ETHYL CORPORATION
RESEARCH AND DEVELOPMENT DEPARTMENT
RESEARCH LABORATORIES · 1600 WEST EIGHT MILE ROAD
FERNDALE 20, DETROIT, MICHIGAN

January 8, 1959

Dr. R. A. Kehoe
College of Medicine
University of Cincinnati
Cincinnati 19, Ohio

Dear Dr. Kehoe:

Enclosed is a translation of a Swiss article, "The Contamination of Air and Dust by Lead from Gasoline From Cars." I came across the abstract and thought it might be of interest; so we obtained a translation. I thought that you might be interested since for the Swiss, in particular, it reads quite favorably on lead.

We will continue to scan publications such as this and where they appear of interest will continue forwarding them to you.

With best regards,

Sincerely yours,

H. E. Hesselberg

HEH:br
Enclosure

THE CONTAMINATION OF AIR AND DUST BY LEAD FROM GASOLINE FROM CARS.

Hans Preiss

Automobiltechnische Zeitschrift, vol. 59, #10, October 1957 pages 304-7.

The Eidgenoessische Materialpruefungsanstalt (EMPA) in Zuerich has been assigned to watch contamination of air and dust by lead-containing products from auto gasolines and particularly in such places where large segments of the population are forced to inhale the exhaust of modern traffic and, also, where certain groups of workers are exposed to the possible effect of lead from fuel such as in garages and gas stations. Analogous investigations were carried out in places in which, aside from lead from gasoline, the air was expected to have a higher lead content from industrial use of lead and its compounds, such as in welding and installation plants, hearths etc. The main results of the experiments which were started in 1948 and continued with interruptions until 1955 will be reported subsequently.

Lead and its compounds is one of the best known industrial poisons. Strict hygienic laws have been passed to protedt workers of plants operating with lead, such as lead works, pigment and battery factories. These deal in particular with respiration protection since lead containing poisons mostly enter the body through respiratory passages. Since even difficultly volatilized, inorganic lead compounds and metallic lead represent a considerable hazard to the operator, how much larger must be the danger of possible poisoning from relatively easily volatizable, organic lead compounds, such as the tetraethyllead which is added to gasoline as an anti-knock agent (to be referred to in the following as TEL).

This concern with respect to high concentrations of TEL is actually well founded. In the first few years of industrial production of pure TEL in the USA a number of poisonings occurred, some even with fatal outcome, until the hazard was reduced by improved installations in those factories and by proper industrial-hygienic measurements. The disquieting results gained at that time where in many places held against lead-containing gasolines and the use of the latter was forbidden legally in some countries. Switzerland was among those countries and it was only in 1947 that the existing ban was counteracted by a special official legislature. This decision was prompted by the sharply increasing demand for gasoline in the post war period and by the impossibility to satisfy this demand with lead-free gasolines of sufficient high octane rating.

The still present hydienic considerations were counterbalanced by the fact that in some foreign countries, especially in the USA, cars had been operated with leaded gasolines on a large scale for 2 decades without producing indications of increased lead poisonings of the population. However, simultaneous with the official admission of leaded gasoline in Switzerland a committee of experts was selected which investigated among other aspects the hygienic effect of the use of leaded gasolines in the operation of cars. This committee assigned the experiments carried out by the EMPA.

Lead in gasoline for cars and its reaction in the engine.

The trend in the construction of automobile engine is towards increasingly higher compression ratios which at the same increases the demands for the knock characteristics of the fuel. Petroleum chemists have stated that owing

to the enormously increased amount of gasoline usage in the post war period productions of fuel with sufficient knock characteristics would not be adequate without the addition of anti-knock agents. Among the usual anti-knock agents, TEL with its specific effectiveness is by far the best. A gasoline base with inadequate knock characteristics is converted into one with sufficient knock rating by TEL additions in amounts of 0.1 to 1%. On the other hand, to obtain equal results with methylaniline, alcohol or benzenehydrocarbons the additions would have to be hundred to thousand times as large.

TEL is added to carburator fuels in the form of a component of the so-called ethyl fluids which are a mixture the composition of which has been changed over a period of time. However, in general it consits of about 60 to 65% TEL and of halogen substituted hydrocarbons. The following is a typical composition of recent times;

TEL	$Pb(C_2H_5)_4$	61.5 wt%
ethylene dibromide	$C_2H_4Br_2$	17.9 "
ethylene dichloride	$C_2H_4Cl_2$	18.8 "
dye solution		1.8

The predominantly poisonous part of the ethyl fluid, the TEL, is a liquid which in the pure form boils at 183°C under 760 Torr and which has a vapor pressure of 1 Torr at normal room temperature. Thus, it is considerably lower as, for example, that of water vapor at the same temperature. It is introduced into the combustion chamber of the Otto motor in gaseous form simultaneous with the gasoline vapors and is burnt there in a homogeneous reaction in the gas phase. In the absence of the halo-hydrocarbons the lead from TEL is converted to lead oxide and lead sulfate - the latter from simultaneous combustion of the sulfur of gasoline - that is, compounds which are not easily volatilized. These would, therefore, deposit in the cylinder and valves and would cause disturbances.

The simultaneous combustion of halo-hydrocarbons liberates chlorine and bromine with which a large portion of the lead, obtained from the combustion of TEL, reacts to form lead chloride and bromide. At the temperature existing during the combustion these compounds are volatile and are expelled from the cylinder. After the exhaust gases have left the combustion chamber they are quickly cooled below point of volatility and melting point of the lead compounds contained in them. While passing through the complicated path of the exhaust system the reaction products of the lead are partially deposited as solid sediments - often mixed with carbon and oil coke - on the walls of the tube or the exhaust pipe; another part finds its way into the lubricating oil and the remainder is pushed to the outside.

The amount of the lead which remains resp. which is thrown into the air depends in the individual case mostly on the type and conditions of the engine and the exhaust system, on the setting of the carburator and the mode of operation to metnion only a few of the more important factors. The reports in the literature indicate that the lead expelled into the air varies within the wide limits of 15 to 80% of the amount added to the lead. A series of experiments carried out on the same engine or car at the hydraulic brake or on the rolling tester have shown that even under the same external conditions (equal load and mode of operation) considerable scattering of the values for the percentage of exhausted lead is found.

This is mainly due to the fact that the time interval at which the samples were taken was relatively short and that the amounts of lead obtained thereby were small. For this reason it was impossible to avoid accidental effects, such as the collection of smaller or larger lead containing particles which had separated from the walls of the exhaust system, the presence or absence of which considerably affected the results of a sample. It has been observed, in general, that smaller amounts of the lead added to the gaoline are exhausted into the air during slower and even mode of operations than during faster and higher engine performance, or respectively during frequent braking following by acceleration. In any case, it did not appear as if the direct measurements of the lead present in the exhaust would produce reliable data concenrning the lead content of the air of a heavily traveled street.

It has been reasoned - based on the lead content determinations of the exhaust gas and multipled by the amount of gasoline used in a certain area - that in certain areas tremendous amounts of poisonous lead compounds are necessarily accumulated. Thus, it can be approximated that, for example, in a town like Zurich 20 tons of lead are annually exhausted into the air.

It is, however, erroneous to assume that this lead necessarily deposits in the area where it is exhausted into the air. The extent the lead compounds deposit or remain in the layer of air close to the ground depends on the form and state of distribution of the exhausted particles of lead compounds and on whether, owing to their small size, they are removed by possible natural air movements from the spot at which they are exhausted, are distributed in space and are diluted to harmless concentrations in the air which is inhaled.

Form and state of distribution of lead compounds in the air.

If TEL evaporates during the spilling of gasoline (tanking) or if gasoline is carelessly used as a cleaning agent then the lead compound attains immediately the vapor form, that is the molecular distribution state, in the air. The TEL vapor thereby acts like a gas and is distributed three-dimensionally in the space by diffusion and air movements whereby the concentration of lead - assuming an adequate supply of fresh air - drops rapidly to harmless values.

To determine the composition, form and size of the particles of lead compounds obtained by the reaction of the TEL in the engine, exhaust gases of the exhaust of engines running under a load on the rolling tester were collected on slides for an electrone microscope and were electrone-optically examined (fig. 1). In this case, the exhausted particles appear to be separated. The joining of several single particles to form agglomerates was occasionally observed in other photographs, but it was only rarely conspicuous. The electrone diffraction diagrams of the dusts thus separated showed lines for lead halides and lead sulfates. The form of the larger dust particles was polyhedral. This form is also probable for the smaller parts which are present in predominant numbers but it cannot be clearly recognised on the pictures owing to the insufficient resolution of the electrone microscope which was used (limit of resolution capacity about 5mμ, limit of 'visibility' about 2mμ, whereby 1mμ = 10^{-6} mm). However, these

particles have similar measurements in all three space directions and differ markedly from occasionally observed soot which appear under the electron microscope as disc-like fragments of hexagonal plates with mostly much larger measurements.

The particle size of the lead compounds is of particular importance. According to the electrone microspope photographs the ranges between about 100mμ and the 'visibility limit'. On the basis of statistical considerations and in view of the performance ability of the electrone microscope it can be concluded that the predominant number of particles have a granule size of considerably less than 20mμ.

The lead compounds in question have edge lengths of the unit cell of their crystalline lattice which range from 4.49 to 9.48 Å; their 'molecular diameter' probably ranges between 2 and 3 Å (10Å = 1mμ). The dimensions of the majority of the various flying dust particles approximate the order of magnitude of these numbers. This extraordinary smallness can be explained on the basis of the fact that the vapor of the lead compounds are quickly quenched from the homogeneous gas phase below the solidification temperature. Therefore, only a minimum of time is available for undisturbed crystallization.

A sedimentation velocity of about 2.10^{-4}cm per second for particles with a granule diameter of 100mμ and of about 1.10^{-6}cm per second for particles with a granule diameter of 5mμ is calculated from the observed particle sizes by assuming an average density of the lead compounds in question of 6.0g/cm². Or, in other words: particles with a granule size of 100mμ require 80 minutes in absolutely quiet air to drop a distance of 1cm, particles of 5mμ require about 10 days. This sedimentation tendency is completely negligable compared to the much larger air velocities such as caused by winds and heat currents. That is, the majority of the lead particles exhausted into the atmosphere do not settle but are removed from the place at which they are exhausted and are distributed like a gas in the air and the free space. It is, therefore, not to be feared that the lead containing dust present in the air would settle at the place of its creation, but instead the largest part is removed into the free atmosphere just as the exhaust from chimneys or the exhaust from unleaded gasolines.

Fig. 1. Electron microscope photograph of the flying dust obtained from the exhaust of a motor operated with leaded gasoline.

How large is then the actual concentration of lead compounds in the air which is breathed in and which is a result of the contamination by engine exhausts and of the natural air replacement?

Lead content in the air.

It was possible to separate the lead containing dust, in spite of its fineness, for test purposes almost completely by filtration or in the high voltage field. The same effect can be achieved with TEL vapors if the TEL containing air is passed through an iodine solution. The effectiveness of these separating methods were clarified and verified in extensive tests.

The chemical analytical processing of these samples, which even after prolonged sampling contained only microgram or milligram amounts of lead, were carried out according to well established methods of analytical chemistry and which will not be further discussed here.

A few typical examples of test results obtained in the street air of Zurich are shown in Table 1. The air samples were always sucked in for an hour at the head level on the sidewalk (1 microgram ($\mu g = 10^{-6} g$). This sampling was usually repeated on the same spot in order to obtain by under-repetition a picture of the scattering which is produced by the accident of external conditions (air movements, weather etc.).

Table 1.

Lead content of street air of the city (Zurich).

Place of sampling	Number of cars per hour	Lead as flying dust μg per m^3 of air
Square with circular traffic, center-of town	240	1.3
"	350	0.8
"	650	0.9
"	600	1.7
"	460	0.7
Street with 15% slope	40	1.8
"	30	4.9
Street tunnel, 200 m long, end of	620	3.5
"	290	4.3
Streettunnel, 200 m long, middle of	700	18.8
Street between tall row of houses	480	0.6
"	810	0.8
expressway without houses	350	0.05

Table 2 shows the lead content of the air of some fully operating garages which are completely equipped to service cars including the tanking of gasoline. The samples were again taken at head level. The duration of sampling amounted to 1 to 8 hours.

Table 2.

Lead content of the air of garages.

Garage	Lead as flying dust µg per m3 of air	Lead as TEL µg per m3 of air
A	24.3	12.0
B	2.7	3.7
C	18.2	37.0
D	9.2	3.7
E	6.6	5.6
F	18.3	20.2
G	20.1	35.4
H	7.5	10.0

To evluate the hazard of the lead content found in the air of the streets and garages it should be noted that the experience of industrial doctors has shown that the tolerance limit of the breathing air of industrial plants - assuming a daily exposure of 8 hours - amounts to 150 µg of lead per m3 of air. This limiting content for chronic lead poisonings has remained unchanged for several years and was again confirmed in 1956 by the 'Conference of American Government Hygienist'. The values of the air in Zurich's streets and garages are far below the cited, critical limits.

Lead content of the sedimented dust.

There are always coarser dusts present on the surface of the street and in the layer of air adjacent to the street which are capable of settling or which have already settled and which are always stirred up again by currents from tragfic. Since the exhaust gases are expelled into this layer of air it could be concluded that a portion of the finer lead particles becomes attached to the larger particles and could settle with them. The question arises in connection with this whether the layers of dust close to the ground would not become enriched in lead in time.

To clarify this problem, settled dust samples were collected in 19 different spots - and always in these same spots - in the streets and squares of Zurich in larger and smaller time intervals from 1948 to 1955. The lead content of these samples was determined. The lowest single value was 0.10%, the highest 7.0% of lead in the dust. The course of the average values of lead content as a function of the time is shown graphically in fig. 2. The diagram contains a second, thinner curve (upper) which represents the approximated measurement for the momentary expulsion of lead at the time of the sampling which was calculated as the product from current amount of cars in Zurich and the average lead content of the gasoline; the latter was obtained from the current controls of the Eidgenossische materialprufungsanstalt.

The two curves show remarkable similarities: they have a slope which is in the first periods quite steep, but later levels out and they also show definite, seasonal variations. These can be explained on the basis of

the fact that there is less traffic in the winter and partially also as due to the lesser lead content of the winter gasolines (alcohol containing). The general trend reflects the increase of the use of gasoline and, thereby, that of lead exhaust. The following conclusions of decisive importance can be drawn from the similarity of those two curves:

number of cars x lead content in the gasoline

% lead content

car x lead-content

lead content in the street dust.

Fig. 2. Change of the average value of lead content of Zurich's street dust with time and also the momentary lead exhaust (the latter as the product of the number of cars and the lead content of gasoline).

The lead content of the dust of the soil is not increased. If this were the case the curve representing the lead content in the dust would have a much steeper slope than the curve representing the momentary lead exhaust. Apparently, rain, wind, and street cleaning are able to prevent this and a type of equilibrium is formed between the exhausted lead and the amount of lead present in the soil dust.

How should the values of the amounts of lead present in the sedimented dusts be evaluated with respect to their poisonous effects? Table 3 will serve to assist in the answering of this question; it shows the lead content of the streets of Zurich during the last sampling period in 1955 and also the settled dust from machine shops and industrial workrooms, the latter being obtained from a molding at head level excluding the sweepings from the floor.

A comparison of the data represented in table 3 shows that the lead content of the street dust is much less than the amounts which are found in the dust of welding shops and work shops as a consequence of the handling of lead and without the interference of leaded gasoline. Finally, the lead content of the street dust is roughly one hundreth of the lead content of dusts found in plants which are known to contain lead hazards. If the lead content of the dusts is assumed to have a relative value with respect to the air in the respective places then the following conlusions could be drawn: with respect to its lead content the air in garages is comparable to that of welding and mechanics workshops, that is to an air

which for generations has been tolerated without difficulty and which can be considered as harmless. The lead contents of the street air are even significantly lower. In order to represent an actual lead hazard the average lead value of the garage air would have to be ten times as large and that of the street air about 100 times as large than was indicated by the measurements which were carried out.

Table 3.

Comparison of lead content in sedimented dust.

Place of sampling	Number of samples	% lead in dust		
		highest value	lowest value	average value
Streets of Zurich	19	7.0	0.7	2.5
7 work shops	15	120	4.0	18.9
11 garages	22	73	1.2	16.1
3 lead hearth	6	390	195	303

1. We wish to express our thanks to the Eidgenoessischen Bleibenzin Komission for the permission to publish the present article.