Leaded Gasoline, a Technical Perspective

When we talk about leaded fuel we are referring to one specific ingredient, tetra-ethyl lead. TEL increases the octane rating of gasoline like no other chemical known. A fuel's octane rating expresses its resistance to detonation – nothing more. Detonation is the technical term for engine knock. If you've never heard an engine detonating, consider yourself lucky. I describe it as the sound of marbles rattling around in a coffee can. Severe detonation can damage an engine in well under a minute. When detonation occurs, part of the fuel literally explodes instead of burning in a relatively slow, controlled manner. Some authors have suggested visualizing detonation as a hammer hitting the piston rather than the firm push of a hand that occurs during normal combustion. This photo of detonation damage comes from Geoff Battick's website.

Two-Stroke Piston Showing Detonation Damage

In addition to hammering the piston, detonation scrubs away the stagnant boundary layer of gases that insulate engine parts from combustion. This greatly increases heat transfer from the combustion gases to those engine parts, quickly elevating their temperature. You can tell detonation is occurring when the exhaust gas temperature **decreases** and, simultaneously, the coolant / head temperature **increases**.

The octane rating system gets its name from one of the reference fuels (iso-octane, chemical formula 2,2,4-trimethylpentane) used to determine the detonation resistance of an unknown fuel. The machine used for this test was designed long ago by the Waukesha CFR company
http://www.waukeshacfr.com/about/

I'm not sure where this photo of the Waukesha Octomatic came from originally. It's not mine, I just stole it off the internet.

When the octane rating of a given fuel is experimentally determined using this variable compression-ratio machine, it's done by comparing a fuel's knock performance against a known mixture of two hydrocarbon compounds: heptane and iso-octane. This basic concept has been in use since 1928, but it obviously was not computerized back then.

Heptane has terrible detonation resistance and is arbitrarily assigned an octane number of zero. Whereas iso-octane is quite good, and arbitrarily gets assigned a value of 100. A fuel's octane number is equivalent to the percentage of iso-octane in the comparison fuel. For example, if the fuel being tested knocked at the same compression ratio as a 15% heptane / 85% iso-octane comparison mixture, it's said to be 85 octane. Actually, there are two different tests, one for research octane number (RON) and another for motor octane number (MON). The octane reported at the pump is the average of MON and RON. Sometime that average is called the AKI (anti-knock index).

By the way, since the octane scale is defined at 100% iso-octane, any “octane” number greater than 100 is actually a “performance number.”

The effectiveness of TEL as an octane booster was discovered in 1923 by Thomas Midgley, Jr. in a truly Edisonian trial-and-error approach. If you read anything by Jamie Lincoln Kitman on this topic, you may think Midgley was the Devil incarnate. But the whole story is more complicated than that. TEL fulfilled a need in WWII aviation that no other compound could. Adding a small amount of TEL (a few milliliters per gallon) to gasoline improves its anti-knock properties enormously.

According to the table below (adapted from Dunstan, *et al.*), a molecule of TEL is over 800 times (118 / 0.142 = 831) more effective than a molecule of xylene at suppressing detonation. (Xylene is commonly used as a backyard chemist's octane booster.)

Compound	Formula	Relative Molar Effectiveness	Usage
Ethanol	C_2H_5OH	0.104	Blending
Toluene	C_7H_8	0.112	Blending
Xylene	C_8H_{10}	0.142	Blending
Aniline	$C_6H_5NH_2$	1	Doping
Tetra-Ethyl Tin	$(C_2H_5)_4Sn$	3.8	Doping
Nickel Carbonyl	$Ni(CO)_4$	35	Doping
Tetra-Ethyl Lead	$(C_2H_5)_4Pb$	118	Doping

The Story of Gasoline, published in 1956 by the Ethyl Corporation, gives us a real-world example:

> *Without TEL, the [sample] gasoline would have an octane number of 74; with 1.5ml, it is 86; and with 3ml it is 90 octane number.*

Just to make the numbers simple, let's assume there's 3.78 milliliters of TEL in a gallon of gasoline. Because there are 3.78 liters per US gallon, that's 1 part in 1000. This makes TEL the most effective octane booster known. (Methylcyclopentadienyl manganese tricarbonyl is only used in small doses.)

Although a small amount of TEL improves a fuel's anti-knock properties significantly, as more and more is added, the octane rating plateaus quickly. It is very much a case of diminishing returns. Heywood's *Internal Combustion Engine Fundamentals* gives an empirical formula for how iso-octane can be improved with increasing amounts of TEL. I tabulated it below:

TEL (milliliters per US Gallon)	Performance Number
0	100
1	108.6
2	112.8
3	115.2
4	117.5
5	119.0
6	120.3

Below is the TEL content for some readily-available leaded fuels. It is becoming more difficult to find TEL numbers, as some sources no longer even list it. For reference, one milliliter (ml) of TEL contains about 1.06 grams of lead.

Fuel	Milliliters TEL per US Gallon
AvGas (100LL)	2
Philips TT111	4
VP C12	4
VP MR8	6

Unfortunately, TEL by itself is highly corrosive and would accumulate inside the engine. What's also needed is a "scavenger" to get the TEL to go out the exhaust system. In *Petroleum and Performance,* Goodger writes:

> *The damage suffered by engines running on 'neat' leaded fuels was found to consist of lead-oxide fouling of the spark-plug electrodes, 'tracking' of the plug insulators, and hot corrosion of the of the exhaust valves and seats, and spark-plug electrodes. Furthermore, cold-corrosion was found to occur after shut-down due to the contamination of the lead combustion products with water, producing acid materials.*
>
> *The energies of the anti-knock agent researchers were now directed towards locating a suitable 'scavenger' to evacuate these lead deposits from the cylinders....*

This scavenger was initially ethylene dibromide (chemical formula $C_2H_4Br_2$) and then a mixture of ethylene dibromide and ethylene dichloride ($C_2H_4Cl_2$). TEL and EDB/EDC together are known as "Ethyl fluid", so the gasoline that used it became know as Ethyl. Ask your grandfather if he remembers the phrase, "Fill it up with Ethyl."

But EDB was not itself without problems. It too is corrosive. Combustion of any hydrocarbon with chlorine creates hydrochloric acid. The same is true of bromine which produces hydrobromic acid. The ratio of TEL to EDB was critical. And even when the ratio was correct, maldistribution problems occur when a single carburetor feeds multiple cylinders. This was especially problematic with large radial aircraft engines during WWII. Ever wonder why spark-ignition aircraft engines have 2 plugs per cylinder? Lead is an electrical conductor. If it accumulates on the spark plug insulator it can short the plug making it inoperable. It's a matter of life and death to have a backup.

In *The Internal Combustion Engine,* circa 1937, D.R. Pye had this to say about leaded fuel:

> *Apart from the organic compounds of metals, a great variety of non-metallic compounds have been experimented with, in the hope of discovering a dope that is not subject to the great drawback of ethyl fluid, its poisonous nature and its propensity for leaving harmful deposits in the engine. For although the association of ethylene dibromide with lead ethide greatly reduces the amount of the deposits, it is not completely effective in preventing them altogether. When used in a proportion not greater than 1/900 by volume, which is the limit allowed commercially, ethyl fluid appears to be fairly innocuous, at any rate for engines of moderate duty; but when the proportion is raised much above this, or the power output and cylinder temperatures of an*

engine are increased by supercharging, troubles from fouled plugs and valves are not slow to appear. Even if the proportion of ethyl fluid is only 1/900, a simple calculation will show that a 50 horse-power engine during a 10 hours run will have something like ¼ lb. of metalic lead supplied to it in the fuel, and even a very small proportion of this left behind in the cylinders cannot fail to lead to trouble in time.

Before moving on to the really bad news about TEL, I want to leave you with this thought from Owen & Coley's *Automotive Fuels Handbook:*

As lead is removed from the gasoline pool it requires more and more energy to make the same volume of gasoline at the same octane quality. Although maintaining a high octane level enables vehicle manufacturers to use high compression ratios and, therefore, achieve a better efficiency, this is pointless if the benefits are more than offset by efficiency losses at the refinery. A number of studies have been carried out to find the balance between these two conflicting factors.

I once asked a chemist friend (I'd credit him, but he wants to remain anonymous) about TEL. His response killed any desire I had to mix my own fuels and made me rethink how I handled leaded fuels.

Tetra-ethyl lead is extremely toxic. It makes many of the other octane boosters, which are also quite toxic, seem like candy in comparison. Personally, I'd rather (and have) handled cyanide, than TEL. It's a contact hazard and it goes right through a lot of glove materials.

TEL can be absorbed through the skin because it's lipid soluble and our skin is a lipid bi-layer. Solvents "de-fat" the skin – that's why your skin can feel cracked and dried after brief exposure to common solvents. When you spill gasoline on your skin, while the fat in your skin is absorbing some components of the gasoline, the gasoline is "rinsing away" some of your fat. The overall transfer of gasoline components to your body is lessened by the rinsing effect. Now take the single most toxic part of that gasoline "solution" (TEL) by itself. You'll still get a "rinsing effect" but you're trying to rinse with the worst stuff. The effective transfer of TEL could be much greater than the change in concentration alone would lead you to believe.

I'm not saying TEL can't be handled safely. The ***correct*** *gloves, sleeve protectors, aprons, goggles (or face shield) and respirator and you're good to go. Skip one or more and you're planning to be "extra careful" which, in my book, is the same as planning to be lucky.*

It is easy to become complacent with health hazards when their consequences aren't immediately apparent. Lead poisoning, like all heavy metal poisoning at lower doses, is systemic and chronic; you won't even feel your brain cells slipping away.

On that note, there is a huge amount of research showing lead is really bad for brain function.

http://www.nmic.org/nyccelp/medical-studies/neurology%20-%20schwartz%20.pdf

This study provides the first evidence that progressive and ongoing decline in cognitive function, particularly functions such as learning and memory, is associated with adult lead *exposure long after exposure ceases.*

http://www.grayenvironmental.com/lead%20exposure%20and%20alzheimers.htm

People who have worked in jobs with high levels of lead exposure are up to 3.4 times more likely to develop Alzheimer's disease, an incurable and fatal degeneration of the brain that causes dementia....

http://www.lead.org.au/bblp/tsld024.htm

The relationship between performance on cognitive tasks and circulating levels of lead in blood and accumulated levels of lead in bone was examined in 141 middle-aged and elderly men. Men with higher levels of blood and bone (tibia) lead copied spatial figures less accurately; men with higher levels of bone (tibia) lead had slower responses for pattern memory. These findings suggest that low levels of lead contribute to impairments in cognitive function among elderly men.

http://www.usatoday.com/news/health/2004-12-07-cataracts_x.htm
(study on lead and blindness)