WHITE PAPER

PROLONG THE USEFUL LIFE OF HEAT TRANSFER FLUIDS IN LIQUID-PHASE SYSTEMS

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ABSTRACT

The degradation of heat transfer fluid is inevitable. What is not inevitable, however, is the time it takes for the fluid to deteriorate. This white paper explores common reasons why heat transfer fluids degrade, how to prolong their useful life, and how to maintain the peak productivity of the entire system.

Heat transfer systems are designed to carry thermal energy away from a heat source using a heat transfer fluid. Systems are designed and components are sized around the physical properties of brand-new, uncontaminated fluid. The ability of a system to maintain its designed performance depends on keeping the fluid in good, like-new condition.

The obvious challenge for operators is that the heat transfer fluid—the lifeblood of the system—will slowly degrade, which can lead to fouled surfaces where the exchange of heat occurs, thus increasing the energy required to maintain temperature, and eventually decreasing productivity. The inevitable outcome is longer downtime periods needed for maintenance, which costs a lot of money. When fluid degradation occurs, its initial properties will have changed and will continue to change as the severity of degradation increases.

The question then becomes: How to keep the system as efficient and productive as it was on the first fill, with a fluid that will degrade over time and use?

This white paper aims to answer that question. Although no expert can keep heat transfer fluid fresh forever, system operators can certainly prolong the retention of fresh fluid properties by avoiding common degradation threats and selecting a better fluid for the application.

Starting with the basics

To appreciate how to retain a fresh fluid's properties, we must first understand the system's operational threats to the fluid's efficacy.

Bulk-oil temperature versus skin-film temperature

There are two operating temperatures to consider as a fluid circulates throughout the system. Understanding these temperature differences in the heat transfer system is necessary for safe and effective system operation.

The first temperature to note is the bulk-oil temperature (T_{bulk}). This is set by the user, as the programmed temperature at which fluid is expected to exit the heat source. For example, in a furnace where the heat transfer fluid flows through a pipe surrounded by heat (as shown in Figure 1), T_{bulk} is the temperature of the oil molecules in the center of the pipe.
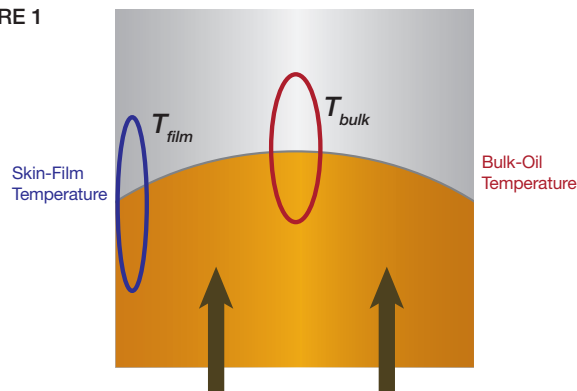
FIGURE 1

FIGURE 1: The bulk-oil temperature is the heater outlet temperature. The skin-film temperature is the fluid temperature at the pipe wall. Use the skin-film temperature, rather than the bulk-oil temperature, as the basis for selecting a heat-transfer fluid.

The second is the skin-film temperature (T_{film}). Also known as the tubeskin temperature, T_{film} is the temperature of the fluid molecules that are in contact with the pipe wall, the heating element, or any surface that separates the fluid from the source of direct heat.

In most cases, T_{film} will be higher than T_{bulk}, but the turbulent flow will try to force a redistribution of heat within the oil.

In well-designed systems—where the oil's flow rate is sufficient (i.e. high Reynolds number with strong turbulent flow) and the heat flux is reasonable (i.e. 12-16 W/in^2 in electrically heated applications)—T_{film} will be only slightly higher than T_{bulk}.

However, if a fluid has a high viscosity or the flow rate decreases (due to a pump problem or a pipe obstruction, for example), the energy required to maintain the necessary T_{bulk} will increase, and cause the T_{film} to become much higher than T_{bulk}. In this situation, a fluid operating near its rated maximum T_{bulk} may suddenly be exposed to a significantly higher skin-film temperature than it can safely tolerate, which accelerates thermal cracking (see below). More importantly, however, as T_{film} approaches the fluid's auto-ignition temperature (AIT), this could create a serious safety hazard.

The gap between skin-film and bulk-oil temperatures is affected by system parameters (e.g. pump size, heater conditions, pipe diameter, etc.); fluid properties (i.e. viscosity, density, thermal conductivity, heat capacity, etc.); and operating conditions (i.e. fluid velocity, thermal energy from the heat source, etc.).

Equipped with this knowledge, we understand the best practice is to consider selecting a heat transfer fluid based on the application's T_{film}, rather than its T_{bulk}, where possible.

Common causes for heat transfer fluid degradation

With temperature differences in mind, we can proceed with exploring the most common threats to the useful life of the fluid (and sometimes the entire system). There are three:

1. Thermal degradation
2. Oxidative degradation
3. Process or external contamination

## 1. THERMAL DEGRADATION OR THERMAL CRACKING

Regardless of the heat transfer fluid type, thermal degradation typically occurs when the fluid molecules receive more thermal energy than they can absorb and carry away at a particular time. The excess energy causes molecules to break down, or crack.

In organic-based heat transfer fluids – such as petroleum oils or chemical aromatics, for example – thermal cracking is the breaking of the covalent carbon-carbon or carbon-hydrogen bonds, which are normally very stable and need a high amount of energy to degrade. Thermal cracking involves a number of steps: initiation, hydrogen abstraction, radical decomposition, and then termination.

This type of degradation is a function of both the oil's inherent ability to absorb heat and the heat flux inside the heat source (i.e. the amount of energy the fluid receives during its residence time in the presence of heat).

Figure 2a illustrates an example of what happens to the molecule in thermal cracking; in this case, the molecule is a typical mineral-oil-based heat transfer fluid. Excess energy breaks the long hydrocarbon molecule (comprising 26 carbon atoms) into two shorter molecules of 12 and 14 carbons. These short molecules are called low boilers, because they have lower boiling points than the 26-carbon molecule. As the concentration of low boilers increases over time, the volatility (i.e. vapor pressure) of the fluid increases and that translates directly to a reduction in properties such as the flash point, fire point and possibly auto-ignition temperature.

FIGURE 2a

$C_{26}H_{54}$
Open-cup flash point: 419°F

C_{14}
Open-cup flash point: 210°F

C_{12}
Open-cup flash point: 160°F
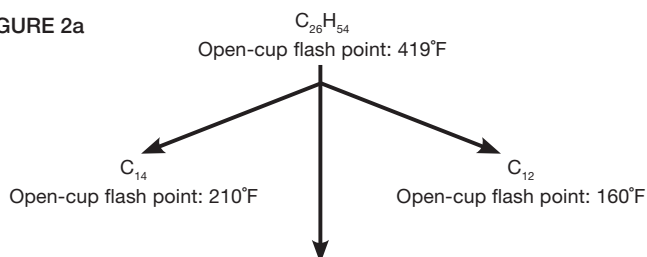
HEAVY CARBON DEPOSITS

FIGURE 2b

FIGURE 2a/b: A hydrocarbon in a mineral-based heat transfer fluid undergoes thermal degradation, which creates lighter hydrocarbons with lower viscosities and flash points, and heavy carbon deposits (FIGURE 2b).

In an open system, where the hot operating fluid is directly in contact with air, a reduction in fire point and flash point could pose a significant safety hazard, and venting or even fluid replacement will be required.

Another concern with thermal cracking is the formation of coke-like residue in the system (as shown in Figure 2). This occurs when thermal cracking forms high boilers, which are high-carbon, low-hydrogen molecules that can polymerize or agglomerate. As these coke-like molecules grow in size and accumulate, it can deposit in the system to obstruct lines and elbows. An abrasive and carbonaceous-type residue can damage pump seals. In systems with electrical heat, the residues will coat the electrical elements; in a furnace, they will form layers inside the heater coil. In both cases, this will act as an insulator.

The residue becomes a problem when the heater, set to a certain temperature, must then produce more thermal energy to pass through not only the pipe wall, but also the carbonaceous layer to get to the fluid. The additional heat raises the T_{film} of the system, causing the gap between T_{film} and T_{bulk} to widen. This creates a cycle of thermal degradation (see Figure 3), where excessive heat causes thermal cracking of the heat transfer fluid, which causes formation of high boilers and build-up of residues on heating surfaces, which in turn forces the heater to produce more energy to maintain the fluid's T_{bulk}.

FIGURE 3

Excessive heat (energy) causes thermal cracking

Heat-transfer surfaces get fouled with residues

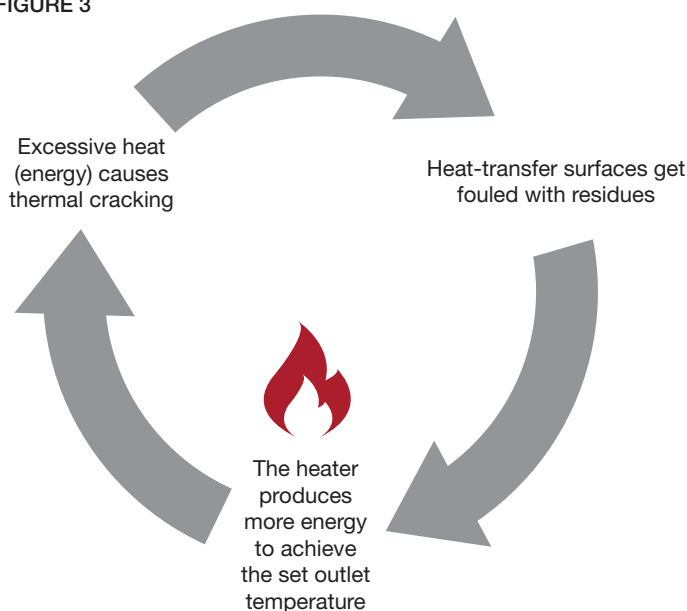The heater produces more energy to achieve the set outlet temperature

FIGURE 3: Thermal cracking of the heat transfer fluid that occurs at the heat source can create high boilers – long molecules that agglomerate and bake on the hot surface of the heat source or pipe wall. Over time, the carbonaceous residue forms a layer on the heat source that acts as an insulator. The heater must then produce more energy to raise the temperature of the fluid to the setpoint temperature, which in turn causes more thermal cracking. Thus, a cycle of thermal degradation occurs.

Even when systems operate at temperatures that are considered relatively mild (well below the fluid's maximum rated bulk-oil temperature), the fluid is not exempt from thermally degrading, thus shortening its useful life.

Addressing thermal cracking

Use the right fluid. Choose a heat transfer fluid with high thermal stability. Petroleum-based fluids formulated with severely hydrotreated white oils, for example, have greater thermal stability when compared to traditional mineral oils. Most problems associated with localized or temporary temperature excursion are preventable.

Vent properly. Venting allows operators to release light, volatile hydrocarbons that are formed during thermal cracking out of the fluid and the system. In most systems of a certain volume, the evacuation of low boilers is done by circulating some of the hot fluid to the expansion reservoir, so that the molecules with a high vapor pressure can naturally migrate into the gas phase and exit the fluid. Depending on the system design, the vapors can then be released into the atmosphere, or condensed and collected into a drum or tank and disposed of in accordance with local regulations.

Fresh fluid will need to be added to maintain the fluid level after venting. The safe addition of fresh fluid must never be added directly into the hot oil stream, but rather into the expansion tank or other cool reservoirs connected to the system fluid. Venting continuously or for extended periods of time is not recommended because the rise in fluid temperature in the expansion tank will accelerate oxidation, which we will discuss below, or it may cause a safety concern as the temperature approaches the fluid's flash point.

Make good use of your vendor's oil analysis program to determine the rate of low boiler generation in any operation. With venting and fluid analysis, one can establish how often and how long the fluid must be vented.

Adopt proper start-up and shut-down procedures. Start-up and shut-down processes account for many instances of thermal cracking. Despite being under pressure to start up as quickly as possible, rapid start-up and improper shut-down can drastically shorten the life of the fluid and decrease the efficiency of the system. Starting a system at ambient conditions and raising the temperature to 400-500°F (204-260°C) should take place over several hours in order to minimize heat flux. The temperature increase has to be mild enough at start-up, at least until the Reynolds number of the fluid becomes high enough to tolerate a higher heating rate.

Shut-down of a heat transfer system, too, can have a destructive effect if the pump is turned off too early.

Even if the heat has been shut off, furnaces contain refractory material that can retain heat for several hours, continuing to heat stagnant oil in the piping and causing it to undergo thermal cracking. It is very important to maintain fluid circulation for several hours after the heat has been turned off—until it has cooled down to 150°F (65°C)—to prevent exposing the fluid to excessive heat.

Tips to ensure thermal degradation will not occur in the system:

- Monitor and control the system's heat flux
- Maintain the pumps and filters
- Use fluid analysis to look for early signs of oil degradation
- Continuously filter the oil with high-temperature glass media filters down to at least 10 μm
- Adopt best practices for start-up and shut-down

2. OXIDATIVE DEGRADATION

Oxidative degradation, known as oxidation, can occur through the reaction of the heat transfer fluid with oxygen in the air. Like other organic matter, exposure to oxygen causes fluid degradation.

Oxidation is largely related to temperature. The higher the temperature, the faster the rate of oxidation. A general rule of thumb is with every 18°F (10°C) temperature increase, the rate of oxidation doubles. By-products of degradation for mineral oil or synthetic chemical aromatic-based fluids can include substances such as carboxylic acids, ketones, aldehydes and other substances.

The first visible evidence of the oxidation process is the gradual discoloration of the fluid (see Figure 4), increase in viscosity and, if left long enough, the formation of insoluble compounds and sludge. Oxidation by-products are not very soluble in oil and they tend to adhere to cooler metallic surfaces or settle in low-flow areas, like the bottom of the expansion reservoir. It is very difficult to completely remove these by-products with cleaning and flushing fluids.

FIGURE 4

FIGURE 4: Progressive discoloration occurs when a heat transfer fluid is exposed to oxygen over time.

Draining the heat transfer fluid will not remove all of the sludge from the piping. At this point, only manual removal or circulation of a chemical cleaning agent through the system will help restore the system's initial efficiency. Residual oxidation by-products, often acidic in nature, will serve as a catalyst to accelerate corrosion and shorten the life of the fresh fluid, if not removed.

Addressing oxidation

Inert gas blanketing. In closed systems, where the hot fluid circulates while cooler oil is exposed to air in the expansion tank, the most effective way to eliminate oxidation is to install an inert gas blanket in the expansion tank. This principle relies on substituting air (containing oxygen) with an inert gas in the only location where warm oil can come into contact with oxygen. No oxygen to react with the oil means no oxidation. The most common gas used for gas blanketing of expansion tanks is nitrogen, but carbon dioxide and argon have been used as well. The pressure of the inert gas is maintained slightly above atmospheric pressure, usually around 2 psig (14 kPa). This device requires ongoing inspection and maintenance to prevent leaks. Leaks will, of course, negate the purpose of the gas blanketing system and release money into thin air.

Fluid choice. Another way to deal with oxidation is to select a fluid that contains the right chemistry of oxidation inhibitors. The type and number of oxidation inhibitors used and the quality vary widely from product to product. Some fluids use conventional anti-oxidants like those found in other gear or hydraulic lubrication applications, while the more sophisticated heat transfer fluids use additive chemistries designed to better withstand the high temperatures of heat transfer systems.

Oxidation inhibitors work in a variety of ways but usually by reacting with free radicals and oxygen compounds (like peroxides) before they can react with the oil molecules. Be aware that some fluids on the market are unadditized and therefore are more susceptible to fouling and have lower oxidation stability.

Systems that use a lot of oil are more forgiving because the oil and antioxidants are constantly being replenished. In which case, experience, benchmarking, and regular used-oil analysis are important for judging oxidation stability to assist in the selection of heat transfer fluid.

Open systems allow hot fluid to come into contact with air all the time, hence the importance of choosing a robust product with antioxidants and preferably one that is designed to deal with air exposure. Even then, frequent change-outs are required and system cleaning or flushing should be done periodically, perhaps as often as every third oil change, if optimal efficiency is a concern.

3. PROCESS OR EXTERNAL CONTAMINATION

Internal process contamination. Contamination can be damaging to system components and to the fluid itself. While logic suggests contamination is unlikely because the pressure is greater on the fluid side, on-site experience shows that process material can enter the fluid stream. The urgency required to fix a leak depends on chemistry of the contaminant, the fluid used and the severity of the situation.

For example, in the oil and gas industry, process hydrocarbon gas can enter the fluid. This gas mixes very well with a mineral-based or chemical aromatic fluid and the viscosity of the entire charge will be reduced, while the volatility will increase. Asphalt is also a commonly seen contaminant that can have the opposite effect and drastically increase oil viscosity and the number of high boilers that foul the piping. Vanadium is a telltale element often seen on oil analysis that indicates asphalt ingression into the oil system.

In some cases, the contaminant may be inert to the fluid but it may react with traces of moisture to form acidic or insoluble compounds that threaten to accelerate corrosion and fluid degradation.

External contamination. Beyond internal process leaks, contamination can occur from the elements, condensation, foreign liquids and airborne ingression. For systems where the expansion reservoir is outside and vented to the atmosphere, it is critical to have a

tank with a 180° goose neck pipe on the top. Though it might sound basic, there have been cases in which the steel cover has fallen off and rain water poured into the expansion tank, resulting in high water content and abrasive dust circulating through the system.

Another common issue is new system contamination. Newly constructed heat transfer systems are cleaned, but seldom flushed before commissioning. In these situations, leftover cleaning agents can accelerate corrosion or fouling or create insoluble residues. For this reason, new systems should be flushed with a suitable and compatible fluid.

Although water in the heat transfer system is easily detected by operators, it is unforgiving and potentially dangerous, as it turns to steam. Water will affect various fluid chemistries is different ways.

In mineral-based, synthetic Group IV PAO oils or chemical aromatics, prolonged exposure to water would cause:

- Hydrolysis or precipitation of oil additives (in additized fluids)
- Accelerated corrosion of internal system
- Accelerated oil degradation (oxidation)
- Pump cavitation and wear
- Gargling noise in expansion tank and knocking in the hot oil piping

Based on real-life oil analysis, we can say that, in general, water does not appear to pose immediate productivity issues in concentrations below 500 ppm (0.05% wt.), although we have encountered more sensitive systems where lower concentrations have a noticeable impact. Results about 1,000 ppm (0.1% wt.) become more alarming and call for investigation and removal.

Addressing contamination

Investigate and fix. All cases of contamination must be investigated and fixed. They should also be reported to your fluid supplier for advice on potential impact on the oil and the additives. Their knowledge of the chemistry of their product helps system operators to assess the situation and formulate a possible course of action. Sometimes the contaminant can be evacuated or boiled off.

Prevention. Seldom do companies or builders factor in the cost of a system flush, since they assume the cleaning and commissioning will be done correctly by the contractor commissioning the system, and that no debris or water from the pressure testing will be left in the piping. Finding out flushing or the drainage of the pressure-test liquid was not done properly only after the system is up and running is too late and it may prove to be costly down the road. Initial flushing costs are even less considered when the fluid of choice is expensive, like silicone-based or perfluoroether fluids. It is a good practice nevertheless, and it will prove worthwhile over time.

Filters. Traditionally, filters are not installed on the oil side beside the pump strainer, probably because of the high flow rates, the large diameter piping and the low estimated value versus cost—since the components have a certain tolerance for solids. However, in recent years, more new system designs seem to be equipped with oil filters. Keep a log book of solids collection in the oil filters or strainers, and include photographs, if possible. The size, texture and color of deposits will tell a story. The deposits must be sent to a research facility or laboratory with sophisticated equipment for accurate identification. Third-party verification is important, as solids could come from more than one source.

Solids from previous fluids could reside in the system for a long time before an event, such as pipe work or partial fluid replacement, loosens them and they finally get carried to the pump strainer or oil filter. It has been observed where a used furnace is purchased and commissioned without being cleaned and flushed prior to connecting it with the main system.

Another case for sending deposits to a laboratory is that, even though solids may have a familiar smell or texture, they could turn out to be something else. What might seem like black, abrasive carbon particles could be copper sulfide, which is caused by the localized chemical attack of sulfur—present in some fluids' base stock—on the copper from the brass valves. In this example, the assumption that the deposits were carbon might result in a lot of money spent replacing fluids or adding filtration, when in reality, it was the valve construction or the selection of the fluid itself that had to change. A switch to a better heat transfer fluid based on highly refined API Group II base oils, containing virtually no active sulfur, proved to be effective.

More routine preventative maintenance

In addition to the degradation-prevention methods listed above, it is important to consider other routine maintenance steps recommended for hot oil circulating systems to prolong the life of the heat transfer fluid. The following reflects a few key considerations.

1. Watch for and act on any alarms on the main heater, whether it's a blinking red light or a notification on the operator console.

2. If not collected electronically, measure key parameters (flow rates, temperatures, pressures, etc.) on gauges at various locations on the system and ensure results are consistent with design specifications.

3. Track energy consumption (electricity, fuel use, etc.), the fluid temperature in the heater and the T_{bulk} at the outlet. If the process temperature requirement remains constant but the heater needs to run hotter to maintain the fluid temperature, it may indicate that the fluid is slowly cracking under thermal stress or deposits are forming on the heat transfer surfaces, reducing efficiency.

4. Record the fluid temperature at the inlet and outlet of the heat source. The difference should be within certain recommended industry and manufacturer guidelines.

"Another case for sending deposits to a laboratory is that, even though solids may have a familiar smell or texture, they could turn out to be something else."

5. Even if everything is running smoothly, it is recommended that an employee "walks the system" on a regular basis. That person might hear a vibrating motor, a pump cavitating, detect an oil leak, or something unusual. Preventing possible issues through planned preventative maintenance will more than cover the cost required to carry out the periodic inspections.

6. Test the fluid periodically. This was discussed earlier, but it bears repeating. Regular testing helps confirm the physical properties of the fluid, including the flash point and any changes that may be occurring. Compare the results against the properties of fresh fluid.

Fluid selection

As demonstrated above, liquid-phase system operators do have some control over the longevity of fluid performance over its lifecycle. In addition to proper system maintenance, one of the most effective control measures an operator can take to maximize the life of the fluid is to select the right one.

There are myriad fluids on the market—typically synthetic or mineral based—each with its own chemical makeup and performance profile that makes it more or less suitable for a specific processing application.

The scope of this paper is not to discuss the advantages and disadvantages of every heat transfer fluid type. It is, however, worth noting the selection stage is important and worth the time for due diligence; the fluid selected has a significant impact on operational success—in productivity and in safety.

A note on investment. Selecting the right heat transfer fluid requires due diligence from multiple stakeholders within an organization—complete with full application analysis. Buyers should resist the temptation to settle on a low base price. Aside from the fact that the fluid plays an important role in the performance of the system, it is also the case that the lowest price tag may not factor in the following variables:

- Costs associated with worker safety, such as training on, equipment for and protection from potential exposure to the fluid (in vapor and liquid form)

- Freight charges for delivery

- Cost associated with pickup, handling and disposal of used oil and drums

- Proven fluid performance beyond fresh oil data. Vendors should be able to prove retention of fresh fluid properties (e.g. thermal stability and oxidation data)

- Capability of the fluid with the current system (e.g. seals, expansion reservoir sizing, etc.)

- Miscibility with current heat transfer fluid, if partial-change out is needed

- Level of liability coverage and expertise the manufacturer offers

- Flexibility of the vendor to work with you on system cleaning or flushing projects, provide adequate fluid inventory and take back excess unused fluid

When to test heat transfer fluids

Assuming the system is running smoothly and there are no concerning reasons to test (i.e. to determine what went wrong), it is still a good idea to get the fluid analyzed on a regular basis. Proactive testing can help detect potential problems early, before a costly reduction in productivity, or worse, a system failure. Testing also allows for better planning, as it may indicate the time frame for a fluid change-out.

Here are guidelines for when to test the heat transfer fluid:

- **During the first year of operation for brand new systems.** Any major issues in the system that can affect the fluid will show up in the test results.

- **Just after a fluid change.** After a week or two, test the fluid even when using the same brand; there will have been enough change in the old fluid properties so that any residue will show up in the test results of the new charge.

- **Annually, at least for large systems.** Schedule a test yearly as a part of the preventative-maintenance routine. The results will provide a current report on file for your insurance company.

When deciding how to test heat transfer fluid, it is advised to send a fluid sample to the fluid supplier's laboratory. They will not only be able to run the tests; they can also interpret the results.

What oil analysts measure

Analysts are looking at the overall condition of the fluid, and to a certain extent, for some insight into the condition inside the circulation system. The best way they can do this is by trending regular samples. Useful information can certainly be extracted from a single data point, but trending provides more valuable data and increases the accuracy of a diagnostic for planning purposes.

At a minimum, a testing program for heat transfer fluids should perform the following tests:

Kinematic Viscosity (ASTM D445-15)
Measures the fluid's resistance to flow. An increase in viscosity indicates the presence of high boilers, and a reduction in the fluid's ability to transfer heat. A decrease in viscosity indicates the opposite: the presence of low boilers (which means a flash and possible auto-ignition temperature drop) and thermal cracking of the fluid may be occurring. The warning limit is a >30% increase; at this point, action should be taken, such as a partial or complete oil replacement.

Acid Number (AN) (ASTM D664-11)
Measures acidic compounds and therefore is an indirect determination of the extent to which fluid has been oxidized. Most fresh fluids have an AN of 0.05-0.10 mg KOH/g. The condemning limit is around 1.0 mg KOH/g, after which point sludge deposits tend to increase.

Cleveland Open Cup (COC) Flash Point (ASTM D92-12)
Measures the lowest temperature at which the fluid's vapor will momentarily ignite (when in contact with an ignition source). When reduced, it often indicates contamination and thermal degradation. The warning limit is <300°F / <150°C.

Insoluble Solids
Determines the concentration of insolubles in the fluid after filtration through a 0.8 micron filter. The measure of organic solids indicates the extent of fluid degradation and potentially how badly the system is fouled. Meanwhile, inorganic solids can indicate system corrosion and contamination. The alarm limit for solids is >0.5% wt.

Water Content (ASTM D1744-13)
Measures the amount of water present in the fluid. The warning limit is 1,000 PPM (equal to 0.1% wt). If these levels are reached, it could indicate a missing cover on the expansion tank or a leaky heat exchanger. In addition to the safety hazard of water boiling and splashing in the expansion tank, a high water content can lead to system corrosion, more rapid fluid oxidation and formation of acidic and corrosive substances described earlier. Water is most detrimental to aromatic fluids, in part because they are generally unadditized, hence lack rust and corrosion inhibitors.

Metals Content (ASTM D5185)
Determines the concentration of approximately 26 elements simultaneously by inductively coupled plasma (ICP). It may indicate a change in additive levels or the presence of wear metals and contaminants. The concentration levels highlight potential corrosion and/or contamination.

Obtaining accurate, third-party-validated measurements of each of these variables will not only enable better informed operational decisions, they will also validate fluid recommendations, which can prove valuable if a change-out requires unplanned downtime and budget.

CONCLUSION

Remember, the system was designed around the properties of fresh heat transfer fluid, so to ensure a safe, predictable operation, operators must try to keep the difference between the current state and what is expected from a fresh fluid within a narrow range. There are many ways operators can proactively keep heat transfer fluid as fresh as possible for as long as possible, to keep the system productive and safe, before inevitable change-outs and thorough system cleaning. We encourage operators make it routine to inspect the system, its components and the fluid, and to regularly have their fluid tested in a lab.