A Study of the Internal Diesel Injector Deposit Phenomenon

Robert Quigley, Robert Barbour, Emma Fahey
Lubrizol Limited, Derby, UK

David C. Arters, William Wetzel, James Ray
Lubrizol Corporation, Wickliffe, Ohio, USA

Summary
The issue of `internal diesel injector deposits' or `IDID' affecting modern diesel fuel injector designs was raised at the last Esslingen Fuels Colloquium in 2009. Unlike convention coking deposits which form on the tips of fuel injectors and within the fuel spray holes, this type of deposit is found within the injector body itself, such as at the armature group, on the piston and nozzle needle and inside the nozzle body. A build up of these deposits can lead to a loss of vehicle drivability and rough engine running, as well as unwanted variations in power and loss of fuel economy. Whilst European OEMs appear principally concerned that IDID formation could hinder future injector developments, many North American heavy duty engine manufacturers have already expressed an urgent concern regarding this issue, with at least one experiencing actual field problems. A number of possible reasons for the emergence of IDID problems have been postulated, including those due to mechanical, fuel or additive factors. However, to date, there has been very little firm evidence that any of these proposed mechanisms actually explain the issue.

This paper will report on a study on internal injector deposits carried out from several perspectives. Firstly, there has been a detailed study to evaluate previously proposed chemical screening tests for fuel additives. Secondly, analysis of fuel injectors and filter deposits from IDID affected engines has been carried out for possible insights into deposit formation mechanisms. A range of fired dynamometer engine testing has also been carried out in an engine known to experience internal injector deposits in field use.

1. Introduction

The issue of `internal diesel injector deposits or `IDID' affecting modern diesel fuel injector designs was raised at the last Esslingen Fuels Colloquium in 2009 [1]. Unlike convention coking deposits which form on the tips of fuel injectors and within the fuel spray holes, this type of deposit is found within the injector body itself, such as at the armature group, on the piston and nozzle needle and inside the nozzle body. These deposits can slow the response of the fuel injector, or cause sticking of moving internal parts, which may result in loss of control of injection event timing, as well as of the quantity of fuel delivered per injection. Hence, a build up of these deposits can lead to a loss of vehicle drivability and rough engine running, as well as unwanted variations in power and loss of fuel economy. Whilst European OEMs appear principally concerned that IDID formation could hinder future injector developments, many North American heavy duty engine manufacturers have already expressed an urgent concern regarding this issue, with a number experiencing actual field problems. [2, 3]

There appear to be at least two different types of internal injector deposits reported. The first comprises of `waxy' or `soap' deposits, while the second type appears to be carbonaceous, or of a lacquered appearance. Many of the problems reported in field use in the United States appear to be of the waxy form, whilst problems highlighted in European engines focus on the lacquer type deposits.

A number of possible reasons for the emergence of IDID problems have been postulated, including those due to mechanical, fuel or additive factors. Ullmann *et al.* [1, 4] reported field incidences of two types of internal fuel injector deposits, a first arising from formation of metal ion soaps and a second type, which generally consisted of sticky brown deposits. The sodium soap type deposits were considered to arise from the use of sodium nitrite pipeline corrosion inhibitors carrying over into diesel fuel and reacting with monomeric fatty acid type lubricity improvers. Sticky brown deposits were postulated to arise from reaction between polyisobutylene (PIB) succinimide deposit control additives and acidic fuel components. This theory was supported by Fourier Transform infra-red (FTIR) analysis of scrapings from affected fuel injector components and a series of glassware experiments involving mixing of neat fuel additive components.

The fuel additive components used in the chemical mixing experiments consisted of three PIB succinimide

variants and three different fatty acid derivatives, namely mono-acidic fatty acids, glycerol fatty acid ester and dimer acid. The latter is the product of dimerisation of monomeric fatty acids under conditions of high temperature and pressure in the presence of an appropriate catalyst [5]. The mono-acidic and ester type materials are currently widely used to improve the lubricity of diesel fuel and have a long history of successful commercial `no-harms' in this application [6]. Dimer fatty acids were also once used as lubricity improvers, but this usage was discontinued some years ago due to unique problems with lubricating oil interactions [7]. Most of the reaction studies carried out by the authors used dimer acid, rather than the other two chemistries, which are now much more widely used in diesel fuels.

Relatively high levels of formic acid were also added to the neat mixtures of additives in a number of experiments. This was done on the basis that partial degradation of fatty acid methyl ester biodiesel blend stocks could result in the presence of formic acid in diesel fuel.

The range of experiments carried out used a reaction temperature of $180^{\circ}C$, with some experiments being stirred and others unstirred. FTIR spectra of the reaction product experiments were compared to those obtained from internal injector deposits with the conclusion that the spectra not only showed the same key absorbances, but also were very similar in overall appearance to the spectra obtained of internal deposits. This was used to support the contention that amide formation between succinimides and dimeric or monomeric fatty acids was the cause of the sticky brown deposits on fuel injector internal parts.

Arters addressed several facets of the IDID problem in a presentation to the Diesel Deposit Workshop at the SAE Fuels and Lubes meeting held in November 2009 [8]. He summarised the results of a series of tests using the CEC F-098-08 Peugeot DW10 procedure on a matrix of fuel additives that had been postulated as being responsible for IDID. These included mixtures of PIB based succinimide deposit control additives with mono-acidic lubricity improvers and dimeric fatty acids. The DF-79-07 reference fuel treated with 1 ppm of zinc metal was used for the testing. After each test had been carried out, fuel injectors were disassembled for inspection. No signs of internal injector deposits were found after any of the tests, even those that might have been considered to be the most likely to cause problems, based on previous reports. This work also presented an examination of fuel injectors from non-common rail heavy duty engines which suggested that internal injector deposits could be found in older design injectors, but were perhaps less critical for proper engine operation in these cases. Finally, a collavboration with the North American OEM Navistar was de-

scribed. This OEM was experiencing problems with developmental engines on test stands. These heavy duty engines were fitted with high pressure common rail fuel injection systems and were experiencing over-fuelling and increases in power above rated load, combined with increased particulate emissions. The problems were encountered with several different ultra-low sulphur diesel fuels. These fuels contained ester based lubricity improver additive and corrosion inhibitor, but not deposit control additives. Treatment of the problem fuels with a novel deposit control additive was able to completely remove pre-existing internal injector deposits during operation of test engines, as demonstrated by a complete restoration of fueling rate and power to rated operation. Deposit control or "keep-clean" performance with the novel deposit control additive was also demonstrated in a second engine at half of the deposit removal dose.

Recently, Schwab et al [9] reported analyses of internal injector deposits taken from failing injectors in OEM test stands and field use in North America, which indicated the presence of sodium salts of low molecular weight hexadecenyl and dodecenyl succinic acids, commonly used as diesel fuel corrosion inhibitors in the United States. Furthermore, the authors reported the use of attempts to simulate the effect of fuel contaminated with sodium salts of alkenyl succinic acid corrosion inhibitors on injector operation in a fired engine. As in the investigation described by Arters, a Peugeot DW10 engine was used, in this case running a slightly modified CEC F-98-08 cycle. Test fuel was treated with dodecenyl succinic acid and solutions of aqueous sodium chloride or hydroxide to generate the sodium salts suspected of causing the problem. It was found that such contaminated fuel did lead to injector sticking and the formation of thin white internal deposits. Analysis of the internal deposits so formed indicated that they contained the alkenyl succinic acid sodium salt. When the testing was repeated with fuel treated with mono-acidic type lubricity improver and aqueous sodium hydroxide no injector sticking or internal deposits were observed.

This paper will report on a study on internal injector deposits carried out from several perspectives. Firstly, there has been a detailed study to evaluate previously proposed glassware screening tests for fuel additives. Secondly, detailed analysis of fuel injectors and filter deposits from IDID affected engines in the United States has been carried out using advanced techniques for possible insights into deposit formation mechanisms. Thirdly, fired dynamometer engine testing has also been carried out in an engine known to experience soap type internal injector deposit formation in field use in the United States.

2. Chemical Screening Tests

As described in the Introduction to this paper, there have been attempts to simulate the infra-red spectra obtained from scrapings of thin layers of internal fuel injector deposits by mixing and trying to react mixtures of neat fuel additives [1, 4]. The basis behind these simulations was the apparent detection of infra-red absorbances attributed to derivatives of PIB succinimide additives in these deposits. The presence of PIB succinimide residues in fuel injector internal surfaces was presumed to be the cause of injector deposit formation and was assumed to arise through chemical reactions between primary and secondary amine groups contained in these materials and other fuel additives, such as mono-acidic based diesel fuel lubricity additives.

Although it seemed rather unlikely that mixing and heating of neat fuel additive materials could correlate to the high levels of dilution that fuel additives are used at, as well as neglecting the role of the bulk fuel, Lubrizol wanted to further understand these additive mixing experiments and their relevance as a predictor of lacquering type internal injector deposits. This was carried out by attempting to reproduce the observations previously reported by Ullmann *et al*. To this end, two PIB succinimides were synthesised, one containing a high level of primary amine and a second containing a tertiary amine and no primary amine. Note that no specific details were given by these authors regarding the chemical identity of the PIB succinimides decribed in their testing. Mono-acidic, glycerol ester and dimer acid type lubricity additives were also selected for the mixing experiments, along with formic acid, as specified in the original papers. A summary of the materials submitted for testing is given in Table 1.

Table 1 Summary of materials submitted for reaction evaluation.

PIB Succinimide	Description	Kv100 (cSt)
1	High Primary Amine Content	800
2	Tertiary Amine. No Primary	514
Lubricity Additive	**Description**	**Kv100 (cSt)**
DA	Dimer carboxylic fatty acid	102
MA	Mono carboxylic fatty acid	5
GO	Glycerol fatty esters	10

The total acid number (TAN), total base number (TBN) and saponification values of the test additives were obtained in order to replicate the 1.2 : 1.0 TBN : TAN mixing ratio of succinimide and lubricity improver stated in the SAE and Esslingen papers [1, 4]. Note that no specific justification was provided for the use of these ratios in the papers. In addition, kinematic viscosity at 100°C (Kv100) was measured for each additive. The mixtures were subjected to FTIR spectroscopy, Gel Permeation Chromatography (GPC) and kinematic viscosity measurements, before and after heating and mixing.

Mixing and heating was initially carried out using a `Tornado' IS6 multipot reactor, which provides powerful overhead stirring for up six reaction flasks at the same time. This is particularly suitable for stirring highly viscous materials and conducting experiments simultaneously under identical conditions. Mixtures were homogenised and heated to 180°C, followed by removal of an initial sample for FTIR analyses and, in some cases, Kv100 measurements. The reaction vessels were maintained under these conditions for six hours, at which point another sample was removed for analysis.

An initial matrix of mixtures was carried out using the conditions described in the above paragraph. Observations for the matrix are shown in Table 2. Looking first at the kinematic viscosity results, an increase in this parameter after the six hour period of heating and stirring might indicate that a reaction had occurred. Out of the six mixtures in the initial matrix, only two showed an increase in viscosity after the reaction period, both of which involved the dimer acid. The greatest increase in viscosity was found with the combination of succinimide 1 (high primary amine content) and the dimer acid. The post-six hour reaction product itself was extremely tacky and elastic. When succinimide 1 was combined with either the mono-carboxylic fatty acid or the glycerol fatty acid ester, a reduction in viscosity was observed.

Table 2 Summary of reaction matrix.

Reactants						
PIBSI	1	1	1	2	2	2
Lubricity Additive	DA	MA	GE	DA	MA	GE
After 6 Hours at 180oC						
Kv100 (cSt)	TV TM*	258	198	715	219	174

Too viscous to measure

Examining the Kv100 results for succinimide 2, higher viscosity is also observed when combined with dimer acid. Since this succinimide cannot form an amide, as it contains only tertiary amine, the most likely explanation is the formation of an ammonium carboxylate salt between the acid and the tertiary amine functionalities.

As was found with succinimide 1, the combination of succinimide 2 with the other two lubricity chemistries actually resulted in a reduction in viscosity compared to the starting materials. This can be seen as a dilution effect, arising from mixing in the viscous succinimide with the much lower viscosity mono-fatty acid and glycerol fatty acid ester materials.

2.1 GPC Chromatographs

A GPC chromatograph obtained from the product of mixing and heating between succinimide 1 and dimer acid is shown in Figure 1. It shows a peak of significant intensity (939 Mp) attributable to dimer acid, while a broader peak at 3086 Mp is around 1000 molecular weight units higher than the starting PIB succinimide and is possibly a 1:1 adduct of succinimide 1 and dimer acid.
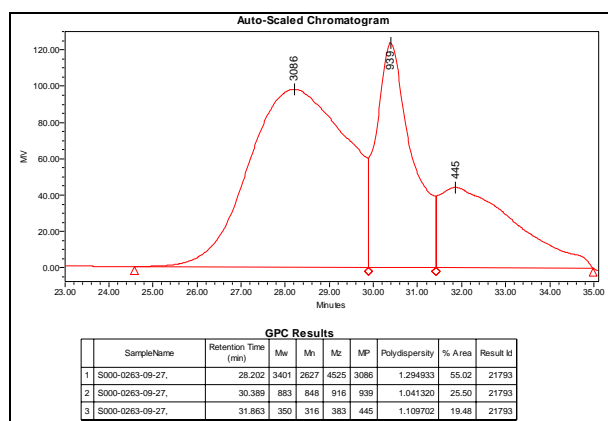

GPC Results

	SampleName	Retention Time (min)	Mw	Mn	Mz	MP	Polydispersity	% Area	Result Id
1	S000-0263-09-27,	28.202	3401	2627	4525	3086	1.294933	55.02	21793
2	S000-0263-09-27,	30.389	883	848	916	939	1.041320	25.50	21793
3	S000-0263-09-27,	31.863	350	316	383	445	1.109702	19.48	21793

Figure 1 Chromatograph of succinimide 1 and dimer acid mixture after stirring and heating.

Figure 2 shows the GPC chromatograph of the reaction product between succinimide 1 and mono-carboxylic acid lubricity improver. A large peak at 457 Mp appears to indicate a large fraction of unreacted mono-fatty acid. A broad peak also occurs at 3025 Mp, which may be a 1:2 adduct of succinimide 1 and mono-fatty acid.

Figure 3 shows a chromatograph of the mixture of succinimide 1 and glycerol fatty acid ester lubricity additive after heating and stirring. Peaks attributable to the mono-, di- and tri-glycerol esters of fatty acid are apparent, along with a higher molecular weight peak at 2530 Mp, which may be an adduct between the succinimide and fatty acid derived from the the glycerol oleates.

In summary, chromatographs of all three mixtures obtained following heating and stirring runs between succinimide 1 and the lubricity improvers showed substantial peaks associated with unreacted fatty acid or ester, along with some evidence of adduct formation in all three cases.
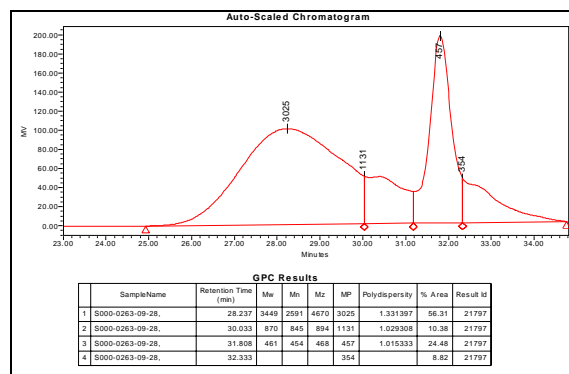

GPC Results

	SampleName	Retention Time (min)	Mw	Mn	Mz	MP	Polydispersity	% Area	Result Id
1	S000-0263-09-28,	28.237	3449	2591	4670	3025	1.331397	56.31	21797
2	S000-0263-09-28,	30.033	870	845	894	1131	1.029308	10.38	21797
3	S000-0263-09-28,	31.808	461	454	468	457	1.015333	24.48	21797
4	S000-0263-09-28,	32.333				354		8.82	21797

Figure 2 GPC chromatogram of succinimide 1 and mono-carboxylic fatty acid mixture after stirring and heating.

GPC Results

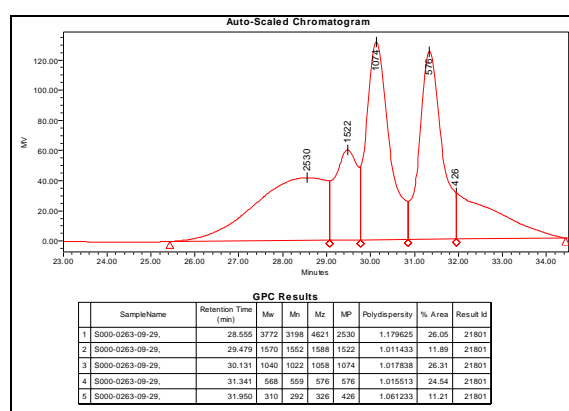|	SampleName	Retention Time (min)	Mw	Mn	Mz	MP	Polydispersity	% Area	Result Id
1	S000-0263-09-29,	28.555	3772	3198	4621	2530	1.179625	26.05	21801
2	S000-0263-09-29,	29.479	1570	1552	1588	1522	1.011433	11.89	21801
3	S000-0263-09-29,	30.131	1040	1022	1058	1074	1.017838	26.31	21801
4	S000-0263-09-29,	31.341	568	559	576	576	1.015513	24.54	21801
5	S000-0263-09-29,	31.950	310	292	326	426	1.061233	11.21	21801

Figure 3 GPC chromatogram of succinimide 1 and glycerol esters mixture after stirring and heating.

GPC chromatographs for the reaction products between succinimide 2 and the three fatty acid based lubricity improvers indicated little to no reaction. This is unsurprising given the purely tertiary amine functionality of this material. Any ammonium carboxylate salts that may have formed are likely to have eluted separately as cation and anion on the GPC column, so probably would not be detected as a single molecular weight fraction. A summary of GPC peak molecular weights observed for individual chemicals and their combined reaction products is given in Table 3.

Table 3 Summary of GPC peak molecular weights (Mp) found for individual chemicals and their mixtures following heating and stirring.

	GPC Mp	DA 1418 / 972	MA 467	GE 1413 / 1037 / 613
PIBSI 1	1958 / 566	3086 / 939 / 445	3025 / 1131 / 457	2530 / 1522 / 1074 / 576 / 426
PIBSI 2	1605	1393 / 924	1746 / 421	1659 / 1399 / 1001 / 590

2.2 Infra-Red Spectra

A summary of key infra-red functional group absorbances relevant to this study is given in Table 4 to aid discussion of the FTIR spectra of the reaction products.

Table 4 Summary of key functional group infra-red absorbances relevant to this study.

Wave numbr (cm^{-1})	Func Gp	PIBSI 1	PIBSI 2	MA	GE	Salt
1230	PIB	Y	Y	N	N	N
1370	PIB	Y	Y	N	N	N
1390	PIB	Y	Y	N	N	N
1470	PIB	Y	Y	N	N	N
1560	Salt	N	N	N	N	Y
1660	Amide	Y	N	N	N	N
1700	Imide	Y	Y	N	N	N
1710	Acid	N	N	Y	N	N
1740	Ester	N	N	N	Y	N

The FTIR spectrum of the reaction product between succinimide 1 and dimer acid, which appeared to be the mixture that showed the most interaction of those tested, is shown in Figure 4. The spectrum of the heated mixture shows similar levels of imide and amide functionality, as would be found in the neat succinimide itself (Figure 5). The main functional difference is the increase of an absorbance characterised by ammonium salt formation with the dimer carboxylic acid at 1560 cm^{-1}. Although there may be some broadening of the amide absorbance, there is little evidence of significant levels of amide formation between the dimer acid and the succinimide. Therefore, the likely reason for the formation of the extremely viscous adduct between succinimide 1 and the dimer acid is dimer cross linking primarily through ammonium carboxylate salt formation, probably also with a lesser degree of amide formation. The predominant

imide absorbance of the succinimide functionality at 1700 cm^{-1} remains prominent in the infra-red spectrum of the reaction product. This is a particularly significant difference compared to the IDID spectra presented by Ullman *et al.*[1, 4]
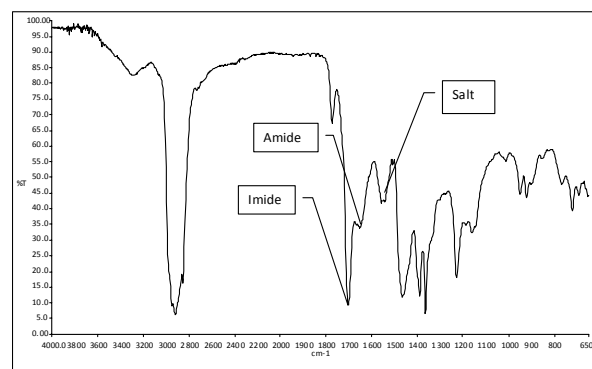

Figure 4 FTIR of succinimide 1 heated with dimer acid for 180°C for six hours.
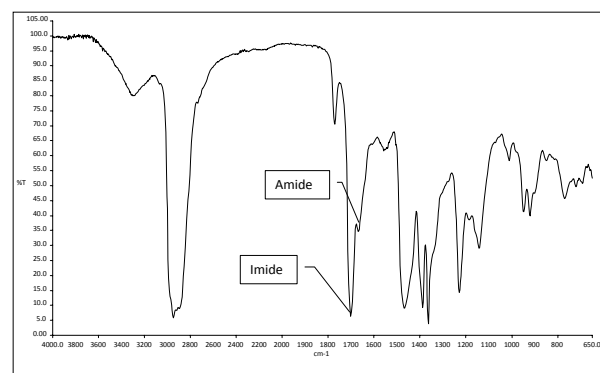

Figure 5 FTIR spectrum of succinimide 1.

The FTIR spectrum of succinimide 1 mixed and heated with the mono-acidic lubricity improver is shown in Figure 6 and reveals absorbances that are due to carboxylic acid salt formation (1560 cm^{-1}), imide (1700cm^{-1}) and amide (1660 cm^{-1}). It would appear that the intensity of the amide absorbance has increased following heating. The imide absorbance remains similar in intensity to that found with the neat succinimide 1, indicating that this functionality has not formed substantial amounts of amide with the dimer acid. Overall therefore, the effect of mixing and heating succinimide 1 with mono-acidic lubricity improver seems to result in an increase of both carboxylic acid salt and amide functionalities, with maintenance of imide absorbance.
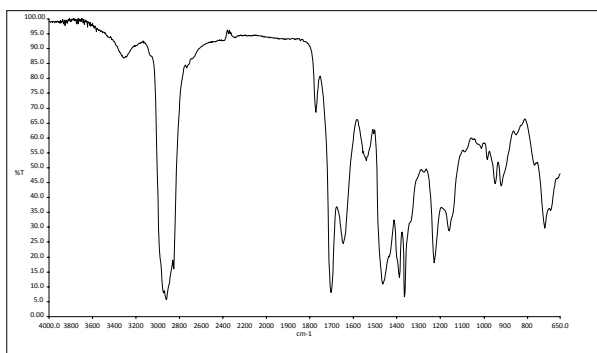
Figure 6 FTIR spectrum of succinimide 1 mixed and heated with mono-acidic lubricity improver.

The FTIR spectrum of the mixture of succinimide 1 and glycerol ester is shown in Figure 7. Once again, absorbances due to amide, imide and carboxylic functionality are evident, along with an absorbance arising from the ester functionality of the lubricity improver.
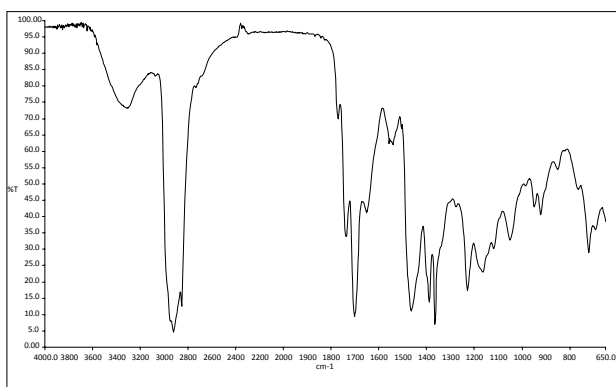

Figure 7 FTIR spectrum of succinimide 1 mixed and heated with glycerol fatty acid ester lubricity improver.

Figure 8 illustrates the FTIR spectrum of succinimide 2 with dimer acid and shows the presence of imide and carboxylic acid salt only. Because succinimide 2 contains only tertiary amine, it cannot react to form an amide with carboxylic functionality and this is borne out by the infra-red spectrum. Similar conclusions can be made for the FTIR spectra of the reaction products between succinimide 2 and the mono-acidic and ester lubricity improvers.

In summary of the findings from these mixing and heating experiments, the most significant effects were found with the dimer acid, with which both succinimide 1 and 2 formed highly viscous materials. Most of this increase in viscosity could be attributed to salt formation, with some possible amide formation in the case of succinimide 1. In the case of succinimide 2, only salt formation is possible and no amide absorbances are evident. In all cases, a very strong imide absorbance is maintained after the reaction period.
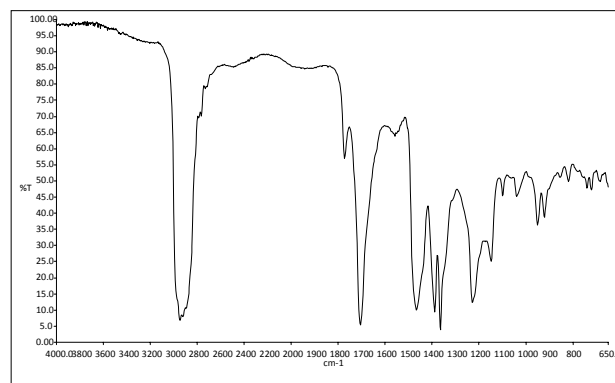

Figure 8 FTIR spectrum of succinimide 2 heated and mixed with dimer acid.

2.1 Non Stirred Mixing Experiments

However, the main contention of the papers authored by Ullman *et al.* is that it is possible to reproduce infra-red spectra of trace internal injector deposits by mixing and heating neat samples of various fuel additives. As mentioned already, one of the most significant differences between actual internal injector deposit spectra and those produced by neat additive mixing experiments is the lack of a strong imide absorbance, which is characteristic of succinimides and is maintained after reaction experiments. Despite attempts to model as closely as possible the conditions published by Ullman *et al*, the FTIR spectra obtained following our mixing experiments did not closely resemble those published by these authors in their SAE and Esslingen papers. As a result of this lack of correlation, further clarification concerning reaction conditions was sought from the authors, who kindly provided further details.

It was suggested that the closest match to actual IDID FTIR spectra might be obtained by mixing together small one to two gram quantities of the succinimide and acid together on a watch glass, followed by placing the sample in an oven without stirring. It was also suggested to use an excess of fatty acid to maximise the level of amide formation and finally, to wash away unreacted components with small aliquots of dichloromethane. As with the previous investigations, the residues were to be analysed using FTIR. This guidance was followed in a series of further experiments that used various ratios of reactants, with and without the presence of formic acid. Experiments were limited to the combination of succinimide 1 and dimer acid, as these were the two components that showed by far the highest interaction of those previously investigated. A reaction time of sixteen hours at a temperature of 180°C was employed. Following removal from the oven and cooling, the product was washed 5 times with 2 ml aliquots of dichloromethane. FTIR spectra and GPC chromatographs were obtained for the unwashed and washed products.

The products of these watch glass reactions were extremely viscous and were not completely homogeneous. A significant amount of material was removed during the washing process, with only a small amount of sample remaining afterwards. Washed products appeared to be slightly more mobile than unwashed ones.

Examining firstly the FTIR spectrum of the reaction carried out in the absence of formic acid, as shown in Figure 9, the ratio of imide to amide appears to be very similar to that of the unreacted succinimide, suggesting that no increase in amide levels occurred during the reaction. Note that this spectrum does appear very similar to that of the unwashed reaction product.
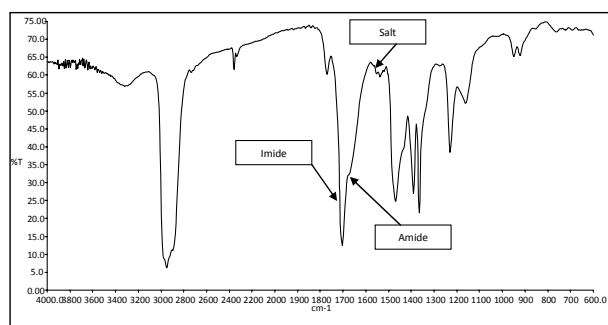

Figure 9 FTIR spectrum of succinimide 1 and dimer acid mixture after heating washed with dichloromethane.

Figure 10 shows the infra-red spectrum of the combination of succinimide 1, dimer acid and formic acid, following washing. Once again, there was no appreciable difference between spectra of unwashed and washed samples. Compared to reaction without formic acid, more amide does appear to have formed, which would be regarded as unsurprising, but imide functionality still appears to predominate. Despite the advised change in reaction conditions, spectra of the reaction products with and without formic acid do not closely resemble those of internal injector deposits reported by Ullmann *et al*.
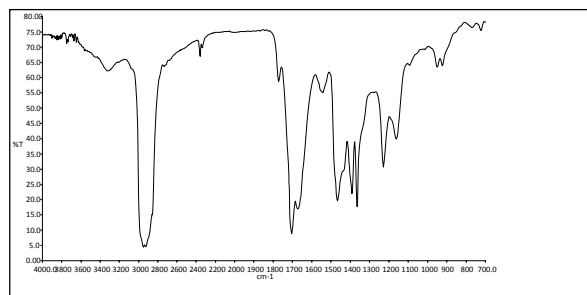

Figure 10 FTIR spectrum of reaction product of succinimide 1, dimer acid and formic acid washed with dichloromethane.

A summary of the main peaks from the GPC chromatographs of the reaction products is shown in Table

5. All of the reaction products have a slightly higher peak molecular weight than the unreacted succinimide 1. In the absence of formic acid, the increase in peak molecular weight was in the order of 30 – 40%. Increases of 80 – 90% in peak molecular weight were observed with formic acid. These observations do suggest that there has been interaction between the succinimide and the dimer acid; however, the chromatograms do not show evidence of significant polymerisation arising from the formation of polyamides. The predominant reaction still appears to be salt formation and while this leads to a significant increase in viscosity, it does not result in the increases in molecular weight that would be associated with high molecular weight polymers.

Table 5 Summary of main GPC peak molecular weights observed after watch glass mixing experiments.

	DA	DA
Solvent Washing	No	Yes
	Mp	Mp
PIBSI 1	2682	2802
PIBSI 1 +Formic Acid	1009, 3684	822, 3772

Finally, the chromatographs do indicate that washing with dichloromethane does remove some lower molecular weight materials, as there is a small increase in peak molecular weight between washed and unwashed samples.

2.2 Section Conclusions

It was not possible to replicate infra red spectra of internal diesel injector deposits through chemical mixing of concentrated fuel additives in the experiments described here. The experiments carried out did indicate, as might be expected, predominant formation of ammonium carboxylate salts between the succinimide deposit control additives evaluated and dimer and monomeric fatty acids, with some possible amide formation in the case of a succinimide containing primary amine functionality.

The dimer acid was the most reactive of the fatty acid derivatives, but as previously pointed out, it is not now used as a diesel fuel lubricity additive and the possibility of dimer acids being produced from monomeric fatty acids in the fuel injector at high dilution levels seems somewhat unlikely. Monomeric fatty acid and ester were both found to be much less reactive than the dimer and did not form the viscous mixtures found with the dimer acid reactions.

In all of the reactions carried out, the imide functionality of the succinimide was preserved, even after ex-

tended heating at 180°C with the fatty acids and formic acid. This is evident from infrared spectra which showed very strong imide absorbances, which are not present in the spectra of internal diesel injector deposits. In addition, none of the FTIR spectra obtained from the heated mixtures of additives resembled those of IDID deposits in overall appearance. Gel permeation chromatography indicated the presence of adducts after mixing and heating of succinimide 1 with dimer, mono-carboxylic fatty acid and ester. These are probably amides, as this method is unlikely to detect the anion and cation of carboxylate salts as a single molecular weight peak. There appears to be some discrepancy between the apparent levels of amide adducts detected by GPC, particularly for the combination of succinimide 1 and dimer acid and the infra-red spectra of this mixture, which showed low levels of additional amide compared to the starting PIB succinimide. Substantial amounts of unreacted dimer or fatty acids were also detected. However, the method did not detect the presence of very high molecular weight polyamines that might be expected to be a precursor to solid lacquer like deposits.

3. Fuel Injector Deposit Analysis

This section describes the results of analysis of failed fuel injectors from the engines of several North American heavy duty OEMs which have been noted [9] to have a consistent chemical composition of the "soap" type, perhaps different than those observed in Europe. The first set of injectors were taken from a recently introduced Tier 2 common rail engine model manufactured by OEM 1, which had been experiencing unacceptable rates of injector failure in different applications and locations. Failed injectors recovered from engines in two different geographical locations and engine applications were analysed. A single blocked filter from one of the locations was also submitted. A section from a needle from one of the failed injectors is shown in Figure 11.
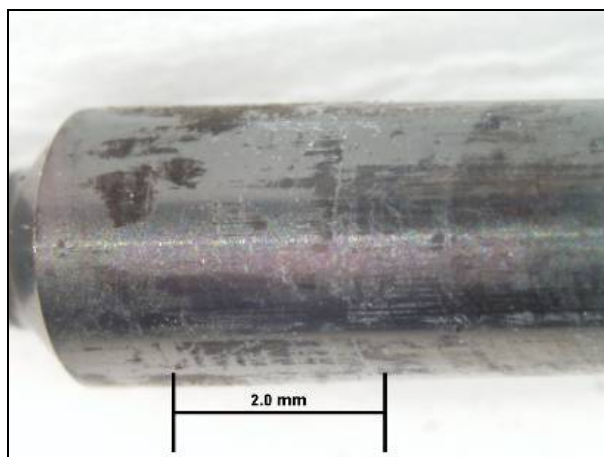

Figure 11 Image of failed injector from OEM 1 Tier 2 engine.

Deposits on the injector needle and piston from the OEM 1 engine model were first examined using scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS). The analysis showed that the elemental composition of the deposits predominantly consisted of carbon and oxygen. Relatively large amounts of calcium (around 9% by weight) were also found, but not large amounts of zinc, sulphur or phosphorus. The EDS quantitative results are shown in Figure 12 (and Table 6). Note that the appearance of iron and chromium are an artefact of beam penetration to the metal surface of the injector.
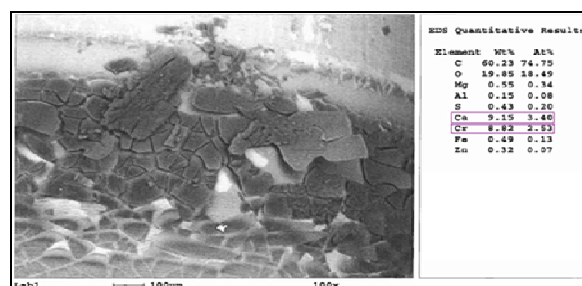

Figure 12 EDS image and quantitative analysis of injector deposit from OEM 1 needle.

A limitation of EDS analysis is that it can only carry out elemental analysis. Therefore, the technique of electrospray ionisation – mass spectroscopy (ESI-MS) was employed in order to try to determine whether specific chemical species or organic molecule fragments were detectable in the injector deposits.

The deposit was extracted into dichloromethane and the result ESI mass spectrum is shown in Figure 13. The scan shows the presence of residues attributable to dodecyl succinic acid (DDSA) and alkylbenzene sulphonate. Residues attributable to dimer acids, fatty acids or succinimide deposit control additives were not detected. However, it should be noted that chemical species present in the injector deposit need to be soluble in the extraction solvent and polar in order to be detected by the ESI-MS method.

The same techniques were applied to both the blocked filter that came from the same location as injector A and a second injector from the other geographic location. Results for these analyses also indicated the presence of DDSA and alkylbenzene sulphonates. A summary of the analyses obtained on the two injectors and the fuel filter is shown in Table 7.
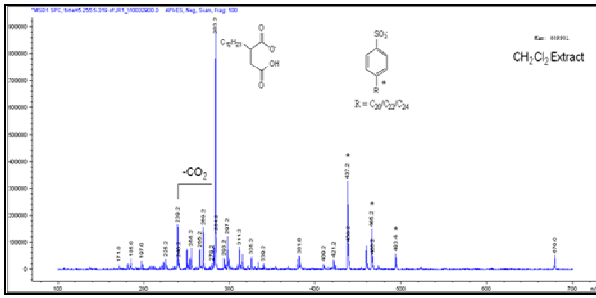
Figure 13 ESI mass spectrum for internal injector deposit extracted in dichloromethane.

Five failed injectors from a second OEM's engine model were also submitted for analysis. The affected injectors were fitted to Tier 3 common rail diesel engines in two different geographic locations. These were reported to have suffered from "sticking" and had been returned to dealerships. For comparative purposes, a non-sticking needle was also obtained. The needle from one of the sticking injectors is shown in Figure 14.

Figure 14 Image of sticking injector from OEM 2 Tier 3 common rail engine.

As with the OEM 1 injectors, SEM/EDS analysis and dichloromethane solvent extraction followed by ESI-MS were carried out. A summary of the analytical results obtained is shown in Table 8.

Examining the analytical results obtained on injectors from OEMs 1 and 2 in more detail, some patterns are evident, but little is consistent across all injectors. SEM/EDS elemental analysis showed that calcium and / or sodium were detected in nearly all of the sticking injectors, with high levels of sulphur and chlorine found in some cases.

Looking at the ESI-MS analysis, no single molecular fragment was found in every sticking injector. However, dodecenyl or hexadecenyl succinic acid residues appear to be detected in most of the extracted injector residues from sticking deposits. Alkylbenzene sulphonate also appears in many of the sticking deposits, but

not other fragments that might be associated with lubricant oil, such as zinc dithiophosphates.

Fatty acid residues were not detected at all in the sticking injectors from OEM 1, whilst oleic, palmitic and stearic acids were detected in both sticking and non-sticking injectors from OEM 2. Residues attributable to succinimide deposit control additives were not seen in any of the deposits from these North American injectors.

Overall, it is difficult to make firm conclusions with regards to these analyses. Therefore, this type of investigation should best be seen as a way of identifying possible contributions to internal injector deposit formation, the actual role of which needs to be then evaluated in engine and vehicle testing for confirmation of any actual contribution that they may make.

4. Engine Test Development

The next stage of the investigation was to attempt to develop a fired engine test that replicated the internal injector deposit issues found in the field, using the injector analyses described in the previous sections to provide pro-fouling candidates. As the main suspected cause of current internal deposit issues in North America are sodium salts of low molecular weight corrosion inhibitors, such as dodecenyl succinic acid, initial development focused on whether internal deposits could be produced in the test engine in the presence of these components.

The test engine chosen is manufactured by OEM 2 and is a 6.8 litre common rail engine compliant with United States Tier 3 off-road emissions regulations. It is one that had already experienced IDID issues in actual field usage. Remediation and prevention of these internal deposits with effective deposit control additive technology in the field had already been demonstrated in this engine model, thereby providing the opportunity to correlate the behaviour of the engine test with known performance in actual usage.

The test cycles for the test development were based on input from OEM and distributors and involved maximising fuel return temperatures and running under steady state conditions at high torque. Each cycle consisted of eight hours running followed by a four hour soak period. Operating parameters monitored were engine power, fuel flow and exhaust temperatures. Fuel filters were also monitored for plugging. After testing, injectors were disassembled to check for signs of piston or needle sticking. Surface chemical analyses were also carried out by SEM/EDS and ESI-MS techniques, as previously described.

Dosing of materials into the test fuel was achieved by several different methods. Firstly, fully fuel soluble, non-interacting additives such as dodecenyl succinic acid, mono fatty acids and/or deposit control additives (DCAs) were added into the bulk fuel storage tank. A second method of addition was employed for treatment of sparingly soluble materials into the fuel through in-line injection at the day tank. This method was used to treat solutions of sodium hydroxide into the test fuel. This method of addition via a second injection system was also used for dosing of DCAs into the fuel for injector deposit removal (`clean up') experiments.

Initial test runs with the engine were carried out using fuel dosed with a stoichiometric blend of sodium hydroxide and dodecenyl succinic acid (DDSA), thereby capable of producing the sodium salts of the DDSA. The results from four such runs are charted in Figure 15. In all four tests, engine power dropped very considerably during operation. This corresponded to decreasing exhaust temperatures (Figure 16).
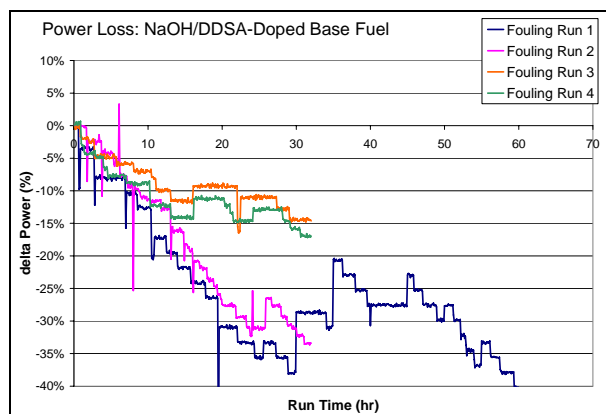

Figure 15 Engine power verses test run time using ULS fuel dosed with sodium hydroxide / dodecenyl succinic acid. (Four test runs are charted.)
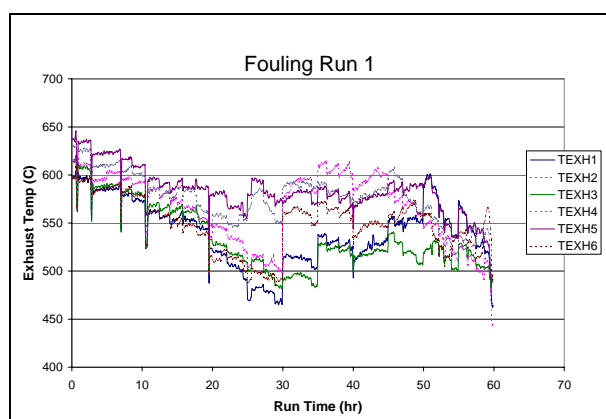

Figure 16 Engine exhaust verses test run time during Fouling Run 1.

Following the demonstration that engine power was adversely affected by the presence of the sodium-DDSA salts, the next test attempted to correlate with the field experience of deposit prevention using DCA

in this engine. The engine was therefore run with the sodium-DDSA salt dosed fuel, but was also treated with a constant use treatment level of the deposit control additive that had been shown to successfully remove internal deposits in the field. The results from this test are shown in Figure 17. The effect of the deposit control additive treatment is clearly to prevent the power loss that was observed in the repeated runs with the base fuel containing the sodium-DDSA salt only. Note that engine power started to decline at around forty-eight hours into this run, which was due to inadvertent discontinuation of the deposit control additive dosing. Exhaust temperatures (Figure 18) were also maintained by the keep clean dose of additive.

Figure 17 Engine power verses test run time using ULS fuel dosed with sodium hydroxide / dodecenyl succinic acid and deposit control additive at "keep clean" treat rate. (The four initial runs without DCA are also charted for comparison.)
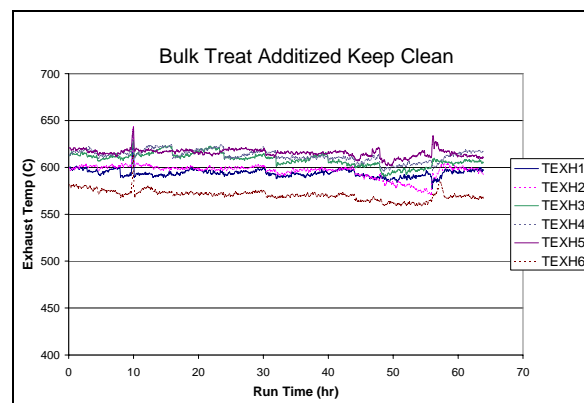
Figure 18 Engine exhaust verses test run time during additized deposit control test.

A final test intended to duplicate OEM experience in the field consisted of an attempt to remove pre-existing deposits from one of the fouled injector sets. Once again, the test was carried out with ultra-low sulphur diesel fuel treated with the sodium-DDSA salt, but in addition, after 32 run-hrs of deposit build up, a high treat dose of the same deposit control additive was added to the fuel. The result of this test is charted in Figure 19, where the plot of engine power versus test cycle shows a very rapid restoration of engine power.
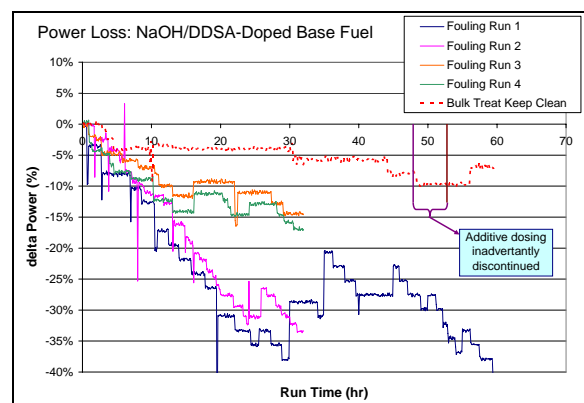
Figure 19 Engine power verses test run time using ULS fuel dosed with sodium hydroxide / dodecenyl succinic acid and deposit control additive at "clean up" treat rate.
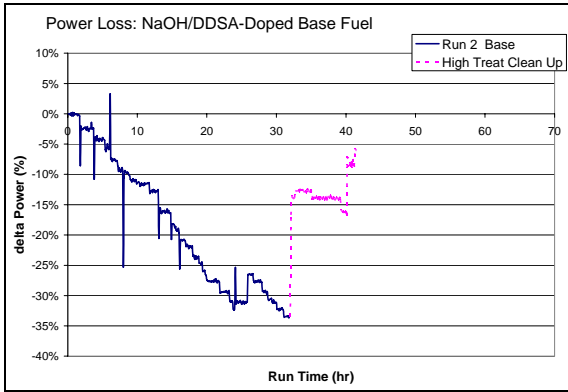
Injectors from the demonstration engine tests were analyzed as before, summarized in Table 9. There are several observations to be made from the results. First, the composition of the deposit is consistent that seen in field injectors with respect to the presence of sodium and DDSA in the deposit. Second, it should be noted that while there are many similarities between the deposit compositions of base and additized runs, the deposit in additized tests was much thinner and was present on a much smaller area of the injector (Figures 19 and 20).

Figure 19 Base fuel fouling run injector needle.

Figure 20 Additized `keep clean` run injector needle

Having demonstrated that internal deposits could be readily formed in the engine test with fuel containing the proper pro-fouling components, a test was undertaken in which the DDSA was replaced by mono fatty acidic components (oleic, stearic and palmitic acids) based on their presence on the surface of field injectors. In this case, no power loss or deposits in the injector were observed. This, along with the bench test experiments carried out earlier in this paper, strongly suggests that the mechanisms proposed in which monacidic components play a role in internal injector deposits are incorrect.

While the test development proved successful in duplicating a sticking phenomenon using the sodium soap mechanism deduced from deposit analysis, the direct tie point to the power loss and exhaust temperature drop was less conclusive. It was determined through sectioning of injector nozzles that some nozzle deposits were also present in the fouling runs. These nozzle deposits are likely to have caused at least some of the observed power loss. Improvements to the procedure are needed to decouple the effects of internal deposits and nozzle deposits on performance, and to enhance the quantification of the performance effects of the internal deposits.

4. Summary

Over the last few years concerns about the occurrence of internal diesel injector deposits have been raised widely both in North America and in Europe. Several different types of internal deposits have been described, with the `soap' or `waxy' type certainly appearing most prevalent in North America. This paper has described several different approaches to better understanding the phenomena involved in this problem. A summary of findings can be given as follows.

Firstly, mixing and heating experiments with neat fuel additive components did not produce mixtures whose FTIR spectra resembled those of internal injector deposits reported by other authors. In particular, the characteristic imide infra-red absorbance was preserved throughout all of the mixing experiments with succinimides and fatty acids described here. In addition, GPC chromatography of the heated mixtures did not show the formation of high molecular polymeric materials, which might be expected in solid lacquer type deposits.

SEM/EDS and ESI-MS analyses of failed injectors recovered from field use in the United States showed that calcium and /or sodium were present in all of the sticking injectors, with high levels of sulphur and chlorine found in some cases. No single molecular fragment was found in all of the sticking injectors analysed, but dodecenyl and hexadecenyl succinic acids were detected in most of the residues from sticking injectors.

A dynamometer engine test procedure was developed using a North American Tier 3 off-road common rail engine that had experienced soap type internal injector deposit problems in the field. The analysis of fuel injector deposits from failed injectors in the field was used to identify possible candidates for testing in the engine with the aim of duplicating an IDID failure mechanism. It was found that treatment of test fuel with sodium salts of dodecenyl succinic acid resulted in substantial power loss in the engine test and internal injector deposits. The dynamometer test was also shown to discriminate using a reference deposit control additive that significantly reduces the amount and effect of internal deposits, in agreement with OEM field and engine test stand experience. The internal deposits generated in the test were also found to be chemically consistent with those found in failing heavy duty fuel injectors in use in North America. Finally, the engine test showed that a suggested mode of deposit formation involving mono-acidic based lubricity additives is unlikely.

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Table 6 EDS quantitative analysis of injector deposit from OEM 1 needle.

Element %Weight By EDS								
C	O	Mg	Al	S	Ca	Cr	Fe	Zn
60.2	19.9	0.6	0.2	0.4	9.2	8.82	0.5	0.32

Table 7 Summary of analytical results for Injectors A and B from OEM 1 engine.

Component	Filter A	Injector A		Injector B	
Region		Needle	Piston	Needle	Piston
Geographic location		1		2	
Elemental Analysis (%wt)					
Na	0	0	0	0	0
Ca	2.7	7.1	9.7	9.2	15.5
S	0.9	0.8	1.8	0.6	0.4
Cl	0	0	0	0	0
DDSA/HDSA	Yes	Yes	Yes	Yes	Yes
Dimer Acid	No	No	No	No	No
Sulphonate	Yes	Yes	Yes	Yes	Yes
Fatty Acid	No	No	No	No	No
Succinimide	No	No	No	No	No

Table 8 Summary of analyses carried out on OEM 2 injectors from Tier 3 common rail engine model.

Component	Injector A		Injector B		Injector C		Injector D		Injector E		Injector F	
Injector	N	P	N	P	N	P	N	P	N	P	N	P
Geography	1		2		2		2		2		2	
Sticking?	Yes		No		Yes		Yes		Yes		Yes	
Element Analysis (%wt)												
Na	0		0	0	0.2	0.4	0.4	0.4	3.6	8.2	13	1.6
Ca	7.1		0	0	0.2	0.2	0.4	0.4	0.5	0.4	0.4	0.3
S	8.6		0	0	0	0	0.1	0.5	0.8	1.1	0.3	0.9
Cl	0		0	0	0	0	1.5	0.2	7.0	10.5	7.4	1.3
DDSA/HDSA	No		No		Yes		Yes		Yes		Yes	
Dimer Acid	No		No		No		No		No		No	
Sulphonate	Yes		No		No		No		Yes		Yes	
Fatty Acid	No		Yes		Yes		Yes		Yes		Yes	
Succinimide	No		No		No		No		No		No	

Table 9 Summary of analytical results for injector from OEM 2 engine dynamometer testing.

Component	Fouling Run		Additized Keep Clean		Additized Clean Up	
Injector	N	P	N	P	N	P
Sticking?[*]	Yes		No		No	
Element Analysis (% weight)						
Na	10.5	9.5	3.8	4.4	6.7	5.6
Ca	0.1	0.1	0	0	0.1	0
S	1.7	0.5	0.1	0.1	0.6	0.5
Cl	0	0	0	0	0	0
DDSA	Yes		Yes		Yes	
Dimer Acid	No		No		No	
Sulphonate	No		No		No	
Fatty Acid	No		No		No	
Detergent	No		Yes[2]		No	

Qualitative measure of force required to remove injector needle from housing.