



HIGH TEMPERATURE FLUIDS—THERMAL STABILITY AND MAXIMUM TEMPERATURE RATINGS



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One of the most critical performance aspects of a fluid designed for high temperature service is its thermal stability. Heat transfer fluids (HTFs) are specifically engineered for high performance and exceptional thermal stability in process operations. But what exactly is thermal stability and how is it determined? How are maximum temperature ratings decided? How important is thermal stability when selecting a heat transfer fluid? How does thermal stability affect fluid lifetime and system performance? This paper seeks to answer these questions and to demystify a topic that is often misunderstood.

THE IMPORTANCE OF ACCURATE TEMPERATURE RATINGS

Thermal fluid systems are a critical component of manufacturing processes all over the world. As such, there is a commonly shared goal of optimizing thermal fluid lifetime to ensure reliability of the process. While the in-service lifetime of the fluid depends on many factors, the reliability and overall cost of operation of the heat transfer system can be directly related to the thermal stability of the fluid. Since thermal stability is proportional to temperature, it is important that temperature ratings be responsibly set by the fluid manufacturer. If maximum temperature ratings are overstated, the end user

may experience high rates of fluid degradation, excessive fluid replacement costs, inefficient processing, system downtime, mechanical component failure, and/or unsafe operating conditions. The end-user should ensure that the manufacturers temperature ratings have been set based on scientific laboratory testing, as well as real-world application performance.

WHAT IS THERMAL STABILITY?

Thermal stability can broadly be thought of as the ability of a fluid to resist irreversible changes to physical properties with changes in temperature. Thermal stability applies to both low and high temperatures, but usually high temperature stability is the focal point for thermal fluids. Thermal stability is directly related to the inherent molecular resistance to temperature induced reactions - fluids with high thermal stability have less pathways available for decomposition or molecular rearrangement vs fluids of lower thermal stability. Impurities in the fluid can also impact stability since they can provide alternative pathways to degradation. The overall thermal stability of a given fluid is therefore dependent on its chemical structure and relative purity. Fluids of high thermal stability undergo fewer physical changes vs. a fluid of lower thermal stability under identical heat-stress conditions. All heat transfer fluids will ultimately experience thermal degradation over time, but fluids of higher stability are more resistant to degradation, providing longer service lifetimes and less potential for unplanned maintenance. Depending on fluid chemistry, degradation byproducts can

vary and so the key considerations are what they degrade to, and how rapidly that degradation occurs.

THERMAL STABILITY VS. OXIDATIVE STABILITY

In many industries, the term thermo-oxidative stability, or more concisely oxidative stability, is often referenced, but it is important to note that thermal stability is strictly different than oxidative stability. Oxidation stability refers to the fluid's resistance to physiochemical changes due to reaction with oxygen in the air. Industrial fluids such as lubricants are formulated to resist oxidation with the addition of antioxidants and other additives which mitigate the oxidation chain reaction. Conversely, thermal stability refers strictly to the inherent stability of the fluid to changes in temperature in the absence of oxygen. Since thermal stability is dependent on chemical structure, there are no additives in the traditional sense that can "strengthen" molecular bonds and improve thermal stability. In fact, many of the additives commonly used in formulating industrial oils are not stable to the high temperatures often seen in heat transfer systems and can be detrimental to the performance and reliability of the fluid. Fluids explicitly engineered for heat transfer service have been thoroughly assessed for extreme temperature performance and will always be backed by full thermo-physical property data over the recommended operating range.

DETERMINATION OF THERMAL STABILITY

While there is no globally accepted industry standard for measuring thermal stability of heat transfer fluids, many regional variations do exist. For years, most heat transfer fluid manufacturers

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have trusted laboratory ampoule testing to determine thermal stability. In North America the commonly referenced method is ASTM D6743. In this test, a small fluid sample is placed in a steel ampoule designed for high temperatures and pressures. The ampoule is purged with nitrogen to remove air and moisture. It is then sealed and held continuously at high temperatures for a set amount of time (usually 500-1,000hrs). Degradation is measured using gas chromatography and flash distillation to quantify degradation products formed under thermal stress. A fluid of high thermal stability will form less degradation byproducts during the test interval, while a fluid of low thermal stability will form more degradation byproducts. Since thermal degradation rate is directly proportional to temperature, thermal stability testing should be performed at various temperatures and a stability curve should be established to understand degradation trends. When properly interpreted, the stability curve is a great guide for what to expect in the field. However, laboratory testing takes place in a controlled environment and cannot account for real-life process variations. Real systems are often shut down and restarted, may experience unexpected temperature excursions, or can be exposed to process contaminants. Therefore, care must be taken to validate laboratory results with real field performance.

The technique of these laboratory tests is also quite important. The test must take place in the absence of moisture and oxygen since they can react and interfere with the interpretation of results. Inadequate purging of the test cells has been known to cause unexpected results and can nullify the experiment. It is also critical that the temperature be uniform during the test interval – minor temperature excursions can have significant effects on degradation.

MAXIMUM TEMPERATURE RATINGS

Every heat-transfer-fluid product bulletin shows a maximum recommended bulk operating temperature and/or a maximum recommended film temperature¹. The maximum bulk temperature refers to the temperature of the fluid as it exits the heater. The maximum film temperature refers to the fluid temperature in the boundary layer — a thin, relatively stagnant film of fluid — at the heating surface and is considered the highest temperature the fluid will experience in the system. In a typical, well-designed system, the film temperature is conventionally estimated to be 40-50°F higher than the bulk temperature². Most production-scale systems have approximately 1% of the total fluid volume in the film layer at any given time. If the temperature of this fluid film exceeds the maximum recommended film temperature, the molecular bonds of the fluid start to break apart (“crack”) and degradation byproducts are formed.

It is important to note that most heaters have an average and a maximum film temperature. If the heater has uniform heat flux, the maximum film temperature will closely track the average. However, most fired heater designs have a radiant section with a higher heat flux leading to higher film temperatures. Therefore, even if the average heat flux of the heater is below the stated maximum film temperature of the fluid, degradation can still occur in localized “hot spots”.

The user should be aware that there are no global standards or regulations on setting maximum temperature ratings for heat transfer fluids and there are many possible methods for determining thermal stability. Some fluid manufacturers set maximum fluid temperatures to coincide with a 5 or 10-year working life, while others may set them based on laboratory ampoule testing, field performance or other criteria. Some fluid suppliers not specializing in heat transfer may set temperature ratings for competitive purposes, with no “real” data to substantiate their claims. Since small temperature changes can have a big impact on fluid lifetime, it is critical that fluid manufacturers set maximum temperature ratings based on as many data points as possible. Data points should include laboratory testing as well as real world performance evaluations. Operation at or near the stated maximum temperature should ensure that rapid degradation of the fluid is minimized.

¹ If a heat transfer fluid data sheet does not contain this information, it is not explicitly designed for heat transfer service and should be avoided.

² Almost all fired heaters have a radiant section which can have a much higher heat flux. Depending on the fired-heater design, temperature differences between bulk and film temperatures can be as high as 100°F.

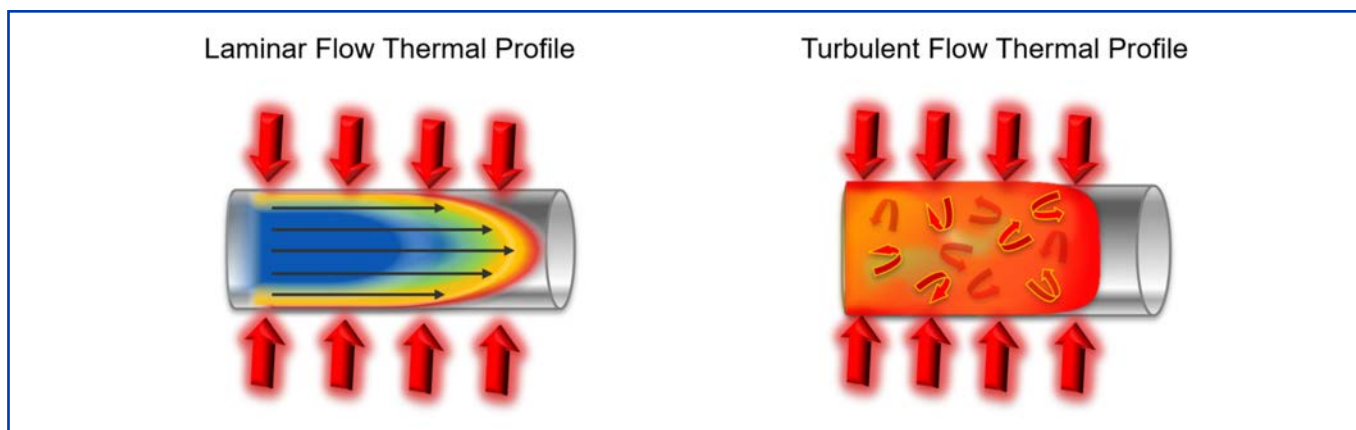


Figure 1: The effects of laminar vs. turbulent flow. At system start-up, the fluid is in laminar flow and the velocity and temperature gradients are at a maximum as is the boundary layer film thickness. As turbulent flow is established, the velocity profile approaches unity, and the temperature gradient is reduced, lowering the film temperature. Turbulent flow is necessary for efficient thermal diffusion when using hydrocarbon-based heat transfer fluids.

Since there are many methodologies for determining stability and varying interpretations of test results, the user may find conflicting stability claims from different fluid manufacturers. For this reason, it is best to choose a knowledgeable and established heat transfer fluid provider who can substantiate performance and stability claims.

FLUID DEGRADATION AND SYSTEM IMPACT

Heat transfer fluids are typically mixtures of specific chemical structures and this structural composition determines the overall thermal stability. Under normal process conditions, there exists a finite quantity of molecules that have achieved sufficient activation energy for degradation to proceed. The higher the process temperatures, the more molecules have sufficient energy to degrade. When degradation does occur, the byproducts that are formed are typically classified as “low boilers” or “high boilers”.

Low boilers are the fragments of molecular scission that are lower in molecular weight vs. the parent fluid. These fragments are of lower viscosity and are more volatile. As low boilers accumulate, fluid viscosity will drop, and vapor pressure will increase. These physical changes to the fluid can be detrimental to system

performance resulting in decreased thermal efficiency, pump cavitation or unexpected venting/pressure relief. Excessive accumulation of low boilers can ultimately damage pump impellers and can create an operational safety hazard due to depressed flash point. Rapid formation of low boilers will also result in high fluid makeup costs since low boilers must be removed from the system and replaced with new fluid.

High boilers are degradation byproducts with a higher boiling point than the parent fluid. High boilers are typically formed when low boilers recombine or polymerize into higher molecular weight fragments. Unlike low boilers, high boilers



Figure 2: Excessive thermal degradation can lead to hard carbon deposits.

cannot be removed from the system with controlled venting, and the only solution for reducing them is fluid replacement. As high boilers accumulate, fluid viscosity can increase significantly affecting fluid pumpability and heat transfer efficiency. Depending on the fluid chemistry, high boilers can remain largely soluble in the parent fluid. Once

solubility limits are exceeded, excessive high boiler accumulation can lead to coking, sludge and tar deposits which can lead to costly system clean-outs and lost production. In general, once high boilers reach 10% concentration, the fluid should be replaced.

STRUCTURE-STABILITY RELATIONSHIP Hydrocarbon HTFs consist of two main fluid classes – mineral oils and synthetic aromatic oils. Mineral oil-based HTFs (AKA “hot oils”) are those formulated directly from refined petroleum fractions. Mineral oil fluids contain a broad distribution of hydrocarbons. Depending on the crude source, the distribution will include varying concentrations of paraffins, isoparaffins, naphthenes, substituted aromatics and polyaromatics. The American Petroleum Institute (API) classifies petroleum base oils into 3 groups:

- Group I – Base oils containing less than 90% saturated hydrocarbons and/or more than 0.03% sulfur
- Group II & III - Base oils containing a minimum of 90% saturated hydrocarbons and maximum 0.03% sulfur

Since Group I fluids contain higher levels of unsaturates and sulfur/nitrogen impurities versus group II and III, they are generally inferior in terms of thermal stability and fouling potential. Reducing the impurities and increasing the saturates content leads to more thermally stable fluids. For this reason, highly refined Group II and III mineral oils are the preferred base for formulating fluids for operation up to 550°F (288°C). The most highly stable mineral oil-based fluids are usually categorized as “white oils” and depending on the composition, may be suitable for temperatures up to 615°F (324°C).

SYNTHETIC HTF’S In heat transfer, synthetic fluids are also referred to as “aromatics” since they are benzene-derived chemistries. Benzene is well known to exhibit exceptional stability due to the chemical concept of resonance. In chemistry, resonance is a term that describes delocalized electron density, and this delocalization of electrons hinders reactivity, making it difficult to break and form chemical bonds with benzene (i.e. more energy is required to physically alter the molecule and therefore aromatic fluids are more resistant to structural changes with temperature vs. mineral oil-based fluids). While benzene is not used in heat transfer, benzene derivatives are, and the resonance concept extends to those chemistries. Synthetic aromatics have been used for high temperature heat transfer service for decades, and several products exist with varying physical properties. Specialized suppliers are usually preferred for these chemistries, which include hydrogenated terphenyls, alkylated diphenyls, aryl ethers, diphenyl oxide/diphenyl blends and more. Depending on the chemistry, these fluids can be suitable for operation up to 750°F (400°C).

MANAGING DEGRADATION

While thermal degradation is ultimately inevitable, protecting the heat transfer fluid from rapid deterioration will lead to a more reliable and cost-efficient process. As such, there are several considerations for reducing thermal stress to the fluid:

- Specify a heat transfer fluid that can handle the maximum design temperatures of the process. This is the most important step in ensuring that the rate of thermal degradation is minimized.
- For new systems, choose a process heater that minimizes excessive film temperatures. Helical coil and serpentine-style heaters are generally best in this regard.
- Ensure that the design flow rate of the heater is always maintained. Most heaters are equipped with a low-flow interlock that will shut down the heater to prevent overheating of the fluid.
- Follow the heater OEM and fluid manufacturers recommendations for system start-up and shutdown procedures. Failure to do so can result in excessive film temperatures and rapid degradation.
- Follow all recommended preventative maintenance schedules as outlined by heater and component OEM's.
- Mitigate oxidation by blanketing the system with an inert gas such as nitrogen. While not directly related to thermal stability, oxidation is exacerbated at higher temperatures and can lead to many other operational issues.
- Design the expansion tank such that low boiling compounds can be safely vented from the system.
- Perform analysis of the fluid at least once per year.

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STABILITY MATTERS

The thermal stability of the heat transfer fluid chosen for a given application is one of the most important parameters in the fluid selection process. Many fluid chemistries are available for different temperature ranges. Since there are no global standards or regulations on how maximum temperature ratings are assigned, it is the responsibility of fluid manufacturers to specify maximum temperature ratings in accordance with the anticipated thermal stability of the fluid. The stability of the fluid should be determined using a combination of scientific laboratory testing as well as established performance in the field. Even properly specified fluids will degrade over time in well-designed systems. Accumulated degradation by-products can have catastrophic effects on equipment, operational safety, and production output. Routine condition monitoring of the fluid allows for proactive management of fluid degradation to prevent catastrophic system failure. Users should be aware that the analytical tests for heat transfer fluids are different than those employed for lubricant analysis. For proper condition monitoring, the user should work directly with the fluid manufacturer to perform the required testing for heat transfer fluids and to ensure that the results are appropriately baselined to new fluid values. Thermal stability is an essential parameter of the fluid — the lifetime and overall reliability of the heat transfer fluid is maximized when it is properly matched to the process requirements and degradation is routinely monitored and managed.

Further Reading

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Founded in 1988, Paratherm—Heat Transfer Fluids has become a leading U.S. manufacturer of specialized heat transfer fluids and system cleaners. The firm offers a wide range of heat transfer fluids (currently 8 fluids and 3 cleaners) covering temperatures from -137°F to +650°F. The company has a network of distributors and warehousing locations throughout North America and globally to offer regional service and quick delivery.

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