October 18, 1939

Mr. J. L. Stecher
E. I. du Pont de Nemours & Co. Inc.
Organic Chemicals Division
Wilmington, Delaware

Dear Joe:

You may remember that during my last visit in Deepwater we discussed the problem of the disposal of the sludge which accumulates in tank cars. I am attaching hereto a copy of our report LTD #39-45 covering the investigation of the composition and recovery of such a sludge.

From the point of view of the hazard involved it is clear that steam distillation is much to be preferred to mere dumping of the sludge itself, irrespective of the location of the dump. A second point in favor of the distillation is that it yields a certain amount of recovered fluid which is pretty good except for a slightly excessive bismuth content which, however, can probably be cut down by appropriate ageing on storage. Even if this is impractical, the blending of a small amount of such recovered fluid in regular production would not significantly raise the bismuth content.

According to our calculations based on figures supplied by Mr. Wasserman, we estimate the sludge collected in tank cars to correspond to 0.08% bismuth on the basis of the lead, which figure I understand is above the average bismuth content of your pig lead. Such a situation, of course, is bound to arise under your present practice, which I understand is to dump the steam still residues of the distillation of sludge from Ethyl Fluid or tetraethyllead right into one of your regular sludge pits. This can only lead to a build-up of the bismuth content of your lead in process, the ultimate refining process really taking place in the Fluid tank cars in that the Fluid minus the sludge as dumped out by our customer, contains less bismuth than the average lead in the plant. Such a procedure seems to put an unnecessary burden on the finished material, and I would like to discuss with you the possibility of taking steps to remedy it.

One step would probably consist in ageing the tetraethyllead sufficiently before it is blended into Ethyl Fluid so that its bismuth content will be much lower, probably around 0.01. A second and independent step which would work in the same direction would be to segregate all sludges separated from tetraethyllead and Ethyl Fluid, a procedure which I understand you are following at present as far as filter-bags are concerned, but which you have been unable to follow in the case of steam still residues after the

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distillation of such sludges. I am not sufficiently familiar with the operation of our plants to make concrete suggestions. Possibly a small enclosure could be set aside in one of the sludge pits for the accumulation of such material (which runs about 50% bismuth). If all such material can be segregated in only one location each in Baton Rouge and Deepwater, you might be able to run a special batch from time to time through the sludge drier as suggested by Heuser. Another possibility would probably be the building of a special small sized smelter which would be capable of handling wet sludge.

Very truly yours,

George Calingaert

GC:[illegible]
cc: Dr. G. Edgar
Mr. J. H. Schaefer
Mr. [illegible] Kehoe

Encl.

LTD 39-45
F. J. Dykstra
305-XP-33, 34, 36
9-26-39
Approved by

RECOVERY OF TETRAETHYLLEAD FROM TANK CAR SLUDGE

PURPOSE

To determine the composition of tank car sludge and to develop suitable methods of recovering tetraethyllead from it.

CONCLUSION

1. Tank car sludge is composed roughly of 50% solid bismuth compounds, 30% Ethyl Fluid, 5% lead salts, and 15% kerosene (used to wash the sludge from the tank car).

2. Ethyl Fluid and kerosene can be recovered from this sludge by steam distillation or by extraction with gasoline.

3. The recovered Ethyl Fluid contains 0.77% bismuth, based on lead, which precipitates out on standing. However, this sludge-forming compound can be removed by air-ageing the Fluid and filtering off the precipitate which forms.

DETAILS

According to a letter from Mr. J. H. Schaefer of August 31, 1939, sludge is formed in tank cars used for transporting Ethyl Fluid at the rate of about 50,000 pounds per year from the Deepwater Plant, and this sludge is estimated to contain approximately 25% tetraethyllead which it is desirable to recover because of its value and in order to reduce present hazards of dumping it. The present investigation was undertaken to determine the probable cause of the formation of this sludge and to devise proper methods of disposing of it while at the same time recovering its valuable constituents.

Analysis and distillation. Five samples of 2 lb. 6 oz. (1075 g.) each were secured from the Manufacturing Department on August 11, 1939.

A first sample of this sludge was filtered on a Buchner funnel, giving a small amount of filtrate and fairly wet filter cake. The filtrate was analyzed for lead, and the cake was treated separately. It was first extracted with hexane to remove tetraethyllead, the hexane solution then being washed with concentrated ammonium hydroxide to remove a small amount of the slightly soluble triethyllead halide. This was followed by extraction with benzene to remove the bulk of the triethyllead halide, and the solid residue was freed from solvent. The three extracts were analyzed for lead, and the solid residue was analyzed for lead, bismuth and halogen. A separate sample of the filter cake was subjected to steam distillation to determine the recovery of tetraethyllead by this method. The results of these tests are shown in Table I.

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TABLE I

Analysis of First Tank Car Sludge Sample

Total weight of sample		1,080 grams		
A.	Filtrate		160	
	1. Et_4Pb (by Pb analysis)	86		
	2. Balance - hydrocarbons, etc.	74		
B.	Filter Cake		920	
	Extraction			
	1. Et_4Pb - hexane sol., NH_4OH insol.	178		19.35%
	2. Et_3PbBr - hexane sol., NH_4OH sol.	3.5		
	3. Et_2PbBr_2 - benzene soluble	21		
	4. Dry extracted residue 3.64% Pb 59.27% Bi 3.52% Halogen (as Br)	484		
	5. Balance - hydrocarbons, etc.	233.5		
	Steam Distillation - Et_4Pb (by Pb analysis)			17.13%
Total Et_4Pb (A.1 + B.1)		264 g. 24.4%		

The high bismuth content of the residue after extraction suggested that the tetraethyllead recovered from the tank car sludge might contain an objectionable amount of bismuth. The analysis of the small samples available yielded negative results (because the analytical method was not sufficiently sensitive) and therefore a sample of unfiltered tank car sludge was subjected to steam distillation to obtain a large sample of recovered tetraethyllead.

TABLE II

Steam Distillation of 510 g. Tank Car Sludge

A. Distillation	Composition of Fractions: 1st fraction 4 hrs.	2nd fraction 3 hrs.
Weight	139 g.	29.3 g.
% Pb	27.4	47.5
% Br	24.6	2.0
% Cl	5.0	
Sp. gr. at 20° C.	1.393	1.330

TABLE II (contd)

	Composition of Fractions	
	1st fraction 4 hrs.	2nd fraction 3 hrs.
B. Calculated composition		
Et_4Pb	42.8 wt. %	74.2 wt. %
$C_2H_4Br_2$	28.8	2.4
$C_2H_4Cl_2$	7.0	
Kerosene	21.3	23.4
Sp. gr. - computed from estimated composition	1.397	1.325

C. Overall composition of total distillate

	Wt. gm.	Wt. % of distillate	Wt. % of sludge	Theories of halides for lead present
Et_4Pb	89.9	47.7	17.6	
$C_2H_4Br_2$	46.7	24.8	9.2	0.90
$C_2H_4Cl_2$	11.1	5.9	2.2	0.40
Kerosene	40.7	21.6	8.0	
TOTAL	188.3	100.0	37.0	

As shown in Table II, the rate of recovery tapered off slowly, and it took seven hours to effect approximate quantitative recovery of the volatile lead present. The distillate was analyzed for Pb, Br, and Cl, and its corresponding composition in terms of tetraethyllead, ethylene dibromide, ethylene dichloride and kerosene is also shown in the table.

Sludge Formation. The fluid recovered by filtration, extraction or steam distillation formed a white precipitate immediately upon exposure to air, and analysis of these precipitates showed a large percentage of bismuth. This sludge formation was investigated in the following manner, using the material recovered by steam distillation:

The precipitate present at the conclusion of the steam distillation was filtered off and a sample of the filtrate was bubbled with air for 14 hours and then allowed to stand exposed to air for three days to form more precipitate. The precipitate so formed was filtered off, bubbling with air was continued for another seven hours, and the material was allowed to stand exposed to air for seven days. Analyses of the precipitates, presented in Table III, show that the first aeration treatment precipitated all the sludge-forming bismuth compounds.

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TABLE III

Precipitate formed by aeration of distillate

		wt. gms.	% Bi	% Pb	% Br
1.	Formed during distillation	0.71	46.5	23.0	
2.	2 days aeration, 3 days storage	0.45	24.7	42.1	4.9
3.	1 day further aeration, 7 days storage	0.23	0	61.0	8.2

Total bismuth precipitated from the distillate — 0.23% based on distillate; 0.27% based on lead.

It should be noted here that bubbling tetraethyllead alone with either air or oxygen results in only an extremely slight amount of sludge formation, similar treatment of Ethyl Fluid results in the ready formation of a sludge, while the presence of bismuth compounds results in an extremely rapid formation of a white, voluminous precipitate. An ignition test of a small sample of the white precipitate after being washed with hexanes and dried indicated that it consisted of an organic bismuth oxide.

DISCUSSION OF RESULTS

The recovery by solvent extraction and by steam distillation is in rough agreement with the results reported in Mr. Schaefer's letter of August 31, in which he stated, "A batch of about 2,000 lbs. of tank car sludge analyzing approximately 25% tetraethyllead was distilled in the experimental building, with the recovery of 600 lbs. of distillate analyzing about 80% tetraethyllead." Naturally, the composition will vary from one tank car sludge to another depending upon the amount of solvent used to wash the sludge from the tank car.

It had been anticipated that the sludge might consist largely of Et_3PbBr, in which case it was expected that steam distillation might yield larger amounts of Et_4Pb than were actually present on account of its formation by the well-known redistribution reaction:

$$2\ Et_3PbBr \quad Et_4Pb + Et_2PbBr_2$$

However, the percentage of triethyllead bromide is very small, approximately 2% in the first tank car sludge sample, and the consistency of the sludge is such that steam distillation did not effect 100% recovery of the tetraethyllead present as such. This accounts for the greater yield obtained by solvent extraction than by steam distillation on the filtered sludge from the first tank car sludge sample.

The halogen present in the original sludge as triethyllead halides and lead halides is calculated as bromine because previous experience has shown that the chlorine content is negligible. The results are somewhat approximate because of the difficulty of securing representative samples of this muddy sludge. From the analytical data presented in Table II, it was possible to reconstruct the composition of the steam distillate. The calculated density of a mixture having the reconstructed composition was in very good agreement with the observed density of the steam distillate. It will be observed that the more volatile constituents were removed by steam distillation during the first four hours, while the recovery of the tetraethyllead and kerosene were probably not complete even after seven hours of steam distillation. The theories of bromine and chlorine present in the recovered fluid, 0.90 and 0.40, differ from those of the original fluid, 0.70 and 0.65, because the ethylene dichloride is the most volatile constituent and partially evaporated from the tank car before the sludge was removed, and the tetraethyllead was not completely recovered because of incomplete steam distillation and decomposition.

On the basis of the above, the material recovered by steam distillation of tank car sludge appears to be close enough in composition to a slightly diluted Ethyl Fluid to make it permissible to work it off in small percentages in regular production Fluid. Its slightly high bismuth content, however, makes it advisable to age the material before blending until the precipitation of bismuth has subsided.

The composition of sludge shows that its formation is due to the presence of bismuth in the original tetraethyllead. Taking the Manufacturing Department's estimate of 80 lb. sludge per tank car, of which 27% is bismuth, there must be 23 lb. of bismuth precipitated per tank car, corresponding to about 0.05% of the lead. The chief problem then appears to be to prevent the presence of this bismuth in the Ethyl Fluid. Its origin is undoubtedly the small amount of bismuth present as an impurity in the pig lead. In addition to keeping the specifications as low as possible, systematic steps should be taken to remove the bismuth from the product. All the sludge collected from filters, whether or not they are steam distilled, should be smelted in a separate furnace from the lead recovery furnace, and the slag or metal recovered should be disposed of. The fact that the tank car sludge contains a lot of bismuth and very little halogen, and the further fact that the aeration precipitates the bismuth preferentially shows that the halogen is not responsible for this precipitation, and therefore it should be possible to eliminate the trouble by proper ageing of the tetraethyllead before blending.

In addition, the high bismuth content of the sludge may make it worth while recovering for the value of the bismuth itself.

P. J. Dykstra
O. E. Kurt
G. Calingaert
10-10-39

AJK

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