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The Nature and Cause of Internal Diesel Injector Deposits and the Effectiveness of Fuel Additives

10 Fuels Lubricants & Fluid Technologies

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ABSTRACT

In the late 1980's the International Maritime Organisation (IMO) started work on reducing air pollution from ships. Since then in a parallel movement to automotive application, the introduction of further legislation and emission regulations have seen the introduction of low sulphur fuels (0.1% sulphur limit inside Emission Control Areas, meaning an unprecedented increase in MGO consumption) and common rail diesel injection equipment.

Increasingly marine grade fuels are nearing the specification of that seen in the automotive industry, such as the potential introduction of FAME into ISO specs. As in the automotive industry, injection equipment manufacturers are also moving to increased pressure and temperature common rail systems. It can be noted that large two stroke engines are now also using Common Rail systems; however these are relatively low pressure at the rail (1000 Bar) and are often designed to operate on both MGO and HFO. Common rail engines not only offer improvement in emissions but are also more efficient and allow more operational flexibility than their predecessors. It is anticipated that next generation medium speed engines will increase the pressure at the rail and will continue to run on both HFO and MGO. High pressure common rail diesel engines are currently seen on MGO only vessels such as high speed Naval or Coastguard vessels.

Within these high pressure common rail fuel systems the formation of internal injector deposits (IDID) is being noted. I This paper describes the nature of IDID, and their potential origins. Different types of IDID and the complexity of these deposits are also discussed. The characterisation of IDID has become an industry priority and a wide variety of analytical techniques have been deployed to try and achieve this. The deposits are complex and ineradicable in nature and often require in-situ analysis. The application of analytical techniques will be described with data from the following techniques

- Scanning Electron Microscopy/Energy Dispersive X ray spectroscopy (SEM/EDAX): This allows general deposit structure to be investigated and semi quantitative elemental analysis both in a mapping and spot form to be determined.
- Hydropyrolysis(Hypy): This technique allows investigation of aliphatic, aromatic and functionalised components of the deposits which may then be analysed by gas chromatography–mass spectrometry (GC/MS).
- Focused Ion-Beam Scanning Electron Microscopy, (FIB-SEM)this technique allows direct structural assessment on the microscale, precise manipulation by use of the ion beam to reveals deep structure, with nanomachining enabling sectioning parts of the deposit for further analysis.
- Transmission Electron Microscopy (TEM): allows deposit structure to be assessed at the 10nm level to show ordering.
- Atomic Force Microscopy (AFM): allows the micro and nano scale topography, morphology and material properties to be investigated.
- Raman Spectroscopy (RS): has allowed the mapping of carbonaceous order in the deposit.
- Fourier Transform infra-red Spectroscopy (FTIR): Using both mapping and spot techniques it indicates functionality on the deposit surface,
- Time of Flight Secondary ion Mass Spectrometry. (Tof-SIMS): provides data on layering in deposits and identification of layers.

Using these techniques, examples of field failures will be described and categorized. The effectiveness of fuel additive in preventing the formation of and removing IDID will also be presented.

INTRODUCTION

Increasingly marine distillate fuels are nearing the specification of that seen in the automotive industry. As in the automotive industry, injection equipment manufacturers are also moving to increased pressure and temperature common rail systems, although in marine powertrains it is still in its infancy. Currently its use is being mainly restricted to pleasure craft, Naval/ Coastguard vessels, ferries and inland water boats. However with ever tightening legislation (0.1% Sulphur fuel as of 1st January 2015), and tightening NOx regulations for new builds, the trend toward use of high pressure common rail injection systems in marine is growing. Common rail engines not only offer improvement in emissions but are also more efficient and allow more operational flexibility than their predecessors. The use of similar systems in automotive powertrains and problems therein since 2005 has allowed a buildup of knowledge which can be used to inform on marine high pressure common rail injectors use in the field.

Most notably in the automotive field, emission regulations with the introduction of Euro 6 [1] in Europe, EPA and CARB in USA [2], and others worldwide [3] have been the key driver in the introduction of even higher pressure common rail injector equipment. As fuel injection pressures have increased in order to meet these regulations there has been a concomitant increase in temperature and shear within the fuel injectors and hence an increase in distressing of fuel within the injector. This combined with the introduction of Ultra-Low Sulphur Diesel (ULSD), resulting changes in fuel solubilsing properties and the blending of biodiesel to meet the renewable fuels mandate has seen a number of reports worldwide of injector problems in the field because of deposit formation [4]. The injector malfunction has manifested itself in:

- No cold start performance
- Higher emissions
- Stalling and misfiring
- Rough idling
- Increased smoke production
- Reduced fuel economy

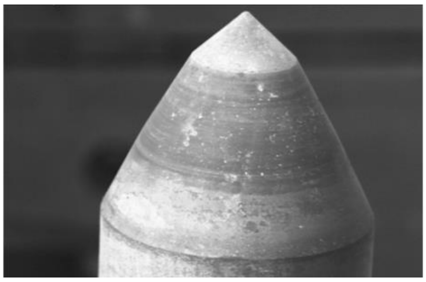
As a result there is significant interest in diesel injector deposits with CRC (Central Research Council, Diesel Performance Group, Deposit Panel, Bench/Rig Investigation sub panel) in the United States and CEN (Committee European de Normalisation TC19/WG24 Injector Deposit Task Force, Engine Test) and the CEC (Coordinating European Council TDG F-110) as well as numerous research groups worldwide investigating this.

Deposits: Originally [5] deposits from the field were noted on the filters of fuel injector equipment FIEs, but then on the injector nozzles and more recently on the internal parts of the injector. In some cases deposits were found in all three locations [6]. Of these deposits it is Internal Diesel Injector Deposits (IDID) which are the current industry focus. There are [7] six industry recognized types of IDID:

1. CARBONACEOUS: Carbon based black in colour

2. AMIDES: Brown coloured polymeric

3. INORGANIC SALTS: e.g. sodium sulphate /chloride



4 AGED FUEL DEPOSIT: “sticky” deposit possible bio origin

5 LAQUER BASED: visualized on some injectors difficult to reproduce may be a carbonaceous precursor?

6 CARBOXYLATE SALTS: white in colour sodium or calcium carboxylate based.

The IDID deposits may be found in various locations throughout the injector body, all of the deposits can be detrimental to the injector operation.

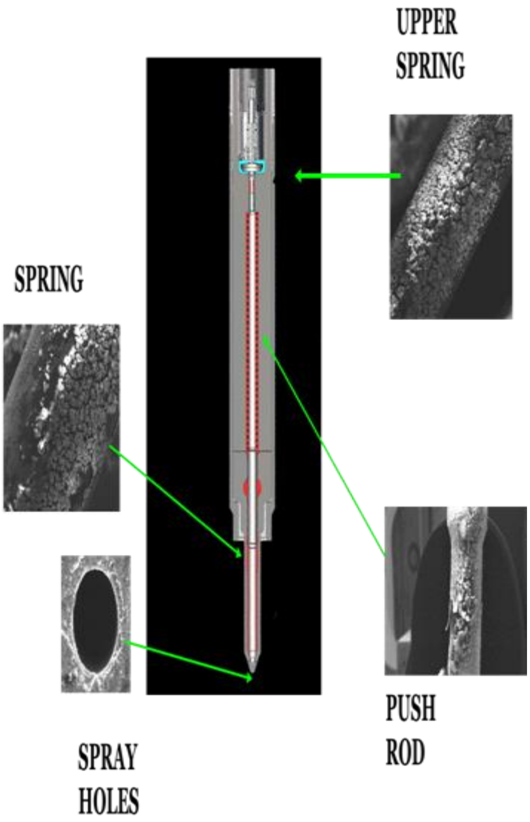


Figure 1 Examples of IDID in injectors.

These and other FIE deposits may be attributed to a number of sources described in figure 2:

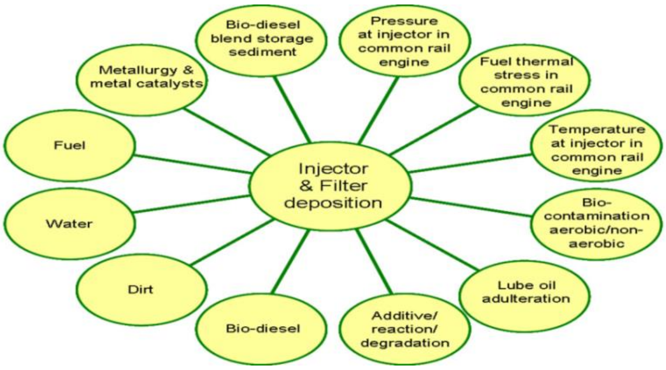


Figure 2

The sources described can of course act both singly and in combination to produce the deposit, in marine there is the added complication of more difficult operating conditions than automotive.

Analytical Techniques

A number of analytical techniques have been applied to understand the nature of IDID deposits which has allowed the development of deposit control additives (DCA) to mitigate deposit effects. Examples of these techniques are:

Scanning Electron Microscopy Energy Dispersive X-ray Spectroscopy Analysis (SEM-EDAX) [7, 8, 9, 10]:

SEM is a widely used technique that produces images of a sample by scanning it with a focused beam of electrons, it has been used extensively to visualise the deposits and their morphology.

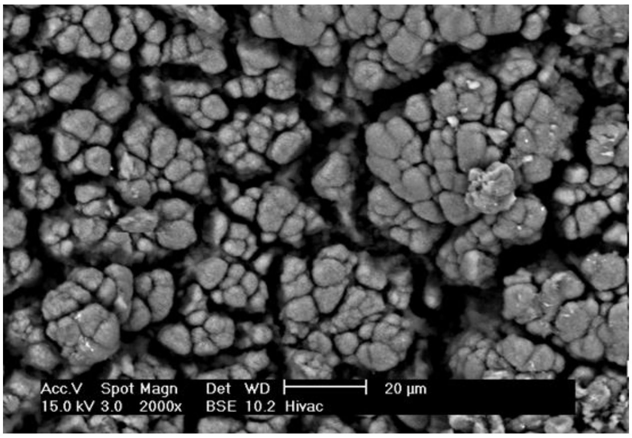


Figure 3 Micrograph of Needle Tip

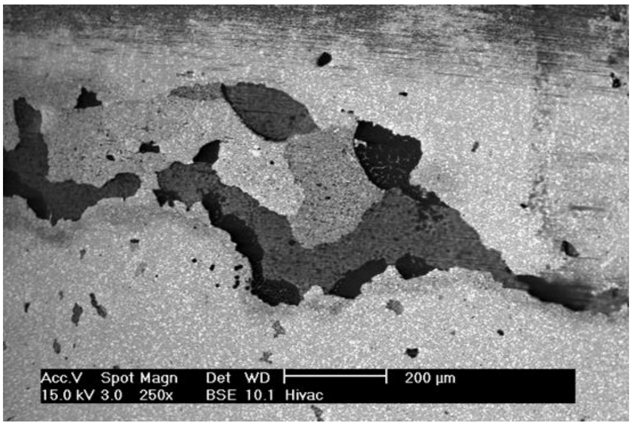


Figure 4 Micrograph of needle body

The SEM images (Figures 3 and 4) show that the deposit can vary in composition across the injector needle with a granular deposit at the tip and a smoother one on the body of the injector.

The use of EDAX further informs on the nature of the deposit even within the same area.

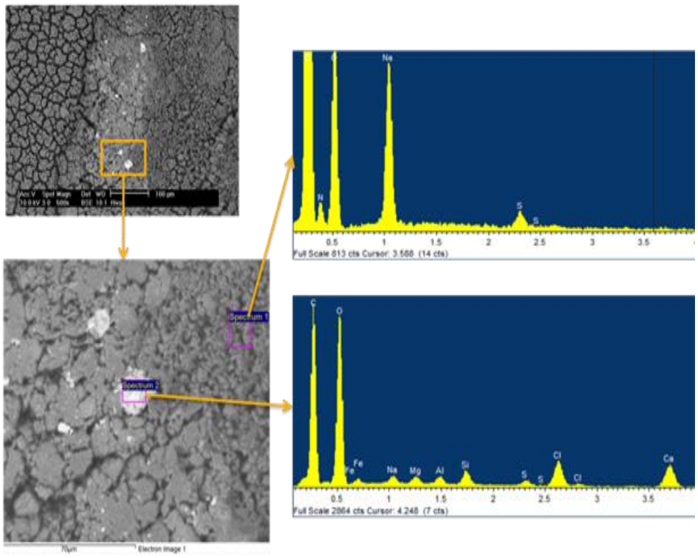
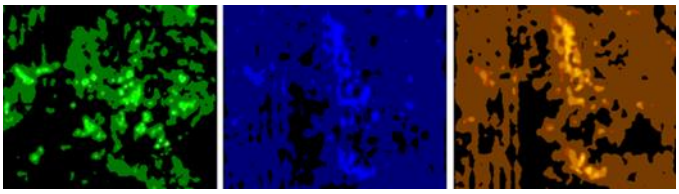


Figure 5 SEM micrograph and EDAX traces of injector deposits

This technique shows the different morphologies of the deposits found and their chemical nature is described by EDAX. The white area shows calcium and chlorine not seen in the darker area (figure 5). The technique can also be used for elemental mapping [10] of the surface. Parts of the needle (figure 6) showed overlay of areas of sodium, carbon and oxygen, consistent with a sodium carboxylate deposit.



Carbon Oxygen Sodium

Figure 6 EDAX Elemental map of part of the injector

Hydropyrolysis (Hypy) [11]: Though not intended for IDID the technique is worth mentioning as it has been used to characterise deposit from the tip of the injector, and thus to inform regarding deposit from the injector orifices. It is a catalytic technique which delicately strips molecules of their functional groups but retains their carbon skeletons and stereo chemistries intact. The resultant products from the hydropyrolysis were subject to Gas Chromatography/Mass Spectrometry (GC/MS) analysis.

Results showed the presence of alkylbenzenes, alkylnapthalenes and alkylphenathranes (figure 7) indicative of species intermediate to final graphitic type structures.

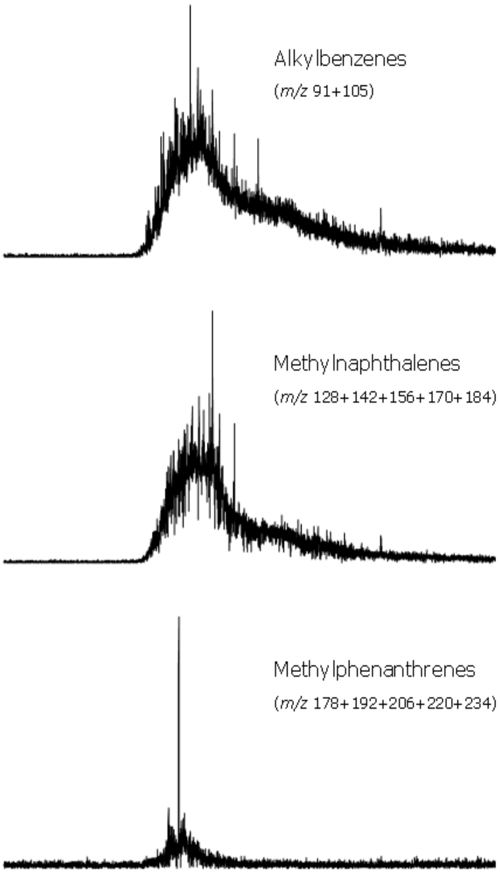


Figure 7 Characteristic Single Ion Chromatograms (SIC) for injector tip Hydropyrolisis product.

Transmission Electron Microscopy (TEM) [7]: TEM describes a sample's topography and morphology on a nanometer scale thus allowing the graphitic nature of deposits to be seen (figure 8):

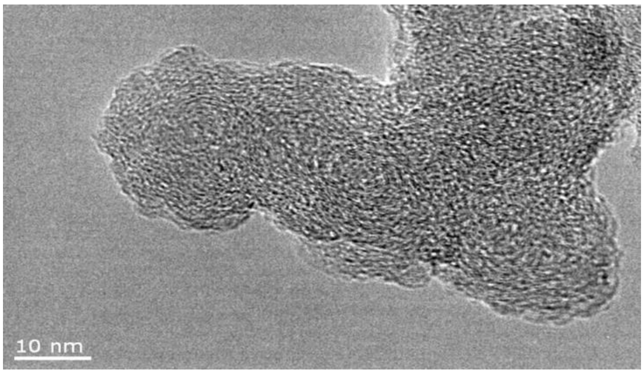


Figure 8 TEM micrograph of injector needle deposit.

Fourier Transform Infra-red Spectroscopy FTIR [12, 13, 14]: though the technique is limited to only detecting molecules with an infra-red signature and at the surface level it has seen use with many groups to identify species on injectors. For example; carboxylic acid salts, inorganic salts, chlorides and sulphates and "aged" diesel fuel residue.

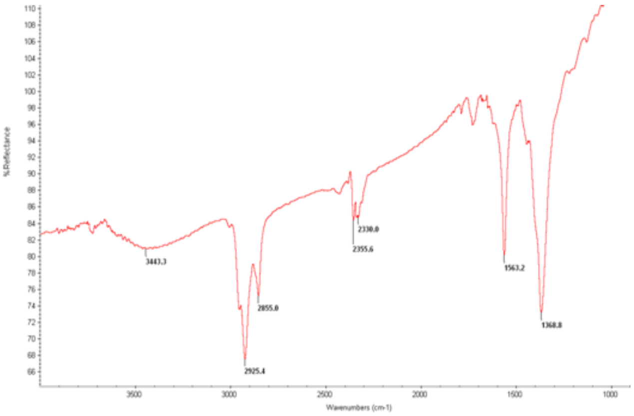


Figure 9 FT-IR trace of deposit from sodium hydroxide and a mono-acid

Figure 9 shows typical carboxylate band at ~1560 cm^{-1}. This shows that, sodium hydroxide; found in many fuels and tank water bottoms is present in a form which can readily interact with the acidic species in the fuel, and a carboxylate salt forms.

Raman Spectroscopy (RS) [7]: Raman spectroscopy unlike FTIR has the ability to observe ordered and disordered carbonaceous deposits and has been used to map an area of an injector needle and showing the variation across it (figure 10), using the change in the intensity of I_G, I_D bands.

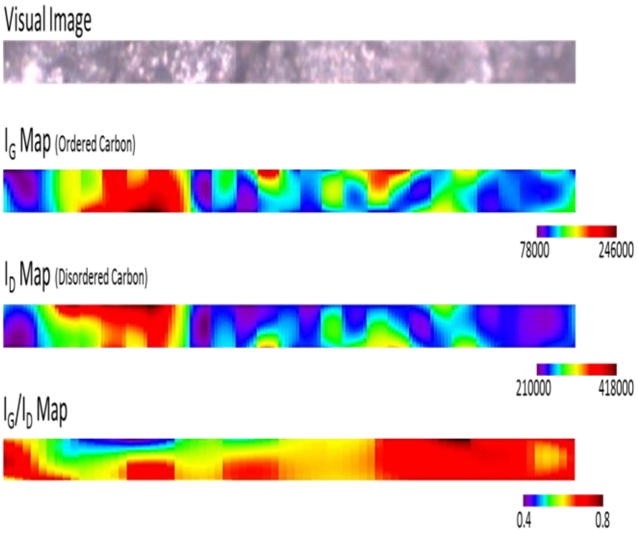


Figure 10 Raman map across injector surface

The ratio I_G/I_D shows how the ratio of ordered to disordered carbon changes across the surface. That is to say that the presence of graphitic and non-graphitic carbon.

Time of Flight Secondary Ion Mass Spectrometry (Tof-SIMS) [15]. The previous techniques are surface based, it was only with the use of this technique which allowed "drilling" below the surface with an ion source that the true nature of IDIDs was noted, in that they are layered. The technique has also shown the presence of aromatic structures within the carbonaceous layers, consistent with a move toward graphitic type products [16].

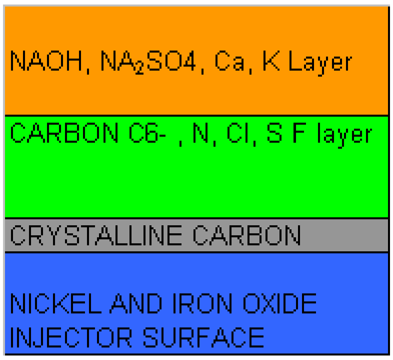


Figure 11 Schematic of depth Profile of injector deposit for Tof-SIMS

Focused Ion Beam Scanning Electron Microscopy (FIB-SEM) [7]: This technique is one of the latest to be applied to IDIDs. All of the above techniques have made progress with regard to understanding IDIDs; however, the deposits have an ineradicable nature in many cases which makes analysis other than in-situ difficult. This technique allows for a cross section to be cut from a deposit using an ion-beam; which can then be subjected to further analysis. Previous to this analysis with the exception of Tof-SIMS the presented surface was analysed, solvent dissolved or scraped. Thus the history of the IDID and its ability to inform regarding formation mechanisms was lost. A description of the technique itself has been given [7] and resultant studies will be the subject of future publications.

Atomic Force Microscopy (AFM) [7]: A scanning probe microscopy technique has enabled morphology and nano-scale properties of IDIDS to be determined. It has informed on important factors such as the adhesion characteristics (figure12) of a deposit layer; which has an impact on its ability to support another deposit layer and may be a factor in how these layers form.

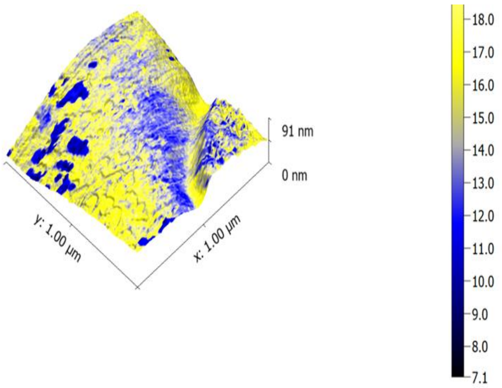


Figure 12 AFM showing adhesive nature of sites within a deposit.

Thermodesorption Photon Ionization Time of Flight Mass Spectrometry Energy Fuels (TPIToF) [17]: this technique has also been used to show the presence of aromatic compounds in IDIDs, this time in deposits on an internal metal ring.

The above work is not a comprehensive documentation of the automotive knowledge on IDIDs There is much work also available on test rigs, and other techniques which have led to automotive's understanding today of IDIDs. The initial application of this knowledge to marine will now be described.

RESULTS

A number of injectors were sourced from a US seaboard operation. The injectors were disassembled and the constituent parts subject to analysis. Most internal parts were found to have deposit on them. The most important components for IDIDs, the injector needle and the push rod were focused on.

Visual

Figure 13 Needle from injector

The needle figure 13) was difficult to remove from the nozzle housing and was found to be covered in a brown residue.

Figure 14 Push rod from injector

The push rod (figure 14) was found to have deposit throughout the length of its body but particularly heavy in parts.

SEM /EDAX:

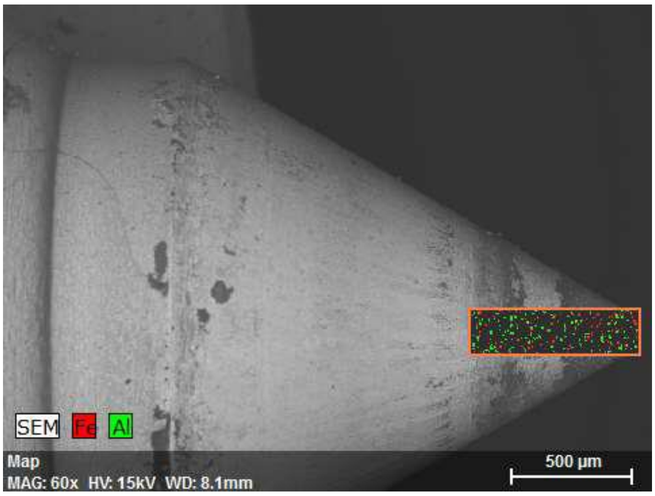


Figure 15 SEM Image and EDAX map of injector Tip

The SEM EDAX images of the injector in (figures 15, 16 and 17) show the presence of carbon, calcium and the injector based steel elements.

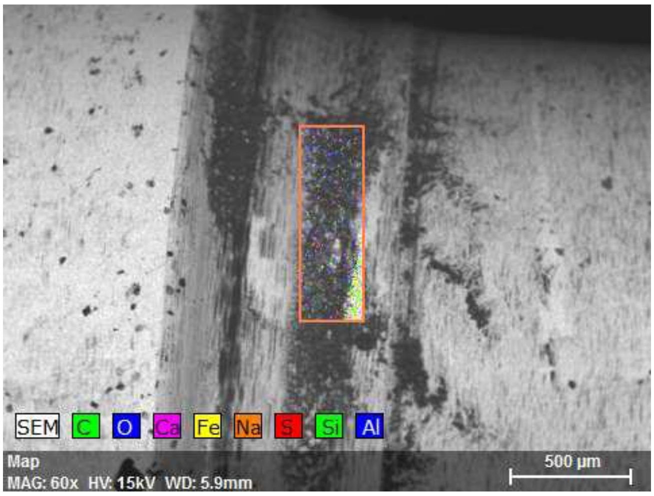


Figure 16 SEM EDAX Image of groove in injector

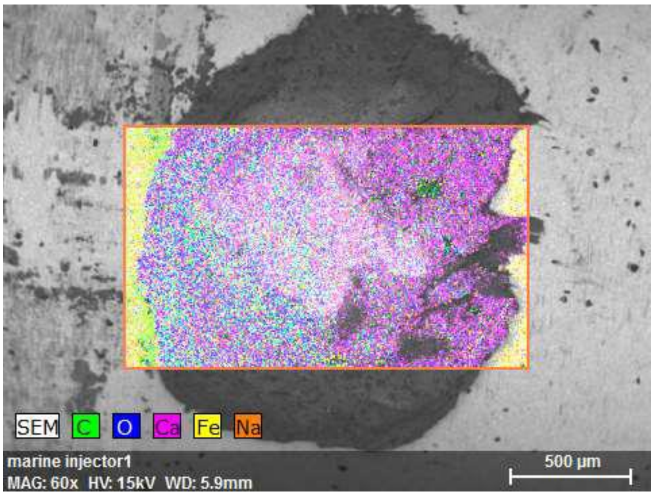


Figure 17 SEM EDAX of particle on Injector body

FTIR Microscopy: Deposit along the needle shows a streak of deposit with island of corrosion and particles as shown in figure 18

Figure 18 Photomicrogarph of injector body.

Infra-red analysis along the body of the injector shows similar spectra, an example of which is shown in figure 19.

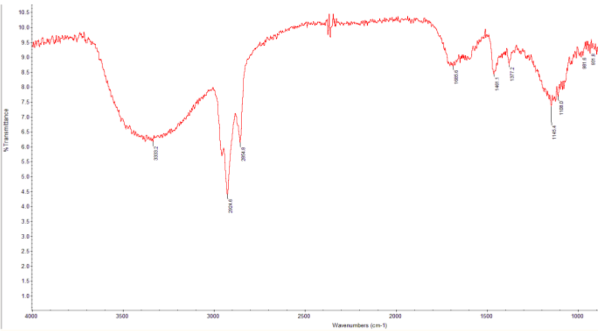


Figure19 Single Point Infra-red Spectrum injector Needle

Infra-red bands are present at ~3333, 2924, 2854, 1685, 1461, 1372 and 1154cm^{-1}.The deposit has a hydroxyl band at 3333 cm-^{1}

The push rod was analysed at the point of heaviest deposit and yielded the following spectrum

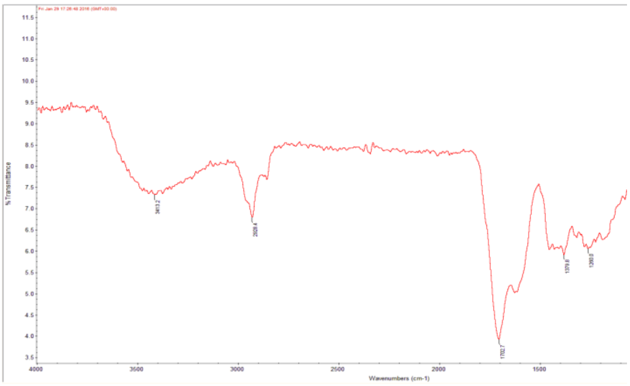


Figure 20 Infra-red spectrum of Push Rod deposit

Infra-red bands are present at ~3413, 2928, 1707, 1618,1379,and1260 cm^{-1}.

The data on the push rod indicates the presence of a carboxlic acid; the injector infra-red bands are broad which makes attribution difficult.

DEPOSIT CONTROL ADDITIVES – INTERNAL DIESEL INJECTOR DEPOSITS

Following incidences related to IDID in the European market; a CEC Test Development Group (TDG) was formed to develop a suitable bench engine test which, could be routinely used for the monitoring and measurement of IDID formation in diesel fuels. A Peugeot DW10C engine with a common rail fuel system design and equipped with Euro 5 compliant production injectors was selected for this engine test [18].

At the time of writing the test method development is close to completion and expected to be published as an approved CEC test method during 2016. It is anticipated that the test will enable investigation of IDID in respect of both metal carboxylate formation and amide lacquers exacerbated by the presence of sodium plus organic acid and low molecular weight PIBSI respectively. The test is expected to be based on a demerit system developed from a combination of different engine parameters measured over a total 30 hours engine running time. The demerit rating scale will be from 0 to 10 with the maximum 10 rating assigned to an engine test where no deviation linked to IDID formation is observed.

Diesel deposit control additives have been developed to combat injector fouling in a range of engine technologies providing protection across a whole vehicle fleet. With the potential for internal diesel injector deposits now becoming a major concern however, it is important to establish that deposit control additives are also able to prevent and remove deposits in this part of the injector.

Using the proposed DW10C engine test method, a number of tests have been performed to determine the ability of additives to prevent IDID. Using reference fuels as suggested in the proposed test method associated with metal carboxylate formation and amide lacquer formation, additive performance tests have been carried out. A summary of the test data is shown in the Table and Figures below.

Basefuel	Contaminant	Additive	Merit Rating (M/10)
Reference Fuel	0.5ppm Sodium* + 10ppm DDSA**	None	4.0
Reference Fuel	0.5ppm Sodium* + 10ppm DDSA**	Yes	10.0

(*) = Sodium as Sodium Naphthenate

(**) = Dodecenyl Succinic Acid

Figure 21: Peugeot DW10C IDID Engine Testing – Metal Carboxylate Formation

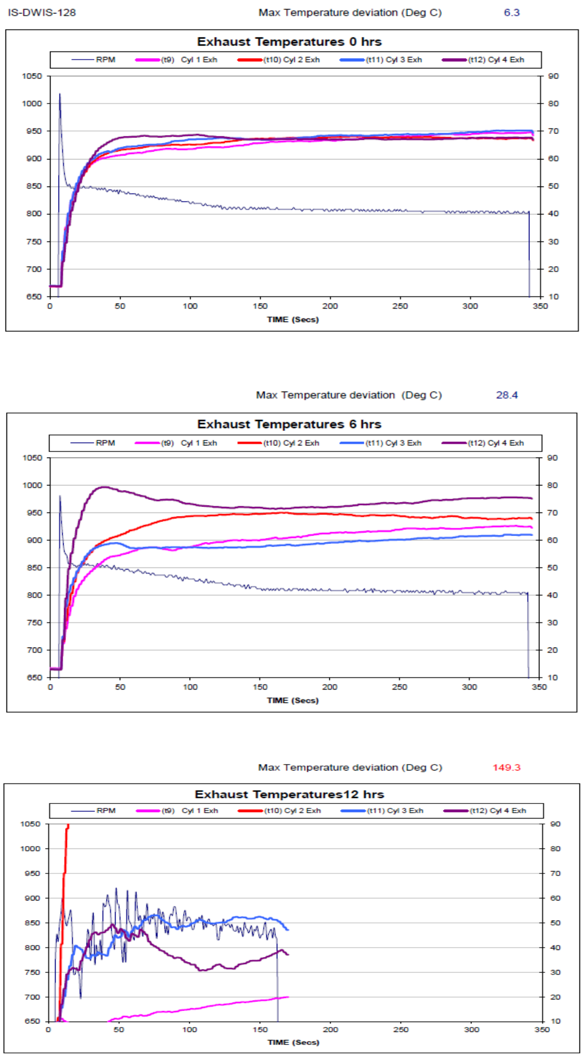


Figure 22: Exhaust Temperature Measurements – DW10C IDID Testing, Basefuel (Na/DDSA)

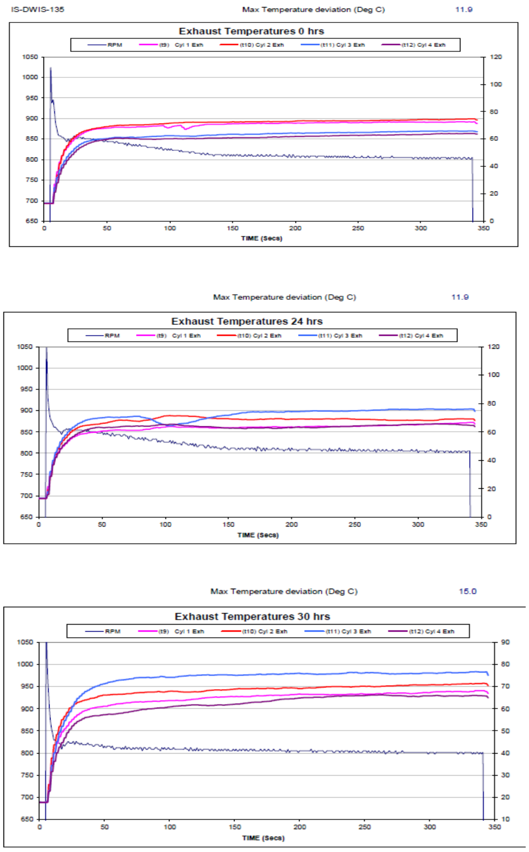


Figure 23 Exhaust Temperature Measurements – DW10C IDID Testing, Basefuel (Na/DDSA) + Additive

Basefuel	**Contaminant**	**Additive**	**Merit Rating (M/10)**
Reference Fuel	10ppm Low MW PIBSI*	None	2.9
Reference Fuel	10ppm Low MW PIBSI	Yes	10.0

(*) = Low Molecular Weight Polyisobutylene Succinmide

Figure 24: Peugeot DW10C IDID Engine Testing – Amide Lacquer Formation

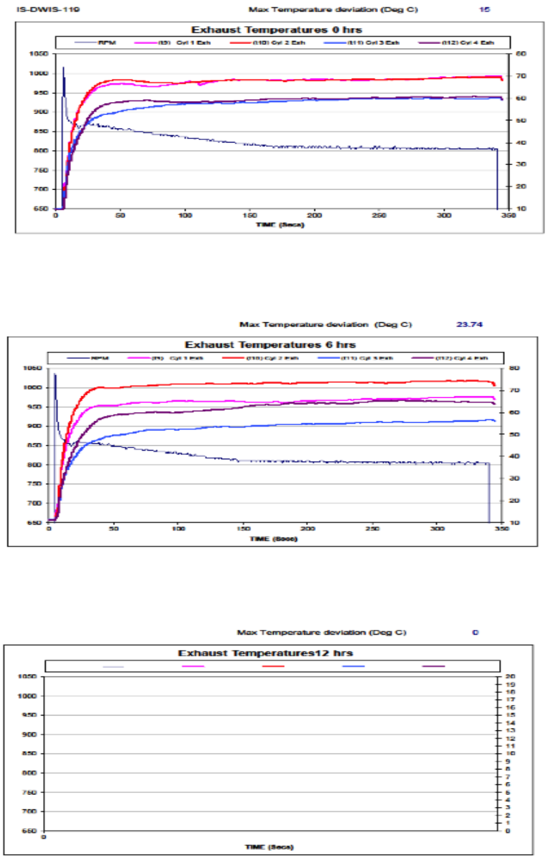


Figure 25: Exhaust Temperature Measurements – DW10C IDID Testing, Basefuel (Low MW PIBSI)

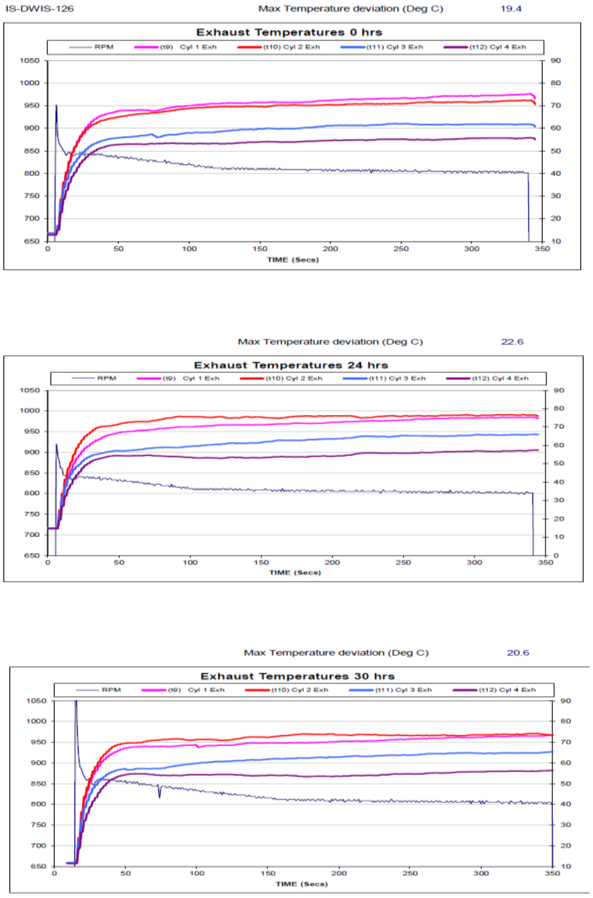


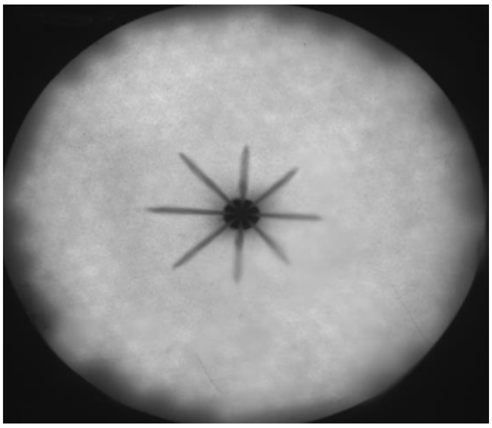
Figure 26: Exhaust Temperature Measurements – DW10C IDID Testing, Basefuel (Low MW PIBSI) + Additive

The above data shows that when the contaminants in the form of sodium and organic acid or low molecular weight PIBSI are added to the reference diesel fuel, significant injector sticking problems are observed. The deviations in exhaust temperature as shown in Figures 22 and 24 highlight the deviation from standard injector operation resulting in the low merit rating for each test. Conversely when the additive is introduced into the same fuels (Figures 23 and 26) and the engine test is ran under identical conditions, the injector operation remains within expected parameters and no major deviations in exhaust temperature are observed, resulting in the highest possible merit rating as measured in the DW10C engine.

Further vehicle tests have also been performed to determine the impact on vehicle performance of internal diesel injector deposits Using a pair of identical Euro 5 heavy duty diesel trucks with a similar vehicle history, over an identical driving cycle and mileage accumulation of 15,000km, the impact of additive addition to the fuel was assessed. This was achieved by fuelling both trucks on the same batch of diesel fuel, but with one truck adding diesel deposit control additive to the fuel.

At the end of the mileage accumulation study, the injectors were removed and subjected to a technique at a 3rd party test facility to observe and study the injector spray and performance from both vehicles.

With Additive



No Additive

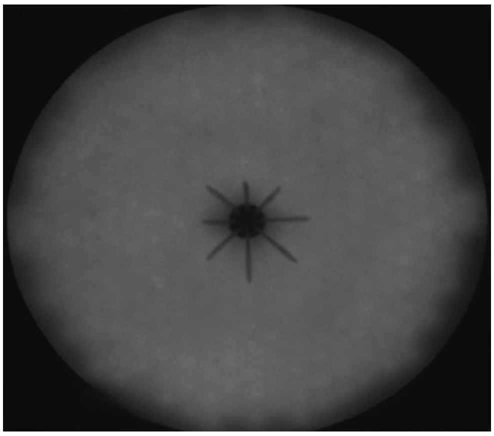
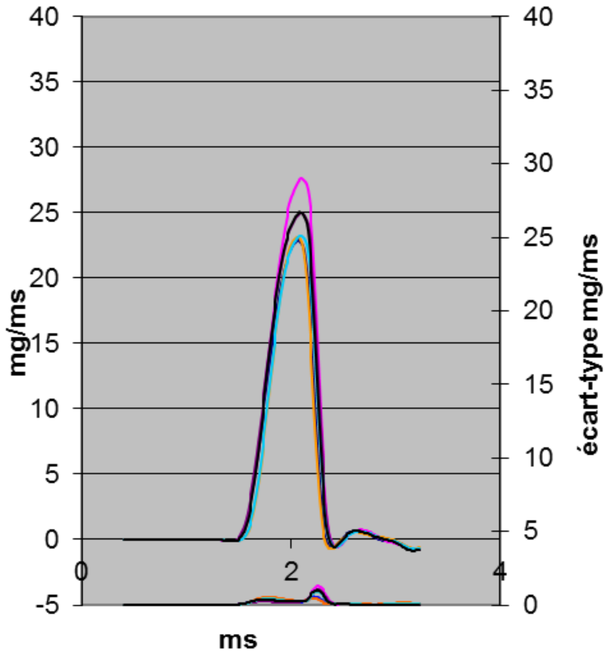


Figure 27: Injector Spray Penetration

With Additive



No Additive

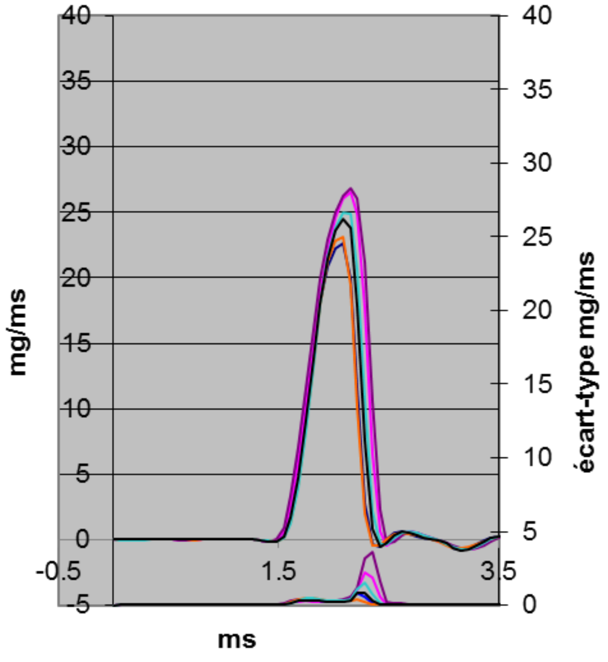


Figure 28: Injector Performance

As can be seen from the above figures the injector spray penetration was far superior in the vehicle fuelled with additive containing diesel; indicating the ability of the additive in removing injector tip deposits. The charts in Figure 28 relate to delays in fuel delivery and injected amount of fuel, with the vehicle fuelled with no additive demonstrating a greater drift in injector performance and suggests evidence of IDID formation. The above data therefore demonstrates in on road vehicle operation, the ability of a diesel deposit control additive to protect fuel injectors against different types of deposit formation and maintain a common rail fuel system in its optimum design condition.

CONCLUSIONS

The automotive area has had common rail IDID injector issues for a number of years now and they have proven to be complicated. An array of analytical techniques has been deployed to try and understand these, The initial data presented here for marine injector equipment shows that the IDID deposit situation is the same as in automotive but that there will be more work required to ascertain the degree of similarity, apart from the presence of carbonaceous material. Similar deposits resulting in operability concerns have been noted in the automotive field. As a result industry standard engine tests have been developed to measure a fuel’s propensity to form IDID. This test can also be used to determine the ability of a deposit control additive to mitigate the formation of IDID and maintain engine and fuel system operability. Successful application in the automotive field also confirms the ability of a deposit control additive to protect a diesel fuel injector against fouling.

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