The role of diesel fuel additives

Simon Mulqueen

THE ROLE OF DIESEL FUEL ADDITIVES IN IMPROVING AND MAINTAINING VEHICLE PERFORMANCE STANDARDS

Abstract
In order to satisfy the requirements of modern vehicle emissions standards, improvements in fuel quality have been necessary. This has led to the incremental development of improved fuel specifications, matching the requirements of new vehicle technology. For example, as European emissions standards, e.g. Euro 5 or Euro 6 have been introduced significant refinery investment has also been necessary to comply with proposed fuel specifications. These changes in fundamental fuel properties, composition and concurrent changes in engine technology have led to changing additive requirements, necessitating the need for novel additive introduction and changes in existing additive chemistry.

More recent advances in engine technology such as the introduction of the common rail diesel engine not only offer improvement in emissions, but are also more efficient than their predecessors. Within these high pressure common rail fuel systems the formation of internal injector deposits (IDID – Internal Diesel Injector Deposits) is however also being noted. Understanding the nature of IDID, and their potential origins can be critical in order to provide optimal protection against their formation. Fuel additives provide benefits to the existing vehicle population and any future additives must cater for both these and new diesel engine technologies.

Diesel engines have been shown to particularly benefit from operation with higher quality fuels containing deposit control additives. Benefits typically result from fuel system cleanliness and if injector fouling in both light duty and heavy duty diesel engines is reduced, then improved air flow and fuel spray patterns will restore lost power and fuel economy.

Tests carried out in both light duty and heavy duty vehicles have shown benefits from additive treated diesel. Both industry standard engine tests and long term vehicle testing have been used to highlight the importance of deposit control.

The paper reviews the role of fuel additives in diesel fuel system cleanliness and the performance benefits.

Keywords: diesel fuels; additives; performance; deposit control; fuel economy
Changes in legislation

Transport fuel specifications in the European Union are controlled by the European Committee for Standardisation (CEN), which was founded in 1961 by the national standards bodies in the European Economic Community and European Free Trade Agreement (EFTA) countries (1). With respect to diesel fuel, a single main standard is enforced for the harmonisation of fuel quality. This standard defines fuel properties as outlined in the EC directive 98/70/EC (2), which resulted from the study carried out in Europe in the early 1990’s, called the European Programme on Emissions, Fuels and Engine Technologies (EPEFE) (3). The key fuel properties specified form the basis of the EN590 diesel fuel standard published by CEN and associated national bodies. This EN 590 standard continues to be reviewed, monitored and updated today through the appropriate CEN working group (4). Table 1 below details the key specification properties for diesel fuel and how this standard has evolved with changing engine technology and legislation requirements.

Table 1: EN 590 Diesel Specifications, 1993. – 2013.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Polycyclic Aromatics, % vol. max</td>
<td>--</td>
<td>11.0</td>
<td>11.0</td>
<td>11.0</td>
<td>8.0</td>
</tr>
<tr>
<td>Cetane Number, min</td>
<td>49</td>
<td>51</td>
<td>51</td>
<td>51</td>
<td>51</td>
</tr>
<tr>
<td>Distillation T95, °C, max</td>
<td>370</td>
<td>360</td>
<td>360</td>
<td>360</td>
<td>360</td>
</tr>
<tr>
<td>Sulphur, ppm, max</td>
<td>2,000</td>
<td>350</td>
<td>50</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>Oxidation Stability g/m³, max</td>
<td>25</td>
<td>25</td>
<td>25</td>
<td>25</td>
<td>25</td>
</tr>
<tr>
<td>Induction Period, hours, min*</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td>FAME Content, % v/v</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>7</td>
<td>7</td>
</tr>
</tbody>
</table>

(*) When diesel fuel contains more than 2 % (v/v) FAME

Although changes in fuel quality have been significant, these modifications have mainly been driven by changes in vehicle emissions legislation. These changes linked to diesel passenger vehicle technology are summarised in Table 2. All dates listed in the tables refer to new type approvals (5).
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Table 2: EU Emissions Standards, Diesel Passenger Cars

<table>
<thead>
<tr>
<th>Date</th>
<th>CO</th>
<th>HC+ NOx</th>
<th>NOx</th>
<th>PM</th>
</tr>
</thead>
<tbody>
<tr>
<td>g/km</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Euro 1</td>
<td>1992.07</td>
<td>2.72</td>
<td>0.97</td>
<td>--</td>
</tr>
<tr>
<td>Euro 2, IDI*</td>
<td>1996.01</td>
<td>1.0</td>
<td>0.70</td>
<td>--</td>
</tr>
<tr>
<td>Euro 2, DI**</td>
<td>1996.01</td>
<td>1.0</td>
<td>0.90</td>
<td>--</td>
</tr>
<tr>
<td>Euro 3</td>
<td>2000.01</td>
<td>0.64</td>
<td>0.56</td>
<td>0.50</td>
</tr>
<tr>
<td>Euro 4</td>
<td>2005.01</td>
<td>0.50</td>
<td>0.30</td>
<td>0.25</td>
</tr>
<tr>
<td>Euro 5a</td>
<td>2009.09</td>
<td>0.50</td>
<td>0.23</td>
<td>0.18</td>
</tr>
<tr>
<td>Euro 5b</td>
<td>2011.09</td>
<td>0.50</td>
<td>0.23</td>
<td>0.18</td>
</tr>
<tr>
<td>Euro 6</td>
<td>2014.09</td>
<td>0.50</td>
<td>0.17</td>
<td>0.08</td>
</tr>
</tbody>
</table>

* - Indirect Injection; ** - Direct Injection

**Engine technology changes**

The resulting changes in engine technology have resulted in the introduction of ever more sophisticated injection equipment along with the necessity for exhaust after treatment devices. Changes in injector technology have resulted in vehicles being particularly sensitive to deposit formation with high speed direct injection (HSDI) diesel engine technology becoming commonplace. A micrograph of changing injector nozzle size for high speed direct injection nozzle engines shown below (Fig. 1) illustrates the increased sensitivity of these components, where injector nozzle diameters for Euro 5 diesel injector designs can now be <100 μm in diameter.

![Figure 1: Euro 3 (left) and Euro 5 (right) Diesel Injectors](image-url)

This ever increasing sophistication with respect to injector design has resulted in a greater tendency for deposit formation in modern engines, with clean injectors being cited as critical in ensuring modern engines comply with specified performance in terms of power, fuel consumption and emissions (6). The use of deposit control additive formulations is therefore an important strategy in ensuring a modern vehicle will function as originally designed.
Diesel deposit control additives – injector tip deposits

With diesel engines, it has always been important to ensure injector cleanliness in order to maintain optimum vehicle performance. As such market requirements for additive performance have focused on injector cleanliness as a performance parameter. The major difference historically has been the engine type in which the evaluation has been carried out; with light duty engines types being the focus in Europe and heavy duty engine types being the focus in the USA. The traditional bench engine tests used for injector fouling in these two markets are shown in the table 3.

Table 3: Market Requirements, Diesel Deposit Control Additives

<table>
<thead>
<tr>
<th>Test</th>
<th>Europe</th>
<th>USA</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Procedure</td>
<td>Requirement</td>
</tr>
<tr>
<td>Fuel Injector</td>
<td>Peugeot XUD9</td>
<td>&lt;50% - 85% flow loss at 0.1 mm needle lift</td>
</tr>
<tr>
<td>Cleanliness</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Power Loss</td>
<td>Peugeot DW10B</td>
<td>&lt;2% power loss in DF79 with 1 ppm zinc</td>
</tr>
</tbody>
</table>

In the past, for European diesel deposit control additive performance requirements, Peugeot XUD9 performance was the critical test requirement. However, a concern over the relevance of this indirect injection engine technology to the current diesel vehicle fleet, along with anecdotal concerns of power loss problems encountered in the market, raised the need for a test assessing performance in modern high speed direct injection engines (HSDI). As a result in 2008, a new test procedure developed by the Co-ordination European Council (CEC) using a Peugeot DW10 engine able to assess power loss as a function of injector fouling was published (7). With this test procedure and engine it was established that a power loss of <2% was important to ensure that there was no deterioration in the optimum performance of this engine.

In the US, the Cummins L10 direct injection heavy duty engine test has been discontinued with no industry standard equivalent for modern high speed common rail engine technology in place. Reports of injector fouling and fuel system deposits are present in the US market however and the sources of these remain a topic of interest and research (8 - 12).

As a result of these concerns over modern engine performance, additive development has therefore taken place to ensure the older engine technology requirements as dictated by the Peugeot XUD9 IDI engine test for example, are satisfied along with ensuring modern engine performance is satisfied in terms of the Peugeot DW10B engine. The ability of an additive to provide deposit control performance in both the DW10B and XUD9 engine is shown in the figures below (Figs. 2 - 5).
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Figure 2: Additive Performance, XUD9 Keep Clean

Figure 3: Additive Performance, XUD9 Clean-Up
As can be seen from the above figures, additive technology has been developed to ensure the whole vehicle fleet is protected. Excellent additive performance is measured in both older XUD9 engine tests and in the modern Peugeot DW10B engine test, demonstrating protection against and restoration of power loss.
Internal diesel injector deposits

Injector nozzle tip deposits and their prevention has traditionally been the focus of deposit control in diesel engines and diesel fuels. More recently however interest has been focused on the deposit found on the internal parts of injectors. These are termed internal diesel injector deposits (IDID) and are currently a main area of industry focus and research. There are six industry recognized types of IDID (13) and some of these are illustrated in the figures from 6 to 10.

Figure 6: Carbonaceous Injector Deposit. Carbon Based, black in colour

Figure 7: Amide Injector Deposit. Polymeric based, brown in colour

Figure 8: Aged Fuel Deposit, ‘sticky’ deposit possible bio in origin

Figure 9: Lacquer Based. Visualised on some injectors, may be a carbonaceous deposit precursor
Figure 10: Carboxylate Salts. White in colour sodium or calcium carboxylate based

These IDID deposits may be found in various locations throughout the injector body and all of the deposits can be detrimental to the injector operation.

Figure 11: Examples of IDID in injector body

These and other FIE deposits may be attributed to a number of sources described in figure 12.
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Figure 12: Potential sources of diesel injector and fuel filter deposits

The sources described can of course act both singly and in combination to produce the deposit. A number of technical papers have been published on this topic to better characterise and understand the nature of IDID (14-17). Following incidences of reported injector sticking problems in Europe, a CEN task force was formed to investigate the issues and identify root causes (18). In general the report concluded that modern passenger vehicles covering high mileage such as taxis and delivery vans were affected the most. Reported systems included, loss of power and acceleration, difficulty in starting particularly in cold conditions, rough running and major driveability concerns which in extreme causes resulted in no engine start. Countries in Europe which were mainly affected included Denmark, Spain and France with the latter being the most affected. The investigation in France confirmed a sodium nitrite based corrosion inhibitor, in use in French multi-product pipelines since 1950, was a potential source of sodium in French diesel fuel. Diesel fuel surveys carried out across Europe confirmed that in general level of sodium in diesel fuel were higher than typically found elsewhere c.f. 0.3 to 0.5 ppm in France and <0.1 ppm rest of Europe. The use of this corrosion inhibitor in the French pipeline was believed to result in the immediate formation of sodium carboxylate soaps in the fuel. The metal carboxylate soaps were believed to be the cause of injector sticking reported in the modern high mileage passenger vehicles.

Other incidences of IDID were reported in the European market where different types of deposit to the metal carboxylate were reported. Here, brown lacquers and varnishes were identified and being linked to the presence of low molecular weight PIBSI in the diesel fuel. The term PIBSI can cover a multitude of different chemical structures and therefore to use such a generic name is potentially misleading. Therefore a number of studies have been performed to better understand the nature and formation of the amide lacquer deposits (14, 17, 19-21).
Following these incidences related to IDID in the European market a CEC test development group (TDG) was formed to develop a suitable bench engine test which could be routinely used for the monitoring and measurement of IDID formation in diesel fuels. A Peugeot DW10C engine with a common rail fuel system design and equipped with Euro 5 compliant production injectors was selected for this engine test (22). The test method development has recently been completed and published as an approved CEC test method during 2016 (23). Currently the published test enables the investigation of IDID in respect of metal carboxylate formation. Further test development is necessary to complete work on the formation of amide lacquers exacerbated by the presence of low molecular weight PIBSI. The test is based on a demerit system developed from a combination of different engine parameters measured over a total 30 hour engine running time. The demerit rating scale is from 0 to 10 with the maximum 10 rating assigned to an engine test where no deviation linked to IDID formation is observed.

**Diesel deposit control additives – internal diesel injector deposits**

As shown earlier, diesel deposit control additives have been developed to combat injector fouling in a range of engine technologies, providing protection across a whole vehicle fleet. With the potential for internal diesel injector deposits now becoming a major concern however, it is important to establish that deposit control additives are also able to prevent and remove deposits in this part of the injector.

Using the proposed DW10C engine test method, a number of tests have been performed to determine the ability of additives to prevent IDID. Using reference fuels as suggested in the proposed test method associated with metal carboxylate formation and amide lacquer formation, additive performance tests have been carried out. A summary of the test data is shown in the table and figures below.

<table>
<thead>
<tr>
<th>Base fuel</th>
<th>Contaminant</th>
<th>Additive</th>
<th>Merit Rating (M/10)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reference Fuel</td>
<td>0.5 ppm Sodium* + 10 ppm DDSA**</td>
<td>None</td>
<td>4.0</td>
</tr>
<tr>
<td>Reference Fuel</td>
<td>0.5 ppm Sodium* + 10 ppm DDSA**</td>
<td>Yes</td>
<td>10.0</td>
</tr>
</tbody>
</table>

(*') = Sodium as Sodium Naphthenate; (**) = Dodecenyl Succinic Acid

Table 5: Peugeot DW10C IDID Engine Testing – Amide Lacquer Formation

<table>
<thead>
<tr>
<th>Base fuel</th>
<th>Contaminant</th>
<th>Additive</th>
<th>Merit Rating (M/10)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reference Fuel</td>
<td>10 ppm Low MW PIBSI*</td>
<td>None</td>
<td>2.9</td>
</tr>
<tr>
<td>Reference Fuel</td>
<td>10 ppm Low MW PIBSI</td>
<td>Yes</td>
<td>10.0</td>
</tr>
</tbody>
</table>

(*') = Low Molecular Weight Polyisobutylene Succinimide
Figure 13: Exhaust Temperature Measurements – DW10C IDID Testing, Base fuel (Na/DDSA) (part one)
Figure 13: Exhaust Temperature Measurements – DW10C IDID Testing, Base fuel (Na/DDSA) (part two)
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Figure 14: Exhaust Temperature Measurements – DW10C IDID Testing, Base fuel (Na/DDSA) + Additive (part one)
Figure 14: Exhaust Temperature Measurements – DW10C IDID Testing, Base fuel (Na/DDSA) + Additive (part two)
Figure 14: Exhaust Temperature Measurements – DW10C IDID Testing, Base fuel (Na/DDSA) + Additive (part three)
Figure 15: Exhaust Temperature Measurements – DW10C IDID Testing, Base fuel (Low MW PIBSI)
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Figure 16: Exhaust Temperature Measurements – DW10C IDID Testing, Base fuel (Low MW PIBSI) + Additive (part one)

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Figure 16: Exhaust Temperature Measurements – DW10C IDID Testing, Base fuel (Low MW PIBSI) + Additive (part two)
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The above data shows that when the contaminants in the form of sodium and organic acid or low molecular weight PIBSI are added to the reference diesel fuel, significant injector sticking problems are observed. The deviations in exhaust temperature as shown in Figures 13 and 15 highlight the deviation from standard injector operation resulting in the low merit rating for each test. Conversely when the additive is introduced into the same fuels and the engine test is run under identical conditions, the injector operation remains within expected parameters and no major deviations in exhaust temperature are observed, resulting in the highest possible merit rating as measured in the DW10C engine.

Further vehicle tests have also been performed to determine the impact on vehicle performance of internal diesel injector deposits. Using a pair of identical Euro 5 heavy duty diesel trucks with a similar vehicle history, over an identical driving cycle and mileage accumulation of 15,000 km, the impact of additive addition to the fuel was assessed. This was achieved by fuelling both trucks on the same batch of diesel fuel, but with one truck adding diesel deposit control additive to the fuel.

At the end of the mileage accumulation study, the injectors were removed and subjected to a technique at a 3rd party test facility to observe and study the injector spray and performance from both vehicles.

![Figure 16: Injector Spray Penetration](image)

As can be seen from the above figures the injector spray penetration was far superior in the vehicle fuelled with additive containing diesel indicating the ability of the additive in removing injector tip deposits. The charts in Figure 17 relate to delays in fuel delivery and injected amount of fuel, with the vehicle fuelled with no additive demonstrating a greater drift in injector performance and suggested evidence of IDID formation.
The greater stability of flow injection after use of the additive has allowed an optimization of injection quality. The above data therefore demonstrates in on road vehicle operation, the ability of a diesel deposit control additive to protect fuel injectors against different types of deposit formation and maintain a vehicle in its optimum design condition.

![Figure 17: Injector Performance](image)

**Conclusions**

The introduction of stringent emissions requirements have resulted in a significant change in the quality of fuel and the engine technology required to achieve these strict standards. Of particular importance is the increased sensitivity of diesel injection equipment to fuel deposits and the need for this sophisticated technology to remain free of injection system deposits.

Fuel additive technology and performance requirements are critical in ensuring modern vehicle performance and consumer satisfaction is maintained. Critical areas that require consideration include:

- Multifunctional deposit control additives are used globally to improve fuel performance and enable product differentiation. These additives offer the motorist improved driveability and performance improvements by maintaining essential engine components in their optimum design condition.
- Suitable test protocols that are relevant to the market place are often used to evaluate additive performance.
The area of diesel deposit formation remains an active area of research and changes in engine and vehicle technology over the last few years has resulted in the reporting of new deposit phenomena.

Fuel additive technology is continually evolving to ensure optimum performance is provided across the whole vehicle fleet and additive selection should consider the different types of deposit protection required.

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