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Attached is an: ____ outline; ____ abstract; X final draft of a technical paper recommended for publication by:

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Title:

Particulate Lead Compounds in Automobile Exhaust Gas

Authors:

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Explanatory Comments

To what extent does this paper present new data or conclusions?
Which items may raise questions of public relations policy?
What objective is to be achieved by presentation and publication of this paper?

No data have been published on the nature of exhausted lead compounds since the 1926-1930 reports of the U.S. Bureau of Mines, Public Health Service, and British Ministry of Health. This paper is the first work in which the amounts, particle sizes and composition of exhausted lead have been determined.

This publication will surely raise questions as to the effects of TEL on atmospheric pollution, smog, and public health. However, Dr. Kehoe feels that these questions will arise anyway, and that we should present actual data before they do. The data will help to obtain approval for 4 ml TEL (and credit us with this effort), since they show that only part of the lead burned is exhausted in airborne size ranges, particularly in metropolitan driving, and that an increase from 3 to 4 ml would increase lead emission by only 1/3 from present low levels. This publication is contingent on obtaining prior direct data, from studies in progress at Midwest Research Institute, to show that TEL has no harmful effect on smog formation.

Please Indicate:

- ☐ Approve
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Comments

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CONFIDENTIAL

Particulate Lead Compounds in Automobile Exhaust Gas

Preface

Since this report has been prepared for potential release outside of the Company, codes have been used to designate the cars and phosphorus fuel additives which were used. These are as follows:

Engine D	1950 Chevrolet
Car B	1954 Ford No. 392
Car M	1953 Cadillac 62, No. 385
Phosphorus Additive A	ICC
Phosphorus Additive B	TCP

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Draft No. 1
D. A. Hirschler & L. F. Gilbert
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Confidential

(Proposed Research Memorandum for Release to Customer Companies)

Particulate Lead Compounds in Automobile Exhaust Gas

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. No studies were made of the exhausted carbon and organic particulate matter.

Approximately 20 to 30 percent of the lead burned in the fuel was retained in passenger car exhaust system deposits and lubricating oil, leaving 70 to 80 percent of the lead to be exhausted over a 20,000 to 30,000 mile period of city and country driving. Lead emission was increased by speed. The lead recovered from the exhaust gas under city-type driving conditions, which included idling, acceleration, deceleration and cruise conditions, normally ranged from 20 percent of the lead burned when the exhaust system was comparatively clean, to as high as 60 percent 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 exhausted lead initially was 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 0.005 micron to several millimeters in diameter. Particles smaller than one micron were by far the most numerous, but accounted for less than 5 weight percent of the exhausted lead. Heavy particles 5 microns and larger, which might be expected to settle rapidly, represented about 25 percent of the exhausted lead under city-type driving but increased to about 40 percent 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 $2NH_4Cl \cdot PbCl \cdot Br$, together with small amounts of $PbSO_4$ and $PbO \cdot PbCl \cdot Br \cdot H_2O$. When phosphorus was present in the fuel, about 3/5 of the lead

was exhausted as $3Pb_3(PO_4)_2 \cdot PbCl \cdot Br$.

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 phosphorus-containing gasoline additives nor changes in fuel sulfur concentration 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 multiple exhaust systems as well as operating factors. Since lower-speed driving conditions as are 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 respect to hygienic standards, and in respect to the amount of lead burned.

Introduction

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 and sulfur. However, no recent work has been reported on the particulate lead compounds which are present also 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 wt. percent lead). TEL has been used in this manner since 1926, 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 necessary to prevent the accumulation of lead oxides in engine combustion chambers. Their function is to convert lead oxide into lead halides, which have greater volatility at engine temperatures and can be expelled from the engine. Therefore, the elimination of lead from engines would 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 it 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 (1, 2, 3, 4). These studies showed that there was no need for concern at normal concentrations of TEL even under the most adverse conditions such as in tunnels, confined garages and in heavy traffic, inasmuch as provisions for ventilation were required to prevent excessive concentrations of exhaust gas and carbon monoxide. 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 no instances in which lead in the air has been more than a small fraction of the accepted concentration limit. These analyses have suggested that much of the lead burned in gasoline is not exhausted in forms which can be suspended in the atmosphere, and because of this 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 three microns in diameter were present rarely, and that most of the suspended particles were less than two microns in size (5). Because of this, the exhausted lead compounds have been classified into two broad size ranges, fines up to 5 microns in diameter, and coarse particles larger than 5 microns. Further classification of the fines into one micron size ranges has been accomplished in most of the work.

The studies of exhausted lead compounds have evolved through several phases. Initially, the exhausted material was collected from single-cylinder engines with only a minimum length of exhaust pipe. Following this, dynamometer tests were made 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 with two cars of different makes. Evaluations were made of the effects of operating conditions and of three fuel variables, TEL concentration, sulfur concentration, and phosphorus-containing additives.