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ABSTRACT

The effect of legislation in driving towards lower emissions has seen significant changes in injector design, (common- rail) and fuel composition (ULSD). This has led to numerous reports of deposits throughout the vehicle diesel system, filters, tanks, pumps and injectors. In recent examples, deposits internal to the fuel injector on the needle have become prevalent and characterisation of the deposits on the injector needle has become an industry priority. A number of studies have made progress on this but the deposits have proven difficult to fully characterise and often have an ineradicable nature, which makes analysis other than in situ difficult. This paper will describe for the first time the application of a number of surface techniques, in combination which not only provide characterisation data but also the ability to provide cross-sectional lifts out of the sample, which may then be the subject of further analysis. The techniques used were:

Focused Ion-Beam Scanning Electron Microscopy, (FIB-SEM): has allowed direct structural assessment on the microscale, precise manipulation by use of the ion beam to reveal deep structure, nanomachining and section parts of the deposit for further analysis.

Transmission Electron Microscopy (TEM): has allowed the deposit to structure to be assessed at the 10nm level to show ordering.

Atomic Force Microscopy (AFM): has allowed the micro and nano scale topography, morphology and material properties to be investigated.

Raman Spectroscopy: has allowed the mapping of carbonaceous order in the deposit.

The insights achieved in understanding of internal carbonaceous diesel injector deposits from the combined application of these techniques is described. Further, the potential such analyses may bring to improving our understanding of the buildup history, origin and relation to other diesel system deposits is also discussed.

INTRODUCTION

The emission reduction driven changes to modern diesel injection systems with increasing pressures and temperatures has yielded injector designs with a greater preponderance to generate deposits. They are also likely because of reduced tolerances to have their operations affected by deposits. The changes in the fuel pool, such as the introduction of ultra-low sulphur diesel (ULSD) in the US, has seen fuels containing more reactive species, more potential deposit precursors and variation in composition which affects the fuels ability to solubilise deposits. Though these changes have manifested themselves in deposits throughout the diesel fuel system [1, 2], in recent years it is internal diesel injector deposits (IDIDs) which have merited the most study because of their impact on the consumer. Through sticking of moving...
internal parts in the injector IDIDs result in the loss of control of injection event timing, and fuel volume which manifests as rough idling, drivability power variations and loss of fuel economy. The sources of IDIDs are many, as shown in Figure 1. These sources have resulted in six types of IDID being recognized, by the industry, though in reality the IDID deposits have been shown to be complex mixtures.[3-6].

The types of IDID recognised are:

- **Carboxylate Salt**: Formed from carboxylates and metals such as sodium and calcium.
- **Polymeric Amides**: These appear brown in colour and polymeric in nature. They have been associated with non-commercial low molecular weight polyisobutenesuccinimides, (PIBSI)
- **Inorganic salts**: e.g. sodium nitrate, sodium chloride and sodium sulphate.
- **Aged Fuel Deposit**: Appear as a tacky, brown or black colour and may be associated with biodiesel breakdown.
- **Lacquer based**: Visualised as coloured blooms on injectors. Fringe patterns suggest thin films. These may be carbonaceous precursors.
- **Carbonaceous**: Usually black containing aromatic rings and buildup of structure. Thought to form through a complex series of mechanisms, involving cycloparafin formation and hydrogen abstraction.

All of these IDID deposits are the subject of significant research effort across the globe, the current industry interest in IDIDs shows no sign of decline. In fact, CRC (Central Research Council Diesel Performance Group-Deposit Panel Bench/Rig/Investigation sub panel), CEN (Comite European de Normalisation TC19/WG24 Injector Deposit Task Force, engine test, and CEC (Co-ordinating European Council TDFG-110) in Europe have sub committees and panels investigating the production and characterisation of these deposits. The deposits are ineradicable in nature and this has meant that in depth analysis of IDIDs has required the use of analytical techniques of increasing complexity [3, 4, 7, and 8], with the first application Time of Flight Secondary-ion Mass Spectrometry (ToF-SIMS) Temperature Programmed Oxidation and Hydropyrolysis to these IDID deposits [3,4] and it is the purpose of this paper to apply a number of other analytical techniques for the first time to inform further on the nature and characteristics of IDID deposits. There is still uncertainty regarding the detailed chemical structure of deposits and the mechanisms involved in their formation. The analytical techniques that are deployed at present are informative but also limiting. For example infra-red spectroscopy describes metal carboxylate deposits, but only at the surface of the deposit, and gives very little information regarding carbonaceous deposits. It is the purpose of the work described here to show other techniques for the first time applied to IDIDs and the unique data they can supply. These will be further explored in future publications and may provide step changes in understanding the nature of IDIDs as Tof-SIMS and hydropyrolysis have [3,4].

**SAMPLE**

The injector needle analysed was from a stuck field injector, from the USA which had used only ULSD. The fuel injector was obtained from the field to build on understanding from earlier work and because of industry focus on internal injector needle deposits. The injector was removed from the engine after the operator had reported operational issues. The fuel injector was from a heavy duty diesel engine in operational service in North America. The problem manifested as power loss, poor drivability, no start, and particulate production from needle sticking. The deposit which caused the sticking problem is shown in Figure 2. The deposit shown was the subject of the analytical techniques described in the body of the paper.

![Figure 2 SEM micrograph of North American Needle](image_url)
EQUIPMENT

Scanning Electron Microscopy (SEM) analysis of several positions on the injector needle was carried out using a FEI XL30 FEG-ESEM, equipped with an INCA microanalysis system (Oxford instruments) fitted with Si(Li) detector, for energy dispersive x-ray (EDAX) chemical analysis. The accelerating voltage used was between 10-15 kV, for the scattered electron and back scattered electron modes with a spot size of 3.0mm. For detection in the wet mode the spot size was 4.0mm. The working distance ranged between 8.8 -10.1 mm. Topography was analysed using Atomic Force Microscopy (AFM), with a Bruker Dimension Fastscan Bio images were acquired in PeakForce™ QNM™ Mode with ScanAsyst™ air Tips (silicon nitride, resonant frequency 70 KHz, spring constant 0.2 N/m)). Samples were analysed at a scan rate of 1.95 Hz, with an engage setpoint of 0.15 V, and the peakforce setpoint between 0.018-0.453 V. The peak force amplitude was 25-100 nm. The images were analysed using Gwyddion™ 2.33 software and were 512 x 512 pixels. The injector needle was embedded in EpoFix™ cold-setting embedding resin and then extracted to leave the deposit resin bound. The resin cast was subsequently microtomed for analysis using SEM, Transmission Electron Microscopy (TEM) and, Raman spectroscopy. Focused ion beam (FIB-SEM) analysis was also carried out using a FEI Quantia 200 3D, using dual beam operation to combine SEM imaging with FIB milling. The accelerating voltages used were 1-5 kV. The sections were cut from resin blocks at 100, 200 and 1000 nm thickness and deposited onto copper TEM grids. The samples were mounted on a TEM stub holder for the SEM and imaged at angles of 0-20 degrees’, with imaging performed using secondary electron imaging mode. High resolution TEM was carried out using JOEL 2100F microscope at an acceleration voltage of 200 kV. The Raman data was collected with a Horiba LabRAM HR instrument, equipped with a confocal imaging capability, laser source wavelengths of 325, 532, 660 and 785 nm and a 600 lines/mm grating. A synapse CCD detector was used throughout. Spectra were collected by recording multiple acquisitions of variable duration for each spectral window. The Raman shift was calibrated using the Raleigh peak and the 520.7 cm⁻¹ silicon line from an Si(100) reference sample.

RESULTS

Scanning Electron Microscopy (SEM).

This technique has been used in numerous studies to characterise IDID [9-12]. The technique can be extended to yield more information specifically imaging using back scattered electrons (BSE). The technique (SEM/BSE) is based on the principle that heavier elements (those of high atomic number) backscatter electrons more strongly than light elements (those of low atomic number). Thus heavier elements appear brighter. This allows the BSE technique to be used to detect contrast between areas with different chemical compositions and densities. The SEM and SEM/BSE images are shown for the same area of the needle tip analysed in in Figure 3 and 4 respectively.

Although the SEM image in Figure 3 very clearly illustrates the topography at the IDID surface, the SEM/BSE image shown in Figure 4 adds additional information regarding variation on the sample surface. Higher magnification SEM/BSE images of the IDID show regions of distinct morphologies and densities as shown in Figure 5. This is indicative of at least two types of deposit being present at the surface layer, indicating different pressure temperature or fuel regimes in the injector at the time of deposition or time induced changes of initial deposits.
The SEM BSE images also have the capability to show the degree of surface damage on the injector needle, an example of which is shown in Figure 6. This may be the result of abrasion or corrosion as shown in Figure 6 [11, 13 and 14].

The concomitant use of Energy Dispersive X-ray analysis (EDAX) allows further understanding of the subtle variations in the surface of deposits. In this case specific areas can be assessed from the SEM/BSE image and information regarding the elements present can be reported. This has been performed for areas 1 and 2 highlighted in the SEM/BSE shown in Figure 5b with the associated spectra produced shown in Figure 7(1) and 7(2) respectively.

The analysis by EDAX shows the presence of and absence of different elements within neighboring regions of IDID. Specifically region 1 shows the presence of potassium not observed in region 2 and increased sulphur. Metals associated with the injector surface and sodium and calcium were also found.

Focused Ion Beam Scanning Electron Microscopy Manipulation (FIB-SEM).

The application of FIB nano machining allows for the first time microscale surface manipulation and sectioning of an IDID. A trench of deposit may be cut out of the surface, and manipulated for further analysis. The technique which is carried out by leaving a central section intact and gradually thinning down at low currents, allowing generation of a cross sectional material slice of desired width and depth which can then be extracted for structural and chemical analysis. The process is described using a series of SEM images taken at key stages in the process in Figure 8. Thus ineradicable deposits may be extracted and manipulated for the first time. Previous analyses of the IDIDs could only be carried out on the presented surface or required physical scraping or solvent dissolution. Thus losing the history of the IDID and its provenance regarding formation. Sequential FIB nanomachining followed by imaging and analysis can provide progressive structural assessment.

Figure 5 SEM/BSE images of the IDID taken at 500X a & c, 2000X b & d magnifications.

Figure 6 SEM micrograph of surface damage.

Figure 7 EDAX spectra for two different regions of an IDID (identified in the SEM/BSE shown in Figure 5b)
Figure 8 A series of SEM images illustrating the FIB milling and sample extraction process from the IDID sample.
Transmission Electron Microscopy (TEM)

Deposit fragments were analysed by TEM to assess ordered carbon structure. Graphitic components were identified similar to those previously found on diesel filters [7], though with much more crystallinity and similar to deposit found for jet fuel [8]. This show the differences in ordered carbon structures found in deposits throughout the diesel engine/fuel system [7, 11], which is important in understanding the process of carbonaceous deposit formation. Figure 9 shows an example of a TEM image obtained for this IDID sample.

Raman Spectroscopy

Raman Spectroscopy can discriminate ordered (G band) and disordered (D band) domains of carbon with examples of both of these observed from an analysis of the IDID shown in Figure 10. These bands (black line) were deconvoluted to give the individual component bands (blue line) to allow the mapping of ordered and disordered carbon domains across an injector.

The ratio of the Ig and Id bands shows how the ratio of disordered to ordered carbon changes over the surface which can also be mapped as a function of position upon the sample surface. This is shown in Figure 11 for the IDID and shows a heterogeneous distribution of ordered and disordered carbon.

Figure 9 TEM Image of Deposit

Figure 10 Example Raman spectrum acquired from an analysis of the IDID

Figure 11 Raman Mapping of the ordered (Ig) and disordered (Id) carbon upon the IDID sample.

The importance of measuring disordered and ordered carbon on the injector needle lies in its ability to describe how far along the mechanism of carbonaceous deposit formation the injector deposit has travelled. That is to say from deposit precursors to ordered archipelago and graphene type structures [5]. In this case disordered carbon indicative of material formed early in the mechanism of carbonaceous deposit formation is found in the presence of ordered carbon deposits which are further on in the mechanistic process.

Atomic Force Microscopy (AFM)

This scanning probe microscopy technique enables the micro and nano scale topography, morphology and a variety of material properties to be investigated. As different carbonaceous regions show different morphologies it allows a broader view of carbonaceous distribution and compliments the ToF-Sims analysis of carbonaceous species in the deposits [17] and the Raman spectroscopic data described in this paper. The AFM analysis of the IDID sample can be used to show the specific size of features on the surface, presenting nanometre scale features of the deposit. Thicker areas of the IDID samples were analysed producing topographical maps of the nanoscale surface features as shown in figures 12, 12a and b.
The AFM technique can be extended to also measure the degree of "stickiness" and rigidity of the deposits over an area. In Peak Force AFM mode simultaneous imaging, topography/morphology may be carried out whilst also making a mechanical and chemical analysis of the surface. The two variables we have looked at are stiffness (Young’s Modulus) and adhesion, although there others, such as dissipation and phase. The technique is performing a force distance curve at every pixel point, and by analysing various components of the curve you can map these values spatially.

These localized differences are described in Figures 14 and 15, with stiffness (logDMT) and adhesion maps. It has already been proven that IDID deposits are built up of a number of layers and the degree of “stickiness” must play a part in the buildup of such layers [3,6].
CONCLUSION

Those involved in the analysis of internal injector deposits cannot be sclerotic in their approach to the analysis of IDIDs. In this study uniquely it has been shown that:

SEM analysis may be enhanced by BSE variation, especially useful in visualising carbonaceous deposits, and changes in morphology with EDAX yielding elemental information.

FIB-SEM has allowed a cross sectional lift out capability and sample milling for sequential structural analysis of multi-layer IDIDs, to be carried out, which has not been possible by current physical scraping and solvent techniques.

TEM showed presence of ordered graphitic structure.

Raman Spectroscopy produced map of ordered and disordered carbonaceous deposits, illustrating some variation across the injector.

AFM, showed the morphology of the IDID, which was not smooth, and areas of rigidity and stickiness which are important factors in deposit build up. It also yielded surface roughness data showing wear and surface degradation.

All of the techniques as well as those described previously [3,4] elided into evidence for the complex nature of IDID deposits and specifically carbonaceous deposits.

REFERENCES


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