ETHYL GASOLINE CORPORATION

RESEARCH LABORATORIES

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DETROIT, MICHIGAN

INTER-OFFICE CORRESPONDENCE

September 12, 1938.

Dr. Willard F. Machle
College of Medicine
University of Cincinnati
Cincinnati, Ohio

Dear Bill:

I am sending you herewith a copy of our report LTD #38-46 covering the steam distillation of some of your sludges. I will be interested to hear from you how our results compare with yours on these same samples.

We are continuing our systematic studies on the stability of lead compounds, concentrating at present on $PbEt_3OH$ and $PbEt_2(OH)_2$.

I am looking forward to your promised visit to discuss some of these matters.

Very truly yours,

George Calingaert

GC:AMC

LTD #38-46
277.XP.1,2,4,5,6,7,
8,9 and 10.
F. J. Dykstra
Sept. 7, 1938.

LEAD CONTENT OF SLUDGES AND WATER BOTTOMS FROM BLENDING AND STORAGE TANKS USED FOR ETHYL GASOLINE

PURPOSE

To determine the lead content of sludges and water bottom samples from blending and storage tanks used for Ethyl Gasoline. Particular emphasis was placed upon the volatile lead, i.e., the $PbEt_4$ already present or formed by steaming of the sludge.

CONCLUSIONS

1. The ten water bottom samples from both blending and storage tanks were with two exceptions, free of soluble lead compounds. The two samples with lead each had only 7 mg. Pb per 100 cc. of solution.

2. The eight sludges from both blending and storage tanks had with two exceptions only small amounts (1%-3%) of lead in them, and only a small part of that could be removed by steaming.

3. Sludges with high lead content, but with or without volatile lead are possible. One sludge contained on water-free basis, approximately 20% lead, of which about 4% could be removed by nine hours of steaming. Another sludge contained 67% lead, of which only a trace was volatile lead.

METHOD

The water bottom samples were simply filtered and analyzed for lead.

The sludges usually containing gasoline, water, rust and solid matter were placed in a distilling flask and enough water added to bring the liquid volume to approximately 300 cc.

The lighter gasoline fractions were first taken off from the side tube of the distilling flask and condensed in ice. The side tube was then closed and all of the vapors refluxed using a water condenser to return the condensate to an ice-cooled trap which separated the water from the oil layer, and returned the water only to the boiler flask. The portion of the trap where the oil layer collected was graduated, enabling readings to be taken. If more than one fraction of oil was desired, the refluxing was stopped long enough to pipette out the oil layer already formed.

After equilibrium was established, the system with a CO_2 cooled condenser and a gas burette in the line was closed. Atmospheric pressure in the system was maintained and the gas, non-condensable in CO_2 ice was measured in the burette.

The refluxing was continued until no more oil or $PbEt_4$ layer was formed. This time varied from three to nine hours, but was usually about six hours.

The products then submitted for lead analysis were the following:

1st - Water-white gasoline fraction.

2nd - Yellow oil layer.

3rd - Filtered Water solution from the boiler flask.

4th - The solid residue, dried over activated aluminum until moderately dry.

DESCRIPTION OF SAMPLES USED

277-XP-1 - Sample 37A-2658.
Bottom sludge from Esso Storage Tank, #9 Standard Oil of N.J., Rockaway, N.J. Bulk Plant. Storage only, never previously cleaned. March 11, 1937.

277-XP-2 - Sample 37A - 3064.
Bottom sludge from the Texas Co., Claymont, Del. Tank #1362 (Blending Tank).

277-XP-4 - Sample 37A - 1713.
Bottom sludge from Standard Oil ofN.J., Rockaway, N.J. Bulk Plant. Tank #4. Essolene (storage only).

277-XP-5 - Sample 37A - 3678.
Dry sludge from Atlantic Refining Co., Franklin, Pa., Tank #340.

277-XP-6 - Sample 37A - 3001.
Bottom sludge from Richfield Oil Corp. of N.Y., Bayonne, N.J. torminal. Blending Tank #2.

277-XP-7 - Sample 37A - 3681.
Bottom sludge Texas Co., Mobile, Ala. Tank #7032.

277-XP-8 - Sample 37A - 3100.
Texas Co., Port Arthur, Texas Refinery. Tank #1086.

277-XP-9 - Sample 37A - 3014.
Side Wall scale from Standard Oil, New Jersey, Paterson, N.J. Bulk Plant. Used for storage only. Tank #1.

277-XP-10 - Water bottom samples:
#1 - Bradford Oil Refining Co., Bradford, Pa. Tank #77, Nov. 12, 1936.
#2 - Sinclair Refining Co., Houston, Texas, Tank #424, Nov. 25, 1936.
#3 - Standard Oil Co. of N.J., Canton Ref., Baltimore, Md. Tank #225. Seven blends since tank cleaned. 5,248 lbs. T.E.L. "Q" Blend, Oct. 26, 1936.
#4 - Cities Service Ref. Co., East Braintree, Mass. Tank #23, Nov. 12, 1936
#5 - Humble Oil & Ref. Co., Baytown, Tex. Blending Tank #716, Nov. 25, 1936.
#6 - Socony-Vacuum Oil Co., Portland, Maine, Tank #32, Nov. 20, 1936.
#7 - The Texas Co., Terminal Baltimore, Md. Tank #7094. Seven "Q" Blends, 4,448 lbs. T.E.L., Oct. 28, 1936.

#8 - Continental Oil Co., Ref. Baltimore, Md., Tank #154, 56 Blends, 100,650 lbs. T.E.L. Oct. 28, 1936.
#9 - Mid-Continent Pet. Corp., West Tulsa, Okla. Tank #313, Nov. 17, 1936.
#10 - Colonial Beacon Oil Co., Everett, Mass. Tank #118, Nov. 18, 1936.

RESULTS

STEAMING OF TANK SLUDGES

Experiment 277-XP-	Sludge (Dry basis) Appr. Gr.	Gasoline Gas Evolved cc.	Gasoline Vol. cc.	Gasoline Pb Content gr.	Oil Vol. cc.	Oil Pb Content gr.	Water Pb Content gr.	Residue Pb Content %
1	45	70	9	0.756	5	0.938	0.233	18.5
2	15	7	7	0.066	1	0.092	0.061	0.9
4	29	16	5	0.004	1.3	0.002	0.027	3.1
5	51	49	nil		drop		0.0003	3.1
6	3	5	4	0.002	0.8	nil	0.023	2.8
7	12	10	68	0.48	1.2	0.08	0.012	3.0
8	42	10	52	trace	2.2	trace	0.044	67.3
9	26	13	nil		drop		0.019	3.2

277-XP-10 Analysis of Water Bottom Samples (100 ccs.)

#1	Blank Pb
2	" "
3	" "
4	" "
5	" "
6	" "
7	" "
8	0.0067 g. Pb/100 cc.
9	Blank Pb
10	0.0075 g. Pb/100 cc.

DISCUSSION OF RESULTS

Gas evolution, which usually accompanies the steaming of the pure lead alkyl halides was not an infallible indication of these compounds. Experiment 277-XP-5 with no volatile lead and hardly any water soluble lead gave a large amount of gas. At least volatile lead and water soluble lead compounds were not formed by the changes which produced the gas evolution.

The 67% Pb residue of 277-XP-8 was black, suggesting strongly precipitated PbS. When some of this residue was dropped in dilute H_2SO_4, H_2S gas was evolved, a test duplicated on pure PbS.

The type of sludge or water bottom sample produced is likely dependent upon the cleaning history of the tank. For instance, the storage tank which had the volatile lead producing sludge of 277-XP-1 had never been cleaned, and one of the water bottom samples, 277-XP-10 #8 with soluble lead had come from a tank in which 56 blends using 100,650 lbs. of T.E.L. had been made.

The tank records of the water bottom and sludges tested are very incomplete, but designated blending tanks did not produce sludges with high lead content, or water bottoms with more than a small amount of soluble lead in them.

The storage tank appears to be a most likely source of dangerous lead containing sludges.

F. J. Dykstra

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AMC