PARTICULATE LEAD COMPOUNDS IN AUTOMOBILE EXHAUST GAS

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Reprinted from
INDUSTRIAL and ENGINEERING CHEMISTRY
July, 1957

57-10

ABSTRACT

A comprehensive study has been made of the amount, composition, and particle size distribution of the lead compounds present in the exhaust gases of automobile engines operated on fuels containing tetraethyllead. The results show that city-type driving tends to exhaust considerably less lead than is burned by the car and that the excess lead which deposits on exhaust system surfaces tends to be exhausted under higher-speed or higher-load operating conditions. The exhausted material ranges in particle diameter from 0.01 micron to several millimeters and is composed mainly of PbCl•Br, α and β forms of NH_4Cl•2PbCl•Br, and $2NH_4Cl$•PbCl•Br. The data provide an explanation for the low lead concentrations which have been reported for urban atmospheres in relation to the consumption of leaded gasolines.

REPRINTED FROM
INDUSTRIAL and ENGINEERING CHEMISTRY, Vol. 49, No. 7, Pages 1131-1142
July, 1957

Lithoprinted in U.S.A.

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The current interest in the contribution of automobile exhaust gas to atmospheric pollution has led to many recent studies of the minor constituents of exhaust gas, such as incompletely burned hydrocarbons, carbon monoxide, and the oxides of nitrogen. However, no recent work has been reported on the particulate lead compounds which also are present to a small degree in most automobile emissions. These lead compounds are present because virtually all automotive gasolines contain tetraethyllead (TEL) in concentrations up to 3.0 milliliters per gallon (0.113 weight per cent lead). TEL has been used in this manner since 1923, and has helped to provide economically the improved antiknock quality of fuels which has been required to keep pace with the introduction of more efficient engines having higher compression ratios.

In addition to TEL, commercial antiknock fluids also contain ethylene dibromide and ethylene dichloride. These compounds, which are known as scavengers, are used to prevent the accumulation of lead oxide in engine combustion chambers. Their function is to convert lead oxide to lead halides, which have greater volatility at engine temperatures and can be expelled from the engine. Therefore, the elimination of lead from engines might be expected to be accompanied by the discharge of particulate oxides and halides of lead.

When TEL first came into use, there was apprehension on the part of public health authorities as to the degree of hazard which its exhaust products might create. Because of this, extensive investigations were carried out in this and other countries to determine the physiological effects caused by exposure to the products of combustion of leaded fuels [5, 6, 7, 8, 9, 12]. These studies showed that there was no need for concern at the normally used concentrations of TEL even under the most adverse conditions such as in tunnels, confined garages and in heavy traffic, inasmuch as the ventilation required to prevent excessive concentrations of exhaust gas and carbon monoxide provided ample dilution. The conclusions reached in these early studies have been entirely borne out by experience in the ensuing years. Not only has no trouble due to lead poisoning developed, but analyses of air in many cities in recent years have shown that the lead concentrations are so low as to be insignificant as judged by current hygienic criteria. These analyses also have suggested that much of the lead burned in gasoline is not exhausted in forms which can remain suspended in the atmosphere, and because of this indication studies have been made to determine the manner in which lead compounds are exhausted from modern cars and from laboratory engines. These studies have been directed toward determining the amount, composition, and particle sizes of the exhausted lead compounds.

Reported investigations of suspended solids in urban atmospheres have shown that particles larger than 3 microns in diameter were present rarely and that most of the suspended particles were less than 2 microns in size [2]. Because of this, the exhausted lead compounds in this study were separated physically into two size ranges, fine particles 5 microns in diameter or smaller, and coarse particles larger than 5 microns. The fines were further classified microscopically into ranges separated from each other by one micron.

In preliminary studies, the exhausted particulate material was collected from single-cylinder engines with only a minimum length of exhaust pipe. Following this, dynamometer tests were made under constant speed and load conditions with a passenger-car engine equipped with its complete exhaust system; and finally to simulate passenger-car service under city-driving conditions, chassis dynamometer tests were made under a city-type driving test cycle with two cars of different makes. In these last tests, the effects of operating conditions and of three fuel variables, TEL concentration, sulfur concentration, and phosphorus-containing additives were studied.

EQUIPMENT AND METHODS

Exhaust Particle Collector

Preliminary studies showed that particulate lead compounds could be recovered satisfactorily from engine exhaust gas by means of an electrostatic precipitator, and that the lead burned by a single-cylinder engine could be accounted for by combining the lead recovered from the exhaust gas with the lead which remained in engine deposits. However, good results were obtained only when the entire exhaust gas stream, rather than a sample, was passed through the precipitator. Exhaust gas sampling was subject to possible error from particle size segregation due to gas velocity differences in the sampled and main streams, from nonhomogeneity of particulate matter in the exhaust stream, and from fusion of lead compounds on the sampling probe. Consequently, in the reported work the entire engine exhaust gas flow was mixed with filtered air for cooling, and then was passed through a modified Westinghouse PO-12 Precipitron for extraction of the particulate matter. Because of the dilution, exhaust gas constituted only about 6 to 12 weight percent of the

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PbCl•Br and lead-ammonium-halide complexes found in the exhausted material.

SIGNIFICANCE OF RESULTS IN RELATION TO ATMOSPHERIC POLLUTION

The emission of particulate matter by automobiles obviously bears on the problem of atmospheric pollution, as do other automobile emissions such as carbon monoxide, oxides of sulfur and nitrogen, and incompletely burned fuel. The importance of these various emissions is a subject currently under study by many laboratories.

The value of the reported work lies in establishing a general pattern of lead emission which might be expected from a car during the idling, accelerating, cruising and decelerating conditions typical of city service. In city driving, a car can be expected to exhaust very little lead while the exhaust system is clean, but over a period of about 5,000 miles its emission of lead tends to increase gradually to the point where 30 to 60 per cent of the lead burned is exhausted; of which from one-half to three-fourths is in particles smaller than 5 microns and 1/25 is smaller than 1 micron. Occasionally when the car may be subjected to higher-speed highway driving or to high-speed full-throttle accelerations, it may exhaust considerably more lead than is burned, with a larger proportion of it in large particles which can settle more rapidly. This emission cleans the exhaust system and returns it to a condition where it again retains a high proportion of the lead burned. This pattern of behavior probably can be modified to some extent by the design of the exhaust system. Current trends toward multiple mufflers and larger exhaust systems, which would run cooler and have lower gas velocities, probably will reduce lead emission in city-type driving at the expense of somewhat increased lead emission under more severe highway-type driving. Similar effects can be expected to accompany the use of lower engine speeds relative to car speed, and of larger engines which operate at relatively lighter load factors in city service.

The foregoing mechanism may well explain why surveys of the lead content of urban atmospheres have shown much lower concentrations of lead than might be expected on the basis of TEL consumption if all of the lead burned became an airborne dust. One of the most thoroughly studied urban atmospheres is that of the Los Angeles area. It has been estimated that in this area 4,680,000 gallons of gasoline were consumed daily in 1954[4]. Published estimates of the daily dispersion air volumes in this area are 4.2×10^{13} cubic feet in clear weather (2000 foot inversion layer) and 6.46×10^{12} cubic feet during periods of severe smog caused by an atmospheric inversion layer at 500 feet[1]. If an average TEL concentration of 2.2 ml per gallon is assumed[10], then uniform dispersion of this entire amount of lead in these air volumes would produce lead concentrations of 9.2 and 59.5 micrograms per cubic meter respectively.

These values may be compared with those from a published study of the suspended matter in Los Angeles air, as measured in 1954 during a four-month period in which atmospheric inversions frequently hindered the dissipation of suspended matter[3]. The concentrations of lead from all sources* including automobiles, as shown by this study, are presented in Table 10.

TABLE 10

Concentration of Lead in Los Angeles Atmosphere[3]

Month	Number of Observations	Lead Conc., Micrograms per cubic meter Average		Range	
		Downtown	Suburban	Downtown	Suburban
August	45	4.1	2.2	1.7-7.6	1.1-4.1
September	60	6.2	4.4	1.4-14.7	0.8-12.8
October	60	7.5	5.0	3.1-13.8	1.9-10.4
November	58	8.3	4.65	3.2-16.4	1.2-11.4

The highest individual lead concentration, 16.4 micrograms per cubic meter, together with other but lower values in the high range, were obtained during periods when the base of the inversion layer remained at 500 feet and lower. In the same study it was also reported that lead concentrations in 30 metropolitan areas ranged, in 1954, between 0.1 and 26.6 micrograms per cubic meter, and averaged 2.15 in 588 individual observations.

Comparison of these observed data with the preceding calculated lead concentrations shows that the measured values are appreciably the lower. However, since only 10 to 50 per cent of the lead burned in city driving is exhausted in fine particulate form, as indicated by the results of the present studies, surprisingly close agreement between calculated and observed lead concentrations can be obtained if the calculations include this factor.

The public health aspects of lead compounds suspended in the air are beyond the scope of this work since these involve many factors in addition to lead concentration, and sources of lead other than the automobile. The present results, however, tend to substantiate the low lead concentrations which have been reported for urban atmospheres, and also provide new information as to the chemical and physical characteristics of exhausted particulate matter and of the factors which influence its emission which will be useful in future hygienic studies.

SUMMARY

Studies to determine the amount, composition, and particle size distribution of the lead compounds present in engine exhaust gases have been made with laboratory engines and with two conventional cars operated on fuels containing tetraethyllead. The exhausted carbon and organic particulate matter were not investigated.

Approximately 20 to 30 per cent of the lead burned in the fuel was retained in passenger car exhaust system deposits and lubricating oil, which left 70 to 80 per cent of the lead to be exhausted over 20,000 to 30,000 mile

*Inasmuch as lead occurs in measurable concentrations in areas remote from urban and industrial centers because of a variety of factors, including airborne particles of dust from the soil; and since the combustion of coal, wood, and waste of vegetable origin contributes lead to the atmosphere, the increment provided by the combustion of tetraethyllead is indeterminate. Evidently the contributions from all sources are subject to dilution in accordance with the vagaries of wind, weather, and the earth's topography, and therefore any attempt at the interpretation of the results of the analysis of atmospheric samples is fraught with serious difficulties.

periods of city and country driving. Lead emission was increased by speed. Under city-type driving conditions, which included idling, acceleration, deceleration and cruise conditions, the lead recovered from the exhaust gas normally ranged from 20 per cent of the lead burned when the exhaust system was comparatively clean, to as high as 60 per cent when the exhaust system was heavily deposited after extensive light-duty service. However, under sustained high-speed driving conditions or during high-speed full-throttle accelerations, the amount of lead exhausted was initially several times greater than the amount burned but diminished in quantity as the exhaust system became cleaner with continued severe service.

The exhausted particles ranged in size from 0.01 micron to several millimeters in diameter. Particles smaller than 1 micron were by far the most numerous, but accounted for less than 5 weight per cent of the exhausted lead. Heavy particles 5 microns and larger, which might be expected to settle rapidly, represented about 27 per cent of the exhausted lead under city-type driving but increased to about 39 per cent under accelerating conditions.

The lead was exhausted principally as mixtures of $PbCl{\cdot}Br$, α and β forms of $NH_4Cl{\cdot}2PbCl{\cdot}Br$, and $2NH_4Cl{\cdot}PbCl{\cdot}Br$. When phosphorus was present in the fuel, about one-fifth of the exhausted lead was $3Pb_3(PO_4)_2{\cdot}PbCl{\cdot}Br$.

The amount of lead exhausted was proportional to the concentration of TEL in gasoline, but particle size distribution and composition were independent of this variable. Neither changes in the sulfur concentration in the fuel nor the presence of phosphorus-containing gasoline additives introduced definite changes in the amount and size of the exhausted lead compounds, and only phosphorus altered their composition.

The quantity of lead exhausted in size ranges which might remain suspended in the atmosphere appears to be reduced by conditions which produce low gas velocities and low temperatures in exhaust systems. These would include design factors such as larger engines and multiple exhaust systems as well as operating factors. Since lower-speed driving conditions as encountered in congested areas tend to minimize lead emission, this fact probably explains why the reported analyses of urban air show lead concentrations which are low in relation to the amount of lead burned.

ACKNOWLEDGMENT

The authors are indebted to many co-workers in the Ethyl Corporation Research Laboratories who made this report possible by their contributions. Among these persons, R. G. Lyben, Karl Beaver, and Loren Knowles developed experimental techniques, and E. B. Rifkin and H. E. Hesselberg assisted in planning the work and interpreting the results.

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