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Spectroscopic Studies of Internal Injector Deposits (IDID) Resulting from the Use of Non-commercial Low Molecular Weight Polyisobutylenesuccinimide (PIBSI)

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ABSTRACT

Since 2009, there has been a rise in deposits of various types found in diesel fuel injection systems. They have been identified in the filter, the injector tip and recently inside the injector. The latter internal diesel injector deposits (IDIDs) have been the subject of a number of recent publications, and are the subject of investigations by CRC (Central Research Council Diesel Performance Group-Deposit Panel Bench/ Rig Investigation sub panel) in the US and CEN (Committee European de Normalisation TC19/WG24 Injector Deposit Task Force) and CEC (Coordinating European Council TDFG-110 engine test) in Europe.

In the literature one of the internal injector deposit types, amide lacquers, has been associated with a poorly characterised noncommercial low molecular weight polyisobutylene succinimide detergent which also lacked provenance.

This work will describe a well characterised non-commercial low molecular weight polyisobutylenesuccinimide, the engine tests associated with it and the spectroscopic analysis of the needle of the resultant stuck injectors. An engine test of a commercial grade PIBSI detergent that showed no sticking will also be described.

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INTRODUCTION

The use of deposit control additives (DCA) to prevent buildup of deposits in fuel injection systems and thus ensure optimum engine operation has a history spanning over three decades. In the 1980s deposits on the injector pintle were noted [1], enabling the technology of fuel additives to reduce diesel injector fouling [2]. Increased emissions from the plugging of spray holes was found in 1991[3], and increased emissions legislation forced changes in fuel and engine design [3, 4]. Recent changes in fuel properties such as solubilsing ability [5] caused for example by the introduction of ULSD and the introduction of more stringent emission regulations along with the increased tolerances, temperatures and pressures in modern diesel injector systems has seen the formation of internal injector deposits (IDID). Thus, more than ever there is a need for high quality, effective DCAs. The most effective and preferred DCA over this period is polyisobutylenesuccinimide (PIBSI). The design and manufacture of such PIBSIs being critical to their performance as a deposit remover and their no harm status.

The nature of IDIDs has been broadly categorised by the industry as:

- Metal carboxylates: carboxylic acid salts of metals such as sodium or calcium.
- Carbonaceous: carbon based deposits from fuel stressing and subsequent degradation.
- Amide based polymeric amide
- Lacquer: films, polymeric.
- “Sticky” deposits: from aged fuels

A number of recent publications have inculcated a low molecular weight PIBSI as a source of IDIDs, associated with injector sticking. [6,7,8,9]. It should be noted that low molecular weight PIBSI would not be regarded as a commercial DCA and certainly not associated with a high quality DCA, and that the term PIBSI can cover a number of chemical structures. The effect of low molecular weight PIBSI has been investigated in bench tests, as well as modified and industry standard engine tests. Recently the Coordinating European Council (CEC) has proposed a new Direct Injection (DI) engine test using the Peugeot DW10C engine. This test adulterates the test fuel with low molecular weight PIBSI to yield injector sticking and although this is not an industry standard it is under serious investigation to become so in the future. These laboratory and engine tests have also shown that commercial PIBSIs specifically designed and manufactured to function as a diesel deposit control additive do not cause internal diesel injector deposits, and act effectively in the prevention of the formation of such deposits. [6, 7, 8, 9].

Field sourced IDID injector deposits have been found to comprise of layers and several different species namely, carbonaceous decomposition products, organic amide lacquers, and metal ion contaminants [11,12,13,14].The composition of these mixtures being determined by the drive history of the vehicle. Further, since low molecular weight PIBSI is not a commercial DCA, it was decided to follow up on a recent publication on low molecular weight PIBSIs [8] to investigate the characteristics of IDIDs resulting from low molecular weight PIBSIs.

METHODOLOGY

In the previous publication [8], a non-commercial low molecular weight PIBSI was synthesised, and used in a DW10B engine test in comparison to a commercial DCA. The low molecular weight PIBSI test resulted in injector needle sticking and the analysis of the IDID that caused the sticking is the subject of this paper. The commercial PIBSI did not cause injector sticking.

Fuels

The base fuel used for all testing was reference fuel RF-06-03. The certificate of analysis for this fuel is given in Appendix 1.

PIBSI Additives

A low molecular weight PIBSI was synthesised in the laboratory according to scheme 1.

The PIBSI was characterised by Gel Permeation Chromatography (GPC) which showed its molecular weight distribution to be bimodal and therefore two distinct number average molecular weights Mn were found. Mn = 596 and 1195.The Chromatogram is shown in figure 2, where a commercial monomodal DCA is also shown for comparison. In previous work, this commercial DCA was shown not to cause injector sticking and indeed, it prevented injector sticking in the presence of low molecular weight PIBSI.

The low-molecular weight PIBSI was also characterised by infra-red spectroscopy (IR), because it has been suggested that significant amide presence in low molecular weight PIBSIs was a contributory factor to their formation of IDIDs. The spectrum figure 3 shows a dominance of imide and the low molecular weight PIBSI was engine tested in this form.

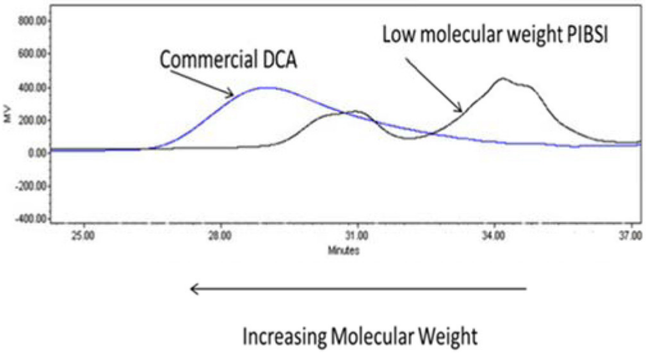

Figure 2. GPC chromatogram for Commercial PIBSI DCA and the Low molecular weight PIBSI used in this test.

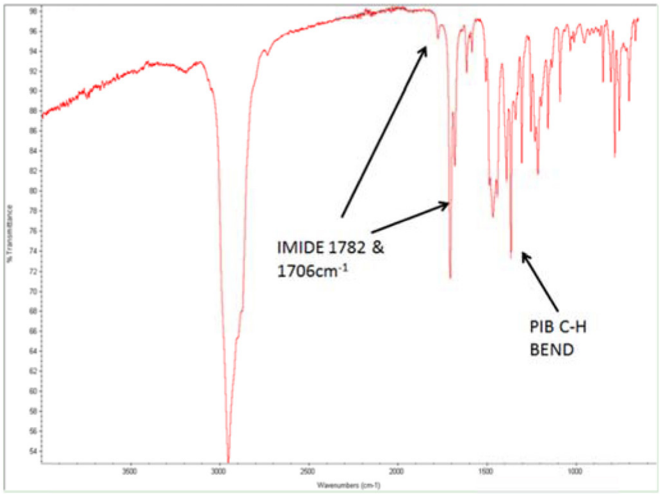

Figure 3. Pre-engine test IR spectrum of Low molecular weight PIBSI.

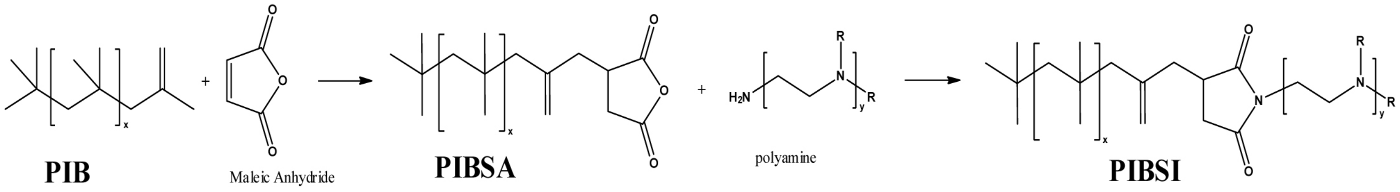

Figure 1. The Synthesis of PIBSI

Engine Test

Tests were conducted using the CEC F-98-08 DW10B engine test [15] to assess the injector sticking tendency of fuel dosed with the low molecular weight PIBSI. A synopsis 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.

On starting the engine the exhaust gas temperatures for each cylinder were recorded. 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 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 and so on until 32 hours of test cycles had been completed or until the engine failed to start which signified serious injector sticking.

To assess injector sticking using the CEC F-98-08 DW10B engine test the fuel was not adulterated with zinc neodecanoate.

Analysis

The needle from the engine test using low molecular weight PIBSI was subject to a number of analytical techniques in this work. The techniques of Scanning Electron Microscopy (SEM), Energy Dispersive Analytical X-ray Spectroscopy (EDAX) and Fourier Transform Infra-red Spectroscopy (FTIR) are well known in this area of study. The use of Hydropyrolysis (HyPy), and Time of flight Secondary Ion Mass spectrometry (Tof - SIMS) is however relatively new [9,10,11,16], hence a description of these techniques is given.

Hydropyrolysis

The hydropyrolysis technique is described in [16], but salient points are described here for convenience. Hydropyrolysis refers to pyrolysis taking place under an atmosphere of high hydrogen pressures; hydrogen pressures of greater than 10 M Pa are typically used. The technique has been developed for its unique ability to release high yields of bound biomarkers from for example coal, whilst minimising the structural rearrangement of those deposits. In relation to deposits formed in diesel engines hydropyrolysis has the capability to identify particular chemistries from the hydrocarbons released.

Tof-SIMS

The technique has been described in detail in an earlier paper by the authors [10]. Briefly, it involves using a primary ion beam to produce a secondary cloud of ions from a target surface. These ions are then extracted into a time of flight mass spectrometer and analysed. The surface can be gradually eroded away by a separate sputter ion beam. A plot of the intensity of a given mass signal as a function of time is a reflection of the variation of its abundance and concentration with depth below the surface. The technique has several advantages including the parallel detection of different chemical species, their mapping over the surface analysed; all of which can be simultaneously performed whilst eroding the surface with a 'sputter' ion beam.

EXPERIMENTAL

Engine Test

The low molecular weight PIBSI sample was tested using the CEC F-98-08 DW10B engine. The exhaust gas temperatures for each cylinder were recorded at the start of the test (SOT) and following each four hour soak period. The treat rate was 500mg/kg to provide IDID in sufficient quantities to assist the analysis.

Figure 4 shows the exhaust gas temperatures for the test. This level of low molecular weight PIBSI was found to cause severe injector sticking after the first eight hours (8 cycles) plus 4 hour soak period.

This is the same as found previously for a 200mg/kg treat rate. The commercial PIBSI under the same test regime showed no injector sticking.

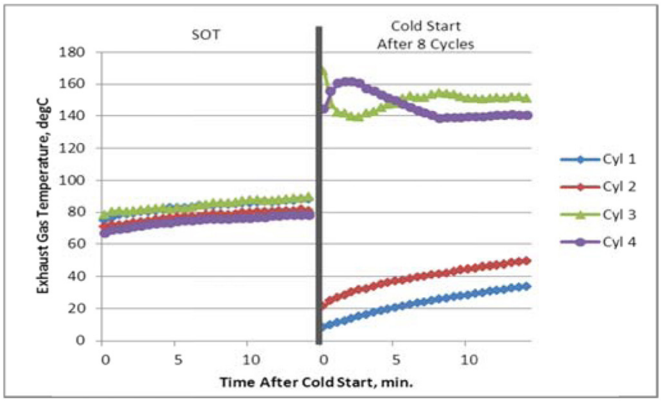

Figure 4. DW10 B, exhaust gas temperatures after 8 cycles plus 4 hour soak with 500mg kg low molecular PIBSI.

The stuck injector needle from the low molecular weight PIBSI test was removed with difficulty and the needle subject to analysis.

SEM/EDAX

The SEM micrograph figures 5 and 6 show the layer of light brown lacquer deposit around the needle tip. Analysis by EDAX showed only metals associated with the injector.

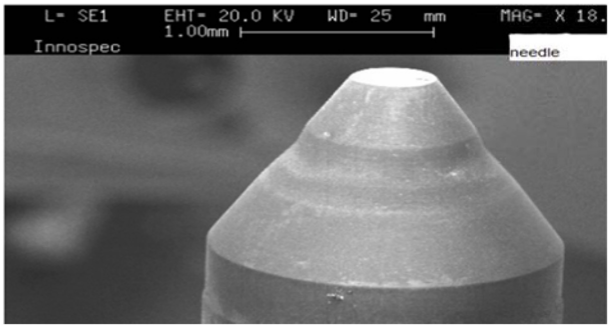

Figure 5. DW10 B, SEM micrograph of Injector Needle

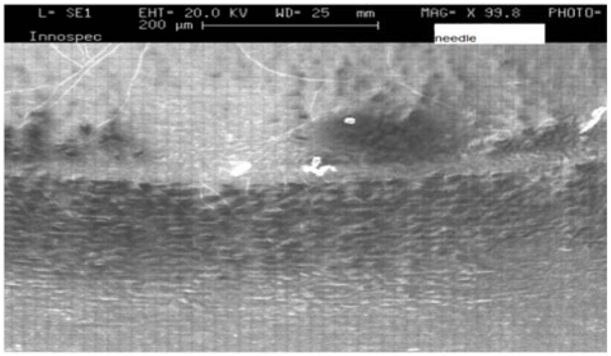

Figure 6. DW10 B, SEM micrograph of Injector Needle

INFRA-RED SPECTROSCOPY

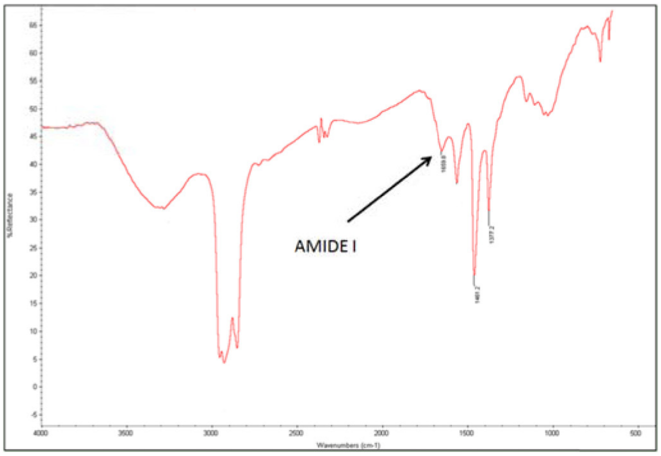

Figure 7. FT-IR spectra of deposit from the DW10b test with low molecular weight PIBSI.

The infra-red spectrum in figure 7 has characteristic amide absorptions at ~1660 cm-1 associated with amide lacquers. The spectrum was recorded directly from the injector needle using a Nicolet ^^^µ^ı microscope in conjunction with a Nexus bench. It is noteworthy that in a previous study [5] that this reference fuel after clay filtration did not produce any deposit with low molecular weight PIBSI. Further, since the original infrared spectrum of low molecular weight PIBSIs shows only some amide presence then the amide part of the deposit formed has to be the result of reaction with acidic species in the fuel.

Tof-SIMS

For depth profiling of the injector deposit, the pulsed Bi3+ primary ion beam had a spot size of < 2 µm diameter and was rastered in a 128 × 128 pixel array. Owing to the insulating nature of the sample, charge compensation using a low energy (20 eV) electron flood gun was applied. The sputtering and analysis ion beams were aligned before measurements so that the spectral analysis area was at the centre of the sputter crater. Depth profiles were subsequently acquired using 'non-interlaced' mode with periods of 100 and 6.9 s of sputtering and analysis respectively, with an intermediate 'pause' period of 0.5 s. The sample repeat areas were undertaken using a 300 µm crater with the central 100 µm area analysed. A standard spectrum for low molecular weight PIBSI was measured by running under cryo-conditions, freezing the PIBSI in liquid nitrogen and then analysing the polymer to avoid volatility problems.

The depth profile of the deposit is shown in figure 8. There are a number of nitrogen containing species, but to attribute layer to PIBSI, an ion of more complex structure is required, and it should be also found in the spectra of the low molecular weight PIBSI. The $C_4H_2O_2N^-$ common ion was found and used to profile low molecular weight PIBSI in the deposit figure 9.

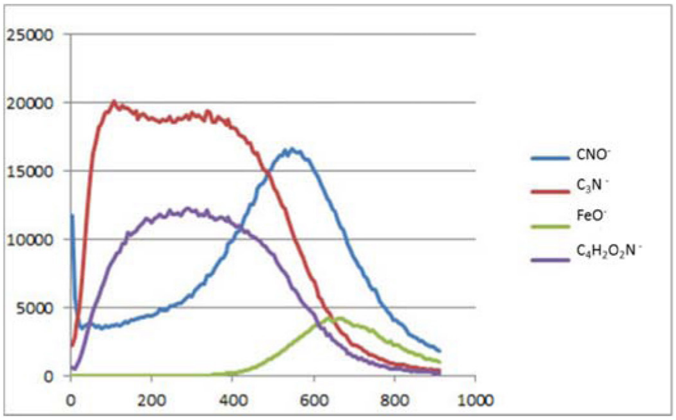

Figure 8. Tof-SIMS depth profile of injector deposit

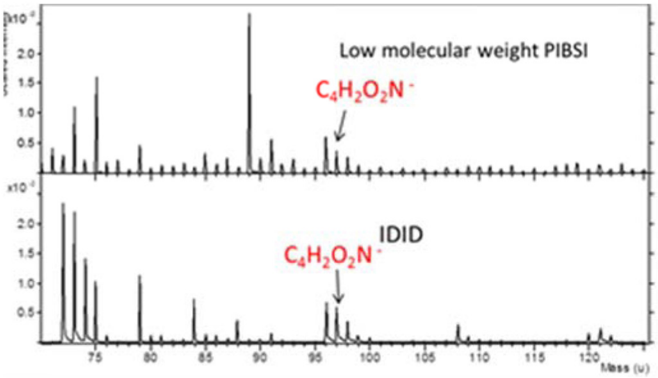

Figure 9. Tof-SIMS mass spectrum ion comparisons between deposit and low molecular weight PIBSI.

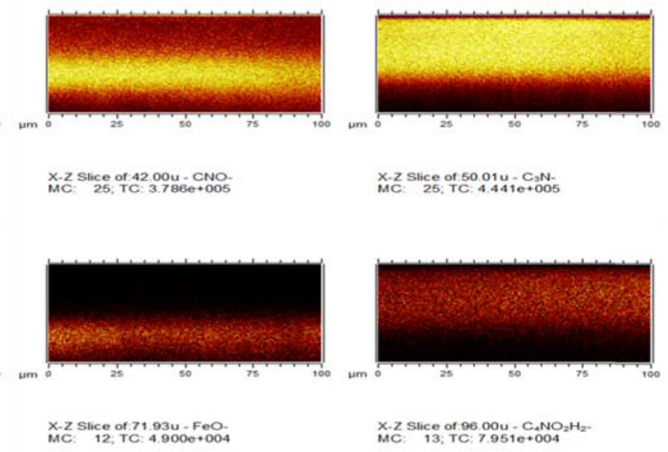

Figure 10. Depth profile images for the above.

The depth profile studies show a surface layer with an associated C3N⁻ ion. Since FTIR shows the surface to be amide in nature, then this would be consistent. The low molecular weight PIBSI in the imide form is found below this surface layer and nearer to the metal surface of the injector.

Hydropyrolysis

The needle was mixed with a sulphided molybdenum catalyst, and placed in the reactor. The reactor was first heated from ambient temperature to 250°C at a rate of 300°C/minute and then to 350°C at a rate of 8°C/minute. A pressure of 150 bar of hydrogen was maintained in the reactor and any products were swept into a silica trap cooled by dry ice. On cooling of the rig, the silica was removed from the trap and analysed. Fresh silica was charged to the trap and with the same hydrogen flow rate and pressure the sample was subject to hydropyrolysis by heating from ambient temperature to 350°C at a rate of 300°C/minute; any material that would be driven off below this temperature would already have been driven off and collected in the previous batch of silica The sample was then heated to a final temperature of 520°C at a rate of 8°C/minute. This higher temperature was held for 2 minutes. Again, after allowing the rig to cool the second batch of silica was removed. The products on each batch of silica were desorbed using dichloromethane and then analysed by Gas Chromatography Mass Spectrometry (GC/MS). GC/MS analysis was performed on a Varian CP3000 GC operating in full scan mode and interfaced to a 1200 M/S; (Electron Impact mode negative ion, 70 E V) Separation was achieved on a VF-1 MS fused silica capillary column (50m × 0.25mm id 0.25µm thickness).Helium was used as a carrier and an oven programme of 50°C (hold for 2 minutes) to 300°C (hold for 20.5 minutes) at a rate of 4°C/minute.

The mass spectrum of the products, figure 11, is shown in both Total Ion Chromatogram (TIC) and Single ion Chromatogram (SIC) modes. A TIC is chromatogram created by summing up intensities of all mass spectral peaks belonging to the same scan. A SOC chromatogram is such that only a selected m/z value or more are detected in the analysis thus enabling further separation of a complex matrix. The spectra show a buildup of aromatic rings SIC m/z 270 deposit precursors. Such precursors and their build up have been described previously (11.16) and are associated with fuel degradation because of high injector and temperature pressures.

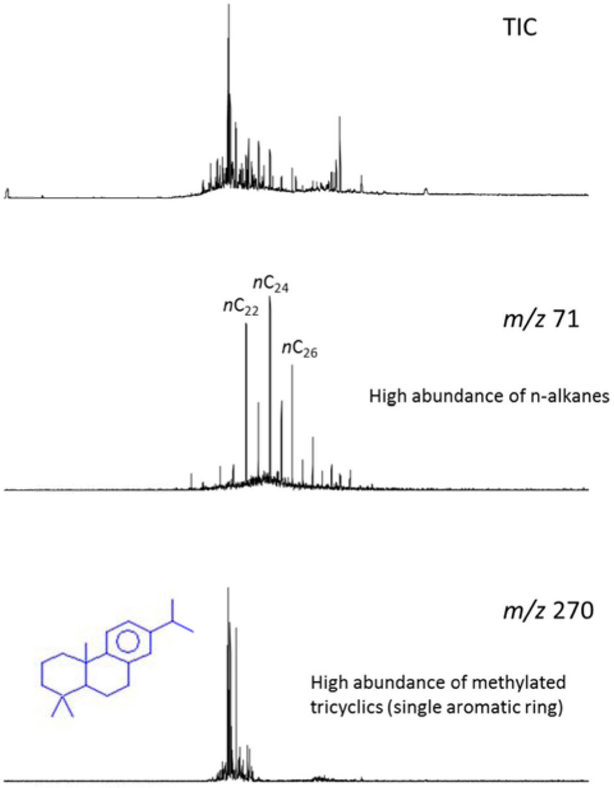

Figure 11. Total ion (TIC) and single ion (SIC) chromatograms for the hydropyrolysis product of the needle deposit.

A comparison of the needle deposit and the original low molecular weight PIBSI figure 12 shows two traces expanded to cover the unresolved complex mixture (UCM) and normalised with each scaled to the largest peak - this shows the relative proportions of the resolved and unresolved components.

The second shows both scaled to the size of the UCM in each, which clearly shows that the UCM from the needle is of higher molecular weight than that from the PIBSI, with the maxima from the needle eluting approximately 8 minutes after that from the low molecular weight PIBSI. This again show higher molecular weight growth in the deposit, which cannot be ascribed to the low molecular weight PIBSI.

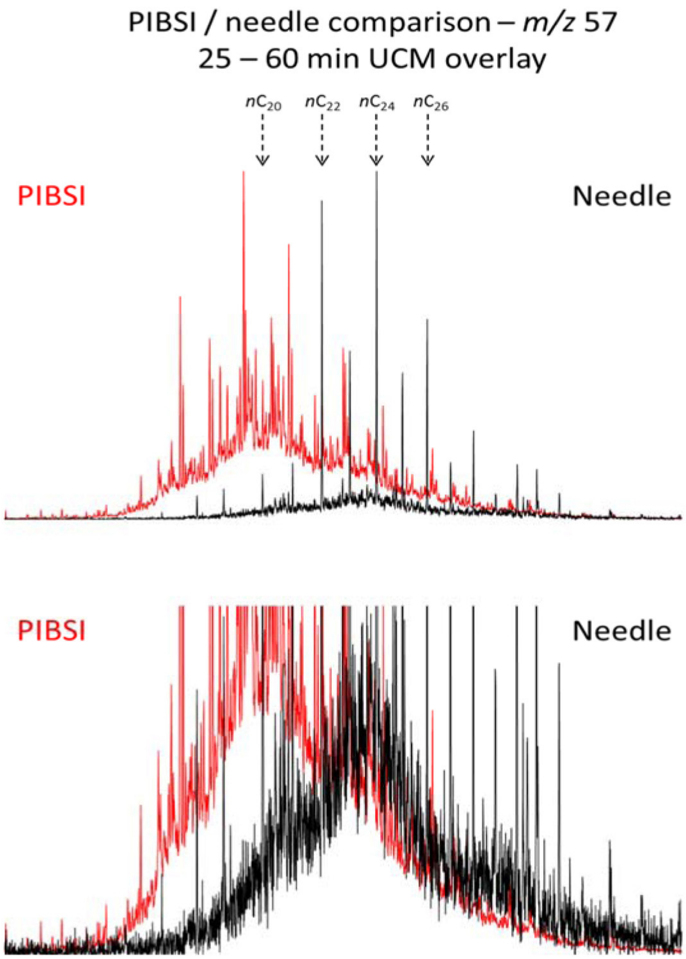

Figure 12. UCM chromatograms for needle deposit and low molecular weight PIBSI hydropyrolysis products.

SUMMARY/CONCLUSIONS

The engine test data clearly shows that low molecular weight PIBSI cause injector sticking because of deposit.

Spectroscopy shows the outer layer of the deposit to be amide in nature but that one of the inner layers is low molecular weight PIBSI. As the low molecular weight PIBSI was in the imide form at the start of the test, it can be surmised that polar species in the fuel under the influence of the injector's high temperature and pressure have formed the amide. This is further supported but previous work that showed that low molecular weight PIBSI does not form deposits when tested with clay filtered fuel [8].

The hydropyrolysis data shows the presence of aromatic deposit precursors. These have been shown to grow to archipelago structures six rings in size by recent work [11]. The IDID on the needle also showed material of higher molecular weight material than the parent low molecular weight PIBSI, which would again indicate a fuel or fuel interaction origin.

In conclusion, the use of low molecular weight PIBSI as a commercial DCA is not recommended. Though the initial spectroscopic evidence indicates the deposit formed by interaction with acidic species in the fuel is amide in nature, the deposit is clearly more complex than that with both aromatics high molecular weight alkanes and PIBSI being present. The low molecular weight species will be sparingly soluble because of their short tail and polar head group, and thus would drop out of diesel. Their high molecular weight counterparts used as commercial DCA are fully soluble, do not drop out of diesel and do not form deposits.

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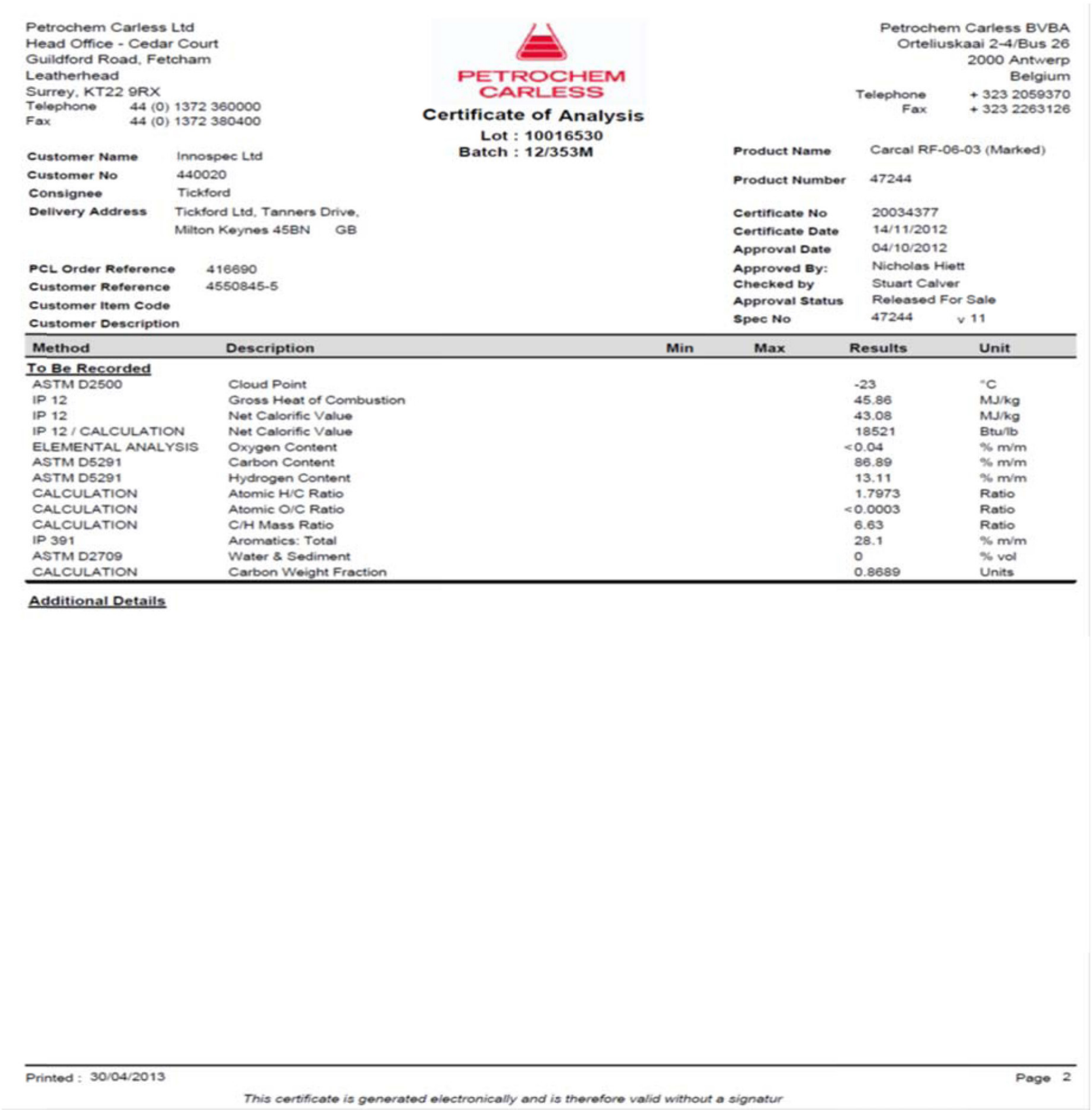
APPENDIX



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PETROCHEM CARLESS

Certificate of Analysis

Lot : 10016530
Batch : 12/353M

Petrochem Carless BVBA
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Fax + 323 2263126

Customer Name	Innospec Ltd
Customer No	440020
Consignee	Tickford
Delivery Address	Tickford Ltd, Tanners Drive, Milton Keynes 45BN GB
PCL Order Reference	416690
Customer Reference	4550845-5
Customer Item Code	
Customer Description	

Product Name	Carcal RF-06-03 (Marked)
Product Number	47244
Certificate No	20034377
Certificate Date	14/11/2012
Approval Date	04/10/2012
Approved By:	Nicholas Hiett
Checked by	Stuart Calver
Approval Status	Released For Sale
Spec No	47244 v 11

Method	Description	Min	Max	Results	Unit
To Be Recorded					
ASTM D2500	Cloud Point			-23	°C
IP 12	Gross Heat of Combustion			45.86	MJ/kg
IP 12	Net Calorific Value			43.08	MJ/kg
IP 12 / CALCULATION	Net Calorific Value			18521	Btu/lb
ELEMENTAL ANALYSIS	Oxygen Content			<0.04	% m/m
ASTM D5291	Carbon Content			86.89	% m/m
ASTM D5291	Hydrogen Content			13.11	% m/m
CALCULATION	Atomic H/C Ratio			1.7973	Ratio
CALCULATION	Atomic O/C Ratio			<0.0003	Ratio
CALCULATION	C/H Mass Ratio			6.63	Ratio
IP 391	Aromatics: Total			28.1	% m/m
ASTM D2709	Water & Sediment			0	% vol
CALCULATION	Carbon Weight Fraction			0.8689	Units

Additional Details

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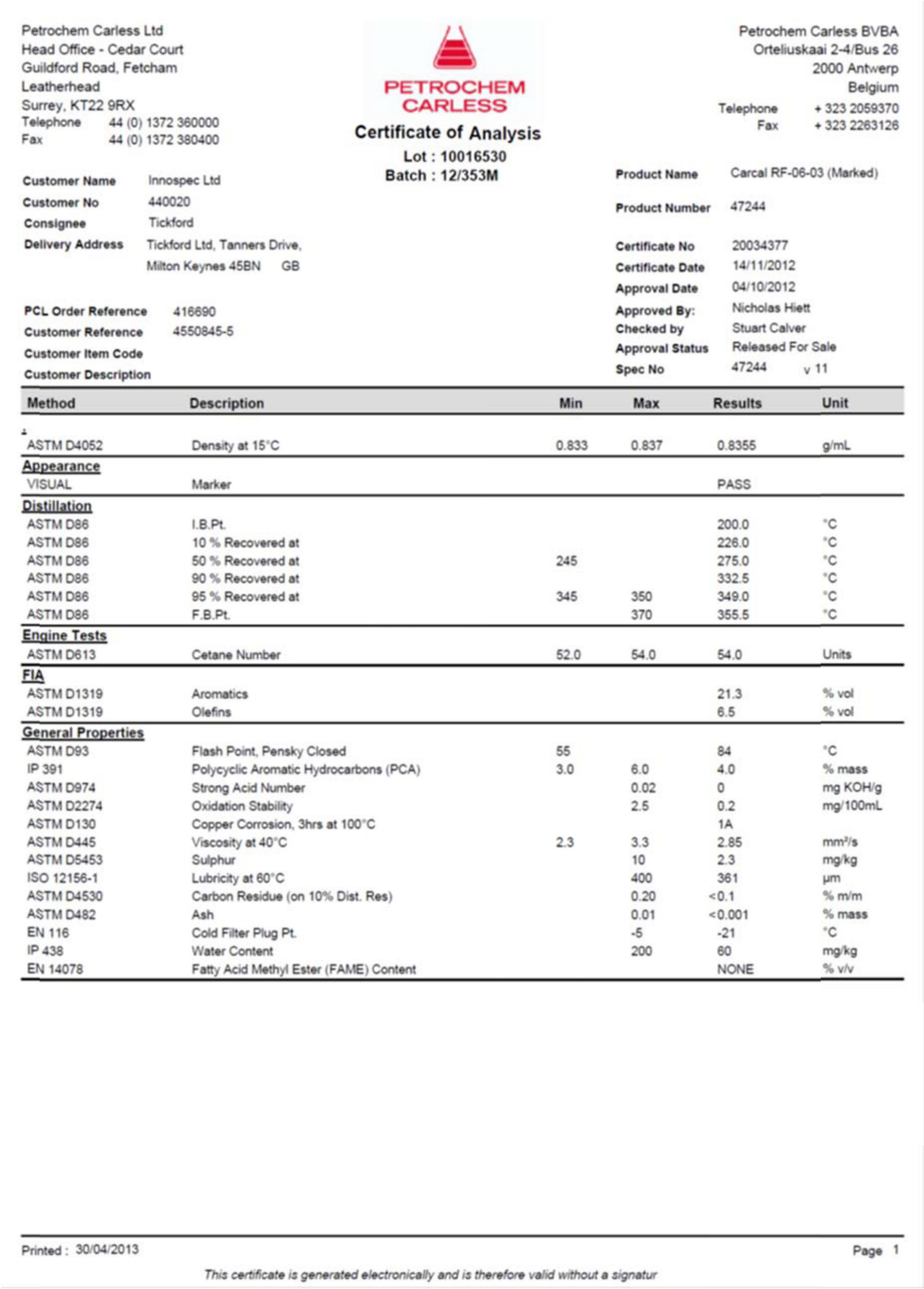
This certificate is generated electronically and is therefore valid without a signatur



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Customer Name Innospec Ltd
Customer No 440020
Consignee Tickford
Delivery Address Tickford Ltd, Tanners Drive,
Milton Keynes 45BN GB

PCL Order Reference 416690
Customer Reference 4550845-5
Customer Item Code
Customer Description

Product Name Carcal RF-06-03 (Marked)
Product Number 47244
Certificate No 20034377
Certificate Date 14/11/2012
Approval Date 04/10/2012
Approved By: Nicholas Hiett
Checked by Stuart Calver
Approval Status Released For Sale
Spec No 47244 v 11

Method	Description	Min	Max	Results	Unit
ASTM D4052	Density at 15°C	0.833	0.837	0.8355	g/mL
Appearance					
VISUAL	Marker			PASS	
Distillation					
ASTM D86	I.B.Pt.			200.0	°C
ASTM D86	10 % Recovered at			226.0	°C
ASTM D86	50 % Recovered at	245		275.0	°C
ASTM D86	90 % Recovered at			332.5	°C
ASTM D86	95 % Recovered at	345	350	349.0	°C
ASTM D86	F.B.Pt.		370	355.5	°C
Engine Tests					
ASTM D613	Cetane Number	52.0	54.0	54.0	Units
FIA					
ASTM D1319	Aromatics			21.3	% vol
ASTM D1319	Olefins			6.5	% vol
General Properties					
ASTM D93	Flash Point, Pensky Closed	55		84	°C
IP 391	Polycyclic Aromatic Hydrocarbons (PCA)	3.0	6.0	4.0	% mass
ASTM D974	Strong Acid Number		0.02	0	mg KOH/g
ASTM D2274	Oxidation Stability		2.5	0.2	mg/100mL
ASTM D130	Copper Corrosion, 3hrs at 100°C			1A	
ASTM D445	Viscosity at 40°C	2.3	3.3	2.85	mm^2/s
ASTM D5453	Sulphur		10	2.3	mg/kg
ISO 12156-1	Lubricity at 60°C		400	361	µm
ASTM D4530	Carbon Residue (on 10% Dist. Res)		0.20	<0.1	% m/m
ASTM D482	Ash		0.01	<0.001	% mass
EN 116	Cold Filter Plug Pt.		-5	-21	°C
IP 438	Water Content		200	60	mg/kg
EN 14078	Fatty Acid Methyl Ester (FAME) Content			NONE	% v/v

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