

Fuel Quality and Diesel Injector Deposits

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ABSTRACT

Internal deposits formed within the fuel injection system have been widely reported in the literature. Several root causes exist, with many deposits consisting of more than one material. The final chemistry depends on the availability of trace fuel contaminants and additives and to a lesser extent hydrocarbon/FAME stability and operating conditions. The present paper identifies the primary deposit morphologies, along with the typical root cause. Metal carboxylate salts, also known as metal soaps are most widely reported and are easily recreated under controlled conditions using compounds present at trace concentrations in some market fuels. The salting reaction may occur at low temperatures in the fuel supply system. It is proposed that the resulting fuel insoluble salt molecules are transported as reverse micelles, occasionally plugging filters but more commonly passing to the high pressure injection system. The micelles collapse at regions of high temperatures, pressures and shear within the injection system to form unstable polar molecules that absorb to nearby metal surfaces as deposits. Nitrogen containing amide deposits have also been widely reported and were recreated through reaction of low molecular weight components present in some PIB based deposit control additives (DCA). Finally, deposits caused by degradation of the hydrocarbon or FAME base fuel are occasionally reported in some markets. Such deposits were recreated and are strongly sensitive to the combined effects of fuel stability and temperature. The composition of deposits caused by FAME stability are chemically similar to that of post-test residue removed from Rancimat tests.

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INTRODUCTION

Deposit formation has been an issue within diesel fuel injection equipment (FIE) since its inception over 100 years ago. [1] Until recently, most industry focus was directed towards nozzle hole coking and to some extent the effects of these early deposits were allowed for in the relatively flexible requirements of the older FIE designs. The effects were of limited concern in the absence of emissions regulations and were primarily increased visible smoke and ultimately power loss due to restriction of nozzle hole flow.

Modern compression ignition engines are designed to meet stringent emissions regulations and are typically "smoke limited", i.e. the maximum fuelling rate is both tightly controlled and limited to prevent excessive soot formation. Injection pressures have increased dramatically, which combined with complex multiple injection strategies demands close control of injection timing and component clearances of less than 1 μm . Fuel pressures of 200 to 300 MPa ensure peak temperatures exceed 150°C due to dissipation of kinetic

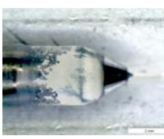
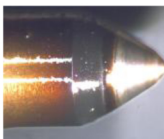
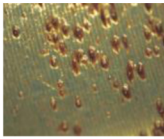
energy, with nozzle tip temperatures being appreciably higher still.

Fuel quality has also changed in response to environmental pressures. Increasingly severe refinery process to reduce sulphur content has affected the ability of the fuel to carry semi-soluble reaction products and also necessitated the use of lubricity additives and in some instances additional corrosion inhibitors. The use of FAME is now commonplace in many regions, bringing less stable components.

These changes have facilitated new reaction pathways in market diesel, which would not have occurred just a few years previously. In addition, the effects of precipitates and deposits are more readily apparent; as even minute changes in operating characteristics become unacceptable in electronically controlled FIE operating as part of a tightly regulated system.

Nozzle hole coking has been controlled through use of PIBSI DCA in some markets and more broadly by careful design of hole geometry, which has the side effect of being an additional constraint on nozzle hole optimization. Incidence of internal injector deposits (IIDs) are now being reported

Table 1. Relationship Between Fuel Chemistry and IID Composition

<u>Fuel Component</u>	<u>Root Cause</u>		<u>Deposit Type</u>	<u>Typical Appearance</u>	<u>Identification</u>
<u>Trace Contaminant</u>	Na > 0.1 mg/kg Acidic material, especially alkenyl succinic acids	Most Concern  Least Concern	<u>Metal Carboxylate Salt</u>		Soapy Deposit Soluble in water EDX: C, O, Na FTIR: 1438, 1415, 1560cm ⁻¹
<u>Additive</u>	Degradation of PIBSI DCA or residual components from PIBSI manufacture		<u>Polymeric Amide</u>		Very hard Impervious to solvents EDX: C, O, N FTIR: 1658 & 1555cm ⁻¹
<u>Hydrocarbon or FAME</u>	Poor stability, especially FAME Inappropriate storage High temperatures.		<u>Aged Fuel</u>		Soft, sticky deposit Soluble in light hydrocarbons EDX: C, O FTIR: 1715-1730 cm ⁻¹
<u>Hydrocarbon Base</u>	Poor hydrocarbon stability. High temperatures and cavitation.		<u>Pyrolised Fuel</u>		Fine black particulate - May form coating - May plug filters EDX: Pure Carbon FTIR: N/A as black

within the FIE, typically within the injector body close to areas where fuel pressure is released. Such areas also tend to be close fitting components in relative motion and so are potentially affected by IID accumulation.

The mechanisms for IID formation are likely to be different to those observed in nozzle-hole coking, since there is no possibility of exposure to combustion gasses or evaporation of fuel from the wetted surface. Instead, it is likely that precipitation of microscopic fuel insoluble materials occurs onto nearby metal surfaces. It is unlikely that the metallic surfaces play an active role, since the IID may be many microns thick effectively shielding the surface from the reaction process.

Sporadic IID issues have been reported in specific geographical areas, indicating that the process is associated with occasional variation in fuel composition. The effects appear consistent across all FIE manufacturers, typically affecting injector dynamics resulting in a measurable change in operating characteristics. The principal chemistries are outlined in [Table 1](#), which broadly correspond to those now being reported in the literature. Each IID may have several root causes, i.e. metal carboxylate salts may result from reaction of sodium from one of several sources with a range of acids. In general, metal carboxylate salts are most common, closely followed by organic amides.

METAL CARBOXYLATE SALTS

OVERVIEW OF METAL CARBOXYLATE SALTS

Metal carboxylate salts have been widely described in the literature and reported by a number of automotive manufacturers in the North American and European markets,

particularly France with transient issues in some other areas. [2,3,4] They form a soft opaque IID, which is often water soluble and may form in fuel with good stability. Typical Fourier Transform Infrared (FTIR) spectra are represented by the red line in [Figure 1](#), with peaks at 1565, 1438 and 1415 cm⁻¹.

The proposed mechanism of metal carboxylate salt IID formation is summarised in [Figure 2](#) and consists of five distinct steps, which are discussed in the following sections. In summary, reverse micelles of metal carboxylate salts may occur within the bulk fuel, remote from the point where deposits are formed, potentially even prior to the vehicle. Evidence is provided to indicate that the micelles are then transported to areas of high temperature and fluid shear, where the deposits are subsequently formed.

FUEL CONTAMINATION

Metal carboxylate salts are readily formed through reaction of sodium with carboxylic acids. [2,3,4,5,6] This combination is believed to be the most common IID precursor, with sodium is present in approximately 75% of IID analysed.[2] Other metallic elements such as calcium and potassium may occur, but are not widely observed.

Potential sources of sodium and carboxylic acids are listed in [Table 2](#). The most likely source is from sodium hydroxide from manufacture of FAME. Other less reactive sources include sodium chloride from salt dryers, sea transportation and de-icing agents and sodium nitrite corrosion inhibitors additives. Metal carboxylate soap IID are particularly prevalent in France, where approximately one third of randomly selected fuels samples have detectable sodium, i.e. a sodium content exceeding 0.1 mg/kg.[2] This is appreciably higher than comparable countries and is believed

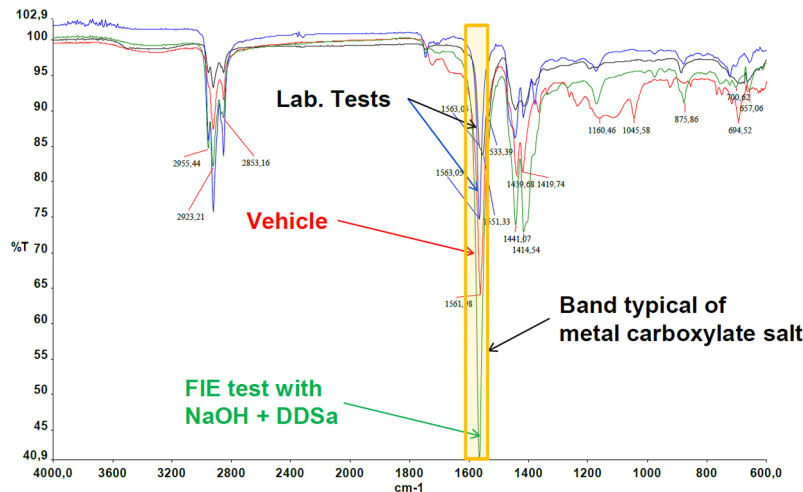


Figure 1. Comparison of FTIR Spectra of Metal Carboxylate Salts from Operating Vehicles, Laboratory Scale Tests, and Electric Motor Driven FIE Tests

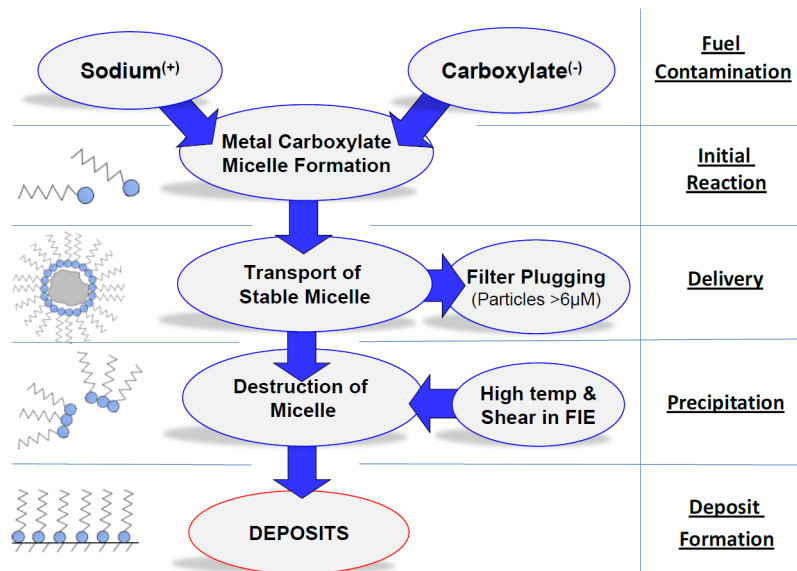


Figure 2. Schematic Diagram Showing Likely Mechanism of Metal Carboxylate Salt Formation

Table 2. Potential Sources of Sodium and Carboxylic Acids

Sources of Sodium		Most Concern ↑ ↓ Least Concern	Sources of Carboxylic Acids	
NaOH	FAME & also in NaNO ₂		DDSa	Corrosion inhibitor
NaNO ₂	Corrosion inhibitor		Fatty acids	FAME Production Lubricity additives
NaCl	Salt dryers		Di Acid	Corrosion inhibitor
	Sea transportation De-Icing Agent			

to be due in part to use of sodium nitrite (NaNO₂) corrosion inhibitors in some multiproduct pipelines.

Sodium nitrite is typically manufactured by treating sodium hydroxide with mixtures of nitrogen dioxide and nitric oxide. As a result, sodium nitrite corrosion inhibitors

normally contain residual sodium hydroxide. The likelihood of IID formation is broadly proportional to reactivity, with sodium hydroxide being more reactive than sodium chloride, however chlorine is detected in some deposits.

Acidic materials are ubiquitous in diesel fuel. The reactivity of sodium hydroxide potentially allows reaction with a range of acidic components, including those typical of fuel aging, mono and dimer acid lubricity additives, as well as corrosion inhibitors.[2] Experience in the European market indicates that alkenyl (hexadecenyl or dodecenyl) succinic acids used as pipeline corrosion inhibitors have particularly strong susceptibility for IID formation. The number of observations of IID in a specific market is plotted in Figure 3, with a strong increase in observations between October and January. Best available information indicates that the observations coincide with the approximately period that dodecenyl succinic acids (DDSa) was used in that market. Similarly, analysis of IID from North American indicated the presence of sodium salts of alkenyl (hexadecenyl or dodecenyl) succinic acids. [3]

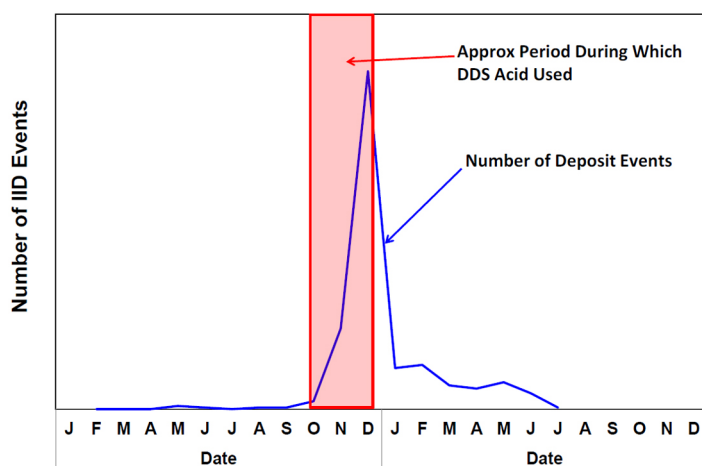


Figure 3. IID Events Observed compared with Use of DoDecenyl Succinic acid (DDSa) in a Specific Market

INITIAL REACTION

Laboratory scale tests were performed to demonstrate that reaction of sodium hydroxide and DDSa to form metal carboxylate salts will proceed at low temperatures, comparable to that during fuel distribution and storage. The tests were performed with 40 ml of additive free diesel fuel containing 5 vol% FAME. DDSa was added to the B5 diesel followed by 30 ml of an ethanolic solution of sodium hydroxide (NaOH). The use of an ethanolic solution improved the solution of the sodium to the blend. The final concentrations of DDSa and sodium were approximately 800 and 474 mg/kg respectively. These concentrations are higher than normally found in field fuels and are used to indicate the potential for reaction under accelerated conditions.

The blend was made in a glass beaker at 40 to 43°C, resulting in visible precipitate in less than one minute. The precipitates were readily removed using 5 µm pore size Millipore type SM filter paper. The blue curve in Figure 1 shows the FTIR absorbance spectrum of the filtered sodium carboxylate salt, which is very similar to the red curve for IID

from an operating vehicle with a strong peak at 1565 cm⁻¹. The salting reaction was observed to accelerate as temperature was increased. Clearly however, the reaction does not require the elevated temperatures within FIE to occur. Additional tests were performed using water, rather than ethanol, as the sodium hydroxide solvent. The salting reaction rate appeared to be reduced. Nonetheless, the resulting precipitate has the correct chemistry as shown by the black spectrum in Figure 1.

DELIVERY

The results of the preceding section indicate that the reaction to form metal carboxylate salts may potentially occur at any point during fuel manufacture, delivery and storage. Nonetheless, deposits are only formed at certain critical locations (typically areas of pressure release and associated high temperature) and are seldom if ever found throughout the low pressure system. Following the initial reaction, it is likely that the metal carboxylate salt forms a reverse micelle, in which the hydrophilic groups are sequestered in the micelle core and the hydrophobic groups extend away from the centre into the fuel.

Electric motor driven FIE tests were performed at the conditions defined in Table 3 to demonstrate that fuels containing relatively high concentrations of metal carboxylate salt are capable of passing through the low pressure system in this manner, only to form deposits at critical regions within the FIE. Prior to each test, 300 mg/kg of sodium oleate was blended into the fuel storage tank. Sodium oleate does not necessarily duplicate all metal salts in field applications. It was used in these tests to ensure metal salt is present throughout the low and high pressure systems, but only results in deposits in critical locations.

Table 3. Operating Conditions for Electric Motor Driven FIE Tests to Evaluate IID

Parameter	Unit	Value
Injection Pressure	MPa	240
Duration	Hours	20
Injection frequency	Hz	19200
Fuel Temperatures		
Pump inlet	°C	90
Back leak	°C	170
Injector on time	µs	250
Sodium Oleate Concentration	mg/kg	300

An initial test sequence was performed with a coarse 25 µm filter in line. Severe IID was produced around areas of pressure release and high temperature, as shown in Figure 4a. No deposit was observed in the remainder of the low and high pressure systems.

A second test sequence was performed with a fine 1 µm filter in line before the FIE, which greatly reduced the amount of IID as shown in Figure 4b. Removal and disassembly of the filter indicates a significant quantity of soap like material on the filter paper. It is proposed that the