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Injector and Fuel System Deposits

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Abstract

Early studies of deposits in injectors and fuel systems were limited to injector nozzle orifice deposits. The majority of these deposits were the result of fuel decomposition during the combustion process and were controlled by deposit control additives (DCA). Modern diesel fuel systems with high pressure common rail architecture and the severe conditions it applies to the fuel, coupled with the introduction of highly refined fuels such as Ultra Low Sulphur Diesel (ULSD) with its different solubilising capacity, has seen an upsurge in deposit formation at various points in the fuel system. Further, historical nozzle deposits were organic in nature whereas the latest deposits have been shown to be not only complex inorganic and organic mixtures but also, in the case of internal diesel injector deposits (IDID), layered in nature. It is also the case that deposits have been found throughout the system, especially on the fuel filters. The results of such deposits are manifested in field problems such as severe issues with drivability, fuel consumption, emissions, and engine failure. Problems in injector systems are now also being observed with direct injection gasoline systems. Although conventional DCAs have their place in combating deposits there are also new generation DCAs that have been developed to combat these deposits. This paper discusses the variety and range of deposits found, their origins and the effectiveness of some of the new DCA chemistries in treating these deposits.

Introduction

The worldwide legislative drive to reduce emissions continues with for example Tier 3 being introduced in the United States, China V in China and the Bharat regulations in India. There are also regulations proposed or coming into effect regarding marine and locomotive transport. The result of this has seen fuel injector manufacturers going to ever-higher pressures and temperatures to attain these targets whilst the fuel manufacturers have had to re-engineer their product with for example reduced sulphur whilst blending non-refinery products such as FAME or ethanol. The outcome of this is a rise of deposits throughout the fuel system. In this paper we will be concerned with the narrow field of diesel and gasoline systems.

The causes of diesel fuel system deposits are described in Figure 1 and continue to be pertinent. One recent example has been vehicle problems as a result of diesel being adulterated with vegetable oil in Argentina [1]. Further with diesel injectors now being at pressures of 2700 to 3000 bar the opportunities for formation of deposits will increase.

The purpose of this paper is to add to the knowledge reported by ourselves [2] and others [3,4] in the study of fuel deposits and their causes.

Figure 1. Sources of Diesel Deposits.

Diesel Deposits

Diesel deposits have been and remain the subject of numerous studies to characterise them and understand their origin [2-5, 12-15,16-20]. The diesel fuel system in a modern common-rail engine has seen deposits in various parts of the injector system and in filters [19,21]. A typical common rail schematic is shown in Figure 2.

The majority of work carried out has centred on the injectors. The Industry Standard engine test procedure (CEC F-98-08) is designed to assess fouling of injector tips. Internal diesel injector deposits (IDID) have been the focus of recent work and are regarded as the most important problem in the industry at present. The types of IDID observed can be categorised as:

- Fuel ageing deposits: tacky brown or black in colour.

- Carbonaceous: black particulates containing aromatic graphite/ene precursors.
- Metal Carboxylates: off white carboxylate salts of sodium.
- Amide lacquer deposits: thin films of deposits, polymeric in nature linked to poor quality low molecular weight PIBSI species.

Deposits are also found on fuel filters and recent work has investigated the inside of the common-rail itself.

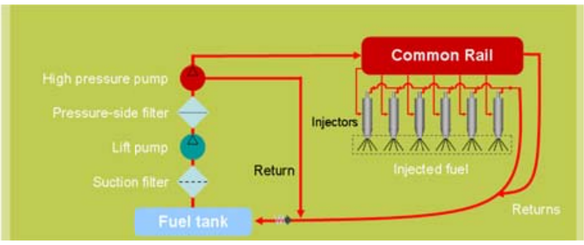

Figure 2. A Typical Common-Rail Schematic

Diesel Injector Tip Deposits

The introduction of the Industry Standard test procedure (CEC F-98-08) to assess the injector fouling tendency of fuels dosed with different deposit control additives has led to the introduction of new chemistries to combat these deposits effectively.

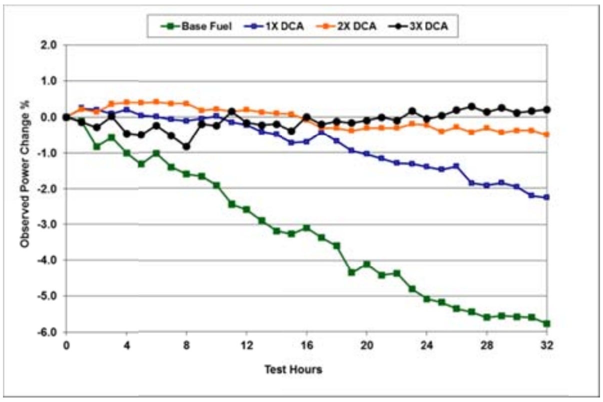

Figure 3. Observed power data from DW10B keep clean engine tests on fuel containing Zn neodecanoate plus novel deposit control additive.

Engine tests conducted using the CEC F-98-08 DW10B engine using RF-06-03 (European certification test fuel) have shown the effectiveness of these novel additives as shown in Figure 3. As per the CEC F-98-08 test procedure the fuel was adulterated with zinc neodecanoate to give 1mg/kg of zinc in the fuel. A brief outline of the procedure is given here. The test used the 1997cm^3, 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. The cycle was repeated to give a total test time of 32 hours.

These novel deposit control additives have also been shown to be effective in cleaning up existing deposits resulting in a rapid restoration of power on addition of the additive after 32 hours. This is shown in Figure 4.

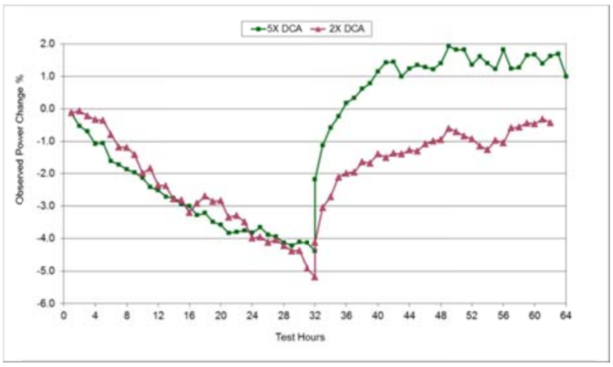

Figure 4. Observed power data from DW10B clean up engine tests on fuel containing Zn neodecanoate plus novel deposit control additive.

Internal Diesel Injector Deposits – Polymeric Amide Lacquers

Polymeric amide lacquer deposits and their link to low molecular weight polyisobutene succinimides (LMW PIBSI) has been investigated in a number of publications [13-20]. In many cases these have investigated an ill characterised LMW PIBSI of unknown provenance.

Recent work [2] on these deposits saw engine testing carried out on a well characterised, lab prepared, non-commercial low molecular weight polyisobutylene succinimide sample, (LMW PIBSI (non-commercial)). The paper described a non-commercial LMW PIBSI which in the CEC F-98-08 Peugeot DW10B engine caused injector sticking. A commercial PIBSI deposit control additive (DCA) was found not to cause sticking in the same test and also prevented sticking when used in addition to the low molecular weight material. The jammed injector needles from the test were subject to a number of analytical tests. The presence of amide on the needle surface was confirmed by infra-red spectroscopy (FTIR).

Time of Flight Single Ion Mass Spectrometry (Tof-SIMS) showed, by spectral comparison with the starting material, that the LMW PIBSI (non-commercial) was present in a lower layer of the injector deposit. This is shown in Figure 5 using the ion $C_4H_2O_2N^-$ which is common to both the LMW PIBSI (non-commercial) and the injector deposit.

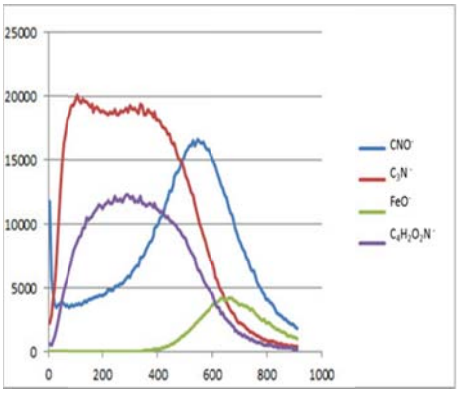

Figure 5. Tof SIMS Depth Profile Study of „stuck“ injector from use of LMW PIBSI (non-commercial).

No Industry Standard test is currently available for IDID. CEN (Committee European de Normalisation) TC19/WG24 Injector Deposit Task Force and CEC (Coordinating European Council) TDFG-110 engine test committees are working to develop an engine test for IDID caused by LMW PIBSI.

Although an engine test will be the final arbiter in any studies there is also a need for a bench test to assist in the understanding of deposits. The Jet Fuel Thermal Oxidation Tester (JFTOT) is the Industry Standard qualification test for the thermal stability of aviation fuel. This technique has been extended to diesel fuel by a number of groups [13-15] including ourselves as an investigative bench test for IDID. Using mapping infra-red techniques we have extended the degree that the test can inform regarding the chemistry of deposit formation. The recent publication [2] detailing engine testing with a LMW PIBSI (non-commercial) also noted work on the lab prepared sample using the JFTOT and a reference fuel. This resulted in deposition on the JFTOT tube. This sample will be used to illustrate the use of infra-red microscopy as a characterisation tool for samples generated by the JFTOT bench test. The infra-red map of the deposit is shown in Figure 6.

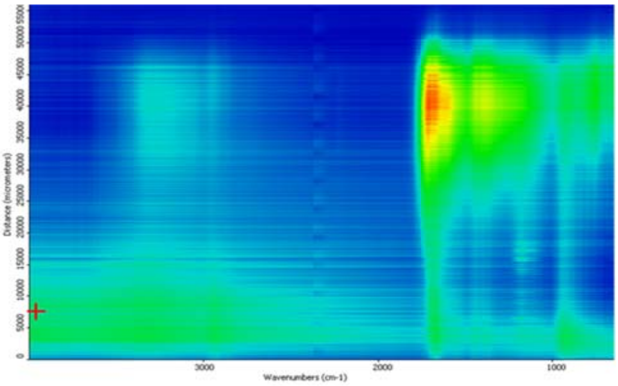

Figure 6. Infra-red Microscope Map of JFTOT Tube Deposit.

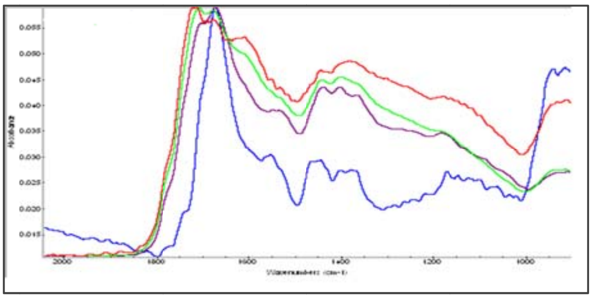

Figure 7. Infrared spectra from varoius points along the JFTOT tube deposit.

The spectra were collected along the tube and a transition can be seen in Figure 7. At the beginning of the tube, amide is predominant with a strong vibration at ~1670cm^{-1}. The further along the tube one travels the imide of the PIBSI comes to the fore with a band at ~1705cm^{-1}. The amide is formed from the acids in the fuel. It may be speculated that the two materials deposit on different parts of the tube because of differences in solubilty in the fuel. Thus a bench test showed both an imide and an amide species exist in a LMW PIBSI (non-commercial) deposit. This agrees with what was found previously on the engine test generated needle [2].

Internal Diesel Injector Deposits – Metal Carboxylates

Internal diesel injector deposits (IDID) from sodium carboxylate sources have also been the subject of investigation. As for the polymeric amide lacquers, there is currently no Industry Standard engine test method. In the US, CRC committee sub panel on IDID (CRC DIESEL Performance Group - Deposit Panel Bench/Rig/Investigation sub panel), and in Europe, CEN TC19/WG24 Injector Deposit Task Force, and the CEC TDFG-110 panel, are working to develop a standard engine test using a “fuel soluble” sodium salt and dodecenylsuccinic acid (DDSA).

Tests were conducted using the CEC F-98-08 DW10B engine to assess the injector sticking tendency of fuels dosed with sodium salts. The tests were carried out using RF-06-03 (European certification test fuel) as received and the fuel was not adulterated with zinc neodecanoate. The engine test procedure was carried out as described above with additional monitoring of the exhaust gas temperatures. 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 work has shown the use of fuel soluble sodium 2-ethylhexanoate in conjunction with dodecenylsuccinic acid (DDSA) 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 commercial deposit control additives were effective in preventing the formation of sodium carboxylate deposits within the injectors.

The change in observed power for each test is shown in Figure 8. The sodium 2-ethylhexanoate/DDSA test failed to start following the first soak period after 8 hours of running.

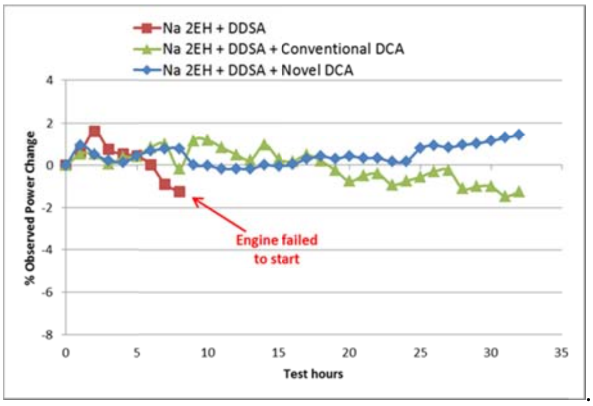

Figure 8. Observed power data from DW10B engine tests on fuels containing Na 2-ethylhexanoate/DDSA, plus conventional and novel deposit control additives.

A commercially available conventional deposit control additive commonly found in diesel fuel globally was added at 2X treat rate 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 9.

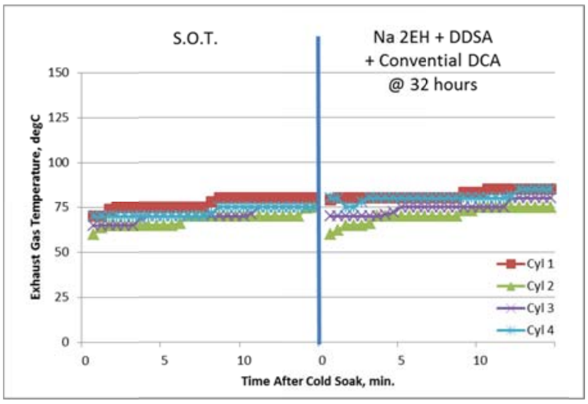

Figure 9. Exhaust gas temperatures from DW10B engine test on fuel containing Na 2-ethylhexanoate, DDSA and conventional deposit control additive.

Next generation novel deposit control additives have also been shown to be effective in preventing injector sticking in the presence of sodium species added to the fuel. A novel DCA was added at 1X treat rate 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 10.

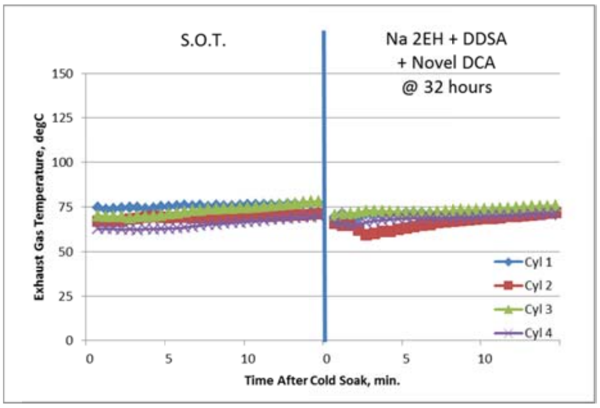

Figure 10. Exhaust gas temperatures from DW10B engine test on fuel containing Na 2-ethylhexanoate, DDSA and novel deposit control additive.

Diesel Common-Rail Deposits

The work above has been limited to the injector part of the common-rail diesel fuel injection system. Preliminary work on analysis of a diesel common-rail will now be described.

In a diesel fuel injection system one of the most important parts is the common-rail, a pressure accumulator where the fuel is stored at high pressure which feeds fuel to the injector system. Though injectors have been investigated [10] until now the rail itself has not been studied. Here we present preliminary data describing the corrosion that has occurred in a common-rail in field use.

A common-rail from a medium duty diesel engine which had suffered a failed injector was recovered from the field in the USA. It had been subjected to use with ULSD until injector failure. The common-rail was cut up and one side of the pipe removed to investigate the inner surface of the rail. This was then mounted on resin and subject to SEM analysis as shown in Figures 11, 12 and 13.

The surface showed general corrosion across the inner surface of the pipe with rust deposits seen across the surface. There was also pitting observed to a depth of 3 to 25 microns.

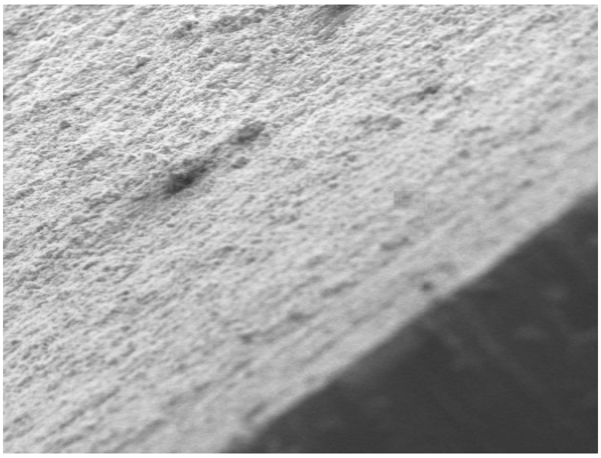

Figure 11. Inner Surface Common-rail Pipe.

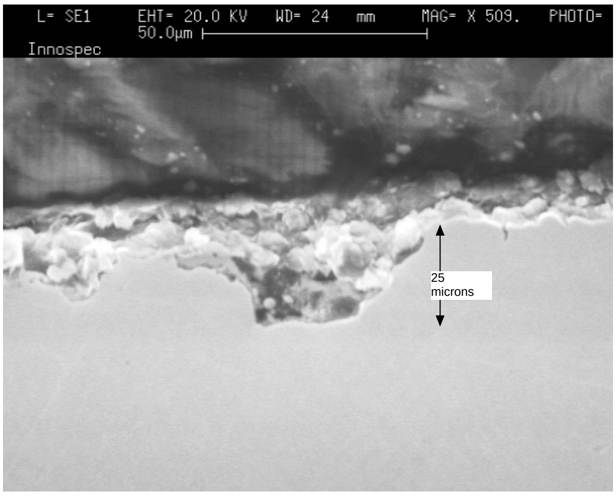

Figure 12. SEM Micrograph of Common-rail Inner Surface with pits 25 microns deep.

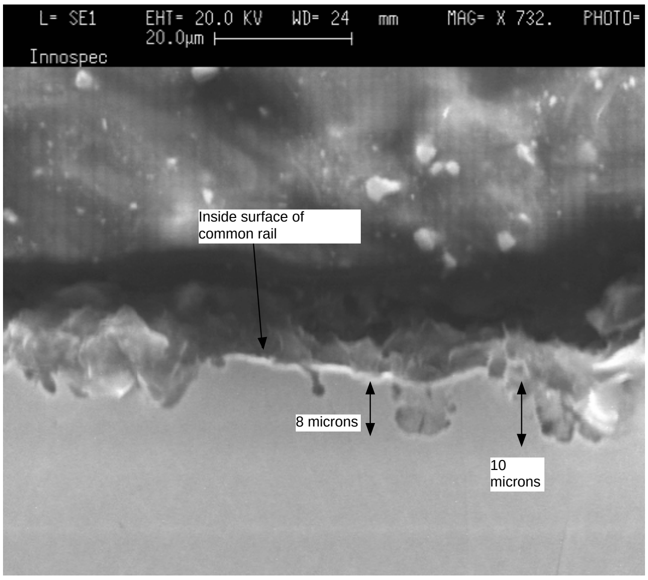

Figure 13. SEM Micrograph of Common-rail Inner Surface with pits 8-10 microns deep.

The presence of such corrosion is of interest from two aspects. One is that it shows the corrosive effect of ULSD on a metal fuel system surface but also the pits formed are active sites for fuel degradation in the fuel system [11]. The corrosion may be the result of water ingress, biodiesel components [12] or disarmament of the corrosion inhibitor additive.

Further investigations will be reported in a future publication.

Diesel Fuel Filter Deposits

Fuel filters are designed to remove particles from fuel and as such can accumulate similar deposits to those observed in the injectors or precursors to those deposits. Filters removed after DW10B testing of fuel doped with zinc neodecanoate showed a build up of black deposits. Filters taken from tests conducted with the addition of novel deposit control additives showed a reduction in these deposits as shown in Figure 14. Clearly these novel deposit control additives are effective in preventing not only injector deposits but deposits throughout the fuel system.

Figure 14. Fuel filters from DW10B engine test on fuel containing Zn neodecanoate with and without novel deposit control additive.

The application of infra-red spectroscopy to the analysis of diesel filter samples has been carried out for many years [22]. The advent of diamond ATR technology has made possible direct acquistion of data from the filter surface routine. An example of a filter from a European diesel filter spectrum is shown in Figure 15.

In addition to bands associated with diesel, the infra-red shows a dominating band at 1565 cm^{-1} assigned to asymmetric COO stretch and in conjunction with a COO symmetric stretch at 1446 cm^{-1}, suggests the presence of carboxylate salts. Although a very useful technique, the caveat that only the surface of the deposit is analysed should always be borne in mind.

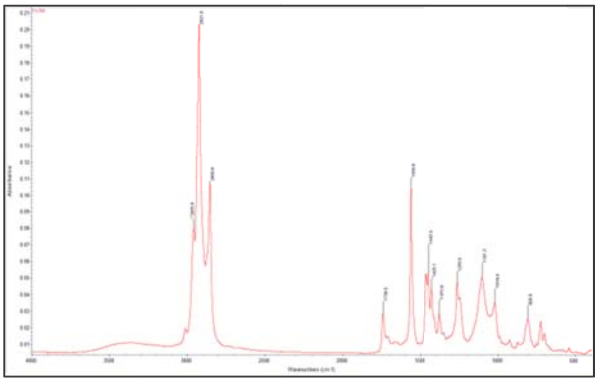

Figure 15. European Field Diesel Filter Direct Surface ATR Spectrum.

The work on diesel has shown that although injector deposits are important, understanding and characterising the deposits formed is analytically challenging. It should also be noted that there are other parts of the common-rail diesel system which require investigation. Hence our previous work on diesel filters [22], and the preliminary work on the common-rail described herein.

Gasoline Injector Deposits

It would be naïve to believe that deposits are restricted to one fuel system alone and there have been a number of recent reports regarding direct injection gasoline injector deposits [5, 6]. The drivers of vehicle fuel economy consumer satisfaction and emissions are pushing gasoline engine manufacturers toward direct injection gasoline engine technology, with estimates of market share of this type of powertrain to be around 20% of the world market by 2020. The number of papers and patents on deposit formation or its prevention has also increased [5-8]. The majority of these have focussed on injector design or fuels, and studies of the chemistry of the deposits at the tip and in the body of the injector. Here we report initial work on a gasoline direct injection injector which had failed.

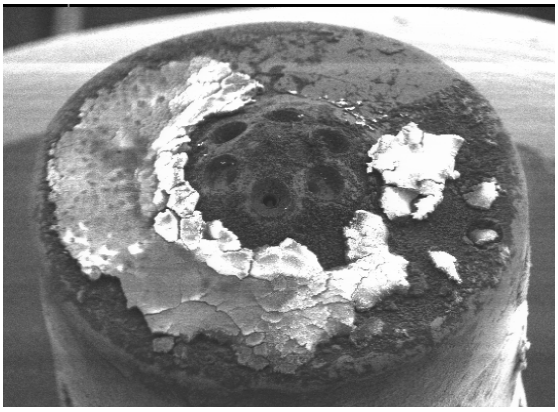

Figure 16. SEM Image of Gasoline Direct Injection Injector Tip.

The SEM of the injector tip, Figure 16, showed deposit around the tip and the injector holes. The anlaysis of the deposit by X-ray fluorescence elemental analysis (EDAX) did not show significant amounts of metals, just traces of molybdenum and calcium. The visual morphology of the deposits would suggest several different chemical species being present.

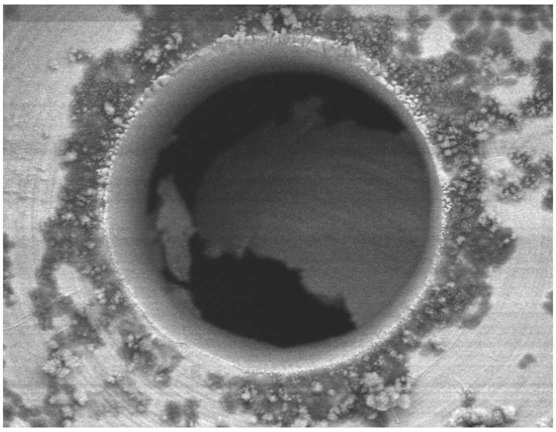

Figure 17. SEM Image of Injector Hole.

The injector holes where all blocked to a certain degree and an example is shown in Figure 17. Again, EDAX analyses showed a lack of metals being present.

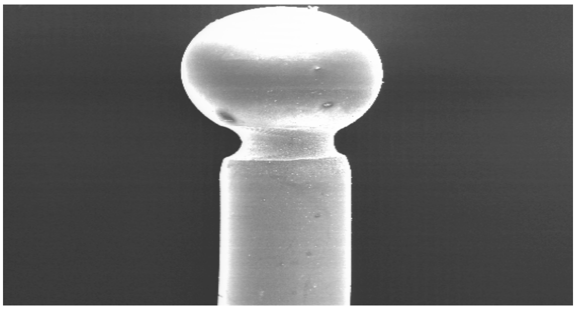

Figure 18. Injector Needle.

The injector needle, Figure 18, had deposit present across the ball and shaft. In this case, trace amounts of lube oil constituent metals (for example molybdenum) were found. Deposits were also noted on the injector spring but again no significant amounts of metals were present. In summary, the deposit on the needle appears to be different in nature to deposits found elsewhere, with a more crystalline nature being observed. The deposits are mainly organic.

Initial data from SEM and Infra-red microscopy studies has shown the deposit to be complex, with both fuel gum, intermediates and carbonaceous deposits present. This study will be fully described in a future publication.

Conclusions

This work has shown that the bench JFTOT test coupled with infra-red spectroscopic mapping techniques can be regarded as a useful test for understanding IDID formation.

The challenge of removing injector tip, IDID and fuel filter deposits has been met by the development of a new generation of DCAs for which successful engine test data is described.

Initial investigations of a diesel common-rail has shown corrosion levels to be high with concommitant pitting of the surface producing active sites which have potential to act as fuel degradation sites.

The current factors causing deposits in diesel systems are also to be found in other fuel systems such as gasoline. The analytical techniques developed for diesel systems are useful to characterise and understand these deposits. Further it would be naive to think that deposits in the future will be restricted to these two fuel systems.

The challenges remain to the DCA producers to keep injectors clean, and to the analytical community to apply techniques to understand the deposits formed. Regarding the latter, work on the application of Focussed Ion-Beam Scanning Electron Microscopy (FIB-SEM), Transmission Electron Microscopy (TEM), Atomic Force Microscopy (AFM) and Raman Spectroscopy, to diesel deposits will be the subject of a future publication.

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