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Understanding Polyisobutylene Succinimides (PIBSI) and Internal Diesel Injector Deposits

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ABSTRACT

Deposit control additives have been added to diesel fuel for over 30 years to prevent the build-up of deposits in the fuel injection system and thereby ensure optimum engine operation. As the complexity of modern diesel fuel injection systems has increased their tolerance to deposit formation has decreased and therefore there is now an even greater need for high quality deposit control additives. The predominant and most effective chemistry for diesel deposit control additives used over the past 30 years is polyisobutylene succinimides (PIBSI). The design and manufacture of these additives is critical to their performance in the field in terms of functioning to control deposits but also from a no-harm standpoint.

Recent work has identified low molecular weight PIBSI as a cause of internal diesel injector deposits (IDID) associated with injector sticking. Low molecular weight PIBSI would not normally be associated with a high quality deposit control additive and the term PIBSI can cover a multitude of chemical structures. This paper presents new work carried out to further understand the relative effects of a range of PIBSI molecules and more precisely understand which low molecular weight PIBSI species can lead to IDID.

Laboratory bench tests have been carried out to test a range of PIBSI to identify those species responsible for IDID. The effects of fuel components and refinery additives have also been investigated. Industry Standard and modified engine tests have been used to demonstrate the effect of low molecular weight PIBSI species. They have also been used to show that a PIBSI specifically designed and manufactured to function as a diesel deposit control additive does not cause

internal diesel injector deposits and will also function effectively to prevent their formation.

INTRODUCTION

The build-up of deposits in diesel fuel injectors is not a new problem. In the 1980s the build-up of deposits on the pintle of a fuel injector was illustrated by Montange et al [1] and the development and introduction of fuel additives to reduce injector fouling occurred [2]. In 1991, Gallant et al [3] noted that deposits caused sticking of close fitting parts and plugging of spray holes leading to power loss and increased emissions. As new emissions requirements led to engine design changes, fuel quality was looked at as a means to reduce injector fouling [3, 4].

Emissions legislation has continued to drive targets lower and fuel injection equipment manufacturers continually redesign injection systems to meet these targets. As a result, fuel injectors have become increasingly complex and the tolerance to any level of deposit is low. Fuel pressures within the injection system are high and temperatures are higher than previously experienced. This combination stresses the fuel and can increase the formation of decomposition products which lead to deposit formation [5].

Fuel legislation has also continued to change with lower sulphur contents and the addition of bio components. These two changes can both have opposing effects with regards the tendency of the components in the fuel to form deposits and the ability of the fuel to solubilise them [5].

Industry Standard engine test methods have been developed to assess the effectiveness of deposit control additives. The Peugeot XUD-9 A/L nozzle coking test has been used for many years and remains an important engine test for this

purpose. More recently, a new Direct Injection (DI) engine test has been developed by the Coordinating European Council (CEC). The Peugeot DW10B test adulterates the test fuel with 1ppm zinc to accelerate deposit formation at the tip of the injectors. No Industry Standard test is currently available to assess the occurrence of internal diesel injector deposits that have been observed in the field although several engines have been used to reproduce the effect. [6, 7, 8]

IDID have been reported [9, 10] to be composed of several different species namely; metal ion contaminants, organic amide lacquers and carbonaceous decomposition products. Some or all can be observed within diesel injectors depending on the history of the vehicle.

Organic amide lacquer deposits have been associated with PIBSI. The term PIBSI can cover a multitude of different chemical structures and therefore to use such a generic name can be misleading. PIBSI will include any species which has been prepared using polyisobutylene (PIB) of any molecular weight distribution which has been reacted with maleic anhydride to form a polyisobutylene succinic anhydride (PIBSA). This is then further reacted with an amine to form the succinimide. The amine can be any amine which contains at least one primary nitrogen group capable of reacting with the anhydride and ring closing to form an imide. In making the intermediate PIBSA, different ratios of starting materials can be used and different processing conditions employed and each will result in a different mixture of compounds. Each of these will then react differently with the amine species and result in an even wider mix. The ratio of PIBSA and amine can also be varied depending on the end application to give optimum performance. All of these products can be referred to as PIBSI.

Initial laboratory studies [9, 11] showed that mixing and heating PIBSI with acidic compounds could generate amides and produce material with a similar FT-IR spectra to deposits analysed from an injector. Subsequent studies [7] showed that although laboratory generated material looked similar by FTIR it did not mean that the initial PIBSI used would produce internal injector deposits. It was noted that other parameters such as the solubility of the additive in the fuel and its effectiveness as a deposit control additive would dictate the tendency to form deposits in injection systems.

Quality and molecular weight have been shown to be important factors in determining whether a PIBSI will form amide lacquers. Low molecular weight production byproducts of PIBSI compounds were identified [6, 12] as the cause of IDID. Barbour et al [6] noted that PIBSI used as deposit control additives are typically made from 1000 molecular weight PIB and that the low molecular weight fraction is only a by-product. Ullmann et al [7] tested two different qualities of PIBSI in laboratory, injector bench and engine tests and showed that only the PIBSI which contained very high levels of low molecular weight species caused significant IDID. The second PIBSI sample with low levels of low molecular weight species did not cause IDID. The use

of the Jet Fuel Thermal Oxidation Tester as a possible test for lacquer formation was also shown. Limited testing in this laboratory equipment produced a similar deposit to that found inside injectors.

FIE bench tests [10] carried out on low molecular weight PIBSI produced a thin layer of deposits identified as amide. Identical tests using PIBSI with “a more normal distribution” did not produce deposits.

Engine tests have also linked low molecular weight PIBSI with IDID. Quigley et al [8] showed IDID formation in a 6.8 litre engine using low molecular weight PIBSI and Barbour et al [6] reported IDID in a DW10B engine operated on fuel dosed with 15ppm low molecular weight PIBSI. Addition of 5% of this low molecular weight PIBSI to a standard molecular weight PIBSI did not create IDID.

METHODOLOGY

Laboratory Test Methods

The Jet Fuel Thermal Oxidation Tester (JFTOT) is used to test the thermal oxidation stability of aviation fuel according to ASTM D-3241. An Alcor JFTOT III was adapted to assess the lacquer formation of different diesel fuel/additive combinations. A volume of fuel was pumped at a fixed rate of 3mL/min through an initial filter unit containing a 4 µm filter paper cut from a diesel fuel filter. The fuel was then passed over an aluminium test piece heated to 260°C. The total test time was 2.5 hours and at the end of test the metal test piece was cleaned with analytical grade toluene and acetone, dried and rated visually for deposit formation.

Engine Test Methods

XUD-9 A/L Engine Tests

Tests were carried out to assess the propensity of fuel/additive combinations to form deposits within an Indirect Injection (IDI) engine according to test procedure CEC F-23-01, referred to in the following discussions as the XUD-9 A/L procedure or method. A brief outline of the procedure is given here; the test uses a 1905cm³, 4-cylinder, naturally aspirated, engine produced by Peugeot Citroën Moteurs. The engine is of the IDI type with a pump-line-nozzle fuel injection system using a Lucas Rotary pump and pintle injectors. The engine is operated on the engine test bench according to a test cycle consisting of four short steady state conditions giving a total cycle time of 270 seconds; the cycle is repeated for a total test duration of 10 hours. At the end of the test the pintle injectors are removed and disassembled, the air flow through the injector nozzles is measured and reported as the flow loss at a needle lift of 0.1mm.

DW10B Engine Tests

Tests were conducted using the CEC F-98-08 DW10B engine to assess the injector sticking tendency of fuels dosed with different PIBSI. A brief outline of the procedure is given

here. The test used the 1997cm³, 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.

When the engine was started 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.

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 I](#).

The JFTOT tests were performed using the fuel as received and referred to as B0 fuel. A blend was also prepared of RF-06-03 with 7%v/v FAME and referred to as B7 fuel. RF-06-03 contains a level of lubricity improver additive to provide engines with adequate protection against fuel pump wear. A series of tests were also carried out using RF-06-03 which had been filtered through a column containing clay designed to remove the lubricity improver additive from the fuel. These are reported under the section ‘Effect of Clay Filtration of Fuel’. It should be noted that this would also remove other polar species present in the fuel.

The XUD-9 A/L tests were carried out using RF-06-03 as received. The DW10B tests were also carried out using RF-06-03 as received. Although the test procedure used to assess injector sticking used the CEC F-98-08 DW10B engine the fuel was not adulterated with zinc neodecanoate.

PIBSI Additives

PIBSI of varying molecular weight distributions were prepared in the laboratory from different molecular weight PIB. For consistency all used the same polyamine and direct comparison of results was achieved by setting all samples to the same active ingredient level. GPC data for each sample is shown in [Figures 1](#) and [2](#) and summarised in [Table 1](#). Each sample will be referred to by the codes in [Table 1](#). For comparison, a sample of a commercial PIBSI specifically designed to function as a diesel deposit control additive and used successfully in the field for over 15 years was also tested. The commercial sample will be referred to as PIBSI DCA to differentiate it from the laboratory prepared samples.

GPC Data

Gel Permeation Chromatography (GPC) was carried out to determine the molecular weight distribution of the laboratory PIBSI samples. Chromatograms are shown in [Figures 1](#) and [2](#) and the data is given in [Table 1](#).

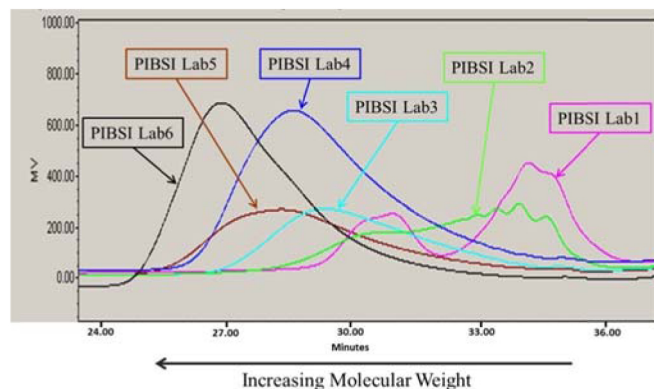


Figure 1. GPC chromatogram for PIBSI Lab1-6

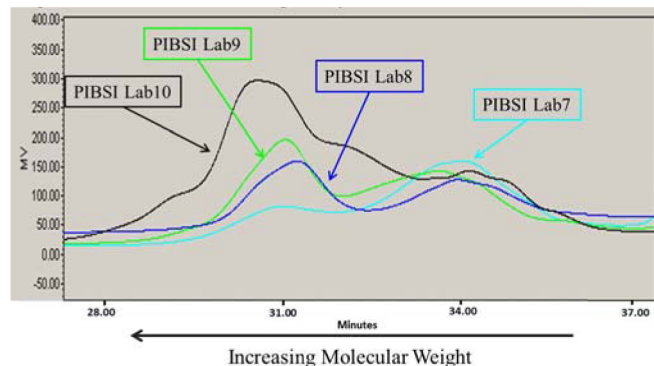


Figure 2. GPC chromatogram for PIBSI Lab 7-10

Table 1. GPC data for PIBSI Lab1-10

Sample Code	Mn
PIBSI Lab1	596, 1195
PIBSI Lab2	801
PIBSI Lab3	1342
PIBSI Lab4	1774
PIBSI Lab5	1913
PIBSI Lab6	3208
PIBSI Lab7	610, 1127
PIBSI Lab8	625, 1156
PIBSI Lab9	626, 1109
PIBSI Lab10	583, 1139

PIBSI Lab1 and PIBSI Lab7-10 are bi-modal in distribution and therefore two distinct number average molecular weights (Mn) are given. Where there is a bimodal distribution it is a clear indication of the presence of a significant proportion of low molecular weight species. The GPC chromatogram for PIBSI DCA is shown in [Figure 13](#).

LABORATORY TESTING

Jet Fuel Thermal Oxidation Tester

The JFTOT is usually used to assess the thermal oxidation stability of aviation fuel. However, it can also be used to assess diesel fuel stability and its propensity to form deposits. In the method fuel is passed over a heated metal test piece and can therefore be likened to fuel passing through a diesel injector. At the end of test, the metal test piece is rated visually for deposit formation.

A series of tests were carried out to investigate the suitability of the JFTOT to reproduce the formation of organic amide lacquers. Tests were run in an Industry Standard Reference Fuel, RF-06-03 as received, blended with 7%v/v FAME and clay filtered. Molecular weight and process variations within PIBSI chemistry were investigated. A PIBSI designed specifically to function as a deposit control additive was also evaluated.

Figure 3 shows a microscope photograph of the lacquer formed on the JFTOT tube from the test of B0 with 350mg/kg of the low molecular weight laboratory PIBSI Lab1.

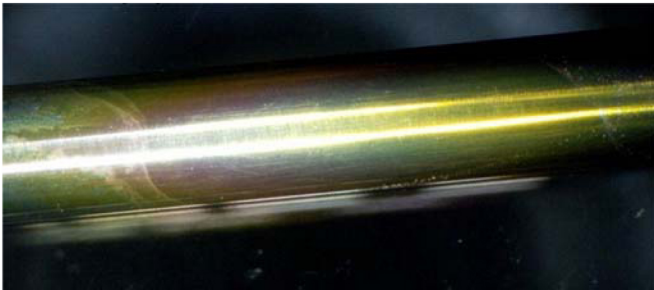


Figure 3. Microscope photograph of JFTOT tube from the B0 + 350mg/kg PIBSI Lab1 test

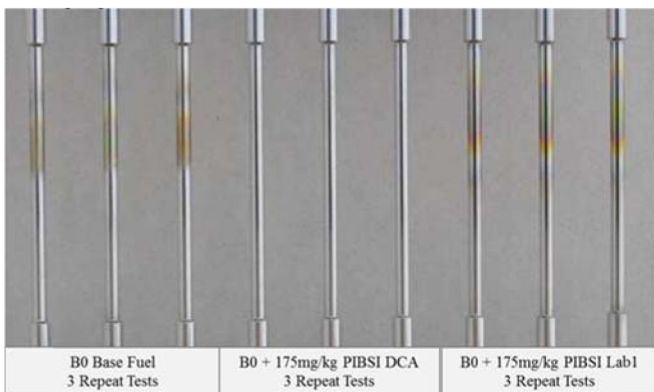


Figure 4. JFTOT tubes, B0 base fuel repeat runs with 175mg/kg PIBSI DCA and PIBSI Lab1

Repeat tests were carried out on the B0 base fuel, B0 + 175mg/kg PIBSI Lab1 and also B0 + 175mg/kg PIBSI DCA.

Consistent results were observed for each set of data and the JFTOT tubes for each run are shown in Figure 4.

Effect of Fatty Acid

Initial tests were carried out with B7 fuel additised with 450 mg/kg mono-fatty acid. PIBSI DCA and PIBSI Lab1 were tested at a high treat rate of 3500mg/kg. Testing was then carried out without the addition of the mono-fatty acid. The JFTOT tubes from each run are shown in Figure 5.

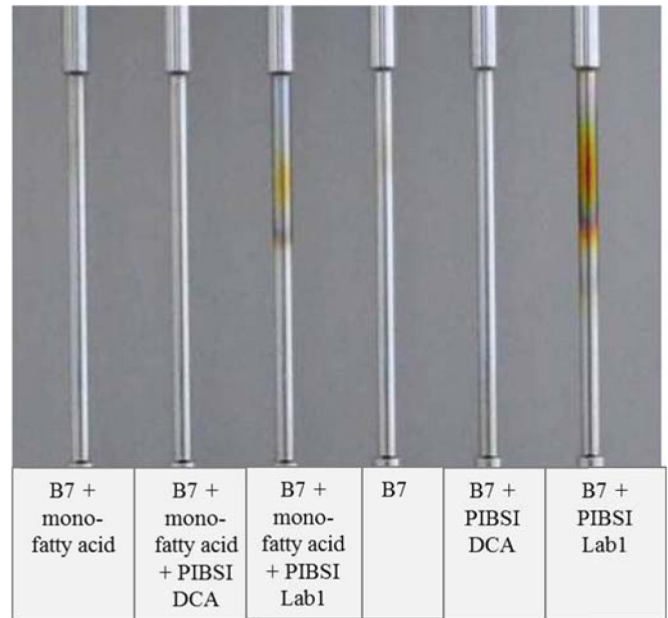


Figure 5. JFTOT tubes, B7 fuel with high treat rates of PIBSI DCA and PIBSI Lab1 with and without mono-fatty acid

Figure 5 shows that the B7 base fuel produced a very low level of deposit and the high treat rate of PIBSI DCA resulted in a clean tube with and without the mono-fatty acid. PIBSI Lab1 resulted in a lacquer being produced both with and without the mono-fatty acid. The addition of the mono-fatty acid to the B7 fuel resulted in less deposit with PIBSI Lab1.

Effect of FAME

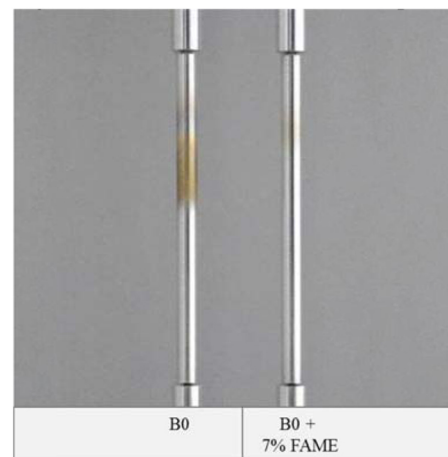


Figure 6. JFTOT tubes, B0 and B7 comparison

A comparison between the B0 and B7 base fuels was carried out and the results are shown in Figure 6. The B0 base fuel

produced a higher level of deposits than the B7 fuel. The addition of FAME can result in a more polar fuel and could therefore be more able to solubilise any deposits formed. For lab testing purposes the use of the B0 fuel was thought of as the worst case and used for subsequent testing.

Effect of Treat Rate

Tests were carried out in B0 fuel with PIBSI Lab1 at various treat rates and the results are shown in [Figure 7](#). It was found that relatively low levels of PIBSI Lab1 resulted in deposit formation. A treat rate of 175mg/kg of PIBSI Lab1 was chosen for further JFTOT testing because the level of deposit was significant enough to be observed.

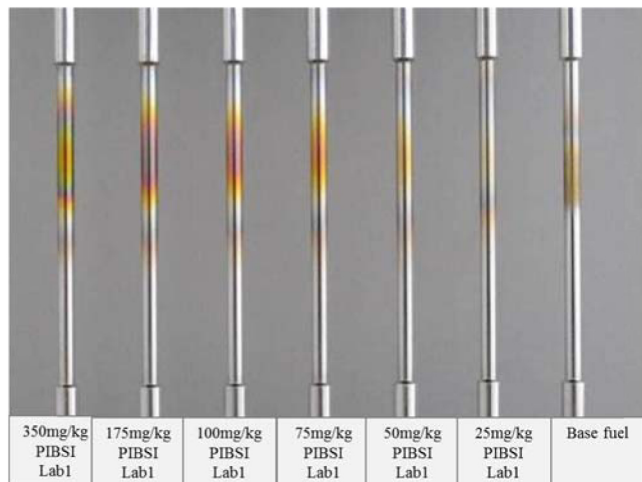


Figure 7. JFTOT tubes, B0 fuel with varying treat rates of PIBSI Lab1

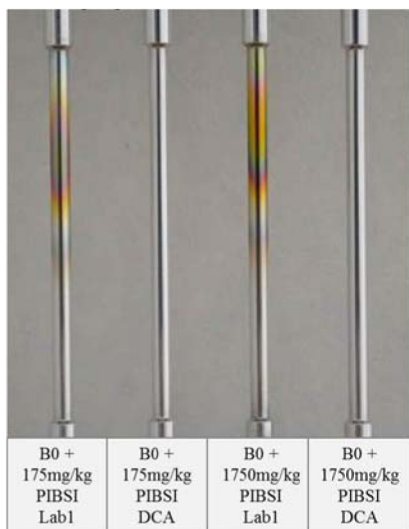


Figure 8. JFTOT tubes, B0 fuel with 175mg/kg and 1750mg/kg PIBSI Lab1 and PIBSI DCA

Reactive dilution of higher Mn material was also investigated by testing PIBSI Lab 1 and PIBSI DCA at 175 mg/kg and 1750 mg/kg and the results are shown in [Figure 8](#). Although the reactive part is diluted for higher Mn material it has no effect on deposit formation.

Effect of Molecular Weight

A series of PIBSI were prepared in the laboratory using different molecular weight PIB but with the same polyamine and ratio of PIBSA to amine. GPC data for each sample is shown in [Figure 1](#). Testing was carried out in B0 fuel at 175mg/kg and the results are shown in [Figure 9](#).

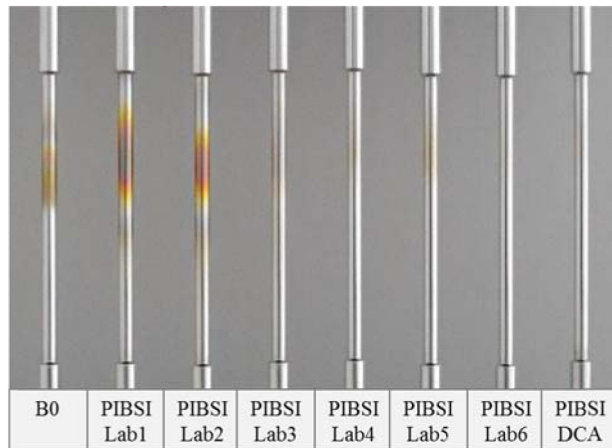


Figure 9. JFTOT tubes, B0 fuel with 175mg/kg varying molecular weight PIBSI

The molecular weight of the PIB used in each case increased from PIBSI Lab 1 through to PIBSI Lab 6. The data showed that PIBSI Lab1 and PIBSI Lab2 produced deposits. The polyamine and the ratio of PIBSA to poly amine were kept the same in each case therefore the influence of the PIB chain length was the predominant factor. GPC data for both PIBSI Lab1 and PIBSI Lab2 show a significant proportion of material with Mn around 600.

PIBSI Lab 3 - PIBSI Lab6 and PIBSI DCA reduced the level of deposit over the B0 base fuel. These products contain low levels of species with Mn around 600.

Effect of Process Changes

A series of PIBSI were prepared using different process conditions but the same polyamine and low molecular weight PIB as used for PIBSI Lab1. GPC data for each sample is shown in [Figures 1](#) and [2](#). Testing was carried out in B0 fuel at 175mg/kg and the results are shown in [Figure 10](#).

[Figure 10](#) shows that the use of different processing conditions to produce PIBSI of nominally the same molecular weight can impact the propensity of the additive to form deposits in the JFTOT. It also shows that not all low molecular weight PIBSI will cause deposits.

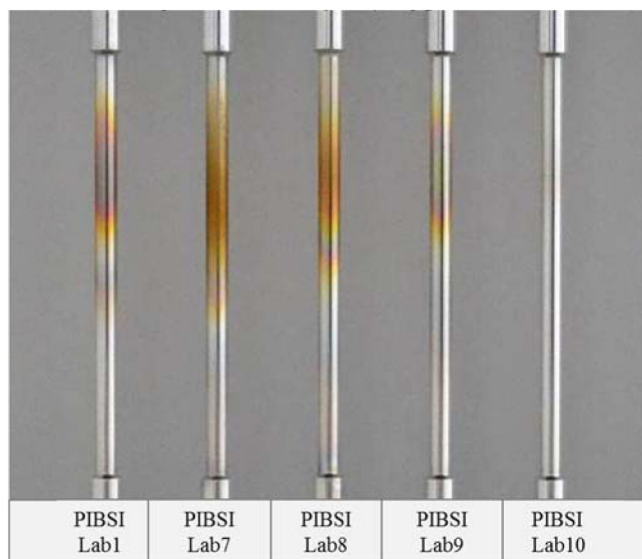


Figure 10. JFTOT tubes, B0 fuel with 175mg/kg low molecular weight PIBSI using varying process conditions

Effect of Addition of PIBSI DCA

PIBSI Lab1 was chosen to determine the effect of adding various levels of PIBSI DCA. The treat rate of PIBSI Lab1 was kept constant at 175mg/kg. Table 2 shows the ratios of PIBSI Lab1 and PIBSI DCA used and the results are shown in Figure 9.

Table 2. Treat rates and ratios of PIBSI Lab1 and PIBSI DCA

PIBSI Lab1, mg/kg	PIBSI DCA, mg/kg	Ratio PIBSI Lab1 : PIBSI DCA
175	0	1 : 0
175	20	1 : 0.11
175	87.5	1 : 0.5
175	175	1 : 1
175	350	1 : 2

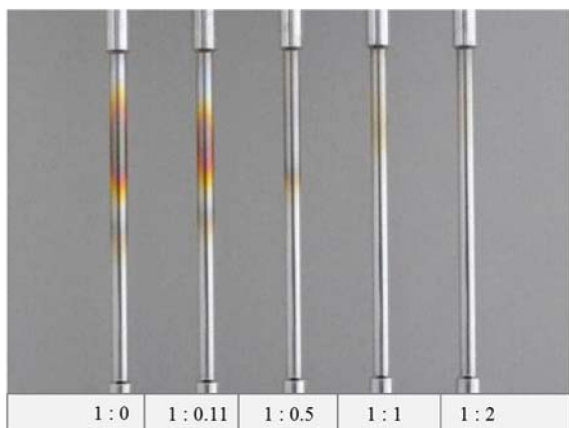


Figure 11. JFTOT test results for ratios of PIBSI Lab1: PIBSI DCA

Relatively low levels of PIBSI DCA were required to control the formation of deposits caused by the low molecular weight species. PIBSI DCA is specifically designed to control diesel deposit formation and in this laboratory testing ~50%*m/m* low molecular weight species could be present before significant deposit formation occurred.

Effect of Clay Filtration of Fuel

The fuel used for the JFTOT testing was deliberately chosen because it is the standard reference fuel used in both XUD-9 A/L and DW10B engine tests. This fuel does not contain any additives with the exception of a lubricity improver to provide protection against engine fuel pump wear. To check that this additive was not having an effect on the results the fuel was clay treated. This involved passing the fuel down a column packed with Fullers Earth clay. JFTOT tests were then carried out using the clay filtered RF-06-03. Tests were conducted for both B0 and B7 and also treated with 175 mg/kg PIBSI Lab1. The 7%*v/v* FAME was added to the clay filtered B0 and was not subsequently clay filtered. The results with and without clay filtration are shown in Figure 12.

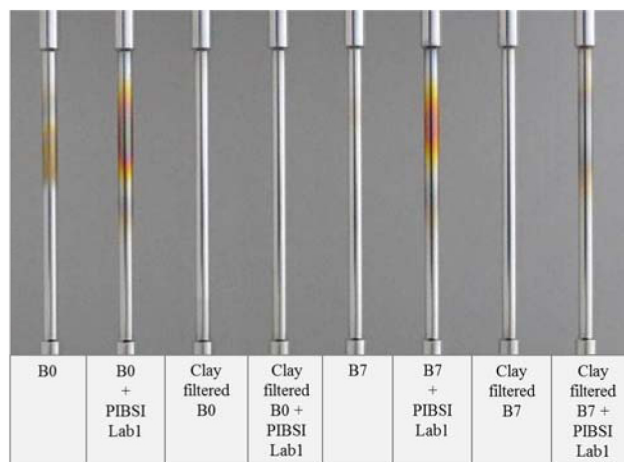


Figure 12. JFTOT tubes results for clay filtration of B0 and B7

The deposit forming tendency of the base fuel was observed to reduce following clay filtration for both the B0 and B7 fuels. While this clay filtration technique will remove the additive species it will also remove any other polar species contained naturally within the fuel. These naturally occurring polar species can include those associated with precursors to deposit formation. No deposit was observed in the B0 fuel on addition of PIBSI Lab1.

Deposits were observed with the B7 fuel on addition of PIBSI Lab1. FAME is known to be prone to oxidation, forming a variety of species including acids. Its addition to a clay filtered fuel could therefore increase the severity of deposit formation in the presence of the low molecular weight amine species.

Addition of Refinery Additives

Acidic fuel additives have been associated with amide lacquer deposits because they can react with amine groups to form amides. A range of typical lubricity improver and corrosion inhibitor additives were tested using the clay filtered fuel treated with typical treat rates of those additives. 175 mg/kg PIBSI Lab1 was added in each case.

Clean tubes were observed in each case and none of the additives tested produced deposits when tested in combination with PIBSI Lab1. This would suggest that amide formation is due to the reaction with acidic species found within the fuel or produced during the degradation of the fuel within the test system rather than with other fuel additives.

ENGINE TESTING

XUD-9 A/L Tests

XUD-9 A/L tests were carried out according to the CEC F-23-01 procedure. PIBSI DCA, specifically designed to work as a diesel deposit control additive, was tested at 2 different treat rates alongside PIBSI Lab1. Blends of the two samples were also tested at the higher treat rate to determine the effect on performance of varying levels of low molecular weight species in a high quality additive known to work in the field. The blend ratios used are shown in Table 3 and GPC data for blend 2 is shown in Figure 13.

Table 3. PIBSI blends used for XUD-9 A/L tests

Blend	PIBSI Lab1 % m/m	PIBSI DCA % m/m	Ratio PIBSI Lab1 : PIBSI DCA
1	10	90	1 : 9
2	25	75	1 : 3
3	50	50	1 : 1

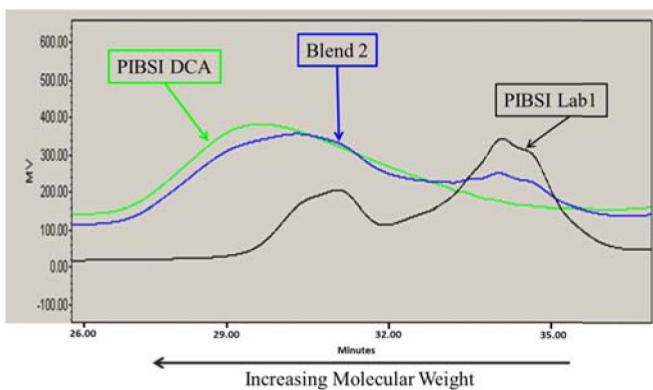


Figure 13. GPC chromatogram for PIBSI DCA, PIBSI Lab1 and Blend 2

At a ratio of 1:3 (PIBSI Lab1 : PIBSI DCA) the low molecular weight species are clearly observed by GPC as shown in Figure 13.

The injector flow loss data for each test is shown in Figure 14. It shows that PIBSI Lab1 does not function as a diesel deposit control additive. It can also be seen from Figure 14 that the % flow loss measured was higher than the base fuel and therefore the level of fouling within the injector nozzles was worse than the base fuel. It was also noted during the assessment of the injector nozzles from the higher treat rate PIBSI Lab1 test that the injector pintles were very stiff in the bodies. This would suggest that the deposit formed is capable of causing sticking even in this older type injector design.

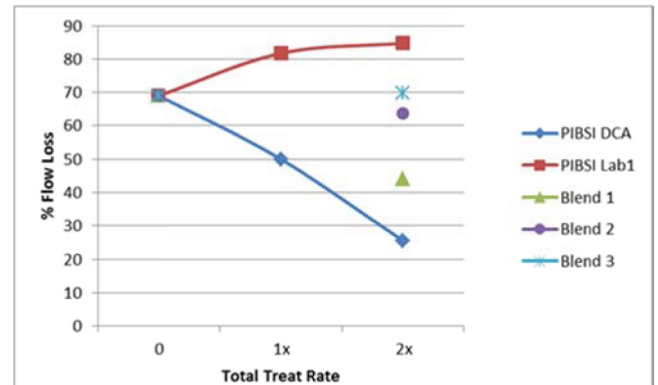


Figure 14. XUD-9 A/L results for PIBSI blends

A microscope photograph of the injector pintle from the high treat rate PIBSI Lab1 test is shown in Figure 15. Typical carbonaceous deposits can be observed on the pintle tip as expected. A layer of light brown lacquer can also be observed further up the pintle.



Figure 15. XUD-9 A/L injector pintle from the high treat rate PIBSI Lab1 test

FT-IR analysis of the deposit is shown in Figure 16 compared with the deposit found in a diesel fuel injector sourced from the field from a vehicle displaying operability problems. In both cases the deposit can be seen to contain peaks at 1664 cm^{-1} , representative of amide lacquer deposits.

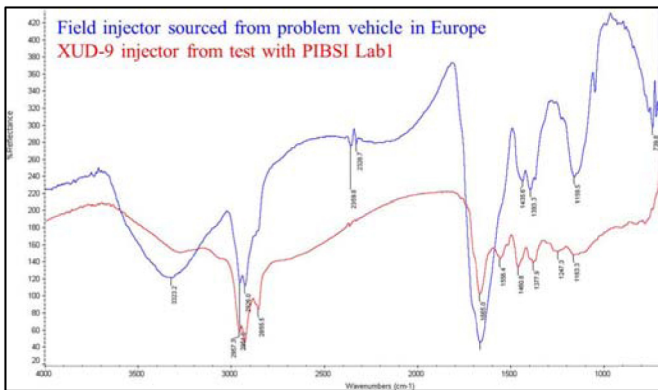


Figure 16. FT-IR spectra of deposit from XUD-9 A/L injector pintle from the high treat rate PIBSI Lab1 test compared with the field injector deposit

Figure 14 also shows that the addition of varying levels of low molecular weight material to an effective PIBSI diesel deposit control additive will severely reduce its effectiveness in the Industry Standard nozzle coking test. Addition of just 10% m/m of PIBSI Lab1 to PIBSI DCA resulted in a drop in performance of over 40% from the PIBSI DCA alone. Low molecular weight PIBSI materials are undesirable from a performance standpoint and high quality, highly effective PIBSI used in the market as diesel deposit control additives are manufactured accordingly.

DW10B Tests

The low molecular weight PIBSI Lab1 was tested using the CEC F-98-08 DW10B engine. The exhaust gas temperatures for each cylinder were recorded at the start of test (SOT) and following each 4 hour soak period. Different treat rates of PIBSI Lab1 were tested to determine the level required to cause injector sticking. Figure 17 shows the exhaust gas temperatures for the test carried out with 200 mg/kg PIBSI Lab1. This level of the low molecular weight PIBSI was found to cause severe injector sticking after the first 8 hours (8 cycles) plus 4 hour soak period.

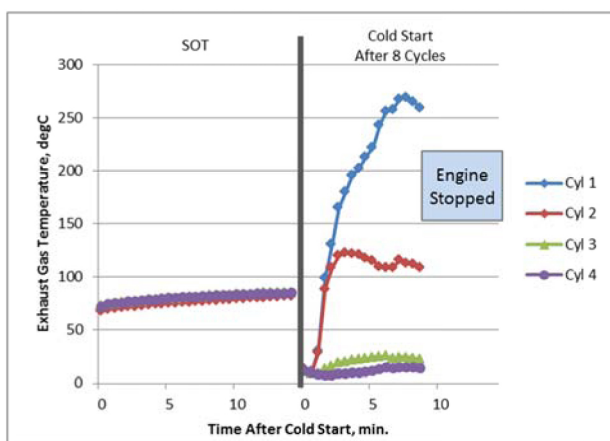


Figure 17. DW10B, exhaust gas temperatures after 8 cycles plus 4 hour soak with 200 mg/kg PIBSI Lab1



Figure 18. DW10B injector from the test with PIBSI Lab1

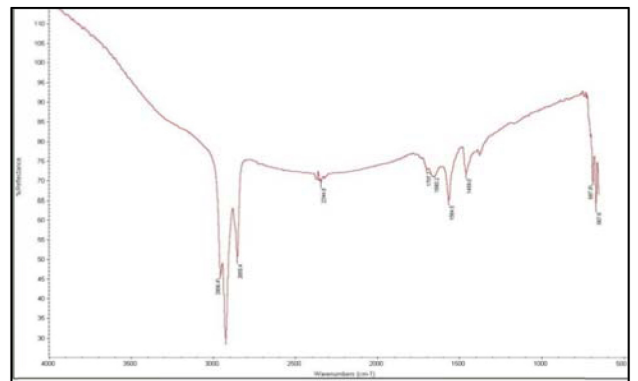


Figure 19. FT-IR spectra of deposit from the DW10B test with PIBSI Lab1

A microscope photograph of the injector is shown in Figure 18. A layer of light brown lacquer deposit can be observed around the needle tip. FT-IR analysis of this deposit is shown in Figure 19 and can be seen to be similar to the deposit found in the field injector and the XUD-9 A/L pintle.

Lowering the treat rate to 75 mg/kg of PIBSI Lab1 extended the test time out to 16 hours (2 sets of 8 cycles + 4 hour soaks). Cylinder 4 was starting to show some erratic behaviour after 8 cycles but the engine continued running normally. The engine failed to start after the soak period following the second set of 8 cycles. This is shown in Figure 20.

No injector sticking was observed when the treat rate was lowered further to 25 mg/kg PIBSI Lab1 and the test ran for the complete 32 cycles.

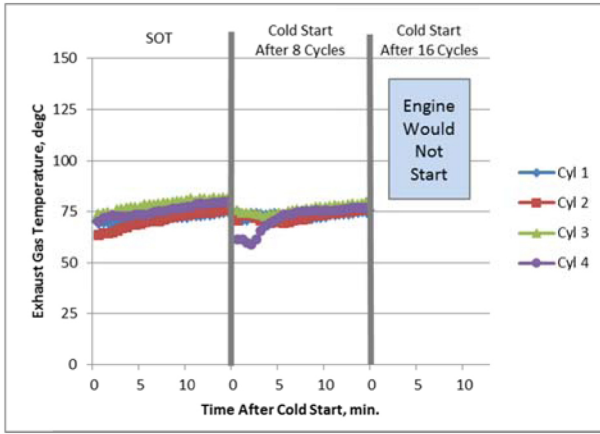


Figure 20. DW10B, exhaust gas temperatures after 16 cycles plus 4 hour soak with 75mg/kg PIBSI Lab1

Effectiveness of PIBSI DCA to Prevent Injector Sticking

A treat rate of 75 mg/kg PIBSI Lab1 was chosen for further testing to determine the effectiveness of the commercial PIBSI deposit control additive (PIBSI DCA) at preventing injector sticking. Three tests were carried out with varying levels of PIBSI DCA as shown in Table 4.

Table 4. Ratios of PIBSI Lab1 to PIBSI DCA in DW10B tests

Test	PIBSI Lab1 Treat Rate, mg/kg	PIBSI DCA Treat Rate, mg/kg	Ratio PIBSI Lab : PIBSI DCA
A	75	320	1 : 4.3
B	75	160	1 : 2.1
C	75	75	1 : 1

All 3 tests continued for the full 32 hours (4 sets of 8 cycles plus 4 hour soaks) without evidence of injector sticking as monitored by exhaust gas temperature. The final set of data for reach run is shown in Figure 21.

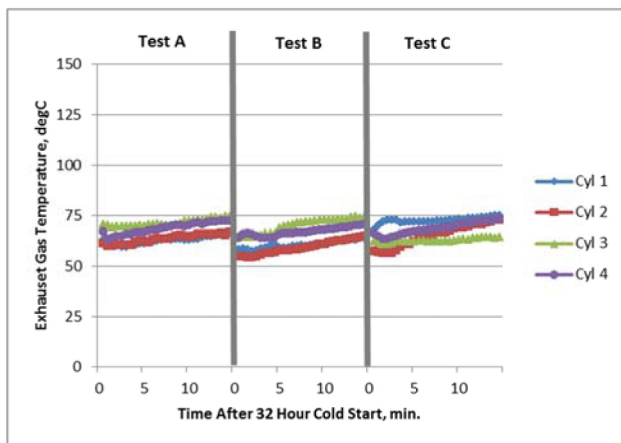


Figure 21. DW10B, exhaust gas temperatures after full 32 cycles plus 4 hour soak with 75 mg/kg PIBSI Lab1 and varying levels of PIBSI DCA

The addition of PIBSI DCA, specifically designed to function as a diesel deposit control additive, prevented injector sticking even when the low molecular weight PIBSI Lab1 was added at a 1:1 ratio.

SUMMARY/CONCLUSIONS

A systematic study has been carried out using the JFTOT laboratory test and the XUD-9 A/L and DW10B engines to understand both the cause and prevention of amide lacquer IDID with respect to PIBSI chemistry.

The JFTOT has been shown to be a useful laboratory tool to assess the relative deposit forming propensity of a range of fuel and additive combinations. Testing of PIBSI prepared from different molecular weight PIB highlighted that only those products containing significant proportions of material with Mn around 600 produced deposits. Significant differences in the level of deposition were observed when different processing techniques were employed to make a range of PIBSI from the same low molecular weight PIB. It should also be noted that not all low molecular weight PIBSI caused deposits. The quality of PIBSI production is therefore very important to ensure amide lacquer deposits are not formed.

XUD-9 A/L engine testing on PIBSI Lab1 showed the low molecular weight PIBSI sample performed no deposit control function. It also resulted in a higher flow loss than base fuel and formed an amide lacquer on the injector pintle. Addition of the low molecular weight PIBSI Lab1 to PIBSI DCA resulted in a significant drop in performance over PIBSI DCA alone because the low molecular weight PIBSI has no effect on carbonaceous tip deposits. Although an older technology, the XUD-9 A/L test remains an important measure of additive performance.

Prevention of injector sticking by IDID was achieved in the DW10B engine through the use of PIBSI DCA, a PIBSI in commercial use for many years with no reported field problems. Ratios of 1:1 and 1:2 PIBSI Lab1:PIBSI DCA prevented injector sticking in the engine. These same ratios in the JFTOT reduced the level of deposit below that of the base fuel and therefore this laboratory method could potentially be used as a guide to determine the propensity of a diesel fuel additive to form IDID.

XUD-9 A/L and DW10B engine test methods both showed the generation of the same type of amide lacquer deposit with a low molecular weight laboratory PIBSI. The engine tests also showed that the commercial PIBSI DCA which contains very low levels of low molecular weight species did not form amide lacquer deposits and that its use prevented IDID formation. Provided PIBSI deposit control additives are properly designed and manufactured to a high quality they will not cause internal injector deposits and can continued to be used in the field without problems.

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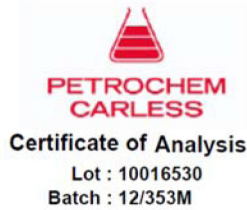
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APPENDIX

APPENDIX 1

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Product Name Carcal RF-06-03 (Marked)

Product Number 47244

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

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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Lot : 10016530
 Batch : 12/353M

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

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

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

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