DCI-11 Corrosion Inhibitor for Gasoline-Alcohol fuels

PLMR 2000-08
Issue 4
9/2007
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1. **Product Description**

DCI-11 is an ashless, non-metallic, phosphorous free additive developed to meet the oxygenate fuel industry’s performance requirements. DCI-11 is the market leader corrosion inhibitor for oxygenated fuels such as gasoline-alcohol, diesel-alcohol and fuel containing MTBE. It is especially effective in ethanol and has a broad acceptance in the fuel grade ethanol industry.

At the recommended treat rate, DCI-11 offers the following benefits:

- Excellent cost effective corrosion protection
- Excellent control of acidity
- Reduction of fuel pump wear
- Long term protection for storage tanks and fuel handling assets
- Corrosion protection for the entire life of the fuel
- Almost two decades of proven field performance
- Excellent protection of critical steel, terneplate, aluminium and brass metals

2. **Typical Properties**

DCI-11 is easily handled at temperatures as low as 0°F (-18°C).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Typical Value</th>
<th>ASTM Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Appearance</td>
<td>Clear, Dark Brown Liquid</td>
<td></td>
</tr>
<tr>
<td>Specific Gravity, 60/60°F (15.6/15.6°C)</td>
<td>0.942</td>
<td>D287</td>
</tr>
<tr>
<td>Pounds / Gallon, 60°F (15.6°C)</td>
<td>7.84</td>
<td></td>
</tr>
<tr>
<td>Flash Point, PMCC, °F (°C)</td>
<td>64 (18)</td>
<td>D93</td>
</tr>
<tr>
<td>Ash Content, wt%</td>
<td>0.0</td>
<td>D482</td>
</tr>
<tr>
<td>Vapor Pressure, psi @ 38°C</td>
<td>2.45</td>
<td>D323</td>
</tr>
<tr>
<td>Viscosity, cSt @ 100°F (38°C)</td>
<td>27</td>
<td>D445</td>
</tr>
<tr>
<td>32°F (0°C)</td>
<td>146</td>
<td></td>
</tr>
<tr>
<td>0°F (-18°c)</td>
<td>559</td>
<td></td>
</tr>
</tbody>
</table>

3. **Treat Rate**

DCI-11 has a recommended treat rate of 10-30 ptb (0.030 - 0.091 gal/1000 gal or 28.5-86 mg/L) in fuel ethanol. DCI-11 should be added to the oxygenate so that a concentration of 2-4 ptb (6-12 mg/L) is provided in the finished gasoline oxygenate blend.
4. Background
Ethanol has been used for many years as a gasoline oxygenate blending component. General Motors has observed increased fuel pump wear in a section of the US vehicle fleet and, as a consequence, performed field studies investigating the quality of the ethanol being utilized in the gasoline pool. As a result GM proposed a change to the specification for fuel grade ethanol\(^1\). The following was recommended:

- Development of an acid detection method – the “pHe method”
- The ethanol manufacturers should control pHe
- Incorporation of a pHe specification into ASTM D4806 and D5798

GM has developed a method to determine pHe, which has been allocated ASTM D6423. Utilizing both this method and the NACE Rust Test TM-01-72, Innospec Fuel Specialties conducted a study to demonstrate certain chemical additives could help meet GM’s concerns. A large number of ethanol manufacturers participated in the program by providing samples of untreated ethanol.

The study demonstrated that a significant fraction of the ethanol pool had low pHe and that during long term storage of ethanol, the pHe decreased due to acid formation. Low pHe strongly correlates with increased corrosivity as demonstrated by poor performance in the NACE (TM-01-72) Rust Test. A Summary of these studies is contained in Innospec’s Fuel Specialties PLMR 9-1999, “Revised Final Report to the Technical Committee of the Renewable Fuels Association”.

5. DCI-11 Prevents Strong Acids Attacking Engine Parts
The alcohol fuel survey demonstrated that for all ethanol with a base pHe greater than 2.5, 30 ptb of DCI-11 increases the pHe to satisfactory levels which meet the ASTM specification of 6.5 to 9.0.

\(^1\) Presentation to spring ASTM D-2 meeting, June 23, 1992, N. Brinkman
5.1 DCI-11 Maintains and Controls EtOH Acidity During Storage
As mentioned previously, the level of acidity as determined by pH, has been found to increase during storage due to oxidative degradation. DCI-11 eliminates the problem by neutralizing strong acids and controlling pH.

5.2 Comparative pH Studies
The ethanol survey included a series of comparative studies in order to demonstrate the effectiveness of DCI-11 versus its major competitors. This involved analyzing the base ethanol and comparing the pH improvement achieved by treating with equivalent concentrations of DCI-11 and alternative products.
Ethanol 1

![Graph showing pH change over time for Ethanol 1 with different inhibitors.]

Ethanol 2

![Graph showing pH change over time for Ethanol 2 with different inhibitors.]

Legend:
- Base EtOH
- 30ptb DCI-11
- 30ptb Competitor A
- 30ptb Competitor B
- 30ptb Competitor C

Base EtOH

30ptb DCI-11

30ptb Competitor A

30ptb Competitor B

30ptb Competitor C
Ethanol 3

Time, (weeks)

pHe

Base EtOH 30ptb DCI-11 30ptb Competitor A 30ptb Competitor B 30ptb Competitor C
6. DCI-11 Protects the Entire Fuel System

Ethanol and gasohols are corrosive to metals most commonly utilized in fuel distribution systems. DCI-11 stabilizes the product and protects hardware from the point of manufacture to the end use vehicle fuel injection systems.

6.1 The NACE Rust Test TM-01-72

The NACE Rust Test (TM-01-72) determines the corrosivity of a fuel and the effectiveness of additives in fuel. This test is a modification of ASTM D665 and can be performed in one day. Typically an untreated fuel is run with several samples of varying treat rates. The samples are placed in a heated bath (100°F) with a mild steel billet suspended in the fuel. These samples are agitated for thirty minutes, at which point 30 mL of deionized water is added to accelerate the corrosion process. The samples are then agitated for 3.5 hours. At the end of the test the steel billets are removed, rinsed with acetone and rated according to the NACE rating scale. This rating is reported as a letter grade and percentage of rust observed on the billet. Unadditized ethanol is normally highly corrosive or will become so with time.

Generally a rating of B++ or better is desired to control corrosion in fuel systems.

<table>
<thead>
<tr>
<th>Rating</th>
<th>Proportion of test surface corroded</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>None</td>
</tr>
<tr>
<td>B++</td>
<td>Less than 0.1% (2 or 3 spots &lt;1 mm diameter)</td>
</tr>
<tr>
<td>B+</td>
<td>Less than 5%</td>
</tr>
<tr>
<td>B</td>
<td>5% to 25%</td>
</tr>
<tr>
<td>C</td>
<td>25% to 50%</td>
</tr>
<tr>
<td>D</td>
<td>50% to 75%</td>
</tr>
<tr>
<td>E</td>
<td>75% to 100%</td>
</tr>
</tbody>
</table>

NACE Rating Scale

![NACE Rust Test Image]
6.1 NACE Rust Test Data

As mentioned previously, low pH ethanol can be correlated with poor performance in the NACE rust test. Only 30 ptb of DCI-11 is required in the denatured ethanol to obtain an “A” rating in an ethanol that resulted in an untreated rating of “E”. DCI-11 also provides excellent corrosion protection in finished gasohol as demonstrated by the chart to the right.

The photograph to the right demonstrates the corrosion inhibition properties of DCI-11 in gasohol. This depicts the condition of carbon steel test specimens (billets) exposed to gasohol in the NACE Rust Test. The top billet was immersed in fuel, which was treated with DCI-11, whereas the billet on the bottom was immersed in the untreated fuel. The billet from the fuel sample treated with DCI-11 shows substantial improvement over that of the untreated fuel.

In extreme cases, vessel ruptures have occurred in carbon steel tanks where untreated ethanol has been stored for extended periods (seam weld locations are particularly vulnerable to accelerated attack due to stress cracking corrosion). DCI-11 protects assets, prevents unnecessary stoppages and averts expensive clean-up costs.
6.2 Comparative NACE TM-01-72 Studies

A series of comparative studies were performed to demonstrate the effectiveness of DCI-11 alongside its major competitors. DCI-11 provides the greatest corrosion protection.
7. **Fuel Pump Protection**

Electric fuel pump failures due to erosion/corrosion have been controlled by the addition of 6 ptb DCI-11 to gasoline/ethanol blends in a specific automotive application where DCI-11 was found to be uniquely effective – an investigation of Walbro 7500 series electric fuel pump failures.

<table>
<thead>
<tr>
<th>Fuel Type</th>
<th>DCI-11 Conc. (ptb)</th>
<th>Pump Failure, (hours)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base</td>
<td>0</td>
<td>10 pumps failed, 58-234 hr.</td>
</tr>
<tr>
<td>Base + 10% EtOH</td>
<td>0</td>
<td>4 pumps failed 88-97 hrs.</td>
</tr>
<tr>
<td>Base + 10% EtOH</td>
<td>6</td>
<td>No failures, 2000 hrs.</td>
</tr>
</tbody>
</table>

Test fluid GP 1140  
Operating Voltage 14.0  
Operating Pressure 40 psi  
Fluid Volume 5 gal

The fluid is changed every 72 hours. Between changes, fluid losses are made up; keeping the pump completely submerged. The pumps were checked every 8 hours. They were turned off and on five times to test whether they jam on start-up. It is rare for pumps to stop during continuous operation, although it has occurred. Normally they will jam during start-up duplicating what occurs in the field.

8. **Crude Oil Pipeline Protection**

The data summarizes corrosion wheel test results on DCI-11 and a competitive product. In the wheel test, using 10% synthetic seawater and a CO₂ purge, DCI-11 provided two to seven times more protection than a competitive inhibitor at 100 mg/L.

<table>
<thead>
<tr>
<th>Concentration</th>
<th>Sour Crude Oil #1</th>
<th>Sour Crude Oil #2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>DCI-11</td>
<td>Competitor D</td>
</tr>
<tr>
<td>3.5</td>
<td>22</td>
<td>18</td>
</tr>
<tr>
<td>8.8</td>
<td>22</td>
<td>2</td>
</tr>
<tr>
<td>35.1</td>
<td>53</td>
<td>29</td>
</tr>
</tbody>
</table>

Wheel Test: Steel coupon weight loss  
Crude Oil/Syn. Seawater, 90/10 vol%  
CO₂ purge  
140°F, 48 hours  
Triplicate tests averaged
9. Materials Compatibility

DCI-11 is compatible with other commonly used fuel additives including antioxidants, metal deactivators, gasoline multifunctional additives and other additives. DCI-11 is compatible with mild steel and stainless steel. Teflon may be used for an elastomer.

10. Storage Stability

DCI-11 is not affected by storage temperatures as high as 110°F (43°C) for prolonged periods. Samples of DCI-11 stored at 110°F showed no evidence of cloudiness or precipitation, nor were the anti-rust or water contact properties affected.

11. Handling Properties

DCI-11 may be unloaded satisfactorily without heating at temperatures as low as 0°F (-18°C). Heating DCI-11 for purposes of accurate metering should not be required at temperatures as low as -20°F (-29°C). The handling of DCI-11 as a function of viscosity versus temperature is illustrated below.

![Viscosity of DCI-11](image)
12. DCI-11 Detection Method
Innospec Fuel Specialties Method 2000-08, July 2000

GAS CHROMATOGRAPHIC ANALYSIS OF
DCI-11 IN ETHANOL

Method Summary
A sample was diluted with water, acidified and extracted with toluene to remove any organic contaminants. The aqueous phase was re-extracted with toluene to ensure no significant quantity of organic contaminants remained. The aqueous phase was then made alkaline with sodium hydroxide to release the DCI-11 and the DCI-11 extracted into toluene for analysis by GC/FID.

Apparatus
Three 50ml separating funnels
Two 5ml glass pipettes
A 2ml glass pipette
Autoinjector vials
500ml volumetric flask
100ml volumetric flask
50ml volumetric flask
HP5890 GC.
HP3396A
HP Autoinjector
Chrom Perfect Direct for Windows

Chemicals
Ethanol absolute
Toluene A.R.
Deionised water
DCI-11
Concentrated Hydrochloric Acid
50% m/m Sodium Hydroxide in water

Chromatographic Conditions
Column - CP Sil 19 30m i.d. = 0.53mm Film 2.0µm
Injector - Splitless (0.8 minutes)
Injection = 1µl using an autoinjector
Carrier Gas - Nitrogen 4ml/min
Detector - FID
Injector Temperature = 200°C
Detector Temperature = 220°C
Oven Temperature - 50°C for 1 minute then 15°C/minute to 225°C
G.C. input range = 1
Retention time = 6.82 minutes
Standard Preparation

A stock standard was prepared by weighing 800µl of DCI-11 into a 500ml volumetric flask and making up to volume in ethanol (0.7536g giving 1507 mg/litre). A 151mg/litre standard was prepared from this by pipetting 5ml into a 50ml volumetric flask and making up with ethanol.

A 30.1mg/litre standard was prepared from the stock standard by pipetting 2ml into a 100ml volumetric flask and making up with ethanol.

Procedure

A 5ml aliquot of the sample (or the standard) was pipetted into a 50ml separating funnel. The sample acidified with 200µl conc. HCl, then 5ml of water and 5ml of toluene were added. The mixture was extracted for one minute and the aqueous phase ran into a second separating funnel, which contained 5ml of toluene. The original organic phase was washed with about 2ml of water then discarded. Any remaining organic contaminants were extracted into the toluene layer during a one-minute extraction and the aqueous phase ran into a third separating funnel. The remaining organic phase was then washed as before. A 5ml portion of toluene was pipetted into the third separating funnel and the mixture made basic by the addition of 500µl of 50% NaOH. After a one-minute extraction the aqueous phase was discarded and the toluene layer analyzed for DCI-11 by GC/FID.

Standard

<table>
<thead>
<tr>
<th>DCI-11 30.1mg/litre</th>
<th>Area (Average of 5)</th>
<th>Relative Standard Deviation %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>42930.6</td>
<td>5.04</td>
</tr>
</tbody>
</table>

The standard was taken through the same extraction procedure as the sample and five separate extracts were prepared. To check the linearity the 151mg/litre standard was run through the extraction procedure giving duplicate results of 156mg/litre and 158mg/litre.

Calculation

\[
\text{DCI-11 Concentration} = \frac{\text{Peak Area Unknown Sample}}{\text{Peak Area Standard Sample}} \times 30 \text{ ptb}
\]
Availability and Technical Assistance

To order Innospec Fuel Specialties petroleum additives, additional literature or product samples, call Innospec Fuel Specialties Customer Service at 800-441-9547.

For assistance in evaluating this product for your application, please call the Innospec Fuel Specialties technical experts at 302-454-8100.
Appendix - Additional DCI-11 Literature Offered by Innospec Fuel Specialties

PLMR 11-95 DCI-11 Corrosion Inhibitor for Gasoline-Alcohol Fuels
PLMR 1-97 Petroleum Additives
PLMR 3-97 Corrosion Inhibitors and Pipeline Monitoring Techniques
PLMR 3-98 Performance of Ethanol in General Motors pH Test
PLMR 9-99 Revised Final Report to the Technical Committee of the Renewable Fuels Association
Additives Brief 95-02 Corrosion Inhibitor Evaluation of Field Samples
Additives Brief 98-05 Dilution of DCI-11