Sodium Contamination of Diesel Fuel, its Interaction with Fuel Additives and the Resultant Effects on Filter Plugging and Injector Fouling

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ABSTRACT

Diesel fuel distilled from crude oil should contain no greater than trace amounts of sodium. However, fuel specifications do not include sodium; there is a limit of five parts per million for the amount of sodium plus potassium in fatty acid methyl esters (FAME) used as biodiesel. Sodium compounds are often used as the catalyst for the esterification process for producing FAME and sodium hydroxide is now commonly used in the refining process to produce ultra-low sulphur diesel (ULSD) fuel from crude oil. Good housekeeping should ensure that sodium is not present in the finished fuel. A finished fuel should not only be free of sodium but should also contain a diesel fuel additive package to ensures the fuel meets the quality standards introduced to provide reliable operation, along with the longevity of the fuel supply infrastructure and the diesel engines that ultimately burn this fuel.

There has recently been an upsurge in reported field problems due to fouling of the fuel injection system in modern diesel engines. This can take the form of deposits in the fuel filters or within the fuel injectors themselves. Recent work proposed a mechanism whereby sodium contaminated fuel can undergo adverse reactions between the sodium compounds and fuel additives leading to the formation of material that can impede the operation of diesel fuel injectors.

This paper presents new work carried out to enhance the understanding of this mechanism and demonstrates that the fate of any sodium contaminant is highly dependent on (i) the fuel additives present in the fuel (ii) the amount of water in the system, (iii) potentially the intensity of fuel/water mixing and (iv) the identity of the sodium salt involved in the reaction. This can lead to sodium accumulating in the water bottoms, forming sodium compounds that go on to plug fuel filters or which may cause injector fouling. The data found may explain the variation in engine test data regarding sodium induced fouling reported in the recent literature.

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INTRODUCTION

Over the last few years there has been an upsurge in the reported incidences of field problems, especially in the US, due to fouling of diesel fuel injection equipment (FIE) particularly fuel filters and fuel injectors [1, 2]. Fouling of FIE is not a new phenomenon [3] and each new occurrence brings about fervent activity to determine the mechanistic causes and to try to take remedial action. The latest reported problems are of no less a concern to the industry and as a result Panel discussions have been held on the subject at numerous SAE Powertrain, Fuels and Lubricants meetings since 2009 [4, 5, 6].

In the US there is currently a CRC committee (CRC Diesel Performance Group - Deposit Panel Bench/Rig/Engine Investigation Sub-Panel) and in Europe the CEN/TC19/ WG24 Injector Deposit Task Force investigating the phenomenon. The CEC is developing test methods to address the issue. Many technical papers have been recently published describing work on a number of investigations into

the character and origins of internal diesel injector deposits (IDID) [7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26]. What is clear is that there is not a single outcome or cause. In the US, the issue appears to be predominantly the build-up of carbonaceous deposits [1, 2, 12] whereas in Europe the concern is more about internal lacquer formation [18]. Differences between the refinery and fuel distribution technologies in these two geographic locations coupled with differences in the diesel vehicle fleet could exaggerate these apparent differences.

Historically, fouling of fuel filters and injectors has been attributed to many different factors including adulteration with low cost hydrocarbon products such as used lubricating oil [27], poorly processed vegetable oils [28, 29, 30], contamination of the fuel with such agents as dirt and rust [31, 32], microbial growth [33, 34, 35], impurities from the refining process (particularly where biodiesel is involved [36]) and also as a result of thermal and oxidative degradation of the fuel [37, 38] which may be exacerbated by the presence of contaminants. Metal contaminants have been shown to catalyse the oxidation of fuel [39] and in one widely used test the fuel is deliberately adulterated with an organic zinc compound in order to promote injector deposit formation [40].

The presence of sodium has also recently been blamed for contributing to fouling problems [13] with calls for maximum sodium concentrations to be implemented. There is an additional argument for controlling sodium concentrations in that it can deactivate the catalyst in certain diesel exhaust aftertreatment devices [41, 42]. Fouling has also been blamed for the interaction of fuel additives and lubricant additives [43, 44] and the interaction between different fuel additives [45]. The former interaction between fuel and lubricant additives was relevant only when the fuel pump was lubricated by the engine lubricating oil allowing for limited mixing of the fuel and lubricant. This problem has been eliminated in modern FIE which relies on the fuel for lubrication. This in itself causes other concerns such as the influence of fuel composition on lubricity [46, 47, 48] and requires careful consideration when formulating fuels and fuel specifications.

As can be noted from the brief outline above the issue of fuel system fouling is an extremely broad and complex matter. This paper concentrates on the specific question of how sodium; in various chemical forms; might affect deposit formation in the presence of various levels of water and different fuel additives.

It has been stated [45] that sodium could enter the supply chain as sodium nitrite used as a corrosion inhibitor at levels below 1 mg/kg. It has also been noted in [43] that "sodium sulphate can be accidentally transferred into fuel during some refinery processes." These sodium compounds were not considered in the current work, but maybe in the future. Sodium hydroxide is used in most fuel refineries as a reagent in the Merox process [49, 50, 51] and to neutralise the acid used during alkylation [50]. This caustic should obviously be

removed before the fuel leaves the refinery but it is possible for isolated incidents to occur where this is not the case. If caustic enters the fuel distribution system there is clearly a strong possibility for acid/base reactions with any acids present in the fuel. Such reactions have been blamed for the formation of soap deposits where the acid has been present as a fuel additive [14].

However, acids, including carboxylic acids are well known as decomposition products of biodiesel [52, 53, 54] and as oxidation products of petroleum diesel [55, 56, 57]. Sodium chloride can enter the fuel either in the refinery (salt driers) or in transportation (tankers that use sea water to flush their tanks, road salt, salt spray, etc.). Water can obviously enter the fuel by condensation of moisture in the air or via poor housekeeping. The industry investigations into this myriad of possible diesel fuel system deposits has led to a search for a standard engine or bench test (CEC; CRC) for IDID using a variety of sodium sources. The level of complexity this brings should not be underestimated. A number of possible sodium carriers have been put forward; for example sodium hydroxide, sodium chloride [25], sodium hydroxide with ethanol (sodium ethoxide), sodium octanoate, sodium napthanate [26] sodium oleate[24], sodium tert butoxide (in ethyl hexyl alcohol) [23] and sodium 2-ethylhexanoate (this work).

Fuel soluble sodium carriers are being recommended to deliver higher sodium levels, give fewer fluctuations in sodium concentration, short term stability and allowing the mixing, storage and sample conditioning parameters of the test to be less critical. The fuel soluble sodium sources are recommended to overcome the lack of reproducibility found with the use of sodium hydroxide/water and fuel emulsions in bench and engine testing for IDID. The following work considers the fate of possible reaction products of such additised fuels when contaminated with aqueous and fuel soluble sodium sources and the subsequent affect on engine performance.

BENCH TESTING

Diesel fuel and water are not miscible. Left to stand, water will separate from diesel fuel and, due to its higher density, will form a water layer at the bottom of the tank. In-line fuel filter/separator units will also promote phase separation. A preliminary set of bench tests were performed to determine whether any products formed from the interaction of the fuel additives and sodium compounds would be present in the fuel or water layer of such a two-phase system. Three fuel additives were used for this part of the work; a di-acid corrosion inhibitor (A1), a dimer-acid corrosion inhibitor (A2) and a mono-acid lubricity improver additive (A3).

Methodology

The fuel additives were commercial grade materials and accordingly comprised moderately complex mixtures. The

measurement of additive in diesel fuel is difficult. Accordingly, it was decided to carry out the experiments using a model solvent. As additives are more soluble in aromatic than aliphatic solvents, toluene was selected Thus, if the additives were extracted from toluene, one could be confident that they would also be preferentially extracted from diesel fuel.

Experiments were performed with toluene solutions of fuel additives which were contacted with aqueous solutions containing sodium ions. GC/MS measurements were made to follow the fate of the fuel additive, for each additive/aqueous phase combination. The additive concentrations in the following solutions were compared:

a. A retain of the original diluted solution in toluene (used as an analytical standard),

b. Samples of the toluene layers after contact with the aqueous phase and

c. A sample back-extracted into fresh toluene by acidification of the separated aqueous layer

The purpose of the different mixing treatments at stage (b) was to check whether the degree of agitation affected uptake.

Method and detection limit

A nominal 0.5g of the individual additives, A1 (0.5002 g), A2 (75 wt% active material, 0.6706 g) and A3 (0.5094 g) were each added to separate, tared 100 cm^3 volumetric flasks. The flasks were then filled to the mark with toluene (Fischer, low-S reagent grade), capped, swirled and inverted as necessary to fully dissolve the added materials. This was determined by visual inspection. These nominal 5,000 mg/l solutions were then subjected to GC/MS. Satisfactory chromatograms were obtained for 10-fold dilutions of each solution. Based on the observed signal-to-noise ratio it was estimated that the method detection limit was 10 mg/l. It was therefore decided to perform the experiments at initial additive concentrations of 100 mg/l. This represents a reasonable treat rate for any lubricity improver.

Extraction by aqueous base

Toluene solutions (100 cm^3, 100 mg/l concentration) of each additive were prepared by dilution from a 1,000 mg/l concentrate. Aliquots (10 cm^3) of each were withdrawn by air pipette and retained for use as analytical standards for each dilution. This is sample (a) for each additive.

Samples (b) were prepared and tested using two mixing methods:

The remainder of the toluene solution was added to three 125 cm^3 sample jars along with 0.9 cm^3 of a 5 wt% aqueous solution of NaOH, taping three jars together and shaking at about 2 Hz for a total of 2 minutes.

The process was repeated and the remainder of the toluene solution added to three 125 cm^3 sample jars along with an X- shaped Teflon-coated stirrer bar and subjecting to the maximum rate of agitation on an IKA-Werke RT10 multiposition stirrer overnight.

The back-extracted samples (c) were obtained using NaOH (0.5 wt%)(10 cm^3). And contact was by stirring the samples on the RT-10 for 60 minutes. Attempts were made to obtain a mass balance for the extraction. Separation was carried out by centrifugation.

Aliquots of each organic layer were then submitted for GC/MS analysis to estimate the level of fuel additive present. The results of these tests are shown in Table 1.

Table 1. Results of NaOH testing.

Additive	Additive concentration in toluene layer after shaking	Additive concentration in toluene layer after stirring	Additive concentration back-extracted into toluene layer from aqueous
A1	< 10 mg/l	< 10 mg/l	> 100 mg/l
A2	< 10 mg/l	< 10 mg/l	> 100 mg/l
A3	< 10 mg/l	< 10 mg/l	> 100 mg/l

For each of the three fuel additives it was not possible to detect any of the material remaining in either of the two toluene phases (b) after extraction by aqueous base. By contrast, the concentration of the additive found in each back-extracted sample (c) was always higher than that of the respective standard. The precision of the experiment and subsequent analysis combined was such that satisfactory mass balance could not be obtained.

This is consistent with much, if not all, of the additive having first been extracted from the toluene phase into the aqueous phase by treatment with sodium hydroxide (presumably by formation of a sodium salt) and then subsequently, on acidification, reverting to the neutral form and being extracted back into the fresh toluene.

Extraction into aqueous saline (NaCl) solution

The procedure for the mass balance was repeated using 1 wt% aqueous NaCl as the potential extractant. In this case 5 cm^3 of the additive solution was retained as a standard for the analysis. The remaining 95 cm^3 of toluene solution was extracted by stirring, as before, but over 5 cm^3 of the aqueous phase. About half of each toluene layer was removed after settling and the remainder was centrifuged along with the respective aqueous layer. After careful separation of the aqueous layer (Pasteur pipette), back extraction into toluene (40 cm^3). All toluene layers were neutralised with aqueous hydrochloric acid (1N, 2 cm^3) before analysis. The results are shown in Table 2.

Table 2. Results for NaCl testing.

Additive	Additive concentration in toluene layer after settling	Additive concentration in toluene layer after centrifuge	Additive concentration back-extracted into toluene layer from aqueous
A1	≈ 100 mg/l	≈ 100 mg/l	< 10 mg/l
A2	≈ 100 mg/l	≈ 100 mg/l	< 10 mg/l
A3	≈ 100 mg/l	≈ 100 mg/l	< 10 mg/l

It was not possible to detect the presence of any of the additives in any of the aqueous samples via attempted back-extraction into toluene on acidification. By contrast, the concentration of each additive in the settled and in the centrifuged toluene sample was indistinguishable from its respective standard. Each of the three additives was essentially non-extractable into 1 wt% aqueous sodium chloride.

This is consistent with either a failure of the fuel additives to react with NaCl or that they did so to form a toluene-soluble material destroyed by contact with acid. Chemical precedent firmly supports the failure to react hypothesis [58]. This would also suggest that neither sodium sulphate nor sodium nitrite would react with the weaker acid additives. Neither sodium sulphate nor sodium nitrate were tested during this programme, but may be tested at a later date to confirm this. This is also supported by unreacted sodium sulphate being found on field injector needles [10].

In summary: the acidic additives will react with basic NaOH but do not react with NaCl.

ENGINE TESTING

To investigate the effects of these different adulterated fuel mixtures the standard Direct Injection, Common Rail Diesel Engine Nozzle Coking Test [40] was used. The test procedure can be summarised as follows: The engine is run to a one hour cyclic test regime described in [59], and shown graphically in Figure 1 for completeness.

This cycle is repeated eight times. The engine is then shut down and allowed to soak for eight hours. It is then restarted and the cyclic operation continued for a further eight hours. These latter two steps are then repeated to give a total engine run time of 32 hours interspaced with a total of 24 hours of engine shutdown.

To eliminate any interference from the presence of zinc; which may not be present in the field; zinc neodecanoate was not used in any of these tests. This test would normally be run using the CEC reference fuel RF-06 which meets the EN590 specification [60]. However, in order to meet the lubricity limits within this specification a lubricity improver additive would normally be included in this fuel, which could interfere

with the engine tests described in this paper. Therefore, a batch of RF-06 was blended by Coryton Advanced Fuels Ltd and supplied without the lubricity improver additive. The analysis of this fuel is provided in Appendix A. In addition to the di-acid corrosion inhibitor (A1) and the mono-acid lubricity improver (A3) used in the bench testing an ester based lubricity improver (A4) was also included in this work. Further, because of industry interest in fuel soluble sodium sources for generation of IDID a fuel soluble sodium 2-ethyl hexanoate compound was used with the mono-acid and ester lubricity improver at the engine testing stage of the investigation for comparison purposes.
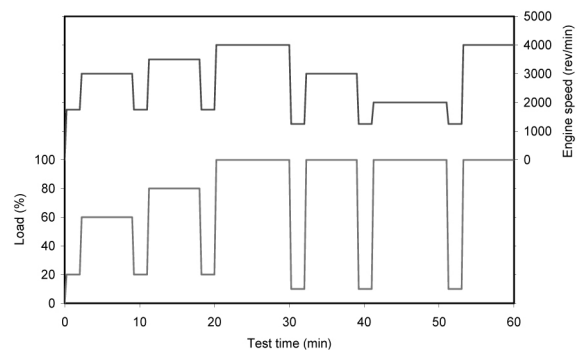

Figure 1. Direct Injection Common Rail Diesel Engine Nozzle Coking Test Cycle.

Monoacid Lubricity Additive and NaOH

The first test was run using the mono-acid lubricity improver additive (A3). The fuel was treated with the lubricity improver at a concentration of 120 mg/kg. A 17.3 wt % aqueous solution of sodium hydroxide was then added to the fuel at a concentration of 1 mole equivalent (approximately 8 mg of sodium per litre of fuel). The mixture was stirred continuously throughout engine testing. After 8 hours of operation the engine began to run erratically, suggesting fuel starvation and the test was stopped. The fuel filter was changed and the test restarted. After a further 5 hours of running the engine again started to show signs of fuel starvation; at this point the test was abandoned. Figure 2 shows the post fuel filter gauge pressure from this test.

It is clear from this figure that the depression downstream of the fuel filter, which is normally less than 10 kPa, begins to rise rapidly after 2 to 3 hours of engine operation and by 8 hours has reached −80 kPa gauge (80 kPa depression). The erratic power measurements could have been caused by fuel starvation or injector blocking or sticking. However, after the fuel filter had been changed the engine power returned to normal indicating no problems with the fuel injectors. The depression downstream of the filter again rapidly increased, indicating filter blocking.

It was concluded that deposit build up within the filter had reduced the fuel flow rate and pressure upstream of the filter. This would reduce the pressure and flow rate out of the high pressure pump, thus reducing the amount of fuel being

injected into the engine cylinders. The power loss was therefore attributed to fuel starvation rather than injector blocking.
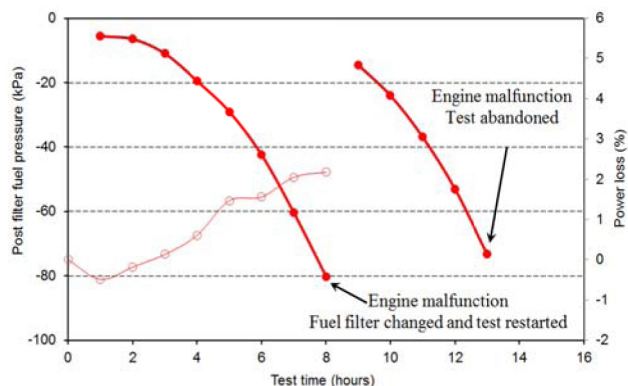

Figure2. Post filter fuel pressure showing filter blocking using NaOH.

Analysis of the fuel injectors at the end of the test did not show the presence of sodium. Analysis of the fuel filter showed significant amounts of sodium. This suggests that the sodium that was added to the fuel had been converted to a form where it was trapped by the filter and did not reach the injectors. Fourier Transform Infra Red (FTIR) analysis showed bands at 1562 cm^{-1}; asymmetric CO_2 stretch; and 1460cm^{-1}; symmetric CO_2; stretch that is indicative of a carboxylate salt, which is shown in Figure 3.
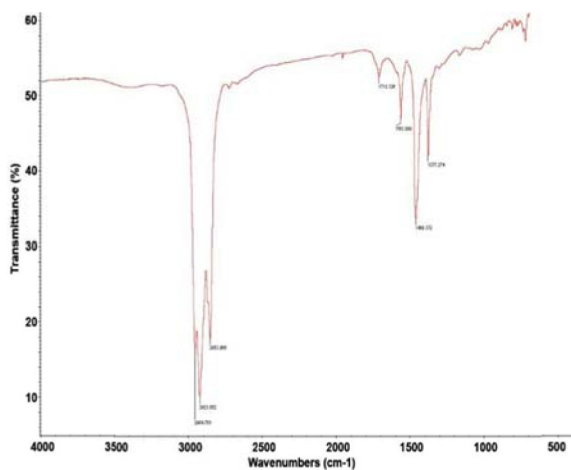

Figure 3. FTIR trace for filter using mono-acid (A3) and NaOH.

The filter from the engine test was cut open and a strip of the filter (approximately 2 cm by 6 cm) removed, and subjected to Energy Dispersive X-Ray Analysis. (EDAX). The EDAX spectrum showed the presence of sodium on the filter and is shown in Figure 4.
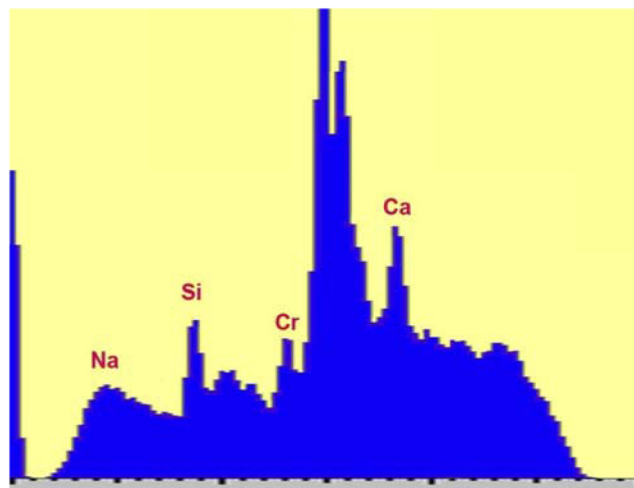

Figure 4. EDAX spectrum for filter using mono-acid (A3) and NaOH.

Calcium was also found. The source of calcium is still unknown as there is no possibility of the lubricant intermixing with the fuel in this engine test. However, there was no indication of zinc which would be expected if the source of calcium was due to lubricant contamination. Further work is required to identify the source of calcium. It is therefore possible that the carboxylate salt as determined by FTIR could be either sodium or calcium salts of organic acids, or a mixture thereof.

Synthetic Di-Acid and Synthetic Ester with NaOH

Tests were also run using the synthetic di-acid (A1) and the ester (A4) in combination with sodium hydroxide. The additive A1 was dosed at 10 mg/kg and additive A4 was dosed at 160 mg/kg. Again, sodium hydroxide was added as a 17.3% aqueous solution and the mixture was stirred throughout testing. Both of these tests ran the full 32 hours with no indication of filter blocking. The corresponding post fuel filter pressure data is presented in Figure 5 along with the power loss data.

The test performed with the acidic additive (A1) in combination with sodium hydroxide resulted in a power loss of approximately 2.4%. Previous work [61] has shown that 1ppm Zn (as zinc neodecanoate) can lead to power or torque loss in excess of 10%. Therefore, the power loss here is below the level that would be expected if the fuel had been adulterated with zinc neodecanoate at 1 mg (Zn)/kg, but does indicate some degree of injector fouling. The test performed with the ester lubricity additive (A4) resulted in power loss of approximately 5%. However, the engine suffered a turbocharger fault towards the end of the test which may account for the increase in power loss over the latter half of the test. It should be noted the turbocharger fault was

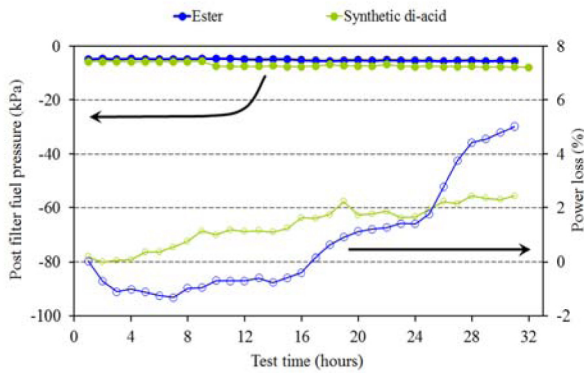mechanically based and not the result of fuel and additive combination.

Figure 5. Post filter fuel pressure without filter blocking using NaOH.

As noted above there was no evidence from the pressure drop across the filter of deposits on the filter element. The FTIR of the filters did not have the band for example at 1562 cm^{-1} that was observed with the test conducted on the mono-acid additive in combination with NaOH. It is assumed that any sodium carboxylate that was formed was sufficiently dispersed to pass through the filter and to reach the fuel pump and injectors.

At the end of the test the fuel injectors were disassembled and subjected to Scanning Electron Microscopy (SEM). There was little evidence of deposit build-up within the holes of the injector. This is the location that has previously been associated with deposit build-up leading to a restriction in fuel flow and hence power loss. However, inspection of the injector needles did indicate the presence of a very thin but fairly uniform layer of deposit. This is evident in the SEM image shown in Figure 6.
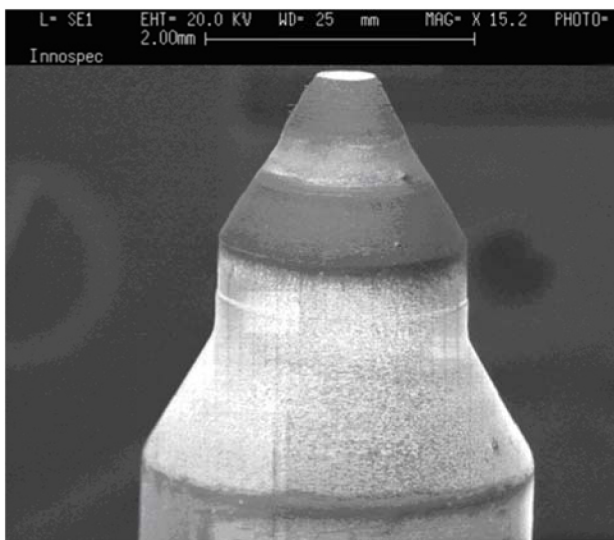

Figure 6. SEM of needle after using di-acid (A1) and NaOH.

The physical nature of this deposition is illustrated in the higher magnification SEM image shown in Figure 7.
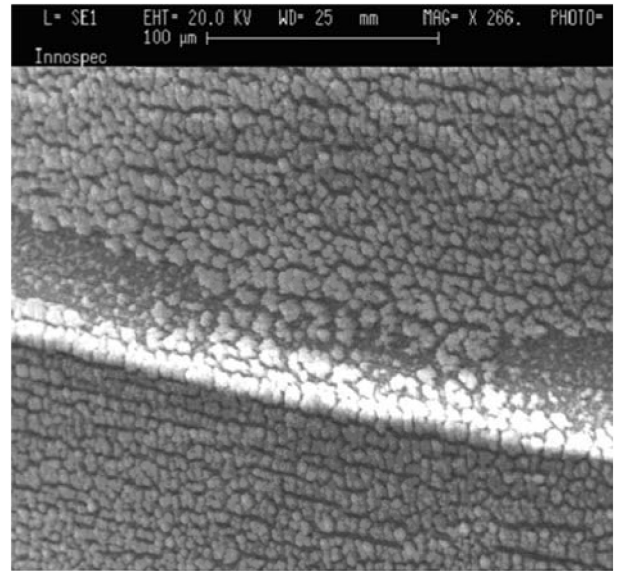

Figure 7. Higher magnification SEM of needle after using di-acid (A1) and NaOH.

Analysis by EDAX showed sodium to be present in these deposits but again there was strong evidence of the presence of calcium. The EDAX trace shown in Figure 8 also shows the presence of silicon, phosphorous and sulphur.
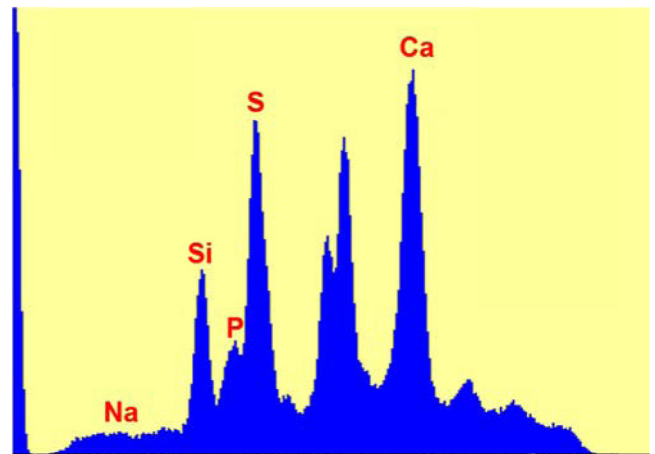

Figure 8. EDAX trace of injector needle having used di-acid and NaOH.

A final test was then carried out using only sodium hydroxide with continuous stirring throughout the test. No additives were added to the test fuel. The fuel filters were observed to block after sixteen hours as shown below, Figure 9.
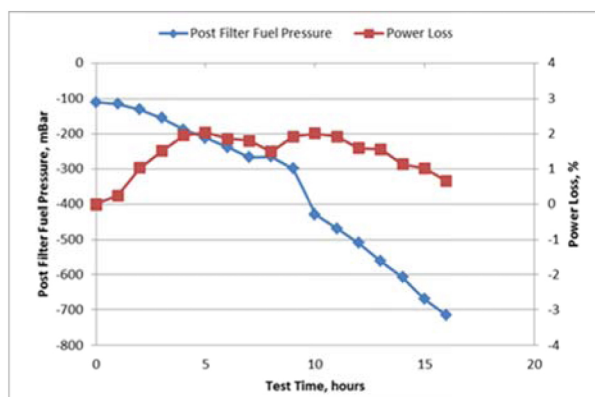
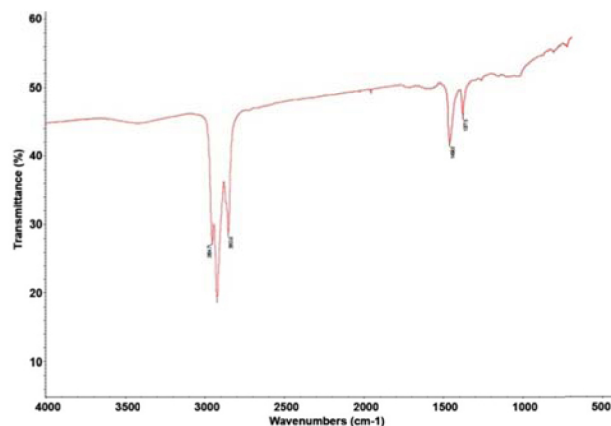*Figure 9. Post filter fuel pressure without filter blocking using NaOH alone.*

Mono Acid Lubricity Additive and NaCl

A test was run with the mono-acid additive (A3) dosed at 120 mg/kg mixed with a 23.4 wt% solution of sodium chloride to give approximately 8 mg/l of sodium in the fuel. Again the test ran the full 32 hours with no indication of filter blocking or injector fouling. The post fuel filter pressure data and the power loss data is presented in Figure 10.
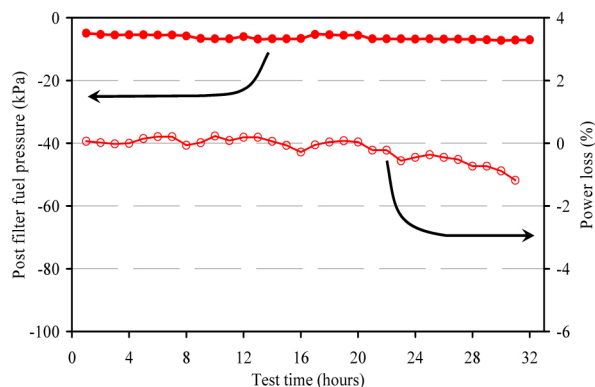

Figure 10. Postfilter fuel pressure showing no blocking using NaCl.

Analysis of the fuel filter element again showed it to be substantially free of deposits. The FTIR trace is presented in Figure 11.

Comparison of Figure 3 and Figure 11 reveals that the bands at 2955 cm^{-1}, 2954 cm^{-1}, 2864 cm^{-1}, 1459 cm^{-1} and 13717 cm^{-1} are all present in both traces but the bands at 1712 cm^{-1} and 1562 cm^{-1} (indicative of the carboxylate salt) are no longer present in the results for the test using NaCl, as shown in Figure 11.

Figure 11. FTIR trace for filter element having used mono- acid plus NaCl.

Analysis of the injectors again showed very low levels of deposit on the tip of the injectors, within the nozzle holes, or on the injector needle. However, careful examination showed the presence of sodium and chlorine; this is noted in the EDAX trace shown in Figure 12.
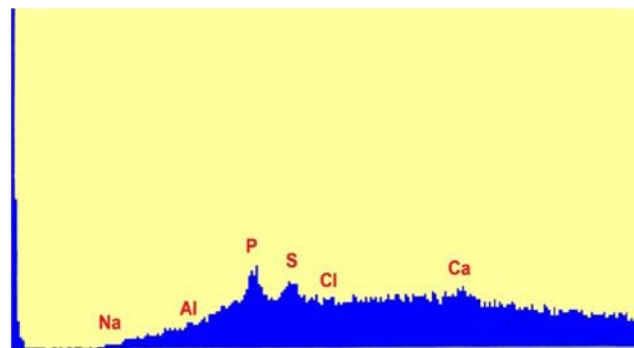

Figure 12. EDAX trace of the injector needle having used mono-acid and NaCl.

These results suggest that sodium chloride is not reacting to form a carboxylate but is passing through the filter and reaching the injector.

Tests with Sodium 2-Ethylhexanoate, a Fuel Soluble Sodium Salt

The final part of the investigation used a fuel soluble sodium salt; sodium 2-ethylhexanoate. Tests were carried out with the mono-acid lubricity improver additive (A3) and the ester lubricity improver (A4). An engine test was run using sodium 2-ethylhexanoate at 0.5 mg(Na)/kg as a blank and no injector sticking was noted. The ester lubricity additive (A4) was tested at 15 mg/kg with 0.5 mg(Na)/kg sodium 2-ethylhexanoate and the full 32 hour test cycle was completed without injector sticking. Power loss and exhaust gas temperatures for both tests are shown in Figures 13 and 14 respectively.
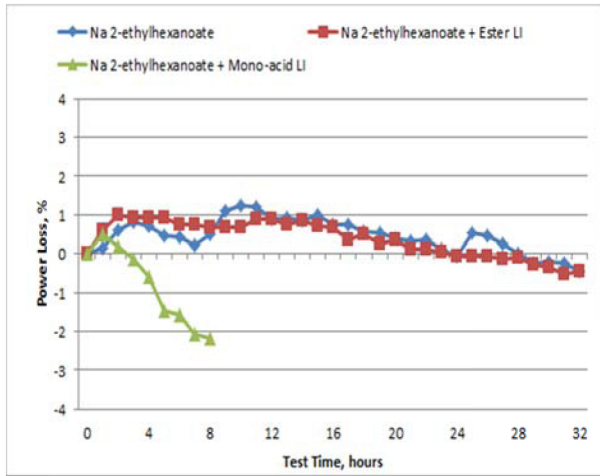
Figure 13. Power loss for sodium 2-ethylhexanoate, sodium 2-ethylhexanote and monoacid lubricity additive and sodium 2-ethylhexanote and ester lubricity additive.
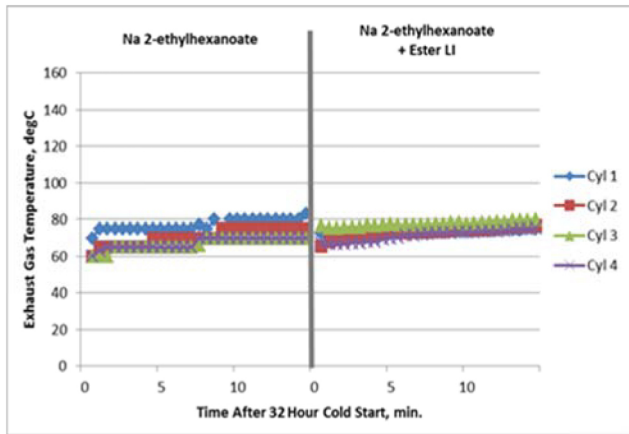

Figure 14. Exhaust gas temperatures for sodium 2-ethylhexanote and sodium 2-ethylhexanoate and ester lubricity additive.

Power loss data is included in Figure 13, and shows a drop in power over the first eight hours.

The RF-06 fuel was run in the DW10 engine with 0.5 ppm (as sodium) of sodium 2-ethylhexanoate and 10 ppm of the mono acid lubricity improver. After the first 8 hour cycle signs of injector sticking were evident from the exhaust gas temperatures as shown in Figure 15.

The injectors were disassembled showing deposits on both the needle and the push rod. The needle was subject to further analysis. The needle was subjected to SEM as shown in Figure16, along with EDAX analysis, provided in Figures 17 and 18.

The presence of sodium was noted. Further mapping of parts of the needle showed overlay of areas of sodium, carbon and oxygen, consistent with a sodium carboxylate deposit.

The needle sticking is attributed to sodium carboxylate and as sodium 2-ethylhexanoate does not show needle

sticking on its own, the cause is sodium carboxylate derived from the mono acid lubricity additive. The summary of the engine test data is given in Table 3.
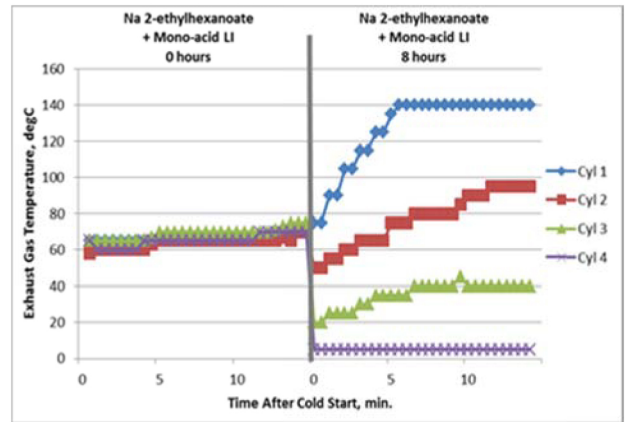

Figure 15. Exhaust gas temperatures for sodium 2-ethylhexanoate and mono acid lubricity additive.

Figure 16. SEM of needle after using mono-acid lubricity improver (A3) and sodium 2-ethylhexanoate.
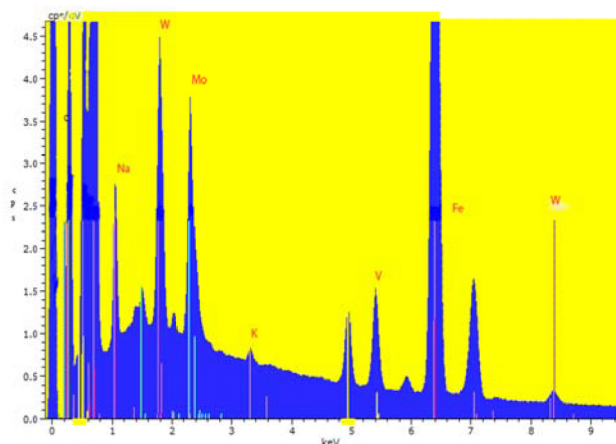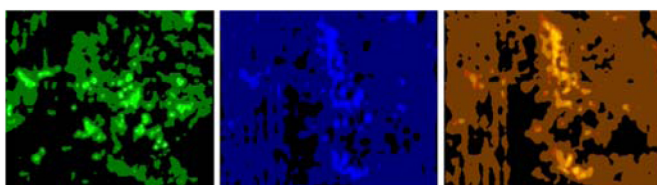
Figure 17. EDAX trace of injector needle having used mono- acid lubricity additive and sodium 2-ethylhexanoate.

Carbon   Oxygen   Sodium

Figure 18. EDAX elemental map of part of the injector after mono-acid lubricty additive and sodium 2-ethylhexanoate.

Table 3. Summary of Engine Test Results.

Sodium source	Lubricity additive	Filter blocking	Injector Fouling
NaOH	Mono-acid	Yes	N/A
NaOH	Di-acid	No	Trace
NaOH	Ester	No	No
NaCl	Mono-acid	No	No
$CH_3(CH_2)_3CH(C_2H_5)CO_2Na$	Mono-acid	No	Yes
$CH_3(CH_2)_3CH(C_2H_5)CO_2Na$	Ester	No	No

DISCUSSION

As outlined in the introduction, fouling of diesel fuel filters and injectors has in the past been attributed to a wide variety of causes. Some of these causes such as adulteration, contamination and microbial growth can usually be avoided by good housekeeping practices. Additional control of microbial contamination can be achieved by the use of appropriate fuel additives. Corrosion of materials used in the fuel supply and storage systems and an associated

assimilation of metal based contamination can be controlled by the appropriate use of corrosion inhibiting fuel additives. Deposit control additives can be used to reduce the accumulation of deposit forming material within the fuel system. Fuel additives are therefore a key component of diesel fuels formulated to avoid problems in current engine technologies.

It has been suggested that the complex mixture of fuel additives mentioned above can contribute to fouling problems.

Furthermore, it has been suggested that mono-acid and dimer-acid lubricity improvers could react with "a metal based corrosion inhibitor" to form soaps characteristic of those found in fouled fuel injectors [45]. Later work [14] using sodium chloride rather than a metal based corrosion inhibitor as a source of sodium ions did not show any injector sticking. This is in agreement with the work reported here where no loss of power was observed by combining a mono-acid lubricity improver with a sodium chloride solution and stirring the mixture throughout the test.

The combination of a di-acid and sodium chloride was shown to produce needle sticking [14]. This was also found to be true when the source of the sodium ions was sodium hydroxide. No data was presented for the combination of sodium hydroxide and mono-acid additives. The work reported here has shown that the combination of a mono-acid lubricity improver with strong base (sodium hydroxide) caused severe fuel filter fouling when the mixture was stirred throughout the test. In the previous work [14] an additional coarser filter (30 µm) was used upstream of the standard fuel filter (4 µm), whereas in this work only the standard 4µm filter was used. It could therefore be postulated that this previous work would have resulted in problematic injector fouling had the fuel filter not caused early termination of the test.

The combination of the specific di-acid (dodecenyl succinic acid) with sodium hydroxide did produce soap formation leading to injector sticking when the fuel/additive mixture was mixed "continually during the test" [16] or "through in-line injection" of the sodium hydroxide [14]. The bench testing reported here suggests that if an acid based additive is mixed with a strong base (sodium hydroxide) then the two will react to produce the sodium soap but that that soap will tend to be in the aqueous phase, i.e. in the water bottom. This would not normally reach the fuel injectors. Sodium hydroxide is, however, more soluble in water than are sodium (and, especially, calcium) salts of carboxylic acids. It is plausible that at high initial levels of NaOH, solid salts of carboxylic acid will precipitate, even from the aqueous phase.

CONCLUSIONS

The accumulation of deposits within the fuel injection equipment of modern diesel engines continues to be a concern to the industry. Recent work has proposed a

mechanism by which sodium compounds contaminating the fuel can react adversely with fuel additives to form compounds that can foul fuel injectors. To further the understanding of the possible interactions between acid based fuel additives and sodium contamination within the fuel a series of laboratory bench tests and engine dynamometer tests were performed to investigate possible causes of fuel filter and injector fouling. The findings were as follows:

• Laboratory bench tests demonstrated that acid based fuel additives dispersed in a liquid hydrocarbon react with aqueous sodium hydroxide; an acid base reaction. It was found that the resultant sodium compounds were always present in the aqueous layer and were not detected in the organic layer.

• A similar set of experiments using sodium chloride instead of sodium hydroxide found that none of the fuel additive was extracted from the organic phase.

• An engine test performed with a commercial treat rate of a mono-acid lubricity improver additive and aqueous sodium hydroxide at a 1 mole equivalent treat rate (with continual stirring), resulted in rapid and severe fuel filter blocking.

• Analysis of the fuel filter strongly showed that the acid lubricity improver had reacted with sodium hydroxide to form a sodium carboxylate which then agglomerated and blocked the filter.

• A similar test, where the mono-acid lubricity improver was replaced with an ester based lubricity improver additive, at a slightly higher treat rate, did not result in filter blocking.

• A test with a di-acid based corrosion inhibitor additive (dosed at a commercial treat rate) and an aqueous solution of sodium hydroxide that was continually stirred throughout the test did not result in significant power loss. Post-test analysis of the fuel injectors did indicate some deposit formation and the presence of sodium. However, calcium was also present and further work is required to understand the source of this calcium.

• An engine test using aqueous sodium chloride as opposed to the strongly basic sodium hydroxide did not result in any power loss and there was no evidence of carboxylate formation. However, the deposition of sodium chloride on the needle may be indicative of trace water presence and in the field, where water levels may be higher; the importance of good housekeeping is paramount

• An engine test using sodium 2-ethylhexanoate and a monoacid lubricity additive resulted in injector sticking. Mono-acid lubricity additives react with sodium sources to cause either filter blocking with a consequent loss of lubricity or internal injector deposits. Testing of ester lubricity additives did not produce injector sticking.

This data has implications for the establishing a standard test for internal injector deposits. Comparison of these with results from the literature would indicate that some workers can get injector sticking under certain conditions with a variety of sodium-acid sources and some cannot. This does not occlude the use of soluble sodium salts in the generation of injector deposits for research, but the interaction of sodium carboxylates with carboxylic acids in fuels is clearly complex. This is not as simple as the published industry standard zinc based CEC F-98-08 test. The exchangeability of the carboxylate ligand of the fuel soluble sodium carrier with the acids in fuel, the mixing, the contact time and the solubilising effect of a particular fuel are among the important factors in engine test sodium carboxylate IDID production. More work is required to understand this.

Good housekeeping is fundamental to minimising any of these contamination issues in the field.

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ACKNOWLEDGMENTS

APPENDIX

CORYTON
advanced fuels

Certificate of Analysis

Fuel Blend No:	CAF-G11/105	**Contact:**
Fuel Type:	CEC RF-06-03 N	**Order No:**
Customer:		**Date:** 18/03/2011

Test	Method	Unit	Limit Min	Limit Max	Result
Cetane Number	EN ISO 5165		52.0	54.0	52.2
Density at 15°C	EN ISO 3675	kg/m³	833.0	837.0	834.0
Distillation					
T50 % v/v	EN ISO 3405	°C	245.0	-	257.3
T95 % v/v	EN ISO 3405	°C	345.0	350.0	345.4
FBP	EN ISO 3405	°C	-	370.0	357.2
Flash Point	EN 2719	°C	55	-	72
Cold Filter Plugging Point	EN 116	°C	-	-5	–18
Kinematic Viscosity at 40°C	EN ISO 3104	mm²/s	2.300	3.300	2.630
Monocyclic Aromatics	EN 12916	% m/m	-	-	11.7
Dicyclic Aromatics	EN 12916	% m/m	-	-	3.5
Tricyclic Aromatics	EN 12916	% m/m	-	-	<0.1
Polycyclic Aromatics	EN 12916	% m/m	3.0	6.0	3.5
Total Aromatics	EN 12916	% m/m	-	-	15.2
Sulphur Content	ASTM D5453	mg/kg	-	10.0	6.8
Copper Corrosion 3 hrs at 50°C	EN ISO 2160		-	1	1a
Conradson Carbon Residue on 10% Dist. Residue	EN ISO 10370	% m/m	-	0.20	<0.01
Ash Content	EN ISO 6245	% m/m	-	0.010	<0.001
Water	EN ISO 12937	% m/m	-	0.020	0.005
Neutralisation (Strong Acid) Number	ASTM D974	mgKOH/g	-	0.02	0.01
Oxidation Stability	EN ISO 12205	mg/mL	-	0.025	<0.01
Lubricity Improver	Report		Report		Not Added
Gross Calorific Value	IP 12	MJ/kg	-	-	45.92
Net Calorific Value	IP 12	MJ/kg	-	-	42.92
Carbon Content	ASTM D5291	% m/m	-	-	85.86
Hydrogen Content	ASTM D5291	% m/m	-	-	14.14
Oxygen Content	Report	% m/m	-	-	0

Date:	18/03/2011
Signed:	

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