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VITOL — May 18, 1949

The purpose of this memorandum is a comparison of our recent results on the volatility of TEL from Vitol with the data presented by C. C. Clark of Thompson Products, Inc. in their Metallurgical Department Report of March 14, 1949. We have also tried to assess the reliability of their work.

In our work nitrogen was passed through the Vitol solutions so that an equilibrium mixture of nitrogen and vapor was obtained. This represents the maximum concentration of vapor that would be obtained in practice. A gas station attendant inspecting a tank of Vitol would be exposed to vapors of about this concentration. On the other hand their tests with deep layers of liquid in beakers which are placed in a relatively slow stream of air certainly do not simulate either the equilibrium situation above or a typical spill in which the liquid is present as a very thin layer. It is also difficult to postulate the exact nature of the evaporation in their experiments, since the solutions are first rather violently disturbed during the sampling procedure and are then permitted to evaporate slowly from a quiescent surface. This type of evaporation is difficult to interpret for even the simplest case of a one-phase system; our work on the air-evaporation of a TEL-heptane solution under similar circumstances (LTD 44-57, especially pages 12 to 14) suggested that non-equilibrium evaporation of the surface layers may play a most important part in the evaporation mechanism. The presence of the disperse phase of the Vitol further complicates the picture since our work has shown that 12% of the TEL is present in this phase, although it is only 0.2% of the total volume. This phase has almost the same density as the rest of the mixture. Although the real state of affairs may actually be quite different, our observations suggest that the disperse phase was distributed through the Vitol during their evaporation experiments in about the following way: just after the sampling, when the solution had been well mixed, the disperse phase was well scattered throughout; the surface area was thus about 0.2% disperse phase, rich in TEL. As time went on the disperse phase gradually settled, leaving the surface essentially free of the disperse phase and therefore much poorer in TEL. However, at a later stage in the evaporation enough methanol had been evaporated from the Vitol to increase the density of the bulk of the mixture so that the disperse phase was now lighter than the other phase. This caused the disperse phase to rise to the surface and perhaps caused the formation of a continuous film. These considerations emphasize the complex nature of the evaporation phenomena in the Thompson Products tests, and the difficulty of relating these tests to realistic conditions.

Ethyl Results

The recent results obtained here are summarized in Figures 1 and 2 which show the lead-methanol distribution and the concentration of TEL in the

saturated air. The contrast between the evaporation of a leaded gasoline and Vitol is clearly shown in Fig. 1. The TEL evaporates very quickly from the Vitol, leaving an essentially lead-free residue, but the TEL evaporates so slowly from the gasoline that less than 1% has come over when 65% of the gasoline has evaporated and only about 5% when 90% of the gasoline has evaporated. (These results correspond to essentially ideal solution behavior.) This means that the evaporation of leaded gasoline leaves behind a heel which becomes progressively richer in TEL as the evaporation proceeds.

The amount of lead in the saturated air is many times greater for the Vitol in the earlier stages of the evaporation (Fig. 2). The two figures are based on experiments under equilibrium conditions in which the air is completely saturated with the mixtures. For this case, both leaded gasoline and Vitol give an amount of lead in the air far in excess of the toxic limit. However, under more realistic conditions, where the air is only partially saturated, it is still evident that there is about 100 times the probability that the lead content of the air from the evaporation of the Vitol will exceed the toxic limit as compared with the leaded gasoline.

Thompson Products Results

The general pattern of the conclusions from our results on Vitol is confirmed by the data presented in the Thompson Products report. Fig. 1 shows the same rapid removal of TEL from the solution because of the enhanced volatility of TEL from Vitol. Their gasoline results are less easily explained, since they report a considerable amount of TEL evaporation (15%) with much less than 50% of the fuel over. This is so contrary to our experience that we think that their analysis of the unevaporated fuel (3.23 cc. TEL/gal.) may be in error. Our former experiments on the evaporation of leaded gasoline were found to be in accord with the physicochemical laws of the ideal solution. These laws would lead us to expect essentially no evaporation of TEL from the solution in the first 2.5 hours. If this is actually the case, the unevaporated fuel analysis should be 2.76 cc. TEL/gal., and the entire curve would then be in agreement with our past experience. However, it is hardly credible that an error of this size could have been made.

It is of interest to note that not one of their four experiments started with the stated 3 cc. TEL/gal. This is shown in the following table:

TABLE - Initial Lead Content

Experiment	ml. solution[1]	ml. TEL[2]	cc. TEL per gallon[3]
Vitol (a)	435	0.212	1.84
Vitol (b)	450	.262	2.20
Blue Sunoco (a)	433	.370	3.23
Blue Sunoco (b)	450	.375	3.15

1 From their Table 2
2 From their Table 1
3 (3785)(Col. 2)/(Col. 1)

Not only do all the results deviate from 3 cc. per gallon, but the Vitol solutions contain an amount closer to 2 cc. than 3. Since the whole experiment depends on lead analyses such as these, this discrepancy in their statements casts considerable doubt on the validity of their work.

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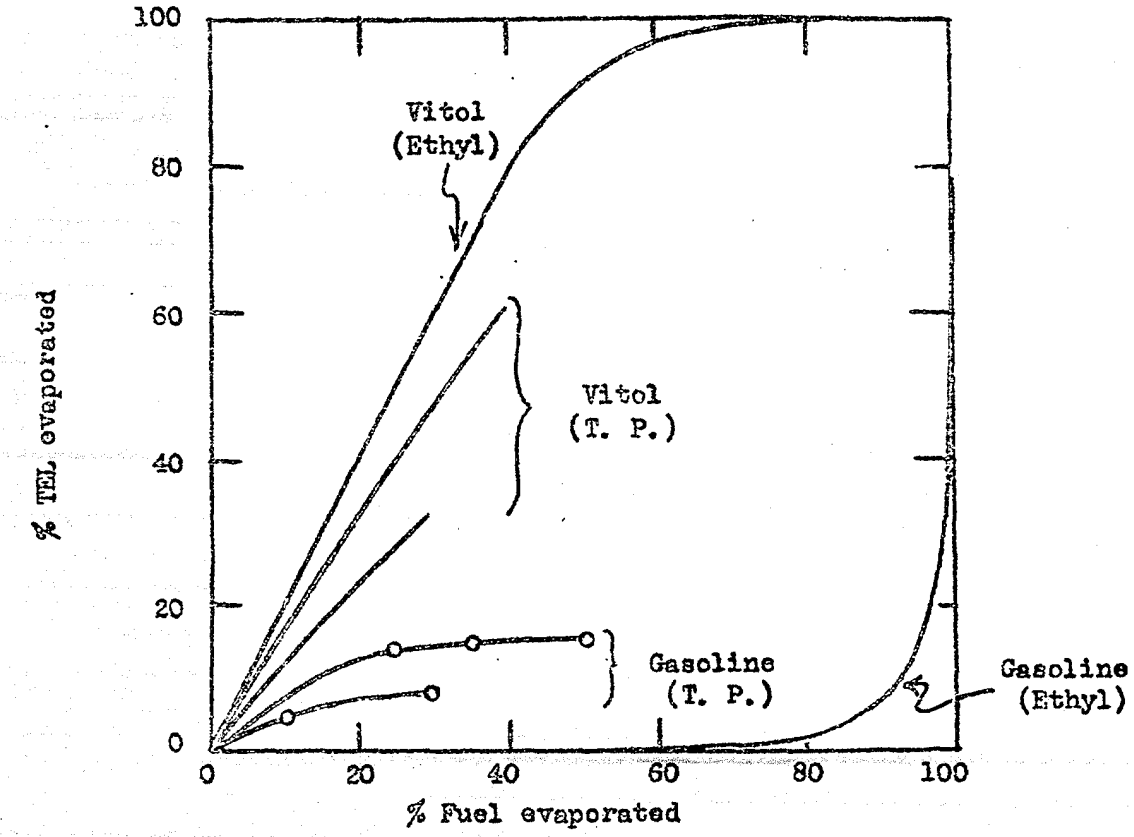

Fig. 1 - Distribution of TEL

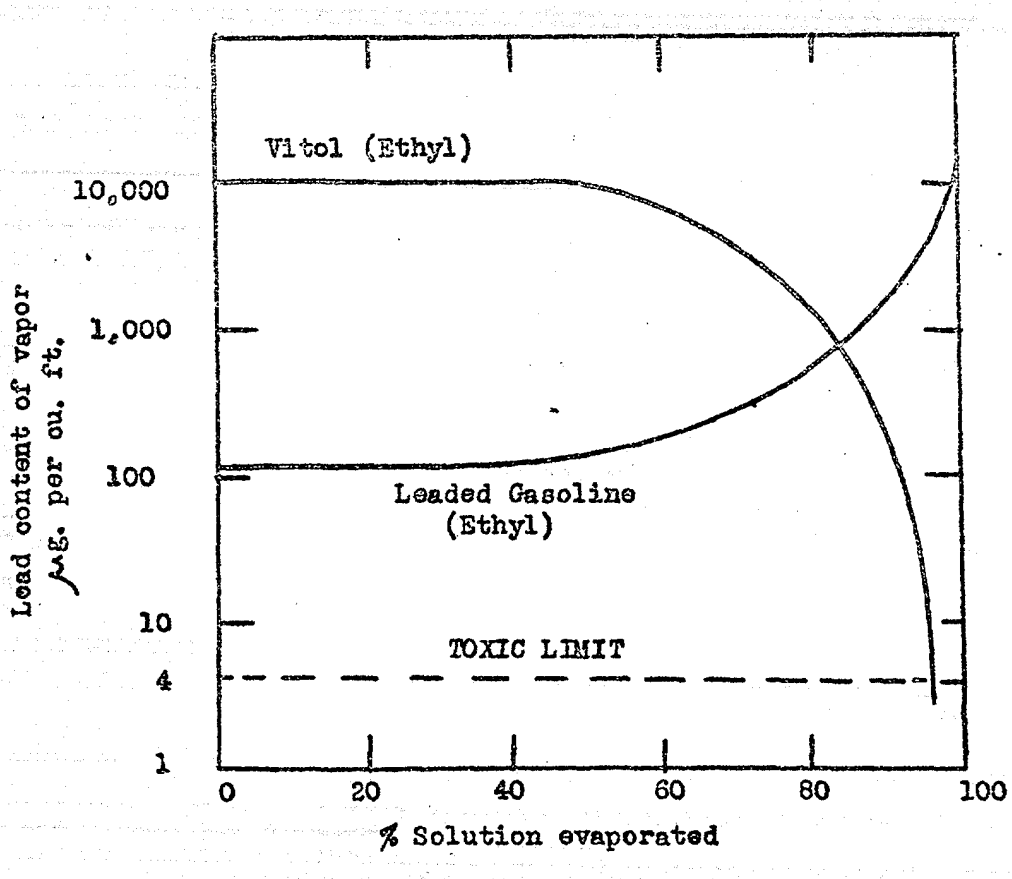

Fig. 2 - Lead Content of Saturated Air