

Internal Diesel Injector Deposits: Theory and Investigations into Organic and Inorganic Based Deposits

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ABSTRACT

Over the last two decades, global emission regulations have become more stringent and have required the use of more advanced fuel injection systems. This includes the use of tighter tolerances, more rapid injections and internal components actuated by weaker injection forces. Unfortunately, these design features make the entire system more susceptible to fuel contaminants. Over the last six years, the composition of these contaminants has evolved from hard insoluble debris, such as dust and rocks, to soluble chemical contaminants. Recent research by the diesel engine manufacturers, fuel injection equipment suppliers and the fuel and fuel additive industry has discovered a major source of the soluble chemical contaminant that leads to injector deposits to be derived from cost effective and commonly used additives used to protect against pipeline corrosion. These deposits have affected engines around the world and across multiple engine sizes in diverse applications and a select few failed injectors are presented. The deposits were studied using microstructure analysis (optical and scanning electron microscopy) and detailed analytical chemistry techniques (infrared spectroscopy and elemental analysis). This paper proposes theories to explain the mechanism by which these contaminants become soluble in the fuel as well as the mechanism by which they form deposits on the metal surface and for both.

CITATION: Trobaugh, C., Burbrink, C., Zha, Y., Whitacre, S. et al., "Internal Diesel Injector Deposits: Theory and Investigations into Organic and Inorganic Based Deposits," *SAE Int. J. Fuels Lubr.* 6(3):2013, doi:10.4271/2013-01-2670.

INTRODUCTION

Increasingly stringent global emission regulations have driven engine and fuel injector equipment manufacturers to push the envelope of design. For engine manufacturers, this means more precisely controlling the mass flow and composition of intake air through the use of advanced turbocharging and exhaust gas recirculation. Similar technological advancements have also been made in fuel injection equipment. In concert with the regulation updates, these systems have been required to inject fuel over a wide range of pressures from 150 bar in 1990 to 2000 bar in 2010. In the 1990's, unit injector systems were actuated by the camshaft at a force of 17600 N for a single injection per combustion event. Today, more modern electronically controlled high pressure common rail systems require 40 N of force and allow for multiple injections per cycle. To meet these requirements, the clearance between internal moving parts has decreased to between 2 and 3 microns. This clearance is now more susceptible to deposits of all composition, ranging from organic based deposits like metal

carboxylates and lacquer, to inorganic based deposits like chloride, sulfate and carbonate salts.

Concurrent with diesel engine and injector design modifications has been the significant reduction in sulfur from diesel fuel. Prior to 2007, the maximum allowable concentration of total sulfur was 500 ppm. After 2007, the EPA required all fuel refiners to start producing fuel with a sulfur concentration less than 15 ppm.[1] Reducing sulfur to this level has many unintended consequences, one of which is decreased corrosion protection. The hydrotreating process that is employed, not only removes sulfur compounds, but also removes beneficial oxygen and nitrogen containing compounds which enhance corrosion protection. Fuel refiners often must add synthetic corrosion inhibitor additives in order to meet fuel corrosivity specifications included in the product acceptance terms of most major pipeline networks. Unfortunately, the most widely used corrosion inhibitor is also the least stable, especially in the presence of contaminants typically found in the fuel distribution system. The lack of proper tank maintenance and cleanliness has been identified as a major culprit that contributes to both deposit and debris induced failures of fuel systems by engine and fuel



Figure 1. Map of reported engine failures due to IDIDs (2007-2013)

injector manufacturers. Over the last year, there has been a concerted effort by multiple OEMs to educate their customers and others in the supply chain about the importance of tank maintenance and to impress upon them the effects cleanliness can have on fuel injector deposits, overall engine reliability and fuel economy.

The formation of both organic and inorganic deposits inside the fuel injector can manifest themselves in a multitude of ways. Once the moving parts (i.e. metering valves or needles) of the fuel injector have been compromised, fueling rates and volumes can change drastically. If the needles or valves seize open, over fueling can occur, causing high levels of smoke. This in turn can lead to excess power cylinder wear, degradation of turbocharger performance and failures of the aftertreatment system. If the needle seizes closed, significant reductions in power or complete engine shutdown can result. Inevitably, these issues result in substantial decreases in uptime and revenue for the end customer.

Reports of rough running, power loss and decreased low temperature operability due to internal diesel injector deposits (IDID) were first witnessed in 2007 and coincided with the introduction of ultra-low sulfur diesel (ULSD) to various regions across the world. Reports and warranty claims seemed to decrease from 2008 to early 2010, and then from late 2010 until now, an increasing number of IDIDs have occurred in fleets of high horsepower marine vessels, mine trucks and rail switcher engines. In smaller displacement engines, IDIDs in a transit bus fleet in a major metropolitan city lead to excessive power loss and high soot loading on the turbocharger and aftertreatment system.

Figure 1 highlights areas of the world where fuel injection failures due to internal deposits have been reported in the literature and by various OEMs. All of the points on the map

have experienced either organic or inorganic deposits. One location in particular, southern California, had injectors that contained both an organic deposit (metal carboxylates) and inorganic deposit (sodium chloride).

Many efforts have gone into indentifying the source of the organic deposit and, more recently, the inorganic deposit. The most common analytical techniques used have been Infrared spectroscopy (FTIR) for qualitative analysis, Scanning Electron Microscopy/Energy Dispersive Spectroscopy (SEM/EDS) for high resolution topography and qualitative elemental analysis and Liquid Chromatography/Mass Spectrometry (LC/MS) for quantitative analysis [2,3]. Lately, Gas Chromatography/Mass Spectrometry (GC/MS) has been reported as an effective quantitative analytical method [4].

ORGANIC INJECTOR DEPOSITS

Organic based IDIDs have been the predominant deposit found on injector parts over the last six years. The organic based deposit that will be discussed herein consists of a metal carboxylate moiety, and of particular focus, will be the mechanisms of formation and deposition of the metal carboxylates.

Carboxylates are the product of an acid/base reaction, involving a carboxylic acid and either water or an alkali metal hydroxide or other similar base, as seen in Figure 2. In the case where the carboxylic acid deprotonates in water, the counter ion is the hydronium ion (H_3O^+) and in the case where the carboxylic acid reacts with an alkali metal base, the counter ion is a metal ion and the resulting chemical is called a metal carboxylate. The equilibrium of these reactions will be discussed below.

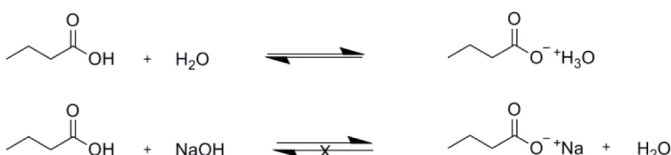


Figure 2. Chemical reaction of a carboxylic acid with water and an alkali metal base

The exact source of the metal carboxylate that has been found on the injectors has been the subject of recent debate. However, the chemical that seems to be consistently observed is either dodecenyl succinate (DDS) or n-hexadecenyl succinate (HDS), with various reports verifying their existence in the deposit with LC/MS. Using DDS as the example, the protonated version of DDS, dodecenyl succinic acid (DDSA), is a cost effective and common pipeline corrosion inhibitor. Unfortunately, this acid is not stable at neutral to basic pH values and is therefore susceptible to deprotonation to the carboxylate. An acid's stability towards a base is generally identified by its pKa. pKa is defined as the pH at which 50% of the acid is protonated and 50% of the acid is deprotonated, and for each unit decrease in pH, the ratio of protonated to deprotonated increases 10-fold.

Using a succinic acid group of DDSA as an example, one of the groups has a primary pKa value of 4.19, as shown in Figure 3. At a pH of 4.19, 50% of one of the carboxylic acid groups will be deprotonated and 50% of the same acid group will be protonated. However, when the pH increases to 7, the amount of deprotonated carboxylic acid increases dramatically, to 99.8%. In translation, when succinic acid is added to pH neutral water, nearly 100% of one of the carboxylic acid groups will be deprotonated.

Figure 3 also shows the pKa values for two structural variants of succinic acid. It shows that the addition on one methyl group to the succinic acid backbone decreases the pKa of the first acidic proton. The addition of a second methyl group, as in the case of ethylsuccinic acid, does not have the same effect. This implies that as the carbon chain lengthens, and the additional methyl group becomes farther away, its electron donating potential has no effect on the stability of the subsequent carboxylate that is formed after deprotonation, and therefore does not change the primary acidic proton's pKa.

However, as the hydrocarbon chain grows by one methyl group, the second pKa continues to increase. This can be attributed to the structural confirmation of the succinic acid backbone. As the backbone and hydrocarbon chain becomes larger, it forces the formation of a hydrogen bond between the carboxylate and the second carboxylic acid, which stabilizes the second dissociable proton, therefore increasing the pKa.

In the case of DDSA, it is important to reiterate that as the chain grows by one methyl group, the pKa for the first acidic proton remains unchanged. As no pKa data exists for chains longer than an ethyl group on the backbone of succinic acid,

it will have to be concluded that the effect of additional methyl groups would have little to no effect on the pKa of the first acidic proton. This information is critical to the assumption that at least one carboxylic acid of dodecenyl succinic acid (C12) will become deprotonated in fuel and could form a metal carboxylate.

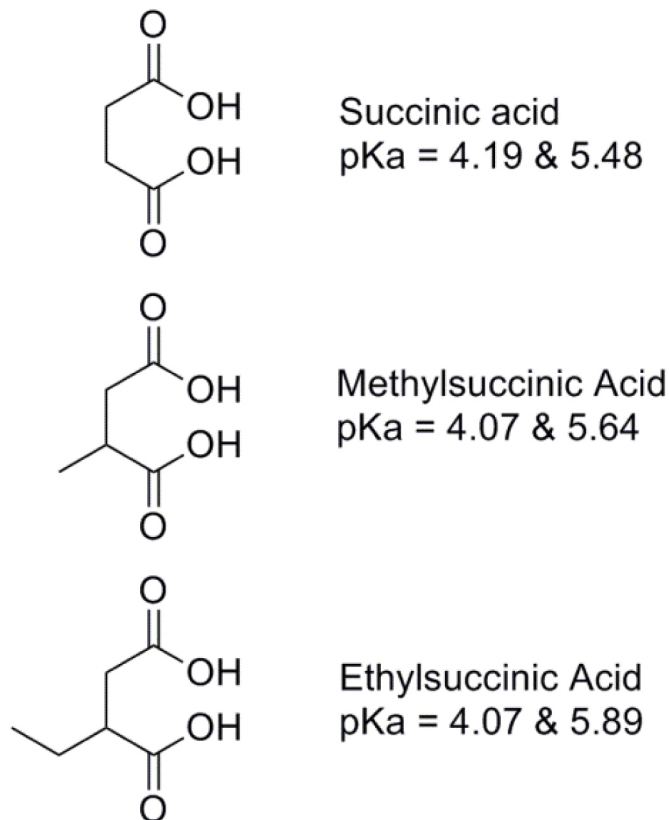


Figure 3. pKa's of Succinic Acid and structural variants [5,6]

It is important to note that the component responsible for the formation of a carboxylate is the base (anion) and not the metal (cation) component. For example, in solution, sodium hydroxide dissociates to a sodium cation and a hydroxide anion. Due to the positive charge on the sodium ion, it is incapable of reacting with the positively charged proton of the carboxylic acid. However, the negatively charged hydroxide ion is electronically favored to react and will remove the proton. Once the proton is removed, the sodium ion will be able to form a stable ionic bond with the negatively charged carboxylate and satisfy the overall net charge balance of the reaction (i.e. net zero charge of reactants and net zero charge of products). When a benign salt, such as NaCl is used, the chloride ion is not a strong enough base and will not remove a proton from the carboxylic acid; thus preventing the sodium cation from forming the metal carboxylate.

In essence, any basic functionality, such as hydroxides, carbonates, and even amine ($-\text{NH}_2$) groups can participate in an acid/base reaction, and the positively charged group (metal

cation, hydronium ion (H_3O^+) or ammonium ion ($-\text{NH}_3^+$) will act as the counter ion.

Inverse Micelle Formation

It is known that water is soluble in diesel fuel up to ~ 200 ppm, and up to ~ 500 ppm in a biodiesel blend. In the case of a fuel sample with a water concentration of 200ppm, this can equate to 600 g of water in 1000 gallons of fuel. It is important to note that the dipole moment of water is roughly 22 times greater than certain components of diesel fuel, suggesting that diesel fuel will not properly solvate the water molecules. Because of this, it is highly unlikely that the water molecules will exist as individual entities, but rather large clusters consisting of 100s to 1000s even millions of water molecules surrounded by relatively polar constituents in fuel, such as the remaining sulfur compounds as depicted in [Figure 4A](#). This phenomenon can be defined using entropy considerations and a variance of the hydrophobic effect.

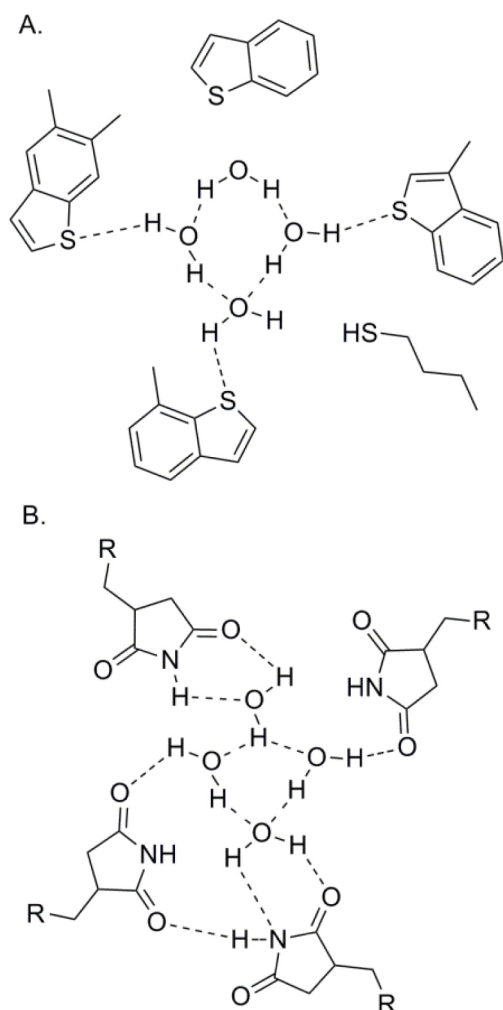


Figure 4. A: Water solvation by sulfur compounds B: Water solvation by detergent additives

In essence, the hydrophobic effect states that non-polar molecules will tend to aggregate in aqueous solutions and exclude water. In contrast, the hydrophilic effect states that polar head groups will tend to aggregate together and exclude the non-polar environment.[7] Both of these terms have roots in entropy, and in this context, describe the hydrocarbon's need to remain in a disordered random confirmation despite the fact that water molecules are forcing it into an ordered, but energetically unfavorable state. [8]

Water's dipole moment, or polarizability, will induce the hydrocarbons to rearrange, or order themselves around the water molecule in a way that is energetically favored. The hydrocarbon's lack of polarizability will prevent this and it will seek a structural conformation that is disordered and away from the water molecule. In order to fill the void left by the hydrocarbon, more polarizable compounds, such as sulfur compounds and detergent additives, will take their place in an attempt to solvate and dissolve the water molecule as seen in [Figure 4B](#). As shown by dotted lines in [Figure 4](#), the sulfur compounds and the heteroatoms of the detergents are able to form hydrogen bonds with the water molecules. This bonding is very stable and more energetically favored than induction and London dispersion interactions that occur between the hydrocarbon chains and water.[9]

Table 1. Dipole moments of water, common fuel and fuel additive components and a metal carboxylate [10, 11, 12, 13, 14]

Dipole Moments of Water, Common Fuel Constituents and Additive Functional Groups (Debye, D)	
Water (H_2O)	1.85
C_4 and higher	0.000
Propane (C_3H_8)	0.084
Toluene (C_7H_8)	0.385
o-Xylene	0.640
cis-Methylsuccinic acid	1.500
Succinimide	1.540
Pentanoic Acid	1.600
Potassium Pentanoate Salt	6.693
Potassium Heptanoate Salt	6.731

To illustrate, [table 1](#) shows the dipole moment of water, common diesel fuel components, as well as the portions of the functional groups used in DDSA (cis-methylsuccinic acid) and fuel detergents (succinimide). Additionally, a carboxylic acid and metal carboxylate are shown for reference. Hydrocarbon chains longer than propane do not have a dipole moment ($D=0.000$) and do not have the ability to stabilize molecules with significant dipole moments, such as water ($D=1.85$). However, the dipole moments of additive functional groups, cis-methylsuccinic acid and succinimide, have relatively high dipole moments ($D=1.50$ and 1.54 , respectively) and possess the ability to polarize around water molecules and stabilize the interaction between the two. When the carboxylic acid is deprotonated and forms a metal salt, as with potassium heptanoate, the dipole moment