

9th November, 1938.

T.R.A. Bevan, Esq.,
Ethyl Export Corpn.,
Thames House.

Antiknock Fluid - Belgium

Dear Mr. Bevan,

In confirmation of our telephone conversation, I am attaching hereto a complete report of the investigation which has been made into the "antiknock fluid" received from Belgium.

You will note from the summary ^{that} this material, when added to a gasoline of 65 octane number in the proportion of 5 ccs. per U.S. gallon produced a rise of 5 octane numbers; the antiknock effect appears to be due to a volatile lead compound, probably tetraethyl lead, of which about 13% is present.

The fluid appears to be a mixture of wood tar with tetraethyl lead, ethylene dibromide and a very small proportion of ether, and is itself of dark brown colour, containing suspended matter. On mixing with gasoline it gives a cloudy liquid. The material as received also contained a small proportion of iron rust, due apparently to corrosion of the container by the fluid.

You will note that the analysis of this new sample differs from that of the former sample which was tested, in that the present sample does possess an antiknock value, but that this is due to tetraethyl lead not present in the former sample; furthermore the composition of the material appears to have been changed in that no alcohols are present.

It would be somewhat difficult to establish whether the lead present in the fluid has been added as T.E.L. or ethyl fluid, but from a review of the analytical figures we feel that it is more probable that it has been added in the form of tetraethyl lead, since there is no indication, for example, of the presence of ethylene dichloride which should be present if ethyl fluid were used to obtain the antiknock effect.

Yours very truly,

RE 0013480

N17451

Sample of alleged "Anti-knock fluid" ex

The fluid has been examined as to its antiknock properties, and, in concentration of 5 ml. per U.S. gallon, has been found to raise the octane number of standard 65 octane spirit to 70.5

The following elements were shown to be present - carbon, hydrogen, (oxygen), nitrogen, chlorine, lead, and iron.

The substance was reddish-brown in colour, having an odour of pyridine bases, and containing a quantity of crystalline material in suspension. On filtration, followed by washing of the residue with industrial methylated spirits, colourless needles were obtained which appeared to be the hydrochloride of a secondary or tertiary organic base.

1% of the sample was soluble in brine; the extract, however, contained no ethyl alcohol. 12% was soluble in hydrochloric acid representing the bases present and 4% was soluble in caustic soda solution representing the proportion of acids present.

The following figures represent the results of the I.P. distillation test (fuming began at 160°C and a crystalline non-volatile substance was separated) :-

<u>Temperature</u>	<u>Percentage</u>
I.B.Pt. 75°C	
80 °C	1.0%
90	1.5
100	2.0
110	3.0
120	4.5
130	7.5
140	18.0
150	27.0
160	34.0
170	40.0
180	44.0
190	48.0
200	49.0
210	51.0
220	54.0
230	58.0
240	65.0
250	74.0
260	82.5

F.B.Pt. 264°C

Recovery 88%

The filtered sample was submitted to fractionisation in vacuo. The results of tests upon the various fractions are summarised in the next Table.

Temp. Range.	Lead Content	Antiknock prop. in conc. 3 mls. per U.S. gallon	Gravity	Remarks.
35-40°C	nil	nil		ethereal odour
120-125°C	nil	nil	1.970	odour resembling chloroform
60-80°C (6 mms.)	nil	nil		
80-100°C (6 mms.)	nil	nil	0.9805	
100-120°C (6 mms.)	nil	nil	1.139	
120-135°C (6 mms.)	nil	nil	1.184	
Residue	present			

The residue was insoluble in spirit; on extraction with hot water the solution gave reaction for lead and chloride.

It seemed, therefore, that the lead compound present in the original fluid underwent decomposition under the conditions of distillation with the separation of lead chloride.

The lead content of the fluid was found to be 8.43% which would correspond to a tetraethyl lead content of 13.11%.

In order to minimise decomposition a rapid distillation of the sample was carried out using the I.P. apparatus. A 30% fraction distilling below 154°C was taken off and both that and the residue were examined as to their antiknock properties. The former, in concentration of 3 ml./U.S. gallon raised the octane number of 65 octane spirit to 67; the latter to 70. Both fractions contained lead.

In an endeavour to prevent decomposition the sample (100 ccs.) was filtered, washed, with hydrochloric acid, water, caustic soda, and filtered through dry filter paper. The dry filtrate was submitted to fractionisation in vacuo. No separation of lead chloride or fuming occurred, the reactive halogen compound having been removed. Results are summarised in the following table :-

<u>Distillation range</u>	<u>Volume</u>	<u>Lead Content</u>	<u>Gravity</u>	<u>Remarks</u>
35-135	25 ml.	positive	2.043	
35-90 (6 mm.)	19 cc.	positive	1.604	
90-110 (6 mm.)	25 cc.	positive	1.228	
90-110 (2 mm.)	13 cc.	negative	1.263	
Residue	slight			fluid

The lead content of the 35-90 (6 mm.) fraction was found to be 20.4% corresponding to a tetraethyl lead content of 31.9%. In concentration of 3 ml./U.S. gallon, the octane number of 65 octane spirit was raised to 75.0.

150-1624
22-40C
10mb.
MARY

The fluid is a dark brown liquid of 1.496 specific gravity, in which suspended material is present, with an odour similar to that of wood tar, and on mixing with gasoline gives a cloudy liquid.

The fluid contains a volatile compound of lead in admixture with wood tar, ethyl ether, and ethylene dibromide. There is present 2% ethyl ether and approximately 33% ethylene dibromide, while over 50% of wood tar containing about 25% organic bases and 10% organic acids is also present. It was proved that a volatile lead compound was present, and as much as 32% was concentrated in one particular fraction by careful fractionation.

The original fluid produced a rise in octane number of 5 when 5 ml. was added to one U.S. gallon of a gasoline of 65 octane number; this indicates that most, if not all, of the antiknock effect of the fluid is due to tetraethyl lead, and it was estimated that 13% of lead tetraethyl was present in the original fluid.