EVAPORATION OF LEAD ALKYLS IN GASOLINE

Summary and Conclusions

This memorandum reviews our previous experiments, calculations, and conclusions. New calculations for the lower alkyls in present day gasolines are being made at Baton Rouge by Henry Wall. These are not likely to change the following general conclusions:

(1) In simple distillation of leaded gasoline, the lead alkyls follow Raoult's Law. Therefore, if the gasoline is known, the progress of distillation can be predicted accurately. This has been well demonstrated experimentally.

(2) Evaporation at room temperature is a different story. When air is saturated by blowing it through the gasoline, the ratio of lead to gasoline in the vapor is, if anything, somewhat higher than predicted.

(3) In this case, the volatility and composition of the gasoline has relatively little effect on the resulting initial concentrations of lead in air. All that matters is the kind and amount of lead alkyl in the liquid.

(4) In non-equilibrium evaporation, where the air is only partly saturated, the lead-to-gasoline ratio in the vapor may be either much greater or somewhat less than it is under equilibrium conditions. The result depends on the particular conditions under which the evaporation occurs.

(5) Evaporation of gasoline containing TEL leaves much more lead in the residual liquid than does distillation. (This results from the different temperatures involved.) Evaporation of gasolines containing TML or mixed alkyls has not been carried out beyond the 10% point.

(6) In all cases, TML is about 100 times as volatile as TEL; the mixed alkyls line up in between. During evaporation of the first 10% of a gasoline containing 3.15 g Pb, the concentration of lead in the saturated air is 2 mg/m^3 for TEL, 36 mg/m^3 for a 50-50 equilibrium mix, and 210 mg/m^3 for TML. By the same token, the final residue of liquid should contain little or no TML.

(7) New experiments on a realistic, full scale are needed to determine the outcome of non-equilibrium evaporation under conditions which might be met in practice. Gasoline in deep layers, in shallow layers, and dispersed on cloth or other absorbents should be exposed to both quiescent and turbulent air. If TEL and TML are compared in each test, the behavior of any mixture can be safely predicted. Many of these tests will involve the formation of large quantities of explosive air-vapor mixtures. These can easily and safely be handled in one of our high-pressure test cells at Detroit.

Vapor Pressure

Figure 1 shows the vapor pressures of the individual alkyls and indicates the range over which they have been measured. The curves are considered to be quite reliable. At room temperature it will be seen that TML is about 100 times as volatile as TEL; the other alkyls line up regularly in between.

Distillation

Given the vapor pressures of the lead alkyls and assuming Raoult's Law, the distillation of the alkyls in any leaded gasoline can be predicted if we have a satisfactory estimate of the molecular weight and boiling point curve of the base gasoline. Methods of estimating this are given in the LTD reports (e.g. 41-53, 44-57, and 50-53).

Figure 2 shows this prediction for each of the five lead alkyls in a 1938 winter grade motor gasoline. Variations in gasoline volatility will change the shape of the curves somewhat, as would be expected; variations in hydrocarbon type will have very little effect. The slope of the curves at any point is a measure of the rate of distillation of the lead alkyl. The maximum rate for TML is seen to be near the midpoint; for TEL, near the endpoint.

These five curves were well confirmed by experiment in a series of bench tests made with a no-reflux still (LTD 39-21). Other tests, made with TEL only, included a steam distillation (LTD 38-6), an Engler distil-

lation (LTD 36-19), and a refinery rerun of 633,000 gal of leaded aviation gasoline (LTD 44-37). All these gave results in good agreement with expectation.

The most convincing proof of our ability to predict the outcome of a distillation was the experiment reported in LTD 39-22. Here, a selected mixture of TEL and other alkyls was added to a base gasoline with the objective of obtaining, on distillation, 10 cuts of equal octane number. In each of two runs, the lead content of the cuts was just as predicted, and their octane numbers were indeed identical.

Equilibrium Evaporation

A number of different tests were made in which air or nitrogen was blown at room temperature through leaded fuel (motor and aviation gasoline and heptane), the effluent being in equilibrium with the liquid. For TEL in avgas or heptane, the runs were carried through nearly to the endpoint. For TEL, TML, and a mixed alkyl in motor gasoline, the runs were stopped at the 10% point.

Figure 3 shows the progress of the evaporation of TEL in avgas (LTD 44-57). Here, the abscissa scales indicate the cumulative amounts of lead and gasoline evaporated as time or air flow goes on; the curves show the momentary concentrations of both lead and gasoline in the effluent air at any time. Both curves are roughly exponential: the gasoline concentration decreasing as the volatility of the residual liquid declines; the TEL concentration in the air rising as its concentration in the liquid builds up to a maximum near the endpoint.

A similar calculation and experiment has not yet been made for TML or a mixed alkyl over the whole range. However, from Figure 2 it is easy to see that the lead-in-air curve for TML would have a quite different slope. It would start at a 100-fold higher concentration, rise quickly to a flat maximum near the gasoline midpoint (where about 10% of the total air has been used), then decline to nearly zero.

It should be possible to concoct a blend of alkyls which would have a nearly flat lead-in-air concentration curve. This was never attempted, but it can be done in a few days time if wanted.

It will be observed that, with TEL, the final 10% of the liquid still contains some 95% of the original lead, compared with only 40% in the case of distillation. This difference is a result of the higher temperatures reached in distillation and resulting higher volatility of TEL relative to gasoline. Both figures are in accord with Raoult's Law.

A decrease in the over-all volatility of the gasoline will, of course, increase the amount of air required for evaporation and thereby lower the concentration of lead in both liquid and vapor in the final stages.

At the front end, however, the fuel volatility is relatively unimportant. Figure 4 (from LTD 41-28) shows the air used and lead volatilized during the evaporation of the first 10% of a motor gasoline containing 3.15 g Pb/gal as the M-410 mixture of alkyls (largely Me_2Et_2Pb and $MeEt_3Pb$). It can be seen that the lead-in-air is nearly constant at a level of some 25 mg/m^3.

Similar experiments on the first 10% evaporated of motor gasolines containing TEL, TML, and various mixed alkyls gave results in fair agreement with expectation (LTD 36-18, 38-20, 41-28). The amount of TML evaporated agreed with Raoult's Law, but for TEL it appeared to be somewhat higher. The same result was obtained with TEL in heptane throughout the evaporation from the 30 to 95% points. (LTD 46-47.) Mixed alkyls from which the TML had previously been stripped gave just about the same concentrations of lead in the air as did the unstripped mixes. This was expected: the increase in concentration of the other alkyls largely made up for the removal of the TML, the amount of which was small anyway.

Early tests on evaporation of TEL from non-volatile solvents such as lube oil (LTD 35-19 or CR-4) and butyl phthalate (LTD 37-23) likewise showed a somewhat faster rate than expected.

Non-Equilibrium Evaporation

There is surprisingly little information in the literature on the non-equilibrium evaporation of binary solutions.

We have made a variety of tests in which air was passed over the surface of gasoline or heptane containing TEL, under conditions where the air became only about 25% saturated with hydrocarbon vapor. In these tests, depending on the conditions used, the ratio of lead to fuel in the effluent vapor varied from a low of 80% to a high of 200% of the value predicted from Raoult's Law (LTD 44-57, 46-47).

When the liquid was stirred only by convection, there was a "surface stripping" effect, giving a high TEL/hydrocarbon ratio in the vapor. (This effect was exaggerated in a test made with TEL in ethylene dibromide, wherein the TEL-rich surface layer has a lower density than the main body of liquid and hence has no tendency to mix with it by convection.)

On the other hand, when the liquid surface was kept nearly identical in composition with its main body, the controlling factor is diffusion of vapor at the interface. In that case, the evaporation of the TEL is retarded by the relatively slow movement of its vapor.

Noteworthy in these tests was the rapidity with which the moving air near the liquid surface picked up vapor from it. In one test, air became 26% saturated in only 18 milliseconds, when flowing at a velocity of 280 cm/sec through a 5-cm length of vertical 4-mm i.d. tube whose inner wall was continuously wetted with a film of liquid.

In an early test (LTD 35-19), lube oil containing 3 ml TEL/gal was poured into a shallow pan to a depth of 1 cm. This was placed in still air in a laboratory room. At the end of two weeks, 90% of the TEL had evaporated.

Hazards

Discussion of the hazards incurred from both lead and gasoline vapor in air is outside the scope of this memorandum. However, it is in order to point out that the surface evaporation tests are important in this connection. They suggest that no great reduction in the hazard of room temperature evaporation can be achieved merely by increasing the ventilation over the liquid surface. What is needed is to remove the vapor from the liquid and then dilute it with additional quantities of air.

Additional Tests Needed

If mixed alkyls are to be used, there should be at least one series of tests made in which TML, Me_2Et_2Pb, and TEL, in one or two typical gasolines, are evaporated to near the end point, using equilibrium conditions.

In view of the marked effect of the experimental set-up in non-equilibrium evaporation, it would seem to be highly desirable to carry out some full scale tests under realistic conditions likely to be met in practice. These would include liquid in deep and shallow layers and dispersed on cloth or other absorbent, exposed to both quiescent and turbulent air. Hazardous air-vapor mixtures can safely be handled in our test cells at Detroit.

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FIGURE 4. AIR EVAPORIZATION OF GASOLINE CONTAINING M-410 MIXTURE

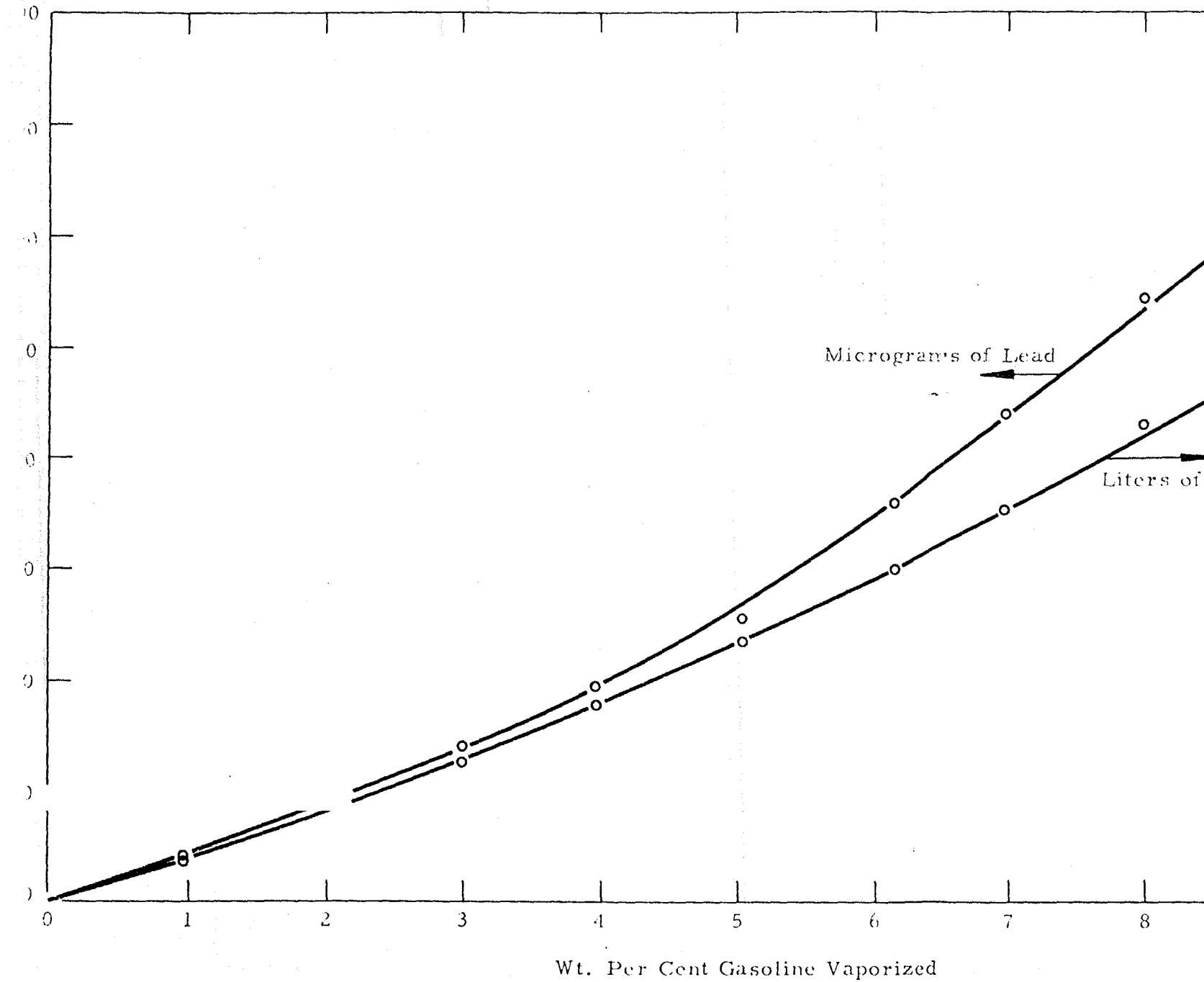

FIGURE 2. SINGLE PLATE DISTILLATION OF LEADED GASOLINE
CUMULATIVE DISTRIBUTION OF LEAD

Red Crown Gasoline Treated With Alkyl Lead Compounds

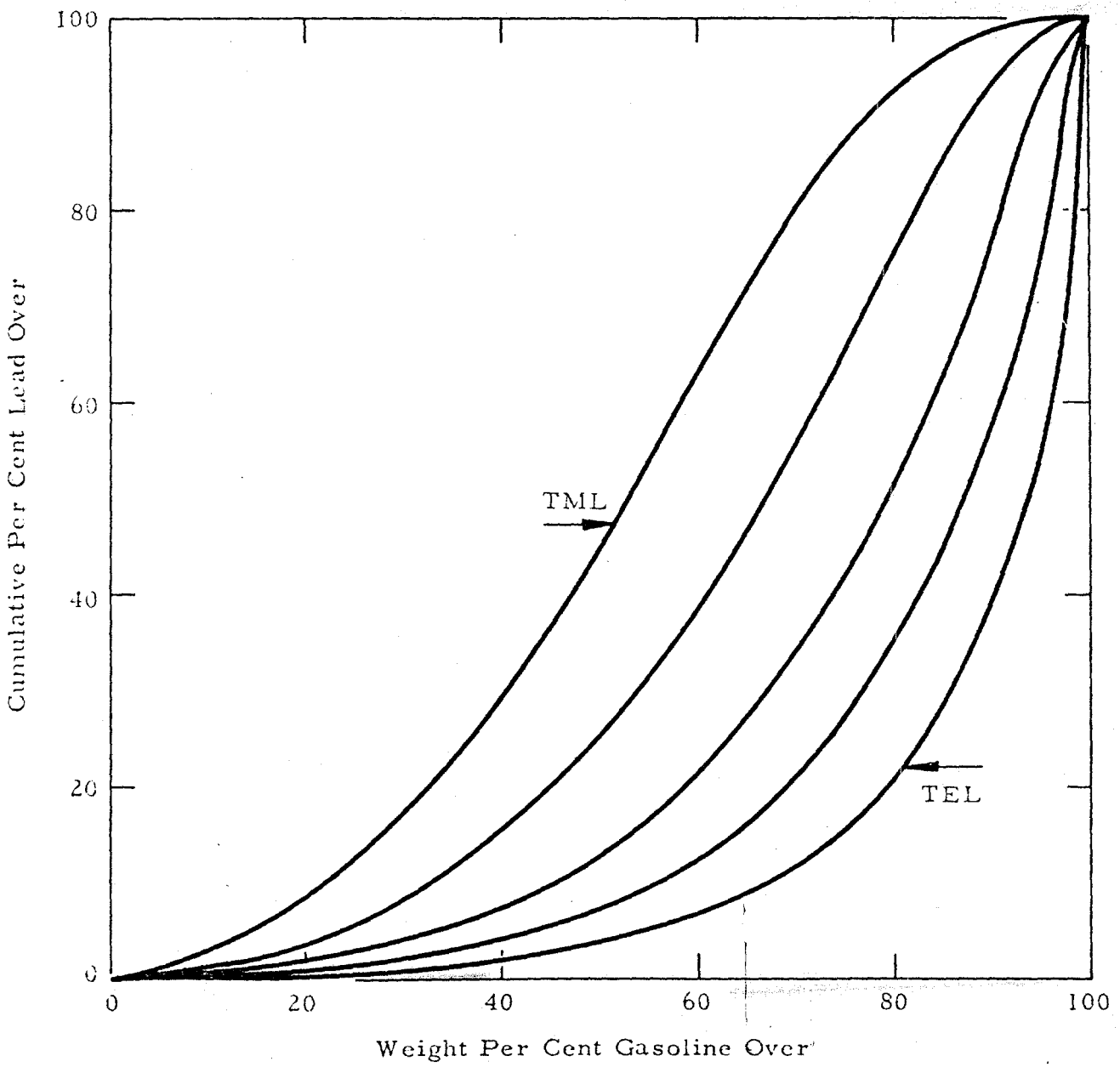

FIGURE 3. CONCENTRATIONS OF GASOLINE AND LEAD IN EMERGENT AIR AGAINST AIR USED OR TIME

Air 100% Saturated

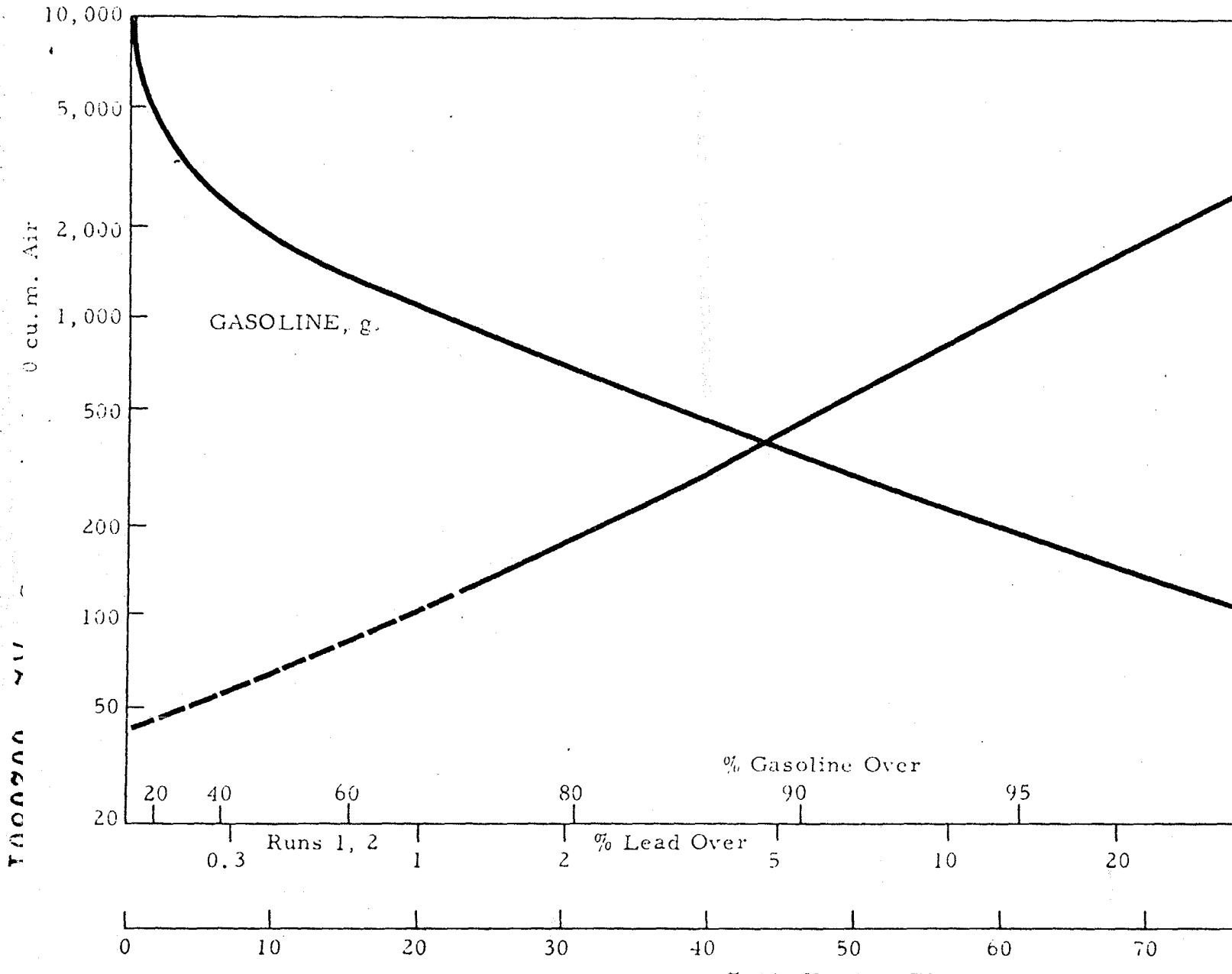

FIGURE 1. VAPOR PRESSURES OF THE LEAD ALKYLS