Technical Insights into Uninhibited Ethylene Glycol

When used as a heat transfer fluid in chiller applications, this chemical can degrade, causing problems and increasing costs. Learn the science behind its properties and why an industrially inhibited ethylene glycol might be a solution.

By Keith Wheeler, Thermo Electron Corporation

Uninhibited ethylene glycol has been a popular heat transfer fluid choice in chillers for many years because of its initial low cost and excellent freeze and heat protection over a wide temperature range. It also has good heat transfer capabilities and low conductivity, not to mention that it is completely miscible with water — an inexpensive and abundant solvent.

Those are the pros. There are, however, disadvantages inherent to uninhibited ethylene glycol, including:

- It is relatively easy to degrade.
- It promotes corrosion after it degrades.
- It is difficult to monitor.
- It absorbs water from the atmosphere.

These disadvantages can lead to frequent fluid changing, which can cost users money in labor and parts. There also can be lost production costs due to shutdown and possible premature failure of the system.

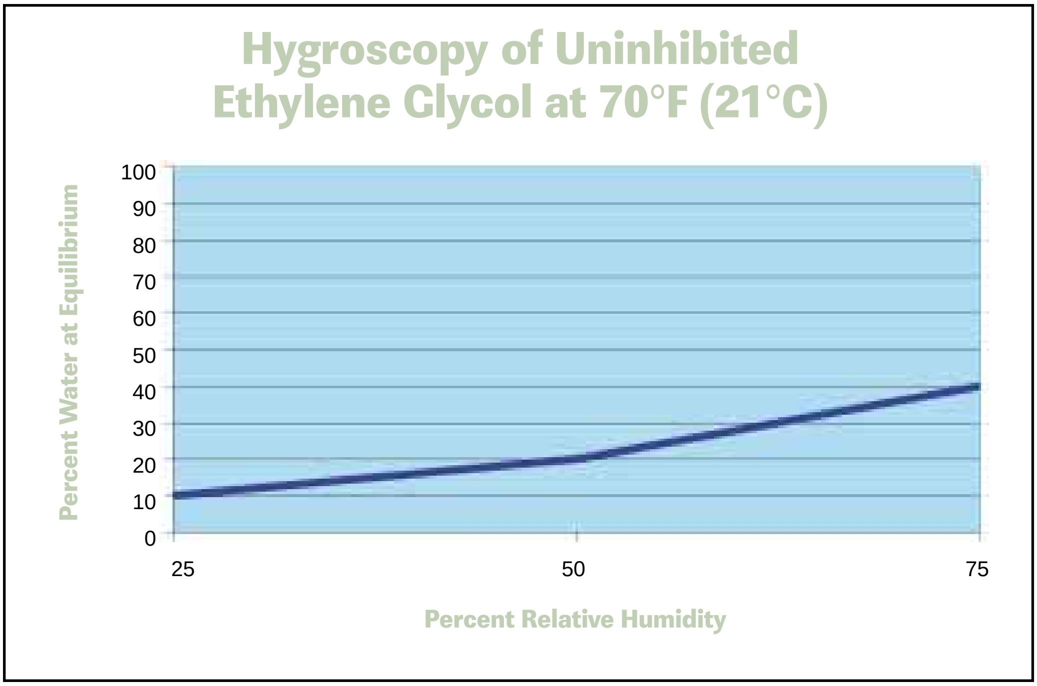
This mechanical seal has been scored due to corrosion byproducts and/or metal contamination of the fluid.

Degradation of Uninhibited Ethylene Glycol

Dow Chemical Co., Midland, Mich., distributes a technical bulletin entitled, “Acidic Thermal Degradation of Ethylene Glycol and Propylene Glycol.”[1] This advisory bulletin references the research of Dr. Walter Rossiter and his team of the National Bureau of Standards, now named the National Institute for Standards and Technology (NIST). Dr. Rossiter and his team conducted experiments that showed uninhibited ethylene glycol will degrade into five organic acids — glycolic, glyoxylic, formic, carbonic and oxalic — in the presence of heat, oxygen, copper and aluminum.[2,3,4] Copper and aluminum act as catalysts in the presence of uninhibited ethylene glycol. The organic acids then will chemically attack copper and aluminum in as little as three weeks under the right conditions to form metal organic compounds in the fluid.

Another extensive study on the degradation of uninhibited ethylene glycol was conducted by John Beavers and Ronald Diegle of Battelle, Columbus Laboratories.[5] They concluded that degradation of uninhibited ethylene glycol occurred in absence of contact with various metals, but degradation was accelerated by the metals' presence.

Many chemical resistance guides list that copper, aluminum and other metals are acceptable for use with uninhibited ethylene glycol. Usually, their recommendations are based on a two-week chemical compatibility study exposing various metals to uninhibited ethylene glycol at various temperatures. The above research indicates that uninhibited ethylene glycol does not begin to degrade and become acidic until after three weeks under extreme conditions (212°F [100°C] and oxygen bubbling into the uninhibited ethylene glycol solution). So, the chemical resistance guides are based on the “solvency” effects of uninhibited ethylene glycol rather than the degraded, acidic uninhibited ethylene glycol effects on metals. The latter is much more corrosive toward metals.



The amount of water absorbed from uninhibited ethylene glycol's environment is proportional to the percent relative humidity.

Corrosion of metals will commence at locations where metal ions are stripped away from the base metal by acidic, uninhibited ethylene glycol. The section of metal that has had its surface metal stripped away now becomes a metal oxide. Also, once metal ions are in solution, they can attach themselves to oppositely charged metals to form a galvanic corrosion cell. Rapid corrosion can commence at these sites in the cooling loop. Corrosion byproducts (metal oxides) then can be swept away to cause damage downstream. Typical problems associated with corrosion in a chiller cooling-loop system are clogging of a particulate filter, damage to mechanical seals and premature failure of the system.

Preventive Maintenance Becomes Difficult

Because uninhibited ethylene glycol can degrade and become corrosive in as little as three weeks, preventive maintenance can be time consuming and costly.

It is almost impossible to achieve an accurate pH reading for 100 percent uninhibited ethylene glycol because it is an organic liquid. pH meters are susceptible to errors and instability when exposed to organic chemicals. According to various manufacturers of uninhibited ethylene glycol, they state this chemical has a pH of 5.5 to 8.0. Most uninhibited ethylene glycol manufacturers do not specify a pH for this chemical; they state not applicable or not available (NA) on the product data sheet or material safety data sheet (MSDS). Others state to dilute the chemical with water to achieve a pH reading. But, by diluting with water, is one measuring the pH of the added water or the pH of uninhibited ethylene glycol/water solution?

A pH reading of an uninhibited ethylene glycol/water solution becomes less accurate with an increase in the uninhibited ethylene glycol concentration. Increasing the water concentration in uninhibited ethylene glycol allows for a more stable and reliable pH reading.

Some inherent problems associated with using a pH meter to measure pH of an organic chemical are:

- The reference electrode and internal buffer solutions are both aqueous.
- The activity of the hydrogen ion can vary dramatically between an aqueous and organic chemical.
- The dissociation of a compound can vary dramatically between an aqueous and organic chemical.
- The external buffer solutions (for probe calibration) are aqueous solutions.

Determining when to change out your uninhibited ethylene glycol by measuring pH to detect an increase in acidity is an unreliable measuring tool.

Atomic absorption spectroscopy (AAS) and inductively coupled plasma (ICP) are two analytical tools that detect specific metals and their concentrations in a fluid. A sample of the uninhibited ethylene glycol can be extracted from an application and analyzed by AAS or ICP to detect the metals that have been chemically attacked by acidic uninhibited ethylene glycol. However, this is a reactive approach because if there is a high concentration of metals found in the fluid, this signifies that the uninhibited ethylene glycol already has degraded and has turned acidic. Corrosion already has occurred and internal system damage is likely to be present.

A gas chromatography/mass spectrometer (GC/Mass Spec) is used to detect organic compounds in a solution. This analytical tool can measure the organic acids that develop when uninhibited ethylene glycol starts to degrade.

Water Absorption

Uninhibited ethylene glycol, like other glycols, is hygroscopic; it will absorb moisture from its environment. The amount of water absorbed from its environment is proportional to the percent relative humidity (figure 1). At 50 percent relative humidity, 100 percent uninhibited ethylene glycol will absorb 20 percent water at equilibrium. This drops the concentration of uninhibited ethylene glycol from 100 percent to 83.3 percent.

Because of this property, ethylene glycol is used as a humectant for textile fibers, paper, leather, adhesives and glue. This desirable property helps make these products softer, more pliable and more durable. However, water absorption can potentially cause many problems in chiller applications.

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Many users of uninhibited ethylene glycol are unaware of its hygroscopic property and often leave the cover off the container. Once this occurs, uninhibited ethylene glycol will immediately initiate water absorption.

Suppose you have a new chiller and you fill it up with what you believe is 100 percent uninhibited ethylene glycol from floor stock. The relative humidity within your building is 75 percent, and the application temperature is -4°F (-20°C). According to your freeze protection guide, you can fill the chiller with 35.5 percent uninhibited ethylene glycol and 64.5 percent (by volume) deionized (DI) or distilled water to achieve freeze protection at -4°F. To be safe, you fill the chiller with 38.5 percent uninhibited ethylene glycol and 61.5 percent DI or distilled water to achieve freeze protection down to -10°F (-23°C). If the environment on the floor is 75 percent relative humidity and the cap has been kept off of the container, the 100 percent uninhibited ethylene glycol can become 71.4 percent uninhibited ethylene glycol and 28.6 percent water. Now, you dilute this solution with 61.5 percent water (thinking you will have a solution of 38.5 percent uninhibited ethylene glycol and 61.5 percent water) and your true concentration becomes 27.5 percent uninhibited ethylene glycol and 72.5 percent water. This concentration only allows freeze protection down to 7°F (-14°C). You now have a solution that you thought would provide freeze protection to -10°F but in reality, it only provides freeze protection to 7°F. The decrease in freeze protection is 17°F (9°C). This error can result in a system failure.

Automotive antifreeze contains silicates and should not be used in chillers.

Conversely, 100 percent uninhibited ethylene glycol is used for heat protection. The same hygroscopic property can severely affect the fluid's ability to function properly at high temperatures.

There are many ways that the surrounding air can find its way into a closed-loop system. Air (humidity) can enter a chiller when the cap to the tank is removed for filling. Also, air can enter when the cap to the tank is removed to visually inspect the fluid level and during subsequent top-offs with uninhibited ethylene glycol. Air also enters the chiller via any left open valves or any leaks (loose hose clamps) in the system. Finally, uninhibited ethylene glycol is viscous and will entrap air when it is poured.

Preventive Steps to Minimize Exposure to Air

- Never leave the tank cap off the chiller.
- Minimize the frequency of removing the chillers tank cap.
- Containers of ethylene glycol should be airtight.
- All hose clamps should be airtight.
- Slowly pour ethylene glycol. Ethylene glycol will entrap air when it is poured. More air will be entrapped if the ethylene glycol is poured vigorously.
- If possible, open the container of ethylene glycol in a low humidity environment.

An Alternative

Industrially inhibited ethylene glycol contains approximately 93 percent uninhibited ethylene glycol, 3 percent water and 3 percent inhibitors. The inhibitors serve two purposes: to protect various metals in the cooling loop from corroding and to buffer the uninhibited ethylene glycol so that it retards the degradation process.

Automotive antifreeze typically contains silicates and therefore should not be used in chillers. Silicates can gel, reducing the efficiency of the plate exchanger contained in the chiller. Also, silicates can damage the mechanical seal of a pump found in a chiller, causing the pump to leak.

Inhibited ethylene glycol does share the same hygroscopic property as uninhibited ethylene glycol. Preventative steps must be followed to ensure minimal exposure to air. A disadvantage to inhibited ethylene glycol, however, is its initial cost.

Using inhibited ethylene glycol in place of uninhibited ethylene glycol can save money over the lifetime of the chiller and tool. If uninhibited ethylene glycol is not allowed to degrade (using inhibitors), then money is saved by less frequent maintenance to the cooling loop system (labor, parts and lost production costs) and change out of the fluid (labor, replacement fluid and lost production costs). **PCE**

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