INTRODUCTION

Steel tanks have been used to store hydrocarbons and alcohols for more than 50 years. The infrastructure to produce, contain, and transport these materials typically involves some form of metallic vessel, tank or pipeline, under a wide range of pressures and flow rates. Commercial grade carbon steel has been used for storage tanks throughout the petroleum marketing distribution network.

Underground tanks are commonly placed at the end use site, such as with motor vehicle fueling facilities. Such tanks are normally shop fabricated in capacities of 50,000 gallons or smaller and operate at atmospheric pressures. In recent years, aboveground tanks are also being installed more frequently for similar end uses and in similar capacities. Aboveground tanks continue to be installed at bulk storage facilities and terminal operation sites. Tanks exceeding 50,000 gallons in capacity are typically field erected.

With the introduction of various environmental regulations, oxygenated components have been blended into gasoline. Alcohols, such as ethanol or methanol, and ethers, such as MTBE or ETBE, are commonly added to gasoline to form oxygenated fuel blends. Steel has long been considered compatible with such fuels. Carbon steel has not required any specific changes to accommodate the storage of reformulated and oxygenated fuels.

Steel Tank Institute is a trade association representing manufacturers of shop fabricated steel storage tanks. STI commissioned a definitive steel corrosion/compatibility study on gasoline blends containing between 5 and 100 percent alcohol. Certain non-metallic components of underground steel tanks, such as nylon bushings at pipe openings and fiberglass reinforced plastic materials used for secondary containment, were also tested by third party testing laboratories to become qualified under national standards.

CORROSION ANALYSIS OF METHANOL/FUEL BLENDS

Earlier studies performed by Steel Tank Institute had shown no compatibility problems with steel of gasolines blended with ethanol.1 As time passed, methanol gained a foothold in certain geographic regions of the United States, and was promoted as the oxygenated fuel of the future. Literature searches indicated that methanol is the more aggressive of the two alcohols.6,8

A company specializing in corrosion testing in the field and laboratory, was hired to perform an investigation of the possible corrosive effects of methanol as an additive to
Specifically, the company was asked to test eight methanol/fuel mixtures. Because methanol/fuel mixtures could possibly contain water, water was added to four of the eight solutions. Table 1, provides the composition of the eight test solutions. Reference Fuel C conforming to ASTM D-471 and composed of 50% isooctane and 50% toluene, was chosen as a baseline material for consistency and testing repeatability purposes.

Test panels were fabricated from steel containing a natural mill scale. This scale had defects where small anodic areas could form. This surface condition is typical of the interior of a steel underground storage tank. In addition, welded panels provided crevice areas that would be more anodic to the larger exposed area of these panels. Both conditions made this test more conducive to corrosion than plain panels with no mill scale.

<table>
<thead>
<tr>
<th>Solution Number</th>
<th>Methanol % by Volume</th>
<th>Reference Fuel C % by Volume</th>
<th>Water % by Volume</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>15</td>
<td>85</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>50</td>
<td>50</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>85</td>
<td>15</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>0</td>
<td>96</td>
<td>4.0</td>
</tr>
<tr>
<td>6</td>
<td>50</td>
<td>48.3</td>
<td>1.7</td>
</tr>
<tr>
<td>7</td>
<td>15</td>
<td>84.6</td>
<td>0.4</td>
</tr>
<tr>
<td>8</td>
<td>84</td>
<td>14</td>
<td>2.0</td>
</tr>
</tbody>
</table>

Water was added to solutions 5 - 8 in quantities to create a fuel blend phase separation, corresponding to a 1/2" level of steel exposure. Since the 84% methanol concentration of solution was found to be too high to create a 1/2" phase separation, a 2% water concentration was used. Two percent water was chosen because some authorities had suggested that this was the maximum water concentration found in 85% methanol(M85) in gasoline. The 15% methanol solution required 0.4% water to produce a 1/2" phase separation at the bottom of the test chamber. The bottom phase corresponded to 8% of the total solution volume. The 50% methanol solution required 1.7% by volume of water to produce a phase separation at the top of the test chamber. The 15% and 50% methanol-fuel solutions without physical introduction of water, absorbed moisture from the atmosphere and developed phase separations within 6 weeks of testing.

The testing laboratory utilized two methods of investigation. The first method to be discussed is an immersion weight loss study. The second, electrochemical methods, were evaluated to determine if they could be used in place of the more standard weight loss tests. Electrochemical methods, never before used with alcohol/fuel blends, provide a short term procedure to obtain corrosion rates of steel within various environments.
**Immersion Study**

Eight plain and eight welded panels were immersed in each of the eight test solutions for up to 24 weeks. These panels were constructed of ASTM A36 HRCQ steel with natural mill scale. The steel was taken directly from a tank fabricator's stock. Overall dimensions of the plain panels were 13" x 4" x 10 Ga (0.135 inches). The welded panels were approximately 13" x 6" x 10 Ga. Ten gauge steel is the minimum thickness used in the manufacture of underground storage tanks per STI standards. All panels were shear cut.

The panels were immersed to the 10-1/2" level, exposing the upper 2-1/2" of steel to the vapor phase of the solutions.

On a weekly basis, the phase separations, solution levels and methanol contents were determined. Also, the solution levels were lowered to half their height and refilled, to simulate the emptying and refilling of storage tanks.

Every four weeks, one plain and one welded panel were removed from each of the eight solutions. These panels were photographed, cleaned, weighed and re-photographed. Panels were evaluated for pitting, welded areas were inspected and percent weight loss was determined. Any corrosion was evaluated by percent weight loss, visual observation, and pit analysis. Trends of increasing activity with exposure time, would be needed to prove the existence of corrosion.

The corrosivity of the test solution was evaluated by the change in appearance of the panels after immersion, weight loss of the panels, pit evaluations of the panels and resistivities of the test solutions. It was thought that an increase in corrosion activity might also be reflected in a decrease in solution resistivity, for blends containing the same methanol content. However, this method was not considered to be accurate enough to determine solution corrosivity.

After evaluation of immersion tests, six of the eight panels exhibited no measurable corrosion which could be attributed to solution exposure. Test panels immersed in Solution 5 (96% Reference Fuel C/4% water) indicated that the bottom phase of this solution was a more corrosive environment than were all the other solutions. Results with this fuel indicated that slight corrosion occurred on the bottom 1/2 inch of the panel during the first four weeks of testing, and decreased thereafter to an immeasurable rate. No measurable corrosion occurred on the steel within the ullage portion of the testing apparatus.

Test panels exposed to Solution 7 (15% Methanol/84.6% Reference Fuel C /0.4% water) showed no measurable corrosion on the upper phase. However, the metal surface exposed to the lower phase, mostly methanol and water, exhibited a loss of mill scale in areas. Mill scale is a natural scale formed steel during the manufacturing process. The steel panel itself did not show signs of corrosion. This observation is consistent with the literature search7,9 and with several tank owners' experiences when switching an existing tank from gasoline to a high percentage methanol fuel blend. This phase was not
considered to be as aggressive as the water phase at the bottom of the 96% Reference Fuel C/ 4% water, discussed above.

None of the other solutions produced any evidence of corrosion on the steel panels.

**Electrochemical Corrosion Rate Study**

Electrochemical test methods proved to be quick and dependable for determining the relative corrosiveness of liquids with adequate conductivity.

Electrochemical corrosion methods are based on the relationship between the weight of metal lost by corrosion, and the amount of current exchanged during the time corrosion occurred. This relationship is expressed mathematically as:

\[ W = kIt \]

where \( W \) = weight in grams  
\( k \) = constant specific to each metal  
\( I \) = average current flow in amperes  
\( t \) = time in seconds during which the corrosion takes place

The two techniques evaluated in this study, polarization and oxygen-reduction, measure the value of current associated with the corrosion process. Neither technique is capable of indicating whether the metal loss is general nor of the pitting type. Electrochemical tests measure only the corrosion occurring in the liquid, not in the gas above the liquid, and only at the rate of corrosion occurring at the time of the test, a further limitation.

For electrochemical testing to succeed, the liquid must have some ability to conduct an electric current. Upon assessing the fuel mixtures, phases with at least 15% methanol provided adequate conductivity.

Corrosion rates were determined and listed in Table 2. With the polarization technique method, a steel coupon measuring 4.5 cm x 2.6 cm x 0.4 cm, with a total surface area of 31.2 cm² was used. With the oxygen reduction current method, a welded steel coupon measuring 12.7 cm x 6.4 cm with epoxy coated edges was used. The immersed surface area was 161 cm². An 85% methanol-15% water solution was chosen here to simulate the bottom storage volume of an M15 fuel blend contaminated with water. The corrosion rate of steel was found to drop 50% of initial rates within a 16-day time period using this method.

Physical inspection indicated that the ratio of non-corroding areas of the steel plate compared to areas where corrosion could be occurring was 300:1. The line marked (3) in Table 2 (Solution 85% methanol/15% water, exposed for 16 days) shows an average rate of corrosion calculated at 3.1 x 10⁻⁶ inches per year. In a worst case scenario where corrosion is not occurring evenly across the entire surface, but instead is concentrated in certain areas (or pitting), the average rate of corrosion would be greater, approximately
9.3 x 10^-4 inches per year. For 10 gage steel, the smallest thickness of steel used in the production of STI registered tanks, this higher corrosion rate corresponds to a service life of 150 years.

With the methanol exposure tests that were conducted, additional physical property tests were not made. Previous studies with ethanol had shown that physical property tests upon steel were not necessary. Samples tested for 15,000 hours in an ethanol gasoline blend were tested for tensile strength both prior to and after immersion. There was less than a 1% variance in tensile strength, indicating no loss of strength or stiffness of the steel when immersed in an ethanol-gasoline blend. The 1% variance fell within the statistical range of material variability for such tests.

<table>
<thead>
<tr>
<th>Original Composition</th>
<th>Surface Corrosion</th>
<th>Average Corrosion Rate, IPY</th>
</tr>
</thead>
<tbody>
<tr>
<td>MeOH % Fuel % H20</td>
<td>Area Sq. Cm.</td>
<td>Current in Microamps</td>
</tr>
<tr>
<td>15 85 TR*</td>
<td>31.2</td>
<td>1.2</td>
</tr>
<tr>
<td>50 50 TR</td>
<td>31.2</td>
<td>1.5</td>
</tr>
<tr>
<td>85 0 15</td>
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<td>1.1</td>
</tr>
<tr>
<td>85 0 15</td>
<td>161</td>
<td>1.2</td>
</tr>
</tbody>
</table>

* Trace of Water
(1) Start of Test period, polarization test, 9-18-89
(2) After 1 day exposure, polarization test, 9-18-90
(3) After 16 days exposure, polarization test, 10-4-89
(4) After 16 days exposure, polarization test, 10-4-89

IPY: Inches Per Year

**TESTING OF NON-METALLIC COMPONENTS OF STEEL TANKS**

Various non-metallic components used with many steel underground storage tanks may come in contact with oxygenated fuels. Non-metallic components of steel tanks must also be designed with an anticipated exposure to oxygenated fuels in mind. Even non-metallic components can corrode, as the National Association of Corrosion Engineers defines corrosion as the deterioration of a material by reaction with its environment. In the case of non-metallic materials, this determination is made by measuring the change in physical properties upon exposure to a specific environment.

For example, nylon bushings are traditionally installed in cathodically protected steel storage tanks to electrically isolate the steel tank from any steel piping. The nylon bushing is threaded into the steel threaded flange. Steel pipe is threaded into the internal threads of the bushing, placing the bushing into compression. With EPA regulations limiting the useful volume of the underground storage tank to 95% of the tank's capacity, bushings are rarely submerged within the liquid today. Nonetheless, the bushings are still...
exposed to splashing from the liquid, they can be submerged during certain tightness
tests, and they are constantly exposed to vapors. Bushings are traditionally tested to
Underwriters Laboratories Standard, External Corrosion Protection Systems for Steel
Underground Storage Tanks. Samples of the bushing are immersed in fluids for 70
hours and cannot exhibit a volumetric change greater than 40% or a shrinkage more than
1%.

Jacketed steel tanks are also becoming more commonplace today. In lieu of a second wall
of steel, some tank fabricators are attaching a non-metallic containment over the primary
steel tank. Again, the containment devices will rarely see a continuous immersion
condition. Since most secondary containment tanks incorporate an interstitial release
detection monitor, and since EPA rules mandate that such monitors be checked every 30
days, the likelihood of exposures beyond 30 days is rare.

Underwriters Laboratories Standard UL 1746 requires jacket samples to be immersed
within 8 alcohols or alcohol fuel blends for at least 30 days, at 100 °F. Fluids include
100% methanol and ethanol, 15% and 50% ethanol or methanol mixed with Reference
Fuel C, and 10% and 30% ethanol mixed with Reference Fuel C. Testing a wide range of
alcohol fuel blends is important as materials can inadvertently be exposed to higher
percentages of alcohol due to phase separation.

The samples must show no signs of blistering, softening, crazing, or other damage that
could impair the performance of the material as a containment mechanism. Physical
properties of the containment material are also tested both prior to and after exposure to
the liquid. Physical properties, such as flexural strength, tensile strength, and Izod impact
are measured. To pass this test, the material must retain 50% of its original physical
property value after being immersed in the various alcohol blends. The logic behind these
tests is complicated due to the chemical nature of plastics, as plastics can exhibit
degradation when exposed to some fluids, particularly with alcohols. These changes can
take place over time, and can usually be predicted for the structure's useful life in a time
span specified under certain testing procedures. Materials which lose physical property
values exceeding 50% of their original as-built property values, are likely to have
softened considerably and the structure could possibly lose its integrity.

Non-metallic materials in common use today for the secondary containment of steel tanks
are made from either fiberglass reinforced plastic using isophthalic polyester resins or
high density polyethylene. Manufacturers have tested both materials successfully to the
UL 1746, Part III criteria. The compatibility tests for FRP jacketed steel tanks were taken
in part from UL 1316, Glass-Fiber-Reinforced Plastic Underground Storage Tanks for
Petroleum Products, Alcohols, and Alcohol-Gasoline Mixtures.

CONCLUSION

Steel structures were commonly used to produce, store and transport fuels in the past.
With the introduction of oxygenated fuels over the past 5-10 years, compatibility
concerns have surfaced and must be addressed. The infrastructure of today and tomorrow
must continue to be useful in the production, storage and transport of such fuels. Steel underground storage tanks have been tested and found to be compatible with ethanol and methanol fuel blends.

**FOOTNOTES**

A) Steel Tank Institute is an international trade association representing fabricators of shop built underground and aboveground steel storage tanks. STI develops fabrication standards on behalf of the industry. STI developed the pre-engineered cathodically protected sti-P 3 ® underground storage tank standard in 1969, the composite ACT-100 underground storage tank standard in 1990, the FRP jacketed Permatank underground steel storage tank system in 1991, the insulated and secondary contained Fireguard aboveground storage tank standard in 1994, and the double wall F921 aboveground tank standard in 1992. An important quality inspection program is provided by STI upon fabricators who build tanks to these standards. Besides publishing important installation and testing recommended practices for shop fabricated tanks, STI also performs critical research and development work on behalf of the industry.

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**BIBLIOGRAPHY**


7) Distribution and Market Experience with Methanol Blends, Dr. Brian C. Davis, Sun Tech, Inc., Presented at the First International Conference on Fuel Methanol, May 9-10,

