

ETHYL CORPORATION

RESEARCH LABORATORIES

1600 WEST EIGHT MILE ROAD

FERNDALE 20

DETROIT, MICHIGAN

cc: H. J. Gibson
J. B. Macauley
R. K. Scales
J. S. Wintringham

September 2, 1948

Dr. Robert A. Kehoe
College of Medicine
University of Cincinnati
Eden Avenue
Cincinnati 19, Ohio

Dear Dr. Kehoe:

1. Air Evaporation of Vitol

We have completed an investigation of the air-evaporation characteristics of Vitol fluid, as suggested at the meeting with the Thompson people in Cleveland on April 20. Our findings are sufficiently different from what we expected that I am transmitting our data to you now in the form of this memorandum, rather than wait until the formal LTD report is issued. Furthermore, we were notified by Mr. Van Hartesveldt that you had given provisional approval to proceed with the Columbus program, and our information may have a bearing on that decision.

You will recall that Dr. Roush of the Thompson Products reported preliminary results indicating that the volatility of TEL in Vitol was about one-fourth that of TEL in gasoline. Our results indicate that a very different situation exists.

We have evaporated samples of Vitol by introducing nitrogen through a sintered disc, so that near-equilibrium conditions exist. The effluent vapors, consisting of nitrogen, methanol, water and the components of the Antiknock Compound were scrubbed through an iodine solution, and the scrubber solutions analyzed for lead. This procedure duplicates that used for TEL-heptane solutions as described in our report LTD 46-47, a copy of which you received at the time it was issued. With gasoline, we found that very little of the TEL evaporated until about 90% of the fuel was evaporated. Consequently dangerous TEL concentrations in the air do not exist during most of the evaporative process, nor would the vapor space in a partly filled container contain high concentrations. On the other hand the residual liquid gasoline becomes higher in TEL content.

The data which we have obtained are presented in the following table and in the attached graphs. Under these conditions of evaporation, vapors from Vitol fluid will contain between 9000 and 12,500 $\mu\text{g. Pb/cu. ft.}$ of air until essentially all the TEL has evaporated. An almost straight-line relationship exists between the amount of lead and Vitol evaporated--2% of the TEL for every 1% of the liquid. Calculations show that evaporation of pure TEL under similar conditions would produce a concentration of 130,000 $\mu\text{g. Pb/cu. ft.}$ of air. The evaporation characteristics of Vitol are, therefore, equivalent to those of 1/10% TEL solution.

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AIR EVAPORATION OF VITOL FLUID AND "ETHYL" AVIATION GASOLINE

Run	Fraction, wt. % of sample	Wt. % Evaporated, cumulative		Concentration of lead in air, μg./cu. ft.	Concentration of TEL in residue ml.TEL/gal.
		Fuel	Lead		
1 Vitol	53	53	97.2	9500	0.19
	30	83	98.2	200	.26
	10	93	98.8	30	.54
	7	Res.	-	-	-
2 Vitol	5	5	11.8	12,500	2.82
	5	10	21.4	12,400	2.64
	5	15	35.2	13,000	2.33
	11	26	61.2	12,100	1.62
	74	Res.	-	-	-
3 Vitol	6	6	10.7	9200	2.58
	11	17	32.0	9200	2.25
	10	27	49.8	9100	1.88
	73	Res.	-	-	-
4 Gasoline	0	0	0	130	4.5
	40	40	(0.5)	160	7.45
	40	80	2.1	480	22.0
	10	90	5.4	1250	42.5
	5	95	13.0	3130	78.5
	3	98	35.5	8540	145.0

Run 1. Vitol fluid, laboratory preparation, no corrosion inhibitor, 3.03 ml. TEL/gal.

Run 2. Vitol fluid, laboratory preparation, no corrosion inhibitor, 3.03 ml. TEL/gal.

Run 3. Vitol fluid, commercial grade, 2.72 ml. TEL/gal.

Run 4. Aviation gasoline, CRC-28R, 4.5 ml. TEL/gal., data from LTD 44-57.

These results, striking as they may seem, are in qualitative agreement with the laws of physical chemistry: as systems approach immiscibility the partial pressures of their components increase considerably and approach the vapor pressures of the pure compounds, a state which is reached when the components become immiscible.

The experiments which we conducted were not designed to duplicate the surface evaporation experienced in a liquid spill, but with this reservation in mind, the following picture of the relative effects of Vitol and leaded gasoline spills can be drawn. In the first place, the evaporation of Vitol will, from the start, introduce considerably greater quantities of TEL into the atmosphere, building up the TEL concentration much faster than is the case with gasoline. In a confined space a real hazard will exist. For example, (1) if one gallon of Vitol is allowed to evaporate to the 50% point, either as the result of a spill or from storage in an open container, into a room of 1000 cu. ft., 2.9 g. of Pb will be introduced into the atmosphere, or 2,900 μg.Pb/cu.ft. On the other hand, under the same circumstances, there would be only 0.048 g. Pb, or 48 μg.Pb/cu. ft. resulting from evaporation of a similar quantity of aviation gasoline. These figures

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are 31 and 0.5 times, respectively, the maximum allowable concentration for 20-minute exposure. (2) The heel remaining in a storage tank containing Vitol or gasoline furnishes another interesting comparison. With Vitol we can expect about 10,000 $\mu\text{g. Pb/cu. ft.}$ of vapor space in the tank, no matter what the size of the heel in relation to the tank. With gasoline even if 80% of the heel evaporated into the vapor space, there would be less than 500 $\mu\text{g. Pb/cu. ft.}$ in the tank atmosphere, and to bring about this condition the liquid hold-up in the tank would have to be on the order of 0.2% of the tank volume, or say 20 gal. in a 10,000-gal. tank which would be unusually low. (3) Still another condition, which may exist in practice, is the build-up of a high lead (TEL) concentration under the semi-enclosed hood of an automobile from the evaporation of Vitol from the storage canister. A mechanic might be subjected to a high concentration very readily from this source.

On the other side of the picture, our experiments show that evaporation of Vitol is a very efficient means of eliminating TEL from the residue, the opposite picture from what occurs in the case of gasoline. Incidentally, we have satisfied ourselves that although the water content of the residual fluid increases, the TEL is removed sufficiently rapidly that no separation occurs due to evaporation. If water is added, however, such as in washing for instance, TEL will, of course, separate immediately.

Thus, from certain standpoints Vitol presents more of a hazard than gasoline, and from others less. Certainly the situation is different. We will be very interested in learning your reaction to these results, and what recommendations you will make concerning the storage, handling and use of this product based on these observations.

2. Further Work

The results recorded above have seemed sufficiently provocative to warrant further work. We plan to carry out the following program, to be completed in about two months:

- 1) Determine evaporation characteristics of Vitol fluid containing 0% and 5% water. If we are at present dealing with borderline immiscibility, these experiments should point it out.
- 2) Determine accurately the partition function of TEL between the alcohol-water and dispersed inhibitor phases. Preliminary experiments indicate the inhibitor contains appreciable, perhaps dangerous, concentrations of TEL.
- 3) Determine the separability of the inhibitor phase. Although Thompson insists the emulsion is permanent, we are still skeptical. We have observed agglomeration of inhibitor droplets, separation on centrifuging and a concentration gradient in commercial Vitol. In view of (2) above, this point needs clarification.

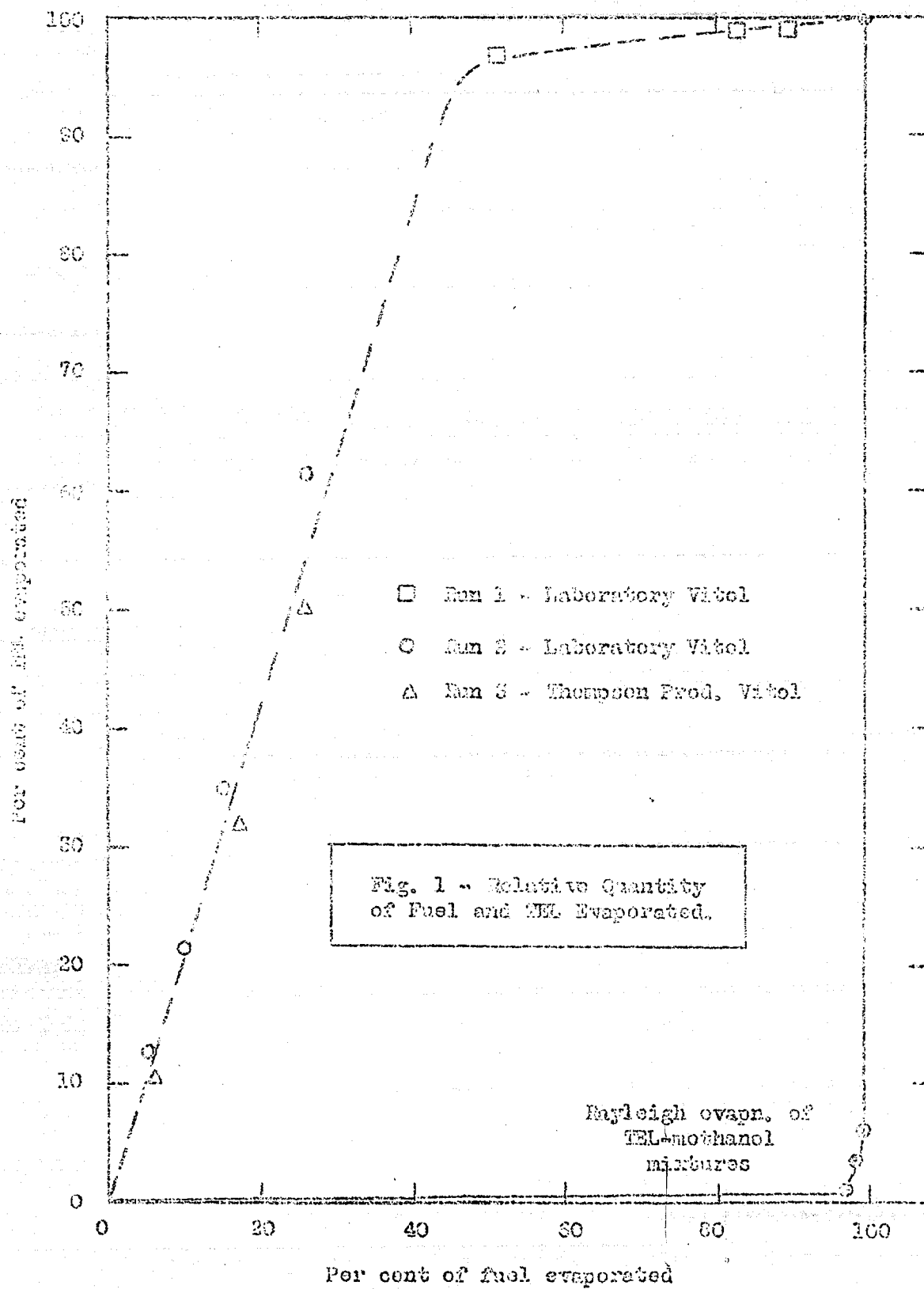
We shall keep you advised of our progress, and send you a copy of our finished report on the work to date.

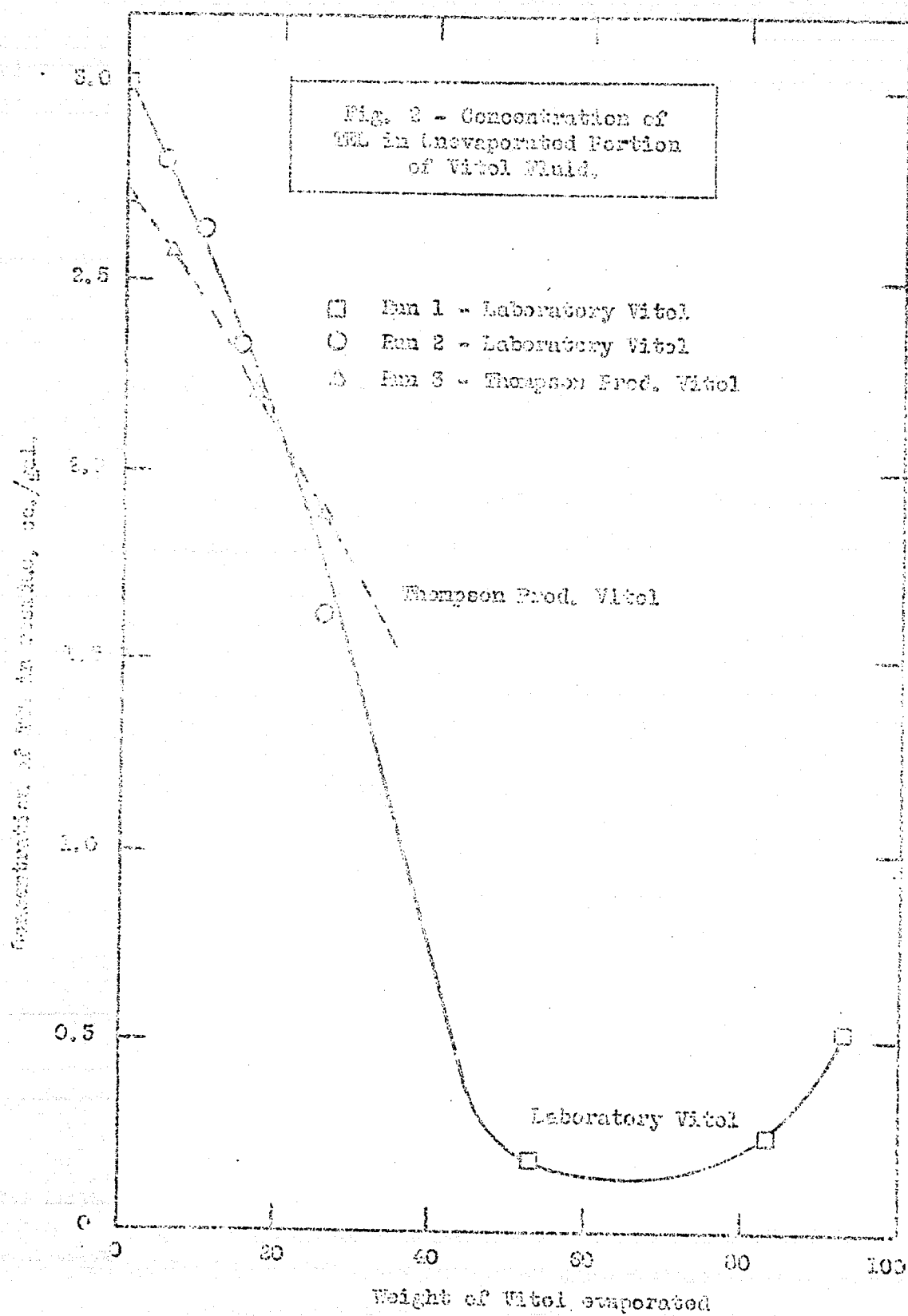
We would be interested in the results of your toxicity studies and in learning the details of your recommendation to Thompson.

Very truly yours,

Robert Thompson

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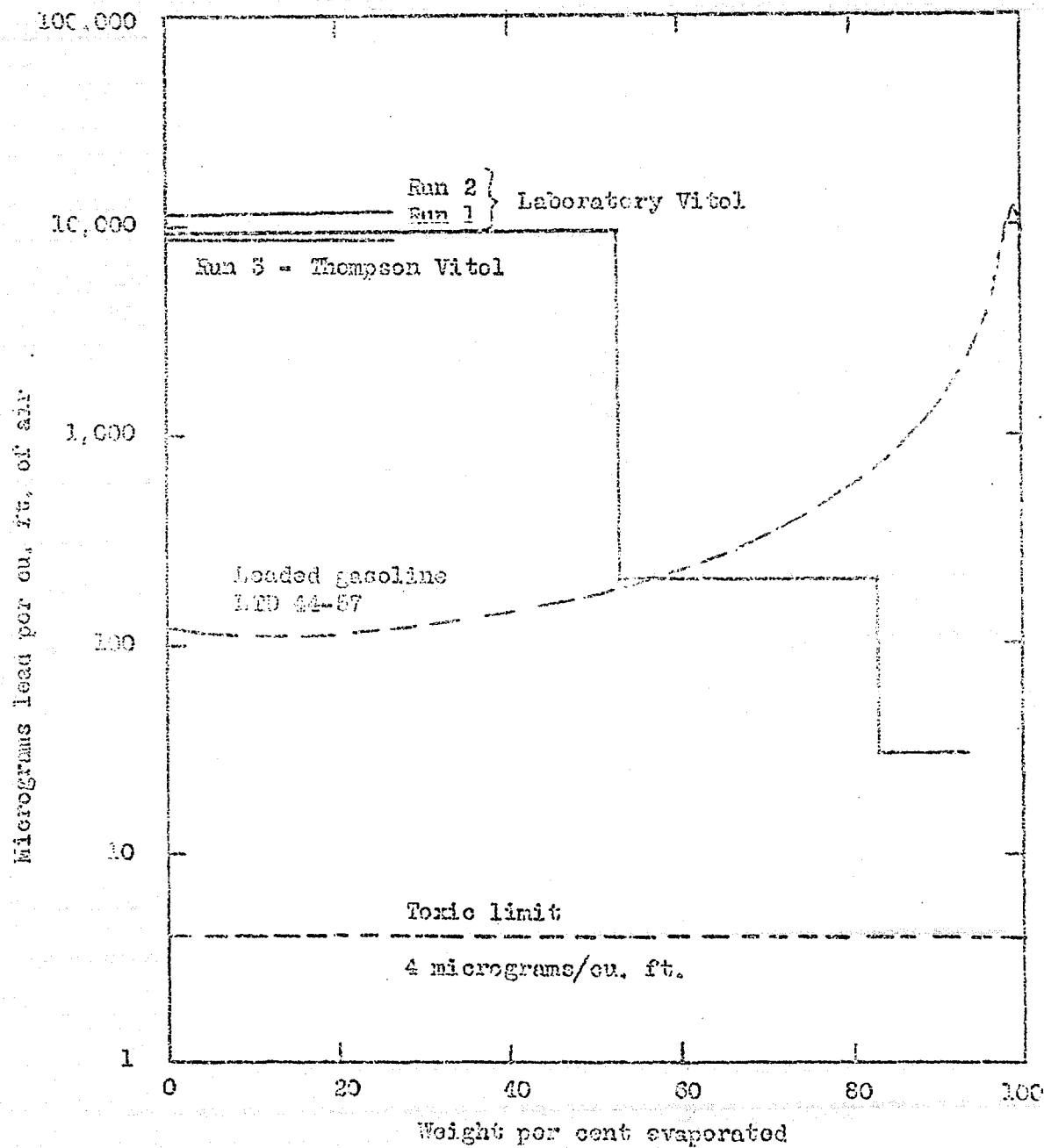


Fig. 3 - Comparison of Load in Air for Evaporation of Vitol Fluid and Loaded Gasoline.