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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 dodeceny succinic 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(C ₂ H ₅)(CH ₂) ₃ 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.

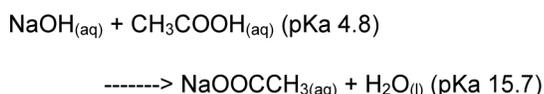
If we consider the field based reaction which the community is trying to mimic;



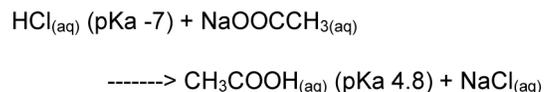
This is a simple “soap” formation process which has been known for many years. Obtaining repeatability in engine testing when contacting aqueous base with fuel has proven to be challenging but the current approach of using “fuel soluble” sodium salts as substitutes is not without difficulty. Essentially, 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.

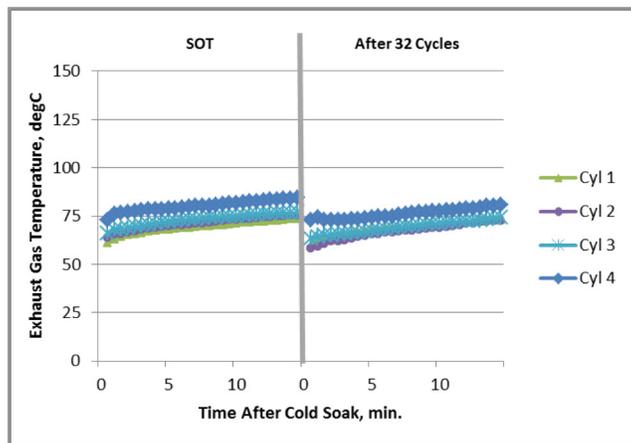


Figure 1. Exhaust gas temperatures from DW10B engine test on fuel containing mono-acid additive and sodium sulphate (aq.).

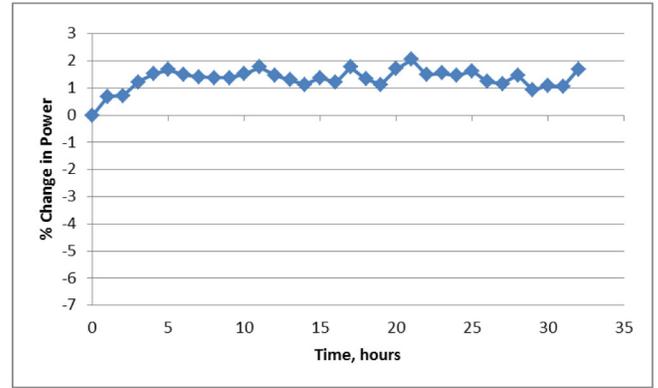


Figure 2. Power loss data from DW10B engine test on fuel containing mono-acid additive and sodium sulphate (aq.).

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.

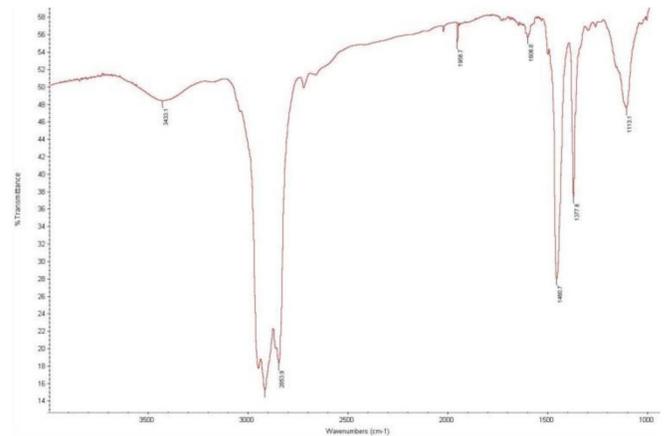


Figure 3. FT-IR trace of fuel filter from DW10B engine test on mono-acid additive and sodium sulphate (aq.).

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

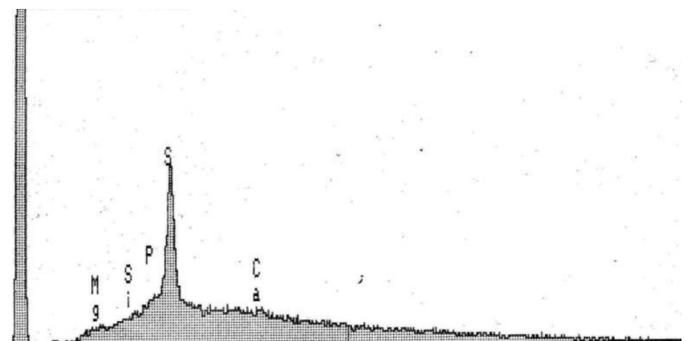


Figure 4. EDAX spectrum from fuel filter from DW10B engine test on mono-acid additive and sodium sulphate (aq.).

Effect of Deposit Control Additives on Sodium IDID

Previous work had shown the use of fuel soluble sodium 2-ethylhexanoate in conjunction with dodeceny succinic acid to cause injector sticking after 8 cycles. Sodium 2-ethylhexanoate alone did not cause injector sticking. To aid solubility in the fuel sodium 2-ethylhexanoate was added as a 10 %w/w solution in 2-ethylhexanol. Further work was carried out to determine if current commercial deposit control additives were effective in preventing the formation of sodium carboxylate deposits within the injectors.

A commercially available deposit control additive commonly found in diesel fuel globally was added to the fuel containing 0.5 mg/kg Na (as Na 2-ethylhexanoate) and 10 mg/kg DDSA. The test ran for the full 32 hours without signs of injector sticking. This is shown in [Figure 5](#).

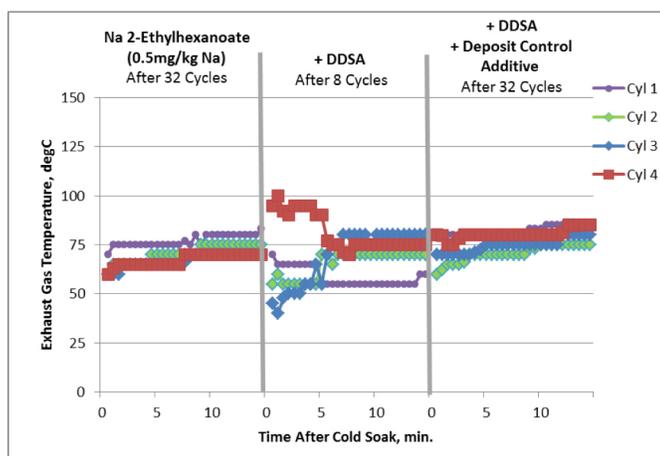


Figure 5. Exhaust gas temperatures from DW10B engine test on fuel containing Na 2-ethylhexanoate, DDSA and deposit control additive.

The data in [Figure 5](#) shows that current deposit control additives are effective in preventing the formation of sodium based IDID.

LABORATORY BENCH TESTS

Fuel Preparation

Samples of four different sodium salts were purchased from laboratory chemical suppliers. The supplier and purity of each sample is shown in [Table 2](#). Sodium 2-ethylhexanoate and sodium naphthenate have both been used as “fuel soluble” sodium sources in engine testing. Sodium hydroxide as an aqueous solution has proven difficult to use in engine testing but is one of the potential sources of sodium in the field. Sodium chloride is another potential source of sodium and has been found in injector deposits but its transport mechanism is not understood.

Table 2. Sodium salts used in laboratory testing.

Sodium salt	Purity (%)	Source
2-Ethyl Hexanoate $\text{CH}_3(\text{CH}_2)_3\text{CH}(\text{C}_2\text{H}_5)\text{COONa}$	97	Sigma-Aldrich
Naphthenate $\text{C}_{10}\text{H}_{17}\text{OONa}$ (example)	8-10 %w/w Na	TCI
Hydroxide NaOH	98	Fisher Scientific
Chloride NaCl	99.9	Fisher Scientific

The base fuel used for all testing was reference fuel RF-06-03.

The effect of the presence of different acidic species in the fuel was investigated by addition of either a mono-acid lubricity improver or a di-acid corrosion inhibitor. The mono-acid lubricity additive was a tall oil fatty acid (TOFA). This consists of a mixture of fatty acids but is depicted in [Figure 6](#) as oleic acid for simplicity. The di-acid corrosion inhibitor used was dodeceny succinic acid (DDSA). The structure of this molecule is also shown in [Figure 6](#). A treat rate of 120 mg/kg was used in each case. Although this treat rate is 10x higher than would be normal for the corrosion inhibitor it was used to ensure sufficient deposit was formed in the lab tests. A test carried out at 10 mg/kg did not result in sufficient deposit to allow analysis.

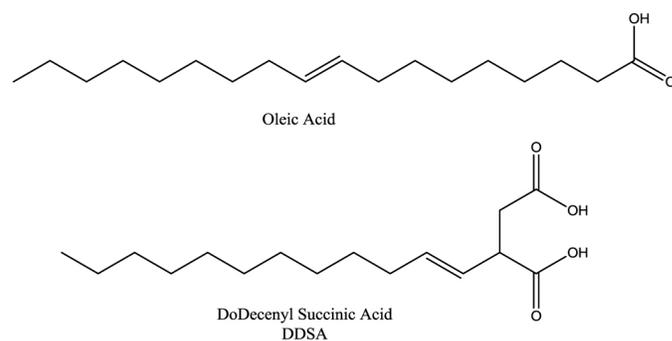


Figure 6. Structures of mono-acid and di-acid additives used in laboratory testing.

The various sodium salts were added to the test diesel fuel dosed with 120 mg/kg di-acid or mono-acid using different addition methods. They were: (1) added direct to the fuel as received; (2) added direct to the fuel as a 10 %w/w solution in 2-ethylhexanol and (3) made up as a 10 %w/w aqueous solution and shaken with the fuel. These were designed to simulate engine test procedures (1&2) where the sodium salt is added directly to the fuel and potential field conditions (3)

where the fuel is exposed to water bottoms in the distribution network. The methods are detailed below.

(1) Direct addition of the sodium salt to the test diesel fuel

Each sodium salt was added in sufficient quantity to equate to 10 mg/kg Na in the test fuel. The level of sodium was set to allow visual rating of deposit formed on the JFTOT tubes. To ensure good contact between the sodium salt and the fuel it was stirred on a hotplate at 750 rpm at room temperature for 1 hour. Due to the poor solubility of the salts in diesel it was likely that un-dissolved sodium was present during testing.

(2) Addition of the sodium salt as a 10 %w/w solution in 2-ethylhexanol to fuel

A stock solution of 10%w/w sodium salt was made by dissolving 1g of sodium salt in 9g of 2-ethylhexanol. Samples were warmed to 50°C in an oven before stirring to ensure maximum dissolution. The 10 %w/w solution of sodium salt was added in sufficient quantity to equate to 10 mg/kg Na in the test fuel and mixed thoroughly. It should be noted that the NaOH and NaCl did not completely dissolve using this method.

(3) Shaking the sodium salt as a 10 %w/w aqueous solution with diesel

A 10 %w/w aqueous solution of each sodium salt was prepared using deionised water. 100 mL of this solution was shaken for 1 minute with 800 mL of the test diesel fuel then allowed to stand for 60 minutes. The fuel layer was separated for testing.

JFTOT Testing

The Jet Fuel Thermal Oxidation Tester (Alcor JFTOT III) was modified to assess the formation of sodium containing deposits derived from different sodium salts and acidic species in diesel fuel. A volume of test fuel was pumped at a fixed rate of 3mL/min through an initial filter unit containing a 4 µm porosity filter paper cut from a diesel fuel filter. The fuel was then passed over an aluminium test piece heated to 260°C. The total test time was 2.5 hours and at the end of test the metal test piece was cleaned with analytical grade toluene and acetone, dried and rated visually for deposit formation.

The deposits formed on the JFTOT tubes were difficult to photograph effectively therefore a visual rating system was devised to record and report the results. The tubes were ranked from 0 to 3 depending on the level of deposit visible. Examples are shown in [Figure 7](#).

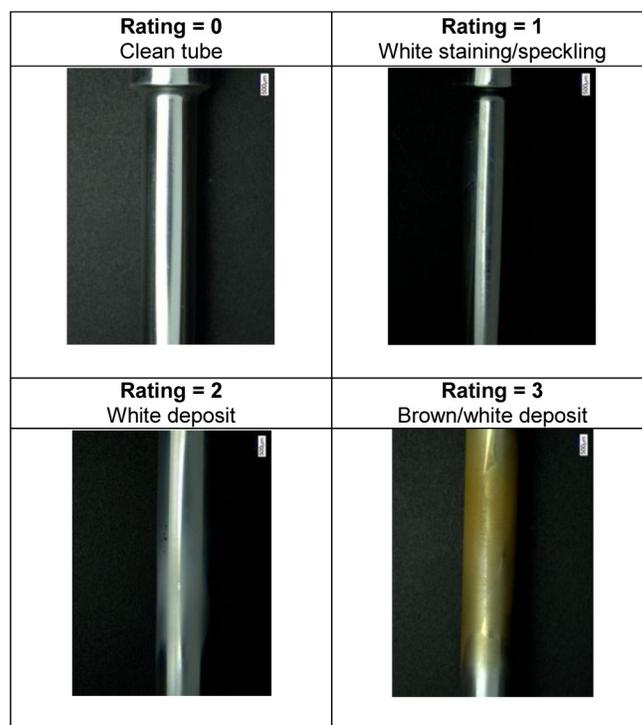


Figure 7. Rating system for JFTOT tubes.

The deposit was also rated depending on where it was situated on the tube relative to the flow of fuel. If the deposit was located on the bottom half of the tube relative to the point where the fuel first flows over the tube it was rated as “L” for lower and if it was on the top half of the tube it was rated as “U” for upper. Some tests resulted in deposit spread over the length of the tube and these were rated with just the number.

Direct Addition of Sodium Salt to Test Diesel Fuel (Method 1)

Tests were carried out according to method 1 to test the effect of the sodium salts on their own and also when either the mono-acid or di-acid were present in the test fuel. The results are presented in [Table 3](#).

Table 3. Visual ratings of JFTOT tubes from direct addition of sodium salts.

Sodium Salt	Acidic Additive	Tube Rating
Na naphthenate	None	3U
	Mono-acid	3U
	Di-acid	2L
Na 2-ethylhexanoate	None	1U
	Mono-acid	0
	Di-acid	2L
NaOH	None	0
	Mono-acid	0
	Di-acid	0
NaCl	None	0
	Mono-acid	0
	Di-acid	0

Sodium naphthenate alone produced a white/brown deposit in the upper part of the JFTOT tube. On addition of mono-acid to the fuel the deposit did not change. When the di-acid was added to the fuel the deposit moved location to the bottom of the tube and was only white in colour.

Sodium 2-ethylhexanoate produced very little deposit when added direct to the fuel on its own or when the fuel contained mono-acid. When added to the fuel containing the di-acid, the level of deposit increased and was again found on the lower half of the tube. Sodium 2-ethylhexanoate is only sparingly soluble in diesel fuel and is generally added as a 10 %w/w solution in 2-ethylhexanol when used in engine testing.

FT-IR analysis of the JFTOT tubes was carried out. The spectrum from sodium naphthenate alone is shown in [Figure 8](#) and the band at 1563 cm⁻¹ is typical of a carboxylate salt.

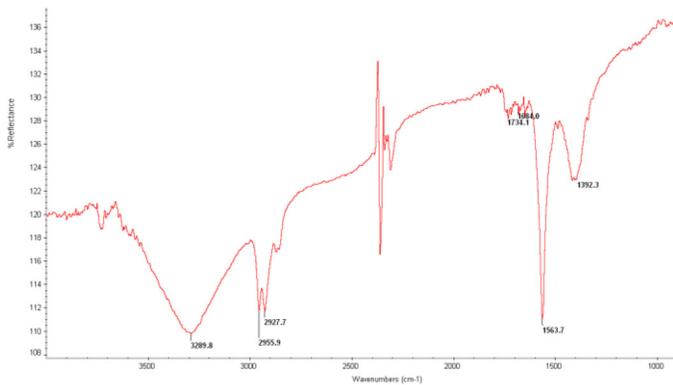


Figure 8. FT-IR trace of JFTOT tube from sodium naphthenate.

The spectrum from the sodium naphthenate/di-acid test is shown in [Figure 9](#) and again the band at 1565 cm⁻¹ indicates that a carboxylate is present. The JFTOT tubes clearly showed a difference in deposit type and location between these two tests but the FT-IR did not allow differentiation between the Na being associated with the naphthenate or the di-acid.

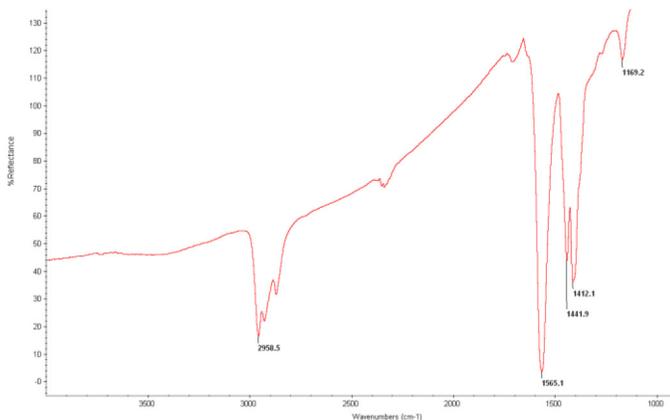


Figure 9. FT-IR trace of JFTOT tube from sodium naphthenate and di-acid.

The tests carried out using NaOH and NaCl did not produce any deposit on the tube. This can be attributed to the lack of solubility of those salts in the diesel fuel, even with acids present in that fuel.

Addition of Sodium Salt as 10 %w/w Solution in 2-Ethylhexanol to Fuel (Method 2)

To aid the dissolution of the sodium salts in the diesel fuel, solutions in 2-ethylhexanol were prepared and tests were carried out according to method 2. The effects of sodium naphthenate and sodium 2-ethylhexanoate were investigated on their own and also when either the mono-acid or di-acid were present in the test fuel. NaOH and NaCl were not fully soluble in the 2-ethylhexanol and therefore were not tested. The results are presented in [Table 4](#).

Table 4. Visual ratings of JFTOT tubes from addition of sodium salts as 10 %w/w solution in 2-ethylhexanol.

Sodium Salt	Acidic Additive	Tube Rating
Na naphthenate	None	3U
	Mono-acid	3U
	Di-acid	2L
Na 2-ethylhexanoate	None	3U
	Mono-acid	3U
	Di-acid	2L

Sodium 2-ethylhexanoate when added as a 10 %w/w solution in 2-ethylhexanol is more soluble in the diesel fuel and a heavier level of deposit was observed. On addition of the mono-acid a similar deposit was observed whereas with the di-acid, the deposit changed in both appearance and location on the tube.

The results for sodium naphthenate were the same as when dosed directly into the fuel.

Shaking Sodium Salt as 10 %w/w Aqueous Solution with Diesel (Method 3)

Tests were carried out according to method 3 to test the effect of the sodium salts as an aqueous solution contacted with diesel fuel. This is the most likely source of fuel - Na interaction in the field. Each salt was tested on its own and also when either the mono-acid or di-acid were present in the test fuel. The results are presented in [Table 5](#).

Table 5. Visual ratings of JFTOT tubes from shaking sodium salts as 10 %w/w aqueous solution with diesel.

Sodium Salt	Acidic Additive	Tube Rating
Na naphthenate	None	0
	Mono-acid	1
	Di-acid	2
Na 2-ethylhexanoate	None	0
	Mono-acid	0
	Di-acid	1
NaOH	None	2
	Mono-acid	1U
	Di-acid	1
NaCl	None	0
	Mono-acid	0
	Di-acid	0

Different results were observed for the various sodium salts when mixed with the fuel as a 10 %w/w aqueous solution.

The FT-IR of the JFTOT tube deposits for the test with NaOH (aq) and di-acid is shown in Figure 10 and the corresponding test with the mono-acid is shown in Figure 11. Both show the typical carboxylate band at ~1560 cm⁻¹ which would suggest that, when the NaOH is present in a form which can readily interact with the acidic species in the fuel, both the mono-acid and di-acid will form sodium carboxylates.

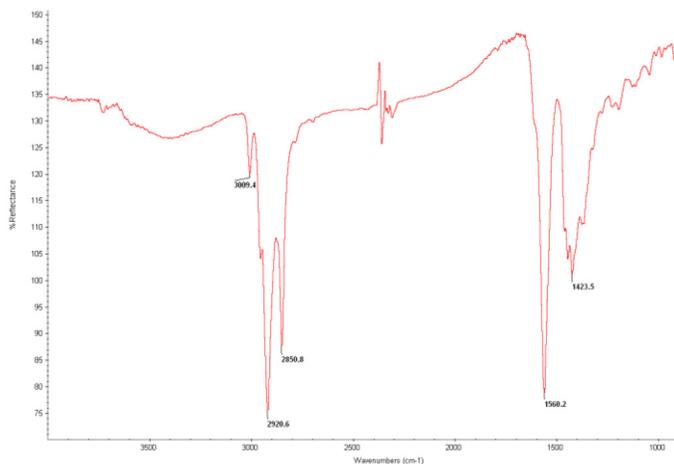


Figure 10. FT-IR trace of JFTOT tube from sodium hydroxide and di-acid.

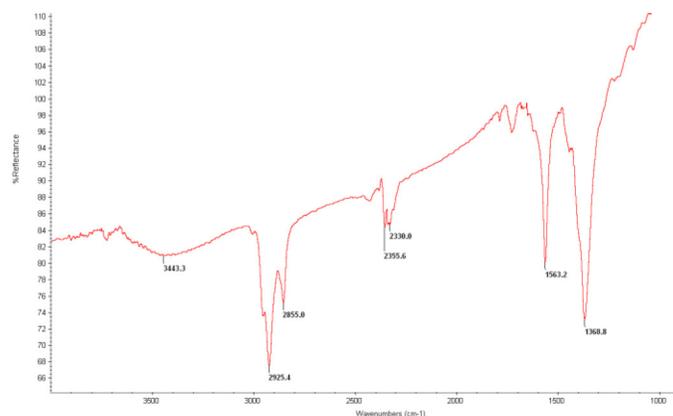


Figure 11. FT-IR trace of JFTOT tube from sodium hydroxide and mono-acid.

The NaCl tests did not produce any visible deposit and suggest strongly that although NaCl has been found in injectors from the field the mechanism of transfer is not due to an acidic additive species in the fuel.

HFRR Testing

A series of High Frequency Reciprocating Rig (HFRR) tests were carried out to try to understand the fate of the Na⁺ ion in the presence of the mono and di-acids. Earlier work [10] had shown that shaking fuel containing a mono-acid with aqueous NaOH resulted in a loss of lubricity performance. This was attributed to the reaction of the NaOH with the mono-acid to form a sodium carboxylate which did not have any lubricity performance. Tests with aqueous sodium chloride did not affect the lubricity performance of the mono-acid. An ester lubricity additive was unaffected by either the NaOH or NaCl. A summary of this work is shown in Figure 12.

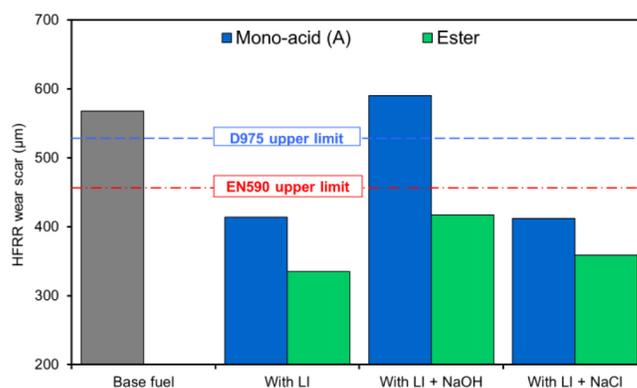


Figure 12. HFRR results from fuel shaken with 5%w/w aqueous NaOH and NaCl with both mono-acid and ester lubricity improvers.

Similar tests were carried out with Na 2-ethylhexanoate. Clay filtered RF-06-03 was used to ensure no other additive species were present. A summary of the results is shown in [Figure 13](#).

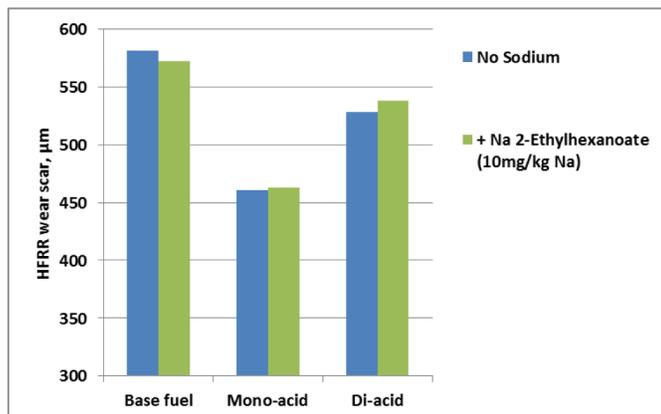


Figure 13. HFRR results for tests with Na 2-ethylhexanoate.

The results showed that the performance of the mono-acid did not change on addition of Na 2-ethylhexanoate which would suggest that direct addition of this sodium salt to the fuel does not result in an exchange of Na to the mono-acid. Note however, that this is a different situation to that likely seen in the field where NaOH is present in water bottoms and a drop in performance is observed.

The di-acid is not normally used as a lubricity improver in diesel fuel. Accordingly, at the treat rates used it did not result in the fuel meeting the industry standard requirement. It did, however, reduce the wear scar over the base fuel result. Addition of Na 2-ethylhexanoate did not affect this result.

The sodium naphthenate tests were not completed due to inconsistencies in the solubility of different batches of the salt. Naphthenic acid is a mixture of acids and therefore the composition may differ from batch to batch. A sodium salt prepared from naphthenic acid may also therefore vary in composition from batch to batch which may impact its solubility in diesel fuel. This will be important in the development of standardised test methods and a tight specification for the sodium naphthenate or naphthenic acid source would be required to ensure consistent results.

SUMMARY/CONCLUSIONS

JFTOT tests using NaCl and acidic additive species did not result in any visible deposit formation although NaCl has been found in field injectors. The transport of near-neutral inorganic salts, such as sodium chloride, through the fuel system to injectors is not readily explicable in terms of carboxylate salt (soap) formation.

In the JFTOT testing, the addition of DDSA to fuel containing a soluble sodium source produced a clear effect on deposit type and location. The corresponding tests with mono-acid lubricity improver did not show such an effect. Such a result is not entirely unexpected:

- The soluble sodium sources are also terminal aliphatic mono-acids which are of similar pKa to the lubricity improver - even if they did exchange they might then behave in similar fashion in this test and
- DDSA has pKa 4.2 so is a stronger acid than the terminal aliphatic mono-acids (pKa 4.8) and so might be expected to exchange.

HFRR testing has shown that addition of a 'fuel soluble' sodium source did not result in the loss of lubricity performance with the mono-acid lubricity improver additive. The same mono-acid in combination with NaOH exhibited a complete loss of lubricity performance.

Whether or not a given acid will exchange sodium with the salt of another acid already in the fuel is not relevant to the field issue. By contrast, how readily an acid mobilises sodium from the available sources, such as water bottoms, is. The choice of sodium source is therefore important when carrying out any surrogate testing, whether in the laboratory or in engine tests, to ensure that results are consistent with field experience.

DDSA has been implicated elsewhere as a 'worse actor' in sodium transport. That issue is separate to this paper. The results in [Table 5](#) for the consequences of contact between aqueous NaOH and fuel and in [Table 4](#) in the absence of added carboxylic acid are, however, relevant to that discussion. They confirm that the combination of the presence of any acidic species in fuel and intimate contact with a source of sodium base runs the risk of causing injector internal deposit issues.

If sodium naphthenate is to be used as a 'fuel-soluble' sodium source then the experience here would strongly suggest that some means to ensure that a consistent material is used needs to be found.

The method of delivery of sodium to the engine is important. The challenge in engine test design is always to generate a repeatable, rapid and clear response, whilst imposing stresses not too far removed from those found in the real-world. This is particularly acute here, where whatever form of test is adopted may well strongly influence the development of future corrosion inhibitors, lubricity improvers and deposit control additives. Nevertheless, this current work has shown that conventional deposit control additives are capable of preventing at least some of these deposits.

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DEFINITIONS/ABBREVIATIONS

CEC - Coordinating European Council
CEN - European Committee for Standardisation
CRC - Coordinating Research Council
DDSA - Dodeceny succinic acid
EDAX - Energy Dispersive X-ray analysis
FT-IR - Fourier Transform Infra-Red spectroscopy
HFRR - High Frequency Reciprocating Rig
IDID - Internal Diesel Injector Deposits
JFTOT - Jet Fuel Thermal Oxidation Test