Defining Thermal Stability

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Understanding maximum temperature ratings and the affects of fluid degradation can help you select a heat transfer fluid with adequate thermal stability.

Thermal fluid systems are used in many industries. Despite different system operating parameters, users share a common desire for optimal fluid life, a factor largely determined by thermal stability. A proper understanding of fluid thermal stability, including determining maximum fluid temperature ratings and the effects of fluid degradation, is important when selecting a heat transfer fluid to achieve reliable heat transfer system performance.

A number of heat transfer fluid chemistries are available. Every heat transfer fluid manufacturer assigns a maximum use temperature to each fluid. This maximum use temperature is determined primarily by the heat transfer fluid's thermal stability. Thermal stability is defined as the ability of a fluid to resist breaking down under heat stress. As such, the maximum use temperature is the suggested maximum temperature to which the fluid can be heated before the fluid begins to break down or degrade at an appreciable rate. A heat transfer fluid with high thermal stability will degrade less than a fluid with low thermal stability and will deliver a longer fluid life than a less stable fluid.

Thermal fluid degradation occurs when enough heat is applied to the fluid to cause the breaking of molecular bonds, which results in a change in the fluid's physical properties. The first products resulting from this thermal cracking are lower in molecular weight and commonly are known as low boilers. High boilers also can be generated when some low boilers recombine to produce higher molecular weight materials. The relative amounts of low and high boiling degradation products vary depending on the fluid chemistry.

BULK, FILM TEMPERATURES

Maximum bulk temperature is the fluid's highest average temperature and usually occurs at the exit of the fluid heater. As a rule of thumb, the rate of thermal degradation will approximately double for every 18ºF (10ºC) increase in the bulk fluid temperature. Therefore, the fluid's life will be cut in half by operating 18ºF (10ºC) above the maximum rate bulk temperature. Similarly, lowering the temperature 18ºF (10ºC) will cut the rate of degradation in half. Given that relatively small changes in temperature can have such a large effect on fluid life at elevated temperatures, one can see why accurately determining the thermal stability limit for a fluid is important.

Film temperature also is an important component of the thermal degradation rate. Maximum film temperature is the highest temperature a fluid experiences in the system. Maximum film temperature normally is found adjacent to the pipe wall at the heating

surface, and typically it is 30 to 60ºF (15 to 30ºC) higher than the bulk fluid temperature. In typical systems, between 15 and 25% of the total fluid degradation that takes place occurs in the film region.

HOW DEGRADATION AFFECTS SYSTEM OPERATION

Both low and high boiling degradation products create an unfavorable environment for efficient heat transfer system operation. Low boiling components can affect system operation in several ways. First, when present in significant quantities, low boilers can lead to pump cavitation. The more volatile nature of the low boilers results in higher heat transfer fluid vapor pressure, which in turn reduces the net positive suction head (NPSH) available at the circulation pump. Severe cases may cause damage to pump seals and, if allowed to continue uncorrected, can damage impellers.

Second, when low boilers are present in excessive concentrations, the heat transfer fluid flashpoint may be lowered. Occasionally, flashpoints below 100ºF (38ºC) have been measured in samples of in-service fluids. Most heat transfer fluid systems are not designed for such low flashpoints. Operating safety may be compromised by such severe flashpoint depression.

Third, the increased fluid vapor pressure resulting from the presence of low boiling components can cause premature and unexpected pressure relief and venting. Should this occur, the increased system pressure would be due to the higher vapor pressure resulting from the presence of low boiling components. The increased system pressure also may cause premature and unexpected pressure relief and venting.

Finally, excessively rapid formation of low boilers will result in unacceptably high fluid makeup costs as the low boilers removed from the system are replaced with fresh fluid.

The presence of high boilers can increase heat transfer fluid viscosity, which will affect the fluid's pumpability at low temperatures and the system's heat transfer efficiency. Unlike low boilers, high boiling compounds cannot be removed from the system easily once they are formed. Hence, high boilers continue to accumulate until the maximum recommended concentrations are reached, thereby signaling the end of the recommended fluid life. If high boiler concentrations are allowed to accumulate beyond that point, sludges and tar deposits can form as the solubility limits for the higher molecular weight compounds are exceeded. One extreme case of sludge formation in a mineral oil system resulted in reduced flow rate to the users. Added costs of operation as a result of these sludge deposit included downtime, repairs, clean-out and lost production.

ACCURATE TEMPERATURE RATING

Obviously, less than adequate thermal stability will result in high rates of fluid degradation and can have a significant effect on both system reliability and overall operation cost. If the maximum temperature rating is overly optimistic, unreasonable degradation rates will occur. This results in increased cost and less efficient system performance than would be experienced if the user chose a fluid that more closely met the system requirements.

Unfortunately, no industry standard method exists for testing thermal stability or establishing a maximum recommended temperature for a heat transfer fluid. Some manufacturers may establish maximum recommended temperature ratings to deliver a 10-year operating life while other suppliers employ different criteria. Furthermore, techniques for analyzing thermally stressed samples vary greatly and can cause confusion when users are presented with apparently conflicting thermal stability claims.

MEASURING THERMAL STABILITY

The thermal degradation rate is dependent upon fluid temperature. At higher temperatures, the energy required to break chemical bonds is more readily available. This yields higher degradation rates. Graph 1 shows typical degradation curve for one high temperature heat transfer fluid.

Thermal stability data is developed for each fluid chemistry in two ways. Compounds first are screened in laboratory ampoule tests. Then, the most promising candidates are installed in actual operating systems to demonstrate their performance.

For laboratory testing, a small amount of heat transfer fluid is placed in a stainless steel ampoule. The ampoule is purged with an inert gas and then held at a constant elevated

temperature for a prescribed time. After heat stressing, the fluid is analyzed using gas chromatography to measure the chemical changes caused by exposure to the elevated temperatures. Ampoule tests are repeated at various temperatures and lengths of time. From this data, a thermal stability curve comparing thermal degradation rate vs. temperature can be created. Properly interpreted, this data can be used to provide guidance in establishing the recommended maximum operating temperature for a heat transfer fluid.

Laboratory testing takes place in an idealized environment where temperatures are well controlled, equipment is clean, and abnormal operating conditions are eliminated. The real world, however, is not quite as controlled; temperatures vary, thermal fluid systems are started and stopped, and fluids may come in contact with air. For these and many other reasons, laboratory tests only can provide guidance about a fluid's maximum temperature rating. Years of real-world testing and actual customer performance are required to validate the tentative conclusions reached in the laboratory and designate a maximum temperature rating with confidence.

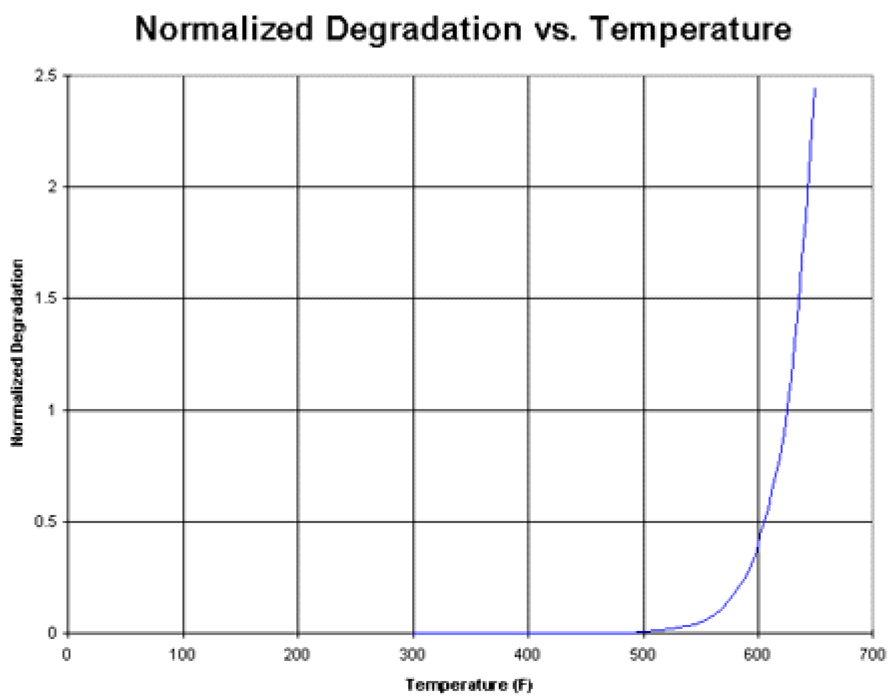
MANAGING THERMAL DEGRADATION

An engineer's goal is to provide a system design that meets the process requirements while providing reliable, cost-effective operation. Protecting the heat transfer fluid from excessive thermal stress will contribute to this goal. Whether the primary heat input source is a fuel-fired heater or a process heat recovery unit, effects of stress to the fluid can be minimized in several ways.

- Select a fluid suitable for the maximum design temperatures so that the thermal degradation rate is maintained at an acceptable level.
- Design the fluid heater and auxiliaries to prevent excessive film temperatures.
- Ensure the fluid is always flowing when the heater is firing. Fluid temperature limits easily can be exceeded in stopped-flow situations.
- Consider using synthetic fluids. Most synthetic fluids have superior solubility characteristics compared to mineral oils.
- Design the expansion tank to permit periodic, controlled venting of low boiling compounds.

Proper management of thermal degradation products requires knowledge of the fluid condition. Fluid analysis should be a normal practice for every system. In a typical system, the thermal fluid should be sampled yearly. Users should note that analytical methods for heat transfer fluids are distinctly different from those applied to lubricating oils. Not all labs are equipped to perform these analyses in a cost-effective manner.

All heat transfer fluids degrade. The key differences among fluids are what they degrade into and how rapidly degradation occurs. Selection of the proper heat transfer fluid--one that has adequate thermal stability-can minimize the amount of thermal degradation a fluid experiences and contribute to high system reliability.



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