Spring 2014

Dear No-Rosion Customer,

Hopefully this letter finds you well, in spite of the relentless winter that just wouldn't seem to end this year…

In our last few newsletters, we've gone into detail regarding the harmful effects of ethanol. It's nearly impossible to find gasoline these days that doesn't contain ethanol. And if the government has their way, E10 gasoline (i.e. 10% ethanol) will soon give way to E15. This has prompted many of you to ask: Why is the government pushing ethanol so hard? And why do refiners use it?

The first of these two questions is complicated. So rather than turn this newsletter into a political diatribe, we'll stick to the second question… And the answer is simple: Ethanol is the <u>cheapest</u> way to boost octane.

<u>Just what is octane</u>? <u>And are there better ways to boost octane than using ethanol</u>?

Octane is a standardized measure of a fuel's ability to resist self-ignition (a.k.a. "detonation") under conditions of <u>heat</u> and <u>pressure</u>. It is quantified using a Cooperative Fuel Research (CFR) engine that has a single cylinder, four-stroke cycle, and variable compression ratio. During this test, the engine operator continuously increases compression until such time as the fuel mixture spontaneously ignites. The results are then compared with those for standardized mixtures of iso-octane and n-heptane, to derive ***Research Octane Number*** (RON).

Motor Octane Number (MON) is another measure of octane, and actually represents a more accurate measure of how gasoline behaves under load. It is determined by running the CFR engine at 900 rpm, versus 600 rpm for RON. It preheats the fuel mixture, and varies the ignition timing, in order to further stress the fuel's knock resistance. Depending on the fuel, MON is about 8 to 10 points (0.8 to 1.0 octane numbers) lower than RON. But there is no direct link between RON and MON. Fuel specifications typically require both a minimum RON and MON. For this reason, you'll usually see the average of both, indicated as "(R+M)/2 Method," on a placard at the fuel pump. This is also referred to as the ***Anti-Knock Index*** (AKI).

These days, most gasoline sold at pumps in the US has an AKI of 87 to 93. Comparatively, gasoline sold in Australia, New Zealand, and all across Europe has a RON of 95 to 100. As you'll note, these countries advertise octane at the pump using the RON methodology, not AKI as we do in the US. And of course, things were much different here in the US prior to 1973, when the EPA banned the use of ***tetraethyl lead*** as an octane boost ingredient in commercial fuel blends…

In the late 50's, the horsepower race in Detroit drove up engine compression ratios. Fuel refiners responded by offering "super-premium" fuels that were high in octane, and rich in **<u>tetraethyl lead</u>.** In 1956, Sunoco introduced "*Dial-A-Grade*" pumps that dispensed five different "Custom Blended" gasolines, ranging from ***Sunoco 190*** (87 octane) to ***Sunoco 260*** (98 octane). Esso introduced its ***Golden Esso Extra*** (101-102 octane), which came in a gold pump. That was followed in the spring of 1957 by Gulf, which introduced its 102 octane fuel that was dispensed from a purple pump. Then Chevron debuted its ***Custom Supreme*** (103-105 octane).

The good 'ol days… When we had REAL choices at the pump! This photo shows a blend selector from Sunoco's "Dial-A-Grade" pump, commonly found back in the '50's and 60's.

As you'll note, every one of the fuels just mentioned contained tetraethyl lead. So just what is ***tetraethyl lead***, and why is it such an effective octane boost ingredient?

To properly answer that question, we first need to understand more about the chemicals that are used to boost octane in gasoline fuel. There are three primary types of octane boost ingredients: (1) **OXYGENATES**, (2) **AROMATICS**, and (3) **ORGANOMETALLICS**.

Let's begin with **OXYGENATES**. When the EPA banned tetraethyl lead due to toxicity issues, refiners started using oxygenates to boost octane. Oxygenates are ether and alcohol, and serve the dual purpose of boosting octane, and also reducing emissions. Their molecular structure is inclusive of oxygen – thus, the name. The most widely used oxygenate is ethanol (CH_3CH_2OH), which has an (R+M)/2 octane rating of 115, and contains 34.73% oxygen by weight. So, as you'll note, on its own, ethanol has a very high octane rating.

But one of the many problems with ethanol is that it is highly volatile. It has a Reid Vapor Pressure (RVP) of 18, which means ethanol is chemically unstable in warm climates. In these locations, other oxygenates have historically been used, such as MTBE $(CH_3)_3COCH_3$, ETBE ($CH_3CH_2OC(CH_3)_3$) and TAME ($(CH)_3CCH_2OCH_3$). They have lower RVP's of 1.5 to 8. But their octane of ratings of 105-110 are lower than ethanol. So they have largely fallen out of favor. Especially MTBE. It smells bad, and started showing up in ground water. It gives water a bad taste at very low concentrations, and renders large quantities of groundwater non-potable.

If we look at the chemical structure of ethers and alcohols, they are essentially hydrocarbons with an extra hydroxyl (OH) group added to one end. When formulated into gasoline, or used by consumers in the form of fuel additives, they reduce fuel economy due to the displacement of hydrogen and carbon atoms by the larger oxygen molecules. The increased molecular-mass of these compounds with the attached hydroxyl is what gives the octane-boosting effect. But the hydroxyl group also makes these compounds polar, water-soluble, and highly reactive. So in addition to being unstable in warm climates, ethanol is also unstable in humid climates!

Ethanol dissolves rubber and plastic fuel lines. It reacts with oxygen in the air via the oxidation process, to form non-combustible gums, which form deposits inside an engine. Ethanol absorbs humidity from the air to form an emulsion that eventually separates into a heavy water layer. This layer sinks to the bottom of fuel tanks, and causes corrosion. And ethanol's hydroxyl group changes the air/fuel mixture, requiring re-jetting and modified tuning of older engines that were originally calibrated to run on gasoline containing tetraethyl lead.

Now that you know all about oxygenates, let's take a look at **AROMATICS**. This group of chemicals has molecules composed of stable benzene ring structures. They are non-polar, and very chemically stable. In fact, they are less volatile and less reactive than most other hydrocarbons in gasoline. This stability is what gives aromatics their octane-boosting powers. Normal gasoline typically contains around 25-30% aromatics, primarily toluene and xylene. Adding more will increase the octane rating, and bring their concentrations up to what is often found in higher-octane European gasoline blends, which are often 40-45% aromatics.

Okay, so aromatic toluene and xylene have none of the side-effects of oxygenates. But by no means are aromatics a panacea. Too much aromatic yields slower combustion rates. This causes fuels high in aromatics to make less power in high-revving engines, for example. In extreme cases, the air/fuel mixture is still burning as it exits the exhaust valve. This is a sure way to destroy emissions-control equipment in a modern engine. Other issues related to cost and ethanol legislation prevent refiners from using just aromatics to boost octane.

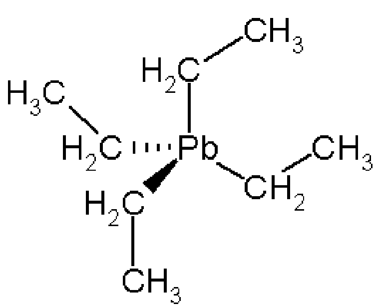
The third and final chemicals used to boost octane are **ORGANOMETALLICS**. They contain covalent bonds between carbon and metal molecules. In liquid form, organometallics possess the peculiar and desirable chemical property of being able to fully suspend a metal in solution. When formulated into a gasoline mixture, the solubilized metal in this mixture provides two very beneficial physical properties, especially to engines of older cars: (a) robust octane, and (b) lubricity.

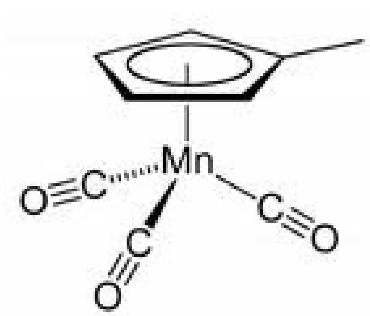
Just what do we mean by "*lubricity*?" Exhaust valve seats in engines built prior to the early 1980's were cast as an integral part of the cylinder head. Back then, the lead in tetraethyl lead gasoline acted as a lubricity buffer against "microwelds" that form between hot exhaust valves and their seats. When the valves open, these microwelds pull apart, taking with them tiny bits of metal. Over time, this causes recession, and results in loss of compression and reduced engine performance. So when lead was phased out by refiners, engine manufacturers switched to hardened valve seats, to prevent this type of recession.

Getting back to the original question: Why is tetraethyl lead such a good octane boost ingredient?

Tetraethyl lead is an **organometallic** compound. Organometallics are extremely concentrated. They offer higher energy content than oxygenated alternatives, and excellent chemical stability. Therefore, one of the greatest advantages of organometallics over other octane boost chemicals is the very low concentrations needed. For example, typical formulations call for only 1 part of organometallic to 1260 parts untreated gasoline. Competing octane boost chemicals must be used in greater amounts, resulting in reduced energy content of the gasoline – especially in the case of the previously referenced hydroxyl groups in ethanol.

Wouldn't it be great if a suitable organometallic replacement existed for tetraethyl lead? Well, it does. It is called **methylcyclopentadienyl manganese tricarbonyl**, or "MMT" for short. But instead of using lead as the metallic constituent, it uses manganese – a highly effective, non-toxic, organometallic octane booster.





Here are molecular diagrams for tetraethyl lead (far left) and MMT. As you'll note, the metallic lead component (indicated as "Pb") shares bonds with carbon. Similarly, the metallic manganese component (indicated as "Mn") shares bonds with carbon. These two substances not only share similar molecular geometries, they also exhibit similar performance when formulated into gasoline.

Most octane boosters contain oxygenates, so beware! Not ours. **No-Rosion Fuel System Octane Booster** is one of only a handful of products available that contains organometallic MMT. But what sets No-Rosion apart from other MMT-containing octane booster products is that it is formulated with a high flash point aromatic carrier. In this way, it boosts octane both via it's organometallic ingredients and it's aromatic ingredients. All other MMT octane booster products available on the market are blended using aliphatic carriers, such as kerosene. Why do other products use oxygenates and/or kerosene? There are a number of reasons…

First and foremost, **cost**. MMT is very expensive. It costs roughly thirty-five times more per volume than oxygenate octane boost ingredients. Likewise, aromatic solvent costs about twice as much as aliphatic solvent.

But there's more to it than just cost. MMT is photo-sensitive, which means that it rapidly degrades when exposed to light. This requires customized blending equipment that is dedicated to the manufacture of this product. And it slows down production substantially, as it requires specialized blending procedures.

MMT also requires a special registration permit from the EPA. The permitting process takes time, requires investment, and adds regulatory and compliance headaches that most manufacturers prefer to avoid.

There are also packaging challenges associated with aromatic solvent. It permeates all types of plastic. So it requires a special High Density Polyethylene bottle that has been treated via fluorination. This process exposes the bottle to elemental fluorine under controlled conditions. Hydrogen atoms in the bottle are replaced with fluorine atoms, creating a fluorocarbon barrier inside and outside the bottle. This prevents the aromatic from penetrating. But it also doubles the cost of bottles. Yet another headache most manufacturers prefer to avoid.

So, what do you get with **No-Rosion Octane Booster** that you don't get with other products? MMT instead of oxygenates. MMT will not require recalibration of carburetors or ignition timing, because it doesn't contain oxygen. It protects non-hardened valve seats. It is safe for catalysts. And it contains aromatic, not kerosene. Whereas aromatic provides additional boost, kerosene has the opposite effect. Additionally, No-Rosion's higher flash point results in lower Reid Vapor Pressure (RVP). This provides additional protection against chemical instability and octane loss in hot environments. Kerosene does not offer this type of protection.

Wondering whether the octane booster product you've been using contains MMT, or oxygenates? Here's how to find out. Request a copy of the Material Safety Data Sheet (MSDS). Manufacturers are legally obligated to provide this information. Most importantly: Beware of octane booster products that contain oxygenates!

Now let's have a look at a modern day "blend selector," which is becoming typical of what you find at the pump... And consider this question: **Which of the blends in the photo below would you choose, and why?**

In the case of this pump, and many others like it these days, the only way you can get octane higher than 89 is to go with E10 or E15. (Look carefully! The 90 octane is E15!) But what if you don't want this much ethanol? That's where we can help. You can purchase lower octane gasoline, which contains less ethanol, and add our **No-Rosion Octane Booster** to get the octane your engine needs. It's the best of both worlds: Lower ethanol content, higher octane. (And protection for non-hardened valve seats in your older cars' engines.)

We hope this info is helpful as you try to best manage the limitations of today's fuel blends for your older (and newer) cars. As always, we're here to help with all your engine fluid maintenance needs.

Thank you for being a customer. We appreciate your support, and look forward to continuing to be of service.

Applied Chemical Specialties, Inc.