

Internal Injector Deposits in High-Pressure Common Rail Diesel Engines

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ABSTRACT

To meet increasingly stringent diesel exhaust emissions requirements, original equipment manufacturers (OEMs) have introduced common rail fuel injection systems that develop pressures of up to 2000 bar (30,000 psi). In addition, fuel delivery schemes have become more complicated, often involving multiple injections per cycle. Containing higher pressures and allowing for precise metering of fuel requires very tight tolerances within the injector. These changes have made injectors more sensitive to fuel particulate contamination.

Recently, problems caused by internal diesel injector deposits have been widely reported. In this paper, the results of an investigation into the chemical nature and probable sources of these deposits are discussed. Using an array of techniques, internal deposits were analyzed from on a number of sticking injectors from the field and from OEM test stands in North America. In each case, the internal deposits were found to be composed mainly of the sodium salts of alkenyl succinic acids. These salts are insoluble in ultra-low sulfur diesel (ULSD) fuel and can exist as very fine particles that pass through fuel filters, flowing to the rail and injectors. Sodium can enter diesel fuel from a number of sources including refinery salt driers, storage tank water bottoms and seawater used as ship ballast. Alkenyl succinic acids are commonly used as corrosion inhibitors to protect pipelines and other parts of the diesel fuel delivery system. Based on the proposed mechanism, an engine test was developed that reproduces the deposits and injector sticking observed in the field and OEM test stands. This test was used to identify alternate corrosion inhibitor and detergent chemistries that significantly reduce the propensity to build sticking deposits in low clearance areas inside high pressure diesel injectors.

INTRODUCTION

Regulations mandating lower pollutant emissions from diesel engines are forcing significant changes both in engine design and diesel fuel composition. In recent years, engine manufacturers have made increasing use of exhaust gas recirculation (EGR), diesel particulate filters (DPF), and high-pressure common rail (HPCR) fuel injection systems. The use of HPCR equipment allows for better fuel atomization and more precise control of the rate, shape and timing of fuel delivery to the cylinder. Safely containing the high pressures and allowing for accurate metering of fuel requires very tight tolerances within the injectors. In North America, HPCR systems are being deployed in an increasing fraction of the overall diesel fleet [1].

Ultra-Low-Sulfur Diesel (ULSD) fuel (less than 15 ppm sulfur) was phased in to the on-road market beginning in 2006. EPA's stated goal in mandating the reduction of sulfur in diesel fuel was to "enable advanced pollution control technology for heavy-duty trucks and buses so that engine and vehicle manufacturers could meet the 2007 emission standards" [2].

Reports of problems with HPCR engines began in 2008. Poor engine operation was observed, with symptoms including poor drivability, rough running, and inability to cold start engines [3, 4]. The problem appeared to be sporadic, with a geographic concentration in the center of the United States. OEMs were affected to different degrees, related to the number of HPCR engines in service and under evaluation. For some OEMs, the problem was limited to engines installed in test cells for pre-production testing. Two distinct types of deposits were identified. One, a hard carbonaceous deposit, was seen on the injector tips and on the outside of the injectors, and was described as a traditional deposit based on

fuel degradation. The other was a waxy, white to yellow deposit that showed up as a thin film on the internal surfaces of the HPCR needles and command plungers, primarily in the lowest clearance areas of the injector internals. Some OEMs saw the deposits on the pilot valve of the injector, another tight tolerance internal area.

In August of 2009, the OEMs, in a letter written to the Coordinating Research Council (CRC), outlined their best understanding of the problem [5]. They identified a possible problem with monoacid lubricity additives, which were being used in some ULSD fuels to improve their lubricating quality. In addition, they expressed the belief that neutral lubricity additive, typically esters, did not contribute to the problem. Some OEMs believed that diesel detergents may be useful in helping to control or eliminate the problematic deposits. While the problem was seen in engines operating on ULSD, not all ULSD fuels were implicated. California in particular was singled out as having no problems, regardless of the lubricity additive utilized. There was a general consensus that lubricity additive type, treat rate, and interaction with other fuel additives or fuel components all contributed to the formation of injector deposits.

Based on these continued concerns, and the inevitable growth in the prevalence of HPCR injected engines in the market, the Diesel Deposit Committee which is under the CRC Light Duty Performance Group was asked to investigate the problem.

When the problems initially surfaced, various groups studied them and reported findings. Work in 2008 by Ullmann, et.al. saw potential interactions with diesel detergents, monoacid lubricity improvers, and sodium ions [6]. Analyses were based on FTIR spectroscopy of deposits and the reaction products of various additive combinations. Sodium carboxylates were identified as a problematic deposit, with the logical conclusion that a monoacid lubricity additive could be involved. Others believed that the problem was mainly related to high injection pressures and fuel thermal stability [7]. While these initial theories had some merit, they were at odds with some observations from the field. The OEMs saw inconsistencies with the onset of the problem - in some applications where monoacid lubricity improvers were used, there were no performance issues related to injector deposit formation. Tests on the thermal stability of problematic fuels showed them to be very stable. Still, these early efforts were useful in pointing out some of the potential interactions.

The investigation outlined in this paper began by surveying the OEMs to build a consistent base of observations which would allow us to broaden our understanding of the factors involved in the formation of injector deposits. Through this survey, it was confirmed that the performance problems observed were limited to HPCR engines fuelled on ULSD.

Problems were seen regardless of the type of lubricity additive used, and whether or not detergent was present. If there was an additive involved, it was likely not a lubricity improver or a diesel detergent. There was the consistent presence of sodium in fuels that caused the problem, although it was only needed at trace levels.

This paper reports findings related to the chemical nature and mechanism of formation of problematic internal injector deposits from vehicles, fuel and filters in North America. Our preliminary research on internal injector deposits found in Europe shows another mechanism may also account for a significant number of problems. These findings will be reported in a separate paper.

MATERIALS AND METHODS

Several OEMs provided failed injectors for analysis. Some of these came from engines running development testing in cells, others came from field service. In addition, other failed injectors were independently obtained from customers in the field. [Table 1](#) provides a list of the injectors, filters and fuels analyzed for this paper. Each injector was disassembled and the critical internal parts (e.g. needle, command plunger, fuel-metering valve) were carefully removed for inspection. In all cases where the internal parts were difficult to remove, we observed deposits covering most of the internal surfaces. After rinsing with heptane to remove any residual diesel fuel, these deposits become white to light brown in color, and were very different in appearance than the black carbonaceous-type deposits often associated with fuel degradation. [Figure 1](#) shows a photograph of a needle removed from an injector returned because of rough running and difficult cold starts. A light colored deposit covering most of the surface, including the low clearance areas, is visible.

In some cases, when failed injectors were unavailable, fuel samples and filters were provided for analysis. Fuel samples were first passed through a glass fiber filter, then the filter was analyzed in the same manner as those received from the field. Each filter was subjected to successive extractions with pentane, toluene, methanol, water. Residual fuel was removed by pentane and toluene. In all cases, the bulk of the deposit solids were soluble in the methanol extraction. After removing the methanol at 100°C under flowing nitrogen, the extracted solids were analyzed in the same manner as the injector deposits.

Several methods were used to analyze deposits. Scanning Electron Microscopy / Energy Dispersive X-ray Spectroscopy (SEM/EDS) were performed with a JEOL JSM-5800LV and were used to study the morphology and elemental make-up of the deposits. Fourier Transform Infrared (FTIR) spectroscopy was performed using a Smiths Detection IdentifyIR FTIR and provided chemical structure information. Mass Spectroscopy (MS), Liquid Chromatography/Mass Spectroscopy (LC/MS)



Figure 1. Needle taken from an UPCR injector that showed symptoms of sticking.

and Mass Spectroscopy/Mass Spectroscopy (MS/MS) were performed on a Waters UPLC / Micromass Q-T of Micro and provided molecular weight and chemical structure information.

SEM/EDS were performed on the deposit while on the injector component. For FTIR and MS analyses, deposit was removed from a selected area by gently scraping with a razor knife. Deposit was analyzed as removed by FTIR or dissolved in methanol or tetrahydrofuran for injection into the MS or LC/MS.

Monoacid-type lubricity improver, ester-type lubricity improver and 2-ethylhexyl nitrate (2-EHN), were obtained from Afton Chemical Corporation. Sodium chloride, behenic acid, and dodecenyl succinic anhydride (both straight and branched carbon chains) were obtained from Sigma-Aldrich Chemical Company. Hexadecenyl succinic anhydride was obtained from Albemarle Chemical Corporation. Alkenyl succinic acids were prepared by reacting the alkenyl succinic anhydride with water. Sodium salts of various carboxylic acids were prepared by combining each acid with an amount of sodium hydroxide (as a 15% solution in water) that neutralized all acid groups. Excess water was removed by flowing nitrogen at 150°C.

Engine testing was carried out using a Peugeot DW10 mounted on a test stand. The DW10 is a 4 cylinder 2.0 liter direct injection turbocharged common rail engine and is used in the CEC F-98-08 Injector Fouling Test. Euro V injectors and the same test cycle (except without soak periods) as employed in the CEC procedure were used in all engine tests. A standard ULSD reference fuel, PC-10, was obtained without additives from Chevron Phillips Chemical Company and used in all engine tests. The sodium content of this fuel was less than 1 ppm. Fuel was supplied to the engine from a drum inside the test cell. Two fuel filters were placed in-line between the drum and the engine, a 30 micron primary-filter and the factory-specified 4-micron secondary filter. Fuel returned from the high-pressure pump and the injectors was passed through a heat exchanger and then recirculated through the 4-micron filter. To bring the fuel cetane number above 50, 1600 ppm by volume of 2-EHN was added to all

test fuels. Sodium was always blended into the fuel as a water solution and was added separately from any carboxylic acids. The contents of the drum (fuel, water, sodium chloride or sodium hydroxide, additives) were mixed with an air motor driven propeller for one hour prior to starting the engine and then continually during each test. The exhaust temperature from each cylinder was recorded throughout each 8-16 hour test. A test was stopped and considered to have failed (one or more injectors sticking) if the exhaust temperature of any cylinder was more than 45°C outside the 4-cylinder average temperature. A test was also considered to have failed if after allowing the engine to cool to ambient temperature, a cold start showed wide differences in cylinder exhaust temperatures. A single cold start was performed after each 8 hour test segment, again with monitoring of individual cylinder exhaust temperatures. Sticking of the needle was confirmed by disassembling the injector and subjectively determining the force required to remove the needle from the nozzle housing.

RESULTS AND DISCUSSION

DEPOSIT ANALYSES

The FTIR spectrum of deposit taken from the surface of the command plunger removed from Injector A is shown in [Figure 2](#).

The grouping of peaks at 1563, 1437 and 1411 cm^{-1} is indicative of a carboxylic acid salt and the spectrum as a whole bears some resemblance to that of sodium palmitate or sodium stearate. However, the hydrocarbon peaks at 2800 to 3000 cm^{-1} are much smaller relative to the carbonyl peak at 1563 cm^{-1} than would be found in a spectrum of natural carboxylate like stearate or palmitate. This would seem to indicate that the deposit salt did not originate from natural fatty acids, which typically have 16-18 carbon atom chains. Therefore, the deposit was likely derived from an acid with significantly less than 16 carbon atoms, or more than one carboxylate group per molecule, or both.

The EDS spectrum of the deposit on the command plunger in Injector A is shown in [Figure 3](#).

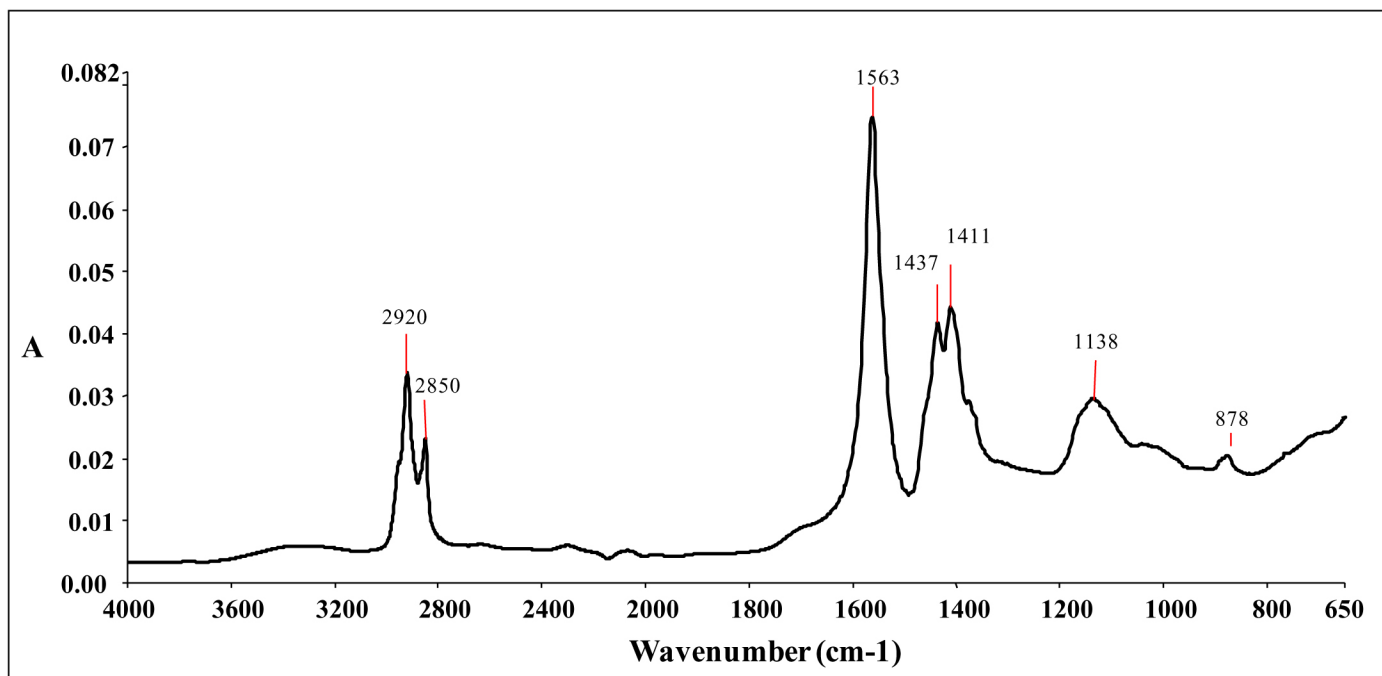


Figure 2. FTIR spectrum of deposit from command plunger removed from Injector A.

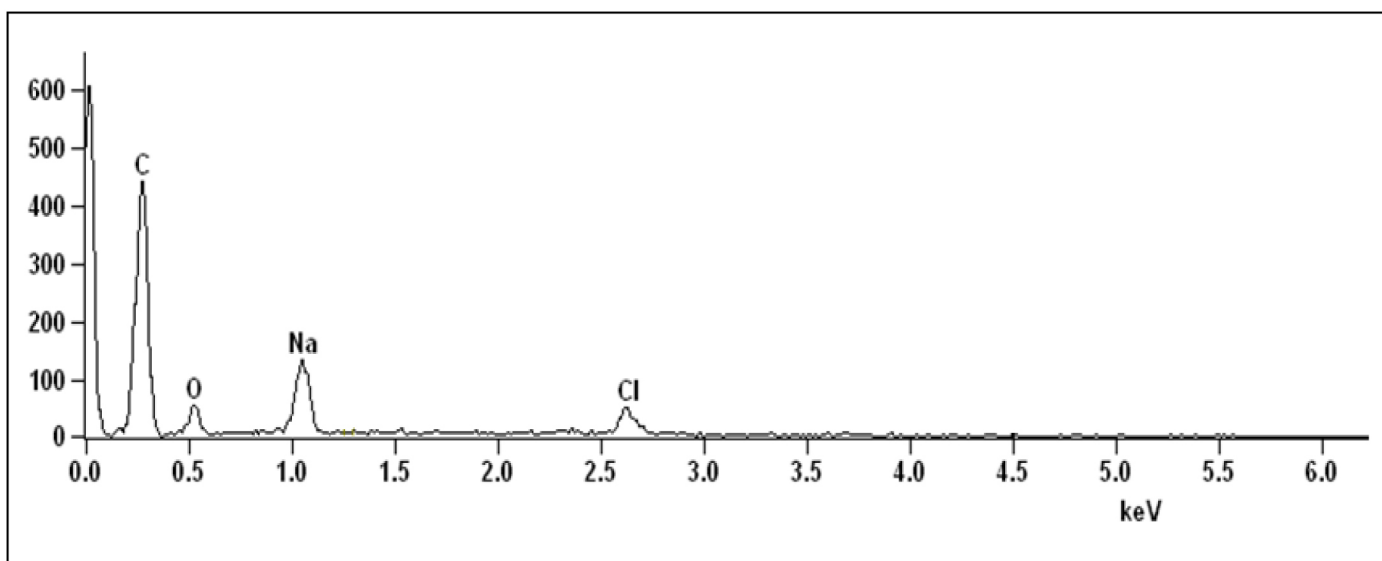


Figure 3. EDS spectrum of deposit on plunger of Injector A. Accelerating Voltage = 7kV.

The major peaks are assigned to carbon, oxygen, sodium and chlorine; identifying sodium as the main counter ion in the carboxylate salt. The presence of a substantial concentration of chlorine in the deposit indicates that sodium chloride was also part of the deposit. Sodium chloride is used as a drying agent at many refineries and could enter the fuel distribution system during a refinery upset. It could also contact the fuel from seawater used as tanker ship ballast.

The negative ion mass spectra of the deposits scraped from Injector A needle is shown in [Figure 4](#).

The major peak in the deposit mass spectrum is at 283 m/z. Singly charged ions of carboxylic acids likely to be found in fuel with this molecular weight are derived from stearic acid (a minor component of mono-acidic lubricity additives) and dodecyl succinic (DDS) acid (a widely used fuel corrosion inhibitor). MS/MS and LC/MS were employed to positively identify the 283 m/z species. [Figure 5](#) shows the MS/MS

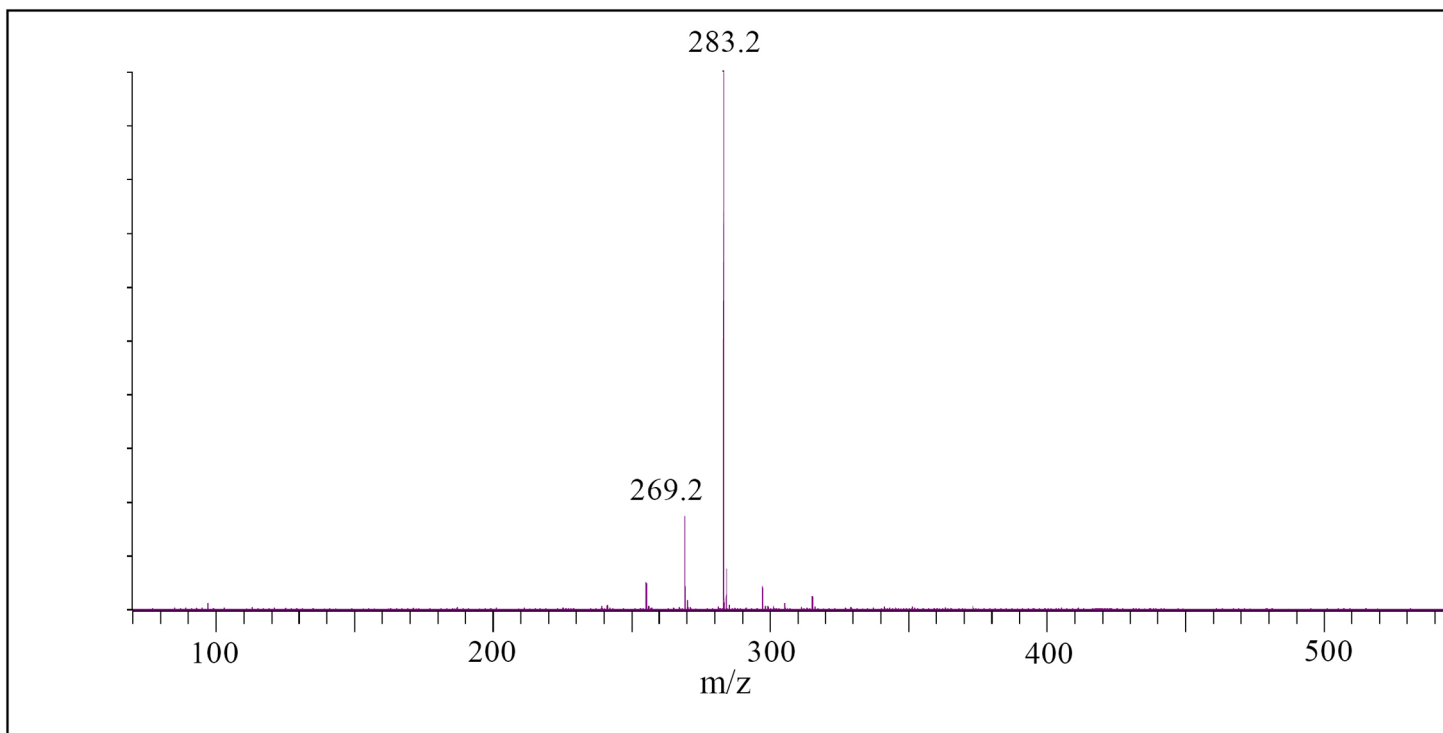


Figure 4. Negative ion mass spectrum of deposit taken from command plunger in Injector A.

fragmentation spectrum of the 283 m/z peak in the A needle deposit.

No significant peaks were observed in the positive ion spectrum of the Injector A deposit. Please note that sodium ions are below the observable mass range for conditions used in this analysis.

The fragment peaks were assigned to the parent ion with a loss of one mole H_2O (265 m/z), one mole CO_2 (239 m/z), one mole H_2O and one mole CO_2 (221 m/z). The peak at 98 m/z was assigned to a maleic fragment with the formula $\text{C}_4\text{H}_2\text{O}_3$. Together with the FTIR and EDS spectra, the matching fragmentation patterns in [Figure 5B](#) and [5C](#) indicate that the deposit was mainly made up of a DDS acid sodium salt. Further confirmation of this was obtained by LC/MS where the retention times of the 283 m/z ion matched that of the DDS acid salt, not the stearic acid salt.

[Figure 6](#) shows the FTIR spectrum of a light colored deposit sample taken from the shaft of the needle in Injector B1. Peaks at 1565, 1439 and 1412 cm^{-1} dominate the spectrum, indicating, as with Injector A, a carboxylate salt was the major species in the deposit. The EDS spectrum ([Figure 7](#)) of this deposit showed an elemental composition of mainly carbon, oxygen and sodium, with trace amounts of magnesium, calcium and sulfur. Sodium was again found to be the main counter ion in the carboxylate salt.

As with the A deposit, the FTIR and EDS spectra of the B1 deposit indicated the presence of sodium carboxylate salts. The major peak in the B1 deposit negative ion mass spectrum ([Figure 8](#)) was at 339 m/z, suggesting the salt was derived from either behenic acid or hexadecenyl succinic acid.

The main peak at 339 m/z is part of a grouping that also includes peaks at 325, 353 and 367 m/z. The peaks in this quartet are separated by 14 m/z, corresponding to one CH_2 unit. Naturally occurring mixtures of fatty acids almost always show differences of 28 m/z, or two CH_2 units, implying that the mixture of carboxylate ions in the deposit was of synthetic origin. A comparison of the MS/MS spectra of the 339 m/z ion in [Figure 9](#) indicates that the deposit spectrum nearly exactly matched that of the sodium salt of HDS acid.

An LC/MS analysis of the 339 m/z mass showed the retention time was the same as the HDS acid salt. It was therefore concluded that the major component in the internal deposit from injector B1 was the sodium salt of hexadecenyl succinic acid.

Similar analyses were performed on deposits taken from other injectors and filters associated with injector sticking. The identity of the major components in each deposit is given in [Table 1](#).