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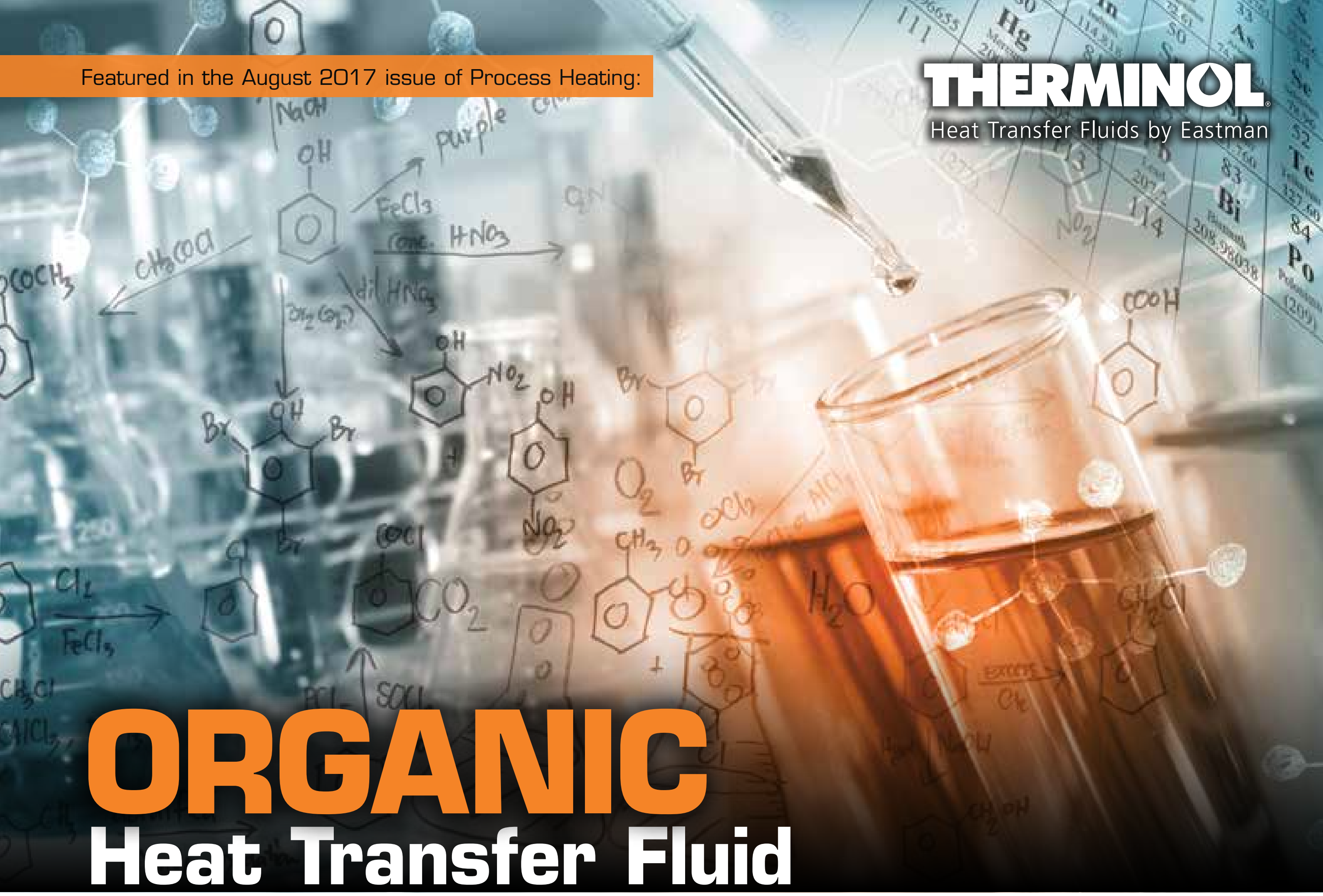
THERMINOL
Heat Transfer Fluids by Eastman



ORGANIC Heat Transfer Fluid Oxidation and Its Prevention

To evaluate oxidation response of various commercially available heat transfer fluids, an oxidation stress test was developed to compare one synthetic aromatic-based heat transfer fluid with other thermic fluids.

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Heat transfer fluid (HTF) systems used in the process industry can be considered the heart of the plant. However, the heat transfer fluids are frequently taken for granted. Commonly, incomplete knowledge about operation and maintenance of heat transfer fluid, or thermic fluid, may result in premature oxidation or thermal degradation. Thermal degradation can be quantified by the percentage of low boiling and high boiling content of the fluid. It is dependent upon the selected chemistry, system design and on-stream time as well as the fluid's operating bulk and film temperatures within the heater.

In general, aromatic-based synthetic fluids are more resistant to thermal degradation than natural mineral oils, which are products of crude petroleum processing. This is apparent as no mineral oil heat transfer fluids are rated to bulk operating temperatures above 620°F (327°C). Normally, mineral oil heat transfer fluids' suitable operating temperatures are limited to 540 to 575°F (282 to 302°C). Synthetic aromatic chemistries are rated up to 750°F (400°C). This permits synthetic aromatic fluids to be used at higher temperatures and for longer durations.

Additionally, contamination and oxidation can promote fluid degradation. Recycling of leaked fluid can compromise the original fluid's service life because it may have been contaminated by foreign particles and may have been oxidized as it cooled.

Organic heat transfer fluids can vary in their response to oxidation depending upon their chemistry. The oxidation stability of organic fluids is an important factor, and it is directly proportional to the life of the fluid in open systems. Basically, this means that higher oxidative stability can result in longer fluid life. Studies have shown synthetic aromatic fluids can offer many times the resistance to the harmful effects of oxidation. In non-inerted, open-to-air expansion tank designs, oxidation will occur when the heated fluid is exposed to air (figure 1).

Many heat transfer system operators falsely believe that cold expansion tank operation can protect the heat transfer fluid from oxidation without fail. The mechanism for air introduction/oxidation into the heat transfer fluid is illustrated as follows:

- Breathing of air (containing approximate 21 percent oxygen) into the thermal expansion tank vapor space with the routine rise and fall of liquid level.
- Absorption of air into the heat transfer fluid within the expansion tank.
- Changing temperature causes volume changes of the heat transfer fluid in the system. Some air-saturated heat transfer fluid is drawn from the expansion tank into the circulation headers.
- The oxygen reacts with the heated heat transfer fluid at greater than 175°F (80°C).
- Oxidation products are formed, with solids formed being the most troublesome to system operational efficiency and system safety.

Open Vent Expansion Tank Operation

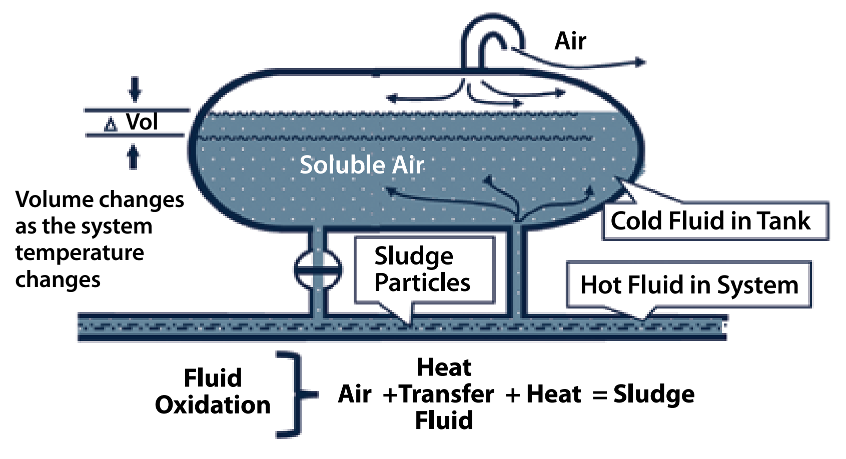

FIGURE 1. In non-inerted, open-to-air expansion tank design, oxidation will occur when the heated fluid is exposed to air.

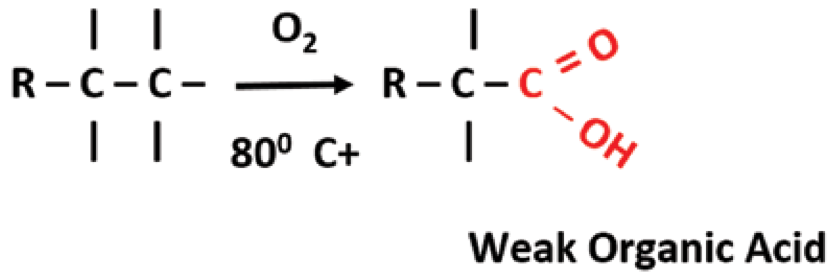

FIGURE 2. The oxidation process is a conversion of hydrocarbons into weak organic acids.

Organic heat transfer fluids will have increasing rates of oxidation as the temperature of the fluid in non-inerted expansion tank increases above 175°F (80°C). The rate of oxidation will accelerate with increasing temperature and duration, and the use of the heat transfer fluid is correspondingly shortened. This can be significantly affected by turbulence within the expansion tank, which increases the intimacy of fluid and air mixing.

The oxidation process is a conversion of hydrocarbons into weak organic acids (figure 2). It is worsened with increasing unsaturation of the fluid.

A key consequence is the formation of polymerization products — or high boilers — is that they can precipitate as sludge/solids. As long as these oxidation products are in solution, there might be an increase in viscosity, which decreases attainable heat transfer coefficients. The weak organic acids produce higher total acid number (TAN), thus leading to increasing rates of corrosion of carbon steel plant equipment, pipelines and, especially, fired heater coils that are exposed to higher thermal stressing. Excess moisture, when combined with higher TAN, is known to further accelerate erosion and corrosion, which can result in failure of heat exchanger tubes, radiator or heater coils, reactor jackets and so on. Ultimately, oxidation not only shortens the fluid life and equipment life, but it can also reduce the effective run time of the process.

To evaluate oxidation response of various commercially available heat transfer fluids, an oxidation stress test was developed under repeated and reproducible conditions. Test apparatus, which could be representative of an actual expansion tank, was developed with controlled temperature and controlled airflow rate over the test fluid surface to accelerate the oxidative stressing. Neutralization number (total acid number) and insoluble solids (filterable solids in 100 ml of test fluid) were measured to evaluate the oxidation resistance of various heat transfer fluids. Other criteria measured include changes in fluid viscosity, corrosion test specimen weight, physical observations and high and low boilers. In the test, it was shown that mineral-based heat transfer fluids were almost solidified due to extreme viscosity that rendered them unpumpable at designed coldest ambient temperatures. The synthetic aromatic-based heat transfer fluid exhibited a smaller observed viscosity increase. Likewise, test tubes used for mineral oil heat transfer fluids were observed to be severely fouled. Such fouled insoluble solids tend to deposit on heat exchange surfaces and subsequently reduce heat transfer effi-

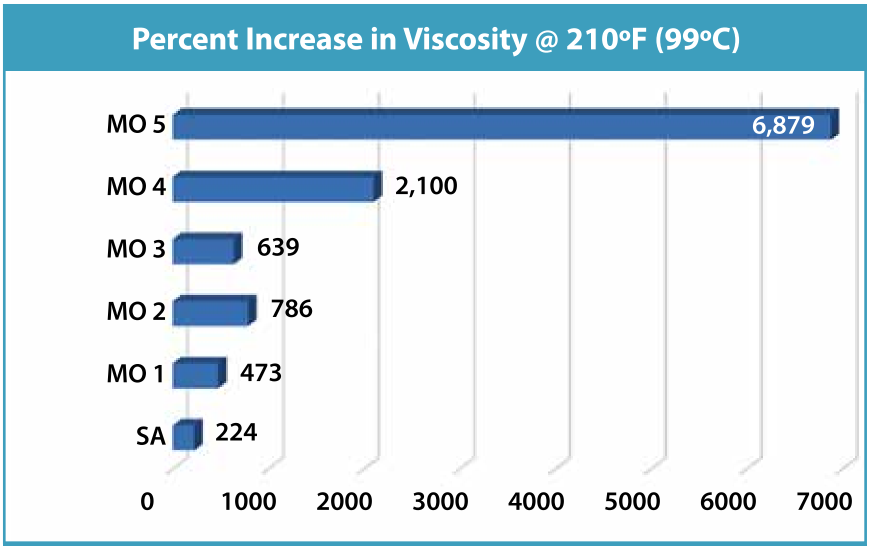

FIGURE 3. The percentage increase in kinematic viscosity of test fluids subjected to oxidation stress testing is depicted here.

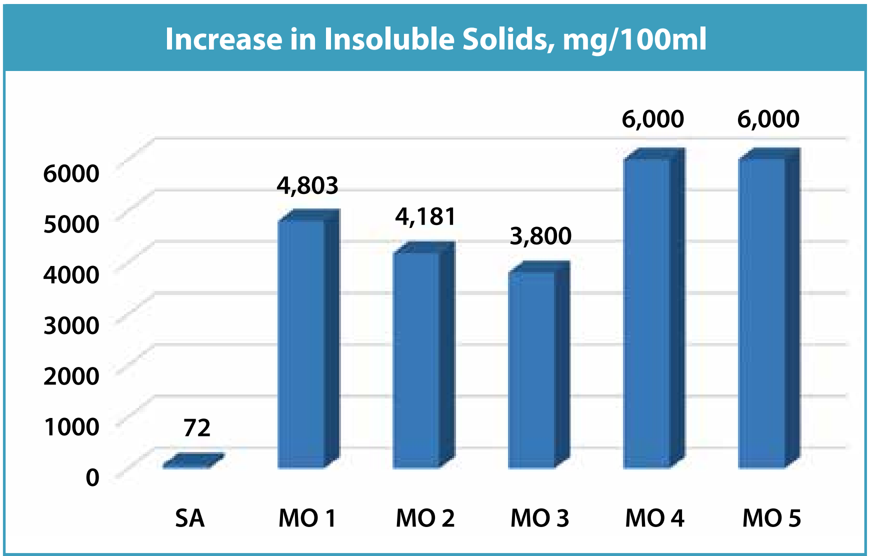

FIGURE 4. Demonstrated in this chart is the increase in insoluble solids content of fluids subjected to oxidation stress test conditions.

ciency of the system. Physical inspection of the synthetic aromatic-based heat transfer fluid test tube showed mild staining.

Graphical presentation of oxidation stress test analysis results is given in figures 3 and 4. Oxidized synthetic aromatic heat transfer fluid, although reported higher in total acid number (TAN), showed a negligible increase in insoluble solids. Mineral-based heat transfer fluids reported insoluble solids in excess of the in-service action limit of 400 mg/100 ml. Most of the mineral oils reported higher percentage increases in kinematic viscosity at 210°F (99°C) and also reported higher percentages of net high boilers increase compare to the synthetic aromatic-based heat transfer fluid.

To conclude, mineral oil heat transfer fluids tested produced more sludge than the synthetic aromatic-based heat transfer fluid tested. The sludge can produce pipe plugging, seal wear and fouling of heat exchange surfaces in heat transfer systems.

The mineral oil heat transfer fluids tested were tars at room temperature. Viscosity measurements were conducted at 210°F (99°C) to make comparisons to the synthetic aromatic-based sample. At room temperature, the synthetic aromatic-based heat transfer fluid had nearly three times its new viscosity and would be pumpable during system startups.

The corrosion rate of metal test specimens for all fluids tested was less than 1 mil/year, which is considered a mild corrosion rate. This should not cause significant system problems.

The synthetic aromatic-based heat transfer fluid contained more acidic degradation compounds than each of the mineral oil heat transfer fluids tested. The acids generated are weak. Results suggest that acids produced in mineral oil heat transfer fluids precipitate as solids quickly due to their lower solubility.

An effective method of inhibiting fluid oxidation is to blanket the expansion tank with an inert gas such as nitrogen or carbon dioxide, or with natural gas. The purpose of inert gas blanketing is to maintain an oxygen-free atmosphere in the expansion tank, and one of positive pressure to prevent air entry. A regulated supply of inert gas with a backpressure regulator on the vent outlet line is necessary to obtain this protection. A pressure relief valve also is required to protect the expansion tank from overpressure due to regulator failure, fire and other causes. Only a static pad of pressure is needed inside the expansion tank to minimize inert gas usage. Maintaining a positive pressure slightly over atmospheric barometric pressure is all that is necessary to prevent air and moisture from entering the tank. A manual vent valve also should be installed for routine fluid maintenance by removing low boilers as needed. ✲

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