Medical Research Division

Esso Research and Engineering Company

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MEMORANDUM

ON

COMPARISON BETWEEN AIR POLLUTION LEVELS CAUSED BY CARS OPERATING ON TML AND TEL GASOLINES

COMPANY CONFIDENTIAL

I. Summary

As part of the over-all evaluation of tetramethyl lead antiknock additive (TML), the lead content of the air around foreign-make cars operating on two fuels containing identical quantities of lead as TML or TEL was studied. This was an exploratory air pollution evaluation done during the period February through March 1960.

The data were obtained simultaneously on the same makes and models of cars during the same driving cycle. This permitted a direct comparison between TML- and TEL-induced lead contamination in the air.

Statistical treatment of the data showed no significant difference between the atmospheric lead levels obtained from either TML- or TEL-containing gasoline.

II. General Discussion

Both inorganic and organic lead compounds have a high order of toxicity. The recommended MAC for lead in air is 0.2 mg/cu.m., with no distinction made between inorganic and organic lead.

To evaluate any incremental lead exposures created by the more volatile TML, as compared with TEL, a sampling program was set up in conjunction with the Products Research Division durability tests on the TML antiknock additive.

The following were sampled: (1) exhaust gases, (2) air directly above the engine with the hood closed, (3) in-car air at the driver's seat at breathing zone height, and (4) air in the general area, four feet behind the car at breathing zone height.

Four pairs of foreign cars were used in the test. These are listed in Table 1.

Table 1

Make	Model	Engine Location
English Ford	Anglia	front
Volkswagen	Sedan	rear
Renault	Dauphine	rear
Fiat	1200	front

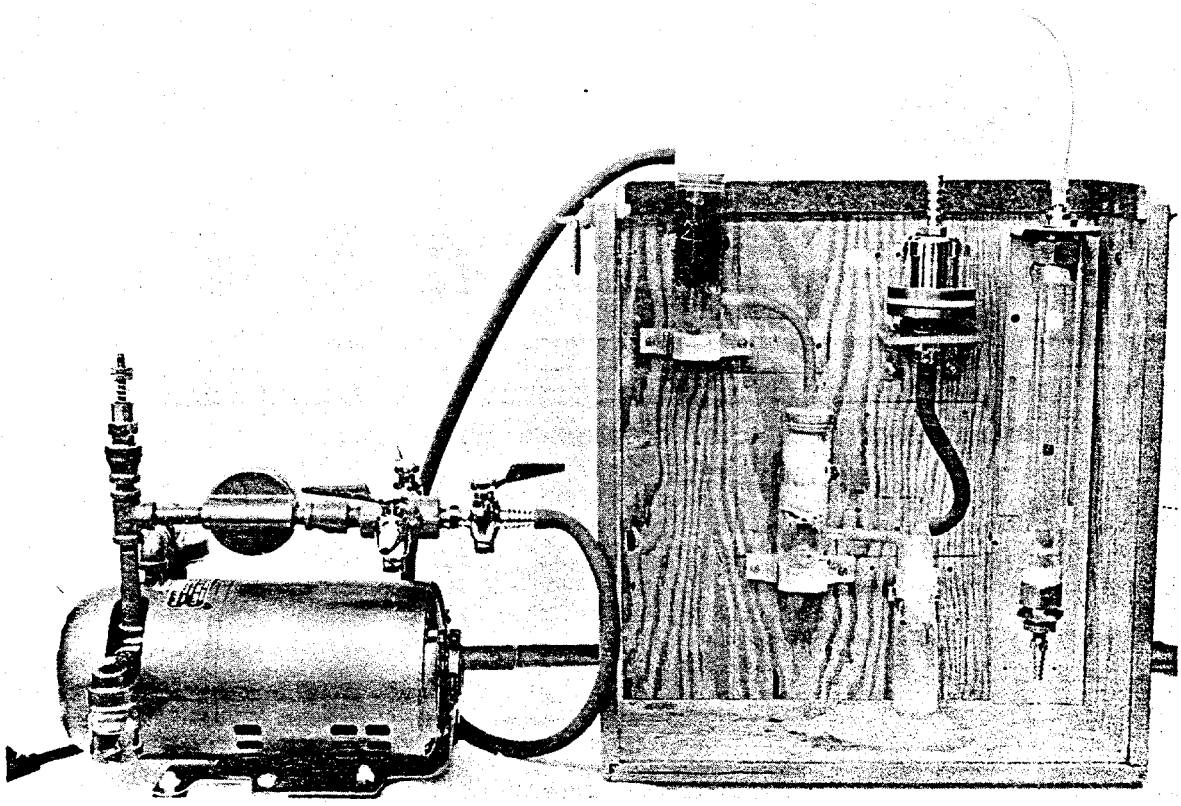
The cars were operated on the MAD units at the Esso Research Center in accordance with a schedule developed by the Products Research Division (see memo dated 1/11/60, P. J. Clarke to G. S. Tobias, Products Research File 3797, Ref. No. 6012836).

A. Sampling Procedure

The sampler was designed to separate organic from inorganic lead, thus permitting the determination of both forms of lead in the air sampled. This equipment is shown in Figure 1.

Figure 1

SAMPLING EQUIPMENT USED



The sampling scheme is simply to meter the total flow with some suitable device, like the rotameter shown. The particulate matter in the air, containing inorganic lead, is filtered on molecular sieve filter paper in a filter holder assembly. The air then bubbles through a collecting solution in an impinger designed for a maximum flow of 14 liters per minute. This impinger contains a solution of KI-I_2 which is a highly efficient medium for capturing organic lead vapor. The air stream is then passed through glasswool and activated charcoal in separate traps to protect the pump from the corrosive effects of iodine vapor carryover.

In practice, when sampling the exhaust gases, condensation in the rotameter made accurate flow measurement difficult. In its place, a 10 liter per minute critical nozzle was placed between the collection devices and the pump. Sample times were varied from ten minutes to over two hours, primarily to collect enough organic lead for accurate analysis. For high flow rates, or where condensation is not a problem, the rotameter is more desirable than the critical orifice, mainly because of its lower pressure loss.

The exhaust samples were obtained from stacks located near the cars. The exhaust from each car was directed into an oversized flexible duct which was connected to the base of a stack. Lead contents found in the stack may not truly represent lead concentration in the exhaust gas because of deposition and dilution in the connecting system, but they serve as good approximations for the purpose of this study.

B. Analytical Procedure

Inorganic lead on the filter paper was analyzed by the Analytical Division using the colorimetric method ATC-920.042T.

Organic lead in the liquid collection medium was analyzed by a colorimetric procedure developed by Snyder, et al[1].

III. Observations and Conclusions

Samples were taken at random intervals in the routine operating cycle. In Tables 2, 3, and 4, adjacent data in the TEL and TML columns, under each sample location heading, were obtained simultaneously.

Table 2

ORGANIC LEAD, microg/cu.m

Engine Location	Exhaust Gas TML	Exhaust Gas TEL	Air Under Hood TML	Air Under Hood TEL	Breathing Zone: Drivers Seat TML	Drivers Seat TEL	4' Behind Car TML	4' Behind Car TEL
Front	-	480	27	80	11	6		
	80*	80	31	21	4	7		
	80	60	9	15	2	4	9	93
	920	1540					8	8
Rear	430	57	27	40			6	6
	670	100	31	120				
	530	530	13	27				

*Estimated

Table 3

INORGANIC LEAD, microg/cu.m

Engine Location	Exhaust Gas TML	Exhaust Gas TEL	Air Under Hood TML	Air Under Hood TEL	Breathing Zone: Drivers Seat TML	Drivers Seat TEL	4' Behind Car TML	4' Behind Car TEL
Front	-	1720	3	7	96	6		
	1870	2670	8	13	22	7		
	4270	4130	6	3	6	3	35	20
	2400	6620					12	14
Rear	8190	3980	20	17			10	6
	3440	1330	90	18				
	4300	3100	50	57				

Table 4

TOTAL LEAD, microg/cu.m

Engine Location	Exhaust Gas TML	Exhaust Gas TEL	Air Under Hood TML	Air Under Hood TEL	Breathing Zone: Drivers Seat TML	Drivers Seat TEL	4' Behind Car TML	4' Behind Car TEL
Front	-	2200	30	87	107	12		
	1950	2750	39	34	26	14		
	4350	4190	15	18	8	7	44	113
	3320	8160					20	22
Rear	8620	4037	47	57			16	12
	4110	1430	121	138				
	4830	3630	63	84				

Comparison of absolute levels obtained within each sub-grouping (e.g., exhaust-front engine) was not possible because of (1) the wide difference in variance between the TML and TEL data within each sub-grouping, and (2) the limited number of data points. It is believed that high levels obtained within each sub-group cannot be discounted in an attempt to normalize the data. Culling of these peaks might lead to erroneous conclusions. Many more test points would be necessary to accurately define the model if in fact this is felt to be necessary.

Grouping of all the data for testing as a population of TML or TEL values was then done. The frequency distribution of the aggregate data for both TML and TEL gasolines was highly skewed toward the higher concentrations This is to be expected since no concentration can fall below 0 and much of the data is near this lower limit.

On logarithmic frequency distribution plotting paper, the data gave similar S-shaped curves. A plot of the deciles from the S-shaped curves versus the normal deviates at these deciles was the technique used to compare the two distributions. They differed only by about 0.1 standard deviation. With such similarity in the distributions of the aggregate data, it is appropriate to use a non-parametric evaluation of the data.

The sampling design and technique employed tended to eliminate car operation as a variable because of a fact that samples were taken during identical operating cycles for both cars. With this approach in mind, the best measure of whether or not the TML-fueled cars were producing more air pollution would be a differential analysis of the tables shown above. That is, one should consider the differences between TML-produced values and the TEL levels, and not the absolute values obtained. The composite table below shows these differential levels:

Table 5

DIFFERENTIAL LEAD, microg/cu.m
(Lead in Air from TML Fuel Minus that from TEL Fuel)

		Exhaust Gas			Under Hood			Breathing Zone: Drivers Seat			Breathing Zone: 4' Behind Car		
		Org.	Inorg.	Total	Org.	Inorg.	Total	Org.	Inorg.	Total	Org.	Inorg.	Total
Engine Location	Front	0*	- 800	- 800	-53	-4	-57	5	90	95			
		20	140	160	10	-5	5	-3	15	12			
		-620	-4220	-4840	- 6	3	- 3	-2	3	1	-84	15	-69
	Rear	373	4210	4583	-13	3	-10				0	- 2	- 2
		570	2110	2680	-89	72	-17				0	4	4
		0	1200	1200	-14	-7	-21						

*Estimated

Non-parametric rank and sign tests of the differential lead generated (see Table 5) for organic, inorganic and total lead concentration in the air were done. These tests showed no significant increase in the air pollution caused by TML-leaded gasoline over that from TEL-leaded gasoline.

The fact that no significant difference appears between the atmospheric concentrations from TML and TEL gasolines is not surprising in view of the experimental set-up at the MAD units in the Esso Research Center. The fuel is piped directly to the cars on the unit eliminating tank-filling loss and possible spillage. Blowby, discharged unburned fuel and carburetor loss are other possible means by which lead can be released into the air. These are not believed to be significant, however, for the reasons given below. As a result, it is to be expected that the lead in the fuel supplied will be exhausted on the basis of lead content in the fuel and not on the lead volatility.

In blowby some of the lead in the gasoline dissolves in the crankcase oil. With the more volatile TML more of this lead could escape by subsequent evaporation. Tests done in conjunction with this study by Products Research Division have borne this out. Crankcase oil from TML-fueled cars had lower lead content than oil from TEL-fueled cars. In terms of air pollution, however, the difference in lead discharged should be small.

The unburned fuel in the blowby and in the exhaust should approximate the composition of the fuel fed.

Carburetor evaporation loss should be small in the foreign cars tested. These cars have small carburetor bowls and at the low ambient temperatures existing during the test program little evaporation should occur.

Thus the quantitative lead emissions from cars studied in this program should be practically similar for both TML and TEL fuels. This has been confirmed by the preliminary data collected in the study.

In the case of an area where gasoline can evaporate and the vapors can concentrate in the air, like a fueling garage, the higher volatility of the TML gasoline will probably produce higher levels of organic lead in the air. This, in fact, has been proven to be true by Cholak[2] in studies in a California garage wherein the taxi fleet using the garage was serviced alternately with the same leaded quantities of TEL and then TML gasolines. The particulate lead concentration remained about the same while the organic lead in the air increased about three times.

In conclusion, the general atmosphere should show little or no significant difference in the air pollution levels created by TML versus TEL gasoline. However, occupational exposure should be checked in locations wherein

the higher volatility of TML could increase the organic lead concentration in air. Such areas and activities would include garages, gasoline storage tank cleaning, gasoline loading racks, service stations, and congested traffic.

IV. References

1. Snyder, L. J., Barnes, W. R., Tokos, J. V.: Determination of Lead in Air. Anal. Chem. 20(8):772-776 (August 1948).

2. Cholak, J. and Kehoe, R. A.: A Report of an Investigation of the Potential Hazards of Exposures to Lead Associated with the Handling and Use of Gasoline Containing an Anti-knock Fluid in which Tetramethyl Lead is Substituted for Tetraethyl Lead. The Kettering Laboratory, Cincinnati, Ohio (November 10, 1959) Confidential Report.

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