ETHYL GASOLINE CORPORATION

MANUFACTURING AND TRAFFIC DEPARTMENT

INTER-OFFICE CORRESPONDENCE

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May 11, 1938

Mr. J. H. Schaefer

Dear John:

We are attaching letter of April 28 from Oscar Lewis to yourself relative to the steaming experiment of Mr. Ball. Our analytical results on the samples forwarded by Ball are as follows:

Sample No.	Color	Total Lead Calculated as T.E.L. (cc. per gallon)	Total Lead Calculated as % Pb.	Total Lead Calculated as % T.E.L.
ST-1	(H_2O portion)		Trace only. Less than 0.0005% (No Pb Found)	
ST-1	(Solid portion)			
ST-2	115%	2.79	0.107%	
ST-3	140	3.22	0.121	
ST-4	160	3.51	0.129	
ST-5	175	3.17	0.116	
ST-6	-	3.65	0.132	
ST-7	220	3.53	0.124	
ST-8	290	3.91	0.139	
ST-9	350	6.84	0.24	
ST-10	-	4.25	0.145	
ST-11	350	3.91	0.126	
ST-12	(H_2O portion)		0.016 —	0.025%
ST-12	(Resinous portion)		0.066	0.104
ST-13	(H_2O portion)		None —	None
ST-13	(Solid portion)		0.0043	0.0067

Samples ST-1 and ST-13 each consisted of a solid portion containing iron scale and a gritty or sandy substance and a water layer above the solid matter. The water was separated from the solid by filtration and each portion tested for lead.

Sample ST-12 contained a resinous or gummy layer with a water layer above. These were also separated and each tested for lead.

In commenting on the analytical results, it is our opinion that Sample ST-9 shows probably too high a figure for lead content but that all other results are within reason. Not much value can be placed in the color strengths since here we run into increases in color due to concentration during steaming and also show color deterioration due to prolonged application of heat. Otherwise, we feel that all analytical figures are self-explanatory.

The report of experimental procedure and the analytical results have been discussed with both Colvin and Biehle and we are including the consensus of our opinions in commenting on this subject. First, the quantity of five gallons of gasoline in a 55-gallon drum seems quite proper since this corresponds to three square feet of refluxing surface per gallon, very nearly the same surface per gallon as found in a standard 60' x 40' (20,000 barrel) refinery tank when there are two inches of gasoline in the bottom. The five-gallon gasoline content also corresponds fairly closely with two inches in a 20,000-barrel tank on the basis of area exposed. For example, in the tank, there were 0.77 square feet of gasoline exposed per gallon, whereas in a 20,000-barrel tank, a 2-inch depth corresponds to an 0.82 square-foot exposure per gallon.

However, two items in the report indicate that the quantity of steam introduced was entirely too great for parallel comparisons. The temperature of 140° was reached in between two and three hours, whereas at the refinery, twenty-four to thirty-six hours are required before reaching that temperature, the theoretical goal. In this test the maximum ran up to 170° for over one hundred hours. These temperatures are Fahrenheit.

Furthermore, the steam condensate amounted to one gallon per hour or in total, twice the content of the experimental tank. To have been consistent with refinery experience, total condensate should not have exceeded ten gallons, basing the quantities on comparable units of refluxing surface.

The one experience in the test which seems out of line with refinery experience is why it took longer to strip out the gasoline than is normal for a tank steaming when using steam quantities so much greater than normal. The explanation may be due to the strong draft or chimney effect venting refinery tanks, which effect is virtually non-existent in a small container.

The statement is made in the report that lead in draw-off water is probably negligible due to the very slight solubility. This does not necessarily follow since lead might be present in suspended or emulsified form in sufficient quantities to affect results, particularly considering the larger than normal ratio of draw-off water to gasoline.

If the reflux ratio in the tank has any relation to the removal of lead by steaming, then the small scale experiment is not comparable to large tank steaming. The ratio of unwetted drum area to free drum volume is almost twenty-five times the same ratio for a 60' x 40' tank. The effect upon refluxing is shown by the fact that in the field the condensate amounts to about three times the volume of the gasoline, while in the small scale experiment, even in the first forty hours, the ratio of condensate to original gasoline was 8:1.

As has been borne out by the analytical results, it is reasonable to suppose that the concentration of lead in the residual gasoline increases as the steaming progresses. Therefore, considerable lead will be distilled in the latter stages of the steaming. In the experiment, the latter stage might be considered the period from forty hours on, when the last 10% of gasoline was distilled. During the last sixty-five hours, approximately sixty-five gallons of condensed steam refluxed into the tank and must have carried quite a bit of the lead with it. The layer of gasoline during the period was not over one-quarter inch in thickness and therefore, re-absorption of lead by the gasoline must have been lower than at first. From these considerations it would not be surprising if a large amount of suspended tetraethyl lead left the drum with the sixty-five gallons of draw-off water.

Finally, in order to interpret the results more intelligently, it would be preferable to retain a material balance during the course of the experiment. In this way it might have been possible to check the results.

There are several factors to be considered in interpreting the results. First, let us assume that the sample of sludge submitted was representative. We estimate the total sand used up to a three-inch level to be equal to 0.4 cubic feet, with an estimated weight of forty-eight pounds at 120 pounds per cubic foot. The lead present in this weight of sludge, as tetraethyl lead, is 1.5 grams based on the 0.0067% of tetraethyl lead for the solid portion of ST-13 and calculated from the assumptions just made. The resinous portion, which analyzed at 0.104% tetraethyl lead, shows a total residue of 0.2 grams as tetraethyl lead based on the 1% of original volume as the residue, and the same gravity as for water. The total residue of tetraethyl lead found in the container is therefore equal to somewhat less than 10% of the original weight of twenty-three grams of tetraethyl lead present.

Thus, it is safe to assume that in the steaming operation at a refinery, at least 10% of the quantity of tetraethyl lead present in the gasoline layer will remain after completion of the steaming and that in all probability the lead residue will exceed this figure.

We are attaching several extra copies of this report for your convenience in the event that you find it advisable to distribute it in its present form.

Yours very truly,

A. P. Stover

Boston, Mass.

STEAM TEST

I. General

In preparing gasoline storage tanks for cleaning, the quickest method in driving out vapors and the remaining gasoline is to steam the tank for at least forty eight hours. The question has arisen as to what happens when leaded gasoline tanks are steamed. A test on a small scale was carried out to bring to light some preliminary data on this subject.

II. Purpose

A. To determine whether or not lead is driven into the remaining gasoline as successive fractions are steamed off in a leaded gasoline tank.

B. To determine whether lead is driven into sludge during this process.

III. Description of test

A. Equipment used -

1 - 55 gallon drum
1 - 300 - 400°F thermometer
Steam connections at 150 lbs. per square inch pressure
Iron rust and scale used as "sludge"
A 12" x 1" rusty iron pipe partially submerged in gasoline and water corresponding to a position of a swing arm.
Water draw off bottles
Sample collecting bottles

B. Preparation.

The drum (hereafter referred to as tank) was placed in a horizontal position with a 2" hole in the top, and a 2" hole cut in the side 6" from the bottom of the tank. At the other end of the tank an 8" removable cover was held in place by stud bolts to assist in sludge removal at the conclusion of the test. A steam jet from a $\frac{1}{8}$" line was connected at the 2" hole at the end of the tank, and a $\frac{1}{4}$" steam line was placed in the top man hole. These were controlled by separate valves. A $\frac{1}{2}$" water draw off was placed 3" from the bottom of the tank on the same end of the 2" hole. Iron rust, scale, sand and water were then placed in the tank until the water level reached the height of the draw-off. A "sludge" sample was then taken.

It should be explained here, that this test was carried out on a small scale for two reasons. We had no appropriation to work with so therefore could provide no elaborate set up such as a large tank, scales, etc. Secondly, we felt closer control could be kept over a small operation such as this one.

On this basis, we used five gallons of Ethyl gasoline in this tank. As we desired to take a sample as each 10% was driven off, we first calibrated the 10% points on a measuring rod with water. The gasoline was then placed in the tank, and the readings checked for a full 100%. The thickness of the level of the gasoline layer on the top of the water was about 2½ inches, and brought the level of the entire contents of the tank ½" below the opening in the end where the steam was introduced. In discussing tank cleaning with various plant operators, we have found that the layer of gasoline on top of water will sometimes run between 1 and 3 inches. We do not maintain that 2½ inches is an average, but we still feel it is within limits of actual practice.

According to the A.P.I. figures, tank steaming is normally run between the temperatures 140 and 170° F. This represents from 20% - 40% steam saturation. This saturation is reported to be satisfactory to make combustible mixtures safe. In keeping with general practice, the temperatures throughout this test were run between these limits. The steam was turned on thru the top man hole, and gradually worked up to 135°F. We introduced steam thru the top in order to effect a smothering action on the vapors in the tank. This is common practice at the beginning of steaming a tank, and this procedure was followed until about 30% was steamed off.

As the tank was steamed, water formed by the condensation raised the level of the water bottom so as to throw off any readings we might get by sticking the tank. It was necessary therefore to draw off any accumulated water thru the tap provided for this purpose. By drawing the water to this level, we reached the zero point on our calibration or measuring rod, and readily determined how much gasoline had been steamed off. The lead solubility in water being extremely low, we believed any water insoluble products would go directly to the bottom of the tank. Inasmuch as we were primarily trying to determine whether or not the lead content of the residual gasoline was increasing, we felt that drawing off water would have little or no effect on the soluble lead in the gasoline. Sampling was carried out thru the same draw off.

This same method of determining the fractions steamed off and sampling was followed throughout the test. We tried to sample at each 10% point, but this was found to be impossible.

The following schedule gives sample identification (St. for steam test) along with temperatures at the time sampling was taking place.

Sample No.	Temperature	Identification
St. 1	---	Sludge before test
St. 2	---	Cities Serv. Ethyl before test
St. 3	135°	After first 10% steamed off
St. 4	117	25%
St. 5	130	30%
St. 6	140	40%
St. 7	142	50%
St. 8	140	60%

Sample No.	Temperature	Identification
St. 9	160°	80%
St. 10	170	90%
St. 11	170	95%
St. 12	170	Residue on water bottom
St. 13	---	Sludge after test

The temperature was lowered to approximately 120°F after the first 10% was taken off, as it was felt the test was running too rapidly. Even though we did lower the temperature the next 10% point was not hit, and we had to take a sample after 25% of the gasoline had been steamed off. We also took a sample at the 30% point. From then on, we hit the 10% points fairly regulatly, excepting the 70% point which came off during the night.

Steaming was not continuous until after the 50% point had been reached, as the fractions were coming at too frequent intervals to allow running over night. Here, a question may be raised as to whether some variable might have been introduced by shutting down from time to time, instead of running a continuous test. We know that when the steam is shut down, the reaction slows down due to lower temperatures, and also that more water is condensed into the bottom of the tank. Aside from this, we cannot see where shutting down would interfere with the purpose of the test. Incidentally, both man holes were closed when the test was shut down.

The following gives a brief log of the test.

Accumulated Steaming Time	Time		Occurrence
0	Tues. Mar. 29,	2:00 PM	Test started
15 minutes		2:15 PM	First 10% off
45 "		2:45 PM	First 25% off
1 hr 45 "		4:00 PM	First 30% off
2 " 30 "		4:45 PM	Steam off
2 " 30 "	Wed. Mar. 30,	10:00 AM	Steam on (Rag plugging man hold saturated with gasoline)
3 hr 30 minutes		11:00 AM	First 40% off
8 " 45 "		4:15 PM	First 50% off
9 " 30 "		4:45 PM	Steam off
9 " 30 "	Thurs.Mar. 31		Steam on (continuous steaming)
16 hr. 30 minutes	Thurs.Mar. 31	4:45 PM	First 60% off
34 hr. 15 "	Fri. Apr. 1	10:30 AM	First 80% off
40 " 30 "		4:45 PM	First 90% off
57 " 30 "	Sat. April 2,	11:00 AM	First 95% off
105 hrs. flat	Mon. April 4,	11:00 AM	Steam off

As can be noted from this log, although the tank was steamed for 105 hrs, over 95% of the gasoline was removed in 59 hours or approximately one half this time. The residue was a viscous substance - about the consistency of petroleum jelly. It is estimated this residue, remaining after 105 hours steaming, represented about 1% of the total volume of gasoline put in the tank.

IV. Comments

Inasmuch as the steam test was carried on in a 55 gallon drum, it is believed this could be used as a basic unit in determining larger tests. For example, it was found that approximately one gallon of water condensed every hour at 20% steam saturation. If a test should be made on a larger tank - by knowing the size of this tank - the condensation of water could be determined by multiplying the size in barrels by one gallon per hour.

It is believed any tank should be steamed at least forty eight hours to free the tank of vapors, if steaming alone is to be depended upon.

H. C. Ball