

# Corrosion inhibitors for ethanol

## Additive solutions

### Background

The use of ethanol as an automotive fuel is certainly not a new idea; after all, Henry Ford designed the Model T to run on ethanol or gasoline. In recent years, however, much attention has been paid to ethanol use as a means to reduce U.S. dependence on foreign oil. Moreover, ethanol helps communities meet federal clean air standards through reformulated gasoline (RFG) programs. Oxygenates, such as ethanol, add oxygen to the fuel, promoting more complete combustion and thereby lowering CO and hydrocarbon (HC) emissions. As a result, the ethanol industry in the U.S. is twenty-two times the size it was in 1980, making the United States the largest producer of ethanol, followed closely by Brazil.

The impetus for additional growth comes from the Renewable Fuels Standard (RFS), part of the Energy Policy Act of 2005. The RFS requires an increasing amount of renewable transportation fuel use, beginning with 4.0 billion gallons in 2006 and increasing to 7.5 billion gallons in 2012. While not all of the renewable fuel utilized to meet this requirement will be ethanol, it is expected that ethanol will comprise a significant portion of the renewable fuel used. By April of 2006, the API estimated that fully 40% of the gasoline in the United States contained some amount of ethanol, up from 33% just a year earlier. The ethanol used for fuel in the United States is

sourced from corn grown in the U.S. (grain ethanol) as well as ethanol made from sugar cane and imported from Caribbean and South American nations. Ethanol is primarily used in gasoline at concentrations up to 10% by volume. However, there are a growing number of flexible fuel vehicles (FFVs) in use that can use E85, an 85% ethanol blend with gasoline. There are currently 4 to 5 million FFVs on the road today, many in private fleets. This market is expected to grow as automakers offer an increasing number of FFV car, truck and SUV models (34 in 2006).

Some of the advantages of using ethanol as a gasoline blend component or as an alternative fuel include those already discussed: a reduced dependence on foreign oil sources and reduced emissions of CO, CO<sub>2</sub>, sulfates, particulates and hydrocarbons.

Additionally, ethanol dilutes the concentration of aromatics in gasoline, thereby reducing the emissions of benzene. Ethanol has a higher octane rating than gasoline and has some detergent properties. Ethanol use also has some disadvantages. It has only about two-thirds the energy content of gasoline, so its use results in lower fuel economy. Ethanol increases gasoline volatility and increases the emissions of aldehydes. However, the ethanol industry has been proactive in seeking ways to overcome these problems in order to make ethanol a viable alternative energy source.

### Additive solutions to ethanol quality issues

Because ethanol for use as an automotive fuel is sourced from a number of domestic and foreign sources, it is of utmost importance to the ethanol industry that the quality of fuel ethanol be standardized. The industry standard for ethanol is ASTM D4806: *Standard Specification for Denatured Fuel Ethanol for Blending with Gasoline for Use as Automotive Spark Ignition Engine Fuel*.

Specifications detailed in this document include (among others) ethanol volume, water content, solvent washed gum content and ethanol pH (pHe). This latter specification is one that can be significantly affected by the use of an additive. The specification calls for the pH of the ethanol to be between 6.5 and 9.0 by test method ASTM D6423. This specification is important to automakers because research has shown that when the pHe is below 6.5, fuel pumps may malfunction as a result of film forming between the brushes and commutators. Also, fuel injectors can fail from corrosive wear and excessive engine cylinder wear can occur. When the pHe is above 9.0, plastic parts used in fuel pumps may fail. In order to bring the ethanol into specification for pHe and thus prevent these phenomena, an ethanol corrosion inhibitor/pH adjustment additive can be added.

The Baker Hughes product of choice is TOLAD™ 3224 corrosion inhibitor. This product not only brings the pH into specification but it also provides corrosion protection. The national trade association for the ethanol industry, the Renewable Fuels Association (RFA), recommends that all of its member companies add a corrosion inhibitor to all their fuel grade ethanol at a treat rate sufficient to provide corrosion protection comparable to that of other motor fuels. The RFA has examined a number of corrosion inhibitors and found that TOLAD 3224 corrosion inhibitor provides acceptable corrosion protection (a B+ in the ethanol/gasoline blend by NACE standard test method TM-01-72) at 13 pounds per thousand barrels of ethanol, the lowest treat rate of the additives recommended by the RFA.

### **TOLAD 3224 corrosion inhibitor**

TOLAD 3224 corrosion inhibitor is a complex of carboxylic acids and polyamine salts which provide convenient and cost effective corrosion protection and pH control in ethanol and ethanol containing blends. It is also an effective corrosion inhibitor in a wide range of fuels, semi-refined products, industrial oils and lubricants. TOLAD 3224 corrosion inhibitor provides corrosion protection in both the hydrocarbon and aqueous phases and is especially useful in situations where excessive static water is a problem. Typical dosage rates are 13 PTB in fuel ethanol.

