ETHYL CORPORATION

INTER-OFFICE MEMORANDUM

TO Dr. R. A. Kehoe

FROM H. A. Beatty

DATE March 20, 1950

SUBJECT LEAD IN ENGINE EXHAUST GAS

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With reference to your letter of March 6 to Dr. Edgar and subsequent telephone conversation with Dr. Calingaert asking for information up to date on this subject, I have reviewed the matter with several of our people here and checked our files, and the results add up about as follows.

(1) Prior to the recent work in Mr. Lovell's group (see paragraph 2), the only data we have are in the 1927 Bureau of Mines report by Sayers et al, with which you are of course familiar. For convenience, I shall note here a summary of their results.

(a) Using either 3 ml or 15 ml TEL per gallon and either trichloroethylene or ethylene dibromide as scavenger, the entire exhaust gas from a Delco engine was mixed with 170 volumes (500 cfm) of fresh air and circulated uniformly through the animal test chamber of 1000 cu ft volume. The engine was operated about 40 hours a week for a year and a half, using 1 lb fuel per hour at about 0.07 fuel-air ratio. Some inspection and analysis of the combustion chamber and exhaust pipe deposits and the oil was made in the early part of the work, but during most of the time the exhaust line was not changed or cleaned. The chamber air was analyzed for total lead at frequent intervals by passing 75-500 cu ft at the rate of 0.5 cu ft per hour through two Cottrell precipitators in series. About 97% of the precipitate was found in the first tube.

(b) The air analyses were somewhat erratic, and averaged close to 50% recovery of the lead input to the engine, the same for both TEL concentrations and both scavengers. The amount of lead lost by way of the lubricating oil and remaining in the combustion chamber and exhaust line may have averaged as much as 20% of the input. There was some accumulation of "scale" particles, too large to be air-borne, in the duct where the exhaust gas and fresh air were mixed, and it is probable that this accounted for the remainder of the lead input. In other words, it seems likely that the Cottrell precipitator gave a reasonably accurate value for the amount of air-borne lead (40 micrograms per cu ft for 15 ml per gallon TEL).

(c) Analyses of the exhaust line deposits and of the scale in the air duct showed halogen as the major constituent, and sulfur as only a minor one, in the lead compounds. There was no analysis of the samples from the Cottrell precipitator other than for total lead.

(d) There was no measurement of particle size of the air-borne dust.

(2) In recent work by Mr. Lovell's group in these Laboratories, the entire exhaust from a single cylinder engine has been passed directly through Cottrell precipitators, with essentially complete recovery of lead. The tests showed in particular that: (a) a substantial part of the lead comes out the exhaust at irregular intervals in the form of fairly large particles, obviously from the break-loose of surface deposits; (b) the deposit on the surface of the precipitator can be converted from oxides to bromide by the action of HBr in the gas stream. (This conversion of solid wall deposits from one lead compound to another has also been shown in the recent work here, likewise in Mr. Lovell's group, in which the products of combustion of an open flame burner are passed down a long exhaust tube.)

(3) We have as yet no information on the fine particles of lead compounds in the exhaust gas stream, as to: (a) particle size, (b) rate of agglomeration, (c) true chemical composition, (d) further chemical reaction in the gas phase with HBr, HCl, SO_2 , etc. (probably nil, once the gas is diluted and cooled), (e) effect on these items of a fog of condensed water vapor, as present in cold weather operation, (f) effect of traffic dust, smoke, etc. in the ambient air.

(4) In normal vehicular operation, the total amount of lead leaving the exhaust pipe will average about 90% of the input, with most of the remainder divided between the exhaust system and the oil. We suspect that the particle size and chemical composition may vary considerably with the engine operating conditions, including such factors as sulfur content of fuel, additives used in oil, fuel-air ratio, variation in engine speed and load, degree of knock, etc. The composition is believed to be lead halides and oxy salts containing halide, sulfate, and carbonate, and the remaining halide is presumably in the form of HCl, HBr. However, this is only conjecture, based on the analysis of solid deposits. We would not expect much variation with either TEL content of fuel or kind and amount of scavenger (within the range covered by our Aviation and Motor mixes, and considering chlorine and/or bromine synonymously as "halide").

(5) The compositions of antiknock fluids in recent years have been as follows, the scavengers being ethylene dichloride and dibromide; 1 T (theory) equals 2 atoms halogen per atom of lead. The composition of the present fluids is <u>not</u> confidential.

Fluid Designation	Date Shipped From	Date Shipped To	T Halogen Br	T Halogen Cl
Motor				
C-Mix	4-30	8-33	0.85	0.30
C-Mix A	8-33	7-34	0.75	0.40
44-Mix	9-33	6-42	0.70	0.45
62-Mix	6-42	date	0.50	1.00
Aviation				
1-T	9-30	date	1.00	0.00