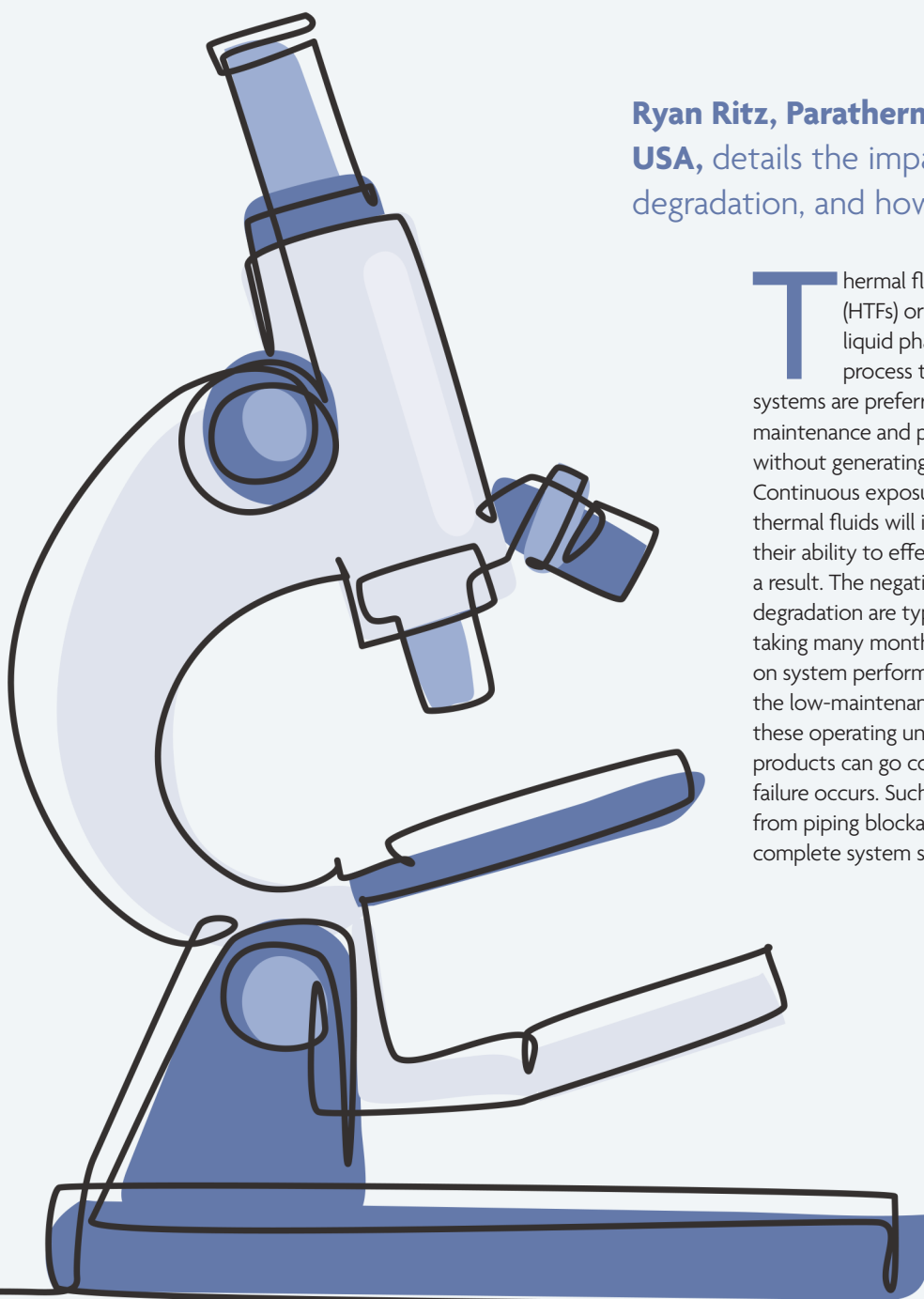


# A closer look at thermal fluid degradation

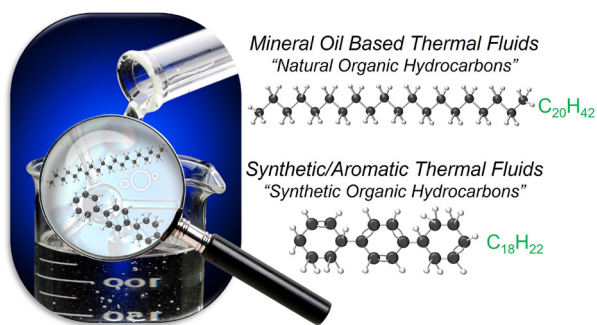
**Ryan Ritz, Paratherm Heat Transfer Fluids, USA,** details the impacts of thermal fluid degradation, and how this can be prevented.

**T**hermal fluids, also called heat transfer fluids (HTFs) or hot oils, have been widely used in liquid phase circulating systems to control process temperatures for decades. These systems are preferred because they are relatively low maintenance and provide consistent, efficient heating without generating high operating pressures. Continuous exposure to high temperatures means that thermal fluids will inevitably degrade over time, and their ability to effectively transfer heat will diminish as a result. The negative effects of this type of degradation are typically slow to transpire, often taking many months or even years before their impact on system performance becomes evident. Because of the low-maintenance 'set it and forget it' nature of these operating units, any build-up of degradation products can go completely unnoticed until a major failure occurs. Such failures are not inconsequential – from piping blockages and fluid leaks at a minimum, to complete system shutdowns, fires and bodily harm at



an extreme. This presents obvious challenges to the coveted values of predictability and damage control in plant maintenance operations.

To overcome these challenges, plant stakeholders need to prioritise gaining a greater upfront understanding of thermal fluid operations and the impacts of fluid degradation. What makes a thermal fluid uniquely capable of serving its purpose relative to any other industrial oils being used at the



**Figure 1.** Molecular structures of hydrocarbon-based thermal fluids.



**Figure 2.** Thermal fluid sludge.



**Figure 3.** Severe build-up of solid carbon.

facility? How does fluid degradation occur? What are the products of degradation and where in the system are they most likely to be generated? How can we identify the occurrence of thermal breakdown and track its effect on fluid performance? A deeper appreciation of the what, how, where and when will create confidence in running an efficient, predictable heat transfer operation without diminishing the low maintenance advantages that these systems are designed to provide. With this goal in mind, this article will focus in on the critical aspects of thermal fluid degradation.

## A closer look at degradation dynamics

Thermal fluid degradation can be defined as the irreversible decomposition of a fluid as a result of thermal stress and/or prolonged contact with oxygen at elevated temperatures. Exposure to heat energy over time alters the inherent molecular structures of the fluid, ultimately resulting in substantial changes to its physical and physiochemical properties. The resulting accumulation of degradation products due to these reactions leads to critical disruptions in fluid performance, working life and equipment functionality. There are two main modes of fluid degradation: thermal cracking (overheating) and oxidation, both of which occur as reaction mechanisms and are therefore subject to the well-established principles of thermodynamics, reaction rates, and thermophysical property correlations.

## Thermal fluid chemistry

The majority of industrial heat transfer products are formulated using hydrocarbon-based chemistries. Because degradation reactions occur at the molecular scale, it helps to understand the chemistry of the fluids from that perspective. Figure 1 provides visual representations of two common molecular structures seen in both natural organic hydrocarbon (mineral oil) and synthetic organic hydrocarbon (synthetic/aromatic) based thermal fluids. Specific molecular arrangements of the various hydrocarbon-based fluid types will determine performance, reaction dynamics, and degradation products.

Mineral oil based thermal fluids (natural organic hydrocarbons) are a product of petroleum distillation and are made up of a ratio of refined alkanes (paraffins) and cycloalkanes (naphthenes) with a targeted array of chain lengths and arrangements. To avoid confusion, Figure 1 is simply showcasing the alkane  $C_{20}H_{42}$  as just one example of a hydrocarbon chain that could be found within the bulk distribution of a mineral oil fluid. Synthetic aromatic hydrocarbons are products of chemical synthesis, and feature ring structures with some degree of double bonding. The chemical composition of each fluid type can be directly correlated to how they will behave in a thermal operation – both in terms of performance, and the manner in which they will degrade.

Truly legitimate thermal fluids are specifically engineered to prioritise quality, heat transfer efficiency, and thermal stability. Impurities and/or superfluous additives will foul out when exposed to heat, and can catalyse degradation reactions. The selective balance of physical properties determines how efficient a fluid will be at transferring heat

energy from the heat source into the fluid, and then out into the operating units. Products formulated using a foundation of robust chemistries will be more resistant to thermal degradation at elevated temperatures.

## Degradation products

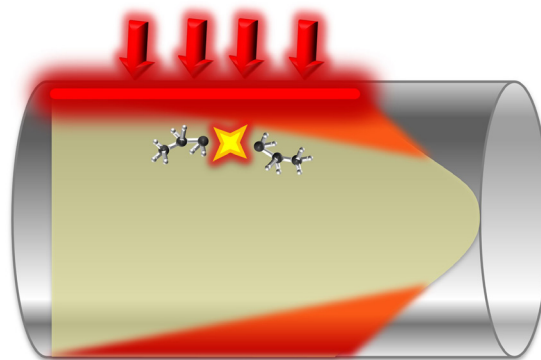
The degradation products that are most commonly generated as a result of thermal cracking and oxidation are the following:

- Low boilers: molecules generated when hydrocarbon chains are broken into smaller fractions that have boiling points lower than the original distribution of fluid molecules. An increase in low boilers generally results in decreased fluid viscosity.
- High boilers: molecules generated when hydrocarbon chains are broken and subsequently reacted with other molecules to create products that have boiling points higher than the original distribution of fluid molecules. Increased high boilers will typically lead to increased fluid viscosity.
- Thermal fluid sludge (see Figure 2): a highly viscous, acidic, tar-like material generated as a result of oxidised fluid combining with solid carbon particles.
- Solid carbon (see Figure 3): a product of ongoing cracking of hydrocarbons into elemental carbon. This can be in the form of suspended fine carbon soot (darkening the appearance of the bulk fluid), larger solid particles, and as a carbon 'shell' fouled onto equipment surfaces.
- Contaminants: high concentrations of additives and/or natural impurities from inferior refinement of raw materials will typically foul out of the bulk fluid far before normal degradation factors come into play. Residual degradation products remaining in a system after fluid changeout are also considered contaminants, and can accelerate degradation reactions in the new fluid charge.

All degradation products will have a negative effect on the performance of the thermal fluid in some way. Low boilers typically contribute to decreased thermal capacity and can cause pressure fluctuations, pump cavitations, and other operating challenges. Solids can block lines and foul equipment surfaces, creating an insulating layer between the heat source and the thermal fluid. Sludge and other high boiling materials will limit fluid flow, plug lines, and can completely solidify or 'gel up' when system temperatures drop. Degradation over time is inevitable, but understanding the factors that lead to more serious consequences helps to minimise the rate at which it happens.

## Focus on the factors: thermal cracking (overheating)

At the most basic level, thermal fluids are designed to perform a somewhat complicated series of tasks. Energy in the form of heat is transferred from the heating source (fired heater, electric immersion element, etc.) through a conductive surface (i.e. the wall of a pipe coil) into the bulk fluid. The fluid then needs to hold onto that energy as it flows through the piping, until it reaches the operating unit and transfers the energy into the process.



**Figure 4.** Degradation hot spot: thermal cracking at the fluid film layer.

Following the principles of the First Law of Thermodynamics, any heat energy that is not transferred out of the heater via bulk fluid movement to be consumed by the process application (or wasted out of a heat exhaust) will ultimately be consumed as energy to break fluid molecular bonds. This occurrence is known as thermal cracking or overheating of the fluid. The heat source is the area of highest energy concentration in the system and thus the primary area where fluid is most prone to thermal cracking. More specifically, thermal cracking is prevalent at the 'film layer' where the thermal fluid is in contact with the heated surface (represented in Figure 4, as the inside wall of a heated pipe coil).

Not only is the film layer the area of highest heat flux, but it is also where the fluid friction is highest and flow is restricted the most. Turbulent fluid flow is critical to allow the fluid to 'wash' the heat energy away from the pipe, into the fluid, and out of the heater. Any factor that inhibits the fluid from effectively transferring the heat energy away from the heated surfaces will lead to some degree of localised thermal cracking. Examples of limiting factors can include insufficient fluid flow set points, poor heat transfer efficiency (inherent to a poorly designed thermal fluid or due to ongoing degradation altering original fluid properties), blocked lines, fouled transfer surfaces, and improper system start-up and shutdown procedures.

Using the previous example of  $C_{20}H_{42}$  alkane representing a typical molecule in a basic paraffinic mineral oil thermal fluid, Figure 5 demonstrates that, as a result of overheating, the hydrocarbon chain is broken into smaller and smaller fractions, each with lower boiling points than the original molecule. The generated low boilers will continue to accumulate, and bulk fluid properties will change drastically as a result of cracking – diminishing heat transfer efficiency. This decrease in efficiency will eventually manifest itself as a loss of temperature output in the operation.

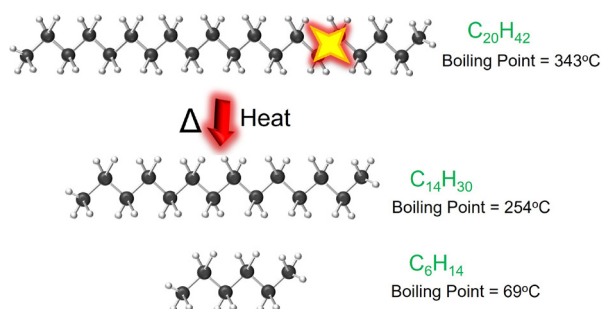
When this happens, the typical immediate reaction of a plant operator is to increase the heater outlet set point to compensate for the losses. This will only compound the problem and accelerate the degradation rate even more (the principles of the Arrhenius Equation apply to degradation, meaning every  $10^{\circ}\text{C}$  increase in temperature doubles the rate of reaction). This downward spiral of events will continue to break down the fluid more and more,

ultimately generating solid carbon and further compromising system functionality.

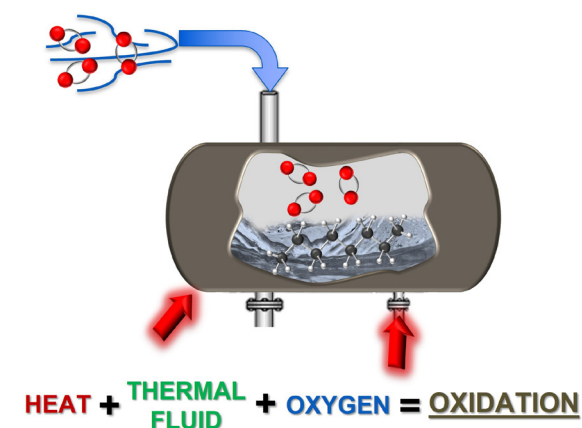
### Focus on the factors: oxidation

Oxidation is a chemical reaction that occurs when heated thermal fluid is continuously exposed to fresh air. Heat energy initiates the breaking of hydrocarbon chains, making the molecules susceptible to further reaction. When in contact with fresh air at elevated temperatures, the degraded hydrocarbons react with oxygen molecules and other stable hydrocarbons to form a variety of new highly-reactive intermediates and byproducts. In a traditional thermal fluid system, the only area that creates the potential for these factors to come together is inside of the expansion tank (see Figure 6). Continued exposure to heat and air under these conditions will perpetuate chain reactions and result in the formation of acidic material (carboxylic acid).

These acids ultimately increase the viscosity of the bulk fluid, decrease the pH, and generate high boilers. The high-viscosity, acidic material can eventually combine with any fine carbon solids that are fouled out of the fluid, and create thermal fluid sludge. Referring back to Figure 3, the negative effects of accumulated sludge in the system become obvious due to the physical nature of this material. Decreased flow dynamics, plugged lines, system cold spots, and high potential for complete system shutdown and extensive maintenance procedures are common when unchecked oxidation reaches that extreme.



**Figure 5.** Example of a thermal cracking reaction mechanism.



**Figure 6.** Degradation hot spot: oxidation occurs in the system expansion tank.

### Evolve: apply knowledge and take action

The purpose of this article was to offer a deeper understanding of how, where, when and why thermal degradation occurs. Fluid degradation over time is inevitable, but applying this knowledge to real-world operations limits the rate at which it happens, and significantly decreases the potential for unidentified issues to compound into a major failure. This knowledge is only effective if used to evolve approaches to running thermal fluid operations.

Knowing that chemistry matters, it is important to choose a fluid that is purposefully engineered to give the best combination of quality, efficiency and thermal stability. Thermal cracking at the heat source can be controlled by monitoring and maintaining design flow rates and temperature set points so that the maximum film temperature capability of the fluid is not exceeded. Fluid is most prone to overheating during system start-up and shutdown, so it is important to slowly ramp up system temperature set points until the fluid viscosity reaches a point where turbulent flow is possible (check with fluid suppliers for specifics on this). When shutting down a system, the system's circulating pump should continue to run after the heater is shut off to remove residual heat from the chamber. Otherwise, stagnant fluid will be left to 'bake' inside the pipe coils.

This article has taken a closer look at fluid oxidation, and examined exactly where it happens and under what conditions: thermal fluid + heat + air = oxidation. Additionally, it has discussed what thermal fluid sludge looks like and how detrimental it can be to a system. If the expansion tank is kept cool (ideally below 70°C), oxidation reactions cannot be accelerated. One consideration could be purging the headspace in the expansion tank with an inert gas to eliminate the presence of oxygen, removing oxidation from the equation.

### Conclusion

Operators should monitor the system, listen, look and make note of any red flags, and question changes in normal system operation, especially heat losses, pressure fluctuations and altered flow dynamics. Attempting to compensate for such changes with a simple temperature or flow adjustment will likely be a detrimental action (all it takes is a 10°C increase in set point to double the rate of degradation). Find a testing laboratory partner that specialises in thermal fluids (as opposed to a standard lube oil analysis) and send fluid samples on an annual basis. This is the most effective way to catch the generation of degradation products early enough to make informed decisions to avoid major failures. Awareness is critical to maintaining an efficient, long-lasting and predictable thermal fluid operation, and it does not take much added effort to make a big difference.