

*See Calingaerts Letter T-3/44
in his file.*

ETHYL CORPORATION

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Chemical Research Laboratory

THE EFFECT OF RERUNNING ON THE TEL AND BROMINE CONTENT OF AVIATION GASOLINE

PURPOSE

To determine the lead and bromine content of the overhead and bottom cuts from the distillation, made by the Socony-Vacuum Company, of a large batch of contaminated aviation gasoline.

SUMMARY

Some 633,000 gal. of finished 100-octane gasoline, nominally containing 4.6 cc. TEL (tetraethyllead) and 3.75 g. bromine per gallon, and having a high gum content, was rerun at below 300°C, taking 96% overhead in two cuts.

The analyses summarized in Table I below show that 26% of the TEL and 95% of the ethylene dibromide was distilled over, and also that the distillation was modified at some stage to give a different proportion of overhead product. A small amount of TEL apparently was lost by decomposition, but 65% of it remained in the 26,000 gal. of bottoms, which thus contained 71 cc. TEL/gal.

The overhead material, with its high bromine-lead ratio, is to be blended with 9 volumes of fresh aviation stock. If Aviation Fluid is then added to make 4.6 cc. TEL/gal., this will give 1.07 theory of bromine in the finished blend, an acceptable amount.

The high TEL content of the bottoms calls for caution in handling, in accordance with the recommendations which have been made by the Safety Department. This has been done by washing out the still with 300,000 gal. of unleaded base stock, reducing the TEL content to 5.60 cc. gal. This material is to be further diluted some 12-fold, and TEL added as needed, to make motor gasoline. One sample of such unfinished material contained 1.14 cc. TEL/gal. of which some 40% was lead from the rerun operation. This sample was accordingly low in halogen content, containing only 60% of the requisite amount. In view of the possible detrimental effect of this, it would seem advisable to add the addition halogen compounds required to make up the deficiency.

INTRODUCTION

On March 31, our safety engineer, Mr. M. I. McCoolley reported to R. L. Goltz that: "The Socony Vacuum refinery at Paulsboro, N. J., was asked by the Government to recondition two tanks of aviation gasoline, 100 octane, containing 4.6 cc. of TEL, that had been

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gasoline contained 30 milligrams of gum and the other contained 68 milligrams of gum, and were turned down as they were above the 6 milligram specification.

"They received 632,940 gallons and recovered overhead 606,394 gallons, by running it through a refined oil still at 40 pounds low pressure steam, and not over 300 degrees temperature. The balance of 25,300 gallons were considered bottoms in the still.

"They put this reconditioned gasoline into two tanks at their refinery. Tank 562 representing 58% of the recovered gasoline contained 0.70 cc. per gallon of TEL, tank 563 representing 42% of recovered contained 2.0 cc. and the bottoms in the still contained 71.0 cc."

It was planned to reblend with new stock in the proportions of 9:1 for the overhead and 400:1 for the bottoms, adding the bottoms to house brand gasoline. For safety in handling the bottoms, the still containing that material was to be considered as a blending tank.

On April 28, Mr. McCoolley reported further that "about 8,000 bbl." of unleaded base stock was circulated through the still into a storage tank; the product, containing "7.6 cc." of TEL per gallon, is used to furnish 25% of the lead requirement in a blend of house brand gasoline.

At our request, samples of the two overhead cuts, the bottoms before and after dilution, and the finished motor gasoline were submitted to this Laboratory and it was decided to determine the distribution of bromine and to confirm the Socony-Vacuum figures for TEL content.

ANALYSIS

Samples from Rerunning Operation

The three samples, our No. M-546, were analyzed as received, being free from sludge: presumably the bottoms sample had been filtered. The overhead cuts had a faint blue color, the bottoms a deep blue. Bromine analyses were made by the sodium biphenyl method (see forthcoming LTD) which should give better than 98% recovery. The results for TEL and bromine are given in Table I.

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TABLE I - ANALYSES OF RERUN MATERIAL

% Recovery calculated for input of 4.6 cc. TEL/gal. in Aviation Fluid

Overhead	Vol.%	Volatility, °F		TEL		Bromine	
		10%	90%	cc./gal.	% Rec.	g./gal.	% Rec.
Overhead							
Tank 562	55.5	130	260	0.80		3.4	
Tank 563	40.3	144	273	1.86		4.2	
Total	95.8			1.25	26.0	3.7	95
Bottoms	4.2*	282	341	70.9	64.7	3.3	3.8
Loss or error	--				9.3		1.4

*By difference.

There were no ammonia-soluble bromine or lead salts in any of the samples, except for a trace of lead in the bottoms sample, 0.5 g. Pb/gal., showing that decomposition products such as triethyllead bromide were absent.

Distillation data are given in Table II. From these as well as the TEL values it is evident that the course of the distillation was changed at some stage in the direction of a higher proportion taken overhead into Tank 563.

TABLE II - DISTILLATION DATA

Sample	Tank 562	Tank 563	Bottoms
Sp. gr.	0.7143	0.7309	0.8236
Distillation			
Initial	97	102	260
10%	130	144	282
50%	196	222	301
90%	260	273	341
Final	310	311	394
Recovery	98.1	98.2	98.0
Residue	0.6	0.7	1.5
Loss	1.3	1.1	0.5

Diluted Still Bottoms and Finished Gasoline

The two samples, our No. M-562, were only analyzed for TEL and halogen, with the results given in Table III.

TABLE III - ANALYSES OF DILUTED SAMPLES

	TEL		Bromine		Chlorine	
	cc./gal.		g./gal.	theories	g./gal.	theories
Diluted bottoms	5.60		0.20	0.04	--	--
Finished gasoline	1.14		.30	.33	0.24	0.57

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DISCUSSION

Rerunning Operation

In calculating the percentage recovery of the TEL and bromine, it was noted that the volumes of rerun material cited above do not balance by over 1000 gal., and that the relative proportions of the two overhead cuts are probably only approximate. Moreover, the discrepancies between the TEL analysis from Socony-Vacuum and from this Laboratory suggest that these cuts were not homogeneous. Also, the exact amount of Fluid in the original is not given. As a result, the calculated recoveries given above in Table I are somewhat approximate.

With this in mind, and in view of the absence of ammonia-soluble bromine salts, it is probable that the recovery of ethylene dibromide was essentially complete. On the other hand, the 9% loss of TEL appears greater than can very well be accounted for by errors in the analysis or the material balance, and decomposition to this extent is not unreasonable in view of the necessarily high temperature and time of heating required for the distillation.

That the distillation operation was changed as the run proceeded is perfectly evident from the volatility data in Table II, as well as from the lead analyses, although Mr. McCoolley was informed that no changes were made. The amount of reflux must have been very small, judging from the percentage of TEL distilled over which is just about that calculated for simple distillation of aviation gasoline. Hence, a very slight change in the reflux could have accounted for the difference between the two overhead cuts.

The distribution of the ethylene dibromide is unexpected, in that its concentration in the bottoms sample, 3.3 g./gal., is nearly as high as in the original, although its boiling point (268°F) is distinctly lower than the average boiling point of the bottoms. However, that result is confirmed by the analysis of the diluted bottoms, which gave 0.20 g./gal. compared with 0.26 g./gal. calculated from the above value.

Reblending Operations

Overhead cuts. - In reblending with 9 parts of new product, it is presumed that addition Aviation Fluid will be added to make up the deficiency in TEL and give 4.6 cc. in the finished blend. This will give a small excess of bromine, 0.07 theory on the average, which is allowable.

Dilution of still bottoms. - The quoted TEL content of 7.6 cc./gal. is presumably a typographical error, and the analytical

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