

Internal Injector Deposits From Sodium Sources

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ABSTRACT

There have been reports of internal injector deposits causing problems in diesel engines in the field from 2008. Such problems manifest themselves as rough idling, power loss, high emissions, high-pressure fuel pump wear, injector sticking, internal component corrosion and engine failure. These reports coincided with the use of common rail diesel injection systems and of ultra-low sulphur fuels introduced because of emission regulation demands.

The injection systems have design features that are more conducive or susceptible to deposit formation such as severe high temperature and pressure operating conditions, the tolerances of critical parts, and lower force internal component actuation. The changes to fuels have also affected the fuels ability to solubilise these deposits. The deposits formed manifest themselves in complex form in the field, often being mixtures of inorganic and organic compounds.

One sub-group of this complex picture that is of current major interest is "sodium soaps", also known as sodium carboxylates. Various sources of sodium have been used to research IDID with varying results. Work with the different sodium precursors, sodium hydroxide and sodium 2-ethylhexanoate (a fuel soluble sodium salt) showed that interaction with monoacid lubricity additives produced filter blocking in one case and injector sticking in the other. With the possible development of a standard engine test it is important to understand the effects of a variety of sodium sources to ensure any future test reflects field problems.

Investigation of a number of sodium salts and their interactions with different acid species in fuels are described in this paper. The effect of water and other factors are also presented. Finally, a commercial deposit control additive that is effective in controlling this type of IDID is provided.

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INTRODUCTION

The current interest in internal diesel injector deposits (IDID) from sodium carboxylate sources shows no sign of weakening. There is currently work in two continents on the subject. In the US there is a CRC committee sub panel on IDID (CRC DIESEL Performance Group - Deposit Panel Bench/Rig/Investigation sub panel) and in Europe the CEN TC19/WG24 Injector Deposit Task Force, and the CEC TDFG-110 panel is developing a standard engine test, using a "fuel soluble" sodium salt and dodecenylsuccinic acid (DDSA). Further, we have recently published [1] data using the diesel engine nozzle coking test [2] that showed sodium hydroxide and mono-acid lubricity improver resulted in filter blocking, and the same mono-acid lubricity improver with a "fuel soluble" sodium salt (sodium 2-ethylhexanoate) gave injector sticking. An ester based lubricity improver was found to cause neither problem.

The recent literature has seen a proliferation of engine testing studies, some using "fuel soluble" sodium salts as candidate reactive precursors for possible interaction with carboxylate group containing species in fuels as shown in [Table 1](#).

Table 1. Sodium sources from the literature.

Sodium Source	Formula
Sodium Hydroxide [3]	NaOH
*Sodium Hydroxide with Ethanol [4] "Sodium Ethoxide"	NaOH + C ₂ H ₅ OH
Sodium Chloride [3]	NaCl
*Sodium Octanoate [4]	NaOOC(CH ₂) ₆ CH ₃
*Sodium Naphthenate [4]	NaOOC ₁₀ H ₁₇ (example)
*Sodium Oleate [5]	NaOOC(CH ₂) ₇ CH=CH(CH ₂) ₇ CH ₃
*Sodium tert-Butoxide [6] (in 2-ethylhexyl alcohol)	NaOC(CH ₃) ₃ in CH ₃ (CH ₂) ₃ CH(C ₂ H ₅)CH ₂ OH
*Sodium 2-Ethylhexanoate [1]	NaOOCCH ₂ C(CH ₃) ₂ (CH ₂) ₄ CH ₃

The “fuel soluble” compounds are marked with * in Table 1 and have been used for a number of reasons in engine testing as a surrogate for aqueous sodium hydroxide. They can achieve delivery of higher sodium levels, provide fewer fluctuations in sodium concentration, offer short term stability and allow the storage and sample conditioning parts of the test to be less critical. This activity has led us to undertake some initial studies of interactions of these compounds with mono- and di-acid additives which may be present in fuel.

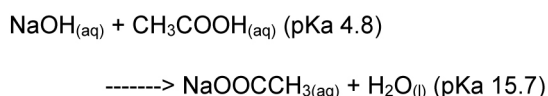
If we consider the field based reaction which the community is trying to mimic;



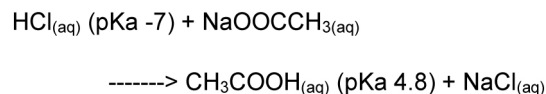
This is a simple “soap” formation process which has been known for many years. Obtaining repeatability in engine testing when contacting aqueous base with fuel has proven to be challenging but the current approach of using “fuel soluble” sodium salts as substitutes is not without difficulty. Essentially, the engine is being used to carry out reaction chemistry throughout the diesel fuel system, from fuel tank to injector tip. In this case there are the added complications of a two phase system, ligand coordination stoichiometry, competing metals, unknown solubility factors, acids from fuel impurities, impurities from water bottoms (including group II metals such as calcium), and elevated temperature and pressure.

Equilibria for reactions in water solution between acids and bases are well understood. This understanding applies irrespective of whether the acids or bases are organic or inorganic. The concept of acid ‘strength’ reflects the extent to which an acid (AH) dissociates in water to form H_3O^+ and A^- . This property can be measured and recorded on a logarithmic scale as a pKa value. Tables comprising lists of pKa values are available [7] and the smaller pKa, the stronger is an acid.

As described above, A^- is referred to as the “conjugate base” of the acid AH. It follows that for AH to ionise to a large extent, then A^- can only remove protons from available H_3O^+ to a very limited extent. Thus a strong acid can only ever provide a weak conjugate base. Mineral (inorganic) acids, such as hydrochloric acid (HCl) have very low pKa (−7); it follows that chloride ion is a very weak base. Thermodynamics drives the equilibrium position of these reactions towards the weaker acid and the salt of the weaker base. pKa values may be used to predict the products of reactions involving mixtures of acids, salts and bases [8]. Thus the reaction of sodium hydroxide and acetic acid yields sodium acetate and water:



Whereas the reaction of sodium acetate and hydrochloric acid yields acetic acid (weaker acid) and sodium chloride (salt of the weaker base):



It is appropriate to sound a note of caution at this point. pKa values are determined using measurements carried out in dilute solution in water saturated with potassium chloride [9] and are intended to be used to predict the course of reactions in aqueous solution. Fuels contain complex mixtures of acidic species, including additives that may themselves comprise mixtures. These acids are frequently of negligible solubility in water and amphiphilic, that is, prone to collect at the water-fuel interface as the polar (acid) ‘head’ group interacting with water and the non-polar hydrocarbon ‘tail’ with fuel. This can set up some distinctly complex equilibria. The water itself may be dissolved in fuel, present as droplets (whether or not surrounded by a monolayer of surfactant as an invert micelle) or as a bulk interface. The ionic strength of the water solution is, in the field, highly variable. In short, it was felt appropriate to investigate these reactions, or at least their outcomes, experimentally. This has been done using a number of JFTOT (Jet Fuel Thermal Oxidation Test) runs and an engine test using fuel deliberately contaminated with sodium salts of organic acids. Engine testing in the additional presence of Deposit Control Additives has been carried out in ‘keep clean’ mode.

ENGINE TESTING - DW10B

Tests were conducted using the CEC F-98-08 DW10B engine to assess the injector sticking tendency of fuels dosed with different sodium salts or by different routes. The tests were carried out using RF-06-03 (European certification test fuel) as received. Although the test procedure used to assess injector sticking employed the CEC F-98-08 DW10B engine, the fuel was not adulterated with zinc neodecanoate. A brief outline of the procedure is given here. The test used the 1997cm³, 4-cylinder, turbo-charged, engine of the DI type with a high pressure common rail fuel system and μ -sac, six-hole injectors. The engine was operated on the engine test bench according to a test cycle consisting of 12 steady state conditions to give a total cycle time of 3600 seconds.

When the engine was started the exhaust gas temperatures for each cylinder were recorded during 15 minutes. The engine then completed 8 test cycles followed by a 4 hour soak period after which the engine was re-started and the exhaust gas temperatures for each cylinder recorded. This is referred to as 8 hour data. The engine then ran for a further 8 hours of test cycles followed by a 4 hour soak period before being re-started and the exhaust temperatures recorded to give 16 hour data.

This continued until 32 hours of test cycles had been completed or until the engine failed to start, which signified serious injector sticking.

Previous testing has shown that different sodium sources will interact differently with acidic species in the fuel, such as mono-acid lubricity improvers or di-acid corrosion inhibitors. Sodium hydroxide has been shown to cause injector sticking with the di-acid DDSA [6] but in the presence of a mono-acid lubricity improver it was found to cause fuel starvation due to a blocked fuel filter [1]. With a sodium 2-ethylhexanoate source, both the mono-acid lubricity improver and di-acid DDSA caused injector sticking and sodium carboxylate was observed on the injector needle. Testing of sodium chloride with a mono-acid lubricity improver did not result in engine running problems over the 32 hour test although EDAX studies showed very low levels of NaCl within the injector [1]. This would suggest that although NaCl does not react with the acidic species in the fuel it can still transport through the fuel system to the injector.

Sodium Sulphate

Sodium sulphate has been observed inside diesel injectors from the field [11] and, like NaCl, would not be expected to react with an acidic species in the fuel. A test was carried out on the RF-06-03 base fuel containing 120 mg/kg mono-acid lubricity improver. 130 mg/L of 18.98 %w/w aqueous sodium sulphate solution was added to the fuel and constantly mixed throughout the test. This is equivalent to 8 mg Na/L fuel and reflects the levels used in previous testing with other Na sources [1]. Exhaust gas temperature data for the test and power data are shown in Figures 1 and 2.

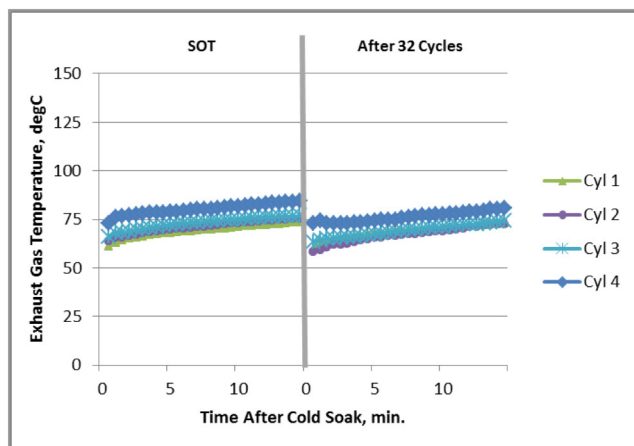


Figure 1. Exhaust gas temperatures from DW10B engine test on fuel containing mono-acid additive and sodium sulphate (aq.).

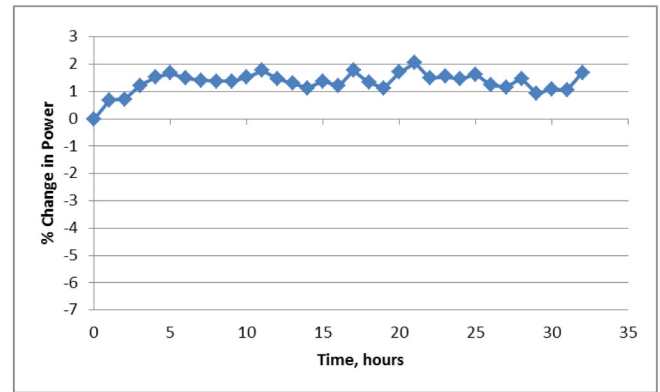


Figure 2. Power loss data from DW10B engine test on fuel containing mono-acid additive and sodium sulphate (aq.).

No power loss or change in exhaust gas temperatures, which would be indicative of injector sticking, occurred during the 32 test hours. Analysis of the injectors from the test showed no deposit. The fuel filter showed the presence of sulphate by FT-IR as indicated by the band at 1113 cm^{-1} which is attributed to an asymmetric SO_4 stretch. The bands at 1460 and 1377 cm^{-1} are attributable to the diesel fuel. This is shown in Figure 3.

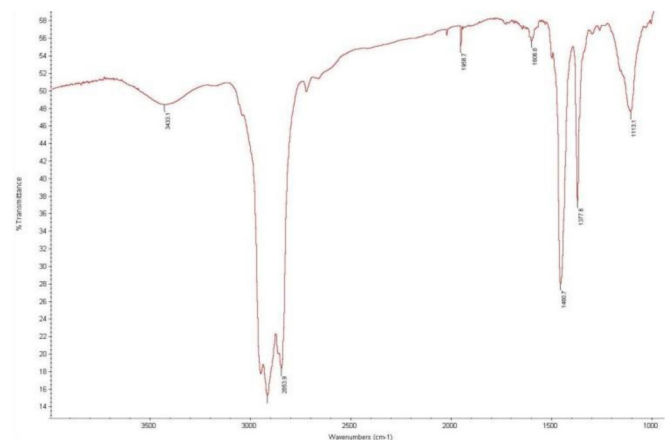


Figure 3. FT-IR trace of fuel filter from DW10B engine test on mono-acid additive and sodium sulphate (aq.).

The filter was also subjected to SEM along with EDAX analysis which showed the presence of sulphur as shown in Figure 4.

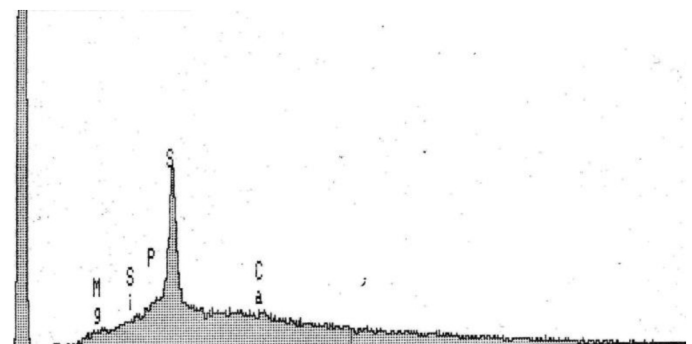


Figure 4. EDAX spectrum from fuel filter from DW10B engine test on mono-acid additive and sodium sulphate (aq.).