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

September 14, 1955

Dr. R. A. Kehoe
The Kettering Laboratory
College of Medicine - Eden Avenue
Cincinnati 19, Ohio

Dear Dr. Kehoe:

Because of the questions you raised yesterday by telephone as to the basic approach we might use in our proposed paper on exhaust gas particles, probably it would be best if we postpone our conference scheduled for next Monday until after these questions have been worked out.

Meanwhile, I'm enclosing my first draft of an outline for the paper to show you the material we will have available. It seems to me that regardless of where we may publish our information, we will have to consider at least some of the public health aspects of the work and its possible relationship to the lead content of urban air. Otherwise, there is the danger of creating an impression in uninformed circles that lead emission is a new and unexplored area for concern. Because of this, I would appreciate your reviewing this outline and considering the suitability of this approach from the standpoint of publication in either public health or automotive journals. Would you be good enough to let me know your general impressions.

Very truly yours,

D A Hirschler

D. A. Hirschler

DAH:mew

cc: R. K. Scales

Encl.

D. A. Hirschler
9-2-55

Proposed Outline for Paper to be Published in
The American Journal of Hygiene

Particulate Lead Compounds in Automotive Exhaust Gas

Introduction

1. TEL is widely used because it performs a useful service.

2. Commercial utilization of TEL involves scavengers for removal of lead deposits; hence particulate lead halide and lead oxide would be expected in exhaust gas.

3. First use of lead was accompanied by investigations by public health authorities in U.S. and England to appraise the magnitude of danger due to breathing of exhaust fumes.

4. Early investigations showed no need for concern. This has been borne out; there has been no lead poisoning, and modern air analyses show the lead content in cities to be far below allowable limits. CO approaches the allowable limit to the same or greater degree than does lead.

5. Current intensified interest in the contribution of the automobile to air pollution makes it desirable to study automobile emissions in respect to lead, and to include composition and size distribution studies, which have not been reported on comprehensively in the past.

6. Particle size determines whether or not solid material can remain suspended in the air over long periods of time. Since Cholak has reported that very little material larger than 3 microns is found in airborne dusts, the exhausted particulate lead compounds have been separated into two classifications: (1) that 5 microns or smaller which is potentially airborne, and (2) that larger than 5 microns which would settle rapidly and not contribute to atmospheric pollution.

~~6. Particle size influences both settling rates and the degree of retention of particles in the respiratory system. The small airborne particles are those least easily retained. Although no discussion of the toxicological aspects of particulate lead compounds will be made, these factors governed the selection of the 5 micron level as the division between fine and coarse particles.~~

7. The work has evolved through single cylinder and dynamometer testing to the use of two full scale cars on the chassis dynamometer. Studies have been made of the effects of operating conditions, and of the following fuel variables: TEL concentration, sulfur concentration and the addition of phosphorus.

Summary

Extensive studies have been made of the discharge of particulate lead compounds in the exhaust gas from laboratory engines and from two conventional cars operated on fuels containing TEL. The principal findings from these studies, in which carbon and organic particulate matter in the exhaust gas were not considered, were:

a. About 20% of the lead burned by the passenger cars was retained in the lubricating oil and in the exhaust system deposits. This indicates that 80% of the lead burned was discharged in the exhaust gas over a 20,000 to 30,000 mile period of city and country driving.

b. Varying percentages of the lead burned were exhausted under different operating conditions. Under light-duty city driving, the exhausted lead ranged from 20% of the lead burned when the exhaust system was comparatively clean to 60% when the exhaust system was heavily deposited. Under sustained high-speed driving conditions, or during full-throttle accelerations following prolonged low-speed service, the amount of exhausted lead was several times greater than the amount burned, but diminished in quantity as the exhaust system cleaned up. Since the minimum lead discharge occurs under the low-speed driving conditions imposed by congested areas, atmospheric pollution by particulate lead is less than might be expected on the basis of gasoline consumption.

c. Exhausted particles were found to range in size from 0.005 microns to several millimeters. Heavy particles 5 microns or larger, which might be expected to settle rapidly and not contribute to atmospheric pollution, were found to account for 20 to 40 weight percent of the discharged lead. Because of this, the potentially airborne lead compounds discharged in city driving would be expected to represent from 1/3 to 1/2 of the lead burned in the fuel, and rapid-settling, large particles would represent about 1/5 of the lead burned.

d. The particulate matter collected was found to consist principally of lead chlorobromide ($PbCl \cdot Br$) and lead-ammonium halide compounds such as $2PbCl \cdot Br \cdot NH_4Cl_{\frac{1}{2}}Br_{\frac{1}{2}}$ and $PbCl \cdot Br \cdot NH_4Cl$. In addition to these compounds, pyromorphite

$3Pb_3(PO_4)_2 \cdot PbClBr$ was also present when phosphorus-containing fuel additives were present.

e. The amount of lead exhausted was found to be proportional to TEL concentration in gasoline, but particle size distribution was not affected. Neither phosphorus-containing gasoline additives nor changes in the sulfur content of the fuel introduced definite changes in the amount and size of the exhausted lead compounds.

f. The experimental findings show that lower-speed driving conditions, as are encountered in the more congested areas, tend to reduce the fraction of lead burned which reaches the atmosphere. This fact probably explains why the reported analyses of city air for total lead from automobiles and all other sources continue to show low values in spite of increased yearly gasoline consumption and higher TEL concentrations. These reported values for lead usually range from 1 to 5% of the commonly accepted allowable maximum lead concentration of 0.15 mg per cubic meter, and in only a few isolated instances under adverse conditions have values near 25% of the maximum concentration been found. On this basis there appears to be little need for apprehension as to the effects of automobile lead emissions on public health, either at present use levels of TEL or at possibly higher levels in the future, and the conclusions of the investigat~~ion~~ors who studied this possibility upon the initial introduction of TEL in 1926 appear justified and still valid.

Experimental Methods

1. Electrostatic precipitators have been used almost exclusively in this work. Precipitator efficiency was found to range from 90 to 95%. Particles were recovered for size classification and analyses by use of coated precipitator parts, which after use were stripped of the coating leaving the inorganic particles suspended in a liquid medium. Organic material was dissolved and not recovered. Separations were made by centrifuge methods, and size classification was made by optical and electron microscope examinations. X-ray diffraction and elemental analysees were used to determine particle composition.

2. Methods of exhaust gas sampling were found to have a large influence on particle size distribution. The most nearly true sample was obtained by maintaining sampled gas flow velocity equal to the velocity of the stream sampled. Since this is difficult to accomplish except under steady-state conditions, a full-flow system for the entire exhaust stream was adopted for cycling tests on the chassis dynamometer.

3. The driving schedule used for chassis dynamometer tests was patterned after typical driving reported for Los Angeles by the L. A. Air Pollution Control District and had a 40 mph top speed.

4. Details of equipment and methods, vehicle operating schedules and exhaust system temperatures will be included in an Appendix.

Basic Studies in Single-Cylinder Engines

1. Collection of material exhausted from a single-cylinder engine, and determination of a lead balance for the engine showed that in short runs (1 to 4 hours) about half of the lead burned was exhausted and the remainder was left in the combustion chamber and oil. No particle size measurements were made. Longer runs showed that after about 30 hours the lead discharge became erratic, and that periodically greater amounts of lead were discharged than was burned.

2. The erratic nature of the lead discharge was studied by the "Scotch Tape impinger" and it was found that the exhaust gas contained a continuous haze of vaporized halides with sporadic bursts of chunks of physically-scavenged material. The latter process was accelerated by thermal shock. The possibility of physical-chemical scavenging was shown, with halogen additives promoting the release of deposit chunks.

Engine Dynamometer Studies

1. Chevrolet engine tests showed (a) dependence of results on operating history (b) effects of speed and load (c) effects of acceleration (d) particle size distribution (e) necessity for full-flow particle collection rather than sampling

(f) effect of 3 and 6 ml TEL concentrations, which gave lead output proportional to lead input (g) particle composition.

Chassis Dynamometer Studies

1. Lead retained in the exhaust system, oil, and engine of the Ford accounted for 21% of input. Probably the Cadillac data will be similar. Muffler weights from HD truck tests (5G1 and 7G1) also show increases from 0.3 to 2.3 lbs in 20,000 to 30,000 miles, showing that even under severe service there is considerable lead retention. Of the lead burned, about 4/5 is left to be exhausted in particulate form. X-ray results show that the composition of deposits in the exhaust system is largely lead chlorobromide.

2. Ford Data

a. The amount of lead exhausted increased progressively with mileage accumulation under mild driving conditions and reached 60% of input. Intervening driving of more severe nature exhausted more lead than was burned and then reduced the lead output in subsequent mild service.

b. Comparison of 3 and 4 ml TEL concentrations indicates that lead output is proportional to lead input, with no effect on particle size distribution or composition.

c. 80% of the particles by count are smaller than 1 micron but 50% by weight are between 1 and 3 microns. Particle weight distribution curves show two peaks; 1 in the 1-3 micron range, and another in a range above 10 microns.

d. Acceleration discharged up to 12 times the lead burned, and high speed driving discharged 1 to 4 times the input. Particle size distribution was similar in all types of sergice.

e. Sulfur variation from .05 to .10 had a negligible effect on amount or size distribution of the lead and changed the composition only slightly toward the lead sulfates.

f. The addition of phosphorus as ICC and TCP may have increased the discharge of fines and total lead but the results are not conclusive in this respect. Phosphorus did change the composition of part of the exhausted material to pyromorphite. The rapidity of this composition change showed that the fine material is largely freshly formed, whereas coarse material is first deposited and then broken off and discharged.

3. Cadillac Data

a. The amount of exhausted lead is somewhat lower than the Ford, but the reduction is mainly due to less coarse material, and fines are exhausted in about the same amount as in the Ford.

b. Particle size distribution in the fines is the same as with the Ford.

c. Although the effects of TEL concentration are rather inconclusive when only the results from consecutive runs on 3 and 4 ml TEL are considered, measurements made after prolonged road service at both TEL concentrations show exhausted lead to be proportional to TEL concentration.

d. Work is still incomplete on the effects of acceleration and high-speed driving. Similarly, the amount of lead retained by the oil and exhaust system is yet to be determined. It is expected that the data will be generally similar to that from the Ford.

4. Particle Composition Data

a. Fines and most of the coarse material are of similar composition and consist of ammonium lead halides, lead halide, and lead oxyhalide. However, the very coarse particles (larger than 50 microns) contain mostly iron oxides and lead sulfates.

b. Solubility data on lead salts found in exhaust gas will be presented.

Discussion of Results

1. Under each type of service, an engine and exhaust system tends to approach an equilibrium condition as to lead retained and lead exhausted. Mild, part-throttle conditions favor low lead discharge and high lead retention, while severe conditions favor high lead discharge and low retention. A lengthy period of conditioning

is required under any given condition if particulate studies are to be representative of that condition. Otherwise, magnified transient effects may be observed while the system is seeking its new equilibrium.

2. Lead discharge from cars in average owner service probably follows a cycle. In city driving the car exhausts little lead while the exhaust system is clean, but the amount exhausted may gradually increase over a 5,000 to 10,000 mile period to the point where 40-60% of the lead burned is exhausted, of which about 3/4 is in potentially airborne size ranges. Then when the car is occasionally subjected to full-throttle service or to high-speed highway driving, considerably more lead is exhausted than is burned, which cleans the exhaust system and returns it to a condition where it again retains a high proportion of the lead burned.

3. The foregoing mechanism probably explains why urban atmospheres have been found to contain lower lead concentrations than might be expected on the basis of TEL consumption. For example, Larson has estimated that 11 tons per day of lead is burned in gasoline in Los Angeles. If this were diluted by the respective clear and inversion air volumes reported for Los Angeles, lead concentrations of .0084 mg/M^3 and .084 mg/M^3 would result. These concentrations are far higher than have been found in any street level surveys of lead content from all sources under the respective conditions. This is not surprising if in city driving something less than half of the lead burned reaches the air in fine particulate form.

4. Trends toward multiple mufflers and larger exhaust systems which would run cooler and have lower gas velocities will probably reduce still further the amount of lead exhausted by automobiles. The current work shows that low speeds and engine outputs, and hence lower exhaust system temperatures tend to reduce lead emission. Similarly, work reported in 1927 by the Bureau of Mines showed that an engine with a 12 foot exhaust pipe exhausted only 2.5% of the lead burned, whereas with a 2½ foot exhaust pipe the engine exhausted 25.6% of the input lead.

5. Fuel additives have different degrees of importance. Lead exhausted is

proportional to TEL concentration, but particle size and composition are not affected. Phosphorus additives alter the composition of the exhausted lead compounds, and possibly tend to increase slightly the output of fine particles. Sulfur appears to have substantially no effect.

Acknowledgements: Beaver, Lamb, Lyben, Gilbert, Niebylski, Analytical Group.

Appendix

1. Exhaust particle collector

Description of system, and data showing precipitator efficiency based on tests in which tandem precipitators and millipore filters were used.

2. Sample handling and processing

Methods, and tests made to determine any influence of processing on particle size.

3. Particle count and weight distribution techniques

Methods used to correct for particles smaller than 0.2 micron and hence invisible to optical microscope. Correction for lost particles.

4. Car cycles, operating conditions and exhaust system temperatures