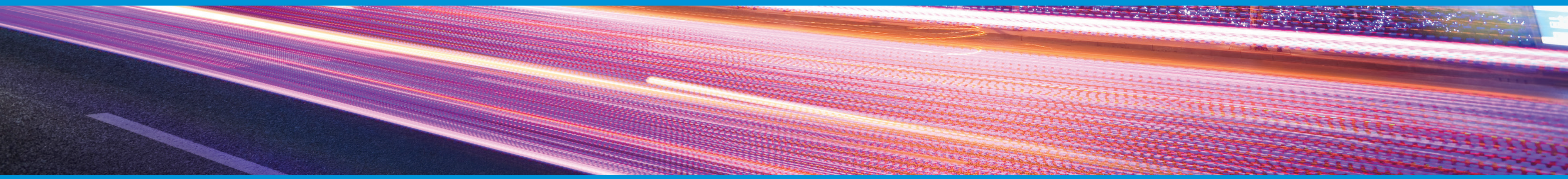
GASOLINE ADDITIVES : WHERE ARE THEY GOING NEXT ?



There's a good chance that you drove a gasoline powered vehicle to work today and you may have even filled its tank at one of the over 150,000 gas stations in the US. With an average commute time of 54 minutes per day for the typical worker in the United States and an estimated 253 million vehicles on the road, there is a reasonable chance that you burned a few of the 378 million gallons of gasoline used daily in the United States [1-3].

Despite this staggering number, a significantly lower number of Americans actually know little about what's in modern gasoline. Modern motor gasoline is more than the low-boiling components obtained during refining of the crude oil, like most people believe. Motor gasoline is a complex formulation that in addition to containing the low-boiling hydrocarbons contains stabilizers, octane boosters, detergents, anti-freeze agents, and a multitude of other substances tailored to increase fuel efficiency, decrease harmful emissions, and maximize the functionality of the vehicles they fuel. These substances are referred to as additives and every major producer of gasoline has its own version of an ideal additives package. These additive packages are often unique and proprietary to the respective companies, and as such the specific compounds in packages, such as BP's Invigorate, ExxonMobil's Synergy, and Chevron's Techron, largely remain the company's trade secret. However, despite the lack of information available on such additive packages, the present paper will describe various classes of common gasoline additives and explain how they were developed, their present status, and where they are headed with respect to use in future gasoline formulations.

Octane Boosters

Octane boosters are one of the more prominent types of additives in gasoline today. Octane boosters are self-explanatory by name: they boost the octane rating of gasoline. In simple terms, higher octane ratings result in more efficient combustion, increased resistance to engine knocking,and allow higher compression ratios to be achieved in gasoline engines, which translate into improved fuel efficiency [4]. A typical gasoline engine runs on a "regular" grade of gasoline, typically marketed with a minimum octane

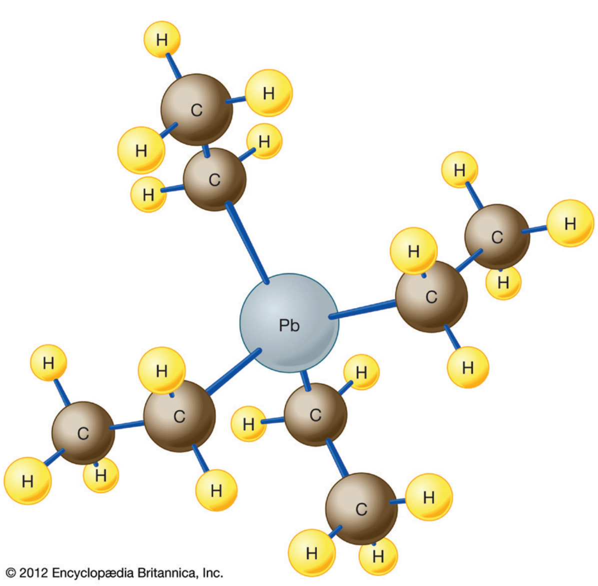


Figure 1. Tetraethyl lead molecule

rating of 87 (using the (R+M)/2 Method; see APPENDIX for more information). Despite a rating of 87, the "gasoline" itself does not have an octane rating of 87, but the additives in the fuel "boost" the octane rating to 87. The first octane booster to make its way into commercial use was tetraethyl lead(TEL) and the gasoline containing it,introduced in 1921,was colloquially known as leaded gasoline. At the time, tetraethyl lead and aromatics, such as benzene, were both known to increase the octane rating of gasoline, and TEL became the booster of choice due to its low costdespite its known health risks at the time [5]. The use of tetraethyl lead in gasoline continued well into late 1990s [6-7]. In 1970 the US government established Environmental Protection Agency (EPA) to regulate emissions. One of the first actions the EPA undertook was to reduce TEL levels in automotive fuel under the U.S. Clean Air Act of 1963 and in two overlapping programs: to protect catalytic converters, which mandated unleaded gasoline for those vehicles; and to protect public health, which mandated lead reductions in annual phases (the "lead phasedown"). Thus,starting in 1974all US gas stations were required to provide an "unleaded" fuel grade to accommodate vehicles with catalytic converters since lead would cause damage to the components thus negatively impacting the exhaust quality. Despite a rollback in the use of leaded gasoline in the 1970s,the use of leaded gasoline in on-road vehicle was not officially banned until 1996.

Fuel companies needed an alternative to tetraethyl lead after the EPA mandated the use of unleaded fueland many turned to alternative compounds, such as methyl tertiary butyl ether (MTBE) and BTEX. MTBE was used to increase the oxygenate content of reformulated gasoline, which boosts its octane rating by facilitating clean combustion, thereby reducing harmful tailpipe emissions. However, MTBE was formally phased out of gasoline use by the EPA in 2005 due to its high water solubility and concerns regarding MTBE contamination of the nation's drinkable water supply. Thus, BTEX,which is a blend of benzene, toluene, ethyl-benzene, and xylene,became alternate octane booster that gained significant use.

At this point, the gasoline companies also began to experiment with other oxygenates that were innocuous to the environment, ethanol being one used most often. The popularity of greater use of ethanol can be ascribed to the EPA ban on the use of TEL and MTBE and the 2007 EPA mandate that gasoline cannot contain more than 0.62 vol. % benzene. According to gasoline industry estimates approximately 95% of the gasoline sold in the United States contains ethanol. The most common commercial blend of ethanol and gasoline is E10 gasoline, which contains up to 10% ethanol. The EPA is currently amending laws to allow the sale of

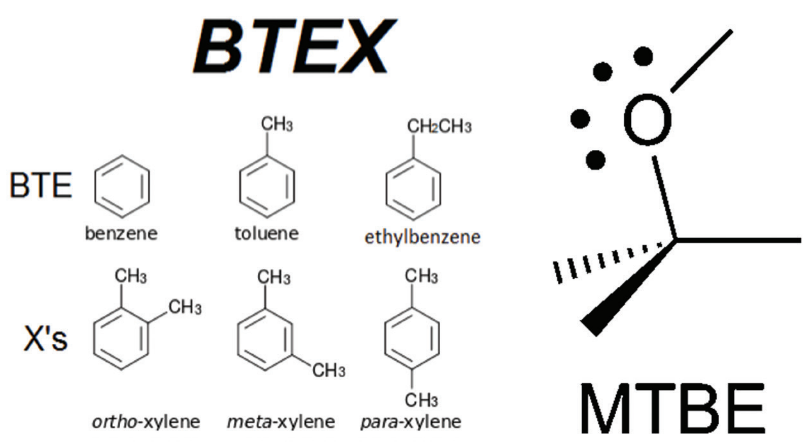


Figure 2.BTEX (left) and MTBE (right) molecules [9-10]

E15 gasoline year-round, which will allow the use of up to 15% ethanol in gasoline[10-11].

This change in legislation foreshadows what is to become the future of the ethanol-blended gasoline. The previous EPA restrictions banned the sale of E15 gasoline between June and September, citing possibility of increased particle emissions into the atmosphere during the summer months. This ban is the primary reason for most gas stations not to offer E15 gasoline at all since switching components and setups to accommodate a partial-year sale is not economically favorable. It is also important to note that the EPA approves the use of E15 gasoline in all vehicles with model year 2001 or newer, despite the fact that many automakers disagree with the EPA's position[11]. This is not the first time that the automakers have disagreed with the EPA regulations as being insufficient with respect to protecting the vehicles affected (this will be expanded upon in the Fuel Injector Cleaners and Detergents section). The new legislation could pave the way for gasoline distributors to economically justify offering theE15 gasoline, but only time will tell if that is the case or not.

Fuel Injector Cleaners and Detergents

Detergents are another class of common additives used in gasoline but have only been commonplace for the past couple of decades. Internal combustion engines consistently fall victim to carbon buildup, notably on the fuel injectors, which are one of the sites where deposits form due to oxidative decomposition of the gasoline components and of the oil components that go past the intake valves. As fuel injection systems became more common over carburetors in the 1980s due to the implementation of catalytic converters, carbon buildup on fuel injectors began to become an increased concern [12].

One of the first and the most commonly-used fuel injector

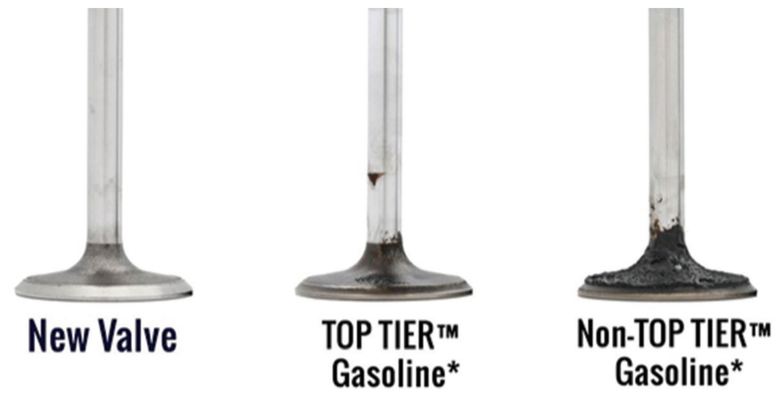


Figure 3. A new valve compared to two valves run for 4,000 miles of simulated driving

cleaneris polyetheramine, or PEA. It was first developed by Chevron as early as 1980 under the name PRC (later renamed Techroline) [13]. After keeping Techroline under wraps for 15 years, Chevron released their product under the trade name Techron® in 1995, a year before the fuel detergents were first mandated by the EPA.Other companies soon followed suit, notably BP with their proprietary Invigorate® and ExxonMobil's Synergy™.

In 1996, the EPA created the Lowest Additive Concentration (LAC) standard to enforce minimum amount of fuel detergent in gasoline [14]. The implementation of the standard for fuel detergents was a strong first step, but many automakers felt that the LAC standard was insufficient. This inspired the collaboration of automakers, such as Toyota, Honda, General Motors, and BMW, to establish a higher standard for detergent additives in gasoline. The result of this collaboration was the creation of the Top Tier gasoline standard in 2004. The Top Tier designation is a significantly stricter fuel detergent standard than the LAC that requires the fuel to use larger amounts of the certified detergent additives[15]. In a study conducted by AAA,Top Tier fuel was shown to be an astounding 19 times better at reducing the engine deposit build up than the non-Top Tier fuel. The use of non-Top Tier licensed fuel in addition resulted in a 2-4% reduction in fuel economy[16]. There are currently 54 different retail gasoline brands that are Top Tier licensed, which translates into 2/3rdof gas stations across the United States, including popular brands marketed by top gasoline suppliers, such as ExxonMobil, BP, Shell, Chevron, Marathon, Sunoco and Conoco[17]. This number is likely to rise further in the coming years as engines become more complicated and the grime and deposit buildup on the engine components becomes less tolerable for peak performance and efficiency [18].

Friction Modifiers

While detergents and fuel injector cleaners tend to draw a fair amount of attention for improving fuel economy and therefore reducing emissions, friction is also a significant cause of the wasted energy and inefficiency in combustion engines. In a typical gasoline engine, approximately 25% of the gasoline burned per engine cycle is burned to overcome friction between the piston and the cylinder wall [19]. The reason for this is that motor oil lubricates most of the engine, but neglects the upper part of the cylinder due to the design of the actual engine. The fuel is the most practical way to lubricate this part of the cylinder because of the fuel delivery being close to the upper part of the cylinder. However, when the gasoline combusts in the cylinder there is no gasoline present to lubricate and the lackof lubrication is the major cause of friction hence wear of the pistons and cylinder walls.

To combat this friction and wear, friction modifiers are added to gasoline. These produce a thin lubricating film on the cylinder wall, which helps in reducing friction and wear. The reduction in friction results in improved fuel economy since less fuel is burned per cycle[19]. ExxonMobil cites the friction modifier in its premium Synergy™ grade gasoline to be a new ingredient that reduces engine wear and tear by up to 30% [20]. Shell makes similar claims about its V-Power NiTRO+premium grade and asserts it to have performance that is significantlysuperior tothat of the standard Lowest Additive Concentration (LAC) gasoline in a wear test (ASTM D6079)[21].

These are bold claims, but how do friction modifiers make such a significant difference in wear within the cylinders? Chevron provides some answers by explaining how their friction modifiers work. According to Chevron, friction modifiers essentially form a "membrane" on the metal surfaces to reduce the friction between them and are similar to biological molecules like cholesterol in that they are amphipathic (contain both hydrophilic and hydrophobic parts). The polar "heads" of the additive molecules attach to the metal surfaces while the fuel-soluble"tails" face outwards and reduce friction [22].

Figure 4. Comparison of results from testing Shell V-Power NiTRO+ against LAC premium gasoline by ASTM D6079

Corrosion Inhibitors, Demulsifiers, and Solvent Fluids

Wear in an engine's metal components is an issue that can affect its overall performance, but corrosion which is also common in automobiles is not of any less importance. Fortunately, corrosion inhibitors are another common type of additives in gasoline that work to prevent the metal components from rusting or corroding. Several of the aforementioned gasoline brands mention the inclusion of corrosion inhibitors in their additive packages, all of which work in a manner similar to that of the friction modifiers, i.e., by forming a thin film over the affected components (intake valves, fuel tank, etc.). These additives work to keep additive package ingredients mixed (solvents), while separating the unwanted substances, typically water, from the gasoline to make removal easier (demulsifiers). These compounds prevent damage to the components that are part of the fuel system by preventing the fuel detergent additives from forming an unwanted film on the engine components (contrary to the films formed in the cylinders for lubrication)[20].

Summary

Gasoline is much more than just a fuel you put in your car. Gasoline is a complicated conglomeration of chemical additives that are engineered to keep engines running cleaner and more efficiently. These additives are designed to keep cars running at their peak performance, yet they are largely ignored by the general population, which remains generally unaware of how much effort goes into fueling their vehicles in the most efficient way possible. From developments to produce cleaner and safer fuel, to breakthroughs in keeping engines protected from damages, gasoline additives are a crucial part of the health of our cars and ourselves, so the next time you fill up your tank on the way home from work, take a minute to think about what's in your gasoline.

Appendix [23]

Minimum Octane ratings are calculated in a few ways. In each case, the number is an index for measuring resistance to engine knocking. The scale used is from 0 to 100 where 0 is equivalent to pure heptane while 100 is equivalent to pure iso-octane (numbers over 100 exist, but are interpolated since they fall out of the scale). The three means of measuring octane rating are the Research Octane Number (RON), the Motor Octane Number (MON), and the Anti-Knock Index (AKI).

RON: measured at a speed of 600 rpm with an intake air requirement of 52°C (mild driving)

MON: measured at a speed of 900 rpm with an intake air requirement of 152°C (harsher driving)

MON is typically around 10 numbers lower than RON

AKI: (R+M)/2; average of RON and MON values

RON is used in most European and Asian countries, while AKI is used in North America

RON and MON are tested using ASTM D2699 and ASTM D2700 in a test engine that follows the aforementioned rpm specifications for each respective test. These numbers are averaged for AKI as there is no test specifically for the AKI value.

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