THERMINOL®

Heat Transfer Fluids by Eastman

Optimizing heat transfer fluid performance

How to avoid costly consequences

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Introduction

Even a perfectly designed and installed heat transfer fluid system is vulnerable to operational stress factors which can deteriorate its performance and can reduce fluid and system component life times. Heat transfer fluids are an essential component of the operation of many high-temperature processes. When the heat transfer fluid isn't performing up to expectations, there can be detrimental impacts to product quality, production rates, heat transfer fluid, and equipment life and it can consume resources in troubleshooting. With the following helpful concepts, a knowledgeable engineer can effectively anticipate and manage these factors and avoid costly consequences.

Selection of the proper fluid for the application

Securing the best and most enduring performance from your fluid actually begins with features beyond the fluid itself. The users of a heat transfer fluid should source their fluid from a reliable, reputable, and responsible supplier. Pay attention to feedback heard from distributors, independent specialists, and other users who have had prior experience with the various suppliers, so that you can benefit from the advantages provided by manufacturers who have a well-established track record, who have well-networked supply and distribution chains, and where experienced customer support specialists answer the phones "live" when you need them. You can also use this feedback to avoid some of the pitfalls that might be present with lower-tier suppliers and fluids. Keep in mind that some suppliers may only be distributors or remarketers who have very limited product and application knowledge. It is always best to buy from the fluid manufacturer having the experts on staff who can answer just about anything related to the safe and effective use of the fluid and its chemistry, or from a distributor having well-trained sales personnel and a strong alliance with the manufacturer.

Engineers will need accurate technical data and physical properties to help support design and troubleshooting efforts. Today, this information is almost always readily available for downloading from web sites, but the technical data should be reviewed as part of the fluid selection process to ensure it provides the needed level of detail. Engineers need quality data, and not just smoothed curves on low-resolution graphs. For safety and environmental evaluations and response, make sure current and complete Safety Data Sheets are also available from the supplier.

Also, the plant engineers will require the supplier's analytical support to run the proper tests on the in-service fluid samples, and have the expertise to fully interpret the test results for providing guidance on when fluid quality adjustments might be necessary, extending the good performance life of the fluid to its maximum. Experienced technical service engineers from the fluid supplier should be able to recognize the early stages of developing problems and counsel the plant engineer on the potential causes so they can be corrected at their earliest and before costly problems develop.

What are those potential fluid-related problems that users might experience? Problems can develop which will be associated with changes in fluid chemistry and its physical properties when the fluid quality deteriorates (ages) from use or contamination. These can include increased corrosion risk, fouling potential, solids/sludge formation, and pumping difficulties.

To best resist the effects of fluid aging and potential system impacts, using a high quality fluid is the appropriate starting point. The following attributes should be considered:

- **Demonstrated performance—**Since the heat transfer fluid is the "life blood" of the high-temperature process, it pays to buy a quality fluid and chemistry to meet the requirements. Consult the fluid supplier and others on the performance records of prospective fluids. Weigh this feedback against the needs of the application, giving due consideration to operating temperature, on-stream time, plant location (for cold start-up factors), possible future higher-temperature requirements, and if other heat transfer fluid systems are at the same plant site, for common fluid inventory stocking.
- **Clearly defined sales specifications—**One means of quality assurance for the end user is the product sales specifications provided by the manufacturer. If needed, the manufacturer should also be capable of issuing certificates of analysis or conformance that the delivered fluids meet those specifications each and every time.
- **ISO-9001 certified processes—**Customers are also protected by manufacturers who have invested in strictly controlled processes certified by independent auditors. If the supplier can provide such certification, such as ISO-9001 conformance, the end user can have added confidence in product consistency.
- **Reliably advertised temperature ratings—**The method of establishing maximum bulk temperature ratings of heat transfer fluids is not mandated by industry standards and is left up to the fluid manufacturer or marketer to assign. There are established test methods for measuring thermal stability of organic heat transfer fluids,[i,ii] but they stop short of prescribing the translation of those results into the published temperature ratings. Consult the fluid supplier about the expected life of the fluid when operated at the maximum temperature rating or at the expected operating temperature for the process. For example, some suppliers may rate the maximum bulk temperature to provide a two-to-three-year life expectancy, where other suppliers may choose to rate for a longer life which could result in a somewhat lower published maximum temperature rating. Keep in mind too, that how the process is operated can influence the actual fluid life experienced. For example, frequent power interruptions can create very thermally stressful conditions for heat transfer fluids that can greatly shorten fluid life even if the normal maximum operating temperature is well within the published maximum bulk temperature limit. Lastly, it should be factored into the fluid selection decision that if a maximum bulk temperature rating is exceeded by roughly 10°C (18°F), the thermal stress is also roughly doubled. This can be expected to significantly reduce fluid life expectancy. Conversely, reducing the operating temperature by the same amount from the maximum bulk temperature rating can be expected to reduce thermal stress by roughly half, thereby significantly increasing the fluid's life expectancy.[iii]

- **Physical properties—**The physical properties (liquid viscosity, thermal conductivity, heat capacity, and density) will be evaluated when determining heat transfer coefficients in support of heat exchange area required, however also consider the vapor pressure of the fluid. Lower system pressures will promote efficient low-boiling degradation products venting and will inherently tend to be less of a leakage problem. A fluid with suitable viscosity at the lowest expected temperature for winter start-up can avoid investment into heat tracing and vessel heating, as well as oversized pump motors.[iv] Fluids having freezing points above the lowest temperature possible will require incorporation of freeze protection into the system design, including the protection of instrumentation sensing lines, and overpressure protection devices.

Measuring the six key parameters of in-service fluid quality

The following are considered the most important measures that can indicate developing problems, enabling potential corrective actions to protect fluid performance/life.

1. **Viscosity** can be readily measured in a fluids lab, typically by ASTM-445,[v] or similar technique. In the ASTM D-445 method, a fluid sample is held at a precisely controlled temperature while the time for a known volume of the fluid to pass through a calibrated tube is measured. From the elapsed time, the viscosity is calculated (Figure 1).

2. **Moisture** content is typically analyzed by the Karl Fischer titration technique.[vi] Moisture content should be kept quite low when operating at high temperatures to avoid issues related to its flashing into water vapor. Inability to maintain low moisture content is an indicator of either an aqueous leak into the system, or perhaps the addition of "wet" make up fluid.

3. The **flash point** of a high-temperature fluid is commonly measured by the Cleveland Open Cup (COC) method, ASTM D-92.[vii] A closed cup technique is also useful in classifying fluids and is run per ASTM D-93.[viii] The flash point is the lowest temperature of the fluid under the test conditions where ignition of the vapors above the liquid can occur, yet evaporation rate is too low to sustain combustion. Flash points are important in electrical classification and hazard analysis. (Figure 1)

Figure 1—Typical instruments for measurement of density and viscosity, flash point, and total acid number (left to right).

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4. **Acidity** of fluids is commonly measured by ASTM D-664,[ix] which is a potentiometric titration. Fluid oxidation results in accumulations of carboxylic acids which lower the apparent pH or raise the total acid number (TAN). Typically, unused organic heat transfer fluids will have a near zero acid number. (Figure 1)

5. **Insoluble solids** content is essentially a measure of the concentration of solids in the fluid at room temperature. Of particular importance are the organic solids which result from exceeding their solubility limit in the fluid. Other solids can include carbon, small portions of gasket materials and metal shavings, and some rust.

6. **Composition/degradation—**Gas chromatography allows the quantification of compounds which have boiling points lower than the initial boiling point (low boilers [LBs]) and higher than the final boiling point (high boilers [HBs]) of the unstressed fluid. This analysis provides a measure of the degree of fluid degradation experienced and can provide an indicator of organic contamination. Gas chromatography typically cannot directly provide a measure of inorganic contamination of organic fluids.

Additional considerations

The proper selection of heat transfer fluid for the process should also consider the potential of intermixing of the process stream(s) with the heat transfer fluid. If this occurs, would chemical interaction be expected? Can the two be effectively separated? Will the integrity of system components be compromised due to chemical incompatibilities?

In general, when a fluid is chosen from a very reputable and established supplier which has the requisite quality assurance systems built-in to its supply chain, has the performance properties and thermal stability well-matched to the application requirements, and where the fluid quality is supported by periodic expert analysis, the new process has the pieces in place for an optimally performing heat transfer fluid. The remaining task is to properly monitor and maintain these advantages over time.

In-use monitoring and actions

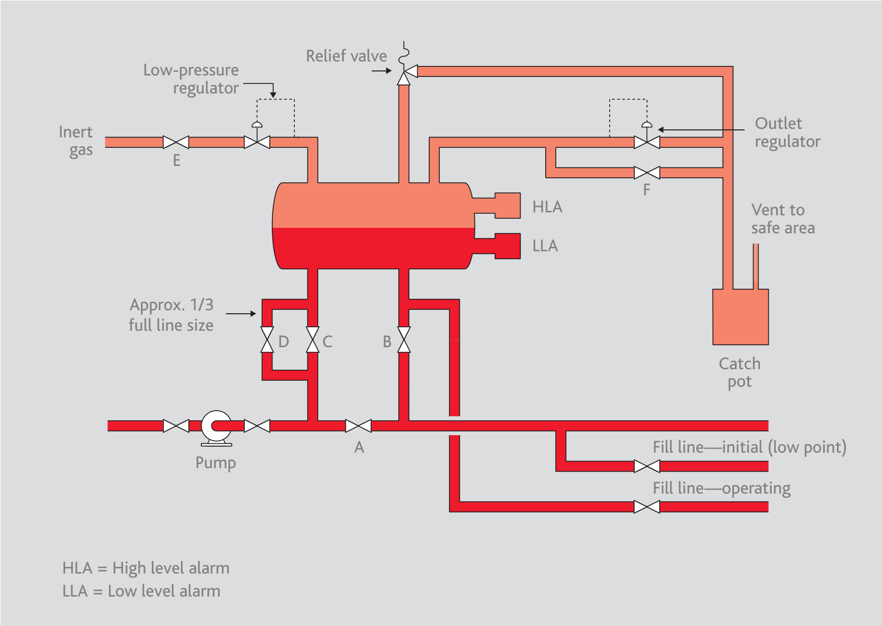
In the preceding sections, we have indicated that heat transfer fluids' properties may change, such that actions would be recommended to either extend the service life of the fluid or prevent occurrence of deteriorating system performance.[x] For each fluid property analyzed, the supplier of the heat transfer fluid may have established specific warning or action limits. Such fluid property limits, provided together with recommendations in an evaluation report, are a composite of the experience in the analyses of used fluid samples and knowledge about heat transfer fluid degradation mechanisms. The actual thresholds for operational problems can vary depending on specific system design factors including inert gas or system pressure, pump NSPHA and NPSHR, pressure drops, etc. In general, when the test results all fall into a "normal" range, the fluid is probably in good condition. If one or more of the tests fall into the "warning" area, the system operator may consider taking appropriate action such as venting, filtration, etc. When the results fall in the "action" area, taking action to return the fluid to a more normal condition either by appropriate fluid treatment or complete drain and refill is more of a necessity.

Understanding that establishing such limits is a composite of experience and that specific system requirements may call for different limits, it's quite understandable that such limits should not be considered to be "rigid." This means—taking as an example a low-boiler upper limit of 5%—that there is no guarantee that systems operating at a low-boiler concentration, e.g., 4.8%, will not experience operational problems such as increased vapor pressure, pump cavitation, or significant flash point drop, but a system operating at a level of 5.2% of low boilers will suddenly suffer from these consequences. Also, it is important to understand that fluid properties and their limits should not be evaluated independently of each other. For example, a system exhibiting a high-boiler content close to or even slightly above the action limit but having the viscosity and insoluble solids content in the "normal" ranges may not require immediate actions. Nevertheless, the key properties and corrective actions for significant deviations of each fluid property measured individually are discussed in the following. A summary is provided in Table 1, page 10.

1. Viscosity

The fluid's viscosity is a measure of its resistance to flow. Fluids of greater viscosity will require higher-pumping horsepower requirements and will adversely affect the degree of turbulence at heat exchange surfaces which can lower heat transfer coefficients. Not only can elevated viscosity reduce heat transfer performance at high temperatures, it can also affect the ability to pump the fluid during cold weather start-up conditions. Viscosity is related to the molecular weight of fluid components. Generally, lower molecular weight components decrease viscosity and higher molecular weight components increase viscosity of the heat transfer fluid. Contamination from leaked process streams, incorrect material added to the heat transfer fluid system, and solvents from system cleaning, as well as thermal stressing and oxidation, may be the source of materials that increase or decrease viscosity. Regardless of any action taken, the causes of viscosity changes should be determined. The typical corrective action to

Figure 2—Features of a common expansion tank design.



address too low a viscosity would be the removal of low-boiling components by circulating the heated fluid through the expansion tank with **inert gas purge** of the vapor space while venting to a safe location (Figure 2). Condensation and collection for proper disposal of the removed low-boiling organics is recommended unless vented to a properly designed flare. Correcting for high viscosity requires either aged fluid removal and replacement or dilution with unused heat transfer fluid.

2. Moisture

When operating at very high temperatures, excess moisture content can prevent the ability to circulate the heat transfer fluid due to its flashing into vapor at the circulation pump intake, creating cavitation. Extended operation with cavitation can lead to excessive heat transfer fluid degradation in heater coils due to lower mass flow rates delivered from the pump. Also corrosion may be induced by elevated concentrations of system moisture. In cooling systems, a high moisture content of the fluid will increase the risk of formation of ice crystals on chiller surfaces. This can decrease the efficiency of heat transfer and deteriorate the overall system performance. On new system start-ups, it is important to remove residual moisture from the system (from hydrostatic testing) to enable the fluid to heat fully to the desired operating temperature. For systems in operation, increasing moisture content may be caused by in-leakage of water from aqueous process steams or from steam systems, or by moisture intake via an expansion tank open to atmosphere. Excess moisture can typically be vented from the expansion tank using the low-boiler venting method (see 1. Viscosity, p. 6). To achieve low ppm moisture levels required for the cooling operation, molecular sieves can be placed in side stream operation.

3. Flash point

While many heat transfer fluids have relatively high flash points, they often are not classified as fire resistant. However, heat transfer fluid systems are usually closed systems. Therefore, a release of fluid should only occur in case of accidents or malfunctions and it is typically safe to operate such well-designed and maintained systems and fluids even at temperatures well above the fluid's flash point. Flash point is a property to be considered in the hazard evaluation of operating systems with combustible fluids. A significantly depressed flash point of the in-service heat transfer fluid may not only increase the fire hazard in case of leakages and the presence of an effective ignition source, it may also affect the area electrical classification of the system in extreme cases. Typically, routine venting of low-boiling thermal degradation products from the expansion tank to a safe location will maintain the fluid's open-cup flash point to within 25°C (45°F) of the flash point of unused fluid.

4. Acidity

High acid numbers could indicate severe fluid oxidation, which is most often a result of hot fluid exposure to air in the expansion tank. But they may also indicate possible contamination from improper material added to the system inadvertently or fluid leaked from the process side of heat exchangers. If the acidity becomes excessive, the system components could corrode and fail. Oxidation and corrosion products can form sludge and deposits that can also decrease heat transfer rates by fouling. A condition of this nature is typically best corrected by removing the material and replacing it with new fluid, with serious consideration given to a system flush to remove residual acidity. If the high acidity was caused by oxidation, inerting the vapor space in the expansion tank should certainly be considered. System inerting has proven to be a highly effective means of protecting against unwanted increases in fluid acidity and oxidative degradation.

5. Insoluble solids

The presence of solvent (typically acetone or pentane) insoluble solids generally indicates contamination from dirt, corrosion products, or severe oxidative or thermal stressing. This condition may cause fouling of heat transfer surfaces which would deteriorate heat transfer performance. Also, plugging of small diameter lines or narrow heat transfer passages could occur. Finally, large amounts of insoluble solids may contribute to wear and plugging of mechanical seals and valves resulting in equipment failure, operational problems, and increased maintenance requirements. If these problems occur, side stream filtration can usually provide ongoing protection against solids-related deposits and their potential consequences. If solids contamination is extremely high, fluid may need to be removed for external filtration and the system may need to be cleaned. Specialized flushing fluids, designed by heat transfer fluid suppliers, can be effective in removing fouling deposits from most synthetic and mineral oil fluid systems. Modest solids content may require filtering with successively finer rated filter element sizes to get the situation under control. A suggested filter rating generally is 10 to 25 micron for ongoing fluid maintenance.

Inert gas blanketing

An effective method of minimizing fluid oxidation is to blanket the expansion tank with an inert gas such as nitrogen, carbon dioxide, or natural gas. The purpose of inert gas blanketing is to maintain a nonreactive atmosphere in the vapor space of the expansion tank, preventing the entrance of air and moisture which can adversely affect fluid life. An uninterrupted supply of inert gas, usually nitrogen, controlled by pressure regulators for both inlet and outlet flow is necessary to obtain this protection. Pressures used should be kept as low as possible 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 to facilitate purging of the expansion tank's vapor space if it becomes necessary.

6. Thermal degradation—low boilers and high boilers

Thermal cracking of the heat transfer fluid will result in components which are lower in molecular weight and commonly are known as low boilers. High boilers also can be generated when some compounds recombine to produce higher molecular weight materials. Both low- and high-boiling degradation products can create an unfavorable environment for efficient heat transfer system operation.

a. Low boilers

Low-boiling components can affect system operation in several ways. First, when present in significant quantities, low boilers can lead to pump cavitation. 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 and viscosity may be lowered. Third, the increased fluid vapor pressure resulting from the presence of low-boiling components can cause premature and unexpected pressure relief and venting. Finally, excessively rapid formation of low boilers will result in unacceptably high fluid make up costs as the low boilers removed from the system are replaced with fresh fluid. Removal of low boilers is typically accomplished by **venting** from the expansion tank to a safe location (Figure 2).

b. High boilers

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, sludge and tar deposits can form as the solubility limits for the higher molecular weight compounds are exceeded. Added costs of operation as a result of these sludge deposits include downtime, repairs, clean-out, and lost production. Corrective action would be either a replacement of the fluid or a major dilution with virgin fluid to maintain fluid properties within normal range.

Venting

Since the expansion tank is usually installed at a high point in the system, it also can serve as the main venting point of the system for excess levels of low boilers and moisture which may accumulate in the heat transfer fluid. To properly vent a heat transfer fluid system, the expansion tank must be capable of accommodating the circulating flow of hot heat transfer fluid. To remove low boilers, the temperature in the expansion tank will be increased and the tank pressure may be lowered while venting. As they flash into the vapor space, the excess low boilers and moisture can be more effectively removed by sweeping out the expansion tank through the vent line to a safe area (preferably via a cooled condenser). Modest pressure decreases help minimize the loss of good heat transfer fluid in the vent stream.

Summary

Changes in fluid properties are often the result of thermal and oxidative degradation. Depending on the stability of the particular heat transfer fluid used, all actions previously described to maintain fluid properties may have to be considered on a regular basis. It has to be acknowledged that all organic heat transfer fluids will degrade. The key differences among fluids are their respective rates of degradation under operating conditions and the nature of the degradation products formed. Selection of the proper heat transfer fluid, having adequate thermal stability along with good system design and operation, can optimize fluid life and performance while helping maintain high system reliability.

Table 1—Summary of in-use heat transfer fluid test results: Interpretation.

Property	Possible cause	Potential effects	Suggested limit
Viscosity changes	Contamination, thermal degradation, fluid oxidation	Poor heat transfer rate, deposits, high vapor pressure, pump cavitation	Depends on fluid chemistry
Moisture increase	System leaks, residue in new or cleaned unit, unprotected vent or storage	Corrosion, excess system pressure, pump cavitation	700 ppm (for heating service)
Flash point decrease	Contamination, high amount of low boiler	Increased fire hazard, change of regulatory requirements	Jurisdictional requirements
Total acid number increase	Severe oxidation, contamination with acid	System corrosion, deposits	0.7 mg KOH/g
Insoluble solids increase	Contamination, dirt, corrosion, oxidation, thermal stress	Poor heat transfer, wear of pump seals, plugging of narrow passages	400 mg/100 mL
Low boiler (LB) and high boiler (HB) increase	Contamination, thermal stress	Pump cavitation, poor heat transfer, excess system pressure, deposits	5% (LB) 10% (HB)

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