who began his long and effective service for Ethyl Gasoline during the summer of 1924, the most of which summer he spent in Dayton. Dr. Kehoe, incidentally, came to Dayton to take under observation the men at the Ethyl blending plant and to make studies of the hazards which existed or might exist there, previously mentioned. Others who followed these tests were Dr. W. Gilman Thompson for the Standard Oil Company of New Jersey and Dr. A. K. Smith for the du Pont Company.

The Bayway Episode

It was while these further tests at the Bureau of Mines were in progress that the upsetting poisoning episode at Bayway, mentioned previously, occurred. In August, 1924, a trial on the semi-works scale of the method of manufacturing tetraethyl lead employing ethyl chloride as alkylating agent, instead of the ethyl bromide then

used at du Pont, had been begun at Bayway by the Standard Oil Company, the plant having been operated for the account of the Ethyl Gasoline Corporation. This was of course a trial of the Kraus and Callis process previously mentioned. On Saturday, October 25, 1924, five of the 45 men working the plant in three shifts were taken seriously ill. This happened in spite of the fact that all had meanwhile been under medical observation. They were taken to the Reconstruction Hospital in New York for treatment. The sickness was however a new one which acted not like conventional lead poisoning but more like delirium tremens. The men affected developed various symptoms, including sleeplessness, low blood pressure, subnormal temperature, low pulse rate, loss of appetite, nausea, muscular weakness, headache, dizziness, and distorted dreams. In the worst cases the victims went out of their heads and had to be put into straight jackets.

There was front-page publicity in the New York papers and in almost every newspaper of the country. On the morning of October 27, a story in the New York Times was headlined

ODD GAS KILLS ONE, MAKES FOUR INSANE.

"Four men were under treatment for delirium in Reconstruction Hospital here yesterday," the story began, "and another was dead from the effects of breathing a gas used to increase the efficiency of gasoline in experiments at the research laboratory of the Bayway plant of the Standard Oil Company at Elizabeth, N. J." Some more expressive writer in another paper dubbed the stuff "looney gas."

The Health Board of the State of New Jersey requested that the manufacture of tetraethyl lead in that state be discontinued (the du Pont lead plant was at Deepwater, New Jersey), and that the sale

of Ethyl Gasoline be temporarily discontinued. The Health Boards of Philadelphia and New York City asked discontinuance of sale also. The Gulf Refining Company, one of the distributors of Ethyl Gasoline at that time, temporarily stopped the sale of it altogether. Midgley and A. M. Maxwell were kept busy visiting boards of health and explaining the difference between the nature of the concentrated tetraethyl lead or Ethyl fluid and the very dilute form represented by Ethyl Gasoline, which then had already been on the market for 18 months without ill effects anywhere. Dispensing of Ethyl fluid through the small ethylizers was discontinued at that time, however, and ethylizing was limited to the bulk form. That this was a courageous thing to do may be apparent from the fact that by that time about 17,000 individual ethylizers were in use.

The advertisement reproduced as Figure 58, page 273, was prepared and sent to all distributors of Ethyl Gasoline with the request that each publish it in his territory at the expense of the Ethyl Gasoline Corporation. The Bureau of Mines very kindly gave out a memorandum to the press for release on October 31 in which the difference between Ethyl Gasoline and the concentrated fluid was pointed out, the tests which they were then conducting were enumerated, and the absence of danger from lead in the exhaust which their tests had already demonstrated was reported to the public for the first time. This naturally helped a great deal to clear the air; but the Bureau could not yet at that time report their results on any dangers that there might be from breathing the vapor of Ethyl Gasoline itself, or from getting the gasoline on the skin while handling it.

ETHYLIZED GASOLINE

For one year and nine months ethylized gasoline has been on sale. It is now being distributed through about 20,000 filling stations covering one-third of the territory of the United States.

About 200,000,000 gallons have been used by more than 1,000,000 motorists with complete safety and satisfaction.

Recently a distressing accident occurred at an experimental plant, where a new process for the manufacture of tetraethyl lead, one of the constituents used in ethylizing gasoline, was under development.

Tetraethyl lead is a poison, as are many raw materials which enter into the manufacture of harmless compounds. Ethylized gasoline consists of 1300 parts of ordinary gasoline containing less than one part of tetraethyl lead.

This statement is issued to make plain the all-important difference between tetraethyl lead, the raw material, and ethylized gasoline, the commercial product.

Ethylized gasoline is more than an improved fuel, giving smoothness to the motor and eliminating knocks: it is a scientific discovery which, in its ultimate development, will contribute largely to the conservation of the world's supply of gasoline.

Exhaustive tests have been conducted which have established the safety of ethylized gasoline when used properly as a motor fuel. These tests have been confirmed by the United States Bureau of Mines, which is making additional studies to determine whether any possible injury can result from continued contact when used for other than motor purposes. Scientific data based on these studies will be submitted to any health commissioner or other public health official on request.

ETHYL GASOLINE CORPORATION

25 BROADWAY

NEW YORK CITY

FIGURE 58

COPY OF ADVERTISEMENT RUN DURING THE POPULAR HYSTERIA ABOUT THE SUPPOSED DANGERS OF ETHYL GASOLINE, FOLLOWING THE BAY-WAY POISONING EPISODE AND THE RESULTING PUBLICITY IN THE NEWSPAPERS.

In contrast to the criticism and adverse propaganda in the popular press, the technical journals almost universally took an impartial or unprejudiced position. Dr. H. E. Howe, editor of Industrial and Engineering Chemistry, for instance, published in the December, 1924, number of that journal a fine editorial on the subject (reproduced in Appendix VI). Also Dr. H. C. Parmelee, editor of Chemical and Metallurgical Engineering, tried to help calm the hysteria of the moment about Ethyl Gasoline.

But nevertheless the propaganda against the product continued, fostered chiefly in the press by the New York World, but also by some labor union publications. This campaign was aided in no small degree by Dr. Yandell Henderson of Yale University, who, when R. E. Wilson had approached him in 1922 about the matter, as related earlier, said that he thought lead-treated gasoline would "constitute an extremely serious health hazard," but offered to investigate the subject for a retainer of \$2,000 per month. Some idea of the part that Dr. Henderson and the New York World played in the campaign of adverse propaganda against Ethyl Gasoline may be got from the several copies of representative newspaper clippings of the time which are included as Appendix VI.

The Surgeon-General's Conference

So great was the effect of the events and of the flood of propaganda upon the public and upon boards of health that in May, 1925, Surgeon General Cumming felt compelled to call a conference of interested people in Washington to consider what ought to be done.

Early in May the Ethyl Gasoline Corporation had announced that meanwhile the sale of Ethyl gasoline would be discontinued voluntarily until such time as the various investigations then in progress and yet to be made could show whether any hazard to the public was really involved in the sale of the product as an automobile fuel. At the time Ethyl Gasoline was temporarily withdrawn from sale, it had been on the market more than 2 years and 300,000,000 gallons had been sold with no known bad effects.

The Surgeon-General's conference met in Washington on May 20, 1925, and was attended by about 75 persons (Appendix VI). "Under the skillful guidance of the Surgeon General, clinical and experimental facts were presented on the industrial and the public health aspects, followed by a free discussion of the whole matter. Fortunately, there was no acrimonious debate, though some of the statements made might better have been left unsaid." (quoted from editorial, Ind. Eng. Chem., 17, 552, June, 1925). Of the pertinent data presented to the conference, the most important was that from the three sources fostered by the Ethyl Gasoline Corporation itself. First, was that from the Bureau of Mines. Second, was the results of an investigation which had been in progress at Columbia University under the direction of Dr. Frederick B. Flinn. And, third, was the results of investigation which Dr. Robert A. Kehoe had for some months been conducting at Dayton.

A full report of this conference and what was said there are contained in Public Health Bulletin No. 158, August, 1925. Among the approximately 75 persons present were many who were antagonistic to the product under consideration, such as the Dr. Yandell

Henderson of Yale, previously spoken of; Dr. Alice Hamilton of Harvard, who had been writing and speaking against the product; N. P. Deppe of Deppe Motors Company, who had long been suing General Motors on carburetion systems; John M. Klein and Lee Sonneborn of the American Oil Company, Baltimore, distributors of benzol-containing gasolines; and a number of labor representatives, university professors, and public health men. Present on behalf of the Ethyl Gasoline Corporation were Messrs. Kettering, Webb, Midgley, Maxwell, Edgar, and Kehoe; also Messrs. C. O. Johns, E. M. Clark, R. A. Van Eaton, F. A. Howard, and Gilman Thompson of the Standard Oil Company of New Jersey; and Messrs. Irene du Pont, W. F. Harrington, Charles K. Weston, and Charles L. Reese of the du Pont Company.

It was during an intermission at this conference that Dr. Alice Hamilton, assistant professor of industrial medicine at Harvard Medical School, and a vociferous opponent of putting lead into gasoline, went up to Mr. Kettering and with fire in her eye told him that he was nothing but a murderer. Why, there are thousands of things better than lead to put into gasoline, she said.

"I will give you twice your salary," Mr. Kettering offered, "if you will name just one such material."

"Oh, I wouldn't work for you!" was her weak and unprofessional response.

The Surgeon General's conference came to a close with the adoption of this resolution:

"It is the sense of this conference that the Surgeon General of the United States Public Health Service appoint a committee of seven recognized authorities

in clinical medicine, physiology, and industrial hygiene to present to him, if possible by January 1 next, a statement as to the health hazard involved in the retail distribution and general use of tetraethyl lead gasoline motor fuel, and that this conference endorses as wise the decision of the corporation to discontinue temporarily the sale of tetraethyl gasoline."

This resolution, which was first introduced by Dr. Haven Emerson of Columbia and Dr. M. Nicoll, Jr., commissioner of health of the State of New York, was adopted after much debate. As originally presented, the last clause was this: "and that until such time distribution of this substance be discontinued," It was only after Dr. Henry F. Vaughan, of Detroit, president of the American Public Health Association, had protested that it was not possible to discontinue the sale of a product already voluntarily discontinued that the clause was changed to the form in which the resolution was adopted.

Investigation by the Surgeon-General's Committee of Seven

The committee of investigation, thus authorized and later appointed by Surgeon General Cumming, consisted of the following men:

William H. Howell, professor of physiology at the Johns Hopkins School of Hygiene and Public Health, chairman.

A. J. Chesley, executive state health officer of Minnesota.

David L. Edsall, dean of Harvard Medical School and chief of the Medical Clinic, Massachusetts General Hospital.

Reid Hunt, professor of pharmacology, Harvard Medical School.

W. S. Leathers, professor of preventive medicine, Vanderbilt University.

Julius Stieglitz, professor of chemistry, University of Chicago.

C.E.A. Winslow, professor of public health, Yale Medical School.

Immediately after the committee had been named, Mr. Webb, on behalf of the Ethyl Gasoline Corporation, tendered personally and in writing to Surgeon-General Cumming "compliments upon the excellence of the committee appointed and our full and unreserved cooperation with him and his committee throughout their investigation. The Surgeon-General replied that there will probably be many occasions during the committee's deliberation when it will become necessary to get certain information and data from us and he would be pleased to communicate to the committee that we, at all times, would be at their service" (Minutes, Special Meeting Board of Directors, Ethyl Gasoline Corporation, June 16, 1925).

The actual conduct of the investigation was put in charge of Dr. J. P. Leake, surgeon of the United States Public Health Service. Dr. Leake organized a corps of workers consisting of the following: Lawrence Kolb, Louis Schwartz, Gleason C. Lake, Charles Armstrong, and W. T. Harrison, surgeons; Claude W. Mitchell, past assistant surgeon; William Mansfield Clark, professor of chemistry; Elias Elvove, chemist; C. G. Remsburg, assistant chemist; Conrad Kinyoun, assistant bacteriologist; J. J. Bloomfield, assistant physical chemist; Wallace Hall, assistant chemist; and William A. Simkins, junior chemist. This group received assistance also from many others, including surgeons G. W. McCoy, L. R. Thompson, and R. R. Sayers of the U. S. Public Health Service; Dr. Lawrence T. Fairhall of the Harvard School of Public Health; W. P. Yant of the Bureau of

Mines; and Graham Edgar of the Ethyl Gasoline Corporation.

Although the general sale of Ethyl Gasoline to the public had been voluntarily discontinued by the Ethyl Gasoline Corporation on May 5, 1925, this group was enabled to conduct an investigation of the product under conditions of actual usage by virtue of the fact that in southwestern Ohio "a supply of ethyl fluid was still in the hands of certain consumers and would be continued in use" (Report of the Committee of Seven, January 17, 1926), Public Health Bulletin No. 163, page 103). As a matter of fact, Ethyl Gasoline remained on sale continuously at certain stations in Ohio and West Virginia. These were the stations of the Refiners Oil Company and those of Spears and Riddle, distributors of the product since early in 1923. During this investigation as conducted, 252 persons were examined in an elaborate program of particulars. The men were composed of 5 groups, as follows:

- Group A. A control group, 36 men, drivers of cars out of the municipal garage of the City of Dayton, using no Ethyl Gasoline.
- Group B. Test group, 77 men, drivers of cars out of the garage of a Dayton public-service corporation (Dayton Power and Light Company) using Ethyl Gasoline exclusively since July, 1923.
- Group C. Control group, 21 men, workers in garages using no Ethyl Gasoline, and gasoline truckers and filling station men who did not handle Ethyl Gasoline.
- Group D. Test group, 57 men, workers in garages using Ethyl Gasoline, and gasoline truckers and filling station men handling Ethyl Gasoline.
- Group E. Control group, 61 men, employed in two industrial plants in which there was known to be serious exposure to lead dust.

Each individual was subjected to a careful clinical examination by four physicians who worked independently and also "blind," that is without knowing the nature of the individual's exposure to lead, if any. In addition smears were made of the subject's blood, for hemoglobin estimation, red-cell count, and count for stippled cells. Also a specimen of each subject's feces was collected and elaborately examined to determine the amount of lead elimination in his case.

Reports of the Committee of Seven and the Bureau of Mines

The general conclusions from this investigation by the Committee of Seven were as follows (Public Health Bulletin, No. 163, "The Use of Tetraethyl Lead Gasoline in Its Relation to Public Health," 1926, page 109):

1. Drivers of cars using ethyl gasoline as a fuel and in which the concentration of tetraethyl lead was not greater than 1 part to 1,300 parts by volume of gasoline showed no definite signs of lead absorption after exposures approximating two years.
2. Employees of garages engaged in the handling and repairing of automobiles and employees of automobile service stations may show evidence of lead absorption and storage, as indicated by the lead content of the feces and the appearance of stippled cells in the blood. In garages and stations in which ethyl gasoline was used the amount of apparent absorption and storage was somewhat increased, but the effect was slight in comparison with that shown by workers in other industries where there was a severe lead hazard (Group E) and for the periods of exposure studied was not sufficient to produce detectable symptoms of lead poisoning.
3. In the regions in which ethyl gasoline has been used to the greatest extent as a motor fuel for a period of between two and three years no definite cases have been discovered of recognizable lead poisoning or other disease resulting from the use of ethyl gasoline.

On the basis of the results of this elaborate program of test, so expeditiously conducted under the able guidance of Dr. Leake, the Committee of Seven reported to Surgeon-General Cumming on January 17, 1926, as follows (Public Health Bulletin, No. 163, page 110):

"Your committee begs to report that in their opinion there are at present no good grounds for prohibiting the use of ethyl gasoline of the composition specified as a motor fuel, provided that its distribution and use are controlled by proper regulations."

Meanwhile, in the summer of 1925, the Bureau of Mines had concluded the further work which it had in progress, as already outlined. Doctor Kehoe had also been pursuing his studies in the field. For the purposes of this history, the work of Dr. Kehoe and the further studies at the Bureau of Mines are sufficiently summarized in the following editorial comment on the just-mentioned report to the Surgeon-General (Ind. Eng. Chem., 18, 112, February, 1926):

"The report . . . confirms the excellent piece of work done some time ago by the Bureau of Mines under the direction of Dr. R. R. Sayre (Sayers) and also the results reported by Dr. R. A. Kehoe of the University of Cincinnati. The results of these investigations had previously been severely criticised and it is, therefore, a pleasure to record the confirmation of their work by the present committee."

The official report of the Bureau of Mines to the General Motors Research Corporation and the Ethyl Gasoline Corporation was issued in full in 1927 under the title "Experimental Studies on the Effect of Ethyl Gasoline and Its Combustion Products." Incidentally, Dr. Kehoe had, in his early work referred to here, made a new and surprising observation, which was that men in normal occupations not having any abnormal exposure to lead showed considerable elimination

of lead (Public Health Bulletin, No. 158, page 20), and he later established this by extensive experiments, even to studying men in primitive society.

The Surgeon-General's Regulations

"The Regulations Proposed Following the Tetraethyl Lead Investigation" were issued promptly by the Surgeon-General. And, under the guidance of Dr. Kehoe and his staff they have ever since been religiously followed by the Ethyl Gasoline Corporation and its licensees. The regulations consisted of four sections, as follows (Public Health Bulletin, No. 163, 1926):

- I. Proposed regulations for the manufacture of tetraethyl lead and the blending of the latter to make ethyl fluid.
- II. Proposed regulations for mixing.
- III. Proposed regulations for distribution of ethyl gasoline.
- IV. Proposed regulations for automobile garages, repair shops, service stations, and filling stations.

The first one of the Proposed Regulations for Mixing was this:

"The maximum content of tetraethyl lead in commercial ethyl gasoline shall be in the proportion of 1:1,260 by volume for commercial tetraethyl lead, or 1:1,300 for Pb (C₂H₅)₄ C.P."

Later, in 1928, there was issued "Changes in the Regulations Proposed for Tetraethyl Lead Gasoline" (Reprint No. 1260 from the Public Health Reports, November 30, 1928). The changes related to the section dealing with distribution, and gave more details concerning the placing of signs on filling station pumps and on all containers of

Ethyl Gasoline sold to consumers. The sign designated to go in a prominent position on each filling station pump dispensing Ethyl Gasoline was to bear the following, which as later events proved was to be placed on about three-fourths of all the filling station pumps in the country, either as such or as some modification of it:

"Contains
Lead
(tetraethyl) and is to be used as motor fuel only,
not for cleaning or any other use.
Avoid spilling"

The investigation of the possible lead hazards associated with the distribution and use of gasoline containing tetraethyl lead, similar to that made by Dr. Leake for the Surgeon-General's committee, was continued afterwards on a larger scale by Doctor Kehoe and his group. During 1927 there were between 400 and 500 persons under observation. Reporting on still further observations made in 1929, Doctor Kehoe concluded thus (Kehoe, Thamann, and Cholak, Jour. Ind. Hygiene, 16, 100, March, 1934):

Three hundred and one men who had incurred the severest and longest exposure to leaded gasoline and its combustion products were studied as to their physical fitness and their lead excretion, during the winter months of 1929-30. No clinical evidences of lead absorption or of lead intoxication were found in any individual, and no indication of lead absorption, as a consequence of the exposure, was detected when the subjects were compared as to their lead excretion with corresponding groups of unexposed persons who had been studied previously.

* * * * *

In view of the negative evidence obtained in this study of persons whose exposure to leaded gasoline and its combustion products was magnified to a point well above that which is possible in the general population, there is no reason to fear the existence of danger to the public health from the distribution and use of leaded gasoline.

It should be said further that the subject of possible health hazards from leaded gasolines was again fought out in England when Ethyl Gasoline was introduced there in 1928. After violent attacks against the product in the press and elsewhere, a Departmental Committee on Ethyl Petrol was appointed by the Minister of Health upon authorization by Parliament. This group of distinguished men studied the reports of all the investigations made on this side; they interviewed Doctor Leake, Surgeon-General Cumming, Doctor Kehoe, Doctor Edgar, and A. M. Maxwell from this side; and they conducted a series of investigations of their own. Number 1 of the conclusions which they reached was this:

The results of our experiments agree with the results of the experiments carried out in the United States of America, whether on behalf of the United States Government Committee or of the Ethyl Gasoline Corporation, and fully confirm the view we expressed in our Interim Report that the findings of the United States Government Committee were justified.

(Interim Report of the Departmental Committee on Ethyl Petrol, H. M. Stationery Office, 1928; Final Report of the Departmental Committee on Ethyl Petrol, same, 1930).

CHAPTER XVII
"ETHYL IS BACK"

The report of the Surgeon-General's Committee, as issued in January, 1926, was generally accepted. And arrangements were made by the Ethyl Gasoline Corporation to resume the sale of Ethyl Gasoline at once. This was done in strict compliance with the regulations proposed by the Surgeon-General, but so far as is known no state passed a law to enforce the regulations. Only in the City of New York, where a resolution prohibiting the sale of Ethyl Gasoline had been passed by the City Board of Health in 1924 and which remained in force until June, 1928, was there restriction on the sale of the product. Expansion of the distribution from that point on was therefore rapid. How rapid it was is indicated by the growing list of distributors contained in Figure 41, page 210.

Thus it was almost exactly three years after the sale of Ethyl gasoline had been begun in February, 1923, and nearly ten years after the beginning of the search for an antiknock agent, that it began to recover from its tribulations and to move forward toward the great success it later achieved. By this time the deficit of the Ethyl Gasoline Corporation had mounted up nearly to \$3,000,000. This did not, of course, include the original development expense. And so Ethyl Gasoline was between three and four million dollars in the red before it got into the black, and much work had yet to be done before any black ink began to appear at the end of its financial statements. But that is a story which will not be followed here.

It may however be mentioned that after the coming of the "Q Brand" in 1933, in which tetraethyl lead was put into regular-price gasolines, the use of the compound expanded rapidly until about three-fourths of all the gasoline sold in the country contains tetraethyl lead. This expansion was aided by the wise and liberal policy of the management of the Ethyl Gasoline Corporation in respect to the prices distributors were charged for the tetraethyl lead.

How, as it became possible to do so, the price charged gasoline producers for tetraethyl lead was gradually and voluntarily lowered is shown below.

1923 to Oct., 1928 — No gallonage charge, 1 c per c.c.

Oct. 1, 1928 to Aug. 15, 1929 — 0.7c gallonage charge,
0.5c per c.c.

Aug. 15, 1929 to Jan. 1, 1930 — 0.6c gallonage charge,
0.4c per c.c.

Jan. 1, 1930 to July 1, 1930 — 0.6c gallonage charge,
0.35c per c.c.

July 1, 1930 to March 1, 1932 — 0.5c gallonage charge,
0.35c per c.c.

March 1, 1932 to July 15, 1933 — 0.425c gallonage charge,
0.35c per c.c.

July 15, 1933 to Jan. 1, 1934 — 0.2c gallonage charge,
0.35c per c.c.

Jan. 1, 1934 to Dec. 1, 1934 — No gallonage charge,
0.33c per c.c.

Dec. 1, 1934 to Nov. 1, 1935 — No gallonage charge, 0.30c
per c.c.

Nov. 1, 1935 to July 1, 1936 — No gallonage charge,
0.28c per c.c.

July 1, 1936 to July 1, 1939 — No gallonage charge,
0.26c per c.c.

July 1, 1939 to May 15, 1940 — No gallonage charge,
0.25c per c.c.

May 15, 1940 to April 1, 1941 — No gallonage charge,
0.23 c per c.c.

April 1, 1941 to April 1, 1942 — No gallonage charge,
0.20c per c.c.

April 1, 1942 to — — No gallonage charge,
0.18c per c.c.

The upward trend of octane number during recent years, particularly after tetraethyl lead was made available for addition to regular-price gasolines around 1933, is shown in Figure 59, page 288. The curves there, which show the averages for the three grades of gasoline are those given by William H. Hubner of the Ethyl Gasoline Corporation (S.A.E. Jour., 47, 409, October, 1940). Tetraethyl lead began to be added to third-grade gasolines about 1938, and the steep rise in average octane number resulting from it is seen on the chart also.

Ethyl in Aviation

Brief mention should perhaps be made also of the large place which tetraethyl lead has played in aviation. As before related, the first purchasers of antiknock agents in any considerable amounts were the aircraft branches of the Army and the Navy. That was back in 1920. Ever since tetraethyl lead has been available it has been used to some degree by military and commercial aircraft. When the Surgeon-General's conference was held in May, 1925, as already related, one of those who attended and put in a plea for the continuance of tetraethyl lead as a much needed material was an officer of the Bureau of Aeronautics of the Navy Department.

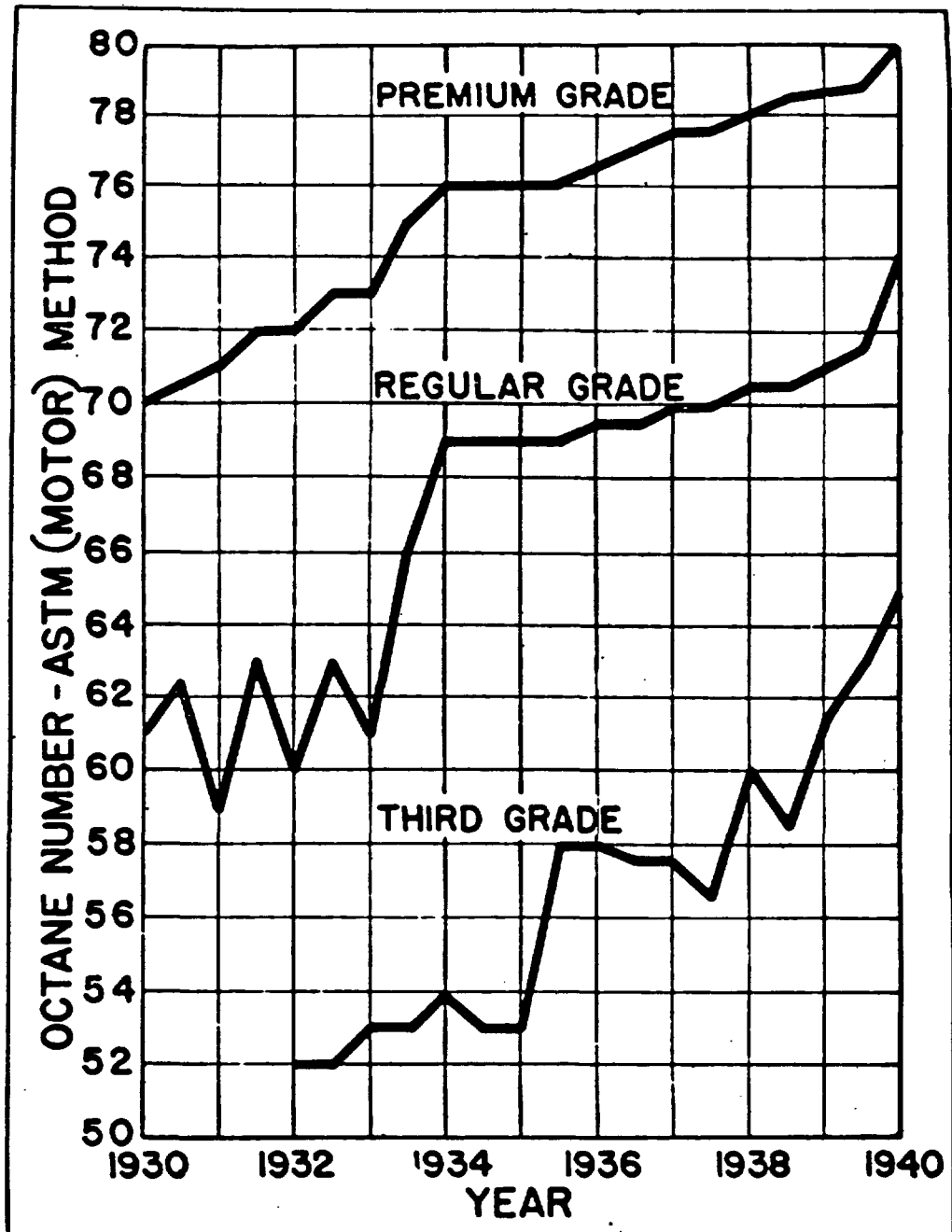


FIGURE 59

THE UPWARD TREND IN THE AVERAGE OCTANE NUMBER OF AUTOMOBILE GASOLINE IN THE UNITED STATES SHOWN FOR EACH OF THE THREE GRADES. PARTICULARLY APPARENT IS THE STEEP RISE IN THE REGULAR-GRADE CURVE AFTER 1933 WHEN TETRAETHYL LEAD BEGAN TO BE ADDED TO SUCH GASOLINES, AND THE SIMILAR RISE IN THE THIRD-GRADE CURVE AFTER 1938 WHEN TETRAETHYL LEAD BEGAN TO BE PUT INTO LOW-PRICE GASOLINES.

At Wright Field in Dayton, one of those concerned with adapting the airplane engines of the Army to use the higher octane fuels made possible by tetraethyl lead was S. D. (Sam) Heron, who now for some years has been a valued member of the staff of the Ethyl Gasoline Corporation. The high-octane gasolines so necessary in military planes and in commercial aircraft have in large measure been made possible by tetraethyl lead. This is particularly so in respect to the 100-octane gasolines containing considerable amounts of synthetic hydrocarbons, for in such hydrocarbons tetraethyl lead is much more effective as an antiknock agent than it is in conventional gasolines. The use of Ethyl fluid for boosting octane number--by permitting, as it does, the dilution of precious synthetics with large amounts of base gasoline much lower in octane number--has made it possible to produce a great deal more high-octane aviation gasoline than would have been possible otherwise.

Iron Carbonyl

During all these years, the only compound that appeared to threaten in any wise the exclusive place of tetraethyl lead as an antiknock agent was iron carbonyl. When on August 15, 1922, nickel carbonyl was found to be an effective antiknock compound (Record 19, page 130), and when later cobalt carbonyl was found to be effective also it was inferred that iron carbonyl would be an effective antiknock agent as well. The nickel carbonyl had been prepared by W. H. Charch, and he made many efforts to prepare also or to buy some iron carbonyl for test. But, although these efforts of his extended over many months, they were altogether unsuccessful, so far as yielding

any iron carbonyl for test was concerned. This, as later developed, was because iron carbonyl can not be made except under high pressure, suitable apparatus for which had not been at Charch's disposal.

On the 18th of November, 1924, Jasper E. Crane, European Manager for the du Pont Company, wrote Mr. Kettering at his Paris address (Mr. Kettering, as previously related, was at about that time in Tunis investigating the bromine possibilities there). Mr. Crane's letter was to the following effect: A director of the Badische Company of Germany (Badische Anilin und Soda Fabrik) had recently been in Wilmington and had told Mr. Harrington and Mr. Pickard of the du Pont Company about a wonderful new antiknock agent which his company had developed. A cable had been sent to Mr. Crane who had then gone to Cologne, Germany, to see Dr. Carl Bosch of Badische about the matter. Dr. Bosch gave Mr. Crane no very specific information, except that they had such a compound and that they should be willing to dispose of it under favorable terms.

After Mr. Kettering got back to Paris, he and Mr. Crane went to Ludwigshafen, Germany, to investigate the matter further. During two days time, November 28 and 29, 1924, they saw Dr. Wilhelm Gaus, Dr. Mueller-Cunradi, and Dr. Carl Bosch. The antiknock effectiveness of the compound was demonstrated to them. The Badische men did not disclose the composition of the compound, but Mr. Kettering guessed that it was iron carbonyl and told Doctor Bosch so. And this, as it later developed, was the composition of the compound. They had been able to make iron carbonyl easily in connection with the manufacture of ammonia and methyl alcohol by the method of synthesis under high pressure which was being conducted there. The

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compound was, in fact, an unavoidable by-product. Dr. Bosch and his men reported that cars had been run as much as 10,000 miles on gasoline treated with the product, that the compound could be made for less than 25 cents a pound in any amount needed, and that it required no corrective agent as did tetraethyl lead. The proposal of the Badische people was that an agreement be made by which the Ethyl Gasoline Corporation would replace the tetraethyl lead in Ethyl gasoline with iron carbonyl and that the resulting savings be divided equally between Badische and Ethyl as profit.

The Badische people were very secretive about the material and extremely reluctant to send any of it over for test on this side. But, when they came to realize that no commitments of any kind would be made without such tests, they did send over a quantity of the compound, and laboratory engine tests of it were begun in the Fuel Section of General Motors Research Corporation in February, 1925 (Monthly Report, February, 1925). It was thus quickly found that, although no noticeable wear of piston rings in the one-cylinder engines resulted from the iron oxide produced by the burning of the compound, the spark plug was quickly shorted out by the conductive coating of iron oxide deposited on the porcelain between the skirt and the center electrode. So a search was begun at once for a possible corrective agent, using the same engines and technique as had been successful in the case of tetraethyl lead. A great many materials were tried, but altogether without success in stopping the shorting of spark plugs.

Then in April, 1925, Dr. Mittasch and Dr. Mueller-Cunradi from Badische came to the laboratory. The difficulties found here

were explained to them. This, they said, was most peculiar, as no spark plug troubles had been experienced during their work in Germany. But Dr. Mueller-Cunradi could and would remain at the laboratory for a time to find a solution for the problem. The next day he gave us a list of suggested corrective agents to try. As it turned out, most of these had already been tested, and the others when tried did not prove at all effective. Accordingly, Dr. Mueller-Cunradi soon went on back to Germany. The results of all these tests are covered in a memorandum prepared by James P. Andrew on April 21, 1925, "Results Obtained in Effort to Prevent the Depositing of Iron Oxide in Engines Run on Gasoline Treated with Iron Carbonyl."

Dr. Mueller-Cunradi seemed to have had an unflattering opinion of the capabilities of the men on this side. This is perhaps illustrated by the following story. When Dr. Mueller-Cunradi met Doctor Edgar, he asked Dr. Edgar when he was in Germany.

"I am sorry that I have never been in Germany at all."

"You are Doctor Edgar, are you not?"

"Oh, yes, I got my doctor's degree at Yale University in New Haven."

"Why," said Dr. Mueller-Cunradi, "I did not know that doctors degrees were given anywhere except in Germany!"

In the Patent Office our application relating to nickel carbonyl and other volatile metal carbonyls ran into interference with the Badische application on iron carbonyl. The interference was composed by agreement between the Ethyl Gasoline Corporation and the Badische Anilin und Soda Fabrik which in brief was as follows: First,

since Badische had an earlier date on iron carbonyl for reduction to practice, the patent on iron carbonyl was to go to them, and was later issued as U.S. 1,646,014, M. Mueller-Cunradi and W. Wilke, October 18, 1928. Second, Badische's right to distribute iron carbonyl was however to be limited to Germany, the rights to iron carbonyl for the U. S. England, and Canada going to the Ethyl Gasoline Corporation. There was then issued to Midgley the patent, U. S. 1,662,323, March, 1928, claim 4 of which reads broadly as follows: "A motor fuel containing a volatile carbonyl of a metal other than iron."

Later on, in 1928, the Research Laboratory of the Ethyl Gasoline Corporation made an extensive series of car tests of iron carbonyl to find out for sure whether the compound could be used in practice. This further investigation was undertaken because of a report from Roy T. Hurley of the Moto-Meter Gauge and Equipment Company, saying that the addition to iron carbonyl of a small percentage of tetraethyl lead greatly reduced the occurrence of spark plug difficulties experienced with iron carbonyl alone. (This suggestion may not have been an original idea of Mr. Hurley's, however, as there is a British patent, 252,018 issued in 1927 and owned by the Badische Company of Germany, which relates to the same subject.) An extensive program of tests was carried out, the results of which showed that, whatever the effect of adding a percentage of tetraethyl lead may have been, the spark plug troubles were again experienced. Experienced also in these tests was increased engine wear, which was so large as to render the use of iron carbonyl definitely impractical.

These later tests by the Ethyl Gasoline Corporation included also an effort to improve the stability of iron carbonyl to light, the compound being naturally extremely sensitive to decomposition by light. But this effort did not prove to be more than moderately successful either. And thus, in spite of extensive efforts to make it so, iron carbonyl has not been found to be a practical antiknock agent. Fuels containing the compound were, however, sold in Germany for some years under the name "Motolin." But even there the use of iron carbonyl is understood to have been altogether discontinued some years ago. However, a number of efforts have recently been made by unauthorized persons to market iron carbonyl as an antiknock agent on this side.

Complaints

From the beginning of the sale of Ethyl gasoline there was opposition to it on the part of various people, on the ground that it damaged engines, notably by causing exhaust valves to burn out. This opposition came chiefly from service stations, garage mechanics, automobile makers—and also, of course, from competitors of Ethyl. And in the early days of the sale of the product there were grounds for the complaints. The effort to combat this opposition began in the days of the General Motors Chemical Company, before the Ethyl Gasoline Corporation was organized in 1924. Issued then was "General Motors Chemical Company Service Bulletin No. 1 - Valves." The purpose of the folder was "to familiarize users and garage men alike" with the changed appearance of exhaust valves when using Ethyl gasoline and to assure them that they need not worry about it. Later on the Ethyl

Gasoline Corporation prepared at least two booklets, called "primers," for use in combating these complaints and propaganda—one in 1927, "Information about Ethyl Gasoline"; the other in 1931, "The Inside Story of Ethyl Gasoline."

The steel used for exhaust valves in the early days of Ethyl Gasoline was not resistant enough to oxidation to withstand even the effects of burning regular gasoline for very long. But slowly matters in this regard were improved as car makers adopted oxidation-resisting alloys for exhaust valves, such as that known as silichrome No. 1. After some time it became possible to get automobile makers formally to approve the use of Ethyl Gasoline in their cars. Thus in the February, 1927, number of The Cadillac Service Man was this item:

ETHYL GASOLINE APPROVED
FOR USE IN CADILLAC CARS
Frequent inquiries are received
by the Service Department regarding
the suitability of Ethyl gasoline
for Cadillac cars.

For the benefit of those who
have occasion to answer similar
inquiries in the service station,
we inform our readers that the
Cadillac Motor Car Company approves
the use of Ethyl Gasoline in cars
manufactured by them.

But the opposition to gasolines containing tetraethyl lead continued in many quarters, and in some it still does persist even today, although it has long ago ceased to be a factor of any considerable importance. The fact is that cars run much further on lead-treated gasolines nowadays without attention to valves than it used to be

possible to run them on plain gasolines. An example of the continuing opposition to lead-treated gasolines is the persistent campaign waged against them for some years in the publications of the Consumers Union. Thus in the July, 1939, number of Consumers Union Reports was this item:

CU must repeat its previous warnings as to the health hazard offered by any leaded gasoline. Although the U. S. Public Health Service has claimed it found no harmful effects from the exhaust fumes given off by engines using leaded gasolines, in CU's opinion the possibility of such a hazard remains and is, in fact, increasing with the wider use of leaded fuels.

Difficulties in Airplane and How Overcome

In aircraft some definite difficulties from the use of leaded gasolines were experienced. These were chiefly the burning of exhaust valves under the very severe conditions of airplane engine operation, rusting of engines in storage after use, and attack on exhaust systems that resulted in scaling. This scaling—it was believed—caused some planes to be set on fire, by incandescent particles carried back on wings and fuselages before the days of all-metal planes. Nevertheless, the attitude of the army aviation people was like that of Mr. F. E. Moskovics, mentioned earlier, when he wrote about tetraethyl lead before a suitable corrective agent had been found: "As bad as it is I should like to get some more." Just so in the face of the difficulties which existed the aircraft people continued to use lead-treated gasolines. In a paper published in 1930, S. D. (Sam) Heron, then at Wright Field, said this (A.S.M.E. Transactions, Aeronautical Engineering, October-December, 1930, page 233):

It is the viewpoint of the Materiel Division that doped fuel of some type is here to stay for high-performance military aircraft engines and that the difficulties attending the use of such fuel can be overcome, as they have been in automobile engines.

These difficulties were gradually overcome by various developments, such as better alloys, stellite-faced exhaust valves and seats, and sodium-cooled or salt-cooled exhaust valves. In fact Sam Heron himself had no small part in solving the problems mentioned.

Patents

Although some of the patents taken out during the research which culminated in Ethyl Gasoline have been mentioned from time to time in this history, not all have been included. And so a list of the nearly 30 such patents, as assigned to the General Motors Research Corporation, is incorporated as Appendix VII. Because of its importance, mention should be made also of the first patent issued to Kraus and Callis, in their work for the Standard Oil Company of New Jersey, covering the method of making tetraethyl lead by using ethyl chloride as a substitute for the ethyl bromide previously employed, U. S. 1,612,131, December 28, 1926.

Conclusion

This seems to be the point where The Early History of Ethyl Gasoline ought to end. The story covers a period of about 10 years. That period runs from the time when the investigation of knock and the

search for a way to cure it began, until—with the end of all the trials endured in answering, to the satisfaction of everyone concerned, the question about whether the presence of tetraethyl lead in gasoline would poison people or not—the use of Ethyl fluid as an antiknock agent had surmounted its last major hurdle, and the endeavor began to be a success. In view of all the difficulties and uncertainties encountered, and of the years of hard work that had to be done during that time, and in view also of the 3 million dollars in red figures on the books at the end of that 10-year period, the title of this story—like that of many another pioneering endeavor—might well have been stated thus: "It's the First Ten Years That Are the Hardest."

A fitting conclusion to the story would perhaps be to list some of the concrete effects of the Ethyl development, as enumerated by Thomas Midgley, Jr., in a recent paper of his, "Problem + Research + Capital = Progress" (Ind. Eng. Chem., 31, 504, May, 1939):

Tetraethyl lead broke down one of the barriers that was blocking the road to automotive progress—the barrier of knock.

It has thus added to the power and performance of over fifty million automobiles.

It has contributed to the constant improvements in quality and the steadily decreasing price of billions of gallons of gasoline annually.

It has made possible the present peaks in performance of airplanes.

It has strengthened our national defense.

It has lowered costs in power farming and truck transport.

It has caused the construction of millions of dollars worth of factories, laboratories, transportation,

and blending facilities, for its manufacture, distribution and use.

It has given temporary and permanent employment to many.

It has uncovered fresh sources of mineral wealth by "mining" the waters of the ocean successfully.

It has aided oil companies in the conservation of petroleum in their gasoline refining processes.

It has paid taxes toward the support of government.

It has made a profit for those corporations that had the courage to go through a long and difficult "shirt-losing period" because they believed that antiknock gasoline would eventually succeed.

APPENDIX I

Extract from Report of May 15, 1920,
entitled "The Motor Fuel Problem"

61-
see p. 69THE MOTOR FUEL PROBLEM

The problem is to increase the available supply of fuels suitable for use in motor vehicles and, at the same time, to conserve the fuel resources of the country, in order to insure the present and future usefulness of motor-driven vehicles.

Possible means of increasing the supply of liquid motor fuels are:

- (1) Production of alcohol for motor fuel
- (2) Production of motor fuels from coal
- (3) Production of motor fuels from oil shale
- (4) Making available for use in motor vehicles a larger percentage of petroleum than can be used at present.

Alcohol has only two-thirds as much heating value per gallon as has gasoline. Forty-six per cent (46%) of all food stuffs produced in the United States in 1918 would have been required to yield enough alcohol to take the place of the gasoline produced in 1919. (See Note 1)

On the basis that all the bituminous coal mined in 1916 could have been coked in by-product ovens and that seventy-five per cent (75%) of the light oil so produced could have been made available for use as a motor fuel, the yield would have been about twenty-five per cent (25%) of the gasoline produced during that year. In 1919, the actual production of material from coal, suitable for motor fuel, was about two per cent (2%) of the gasoline produced. (See Note 2)

The shale deposits in this country are enormous. But, for refining oil shale, large initial investment and construction on a very large scale would be necessary. It would be several years before the industry could come into quantity production, and an increase in available motor fuel must come within the near future if the use of motor-driven vehicles is not to be curtailed. The deposits of oil shale should be considered as a future source of motor fuel but a source which cannot possibly be available for several years.

Note 1:

Total possible production alcohol, 1918, gals.---12,820,400,000
Production of gasoline, 1919, gallons----- 3,957,857,097

Ratio heating value of $\frac{80,000 \text{ b.t.u. per gal.}}{120,000 \text{ b.t.u. per gal.}} = \frac{2}{3}$
alcohol to that of gasoline

Note 2:

Data from "Internal Combustion Engine Fuels" by E. W. Dean,

While some motor fuel may be obtained from the sources given immediately above, petroleum is the cheapest, most abundant, and best source of such fuel. Doctor E. W. Dean, Petroleum Chemist, United States Bureau of Mines, says, "The nation certainly needs to increase its engine-fuel resources and no step in this direction should be hindered. It should be recognized, however, that petroleum gasoline is a type of fuel for which present equipment has been designed and for which it is eminently satisfactory." (See Note 3)

The best solution of the motor fuel problem is to make available for use in gasoline motors a much larger percentage of the crude oil than the twenty-five which is now used. This may be done by:

- (a) Cracking the heavy petroleum distillates.
- (b) Making it possible to burn straight petroleum distillates of a much higher end point than it is now possible to run in motors of standard compressions.

Cracking is very wasteful from a fuel-conservation standpoint, and it is not profitable unless there is a wide margin between the price of fuel oil and that of gasoline.

The best means of increasing the available fuel supply and, at the same time, of conserving the nation's fuel resources is to burn larger percentages of the crude oil in motors in the form of straight distillates. Such a procedure would both simplify and cheapen refining, but the burning of distillates of high boiling range presents difficulties from knocking at normal compressions, in starting, in atomization and distribution, from crankcase dilution, and from carbonization.

Work so far conducted in this laboratory has shown that:

- (1) High boiling petroleum distillates, even up to fuel oil, may be run in motors of standard compressions without knocking. This result may be obtained in a number of ways, the best of which is to add to the fuel a small percentage of "anti-knock", of which aniline, toluidine, and xylydine are the most practical.
- (2) Motors can be started on high boiling petroleum distillates by use of the Good suction burner, or by priming the cylinders with small amounts of volatile fuel.
- (3) Heavy fuel can be finely atomized by mechanical means, and it can be properly distributed by making use of the Good suction burner.

Note 2 (continued):

Jour. S.A.E., February 1920, page 117, and from article in "Oil and Gas Journal", April 9, 1920, by A. W. Ambrose, U. S. Bureau of Mines.

Note 3:

Quoted from the first reference given in Note 2.

APPENDIX II

Cost of Fuel Research from
July 1, 1917, to February 29, 1920

FUEL COSTS FOR PERIOD JULY 1, 1917 to
FEBRUARY 29, 1920

JULY 1 to DEC. 31, 1917

Direct Salaries for above period	1,958.70	
Direct Overhead 198.96%	3,397.09	
113 hours Laboratory work at 3.811 per hour	<u>430.95</u>	6,286.74

JANUARY & FEBRUARY 1918

Direct Salaries	630.00	
Direct Supplies	31.95	
Direct Overhead 66.6266%	<u>419.59</u>	1,081.54

MARCH 1918

Direct Salaries	372.50	
Direct Supplies	486.51	
Direct Overhead 48.625%	<u>181.08</u>	1,040.09

APRIL 1918

Direct Salaries	400.00	
Direct Supplies	114.38	
Direct Overhead 63.217%	<u>252.88</u>	767.26

MAY 1918

Direct Salaries	466.50	
Direct Supplies	496.84	
Direct Overhead 63.7396%	<u>297.35</u>	1,260.69

JUNE 1918

Direct Salaries	322.50	
Direct Supplies	196.19	
Direct Overhead 50.677	<u>163.43</u>	682.12

JULY 1918

Direct Salaries	410.00	
Direct Supplies	381.85	
Direct Overhead	<u>206.15</u>	998.00

AUGUST 1918

Direct Salaries	493.50	
Direct Supplies	528.79	
Direct Overhead 60.256%	<u>297.36</u>	1,319.65

SEPTEMBER 1918

Direct Salaries	388.08	
Direct Supplies	734.28	
Direct Overhead 56.0706%	<u>217.60</u>	1,339.96

OCTOBER 1918

Direct Salaries	800.00	
Bonus paid for previous 6 months	152.88	
Direct Supplies	712.24	
Direct Overhead	<u>490.41</u>	2,155.53

NOVEMBER 1918

Direct Salaries	565.00	
Direct Supplies	731.29	
Direct Overhead 47.4105%	<u>267.87</u>	1,564.16

DECEMBER 1918

Direct Salaries	571.09	
Direct Supplies	626.70	
Direct Overhead 70.8313%	<u>404.51</u>	1,602.30

JANUARY 1919

Direct Salaries	506.25	
Direct Supplies	399.82	
Direct Overhead	<u>421.36</u>	1,327.43

FEBRUARY 1919

Direct Salaries	372.50	
Direct Supplies	205.90	
Direct Overhead	<u>463.57</u>	1,041.97

MARCH 1919

Direct Salaries	360.26	
Direct Supplies	372.09	
Direct Overhead	<u>396.28</u>	1,128.63

APRIL 1919

Direct Salaries	680.00	
Direct Supplies	270.96	
Direct Overhead	<u>825.20</u>	1,776.16

MAY 1919

Direct Salaries	360.00	
Direct Supplies	278.18	
Direct Overhead	<u>595.87</u>	1,234.05

JUNE 1919

Direct Salaries	405.00	
Direct Supplies	80.34	
Direct Overhead	<u>489.67</u>	975.01

JULY 1919

Direct Salaries	845.00	
Direct Supplies	212.53	
Direct Overhead	<u>1,122.60</u>	2,180.13

AUG. 1st to SEPT. 15, 1919

Direct Salaries	405.00	
Direct Supplies	<u>80.34</u>	485.34

SEPT. 15 TO DEC. 31, 1919

Direct Salaries	1,250.00	
Direct Supplies	2,204.16	
Direct Overhead	2,071.35	
General Overhead	<u>1,765.06</u>	7,290.47

JANUARY & FEBRUARY 1920 (RESEARCH DIV)

Direct Salaries	1,447.50	
Direct Supplies	173.04	
Direct Overhead	2,077.16	
General Overhead	<u>553.24</u>	4,250.94

JANUARY & FEBRUARY 1920 (PLANT NO. 3)

Direct Salaries	18.90	
Direct Supplies	13.48	
Direct Overhead	32.87	
General Overhead	<u>7.22</u>	72.47

Plus Expense connected with Oil Deal in West chargeable against fuel work	11,506.29

Plus Cost on Fuel Pump & Trap Job for Fuel Work	<u>1,073.06</u>

T O T A L	54,439.99

S U M M A R Y

Direct Salaries	14,028.28
Direct Supplies	9,762.71
Overhead	17,916.77
Bonus paid applicable to job	152.88
Oil Deal	11,506.29
Fuel Pump & Trap Job	<u>1,073.06</u>

T O T A L	54,439.99

APPENDIX III

Copy of Letter Written to Charles L. Reese
of the DuPont Company by Thomas Midgley, Jr.,
June 9, 1920

COPY
GENERAL MOTORS RESEARCH CORPORATION
DAYTON, OHIO
June 9, 1920

Mr. Charles L. Reese,
du Pont Chemical Co.,
Wilmington, Del.

Dear Mr. Reese:

File RW-126-4

I am in receipt of your favor of June 1st, and have gone over this matter pretty thoroughly with our research men with regard to the general situation covering aniline. We thoroughly appreciate that, should a requirement for some odd number of millions of gallons of aniline suddenly come into existence, the du Pont Chemical Company, or for that matter the entire chemical industry could not possibly meet this sudden demand.

It does not seem, however, that such a tremendous demand can be created by any of the methods which we consider practical for the introduction of aniline as an aid in solving our motor fuel problem.

First. Let us consider the rather impossible method of introducing aniline at the refinery as an integral part of our motor fuel. To give relief to our present gasoline situation some 80 million gallons of aniline per year would be necessary. This amount is entirely outside of the limits of possibility for some years to come.

Second. Consider the use of aniline as being added to heavier distillates for special use in tractors and possibly some trucks. This program would necessitate not only the addition of aniline to the fuel, but special devices which could only be embodied in new tractors and trucks; therefore, we could see the use of aniline growing as these cars were manufactured and sold. This total requirement might some day become a million or more gallons of aniline per year, but this demand could not come suddenly.

Third. The possible use of aniline by injecting the aniline separately from the fuel, in which the injection is accomplished only at the time the addition of aniline is necessary, thereby resulting in the use of about one-tenth the amount of aniline used in the first and second methods. Consequently to handle our present fuel consumption would result in a maximum demand for 8,000,000 gallons of aniline per year. We realize that this is a rather large quantity of aniline, which could only be produced by the additional investment of capital, but we do not see how we can possibly effect a sudden equipment of all the present automobiles. In fact, probably less than 50% of our automobiles need this device; of these 50%

some two-fifths are at present operating on gasoline which does not need the addition of aniline in the present equipment; and of the remaining 30% we doubt if more than one-third could be sold in injector equipment, which would bring the total requirement for aniline on this basis to some 800,000 gallons, which we do not believe would be difficult for a good sized aniline plant to produce per year. Understand that this demand could not come suddenly, but would have to grow.

Fourth. Were the method outlined under No. 3 complete unto itself, it would scarcely be worth the trouble of alleviating the motoring public in this manner, but when the small package distribution of aniline and its use by the injector method has been established, it will be possible to place on the market a motor of considerably higher compression than those now in use, and obtain thereby much greater economy of operation. As we are inclined to feel that economy must necessarily be the keynote of motor car development of the future, we believe that such a use of aniline is highly to be desired and therefore encouraged with present equipment.

Answering your letter in detail:

The above outlines our view point at this time on the use of aniline as a fuel improver. Our experiments upon the injector are progressing satisfactorily. We are fairly certain of the figures above, (i.e., one-tenth of the amount needed when injecting as is needed when aniline is mixed directly with the fuel), will come very close to the quantity necessary.

With regard to estimating how much aniline may be required for this purpose in the next six months, you will readily see from the plan of No. 3, that it would probably be necessary only to stock dealers with this material at various points. What this amount of aniline would be we do not know. It would depend upon the size of the package, etc., and we would scarcely expect it to exceed a few thousand gallons.

With regard to placing aniline on the market, we have not formulated any program whatsoever. We must first determine almost our entire fuel campaign in the future, in order to know what is the right thing to do, and the determination of this rests very largely with the demands upon the General Motors Corporation by the public.

We have not brought to issue as yet any patents covering the use of aniline as a knock suppressor. We have, however, in the patent office at the present time some applications on the use of knock suppressors, among which are claims covering the use of aniline. There are broad claims covering the addition of anti-knock material to the fuel, which cover any anti-knock material which may be so added.

We do not believe these applications would protect the du Pont Company, as they are confined to the use of aniline and not to its production, and while we believe we could stop other people from using aniline, it would be difficult to specify any particular make of aniline. However, we believe this is a matter for our respective patent attorneys to decide, as they are better qualified to give an opinion upon a point of this kind.

Regarding the possibility of a better knock suppressor than aniline making its appearance, this is always and must always be a potential possibility, but I think we can remove it as a probability. If our theories covering the cause of knocking are correct, then we can at once eliminate the possibility of any compound being a reasonably active suppressor that does not contain a benzene ring. Therefore aniline is the logical material. However, if our theories concerning knocking are incorrect, it is difficult to conceive of an organic compound we have not already tried which could be produced at anything like the cost of aniline. With regard to inorganic knock suppressors, these would not seem very likely to give us trouble, since the necessary physical properties of successful anti-knock materials are not found in many inorganic compounds. We have found but one, namely iodine, which is entirely too expensive, so that while we readily admit the possibility of a knock suppressor being discovered which would be better than aniline, we do not believe it is likely—certainly not within the next year or two.

With regard to a search being made of the literature and patent files, that search has been properly conducted and no suggestions concerning anti-knock materials have ever been discovered. Of course it has been well known for years that the injection of water performed similarly to the way in which our anti-knock materials do, but not in the same degree. In so far as we have been able to learn no one else has ever worked on the development of a knock suppressor.

As nearly as we can ascertain the motor fuel situation is about as follows:

This year will see the maximum production of petroleum that this country will ever know. The demand for gasoline, however, is increasing approximately at the rate of 40% per year. No serious steps have been taken to curtail this demand and it is recognized by all who are familiar at all with the fuel situation that a serious shortage is probable.

The practice in the past has been for the oil companies to raise the end point of gasoline whenever a shortage was impending. At the present time, however, this is impractical, not because motors would not handle this fuel in a semi-satisfactory manner, but

because other petroleum products such as kerosene, gas oil, etc., are likewise in demand and the supply of gasoline could more profitably be increased by cracking the fuel oil out than it could be increased at the expense of the kerosene cut. Therefore it seems reasonable to expect that a shortage of gasoline will develop within a year from this summer, but that the quality of gasoline will scarcely be altered. However, the gasoline situation is such a shifting kaleidoscope that while this is the outlook at present, it is very difficult to be sure of what the situation may change into in the next few months. There seems to be only one thing fairly definitely established, and that is that the quality of the gasoline will not materially change. It is barely possible that it may change for the better, due to the extensive cracking programs on the part of some of the large oil companies.

Trusting this letter contains the information you desire,
beg to remain

Very truly yours,

Thomas Midgley, Jr.,
Asst. Director of Research.

TM Jr./AN

APPENDIX IV

Partial List of the Compounds Tested
in the Search for an Antiknock Agent

LIST OF MATERIALS TESTED WHICH SUPPRESS KNOCK
Prepared June, 1925

<u>Metallic Element</u>	<u>Compound</u>	<u>Effect on Knock</u>	<u>Record & Page</u>
<u>Lead</u>	Lead triethyl phenyl	Powerful . .	19-152
	Lead hexaethyl?	Powerful . .	19-157
	Lead triethyl mercaptan	Powerful . .	19-157
	Lead diethyl di-iodide	Powerful . .	19-166
	Diplumbic hexaethide	Powerful . .	19-166
	Triethyl lead mono-dichlor acetate .	Antiknock . .	19-180
	Triethyl lead mono-trichlor acetate .	Antiknock . .	19-183
	Triethyl lead mono-monobromacetate .	Antiknock . .	19-188
	Lead triethyl methyl	Powerful . .	19-190
	Lead triethyl propyl	Powerful . .	19-191
	Lead triethyl bromide	Powerful . .	19-204
	Lead diethyl diphenyl	Powerful . .	19-206
	Triethyl lead	Powerful . .	Charch
	Lead diphenyl dibromide	Antiknock . .	Charch
	Lead diphenyl di-iodide	Powerful . .	Charch
	Lead diphenyl dichloride	Antiknock . .	Charch
	Lead diphenyl dimethyl	Powerful . .	Charch
	Lead diethyl dichloride	Powerful . .	Charch
	Lead xanthate	Some suppression	Charch
	Tetra-n-propyl lead	Powerful . .	19-32
	Tetrabutyl lead	Powerful . .	19-110
	Tetraphenyl lead	Powerful . .	19,110,207
	Lead tetraethyl.	Powerful . .	13-200
	Tetra-methyl lead	Powerful . .	13-207
	Tetra isopropyl lead	Powerful . .	13-280
<u>Aluminum</u>	Aluminum ethyl iodide	Slight suppression	Charch
<u>Bismuth</u>	Trimethyl bismuthine	Powerful . .	Charch
	Triphenyl bismuthine	Suppressed . .	19-130
<u>Titanium</u>	Titanium tetrachloride	Antiknock . .	19-208
<u>Tin</u>	Tin diethyl di-iodide	Antiknock . .	Charch
	Tin tetra-iodide	Antiknock . .	Charch
	Tin tetra-chloride	Antiknock . .	Charch
	Stannic ethide (tin tetraethyl) . .	Suppressed . .	13-177
<u>Selenium</u>	Selenium tetra chloride	Powerful . .	Charch
	Selenium bromide (Se ₂ Br ₂)	Antiknock . .	21-60
	Selenium oxychloride	Powerful . .	13-25
	Diphenyl selenide	Powerful . .	13-28
	Dipropyl selenide	Powerful . .	13-28
	Diethyl selenide	Powerful . .	13-28

<u>Metallic Element</u>	<u>Compound</u>	<u>Effect on Knock</u>	<u>Record & Page</u>
<u>Iron</u>	Iron penta-carbonyl	Powerful	--
<u>Antimony</u>	Antimony (metal)	Slight suppression	8-9
	Liver of antimony	Suppressed	8-11
<u>Arsenic</u>	Triphenyl arsine	Suppressed	13-173
	Triethyl arsine	Suppressed	13-174
<u>Tellurium</u>	Diethyl telluride	Power, suppression	13-26
	Dipropyl telluride	Power, suppression	13-27
	Diphenyl telluride	Suppressed	13-30
	Dimethyl telluride	Powerful suppress.	20-10
<u>Nickel</u>	Nickel xanthate	Some suppression	Charch
	Nickel carbonyl	Powerful suppress.	19-130
<u>Potassium</u>	Potassium iodide (solid)	Lessened	8-10
<u>Cobalt</u>	Cobalt xanthate	Some suppression.	Charch
<u>Zinc</u>	Zinc xanthate	Some suppression.	Charch

<u>Non-Metallic Elements</u>	<u>Compound</u>	<u>Effect on Knock</u>	<u>Record & Page</u>
<u>Chlorine</u>	Phenyl chloride	Some suppression.	13-131
	Amyl chloride	Very slight sup.	13-132
	Halowax oil (10%)	Suppressed	--
<u>Iodine</u>	Iodine (element)	Suppressed	8-8
	Ethyl iodide	Suppressed	4-1
	Potassium iodide (solid)	Suppressed	8-8
	Phenyl iodide	Suppressed	13-27
	Amyl iodide	Suppressed	13-129
<u>Fluorine</u>	Phenyl fluoride	Slight suppression	13-142
<u>Nitrogen</u>	Diphenylamine	Suppressed	10-107
	Alpha naphthylamine	Suppressed	13-11
	Beta naphthylamine	Suppressed	13-11
	Ortho, meta, and para toluidines	Suppressed	13-10
	Mono-methyl aniline	Suppressed	10-66-67
	Dimethyl aniline	Slight suppress.	10-66-67
	Paratoluidine	Suppressed	10-66-67
	Orthotoluidine	Suppressed	10-66-67
	Acetanilide	Very slight supp.	10-66-67
	Benzanilide	Very slight supp.	10-66-67
	Alpha naphthylamine	Very slight supp.	10-66-67
	Beta naphthylamine	Suppressed	10-66-67

Non-Metallic Elements	Compound	Effect on Knock	Record & Page
(Con'd)			
<u>Nitrogen</u>	Phenylene diamine (saturated) . . .	Suppressed . . .	10-66-67
	Amyl aniline	Suppressed . . .	10-95
	Butyl aniline	Suppressed . . .	10-115
	Propyl aniline	Suppressed . . .	10-108
	Ethyl aniline	Suppressed . . .	10-104
	Ethyl phenylamine	Suppressed . . .	10-108
	Amyl phenylamine	Suppressed . . .	10-110
	Xylidine	Suppressed . . .	10-110-113
	Methyl toluidine	Suppressed . . .	10-114
	Methyl xylidine	Suppressed . . .	10-116
	Diethyl aniline	Suppressed . . .	10-116
	Cumidine	Suppressed . . .	10-138
	Allyl amine	Suppressed . . .	10-267
	Ethyl amine	Suppressed . . .	10-15
	Azobenzene	Very slight eff. . .	10-130
	Azoxybenzene	Very slight eff. . .	10-130
	O-tolyl azophenol	Very slight eff. . .	10-130
	O-tolyl azophenol acetate	Very slight eff. . .	10-130
	Diazoamidebenzene	Slight effect . . .	10-130
	Amide azo benzene	Slight effect . . .	10-130
	Mono-methylaniline	Suppressed . . .	10-131
	Mono-ethylaniline	Suppressed . . .	10-131
	Toluene diamine	Suppressed . . .	10-271
	m-Toluidine	Suppressed . . .	13-10
	b-Naphthylamine	Suppressed . . .	13-11
	Meta-xylidine	Suppressed . . .	13-13
	Triethyl amine	Slight suppression . . .	13-154
	Ethyl benzyl aniline	Very slight supp. . .	13-210
	Monoethyl a-naphthylamine	Suppressed . . .	13-210
	Phenyl a-naphthylamine	Suppressed . . .	13-210
	Aniline	Suppressed . . .	8-17
	Ortho amino phenol	Some suppression . . .	20-2
	Phenyl methyl nitrosamine	Some suppression . . .	20-2
	Triethyl amine	Very slight . . .	20-12
	Diethyl amine	Suppressed . . .	—
<u>Hydrogen and Carbon</u>			
	Hydrogen	Suppressed . . .	1-2
	Isoprene (11%)	Slight suppression. . .	1-about 5
	Toluene (12%)	Slight suppression. . .	10-68
	Dimethyl benzene (ortho) (12%)	Slight suppression. . .	10-68
	Dimethyl benzene (para) (12%)	Slight suppression. . .	10-68
	Cyclohexane (12%)	Slight suppression. . .	10-68
	Diphenylmethane	Slight suppression. . .	19-273
	Triphenylmethane	Slight suppression. . .	19-274
	Triphenyl ethyl methane	Slight suppression. . .	19-275
	Diphenyl methane	Slight suppression. . .	19-276
	Diphenyl diethyl methane	Slight suppression. . .	19-286

Non-Metallic Elements	Compound	Effect on Knock	Record & Page
<u>Carbon, Hydro- gen and Oxygen</u>	<u>Alcohols & Hydroxy Compounds</u>		
	Merck's cresol	Suppressed	
	Water	Suppressed	8-14
	Ethyl alcohol (5%)	Slight suppression	10-67
	Butyl alcohol (6%)	Slight suppression	10-67
	Amyl alcohol	Slight suppression	10-67
	Phenol	Slight suppression	10-67
	m-Cresol	Slight suppression	10-67
	Xylenol 1:3:4	Slight suppression	10-67
	Veratrol	Slight suppression	10-67
	Benzyl alcohol (12%)	Slight suppression	10-67
	Diethyl methyl-carbinol	Slight suppression	10-67
	Hydroxybenzene	Very slight effect	10-130
	Hydroxybenzene benzoate	Very slight effect	10-130
	o-tolyl azophenol	Very slight effect	10-130
	o-tolyl azophenol acetate	Very slight effect	10-130
	Steam	Suppressed	10-175
	Anisole	Slight suppression	20-12
	Phenol	Some suppression	20-12
	<u>Ethers</u>		
	Diphenyl ether	Some suppression .	13-123
	<u>Organic acetates</u>		
	Methyl acetate (12%)	Slight suppression	10-69
	Amyl acetate (12%)	Slight suppression	10-69
	Camphor	Slight suppression	1-47
<u>Phosphorus</u>	Triethyl phosphine	Slight suppression	13-158
	Triphenyl phosphine	Suppressed	13-160

LIST OF MATERIALS TESTED FOR ANTI-KNOCK
EFFECT AND FOUND TO BE NEUTRAL

<u>Metallic Element</u>	<u>Compound</u>	<u>Effect on Knock</u>	<u>Record & Page</u>
<u>Lead</u>	Lead tetra-stearate	None	19-166
	Di-ammonium lead hexachloride.	No effect	Charch
	Lead diphenyl diacetate	Not an antiknock	Charch
	Colloidal lead	Not an antiknock.	Charch
	Pb ₂ Fe(CN) ₆ NO ₃	No effect	Charch
	Benzaldehyde lead	No effect	Charch
	Lead ferricyanide	No effect	Charch
<u>Mercury</u>	Mercuric xanthate	No effect	Charch
	Calomel (solid).	None	8-8
	Mercuric chloride	None	8-9
	Mercurous acetate (solid)	None	8-9
	Diphenyl mercury	No effect	13-27-250
	Mercuric chloride	No effect	8-17
<u>Aluminum</u>	Aluminum triethyl	None	19-157
	Aluminum stearate	No effect	21-46
	Aluminum sulfate (solution)	No effect	20-4
	Aluminum nitrate (solution)	No effect	20-6
<u>Bismuth</u>	Triphenyl bismuthine dichloride	Little, if any, effect	Charch
	Triphenyl bismuthine dibromide	Little, if any, effect	Charch
	Bismuth nitrate (solution).	No effect	20-4
	Bismuth chloride (solution)	No effect	20-4
<u>Tin</u>	Tin tetra-bromide	Almost neutral	Charch
	Tin dioxide	No effect	21-46
	Colloidal Sn	No effect	1-about 100
<u>Iron</u>	Colloidal iron	Not an antiknock	Charch
	Ferric sulphocyanate	No effect	Charch
	Ferrous dimethylglyoxime	No suppression	Charch
	Ferric xanthate	No effect	Charch
<u>Gold</u>	Gold trichloride	No effect	Charch
<u>Zirconium</u>	Zirconium tetrachloride	No effect observed	21-4
<u>Arsenic</u>	Arsenic tetraethyl hydroxide	No effect	21-16
	Arsenic tetraethyl iodide	No effect	21-17
	Ammonium arsenite (solid)	None	8-9
	Arsenious acid	None	8-9
	Arsenic trioxide (solution)	No effect	20-4
<u>Platinum</u>	H ₂ PtCl ₆ 6H ₂ O	No effect	21-18
	Platinum chloride	No effect	Charch

<u>Metallic Element</u>	<u>Compound</u>	<u>Effect on Knock</u>	<u>Record & Page</u>
<u>(Cont'd)</u>			
<u>Platinum</u>	Dicarbonyl chloroplatinite . . .	No effect . . .	Charch
<u>Tungsten</u>	Tungsten hexachloride . . .	No effect . . .	Charch
<u>Vanadium</u>	Vanadium oxide (V ₂ O ₅) . . .	No effect . . .	21-46
<u>Nickel</u>	Nickel dimethyl glyoxime . . .	No effect . . .	21-57
	Ni(CN) ₂ C ₆ H ₅ NH ₂ NH ₃ . . .	No suppression . . .	Charch
	Ni(CN) ₂ C ₆ H ₅ NH ₃ . . .	No suppression . . .	Charch
	Colloidal Ni . . .	No effect . . .	1-about 100
<u>Thorium</u>	Chloride (ThCl ₄) . . .	No effect . . .	21-91
<u>Germanium</u>	Germanium tetra-ethyl . . .	No effect . . .	21-91
<u>Copper</u>	Copper dimethyl glyoxime . . .	No suppression . . .	Charch
	Colloidal Cu . . .	No effect . . .	1-about 100
	CuCO ₃ (solid) . . .	None . . .	8-8
	Copper salt of monobutyl phthalate . . .	No effect . . .	19-46
	Copper acetate . . .	No effect . . .	8-17
	Copper sulfate (solution) . . .	No effect . . .	20-6
	Copper chloride (solution) . . .	No effect . . .	20-6
<u>Cobalt</u>	Cobalt succinimide . . .	No effect . . .	Charch
	Cobalt carbonate . . .	No effect . . .	8-8
	Cobalt nitrate (solution) . . .	No effect . . .	20-6
	Cobalt chloride (solution) . . .	No effect . . .	20-6
<u>Sodium</u>	Sodium xanthate . . .	No effect . . .	Charch
	Sodium benzoate (solid) . . .	None . . .	8-10
	Sodium cyanide . . .	No effect . . .	10-21
	Alcoholic sodium hydroxide . . .	No effect . . .	10-92
<u>Zinc</u>	Zinc ethyl . . .	No effect . . .	9-64
<u>Silver</u>	Silver nitrate . . .	No effect . . .	8-17
<u>Cadmium</u>	Colloidal Cd . . .	No effect . . .	1-about 100
<u>Antimony</u>	Antimony methyl . . .	None . . .	8-16
<u>Barium</u>	Barium nitrate . . .	No effect . . .	20-4
<u>Cerium</u>	Cerous oxalate . . .	No effect . . .	10-198
	Cerium nitrate (solution) . . .	No effect . . .	20-6
<u>Fluorine</u>	Amyl fluoride . . .	No effect . . .	19-196
	Hydrogen fluoride . . .	Practically no effect . . .	19-232
<u>Helium</u>	Helium . . .	Dilution effect . . .	21-18

Element (Cont'd)	Compound	Effect on Knock	Record & Page
<u>Argon</u>	Argon	Dilution effect	21-29
<u>Sulphur</u>	Benzyl sulphide	No effect . . .	Charch
<u>Phosphorus</u>	Phosphorus oxychloride	No effect . . .	20-10
<u>Carbon, Hydrogen & Oxygen</u>	Ethyl carbonate	No effect . . .	19-178
	Diethyl phthalate	Not an antiknock	19-291
	Ethyl xanthate	No effect . . .	Charch
	Oil of cloves	No effect . . .	21-97
<u>Alcohols and Hydroxy Compounds</u>			
	Alpha and beta naphthols	None	-
	Hydroquinone	No effect . . .	10-67
	Beta naphthol	No effect . . .	10-67
	Glycerol	No effect . . .	10-67
	Isoborneol	No effect . . .	10-130
<u>Organic acetates</u>			
	Ethyl acetate	No report . . .	1-47
	Methyl acetate	No effect . . .	10-142
<u>Sulphur</u>	Sulphur (solid)	None	8-8
	Sulphanilic acid	None	-
	Diphenyl sulphide	No effect . . .	13-146
	Diphenyl sulphide	Very slight . . .	20-12
	Hydrogen sulfide (vapor in air inlet)	No effect . . .	20-14
<u>Acids</u>	Oleic acid	None	8-7
	Boric acid (solid)	None	8-9
	Arsenious acid	None	8-9
	Tannic acid	No effect . . .	19-33
	Formic acid	No effect . . .	10-129
	Lactic acid	No effect . . .	10-129
	Tartaric acid	No effect . . .	8-17
	Molybdic acid (solution)	No effect . . .	20-6
	Acetic acid	No effect . . .	-
<u>Aldehydes</u>	Propaldehyde	No effect . . .	10-129
	Acetaldehyde	Very little, if any effect	
	Benzaldehyde	Little effect. In large % inducer pre-ignition.	
	Furfuraldehyde	Little or no effect. In large percentages induces preignition.	
<u>Silicon</u>	Silicon tetraethyl	Very slight if any effect	13-198

Element (Cont'd)	Compound	Effect on Knock	Record & Page
<u>Miscellaneous</u>			
<u>Materials</u>	Beechwood creosote	Vague report	1-about 47
	Terebene	No effect	1-about 50
	Blandol	No effect	1-about 50
	Acetone (60%)	Pre-ignition	—
	Kerosene treated with AlCl ₃	No effect	—
	Residue from cracked turpentine.	Stopped motor	—
	Rosin	None	13-25
	Ammonia (very slightly soluble).	No apprec. eff.	10-13
	"Bachite" (catalytic carbon)	No effect . . .	10-198
	du Pont's "White Oil"	No effect . . .	10-222
	"Resin C" (Barnett)	No effect . . .	13-26
	"Resin G" (Barnett)	No effect . . .	13-26
	Divinylacetylene	No effect . . .	19-152
	Borax (solution)	No effect . . .	20-6
<u>Chlorine</u>	Chloroform	No effect . . .	1-about 60
	Chlorinated kerosene	No effect . . .	1-about 60
	Ethyl chloride	Very slight effect	1
	NaCl (solid)	None	8-8
	Calomel (solid)	None	8-8
	Mercuric chloride	None	8-9
	Monochlor benzene (12%)	No effect. . .	10-68
	Ortho dichlor benzene	No effect. . .	10-68
	Pinene hydrochloride	No effect. . .	10-130
	Chloral hydrate	No effect. . .	10-194
	Stannous chloride	No effect. . .	10-198
	Mercuric chloride	No effect. . .	8-17
	Barium chloride (solution)	No effect. . .	20-4
	Chloral hydrate	No effect. . .	10-194
	Bismuth chloride (solution)	No effect. . .	20-4
	Calcium chloride (solution)	No effect. . .	20-6
	Cadmium chloride	No effect. . .	20-6
	Cobalt chloride (solution)	No effect. . .	20-6
	Copper chloride (solution)	No effect. . .	20-6
	Phosphorus oxychloride.	No effect. . .	20-10
	Phenyl chloride (vapor in air inlet)	No effect. . .	20-14
<u>Bromine</u>	Ethyl bromide	Choked engine	4-7
	Ethylene bromide	"Tendency to stop engine"	4-8
	Ethylene bromide	Power reduced	—
	Potassium bromide (solid)	None	8-10
	Mono brom benzene (12%)	No effect . . .	10-68
	Para dibrom benzene	No effect . . .	10-68
	Dimethyl dibrom benzene	No effect . . .	10-68
	Ethyl bromide	No effect . . .	10-21
	Bromine (5% in kerosene)	No effect . . .	8-17
<u>Iodine</u>	Cyanogen iodide	No effect . . .	10-21

<u>Element (Cont'd)</u>	<u>Compound</u>	<u>Effect on Knock</u>	<u>Record & Page</u>
<u>Nitrogen</u>	Nitrobenzene	No effect	1-47
	Benzidine	None	-
	Orthonitrophenol.. . . .	No noticeable effect	20-2
	Sulphanilic acid.	None	-
	Pyridine	None	-
	Methyl cyanide	None	10-48
	Benzonitrile	None	10-78
	Benzidine	No suppression.	10-66-67
	Piperidine.	No effect.	10-138
	Beta-amino-anthraquinone	No effect.	10-222
	Cyanogen iodide	No effect.	10-21
	Quinoline	No effect.	10-24
	Acetonitrile	No effect.	10-48
	Acetamide	No effect.	10-129
	Propaldehydecyanhydrin.	No effect.	10-129
	Nitrobenzene	Little if any effect	13-3
	Triphenyl amine	No effect.	13-156
	Anthranilic acid.	No effect.	20-2
	Phenyl hydrazine.	No effect.	20-2
	Furfuramide	No effect.	20-12
<u>Nitrates & Nitrites</u>	Orthonitrophenol.	No noticeable effect	20-2
	Cobalt nitrate (solution).	No effect	20-6
<u>Hydrogen & Carbon</u>	Naphthalene	No effect.	10-68
	Phenanthrene	No effect.	10-68
	Diphenyl	No effect.	10-68
	Phenyl toluene	No effect.	10-68
	Ethyl benzene (12%).	No effect.	10-68
	Pinene	No effect.	10-130
<u>Potassium</u>	Potassium bichromate (solid)	None	8-10
	Potassium chromate (solid).	None	8-10
	Potassium ferrocyanide (solid)	None	8-10
	Potassium nitrate (solid)	None	8-10
	Potassium carbonate (solid)	None	8-10
	Potassium bromide (solid)	None	8-10

LIST OF MATERIALS TESTED WHICH INDUCE KNOCK

<u>Element</u>	<u>Compound</u>	<u>Effect on Knock</u>	<u>Record & Page</u>
<u>Mercury</u>	Mercury diethyl	Knock inducer	19,152, 288,290
<u>Uranium</u>	Uranyl chloride	Knock inducer	19,297
<u>Antimony</u>	Antimony triethyl oxide	Knock inducer	21-4
	Antimony tetraethyl hydroxide	Knock inducer	21-15
<u>Boron</u>	Boron trichloride	Slight inducer	Charch
<u>Sulphur</u>	Allyl isothicyanate.	Slight inducer	Charch
	Phosphorus trisulphide.	Inducer	Charch
	Nitrogen sulphide N_4S_4	Powerful induc.	Charch
	Sulphur oxychloride.	Increased . .	13-25
	Diethyl sulphide	Increased . .	13-144
<u>Phosphorus</u>	Phosphorus trisulphide	Inducer . . .	Charch
<u>Nitrogen</u>	Ammonia	Slight inducer	19-224
	Diazobenzeneimide	Inducer	Charch
	Orthonitrotoluene	Increased . .	—
	Ethyl nitrate	Induced . . .	—
	Propyl nitrite	Induced . . .	13-49
<u>Chlorine</u>	Carbon tetrachloride	Increased . .	8-3
	Sulphur oxychloride	Increased . .	13-25
	Chlorine (gas in air inlet)	Increased . .	20-12
	Carbon tetrachloride (vapor in air inlet)	Increased . .	20-12
	Chloroform (vapor in air inlet)	Increased . .	20-12
<u>Bromine</u>	Phenyl bromide	Increased . .	13-126
	Ethyl bromide	Increased . .	13-128
	Amyl Bromide	Increased . .	13-128
	Bromine (vapor in air inlet)	Increased . .	20-14
<u>Nitrates & Nitrites</u>	Orthonitrotoluene	Increased . .	—
	Ethyl nitrate	Induced . . .	—
	Propyl nitrite.	Induced . . .	13-49
<u>Carbon, Hy-</u>	<u>Ethers</u>		
<u>drogen & Oxy-</u>	Diethyl ether	Increased . .	13-148
<u>gen</u>	<u>Organic acetates</u>		
	$CH_3COCH_2COOC_2H_5$ (12%)	Increased . .	10-69
<u>Copper</u>	Copper resinate	Increased . .	8-4

APPENDIX V

SUMMARY REPORT ON THE INVESTIGATION
OF THE SPARK PLUG CORROSION AND EX-
HAUST VALVE DEPOSIT PROBLEM

ETC 37121

REPORT ON CORRECTION OF SPARK PLUG EROSION AND VALVE DEPOSITING
TROUBLES INCIDENT TO TREATING GASOLINE WITH
LEAD COMPOUNDS

By T. A. Boyd, J. P. Andrew, and C. J. Allen. October 25, 1924.

THE PROBLEM TO BE SOLVED

When an alkyl lead compound is burned in a gasoline engine, the lead goes mainly to PbO . In the finely divided state in which it is formed PbO frits at $700^{\circ}C.$, and its melting point has been variously given as 776° , 879° , 808° and $906^{\circ}C.$ Thus two problems are introduced in the internal combustion engine.

1. An erosion of the spark plug electrodes, which are made of a nickel containing alloy, and a gradual softening of the porcelain, which forms the electrical insulation of most spark plugs.
2. A deposition of solid lead compounds, mostly PbO , on the faces and stem of the exhaust valves. The effect of this, of course, is to hold the valve a small distance off its seat permitting a leakage to occur, thus cutting down the power of the engine, and in time injuring the valve seat.

It was to find some means of preventing depositing on valves and erosion of spark plugs that this investigation was conducted.

THE RESULTS OBTAINED

It has been found that bromine compounds are the only materials that prevent the depositing of lead compounds on exhaust valves, and at the same time correct the erosion of spark plugs to a satisfactory degree. Chlorine is fairly effective, but unless used in high concentration relative to the lead present it does not prevent the deposition of lead oxide on exhaust valves although it seems to protect the spark

plug electrodes fairly well. Fluorine and iodine are effective also, but not so good as bromine. Sulphur, too, shows some reactivity with lead in the engine, but in its ultimate effect it exerts very little protection either to exhaust valves or to spark plugs. Of all other materials tested, of which there were many, as may be seen from the list given on the last few pages of this Appendix, none was found that exerted an appreciable protective action:

BRIEF ACCOUNT OF THE METHODS USED IN THE INVESTIGATION

At the outset in the study of this problem there seemed to be two possible ways of solving it. These were:

- (a) To introduce some material into the combustion reaction that would cause the formation of a lead compound of very high fusion point, so as to prevent its sticking to the exhaust valve or fluxing away the spark plug electrodes.
- (b) To introduce some material into the reaction to cause the formation of a lead compound of sufficient volatility to vaporize from the hot exhaust valve and to correct the spark plug erosion at the same time.

In either case, of course, the compound must have sufficient reactivity with lead in the form in which it exists in the combustion reaction to form the suitable compound.

The actual investigation was begun in June, 1922, by running single cylinder engines on gasoline treated with the tetraethyl lead plus different amounts of other materials added as possible corrective agents. The engines were run for a given period, the lengths of which varied at different times during the investigation from 8 to 48 hours, on each mixture. At the close of each run the exhaust valve and spark plug were

removed and examined. During the early stages of the work the observations were largely qualitative in character, but as the investigation progressed a more quantitative examination was made, particularly of the exhaust valves. The weight of material deposited on the exhaust valve was determined for each mixture, and the thickness of the deposit on the seat of the exhaust valve was measured. Finally, after it had been found that chlorine and bromine were the only materials that offered any possibility of commercial application, careful determinations were made of the weights and chemical composition of material deposited when various combinations of chlorine and bromine were used.

Air cooled engines were employed throughout the laboratory investigation. Up until October 19, 1923, the runs were all made on the engines in the regular dynamometer room of the laboratory. After this date all of the single cylinder engine tests were made on the twelve engines located in room five of the Fuel Section and shown on a later page, in Figure 1 of this Appendix. These are 600-watt copper cooled Delco-Light engines, standard, except for the fact that each engine is equipped with a 3/4" adjustable Schebler carburetor. The tests on these engines were run 24 hours a day, and for the most part the period of each run was 48 hours. A new spark plug and a new exhaust valve were used in every test. The runs were usually made in duplicate, and frequent tests were run on straight gasoline and on gasoline treated with tetraethyl lead alone to serve as a basis of comparison.

During the course of this investigation a great many road tests were run also. These were conducted by the Research Garage. No report will be made of this work herein, other than to say that in general the results obtained on the road checked those secured in the laboratory to

a reasonable degree.

The most valuable information was obtained by the methods outlined above. But the study was conducted in the laboratory in a number of other ways also, the principal investigations having been as follows:

1. Study of the combustion of various mixtures of tetraethyl lead and other compounds by means of blow torch flames impinging on steel plates. This investigation did not yield results of value, chiefly on account of the inability to make a blow torch operate steadily on gasoline containing lead tetraethyl. The lead compound decomposed in the hot nozzle where the gasoline was vaporized, thus gradually stopping it up and changing the character of the flame. This investigation was pursued to a greater extent at Mass. Inst. of Tech. than here, but even there the results obtained did not add anything to the data obtained in the laboratory engine tests, and in some cases they did not agree with the results obtained in practice.
2. Study of the combustion of gasoline treated with tetraethyl lead and various halides in a steel bomb, using oxygen as the combustion medium. The data collected consisted of the composition of the products of combustion, both in the gas and as a solid deposit in the bomb. On account of inability to prevent excessive corrosion of the bomb by the halogen acid and water formed in the combustion, with consequent difficulties of analysis, this work did not yield anything of particular value over and above that gained from the engines, and hence it will not be reported further herein.

3. Quantitative examination of the products formed by burning lead tetraethyl and organic halides in an engine. This work, (covered in detail in a previous report), yielded the following facts as its most valuable information.

- (a) When any one of several organic chlorides, and even molecular chlorine itself, is admitted to the engine in amounts up to 5% of the fuel the product exhausted by the engine contains no free chlorine, but only HCl.
- (b) When organic bromides are burned in the engine as in
 - (a) there is no free bromine in the exhaust.
- (c) When small amounts of molecular bromine are admitted to the engine with the inlet air, none of it appears in the exhaust as free bromine. But when the amount is increased to some larger, although not quantitatively determined ratio, bromine does appear in the engine exhaust as such.
- (d) When the fuel contains both lead tetraethyl and an organic halide the amount of hydrogen halide formed indicates that the lead is converted into lead halide roughly in accordance with the following table:

Amt. of Organic Halide Present in Relation to the Lead as PbX ₂	Percentage of the Lead Present Converted to the Halide	
	<u>With Chlorine</u>	<u>With Bromine</u>
1 theory	45	55
1.5 theories	55	75
2 theories	60	90

PRESENTATION AND DISCUSSION OF RESULTS OF ENGINE TESTS

Efforts to solve the problem along the first of the lines, (a), as per page 325, did not prove successful. The highest fusing lead salt whose formation seemed possible was lead sulphate, which fuses at 1000°C . (Although PbS fuses at a higher temperature 1035° , it is apparently oxidized to PbSO_4 on the valve.) In motor tests using sulphur compounds it was found that heavy deposits of lead sulfate were formed on exhaust valves, but that sulfur compounds were not sufficiently reactive with lead to protect the spark plug electrodes.

Research along the second line, (b), as per page 325, has shown that the halogens are the only elements that give lead compounds of sufficient volatility to vaporize from exhaust valves, and that have at the same time the necessary degree of reactivity with lead to protect spark plugs. Vapor pressure data on lead chloride and lead bromide are shown graphically in Figure 2 of this Appendix. The difference in volatility between the chloride and the bromide does not have much significance in this case, though, because as will be seen later PbCl_2 is sufficiently volatile to be removed from exhaust valves almost completely. It was found further that bromine is the only one of the halides that is sufficiently reactive with lead to prevent to a satisfactory degree the formation of the undesirable lead oxide. This may be seen from the figures in the following tabulation:

<u>Fuel Mixture</u>	<u>Weight of Deposit on Exhaust Valve in Grams After 48 hours Continuous Running on Gasoline Plus 6 c.c. PbEt_4 Per Gallon</u>
Straight lead in gasoline	3.0
Lead plus fluorine (2 theories) in gasoline	2.15
Lead plus chlorine (2 theories) in gasoline	0.85

<u>Fuel Mixture (Cont'd)</u>	<u>Weight of Deposit, etc. (Cont'd)</u>
Lead plus chlorobromide (1.6 theories) in gasoline	0.45
Lead plus iodine (2 theories) in gasoline	0.25
Lead plus bromine (1.5 theories) in gasoline	0.10
Straight gasoline	0.10

A great deal of work was done during the course of the investigation in an effort to catalyze the action of chlorine in some way so as to make it as reactive as bromine. Upon hypothetical grounds it seemed that this should have been possible (see previous reports). It was found, however, that no noticeable effect was produced by any of the large number of materials that were tried, and which are listed later on in this Appendix.

The results of the systematic and careful examination of the deposits from exhaust valves from engines run on various mixtures of chlorine, of chlorobromide, and of bromine with lead tetraethyl in gasoline are shown graphically on the later pages, Figures 3 to 7 inclusive.

Each point on the curves represents the average of the deposit from at least six engines, and many of them give the average of 12 engines. Each engine was run 48 hours continuously on 6 c.c. of lead tetraethyl per gallon, (twice the amount used in practice), and the halide as indicated on the abscissa scale in theories of amount required for PbX_2 . The horizontal dotted lines at the bottoms of Figures 3 to 6 inclusive indicate the average total weight of deposit scraped from the exhaust valves that were run on straight gasoline as fuel. Ethyl Fluid 3-E, which was run in various concentrations as per Figure 7, was composed of three parts tetraethyl lead and two

parts ethylene chlorobromide (1.6 theories) by volume. With this brief explanation the charts on later pages of this Appendix are self-explanatory.

Figures 8 and 9 of this Appendix are photographs giving some idea of the appearance of exhaust valves and spark plugs after 48 hours continuous running on -

- (a) Straight gasoline.
- (b) Gasoline plus 6 c.c. PbEt_4 alone per gallon.
- (c) Gasoline plus 6 c.c. PbEt_4 per gallon plus 2 theories chlorine.
- (d) Gasoline plus 6 c.c. PbEt_4 per gallon plus 1.5 theories bromine.

Note that the center electrode of one of the spark plugs run with gasoline plus 6 c.c. tetraethyl lead alone per gallon is entirely gone, and the porcelain is covered with a thick brown glass. The electrodes of the other spark plug run with lead alone are in bad shape also. On the other hand it may be seen that all the other spark plugs are still in good shape. Although, the pictures are necessarily small, the characteristic differences in the conditions of the exhaust valve with the various mixtures may easily be seen.

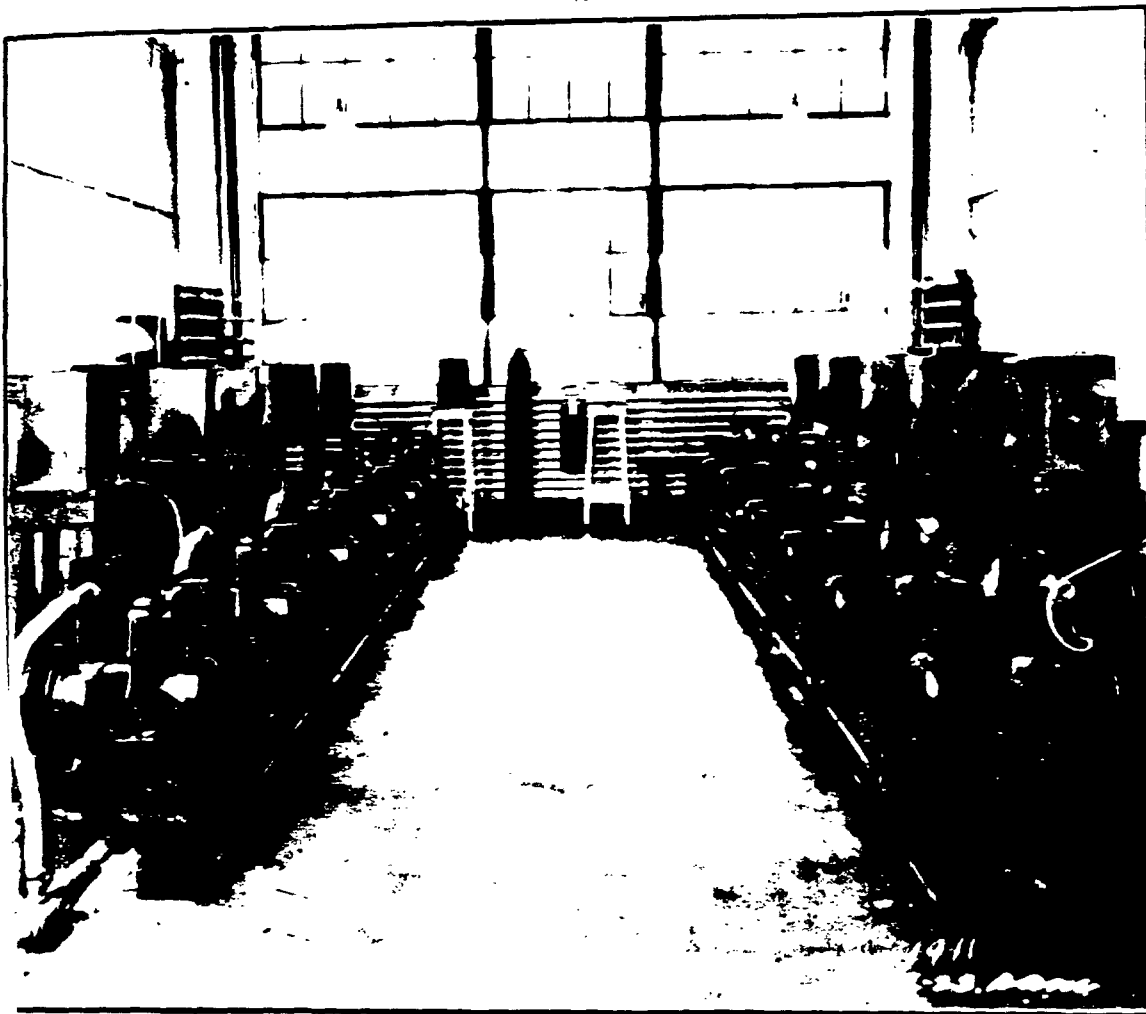


FIG. 1, APPENDIX V

BATTERY OF 12 ONE-CYLINDER, AIR-COOLED, DELCO-LIGHT ENGINES
USED IN THE LONG SEARCH FOR AN AGENT TO CORRECT THE SPARK-
PLUG EROSION AND EXHAUST-VALVE DEPOSIT TROUBLES EXPERIENCED
WITH TETRAETHYL LEAD BY ITSELF.

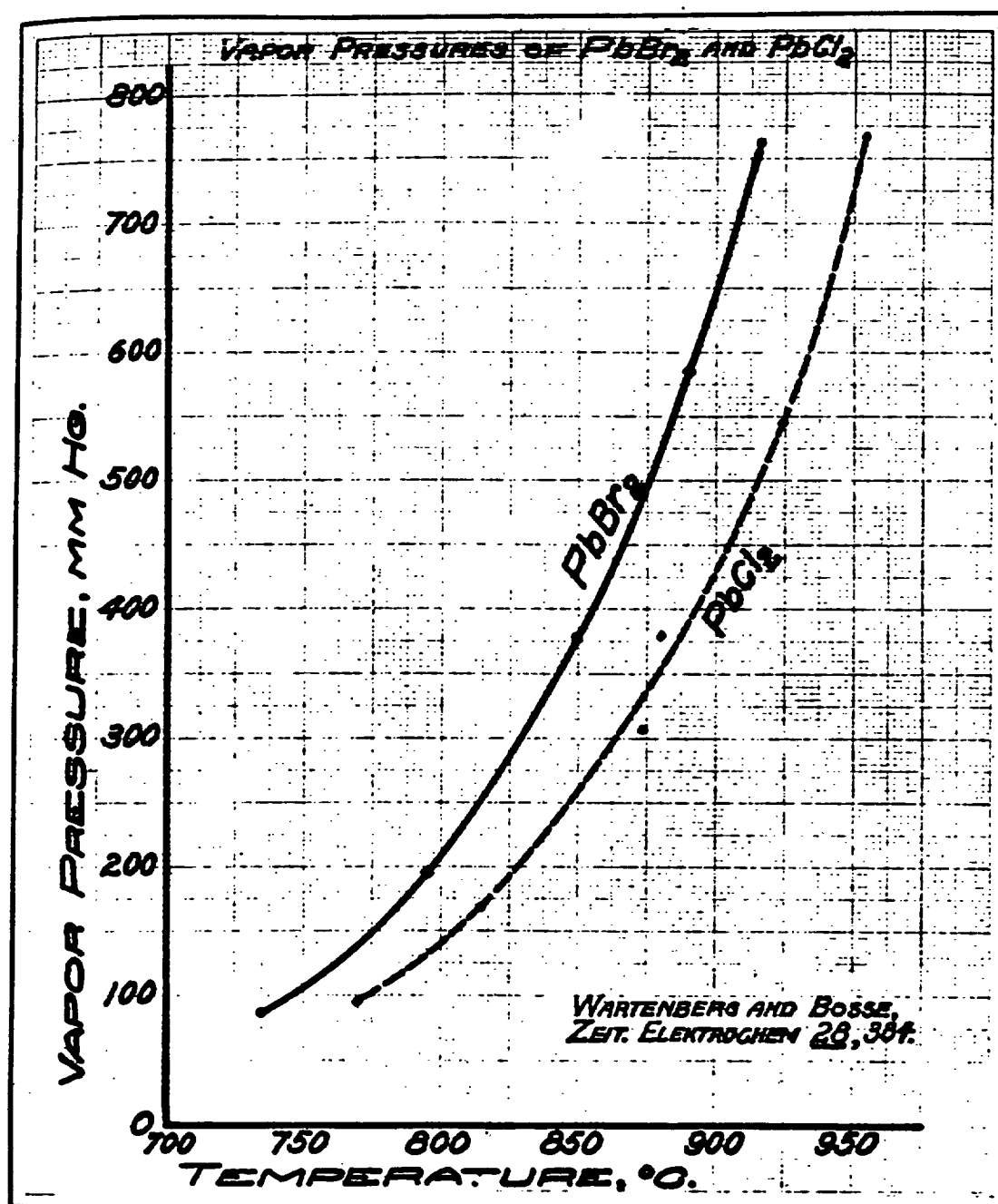


FIG. 2 APPENDIX V

PLOT OF THE RELATIVE VAPOR PRESSURES OF LEAD BROMIDE AND LEAD CHLORIDE, SHOWING THAT THE BROMIDE VAPORIZES MORE READILY THAN THE CHLORIDE.

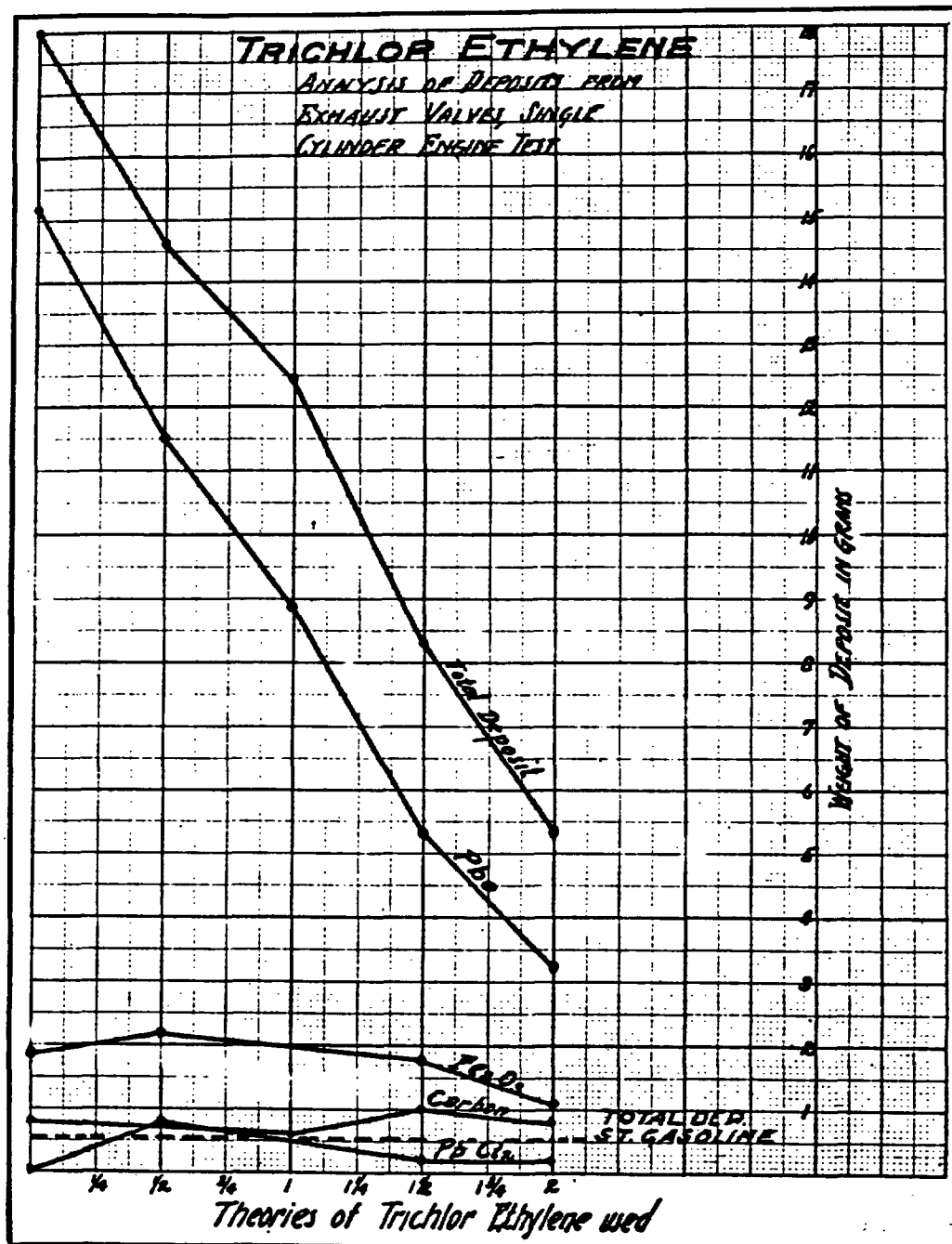


FIG. 3, APPENDIX V

PLOT OF THE EFFECTIVENESS OF A COMPOUND CONTAINING CHLORINE ALONE FOR REDUCING DEPOSITS OF LEAD ON EXHAUST VALVES. ALTHOUGH WEIGHT OF DEPOSIT FALLS RAPIDLY WITH INCREASING AMOUNT OF TRICHLOROETHYLENE, IT IS NOT ALL REMOVED EVEN WHEN CHLORINE IS PRESENT IN TWICE THE CONCENTRATION NEEDED THEORETICALLY TO FORM LEAD CHLORIDE.

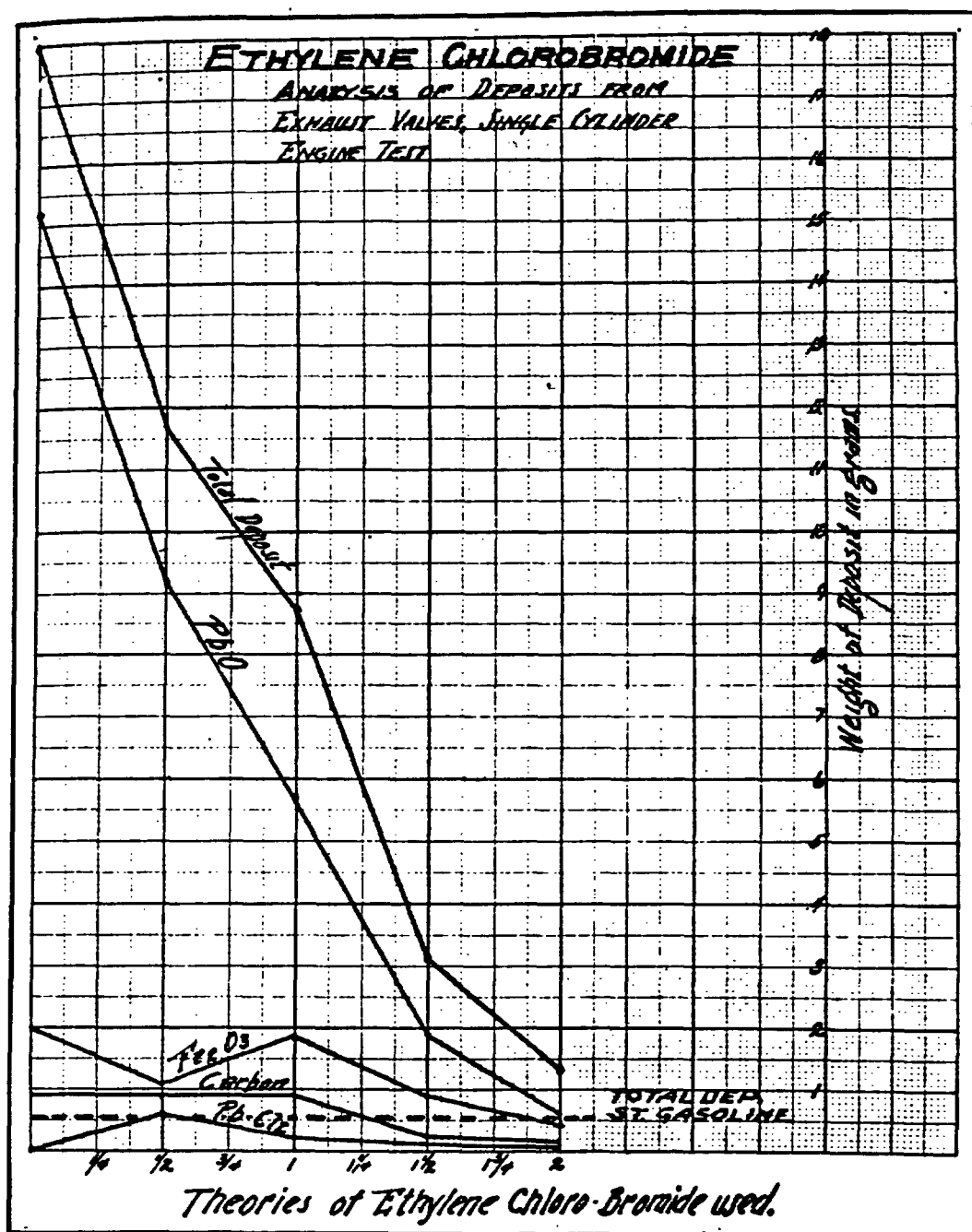


FIG. 4, APPENDIX V

PLOT OF THE EFFECTIVENESS OF A COMPOUND CONTAINING HALF CHLORINE AND HALF BROMINE FOR REDUCING DEPOSITS OF LEAD ON EXHAUST VALVES. COMPARISON WITH FIGURE 3 SHOWS THAT REPLACING HALF THE CHLORINE IN THE CORRECTIVE AGENT WITH BROMINE IMPROVED ITS EFFECTIVENESS.

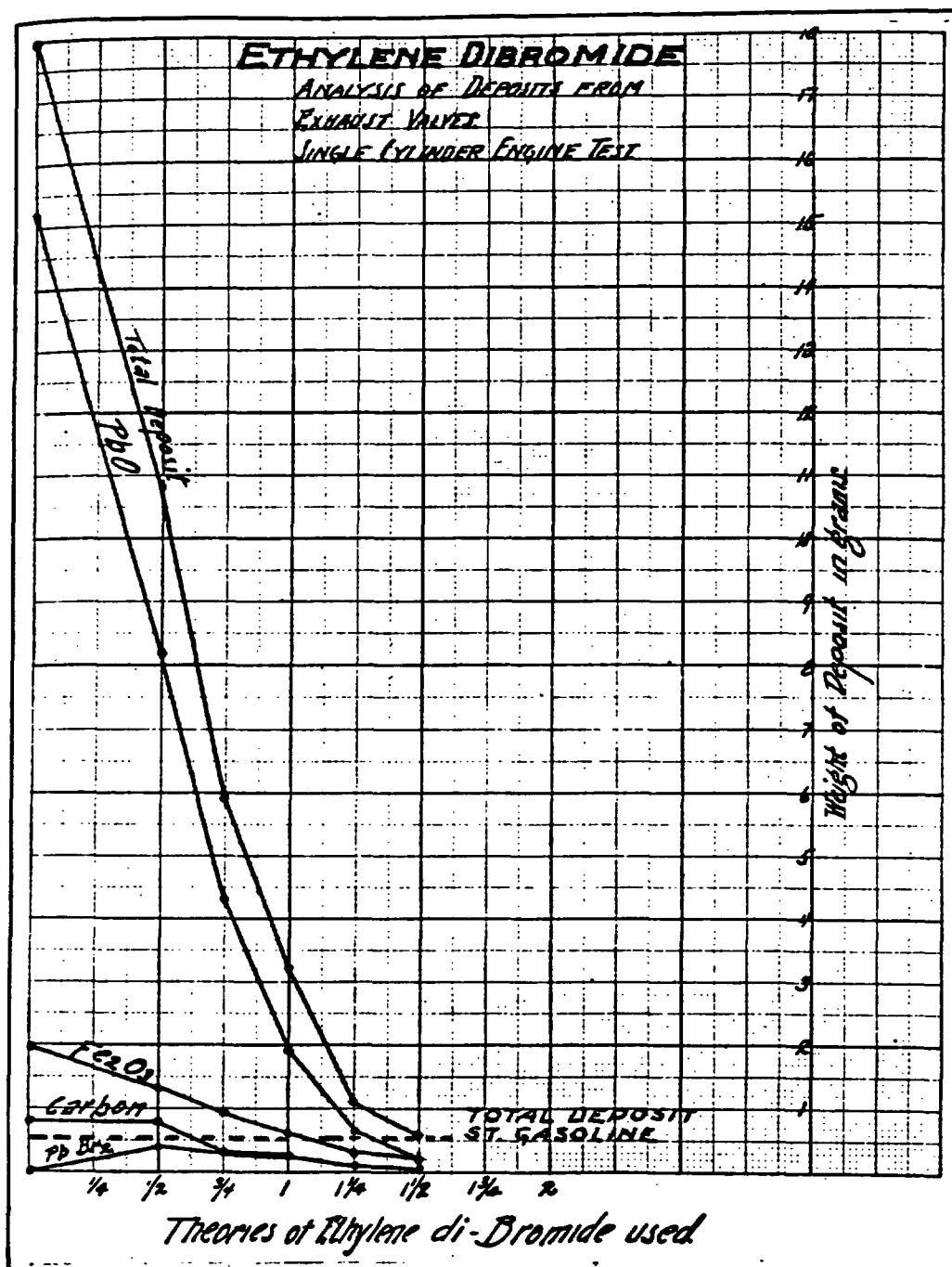


FIG. 5, APPENDIX V

PLOT OF THE EFFECTIVENESS OF A CORRECTIVE AGENT CONTAINING BROMINE ALONE FOR REDUCING DEPOSITS OF LEAD ON EXHAUST VALVES. COMPARISON WITH FIGURES 3 AND 4 SHOWS THAT COMPLETE SUBSTITUTION OF BROMINE FOR CHLORINE IN THE CORRECTIVE AGENT IMPROVED EFFECTIVENESS STILL FURTHER.

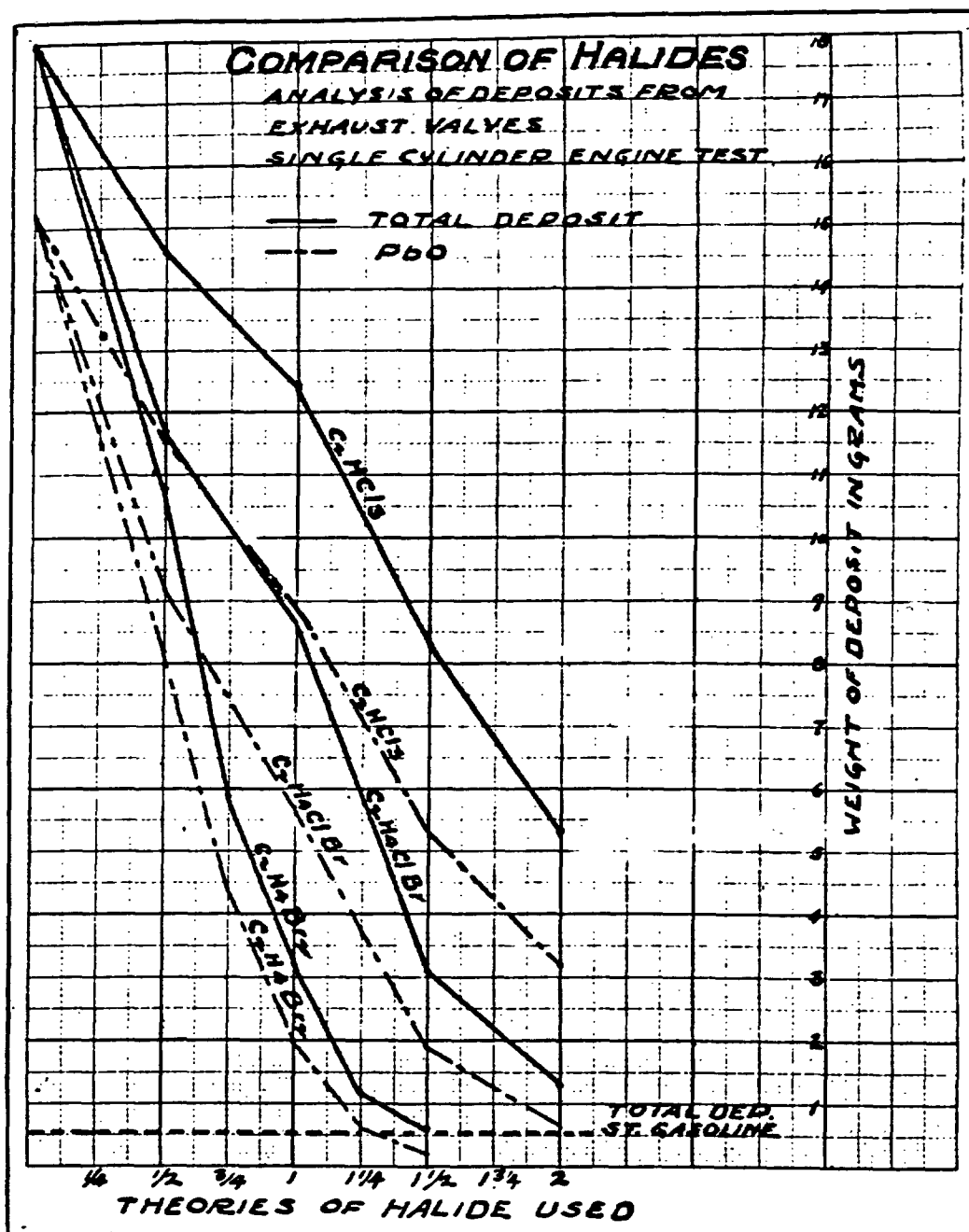


FIG. 6, APPENDIX V

DIRECT COMPARISON OF DEGREES OF EFFECTIVENESS OF CORRECTIVE AGENTS CONTAINING CHLORINE ALONE, HALF CHLORINE AND HALF BROMINE, AND BROMINE ALONE.

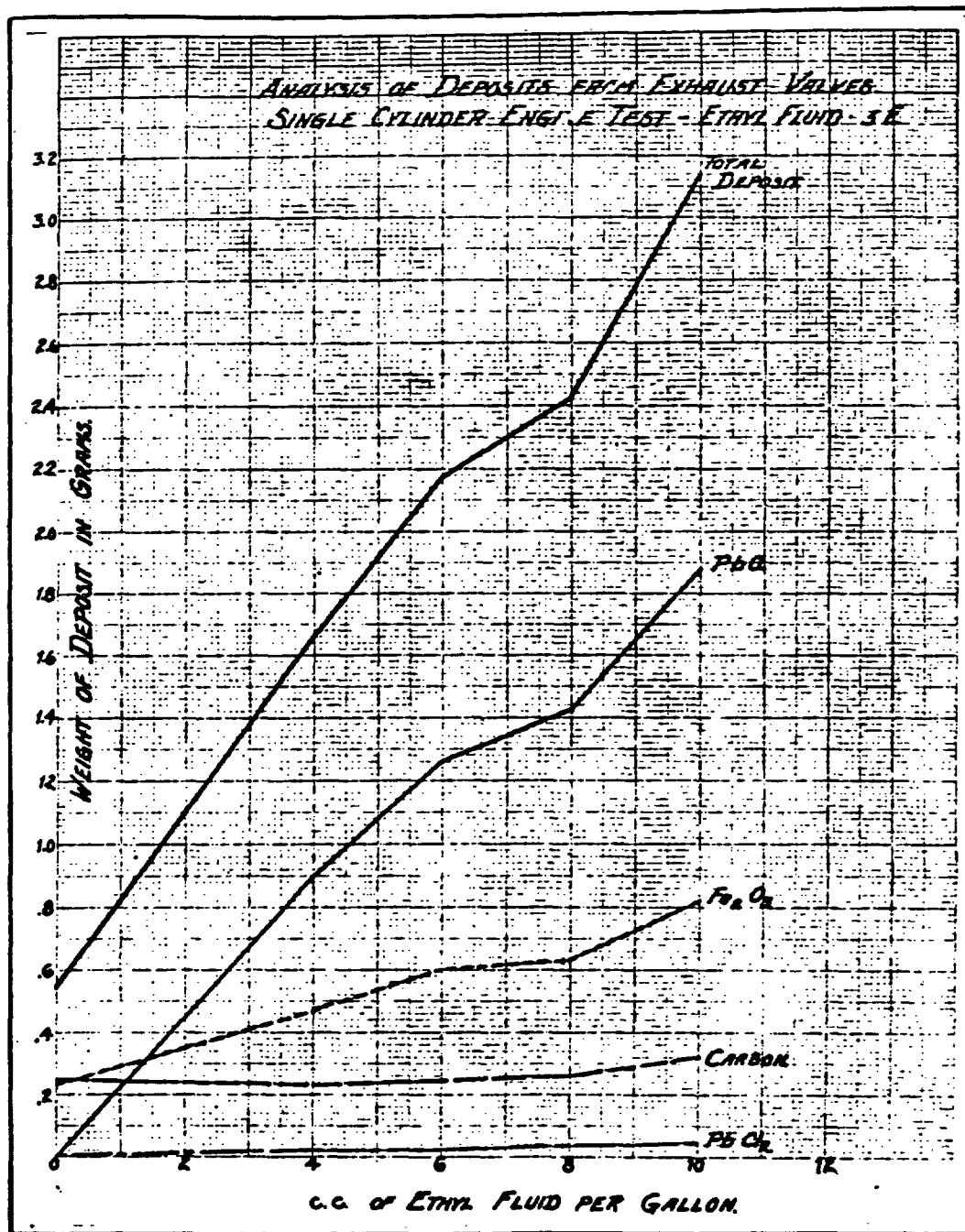


FIG. 7, APPENDIX V

CHART SHOWING, FOR ETHYL FLUID 3-E, HOW WEIGHT OF DEPOSIT ON THE EXHAUST VALVE INCREASED WITH NUMBER OF CC'S OF ETHYL FLUID PER GALLON OF GASOLINE. ETHYL FLUID 3-E CONTAINED BY VOLUME 3 PARTS TETRAETHYL LEAD AND 2 PARTS ETHYLENE CHLOROBROMIDE.

ETHYL GAS DEVELOPMENT

*Progress in Correcting Spark Plug Erosion
and Valve Deposit Troubles.*

*Sample spark plugs and exhaust valves from single
cylinder engines after running continuously at
1400 r.p.m. for 48 hours on various fuels.*

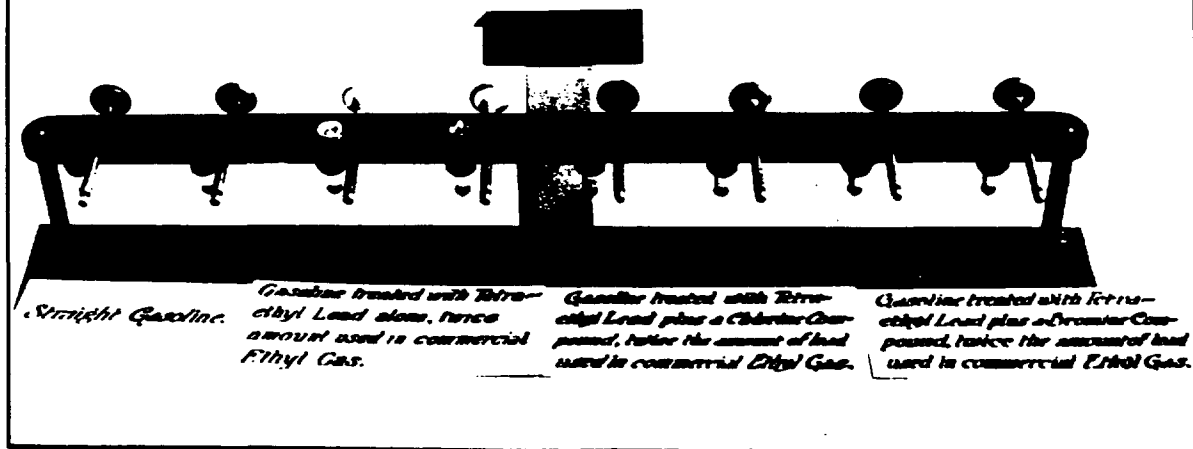


FIG. 3, APPENDIX V

CONDITIONS OF EXHAUST VALVES AND SPARK PLUGS AFTER
48 HOURS CONTINUOUS RUNNING ON FUELS OF THE FOUR
DIFFERENT COMPOSITIONS GIVEN ON THE CARDS AT THE
BOTTOM.

[illegible]

3.3001 Various Compounds & Mixtures

acetamide
acetic acid
acetic anhydride
acetophenone
acetyl chloride
acetyl isothiocyanate
aluminum ethylate
anisole
anthranic acid
antimony trichloride
arsenic trichloride
arsenic triphenyl
benzaldehyde
benzylacetate
boric acid

Carbon disulfide + amyl alcohol

Camphor

Carbon disulfide

Carbon disulfide + carbon dioxide (Catalytic agent)

Carbon disulfide + carbon dioxide (Catalytic agent)

Carbon disulfide + carbon dioxide (Catalytic agent)

Carbon disulfide + carbon dioxide (Catalytic agent)

Carbon disulfide + ethyl carbonate

Carbon disulfide + ethyl iodide (Catalytic agent)

Carbon disulfide + ethyl iodide

Carbon disulfide + ethyl iodide

Carbon disulfide + isopropyl nitrate

Carbon disulfide + carbon dioxide (Catalytic agent)

Carbon disulfide + carbon dioxide (Catalytic agent)

Carbon disulfide + carbon dioxide

Castor oil

Cresole

Diethyl malate

Diethyl malate

Diethyl ether

Diethyl ether

Diethyl ether

Diethyl ether

Diethyl ether

Diethyl ether + carbon disulfide

Diethyl ether

Diethyl ether + carbon disulfide

Diethyl ether

Diethyl ether

Diethyl ether

Diethyl ether + carbon disulfide

Diethyl ether

Diethyl ether + ethyl iodide

Diethyl ether

Diethyl ether

Diethyl ether

Diethyl ether

Diethyl ether

Diethyl ether

Diethyl ether + carbon disulfide

Diethyl ether

Diethyl ether

Diethyl ether

Diethyl ether

Diethyl ether

Diethyl ether

Diethyl ether + carbon disulfide

Diethyl ether

Diethyl ether

Diethyl ether

Diethyl ether

Diethyl ether + ethyl iodide

Diethyl ether

To:

From:
L. E. Blanchard, Jr.

ETC 37144

APPENDIX VI

REPRESENTATIVE ITEMS FROM THE PUBLICITY
ABOUT THE BAYWAY POISONING EPISODE

ANOTHER MAN DIES FROM INSANITY GAS

Eight Other Standard Oil Workers Suffering From Poison Said to Be Tetra-Ethyl Lead.

EXPERT ISSUES A WARNING

Dr. Yandell Henderson Sees Menace to Public in Use of Lead in Gasoline.

FEARS ITS USE IN AUTOS

Company Issues Statement Denying Negligence—All Laboratory Employees to Be Examined

The second death from insanity-producing gas at the Standard Oil plant at Elizabeth, N. J., was reported yesterday. The victim was Walter D. Smith, who died violently insane at the Reconstruction Hospital in this city, to which he had been removed from Elizabeth. His symptoms were identical with those of Ernest Olgert, who died of the deadly gas on Saturday.

A total of eight patients were under treatment at the Reconstruction Hospital, all more or less damaged from the fumes which seemed to have such a mysterious effect on the brain and nervous system.

Dr. Yandell Henderson, Chief Medical Examiner here, said he suspected from the symptoms that death had been caused by tetra-ethyl lead, but that the autopsy had revealed no evidence as yet. He said the detection of death from lead gas was one of the most difficult kinds of biological chemistry and that it might require four or five weeks to establish the agent which had produced death.

Dr. Randall Henderson, Professor of Applied Physiology at Yale, and one of the greatest authorities on the action of gases on the human body, said the symptoms from which the two victims had suffered made it evident that the poison was tetra-ethyl lead. He said the Standard Oil Company was selling gasoline containing this substance in some States, and that he regarded it as one of the greatest menaces to life, health and reason, because of its insidious character of the gas.

No high Standard Oil official could be found last night to reply to his own charge to Dr. Henderson's charge, but a representative of the company, who would not be credited by name, characterized Dr. Henderson's accusation as "nonsense." He said it was true that the Standard Oil had used a lead preparation to increase the efficiency of gasoline, but that careful tests had shown it to be safe in such attention as it could give the air.

"It has been known for several years,"

Dr. Henderson said, that the mixture of tetra-ethyl lead would produce the effect. The General Motors Company, ten years ago, asked me to make a report on the substance. I reported that it was exceedingly dangerous to life and health, and that it would be criminal to use it as a hazard on the general public, unless it was perfectly safe.

Police Attache Brule and Norrie, of Montreal, said the most dangerous form of lead poisoning, by being volatilized, the lead is introduced quickly into the blood through the lungs and enters its attack on the brain and nerves. Those who have suffered from malaria as a result of breathing the gas in this laboratory have had gas poisoning in its most acute form.

Are they likely to recover completely? Dr. Henderson was asked. They are not, he said. They may recover, but in all probability they have suffered permanent damage. Dr. Henderson said that milder cases of lead poisoning lead to paralysis and other severe symptoms, and breathers of small amounts might suffer from later symptoms.

"This is one of the most dangerous things in the country today," he said, "and although this is the first case that has been widely known, there have been several other similar cases. There is such an outbreak at a plant in New York State recently. I have private information on that subject which I am not at liberty to disclose."

"I know from good information that the Standard Oil Company, while it had said none of this substance had been used in New York State, has said it in other States. In my opinion, cities like New York City should take energetic measures to protect the masses against the danger which is involved in this."

If an automobile from another State with this gas should have trouble along Fifth Avenue and release a quantity of gas with the lead mixture, it would be likely to cause gas poisoning and cause deaths along the avenue.

If one of this kind were released in a park, it probably would have disastrous results on those who breathed it.

The gas has a slight odor, but it is not sufficient to warn the breathers that the fumes are dangerous. As the symptoms do not occur immediately, he does not know his danger and the damage that will be done later.

During the investigation of this substance a number of investigators, chemists and doctors have been poisoned. I regard it as a matter of vital importance that the health authorities of New York City should protect themselves in this matter without delay.

Dr. Norrie said he was regretful of the danger pointed out by Professor Henderson, but that there were being taken to meet it.

Dr. Henderson is one of the greatest authorities on this subject and I believe that what he says is correct, I said Dr. Norrie. "Within the last six weeks I have been warned that there is a menace of this kind. So far as we have been able to ascertain, no automobile burning gasoline containing this lead has entered New York City."

"I have been informed that they have been putting on the market in some places a gasoline containing about 5 percent of lead and that, in my opinion, is not a safe product, especially in this city, in which such quantities of gas are discharged into the air from automobiles all the time."

Five Patients Being Well.

Dr. Norrie said he would call on the Standard Oil Company to furnish all possible information bearing on the cause of death of the man who died in this city.

But researchers and others who may want chemical proof of the cause of death will have to wait possibly a month because of the extreme complexity of the chemical analysis necessary to establish lead gas poisoning.

Dr. E. Flint, house surgeon at the Reconstruction Hospital, said five gas sufferers still were under treatment here.

They are all doing nicely," he said, "and our expectation is that they will recover. For the most part they are rational, but they still have fits of insanity. This is a new disease and there is no known treatment for it. The symptoms bear a strong resemblance to a typhoid fever, but do nothing else."

Investigator A. J. David of Elizabeth continued his investigation to discover whether there had been any criminal negligence.

"I have found out one thing," he said, "and that is that these deaths took place not in the course of experiments but in the course of manufacture. The Standard Oil Company at this plant is mixing other chemicals with gasoline and putting it on the market to increase the efficiency of the gasoline. This is being done in the course of regular production, not experiment."

Whether the gasoline thus treated was being sold in New Jersey has not been established.

The Standard Oil Company of New Jersey denied that it had been guilty of negligence in a statement issued from the main office at 24 Broadway yesterday. This statement follows:

"For several years past the development department of the Standard Oil Company of New Jersey, under the guidance of the foremost chemists and engineers obtainable, has been engaged in an effort to find a substance which could be successfully used with straight gasoline to overcome certain inherent difficulties of motor car operation. When such a substance was discovered, it was immediately subjected to a similar large-scale development department because it was in the possibility of being successfully used with straight gasoline in a temporary laboratory was equipped in the research building at the Bayway plant and work was begun there on a small scale."

"It was planned to use these quarters for six months only, by the end of which time it was expected that enough would have been learned about the process to warrant the erection of a permanent building especially designed and equipped for commercial production. It had been tentatively decided to erect such a building at Chicago if the experimental work going on at Bayway indicated a successful solution of some unusual manufacturing problems."

"As in the production of bromine, nitroglycerine and certain other chemical substances, the manufacture of the new fluid involved certain dangers. Against these every precaution was taken by the development department. The foremost authority on occupational diseases, acting as medical consultant of the Standard Oil Company of New Jersey cooperated with the company's medical department and the local physicians at the Bayway plant to make the work safe. The doctors arranged for frequent examinations of all those who worked in the laboratory and kept a sharp lookout for symptoms peculiar to gas poisoning. When minor illnesses arose from time to time, the men affected were at once transferred to other work."

Laboratory Ordered Closed.

"On Saturday morning five employees who had been under medical care became seriously ill. The medical department immediately closed the laboratory and ordered that no more men be allowed to work there pending the conclusion of an investigation of the cause of the illness. The patients were sent to the Reconstruction Hospital in New York City to give them the best possible attention. One of the peculiarities of this form of poisoning is that certain men appear to be immune while working alongside others who have become ill. Another is that the cumulative effect of unappetized exposure to fumes has been impossible to detect until illness sets in."

"As in other big industries, the Standard Oil Company of New Jersey has kept a large force of physicians and chemists employed in experimental studies, some of which are necessarily attended with danger. For this reason it has given a great deal of attention to safety measures and no employee has ever been exposed to unguarded exposure against illness or accidents. That such an accident as these deaths occurred in spite of precautions is greatly deplored by the company."

"It was explained that the increased efficiency of this newly increased gasoline combination made it possible for automotive engineers to produce a more powerful engine than any yet known, and that plans for putting this new engine on the market have advanced substantially with the experiment on the background."

The lead is said to be the speed of the combustion, deliver away from the pistons and decreasing carbon deposits.

It was said the new motor made to handle the lead-gasoline could obtain great power from this new-expanding substance, but some hammer blow to pieces if run on ordinary gasoline.

Forty-five men were engaged in the experimentation, consisting of three shifts of fifteen men each. All were subjected to the same influences from the new gas. Those that took ill manifested different symptoms, but in general they were first an insomnia, then general restlessness, lowered blood pressure, and finally brain congestion. In some instances the illness came rapidly; in others it was of cumulative character, but progressed so gradually as to escape detection. The medical specialists in charge did not become alarmed until last Thursday, and then believed that the strange malady will be hard to treat until last Saturday, when a sudden turn took one man's life.

Dr. James and Thompson said two physicians were on the ground all the time at the Elizabeth plant, including a staff of nurses, an emergency hospital, and an ambulance service hastening to the city hospital or to the city hospital. Each of the forty-five men employed was watched closely for change in blood pressure or other symptoms. The new form of gasoline, they said, had, so far as they could tell, no action, and pending an autopsy it would be impossible to tell exactly what was the cause of death in two instances and illness in seven others.

The Standard Oil Company of New Jersey has had in effect for many years an employee welfare plan calling for ambulance, benefits and insurance for persons injured or killed while in the company's service. The families of the two men who died, it was said, would consequently be cared for and no money would be spared in treating the patients now in hospital.

The family of William McKinley, one of the victims at Reconstruction Hospital, who has been in a straitjacket, were notified to come to the hospital yesterday because there was danger of a fatal complication, but it was later reported that he was improved.

The Standard Oil's development laboratory, where the poisoning occurred, remained closed.

How to Be Killed.

Forty men, all of whom had been in any way exposed to the "insanity gas," were ordered to take a physical examination at the plant today. It was reported that the medical examiners suspected a slight degree of poisoning in several cases. It was reported that many others were to be sent to Reconstruction Hospital for treatment, but this was denied.

Dr. C. O. Johnson, Director of the development laboratory, was asked about a report that six rats and six pigeons died in the gas when the laboratory was opened and all died.

"I don't know about that," he said. Edward Rodgers of 442 Cherry Street, Elizabeth, quit work in the laboratory three weeks ago because of illness and has since been confined to bed at his home. Members of his family said today he had shown no improvement and that he continually complains that he is being persecuted and takes them in that kind of delirious way."

NEW YORK TIMES, TUESDAY, OCTOBER 28, 1924.

BAR ETHYL GASOLINE AS 5TH VICTIM DIES

City Health Authorities Forbid
Its Use—Sold in 10,000
Filling Stations.

DENIES IT'S "MYSTERY GAS"

Inventor of Compound Declares
Dangerous Nature Was
Long Known.

HAD CAUSED DEATH BEFORE

Standard Oil Officials Say Workers
Were Warned, and That It Is
Harmless in Dilution.

Herbert Fuson of 516 Grier Avenue, Elizabeth, N. J., died in a straight jacket violently insane at Reconstruction Hospital yesterday morning, the fifth victim of the deadly tetraethyl lead fumes generated in the Standard Oil plant at Elizabeth, N. J., where the tetraethyl lead was being added to gasoline to increase its efficiency.

The gasoline thus treated with tetraethyl lead was barred from New York City as a public menace by resolution of the Board of Health yesterday, and similar action was taken in various parts of New Jersey.

Thirty-six persons were under treatment or observation in hospitals and eight in their homes yesterday because of exposure to the gas. With the five dead, this made a total of forty-nine persons who had been placed in the peril of this insanity-producing substance.

In an official statement yesterday the Standard Oil Company of New Jersey denied that the poison which has wrought this havoc was a "mystery gas" and said that its qualities were well known. It was admitted that it was known that this gas had collected a previous tool of death and insanity before the forty-nine employees were exposed to it at the Elizabeth plant. This plant continued to be closed yesterday, and the investigation of County Prosecutor David of Elizabeth into the possible criminal aspects of the case continued.

Sold in 10,000 Stations.

Although the perils involved in making the lead-gasoline were admitted by the Standard Oil Company yesterday, it denied that such perils existed in the use of this gas in automobiles. Such gasoline, greatly diluted, is in use in more than 10,000 filling stations and garages, and no ill effects have thus far been reported, according to the Standard Oil Company. Acting on information that this product was dangerous, however, the health authorities of this city barred it yesterday. Dr. Yandell Henderson of Yale, whose opinion on the action of the gas on human breathers was sought by the manufacturers and then rejected

asserted that the absence of reports of injury due to breathing this gas in automobile exhaust fumes was no indication that those fumes were not dangerous. He said that this poison was so insidious that the breakdown in health might occur long after the breathing of the poison so that insanity or milder symptoms might not be connected with the true cause.

Thirty-two of the employees of the plant were at the Reconstruction Hospital yesterday. Some of them have developed no symptoms at all and were removed to the hospital only as a precaution.

"Some of them are suffering from headaches," said Dr. C. K. Flint, house physician of the hospital. "Others have some mental disturbance. It might be called a mild delirium or might be called dizziness. Low blood pressure is another symptom by which injury from the gas is detected. None of the thirty-two here at present is in a serious condition and we expect no more fatal results."

Nervousness a Symptom.

Extreme nervousness is one of the early symptoms, but it is difficult in some cases to discriminate between nervousness caused by the gas and that due to anxiety naturally experienced by those who have been exposed to it, according to Dr. Flint.

These patients are being treated with intravenous injections of hypophosphite of soda which is believed to combine with the lead and produce harmless substances, but the five deaths at the hospital on successive days have diminished the prestige of this remedy. Dr. Flint said, however, that it is thought to be beneficial to those now receiving the treatment.

These deaths, together with the warnings of Yandell Henderson and other investigators of the alleged dangers lurking in the use of the tetraethyl lead gas, called the calling of a special meeting of the Board of Health of New York, at which this resolution was adopted:

"Whereas it has been brought to the attention of the Board of Health that compounds of lead or other deleterious substances are being added to gasoline in tanks of motor vehicles and motor engines generally for the purpose of increasing gasoline or motor efficiency; and

"Whereas it is the opinion of the Board of Health that 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 and motor engines; be it

Resolved, That the Board of Health does hereby prohibit and forbid the use of gasoline for any of the above purposes to which either compounds containing lead or other deleterious substances have been added, and also does hereby prohibit and forbid the addition of substances to gasoline intended to be used for such purposes."

Health Commissioner Frank J. Monaghan afterward held a conference with a number of health officials from New Jersey at which it was decided to make a further study of the effects of tetraethyl lead in automobile engines to discover whether it presented a menace in garages, repair shops and congested streets, as has been alleged by scientists and denied by the manufacturers. The health officers in Union County were all requested by Prosecutor David to stop the sale of gasoline combined with lead.

Defended by Inventor.

Thomas Midgely Jr., discoverer of the use of tetraethyl lead for increasing power in gasoline, defended his compound at an interview yesterday at the offices of the Standard Oil Company, at 14 Broadway. To prove that the substance was not dangerous in small quantities he rubbed some of the tetraethyl lead on his hand. He said that two fatalities had occurred at the Dayton plant of the General Motors Chemical Company, which also has been making this gasoline compound.

Mr. Midgely said the Bureau of Mines had been asked to make a most thorough investigation of the effects of tetraethyl lead gas poisoning, and that the bureau had been conducting tests in this connection for about ten months. According to an official of the Standard Oil Company, the bureau will make a statement on the results of these tests in two or three days. The tests are being made, Mr. Midgely said, at the request of the General Motors Corporation.

tion, which, with the Standard Oil Company of New Jersey, owns the Ethyl Gasoline Corporation.

Not only had the employees of the Dayton research plant been under observation after handling the fluid; two of these cases proving fatal, but similar difficulties in erecting adequate safeguards for employees had been met with at the du Pont laboratories, Mr. Midgely revealed. He said that the experience in combating the effects of the tetraethyl had been general wherever the process had been carried out. Without, he said, desiring to attach any blame to the employees, it had been found at the Dayton plant that the men, regardless of warnings and provision for their protection, had failed to appreciate the dangers of constant absorption of the fluid by their hands and arms.

Manufacture Not Perfected.

Dr. J. Gilman Thompson, consulting physician for the Standard Oil Company, who was present at this interview, gave out the following typewritten statement on the subject:

"Tetraethyl lead is a substance first known to chemists in 1854. Since that time it frequently has been experimented with in chemical laboratories where it was known to be, in concentrated form, poison. It is a compound of metallic lead and one of the alcohol chemical series. Its recently discovered use for greatly promoting the efficiency of gasoline engines has led to its manufacture on a commercial scale through processes still more or less in a stage of development. This has occasioned unforeseen accidents which as processes and apparatus are further perfected should be avoidable in the future. One of these has been the sudden escape of fumes from large retorts and the inhalation of such fumes gives rise to acute symptoms, particularly congestion of the brain, producing a condition not unlike delirium tremens. Although there is lead in the compound, these acute symptoms are wholly unlike those of chronic lead poisoning such as painters often have.

"There is no obscurity whatever about the effects of the poison and characterizing the substance as 'mystery gas' or 'insanity gas' is grossly misleading.

"In the recent cases of poisoning occurring among employees of the Standard Oil Company of New Jersey, there were five which resulted fatally before the delirium could be controlled. The other patients were affected in mild degree, but promptly were brought to the Reconstruction Hospital in New York, because that institution is devoted exclusively to the treatment and investigation of industrial diseases and accidents. Here new methods of curative treatment have been discovered which are proving highly successful.

"It should be emphasized that the product as destined for final use in gasoline engines has to be greatly diluted, usually with 1,000 parts of gasoline. This extremely diluted product has been for more than a year in public use in over 10,000 filling stations and garages, and no ill effects thus far have been reported."

Standard Oil officials expressed the opinion that the Dayton plant, closed after the fatalities, probably would not be reopened. The work on which the men who were stricken were engaged will be carried on at the du Pont plant, it was said.

Believe the Men Knew Danger.

Asked what would be the reaction of the Standard Oil Company to possible claims of families of men who died from the poison that the stricken men were never aware of the extent of danger involved in their work, officials of the company replied that the rejection of many men as physically unfit to engage in the work at the Dayton plant, daily physical examinations, constant admonitions as to wearing rubber gloves and using gas masks and not wearing away from the plant clothing worn during work hours should have been sufficient indication to every man in the plant that he was engaged "in a man's undertaking."

NEW YORK TIMES
OCTOBER 31, 1924

NO PERIL TO PUBLIC SEEN IN ETHYL GAS

Bureau of Mines Reports After
Long Experiments With
Motor Exhausts.

MORE DEATHS ARE UNLIKELY

All the 34 at Reconstruction
Hospital Are Believed to Be
Out of Danger.

LITTLE USED IN THE CITY

Tetra-Ethyl Compound Sold to Only
Two Firms, Which Are Experi-
menting, Says Standard Oil.

None of the surviving sufferers from tetraethyl lead poisoning appears to be in serious danger and it is believed that the death list of five will not be increased, according to reports from Reconstruction Hospital.

Four new patients were added to this group, making a total of thirty-six at the hospital, but two of these were discharged later as being entirely free from symptoms of the poison.

"The patients here now appear to be out of danger," said Dr. C. K. Flint, house physician of the hospital. "Some of them have no symptoms and are here for observation only, and none has developed any serious trouble. We are hopeful of full recovery in all these cases."

Dr. Flint said it had not been established certainly whether the lead or the higher alcohol in the tetraethyl lead was the cause of the illness and deaths. The lead is combined with one of the alcohol groups. According to Dr. T. A. Wallace of 141 Fifth Avenue, the gas, after being breathed into the lungs, could be reduced in the blood stream to pure alcohol, producing a form of acute alcoholism. Brig. Gen. Amos O. Fries, chief of the Army Chemical Warfare Service, reported, on the other hand, that an investigation of the use of this gas for poison gas warfare had shown that lead was the agent which produced the poisoning.

Samples of the so-called "loony gas" were used at the Edgewood Arsenal six months ago to see whether this reason-destroyer had any promising possibilities for war, and also to discover antidotes and other protections against it. It was found that it was dangerous unless the greatest precautions were taken in handling it.

Sent in Pure Form to Garages.

The tetraethyl lead, which is dispensed from 10,000 filling stations at present, according to the Standard Oil Company, is diluted about 1,000 times

for use in gasoline. The tetraethyl lead is sold in its pure form, however, to the garages and filling stations, so that it is handled locally at thousands of places. Elaborate directions and warnings are sent out to those who handle the substance in its concentrated form. It is mixed with a red coloring to serve as a warning of the care necessary in handling and to prevent its use for cleaning and other purposes for which ordinary gasoline is used in the home.

Philadelphia yesterday followed the example of New York City by prohibiting the sale of gasoline containing the tetraethyl lead. At the same time a report of the Bureau of Mines was made public at Washington with the conclusion that the danger to the public from lead in the exhaust of automobiles is "seemingly remote." The report does not deal with the dangers in handling the substance at the service stations or other risks aside from that incurred by the general public in breathing air contaminated by automobiles.

The Bureau of Mines carried on its investigation at Pittsburgh where a number of compounds supposed to increase the efficiency of gasoline were tested. "One of the commonly used 'antiknock' compounds," the report said, "is known as tetraethyl lead. This is added to gasoline in quantity of less than one part of tetraethyl lead in one thousand parts of gasoline by volume and this mixture is sold on the market as ethyl gasoline."

Problems Relating to Health.

"The problems of the health hazard due to the use of tetraethyl lead may be divided into three parts:

"1. The hazard in the manufacturing and handling of the concentrated tetraethyl lead. This hazard occurs in the manufacturing plant.

"2. The possible hazard in handling the ethyl gasoline (one part of tetraethyl lead to one thousand parts of gasoline). This possible hazard may affect those handling ethyl gasoline.

"3. The possible hazard due to the exhaust gases from automobiles using ethyl gasoline. This possible hazard concerns the entire public.

"The scope of the work undertaken by the Bureau of Mines included an investigation of all possible hazards as outlined in the above. The first two parts, namely, that of the danger in the manufacture and handling of the concentrated tetraethyl lead and the possible risk in handling the ethyl gasoline as sold to the automobile user, are now being investigated. Sufficient data have not been obtained to draw conclusions to date. As soon as this investigation has been completed the results will be made public.

"The last part of the above outlined problems, namely, the possible hazard due to the exhaust gases from automobiles using ethyl gasoline as ordinarily sold, has been carried on for more than ten months.

"The plan of investigation was that of exposing various types of animals (rats, guinea pigs, rabbits, dogs and monkeys, over 100 in all), to a definite concentration of exhaust gas from an engine using Ethyl gasoline. The concentration of exhaust gas in air used was that which when coming from the average automobile would be four parts carbon monoxide in ten thousand parts of air; this concentration would be allowable for but a period of one hour's exposure from the standpoint of carbon monoxide. (The concentration of exhaust gas in air used was such as to exceed that known to exist in ordinary traffic of a city street.) The carburetor was adjusted so that the carbon monoxide content of the exhaust gas from the engine used was less than one-half that found in the average automobile exhaust gases.

Showed No Sign of Poisoning.

"The animals were divided into three representative groups. The first two groups were exposed for periods of three and six hours respectively, and the third group not exposed but used as controls. The animals were thus daily exposed for three and six hours over a total period of approximately eight months to a known concentration of exhaust gas. These exposures were such that the lead content of the air breathed

by the animals was similar to that which would result from exhaust gases of an average automobile using ethyl gasoline diluted so as to contain about four parts of carbon monoxide to ten thousand parts of air (the permissible exposure for one hour from the standpoint of carbon monoxide poisoning). This was a considerably higher concentration of exhaust gas than could ordinarily occur.

"The animals were observed throughout the entire test period for symptoms of lead poisoning, as colic, paralysis, loss of appetite and loss of weight. Also a careful examination of the blood was made for characteristic signs of lead poisoning. At various times animals were killed and the entire tissues examined for effects of lead and analyzed for stored-up lead.

"After a period of approximately eight months daily exposure to the above conditions there was no indication of lead poisoning. The animals continued to grow and mature at a normal rate. One of the dogs gave birth to five puppies. There were continued on test with the mother, and in the course of the test matured normally. The absence of lead poisoning may be due to the small amount of lead present in the exhaust gas air mixture. Furthermore, observations made on man showed that most of the lead in exhaust gases coming from ethyl gasoline when inhaled is again exhaled.

"The investigation carried out indicates the danger of sufficient accumulation in the streets through the discharging of scale from automobile motors to be seemingly remote.

"The investigation of the possible hazards of lead poisoning from exhaust gases is being continued at the Pittsburgh station of the Bureau of Mines, together with the first two phases of this study."

Little of It Used Here.

The resolution of the Board of Health, prohibiting the sale of ethylized gasoline in the city, will have no immediate effect, as there have been no sales of the product here, the only deliveries in New York City having been those to three automobile companies which wanted to make tests on their cars, according to the Standard Oil Company of New Jersey.

At the offices of the company it was stated yesterday that the sale of ethylized gasoline has been more general in other parts of the country, particularly in the Middle West, where the Standard Oil Company of Indiana has been a large distributor through its own service stations. Because of the demand for the product, it was explained, supplies have been inadequate to supply the local territory.

A number of other companies have been marketing ethyl fluid in conjunction with gasoline. The Standard Oil Company of New Jersey, which is equal owner with the General Motors Company of the Ethyl Gasoline Corporation, owners of the patents on the fluid, has cut its marketing well under way in the South Atlantic Coast district in Maryland, Virginia and the District of Columbia. The company is now starting to introduce it at the service stations in New Jersey.

**NEW YORK TIMES,
NOVEMBER 1, 1924**

NEW YORK
WORLD

NOV 27 1924

STANDARD CEASES MAKING ETHYL GAS IN JERSEY PLANT

**Bayway Work to Be Removed
to Middle West as the Result
of Five Deaths From Poison.**

**SAFE WAYS OF HANDLING
NOW KNOWN, SAYS CHEMIST**

**Dr. Howe of the American
Chemical Society Says Gas
Is Too Valuable to Abandon.**

The production of tetra-ethyl lead has been discontinued, probably permanently, by the Bayway, N. J., plant of the Standard Oil Company of New Jersey. It was stated yesterday by Dr. Andrew F. McBride, State Commissioner of Labor, in a report to Gov. Silzer, giving the results of his investigation of the manufacture of "looney gas" and the consequent death of five employees of the Bayway plant.

At the Bayway plant, officials said

SUFFALO, N. Y.
EXPRESS

NOV 27 1924

Folly to Stop Looney Gas Manufacture, Chemist Says

**Dr. Harrison E. Howe insists danger no greater
than risks in many processes.**

New York, Nov. 26 (A. P.).—Manufacture of tetra-ethyl lead, so-called looney gas, should not be discontinued, despite the dangers involved. It is asserted in a report made public today by Dr. Harrison E. Howe of Washington, D. C., editor of the official journal of the American Chemical society, following an investigation into the recent deaths of five workers at the Bayway, N. J. plant of the Standard Oil company.

privately yesterday, instructions had been given to dismantle the plant. These officials, who refused to give their names, said as soon as a site could be selected, the plant would be set up in the Middle West, and the manufacture of ethyl gasoline continued.

Coincident with Dr. McBride's report, the American Chemical Society announced the results of an independent investigation by Dr. Harrison E. Howe of Washington. Dr. Howe declared he "found no evidence to justify even the occasional demand that no more ethyl gasoline be manufactured." He said now "the price for an important economic advance has been paid." It would be "folly" not to continue.

Dr. McBride's report said he was opposed to any attempt to manufacture tetra-ethyl lead by the same methods used in the past, as "experience has demonstrated workmen cannot be safeguarded against the effects of poisonous contact." At the same time, Dr. McBride stressed that the Standard Oil Company had complied with the State sanitary laws in every particular.

Dr. McBride pointed out that ordinary workmen cannot be expected to use successfully the methods to protect themselves that skilled scientists use, even if all the protective apparatus is furnished them.

The report concluded, "I have been assured by a representative of the Bayway plant that the old process will not be used again; and no effort will be made to manufacture this material without first notifying the Department of Labor of New Jersey of the fact."

The report covered in addition the E. I. du Pont de Nemours Company, at Carney's Point, N. J., where three workmen died, with similar findings.

According to the report of the American Chemical Society more than

200,000,000 gallons of ethyl gasoline have been used by the public in the last two years, and it has been sold at 20,000 filling stations "without apparent injury or loss of life."

The report said "unquestionably the manufacture of tetra-ethyl lead is dangerous." It points out that this hazard is no greater than in many manufacturing processes, and manufacture under strict control and adequate supervision is now possible.

Tetra-ethyl lead has been distributed in the form of ethyl fluid, the reports said, in small cylinders sealed with a tin cap, which is punctured by a spike before it is poured into the delivery hose at a service station. Any hazard involved in distribution in this way, the report declared, will now be reduced to the vanishing point.

men engaged in the work are so informed and receive extra compensation.

Their condition is carefully watched by physicians. This type of poisoning differs from that of other lead compounds in that the tetra-ethyl lead seems to enter through fatty tissues and to be deposited as such in various parts of the body, including the brain, where it remains unchanged.

Nevertheless, the report maintains, the dangers are "no greater than in many manufacturing processes" and adds that by the time the lead reaches the material, "the hazard is reduced to so near the vanishing point by dilution, that in the future no ethyl fluid will be sold as such, but ethyl gasoline, ready for use, will be received and dispensed as in any other gasoline."

Discontinuance of the manufacture of the compound would be folly if it is stated, the price now having been paid for an important economic advance. It is further pointed out that more than 200,000,000 gallons of ethyl gasoline have already been distributed by 20,000 filling stations in 22 states without apparent injury or loss of life. Unquestionably, the manufacture of tetra-ethyl lead is hazardous, the report states. "The

EDITORIALS

Tetraethyl Lead

FOLLOWING the unfortunate loss of life among employees of the Standard Oil Company at Bayway, N. J., various accounts of which have appeared in the daily and technical press, there were many manifestations of hysteria in which a few scientific men had a part. Fortunately, other scientists were in a position to prevent hasty action and made remarkably clear reports for the proper guidance of boards of health. It seems well to set down here a few of the facts in the case.

Tetraethyl lead, discovered in 1854, has long been known as a highly toxic substance. It is in no sense a mysterious substance, although named "mystery gas" by the daily press. In concentrated form it is about one-twentieth as potent as bichloride of mercury, and one twenty-fifth as toxic as mustard gas. The discovery that its use in gasoline would permit the employment of motors of much higher compression, and consequently of improved economy, has made it a substance of great economic importance. Data indicate that with an engine designed for high compression as much as twenty-five per cent of our petroleum can be conserved and the amount of carbon monoxide reduced, owing to the lessened consumption of fuel per motor.

Tetraethyl lead is manufactured by one of our largest and most experienced makers of chemicals, who has demonstrated that this compound can be produced with safety to all who are engaged in the process. During the developmental work three men have been lost, but with a better understanding of the effects of tetraethyl lead, illness has been steadily reduced among the workmen until, like many other toxic materials, it can now be produced in large quantity with safety.

Ethyl fluid is the form in which tetraethyl lead has been distributed. This is tetraethyl lead dissolved in an organic bromide or chloride, such as ethylene dibromide. This solvent is also toxic, and ethyl fluid has until now been dispensed in small cylinders sealed with a tin cap and punctured by a spike when the cylinder is inverted over an iron cup on the delivery hose at the service station.

Ethyl gasoline is the material used by the motorist. The proportion of tetraethyl lead to gasoline is from one in one thousand to one in fourteen hundred, a dilution which makes a perfectly safe mixture. Such gasoline has been in public use for two years and two hundred million gallons have been dispensed by twenty thousand filling stations in twenty-two states without apparent injury or loss of life.

The products of combustion contain lead compounds, principally the oxide, much of which remains in various parts of the engine and its exhaust system, but a part of which is thrown into the air.

Obviously, there are hazards involved: these being, first, in manufacture; second, in distribution and handling; third, in the use of the treated gasoline; and finally, the possible hazard to the public on account of the lead compounds thrown into the atmosphere. What does the evidence on these hazards indicate?

Unquestionably the manufacture of tetraethyl lead is hazardous. The men engaged in this work are so informed and receive extra compensation. Their condition is carefully watched by physicians. This type of poisoning differs from that of other lead compounds in that the tetraethyl lead

seems to enter through fatty tissues and to be deposited as such in various parts of the body, including the brain, where it remains unchanged. It does not appear to be cumulative and disappears by way of perspiration and body fluids if the man affected is promptly removed from contact with the material. The men who lost their lives were examined frequently for plumbism and forty others affected at the same time have been saved. The hazards, moreover, are not greater than in many manufacturing processes. By working in completely closed systems safety is obtainable, and perhaps the greatest hazard is the indifference which not only workmen but even chemists come to have for dangerous work with which they are familiar. Indeed, the ethyl fluid is ordered to prevent men from using it as they use any other gasoline for washing hands. It has been demonstrated, however, that manufacture under strict control is possible and, as adequate supervision is constantly exercised and the dangers are known, we must look further for hazards affecting large numbers.

Distribution of ethyl fluid involves a large number of men who are very likely to be careless. To date injury to most of these men operating twenty thousand filling stations distributing ethyl gasoline has been reported. Nevertheless, the hazard is reduced by dilution to so near the vanishing point that in future no ethyl fluid will be sold as such, but ethyl gasoline ready for use will be received and dispensed as is any other gasoline.

The motorist meets no hazard in the use of ethyl gas and clearly he shares only such hazards as may threaten the general public. The public wants to know how liable it is to lead poisoning from the discharge into the atmosphere of some two or three tons of lead compounds per million gallons of ethyl gasoline burned. But the public is not nearly so concerned as are the manufacturers, who realize to what extent they would be the subject of attack should it develop that the public is endangered by the use of this fuel. Consequently, a year ago investigations were begun at the request of the manufacturers at the Massachusetts Institute of Technology and Columbia University, and independently at the Bureau of Mines. In addition, the company continued its own research. One investigation showed that the dust in the vicinity of the Grand Central Station in New York, where ethyl gas has never been used, contains more lead than dust from Detroit, where this fuel has been in service two years. The Bureau of Mines has announced the results of its careful investigation, during which more than one hundred animals of various types were exposed to a definite concentration of exhaust gas from an engine using ethyl gasoline, care being taken to adjust the carburetor to lower the content of carbon monoxide to less than one-half that found in the average automobile exhaust. Various examinations were made from time to time for symptoms of lead poisoning, such as colic, paralysis, loss of appetite, and loss of weight, the condition of the blood, and the possibility of stored-up lead in various body tissues. After a period of approximately eight months' daily exposure to these conditions there was no indication of lead poisoning. The animals continued to grow and mature at a normal rate. One of the dogs gave birth to five puppies. These were continued on test with the mother and in the course of the test matured normally. The absence of lead poisoning may be due to the small amount of lead present in the exhaust gas-air mixture. Furthermore, observations made on man by the Bureau of

Mines showed that most of the lead in exhaust gases coming from ethyl gasoline if inhaled is again exhaled. The investigation indicates the danger of sufficient lead accumulation in the streets through the discharge of scale from automobile motors to be seemingly remote.

We fail to find evidence, therefore, to justify even the occasional demand that no more ethyl gasoline be manufactured. We profoundly regret that the development of this economically important substance has cost the life of any one, and it does not add to the blow to those bereaved to point out that all poisoning has been accompanied with a loss of life. The price having now been paid, and lessons learned which might not have been learned without it, would it not be fully to demonstrate the use of the material after such sacrifice? We are so ready to denounce the use of ethyl gasoline, for it has a clean record in use. If we wish to do something really worth while, let us find a way to pro-

tect the public against the deadly carbon monoxide which takes its frequent victims. However, the case is not closed and the investigation is being continued by the Bureau of Mines and others equipped to conduct such investigations. The literature shows that lead is a substance to be watched carefully. Legge and Goadby, in one of the International Medical Monograph Series on lead poisoning and lead absorption, stress the toxicity of all lead compounds and state that lead coming in contact with the membranes of the respiratory system is far more dangerous than ingested lead. But in our investigation of potential lead poisoning for the public at large, let us not forget that there are many sources of lead dusts. We cannot single out tetraethyl lead for attack but must reconsider the use of lead paints in view of the data on the occurrence of lead in the dust of the average city.

We would like to see a larger number of those qualified to conduct thorough investigations of the possibility of lead poisoning become interested in this particular problem, do their work independently, and submit their results to an impartial group for interpretation. In the interim, there seems to be nothing to justify the hysterical statement that we are threatened with the same fate which overtook those in contact with the highly concentrated material. It is an instance where we would do well to keep our feet on the ground and not lose our heads.

Change of

After December 30, fees will be located Seventeenth Street a new Washington, D. C. for the convenience of all to call upon the B. and as when in Wash. office in the same building. Note the address of the Bureau.

Time

New York Times

7 - 1925

DEMANDS FAIR PLAY FOR ETHYL GASOLINE

Hysteria Should Not Be Allowed
to Bar Thorough Test of
Product, Editor Says.

CALLS FOR SANE OPINION

Ban on Sale of Fuel as Dangerous
to Health Advocated by Cor-
nell Professor.

Dr. H. C. Parmelee, editor of Chemical and Metallurgical Engineering, appeared to the chemical industry yesterday to demand fair play for ethyl, or leaded, gasoline, which is under attack as a menace to health.

"The chemical industry," said Dr. Parmelee, "can scarcely afford to sit idly by and view with equanimity the casual manner in which the fortunes of one of its branches have been rudely thrown into the balance by the hysteria of a newspaper and a physiologist. Whatever the merits or demerits of tetraethyl lead and ethylated gasoline, the products should not be summarily condemned as a menace to health, nor should the manufacturers be pilloried as inconsiderate profiters, without a thoroughgoing investigation."

"The research and development that produced tetraethyl lead were conducted in a fine spirit of industrial progress looking toward the conservation of gasoline and increased efficiency of internal combustion motors. The business was no fly-by-night venture, and its known hazards were safeguarded to the best of human ingenuity and ability. Its casualties were negligible compared to human sacrifice in the development of many other industrial enterprises."

"It is little short of a calamity, therefore, that the train of events of the past two months has developed a public controversy over this product that has been characterized by incompetent and hysterical testimony. One can imagine how chemical progress in the past might have been hampered by a similar crusade by self-appointed guardians of the public health. City gas and motor oil—neither still claim their victims almost daily, but escape the tender ministrations of the crusader."

"What is needed in the present situation is sanity and judicial consideration, and for these elements we must look to the conference called in Washington on May 20 by Surgeon General Hugh S. Cummings of the Public Health Service. It has been publicly stated that the conference will include physicians, pathologists, representatives of the automobile industry and chemists. We have urged General Cummings to recognize the importance of the last-named group. Inasmuch as a branch of the chemical industry is on trial, competent and impartial representatives of the industry as a whole should not only be among the witnesses, but on the jury."

"The chemical industry has no desire to be either a nuisance or a menace, but it does want a reasonable degree of assurance that it is not to be tried and convicted by incompetent critics or forced to abandon its legitimate pursuits by misguided zealots."

DU PONT TELLS OF THE GAS.

His Company Had Fatalities, but
Has Lessened Dangers.

Special to The New York Times.

WILMINGTON, Del., Oct. 30.—Death from poisonous gases encountered in the manufacture of motor fuels by the Standard Oil Company and the possibility of similar occurrences here were commented upon today by Irénée Du Pont, President of the E. I. Du Pont de Nemours Company.

In an interview today he said that in the earlier experimental stages of manufacturing tetraethyl lead some accidents and fatalities had occurred, but when the experimental stage had been passed these accidents ceased.

"Tetraethyl lead, which the Du Pont Company is manufacturing on a commercial scale," he said, "and which is reported as the cause of the recent unfortunate accident at the Bayway plant of the Standard Oil Company, should not be confused with ethyl gas, an improved motor fuel which contains less than one-tenth part of 1 per cent. of tetraethyl lead."

"Tetraethyl lead is poisonous and its manufacture involves risk, but no more so than many chemicals manufactured and used in enormously greater amounts."

"The du Pont Company, during the experimental period, experienced much trouble with men becoming poisoned, even to the extent of fatalities. During the past year of production, when more than 100 men have been employed continuously, the difficulty has diminished steadily. In the past several months, under full production, only slight difficulties have been encountered. Experience has taught the necessary protection, both in plant and medical care."

"We find that workmen cumulatively poisoned by this material invariably indicate it in the incipient stages, before any harm is done by a marked symptom. Doctors in the employ of the company continually make test on workers engaged in this process."

**NEW YORK TIMES,
OCTOBER 31, 1924**

WASHINGTON, May 8.—A ban on the sale of gasoline containing tetraethyl lead was advocated today by Dr. Charles L. Dana, Professor of Nervous Diseases at the Cornell Medical College, in an address at the Congress of American Physicians and Surgeons.

Although no evidence has been produced to show that the gasoline had affected the health of service station and garage employees, he said, the product had not been on the market a great length of time, and it was too early to classify it as a menace.

Dr. Dana created some of the cases of poisoning that occurred last Fall in the New Jersey laboratories where tetraethyl lead was being manufactured. Of the forty persons made dangerously ill, he said, none had yet recovered, although he believed the majority would eventually be restored to complete health.

DANGEROUS LEADED GASOLINE (TETRAETHYL) SALE STOPPED AFTER FIGHT BY THE WORLD

PRO AND CON—Manager of Tetraethyl Corporation
and Yale Scientist Who First Attacked Its Product



THOMAS MIDGLEY, JR.



Prof. YANDELL HENDERSON
Photograph by Keystone View Co.

Corporation Ends Trade To-
Day in Answer to Appeal,
Pending Washington Con-
ference on Peril to Health
in the Ethylized Fluid

**STATE HEALTH COUNCIL
TO SIFT ISSUE TO-DAY**

Dr. Yandell Henderson of Yale
Took a Large Part in
the Crusade

The campaign which The World has waged almost single-handedly against sale of tetraethyl leaded gasoline, pending scientific determination of the charge it is a menace to public health, brought a statement from the Ethyl Gasoline Corporation last evening that it would suspend sales indefinitely, beginning to-day.

This action was taken a few hours after The World sent telegrams to officers of the company and to directors of the Standard Oil Company of New Jersey and the General Motors Corporation, which jointly own the Ethyl Gasoline Corporation, asking if they did not agree sale of the fluid should be suspended immediately.

Columbia Report Asked For

The World also asked if they did not agree that the report which Columbia University experts have made on their investigation of the fluid's relation to public health should be made public immediately, in order that the public might be warned against further use of the product.

No answer to this query could be obtained. The university stood on its declaration that it would send the report to Surgeon General Cummings of the Public Health Service, at which and a conference of experts will meet at Washington May 26, for consideration.

NEW YORK WORLD, 5-5-25

N.Y. World - 5-6-25

PROF. HENDERSON WANTS U. S. CURB ON DEADLY GASES

**Lauding Successful Campaign
by The World, He Points to
Gap in Safeguards to Health**

TETRAETHYL SALE AT END PENDING INVESTIGATION

**Dr. Nicoll, Health Commis-
sioner, to Represent New
York State at Conference**

With sale of tetraethyl leaded gasoline suspended throughout the country yesterday, as a result of the crusade waged in the interest of public health by The World, chemists pointed out the need of Federal legislation to guard against just such a situation as has arisen in sale of a product the safety of which is now in scientific controversy.

Though the Food and Drug Law of the United States Government protects the public against impurities in food and drugs, there is no law to protect against danger in other articles of every-day commerce.

On Sale Two Years

Local Health officials may bar the sale of tetraethyl leaded gasoline or other products dangerous or of doubtful safety, it is pointed out, but there is no effective national agency to deal with the problem.

Because of the lack of such an agency the Ethyl Gasoline Corporation has been able to sell its product for two years, although evidence favorable to it came chiefly from the company's own experiments and from an inconclusive investigation by the United States Bureau of Mines.

Henderson Lauds The World

It continued selling the fluid after such an authority as Prof. Yandell Henderson of Yale had warned of the danger and after Drs. Edsall and Drinker of Harvard had criticized the method of the Bureau of Mines investigation. It suspended sale when The World—acting solely as a private agency performing a public service, as Prof. Henderson pointed out—began a crusade to halt distribution until the doubt regarding safety had been cleared away and when Columbia University experts found dilutions of the product highly dangerous.

SEES CAR MONOPOLY IN ETHYL GASOLINE

**Prof. Henderson Says That
Is in Prospect.**

New Haven, May 6.—Prof. Yandell Henderson of Yale, head of the laboratory of applied physiology, said the subject of leaded gasoline for automobiles "is probably the greatest single question in the field of public health," in a statement to the Yale News today. He said that the sale of financial interests involved is stupendous. "It is not a matter of millions or even hundreds of millions, but literally of billions."

Prof. Henderson said, in a portion descriptive of the preparation of leaded gasoline that, except in New York city and its immediate neighborhood, it was being introduced everywhere throughout the country as fast as it can be supplied. He also said that it is now sold "at little or no profit" and that the profit in the future will consist in control of the gasoline business and control of the automobile industry.

Prof. Henderson said: "The power or combination of powers that holds the patents on tetra-ethyl lead will be the only one that will be able to make cars that we all will want to buy, the improved cars for which we will discard those we now have. That power will also control the only fuel on which those cars will run. The financial stake is almost immeasurably great."

In praising The World's campaign, Prof. Henderson called attention to the gap which exists in the method of public protection against such dangers.

Columbia University, it was learned yesterday, has sent its "progress report" to Surgeon General Cumming. This term does not mean that the report rests on incomplete scientific data. The findings are definite and detailed. What is lacking is a tabulation and complete description of the experiments performed. The report deals only with the diffusion of the fluid as used in automobiles, and not with exhaust fumes or discharges.

At a meeting of the State Public Health Council here yesterday, Dr. Mathias Nicoll, State Health Commissioner, was elected to attend the Washington conference May 26. Since the company has suspended sales, the council took no action to bar the fluid in this State.

N.Y. Post - 5-6-25

'AUTO INDUSTRY PREY OF LEAD 'GAS' POWERS

**Prof. Henderson Says Interests
That Control Tetra-Ethyl Prod-
uct Will Grip Nation**

HE FINDS BILLIONS AT STAKE

New Haven, May 6.—Professor Yandell Henderson of Yale, head of the laboratory of applied physiology, said the subject of leaded gasoline for automobiles "is probably the greatest single question in the field of public health," in a statement to the Yale News today.

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The World

EDITORIAL SECTION

NEW YORK, SUNDAY, MAY 2, 1938

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AGAINST AND FOR STYL. GAS

**"Virtual Atom Smasher" by Lead Poisoning.
In Prof. Youdehl Mandroon's
Dark View of the Future**

How Much Speedy Lead Dust From Motors' Exhausts Floating in the Air, Is the Vital Question

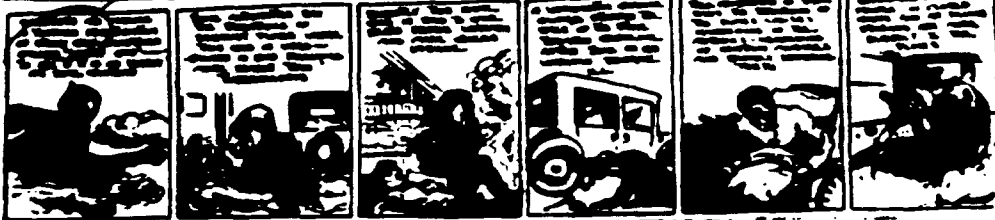


Prof. Yusef Mawhood in the Laboratory at Yale and Thomas M. Kelly Jr., Director of Blood Center

Two Men At Investigating Ethyl Gasoline

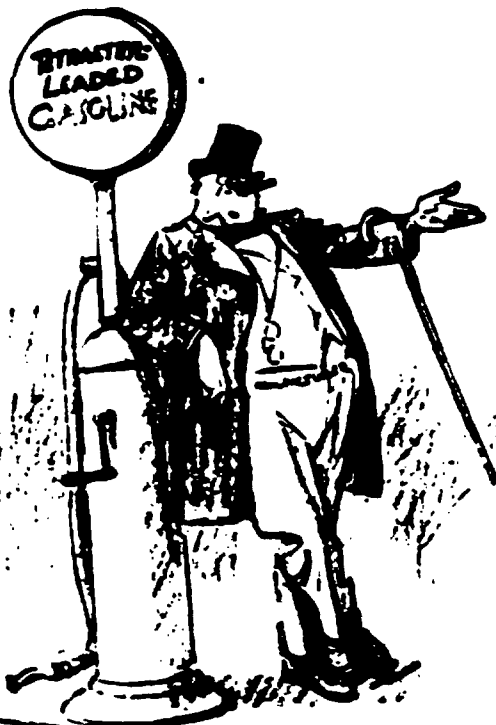
"LOONEY GAS" A PERIL TO MOTORISTS

By HAL COFFMAN



WORLD - (RM)

MAY 6 1935



NOT WAITING FOR AN INVESTIGATION

**CONFERENCE AT WASHINGTON
ENDORSSES WORKERS DEMAND
FOR BAN ON DANGEROUS 'GAS'**

Tetra-Ethyl Gasoline Off Market, Scientists Will Investigate Report to be Submitted

By International Labor News Service
WASHINGTON, D. C., May 6.—A conference of the International Labor Office today endorsed the demand of workers for a ban on the use of tetra-ethyl gasoline in motor vehicles. The conference, which was held in Washington, D. C., today, was the first of its kind since the outbreak of the world economic crisis. It was attended by representatives of 15 different countries, including the United States, Great Britain, France, Germany, Italy, Japan, and the Soviet Union. The conference was convened by the International Labor Office, which is a part of the League of Nations. The workers' demand for a ban on tetra-ethyl gasoline was based on the fact that this type of gasoline is highly flammable and explosive, and it is a health hazard. The conference agreed to send a report to the League of Nations, which will be submitted to the League's Health Committee. The report will recommend that tetra-ethyl gasoline be taken off the market and that scientists be allowed to investigate the health hazards of this type of gasoline. The conference also agreed to call on the governments of the world to take steps to protect the health of the public by banning the use of tetra-ethyl gasoline in motor vehicles.

Leader
Springfield

JUN 28 1925

MANUFACTURER REPLIES TO AN ATTACK AGAINST ETHYL GAS

Consideration of Public Health Should Have Been Given,
Says Statement—Makers Claim They Are Selling It
Without Profit in Order to Introduce It.

Orders for the suspension of the sale of ethyl gasoline, temporarily, at least, which have been sent throughout the United States by the Ethyl Gasoline Corporation, give peculiar interest to a statement of the attitude of the corporation, made public just before the order was issued. The statement was issued by Thomas Midgley, Jr., vice president and general manager of the corporation, and comments on the attack recently made on the corporation by Prof. Vandell Henderson of the department of applied physiology of Yale University.

"New York newspapers recently published accounts of the speech of Dr. Vandell Henderson attacking the Ethyl Gasoline Corporation, its products, its shareholders, methods of doing business and morals," the statement said. "The main topic of Dr. Henderson's speech is, or should have been, the consideration of the hazard to public health arising from the use of ethyl gasoline. If the statement had been confined to an expression of Dr. Henderson's opinion on this subject there would have been no occasion for any statement by the Ethyl Gasoline Corporation, since Dr. Henderson's views on this point have already been widely promulgated by him. The Ethyl Gasoline Corporation desires, however, to make clear the facts concerning the other matters in connection with its business which were discussed by Dr. Henderson.

"Dr. Henderson states that the purpose of the 'interests' behind the Ethyl Corporation is to monopolize the production of motor cars and the sale of motor fuel. The facts are as follows: The product of the Ethyl Gasoline Corporation is ethyl fluid, the chemical which, when added to gasoline in the percentage of about one-tenth of 1 per cent, stops the detonation or 'knock' which is experienced to a considerable extent when operations automobile motors under conditions of hard service. The occurrence of this knock is the one important thing which has for a generation past prevented the building of more efficient gasoline engines. The General Motors Corporation recognized this problem some seven or eight years ago and started research in its laboratories at Dayton, Ohio, to determine the cause of this knock and any possible means which might be used to correct it and thereby permit more efficient motors to be built. The result of seven years of work along this line was the final discovery that the knock was caused by certain combustion characteristics of gasoline, which, as everyone knows is the only fuel which may be relied upon as permanent and adequate for the automobile. It was further discovered that the addition of certain

rates and theretofore almost unknown chemicals to gasoline would prevent this knock.

"The results of this research work were freely published and have already been of immense benefit to the automobile industry in the better understanding of the problems of engine design and the production of more efficient engines and better motor fuels. The sole direct benefit which the General Motors Corporation received from the expenditure of this work was that it did own patent rights covering particular materials which could be added to gasoline to accomplish the desired result. It has, and can have, no monopoly of the more efficient types of motors which this new fuel will make possible. Indeed, such motors have been in use with special fuels for many years for racing, and aeronautical, and other purposes. No basic patent on such motors are or can be held by any company.

"It may be of interest in this connection to know that the engines for the airship Shenandoah are of an efficient, high compression Packard aviation motor, and that the Shenandoah has for some time past been using, and is now using, ethyl gasoline, as being the fuel best suited for this type of high efficiency motors. The world's speed record for automobiles, recently made by Tommy Milton, in California, was obtained by the use of ethyl gasoline, in a high-compression motor of another make.

"Many other examples could be cited to prove thoroughly the advantages obtained by the use of this fuel in such motors. Such motors are built by various motor manufacturers in no way associated with the Ethyl Gasoline Corporation.

"The Standard Oil Company of New Jersey started on the same line of research work referred to as having been initiated by the General Motors Corporation, some two years later, and followed this line of research independently, but in close co-operation with the General Motors Corporation, until the summer of 1924. At that time, it was conceived to be not only to the best interest of these companies, but to the interest of the more rapid progress of this economic improvement to merge these two lines of effort, through the organization of the Ethyl Gasoline Corporation, the General Motors Corporation, had previously entered into contracts with many large oil refiners for the sale of its antiknock product and at the time of the organization of the Ethyl Gasoline Corporation, the Standard Oil Company of New Jersey specially stated that its connection with the Ethyl Gasoline Corporation would have no effect

whatever on the marketing policy of that corporation, and that, far from seeking to obtain any monopoly of the sale of ethyl gasoline, the purpose and policy were to license the entire petroleum industry. At present, not only the Standard Oil Company of New Jersey, but a number of companies, both large and small, and in no way associated with the Standard Oil Company of New Jersey, are selling ethyl gasoline.

"These facts, we believe, adequately meet the statements made by Dr. Henderson bearing on the alleged monopolistic purpose of the General Motors Corporation and the Standard Oil Company of New Jersey, as effected through the ethyl gasoline business. With regard to Dr. Henderson's statements concerning the attitude of the Bureau of Mines, one can draw only the inference that he wishes to insult gratuitously the scientific arm of the government, the propriety of which has never been questioned.

"If Dr. Henderson wished the public to draw the conclusion that because a part of the cost of a scientific investigation is defrayed by an industry which is interested in it, the results are to be regarded with suspicion, he may wish to explain why it was that he himself, unsuccessfully sought a retainer from the General Motors Corporation, to make such an investigation. General Motors Corporation preferred to entrust such an investigation to an arm of the government than to a private investigator paid by it.

"Dr. Henderson is quite right in stating that the business of the Ethyl Gasoline Corporation is not at present conducted at a profit. Neither was there any hope of an immediate profit in the expenditures called for by the years of research work which the stockholders of this corporation put in. The Ethyl Gasoline Corporation hopes and believes that it will at some time be able to conduct its business at a profit, which profit, however, compared with the resultant savings of the public, through the conservation of gasoline, will be considerable. Its stockholders do hope to benefit in an indirect manner and to the same extent to which the public, the petroleum industry, and the automotive industry will all benefit through the conservation of motor fuel.

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SCIENTISTS TO PASS ON TETRA-ETHYL GAS

Meet in Washington Today to
Determine Whether Its Use
Menaces Public Health.

MANY INTERESTS INVOLVED

Automotive Industry Deeply Con-
cerned in Question of Its Em-
ployment as Motor Fuel.

Special to The New York Times.

WASHINGTON, May 19.—The conference called by Surgeon General Cumming of the Public Health Service to ascertain whether tetraethyl gasoline is dangerous to its users and handlers will commence all of that day and Thursday.

The Surgeon General reiterated today that no matter what inquiries had been made, he was open-minded on the matter and would govern his inquiry accordingly. He said again he sincerely hoped that if it should be found that tetraethyl gas was deleterious to the public health, some substitute possessing the same efficiency, but without any bad effects, would be developed.

All manner of interests will be represented when the conference starts work, including the automotive trade, medical associations, health commissions, gasoline manufacturers, universities which have concerned themselves with research in connection with the fuel, the navy and the chemical warfare service.

Delegates Expected.

A list of the organizations and their representatives expected follows:

American Automobile Association, A. F. Federita.
American Chemical Society, Dr. D. E. Howe.
American Electro Chemical Society, Colin G. Pink, Secretary.
American Federation of Labor, A. L. Berres, Secretary.
American Metal Trades Department, Miss Grace Burnham, Director.
Workers' Health Bureau.
American Institute of Chemical Engineers, J. C. Olsen, Secretary.
American Medical Association, Dr. William Parry, President.
American Oil Company, Lester A. Harris.
American Petroleum Institute, Robert Welch, Secretary.
American Public Health Association, Dr. Henry Vaughan, Dr. George A. Soper.
Baltimore Department of Health, Dr. J. H. Schrader.
Brown University, Professor C. A. Kraus.
Chemical Warfare Service, E. B. Vedrier.
Bureau of Chemistry, Chicago, Commissioner of Health.
Cincinnati College of Medicine, Dr. Robert A. Kehoe.
Ohio State Department of Health, Dr. E. H. Hayhurst.
Columbia University, Haven Emerson, Professor of Public Health.
Frederick B. Pitts, Professor of Physiology.
F. du Pont de Nemours & Co., Irene du Pont, W. F. Harrington.

Ethyl Gas Corporation, Gilman Thompson, Chairman of Medical Investigation Committee; C. F. Kettering, President; Thomas Midgley Jr., Vice President; Dr. Graham Edgar, Chemist, General Motors Corporation.
Harvard University, Dr. Joseph C. Aub, Medical School; Dr. Cecil Barker, Professor of Physiology; Dr. David Edsall, School of Public Health; Dr. Alice Hamilton, Professor of Ind. Medicine; Dr. Reid Hunt, Professor of Pharmacology.
Johns Hopkins University, Dr. W. H. Howell, Professor of Physiology, School of Hygiene and Public Health; Dr. Ell Marshall, Professor of Pharmacology, Mellon Institute, University of Pittsburgh; Dr. W. A. Grub, Bureau of Mines; Dr. R. R. Myers.
National Research Council, Dr. Ludwig Heiktoen, Chairman Division of Medical Sciences; E. W. Washburn, Division of Chemistry and Chemical Technology.
National Safety Council, W. H. Cameron.

Navy Department, Bureau of Aeronautics, Lieutenant H. M. Mullinix.
New York Academy of Medicine, Dr. James B. Clements.
New York City Department of Health, Dr. Frank J. Conaghan, Commissioner of Health; William H. Park, Director Bureau of Laboratories.
New York State Department of Health, Dr. M. Nicoll, Commissioner of Health.
Francis P. Patterson.
Philadelphia Department of Health, Dr. C. M. Robinson, Division of Chemistry.

Scientific American, Senator Shipstead, Society of Automotive Engineers, Harry Fleming, Secretary.

Standard Oil Company of Indiana, Allan Jackson, Vice President.
Standard Oil Company of New Jersey, Dr. C. O. Johns.

State and Provincial Health Authorities, R. Olin, Secretary and Treasurer.
Mitsubishi Corporation, A. J. Chamber, E. J. Miller.
Reconstruction Hospital, New York City, Dr. M. D. Tourant.

University of Chicago, Professor E. O. Jordan.
University of Wisconsin, Dr. Lowenhart, Professor of Physiology.

Western Reserve Medical School, Cleveland, Professor Gerald Soliman.
Yale University, W. H. Hazard, Laboratory of applied physiology; Yandell Henderson, Professor of physiology; E. A. Winslow, Professor of public health.

Sees Billions of Dollars Involved.

The scientists who will confer at Washington today with Surgeon General Cumming on the use of tetra-ethyl lead in gasoline will have in their hands the fate of an industrial development involving "literally millions of dollars," according to Professor Yandell Henderson of Yale, a leading opponent of the use of the lead compound.

The efficiency of gasoline is so greatly increased by the addition of tetra-ethyl lead that it will be universally used and will result in the general substitution of high-compression motors for those now in existence, according to Professor Henderson, providing the use of the lead compound is permitted. Such universal use, the professor holds, probably would cause widespread lead poisoning, which, in his opinion, is a worse disease than tuberculosis.

While the tetra-ethyl lead can be used with advantage in ordinary motors, the General Motors Corporation, according to a statement made yesterday by A. S. Maxwell, sales manager of the Ethyl Gasoline Corporation, is preparing to introduce special motors for the so-called ethyl or leaded gasoline which will triple the best mileage a gallon of gasoline will give today. Mr. Maxwell said these interests in the product believed the scientists would find no cause to fear any public health danger in its use.

Introduction of special motors for using the ethyl gasoline must wait, according to Mr. Maxwell, until the treated gasoline is in general use, because the new high-compression motors must be fueled with ethyl gasoline only. The use of ordinary gasoline soon would wreck them. The motorist using the

high-compression engine must, therefore, be sure of being able to get a supply of the leaded gasoline wherever he travels.

"It has always been known that high compression greatly increased the efficiency of gasoline," said Mr. Maxwell. "We only get 2 or 3 per cent out of gasoline under ordinary conditions today. If complete combustion were obtainable, one gallon of gasoline in a 25-horsepower motor would drive an automobile for 250 miles."

"This great waste of efficiency has been realized for a long time in the automotive industry. Attempts have been made to remedy it with high-compression engines, but, while they obtained greater power per gallon from the gasoline, they also increased the 'knock.' If the high-compression motors developed for ethyl gasoline were used with ordinary gasoline, the knock would drive the piston right through the head of the cylinder."

"The problem was to find some way of making the combustion uniform and even, so that it exerted a push instead of a slap. The research men went right up and down the line among the chemicals and tried more than 2,000 compounds. Finally, Mr. Midgley discovered the effect of tetraethyl lead in making the combustion even and going away with the flame-slap."

"Tetraethyl lead had been known since 1874, but it was purely a laboratory curiosity with no known usefulness. There was no method of making it in quantity, and the price at first was \$200 a pound. This led to further research with the aim of making quantity production possible. The Standard Oil company of New Jersey made great strides in this research, and the result was that that company and the General Motors came together and formed the Ethyl Gasoline Company."

"It can be made so cheaply now that the ethyl gasoline can be sold at an increase of only three cents a gallon on ordinary gasoline. While it is true that tragedies have occurred in poisoning it, we believe that the safeguards now in use make it possible to produce it without great risk."

APPENDIX VII

LIST OF GENERAL MOTORS CORPORATION
PATENTS RELATING TO THE ETHYL ENDEAVOR

PATENTS RELATING TO ANTIKNOCK AGENTS

As Assigned to General Motors Research Corporation

-
- U. S. 1,467,222, September 4, 1923, Fred E. Aseltine,
Injector for antiknock agents.
- U. S. 1,501,568, July 15, 1924, Thomas Midgley, Jr.
Aniline injector.
- U. S. 1,539,297, May 26, 1925, George H. F. Calingaert.
Method for producing lead compounds.
- U. S. 1,544,922, July 7, 1925, Thomas Midgley, Jr.
Ethylizer or fuel-mixing apparatus.
- U. S. 1,567,159, December 29, 1925, Brian Mead.
Method for producing lead compounds.
- U. S. 1,571,862, February 2, 1926, Thomas Midgley, Jr.
Prevention of fuel knock (aniline patent).
- U. S. 1,573,846, February 23, 1926, Thomas Midgley, Jr.
Method and means for using motor fuels (first lead patent)
- U. S. 1,575,436, March 2, 1926, Thomas Midgley, Jr.
Method and means for using low-compression fuels
(selenium patent).
- U. S. 1,575,437, March 2, 1926, Thomas Midgley, Jr.
Method and means for using low-compression fuels
(tellurium patent).
- U. S. 1,575,438, March 2, 1926, Thomas Midgley, Jr.
Method and means for using low-compression fuels
(arsenic patent).
- U.S. 1,575,439, March 2, 1926, Thomas Midgley, Jr.
Method and means for using low-compression fuels
(antimony patent).
- U. S. 1,575,440, March 2, 1926, Thomas Midgley, Jr.
Method and means for using low-compression fuels
(phosphorus patent).
- U. S. 1,575,441, March 2, 1926, Thomas Midgley, Jr.
Method and means for using low-compression fuels
(cadmium patent).

- U. S. 1,575,442, March 2, 1926, Thomas Midgley, Jr.
Method and means for using low-compression fuels
(bismuth patent).
- U. S. 1,575,443, March 2, 1926, Thomas Midgley, Jr.
Method and means for using low-compression fuels
(titanium patent).
- U. S. 1,575,444, March 2, 1926, Thomas Midgley, Jr.
Method and means for using low-compression fuels
(tin patent).
- U. S. 1,578,731, March 30, 1926, Carroll A. Hochwalt.
Process of producing dialkyl selenides and tellurides.
- U. S. 1,592,953, July 20, 1926, Thomas Midgley, Jr.
Method and means for treating motor fuels ("solid"
tetraethyl lead).
- U. S. 1,592,954, July 20, 1926, Thomas Midgley, Jr.
Fuel (use of organic halides as corrective agents).
- U. S. 1,592,955, July 20, 1926, Thomas Midgley, Jr.
Motor fuel (phenyl lead patent).
- U. S. 1,605,663, November 2, 1926, Charles F. Kettering and Thomas
Midgley, Jr. Motor fuel (second aniline patent).
- U. S. 1,605,664, November 2, 1926, Charles F. Kettering and Thomas
Midgley, Jr. Motor fuel (naphthylamine patent).
- U. S. 1,622,228, March 22, 1927, Thomas Midgley, Jr.
Process of making organic lead compounds.
- U. S. 1,622,233, March 22, 1927, George Calingaert.
Process of producing alkyl compound of lead.
- U. S. 1,635,216, July 12, 1927, Charles F. Kettering and Thomas
Midgley, Jr. Method and means for using low-com-
pression fuels (iodine patent).
- U. S. 1,662, 323, March 13, 1928, Thomas Midgley, Jr.
Motor fuel (use of a volatile carbonyl of a metal
other than iron).
- U. S. 1,662,355, March 13, 1928, James P. Andrew.
Bromine recovery (use of twice theoretical amount of
chlorine).
- U. S. 1,668,022, May 1, 1928, Thomas Midgley, Jr.
Motor fuel (use of halowax oil or halogenated
lubricating oil).

U. S. 1,787,419, December 30, 1930, Thomas Midgley, Jr.
Method for using motor fuels (process patent on
volatile compound of a metal).

Trade-Mark 187,410, August 5, 1924. Ethyl.

APPENDIX VIII
SOME SUPPLEMENTARY ILLUSTRATIONS

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New Compound Placed in Gasoline to Add Power; Tests Will Be Checked

Practical use of the ethyl gas compound, developed at the General Motors Research laboratory, to increase the mileage of gasoline and remove the "knock" is now being made by the Refiners Oil Co., Sixth and Main sts.

The compound gives ordinary gasoline the features found now only in so-called "high test" gasoline, it is said. It was held significant that the price of the high test fuel dropped five cents in price Wednesday on the eve of the marketing of the "compound" gasoline, which is being sold at 25 cents a gallon.

First sales of the gasoline containing the compound were made Thursday morning by the Refiners company. A check of all motorists using the fluid will be made to determine the actual value of the compound.

Experiments conducted at the

laboratories showed it to be highly successful, it is said.

Thomas F. Midgley, jr., one of the men credited with originating the compound, is supervising the tests conducted by the Refiners company.

According to Mr. Midgley, ethyl gas in the gasoline gives greater strength to the mechanism of a car especially when climbing hills and, in most instances eliminates the necessity of shifting of gears to make the grade. He also said with its use the "knocks" are taken out of a motor, assuring smoother riding.

Refiners Oil Co. officials said Wednesday should the ethyl gas prove successful it will be installed at all of its stations which are located in 12 Ohio cities. The fluid was placed in 1000 gallons of gasoline at the Sixth and Main sts: station Wednesday afternoon

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Mrs. Catherine Ballman

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Dayton
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DAYTON DAILY NEWS, FEBRUARY 1, 1923

THIS HISTORIC ITEM ABOUT THE BEGINNING OF THE SALE OF ETHYL GASOLINE TO THE PUBLIC APPEARED IN THE DAYTON DAILY NEWS ON THE AFTERNOON OF FEBRUARY 1, 1923.



CHARLES F. KETTERING IN HIS OFFICE AT THE
MORaine CITY LABORATORY IN 1924, ABOUT THE
TIME THE ETHEL GASOLINE CORPORATION WAS
FORMED.



THOMAS MIDGLEY, JR., A PHOTOGRAPH TAKEN
ABOUT THE TIME OF THE DISCOVERY OF TETRA-
ETHYL LEAD AS AN ANTIKNOCK AGENT.



DR. F. O. CLEMENTS (CENTER), WHO WAS TECHNICAL DIRECTOR OF THE RESEARCH LABORATORY FROM THE TIME OF ITS ORGANIZATION BY MR. KETTERING IN 1916, THROUGHOUT THE PERIOD DURING WHICH ETHYL GASOLINE WAS DEVELOPED, AND WHO WAS ASSISTANT SECRETARY OF THE GENERAL MOTORS CHEMICAL COMPANY. THIS PHOTOGRAPH, WITH MR. KETTERING AND DEWILLIE, WAS TAKEN IN 1939.

ETC 37166



T. A. BOYD, A PHOTOGRAPH TAKEN
ABOUT THE TIME OF THE WORK ON
TETRAETHYL LEAD.



CAROL A. HOCHWALT, A PHOTOGRAPH
TAKEN ABOUT THE TIME HE WAS ASSISTING
SO EFFECTIVELY IN THE CHEMICAL WORK
ON TETRAETHYL LEAD.

APPENDIX VII



THIS PICTURE OF THOMAS MIDGLEY, JR., C. F. KETTERING, AND T. A. BOYD WAS TAKEN ON FEBRUARY 2, 1924, DURING THE CELEBRATION AT MIDGLEY'S NORTHINGTON, OHIO, HOME OF THE TWENTIETH ANNIVERSARY OF THE FIRST SALE OF ETHYL GASOLINE TO THE PUBLIC. THE PICTURES SEEN IN THE BACKGROUND ARE ENLARGEMENTS OF SOME OF THOSE INCLUDED IN THIS HISTORY.



MIDGLEY AND FRED L. CHASE, PHOTOGRAPHED TOGETHER ON FEBRUARY 2, 1943. CHASE WAS THE MAN WHO THAT DAY BACK IN 1917 GAVE MIDGLEY THE IODINE, WHICH TURNED OUT TO BE THE FIRST ANTIKNOCK AGENT, WITH THE SUGGESTION THAT IT OUGHT TO DYE KEROSENE THE RED COLOR HE WANTED.



STANDING BACK OF MIDGLEY AND MR. KETTERING IN THIS GROUP, GATHERED AT MIDGLEY'S HOME ON FEBRUARY 2, 1943, FOR THE ANNIVERSARY CELEBRATION MENTIONED PREVIOUSLY, ARE, FROM THE LEFT, A. M. MAXWELL, DR. ROBERT A. KEHOE, EARLE W. WEBB, AND GRAHAM EDGAR.

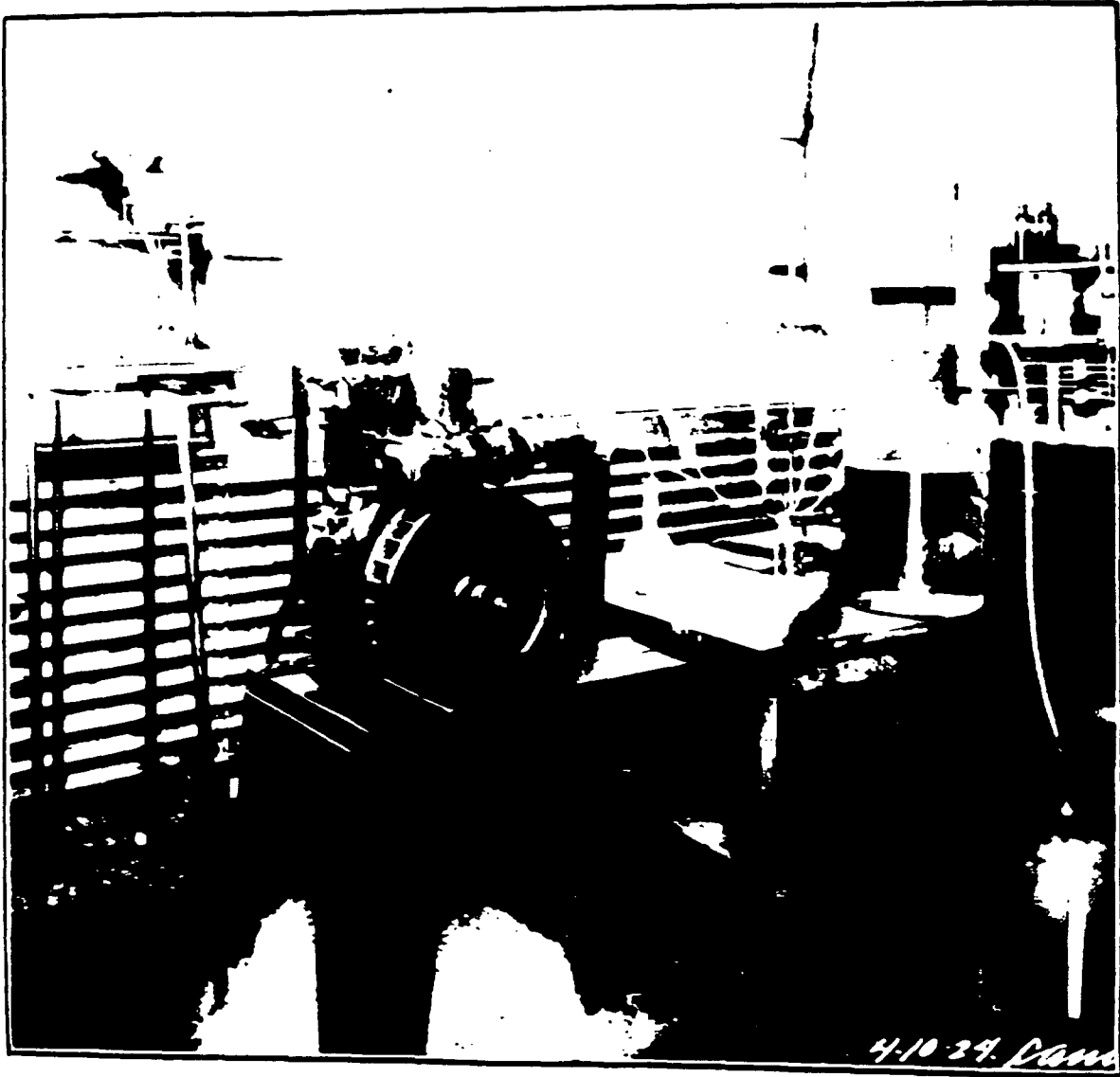


BEHIND MIDGLEY AND MR. KETTERING IN THIS PICTURE, ALSO TAKEN AT MIDGLEY'S HOME ON FEBRUARY 2, 1943, ARE THE FOLLOWING, READING FROM THE LEFT: HARRY MACK, CHARLES A. THOMAS, DR. ROBERT A. KEHOE, N. D. SIEBENTHALER, JOE W. MORRISON, GRAHAM EDGAR, CHARLES P. HARDING, ROBERT JORDAN, AND CARROLL A. HOCHWALT.



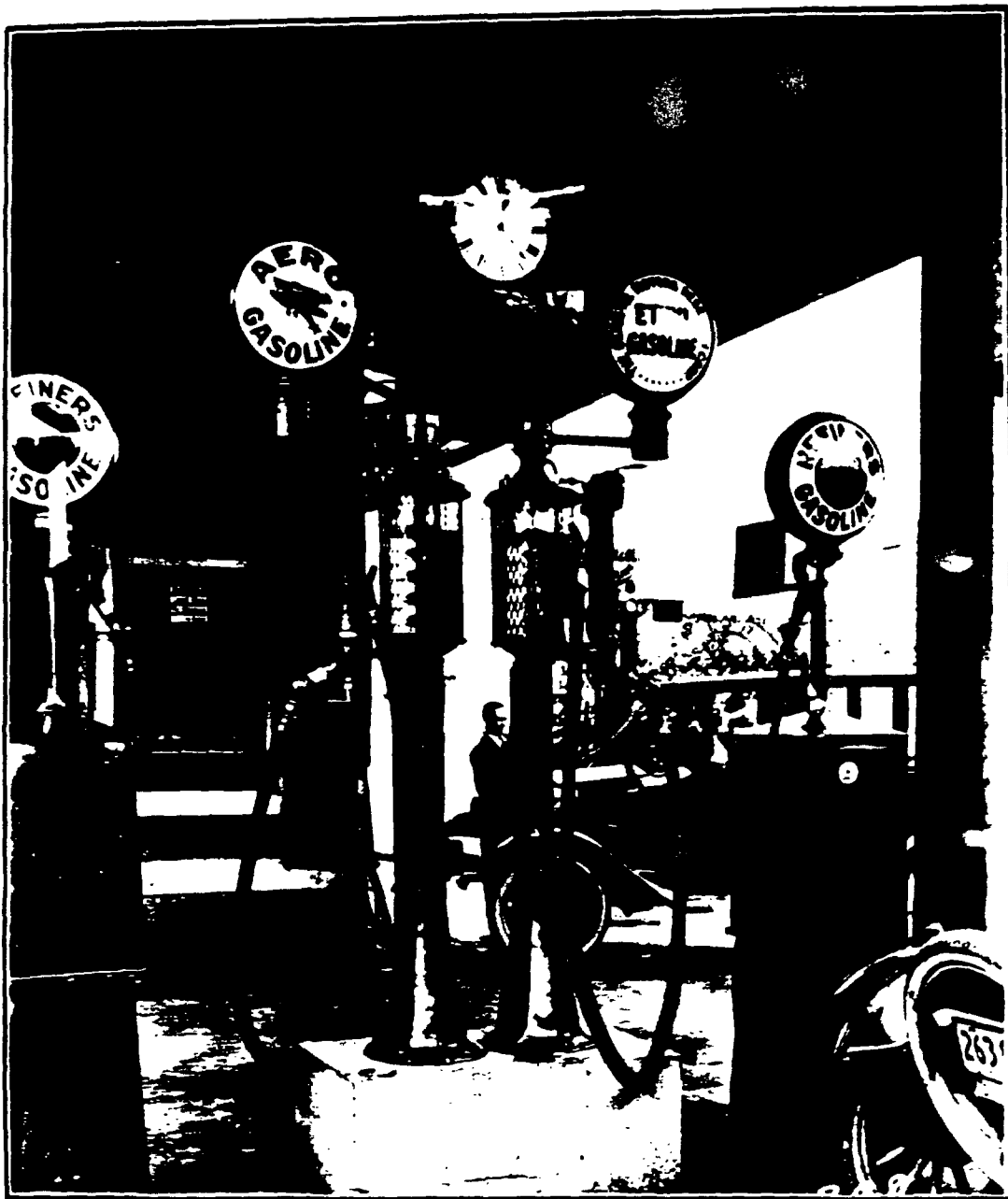
IT WAS HERE IN THIS ONE-CYLINDER, DELCO-LIGHT ENGINE THAT TETRAETHYL LEAD WAS TESTED FOR THE FIRST TIME. THEN, AS IN THIS PICTURE TAKEN TWO YEARS LATER, THE OPERATOR WAS T. A. BOYD.

ETC 37173

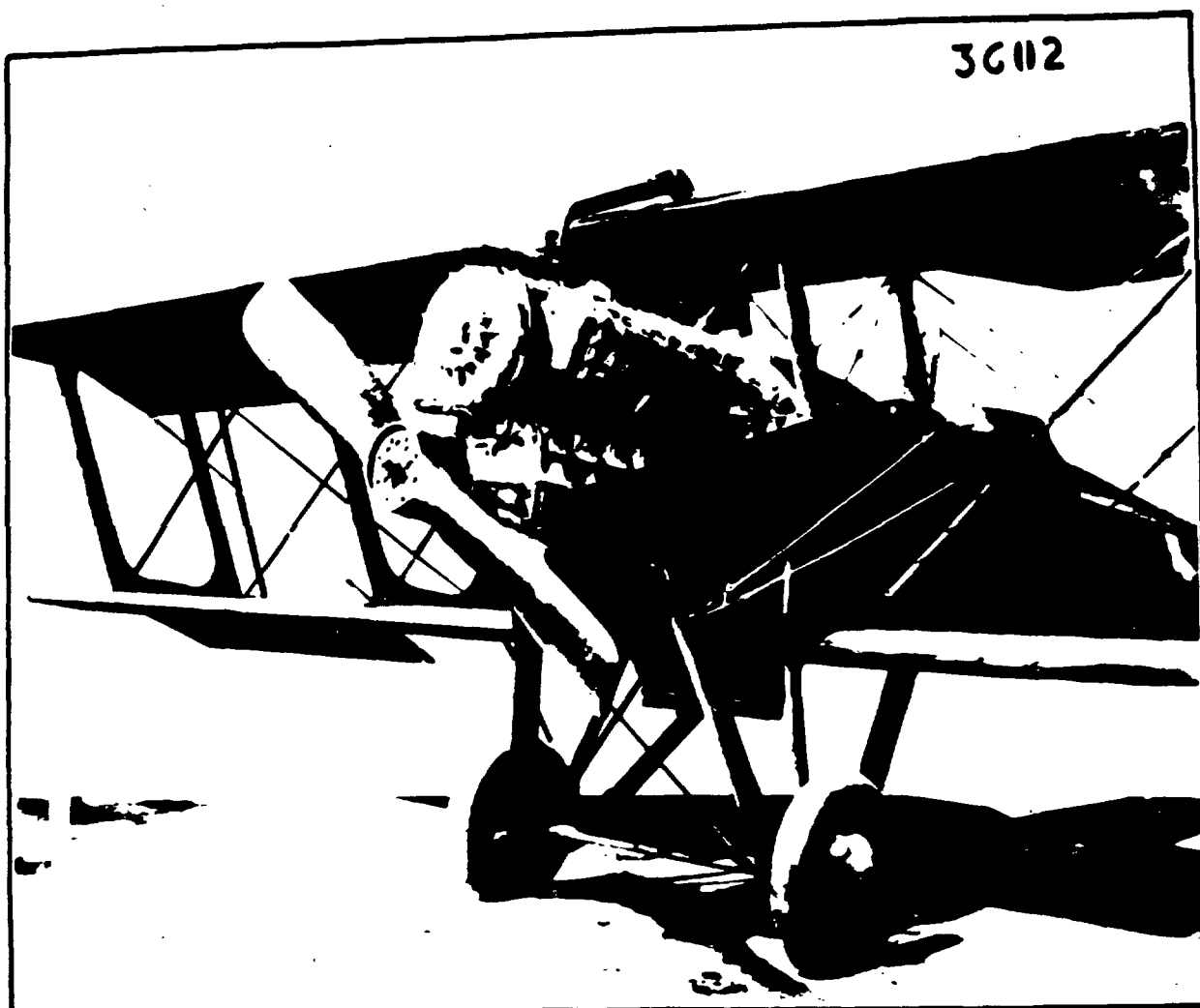


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THE FOLLOWING INFORMATION WAS OBTAINED FROM A SEARCH OF THE
 RECORDS OF THE BUREAU OF INVESTIGATION, U. S. DEPARTMENT OF JUSTICE,
 AT WASHINGTON, D. C., ON APRIL 10, 1934, IN CONNECTION WITH THE
 INVESTIGATION OF THE ALLEGEDLY COMMITTED BY THE ABOVE NAMED
 SUBJECTS, AND THE RESULTS OF THE SEARCH ARE SET FORTH IN THE
 FOLLOWING REPORT.



ANOTHER CONTEMPORARY VIEW OF THE FILLING STATION OF THE REFINERS OIL COMPANY AT SIXTH AND MAIN STREETS, DAYTON, OHIO, IN WHICH ETHYL GASOLINE WAS FIRST SOLD TO THE PUBLIC. THE PUMP FROM WHICH ETHYL GASOLINE WAS DISPENSED IS SECOND FROM THE RIGHT.



AIRPLANE IN WHICH, ON FEBRUARY 27, 1920, MAJ. R. W. SCHROEDER ASCENDED FROM MCCOOK FIELD AND MADE AN ALTITUDE RECORD OF 36,020 FEET, NEARLY 7 MILES, USING GASOLINE CONTAINING XYLIDINE AS ANTIKNOCK AGENT. THIS WAS A LE PERE P-53 BIPLANE, POWERED BY A LIBERTY ENGINE. IT IS UNDERSTOOD TO HAVE BEEN THE FIRST AIRPLANE IN THE UNITED STATES TO BE EQUIPPED WITH A TURBO-SUPERCHARGER, THE SUPERCHARGER HAVING BEEN MADE BY THE GENERAL ELECTRIC COMPANY. THE XYLIDINE, FURNISHED BY MIDGLEY, WAS FOUND NECESSARY TO PREVENT KNOCK AND PREIGNITION UNDER THE CONDITIONS OF SUPERCHARGE REQUIRED FOR THE FLIGHT. THIS PICTURE WAS OBTAINED THROUGH THE KINDNESS OF MAJ. G. E. A. HALLETT, WHO, AS CHIEF OF THE POWER PLANT SECTION, MCCOOK FIELD, AT THE TIME OF MAJ. SCHROEDER'S FLIGHT, HAD MUCH TO DO WITH ITS SUCCESS.

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