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ETHYL GASOLINE CORPORATION

RESEARCH LABORATORIES

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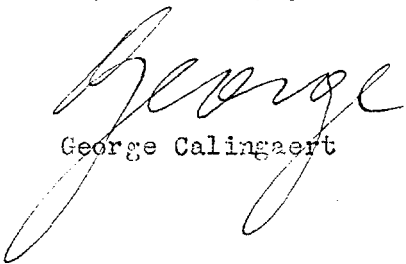
June 26, 1939

Dr. Robert A. Kehoe

Dear Bob:

I am sending you herewith a copy of our report LTD #39-27 entitled "Sludge Formation in Ethyl Gasoline". This work was carried out at the suggestion of Dr. Machle to get some idea of the amount and nature of the sludge formed in Ethyl Gasoline. Somewhat to our surprise the sludge formation was decidedly small and most of it remained in the gasoline. Insofar as this work is significant, I would say that we would not expect much lead sludge in Ethyl Gasoline storage tanks unless the tank has been spiked. Your comments will be appreciated.

Very sincerely yours,


George Calingaert

GC:AMC
Encl.

KE 0022258

SLUDGE FORMATION IN ETHYL GASOLINE

PURPOSE:

To study the formation and nature of sludge produced in Ethyl gasoline during its storage in vented mild steel tanks.

CONCLUSION:

Seventeen months storage of Ethyl gasoline (containing 3.12 gm. Pb/gal. added as 70-45 Ethyl fluid) in a 55 gallon vented, half-filled steel drum produced a decomposition of 3.1% of the original tetraethyl lead with 74% of the decomposed tetraethyl lead soluble in the gasoline and the remaining 26% present in the sludge. *85.6 gm Pb in*
0.81%

25 gms. (dry basis) sludge had formed, of which only 3% was lead and the remainder was rust. Half of the lead in the sludge was organic and the other half inorganic lead compounds. *1 1/2 % org. Pb in sludge*

Rust was found in a depression on the bottom of the drum but the sides were free of rust. Only traces of water had condensed in the drum.

METHOD:

Ethyl gasoline was made by mixing 235 cc. Red "44" (70-45) Ethyl fluid with 50 gallons of White Red Crown winter grade gasoline in the blending tanks for forty minutes. This gasoline was then pumped into a new gasoline-rinsed 55 gallon mild steel drum. The filled drum in ^{an}upright position and with ^{the}bungs moderately tight was left in the storage shed at the Milwaukee laboratory from January 7, 1938 until February 10, 1938. The drum was then sent out to the Eight-mile laboratory where it was stored outside in the open in an upright position from February 10, 1938 to May 31, 1939. Approximately 22 gal. of gasoline was removed and a small copper tube vent pipe installed on February 10, 1938. The drum was shaken at irregular intervals, usually daily.

Samples of the gasoline were removed for lead analysis at the end of 1, 4, 7, 10 and 17 months. The last three samples were also extracted with 20% NH_4OH to determine the amount of lead alkyl halides in the gasoline.

About 22 gallons of gasoline was left at the end of the experiment. It was removed and the sludge and rust were rubbed loose and rinsed out with gasoline and 2% NH_4OH . All of the gasoline was filtered and the sludge which was collected was then dried in a vacuum dessicator, weighed and analyzed. The 2% NH_4OH rinse was also analyzed for lead to determine approximately the amount of sludge which had not been removed from the drum but from which the NH_4OH had extracted the organic lead.

RESULTS:

Lead Content of Gasoline - g./gal.

<u>Time - Mo.</u>	<u>Total Pb</u>	<u>Pb sol. in 29% NH₄OH</u>
0	3.12	
1	3.20	
4	3.27	
7	3.75	0.049
10	3.84	0.051
17	4.46	0.094

Sludge Analysis

Total sludge (calc'd. from NH ₄ OH rinse)	25 gm.
Sludge removed from drum (dry basis)	7.88 "

Analysis of dried sludge

Total lead	3.01%
Soluble in NH ₄ Ac solution	1.93%
Soluble in 2% NH ₄ OH solution	1.72% -

Steel Drum Inspection

There was little water in the residue taken from the drum. The residue or sludge consisted mostly of scaly pieces of rust, which had been scraped from the bottom of the drum. The sides of the drum were in perfect condition, the only rust being in the depression in the bottom of the drum.

DISCUSSION OF RESULTS:

The total lead concentration in the gasoline increased from 3.12 to 4.46 gm. Pb/gal. because of the evaporation of the lighter ends from the gasoline. The lead alkyl compounds (bromides, chlorides, carbonates and hydroxides), soluble in the gasoline but extractible by the NH₄OH, increased steadily until they reached 2% of the total lead due to the reaction of tetraethyl lead with the halogen carriers in the Ethyl fluid (ethylene dibromide and ethylene dichloride) and their decomposition products.

The sludge, consisting mostly of rust, contained 3% Pb, about half of which was inorganic and the other half organic lead compounds, insoluble in gasoline ((Et₃Pb)₂CO₃, etc.). Since neither ammonium acetate nor ammonium hydroxide are perfect solvents for inorganic and organic lead compounds, respectively, they probably give only an approximation. It is interesting to note that of the 3.1% of the original tetraethyl lead which had decomposed, 74% of the product was soluble in gasoline and 26% was found in the sludge.

Breathing of the drum, due to alternate heating and cooling, introduced sufficient water to rust the bottom of the drum moderately. The heating and cooling were accentuated because the drum was painted black on the outside and exposed to sunlight for part of the day. It was well ventilated by means of a copper tube. In view of previous complaints, it is interesting to note the absence of rust on the sides of the drum exposed to air above the gasoline.

F. J. Dykstra

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6-14-39

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