MARLOTHERM ®- News Letter No. 20

Chemical Structures and Thermal Stability of Organic Heat Transfer Fluids

Introduction

All organic chemical structures undergo thermal degradation as heat is applied. At any given elevated temperature there is some level of degradation that occurs depending upon the structure of a particular heat transfer fluid or oil. Non-aromatic versus aromatic chemical structures and then the degree of aromaticity determines the thermal stability ranking at increasing temperatures. Basically, the thermal stability of commercially available heat transfer fluids or oils increases starting with the weakest C-C chemical bond to the strongest aromatic structure as follows:

C-C << Aromatic

In addition to the thermal stability hierarchy of organic heat transfer fluids and oils, commercial products tend to follow the organic chemistry ”rule of thumb” which is for every 10 °C increase in temperature, the rate of reaction doubles. In the case of the heat transfer fluids and oils, it applies to the rate of thermal degradation under controlled test conditions after reaching a temperature level where there is measurable change in a particular chemical’s structure.[1] Beyond that level or threshold, the degradation rate is exponential as the temperature increases in approximately 10 °C increments.

While organic heat transfer media are selected for their resistance to thermal stress, they will start to thermally decompose into low and high boiling fractions at some elevated temperature. The lowest boilers should be vented out of the heat-transfer system to avoid pump cavitation, and under certain conditions their presence can lead to regulatory and safety problems. The high boiling degradation fractions also exhibit high viscosities. Those fractions in aromatic fluids tend to be soluble in the original chemical structures and do not separate during operation. The high boiling degradation fractions of non-aromatic structures, however, tend to be insoluble in the mass of the original chemical structures. These insoluble, high viscosity fractions move to the interior pipe walls and can lead to laminar flow conditions. That further exacerbates the thermal decomposition problem at the heat source eventually leading to the formation of organic sludges, carbonaceous deposits and coke development. Poly alpha-olefins, paraffinic and most highly branched aliphatic structures such as mineral oils used as heat transfer fluids are very susceptible to these formations at temperatures above 290 °C (550 °F) because of their weak aliphatic structures.

The higher the degree of aromaticity, the better the thermal stability of the organic heat transfer fluid. Those fluids that are suitable for use at bulk outlet temperatures above 300 °C (~570 °F) are highly aromatic in chemical structure. Most commercial aromatic types do, however, vary in their thermal stress resistance because their individual structures vary in the degree of aromaticity. In the same way, the solvency power of aromatic heat transfer fluids is superior to that of non-aromatic structures, particularly for degradation fractions. For example, the highly aromatic dibenzyl toluene structure of MARLOTHERM® SH is more thermally stable and solvating as compared to non-aromatic structures and even to the aromatic structures of hydrogenated terphenyls and styrenated tetraline.

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[1] DIN 51528 Testing of Mineral Oils and Related Products - *Determination of thermal stability of unused heat transfer fluids.*

Modes of Operation

Poly alpha-olefins and petroleum-derived oils can only be used in liquid phase heat transfer systems because of their thermally weak chemical structures and wide boiling point ranges.

The degree of aromaticity and boiling points of the synthetic organic high temperature fluids commercially available are used to distinguish between the modes of operation, liquid and vapor phases. Several products having aromatic structures with boiling points below their maximum allowable bulk outlet temperatures can be used in vapor phase heat-transfer systems because of their excellent thermal stability. These can also be used in pressurized systems to keep them in liquid state. Examples are the biphenyl/diphenyl oxide eutectic mixture and benzyl toluene (e.g., MARLOTHERM® LH). While essentially one (1) and two (2) in thermal stress resistance of commercial fluids at temperatures greater than 300 ^{o}C (572 ^{o}F), operations using these particular fluids present specific safety, maintenance and operating problems that must be addressed during the system design.

The simplest and safest operations are achieved by using the highly aromatic fluids below their boiling points regardless of the bulk outlet temperature. This mode is described as non-pressurized, liquid phase (but under forced circulation) heat transfer systems. Except for very low boilers generated that should be vented, the thermal decomposition materials, low and high boilers, exhibit varying degrees of solubility in the remaining non-degraded mass of these aromatic fluids. The more aromatic in chemical structure, the better the solubility. The solubilizing characteristics minimize the formation of organic sludges, coke and carbonaceous deposits. Here again, MARLOTHERM SH is superior because it has better solvency power compared with other fluids used below their boiling points at temperatures $\geq$ 300 ^{o}C (572 ^{o}F).

Low and High Boiler Formation

The chemical structure determines weight percentages of low and high-boiling fractions generated as a result of thermal stress being applied at given bulk outlet temperatures. Based on laboratory tests and in-plant experience with heat transfer fluids and oils, information is available to project the expected low to high-boiler fractions for a given product under plant operating conditions. The total amount generated and ratios are needed to determine:

- Rate of top off due to low boiling generation
- Effects on flash points and autoignition temperatures
- Viscosity changes due to the accumulation of high boiling fractions
- Change out points for heat transfer fluids and oils

This information is also needed to determine the overall economics of one heat transfer fluid or oil compared with another product at different bulk outlet temperatures. High low-boiler generation means a high annual top off rate and associated higher operating costs. MARLOTHERM SH is unique in the low level of ventable fractions generated and a system charged with it requires less topping off over the use life of this fluid.

Heat Transfer System and Fluid/Oil Use Life Economics

Estimating the use life economics of a heat transfer fluid charge is difficult because of the dynamic nature of high temperature heat-transfer systems. Before projecting the use life of a particular fluid, a great deal of information is needed - be careful. For the fluid or oil supplier to make the best overall recommendation, the operational bulk outlet temperature range must be defined accurately. If a heat transfer system is expected to operate at ~290 ^{o}C (550 ^{o}F), it should not be specified that ~340 ^{o}C (650 ^{o}F) is maximum bulk outlet temperature but rather in the range of 300-310 ^{o}C (572-590 ^{o}F). Some additional design information that will assist the supplier in selecting the fluid or oil best suited for a non-pressurized or pressurized, liquid phase heat transfer system follow:

- No air impingement so that oxidation does not occur[2] – recommend that expansion vessels should be inert gas blanketed
- High flow velocities to maintain turbulent flow - the recommended minimum through connecting pipes at 2-3 m/sec (6-10 ft/sec) and the heat source at 3-4 m/sec (10-13ft/sec)
- High Reynolds numbers - recommend > 4000
- Heat flux of fired and electrical heaters - maintain a range of 3-4W/cm^2 (8000-11,000 BTU/hr·ft^2)
- Watt densities of electrical heaters - below 4.5 W/cm^2 (~30W/in^2) and better, 3.0W/cm^2 (~20W/in^2)
- The number of heat users and the expected heat load - if new users are added to a marginal system, increasing the fluid or oil bulk outlet temperature usually results in problems

The heat transfer fluid or oil supplier should provide the physical property data along with the following guideline information:

- Maximum bulk outlet temperatures - define meaning such as "it will last 1 year, etc. without top off under controlled conditions at that temperature" and special design considerations may be necessary
- Maximum bulk outlet temperature - define range above the bulk outlet temperature
- Lower pumping limits - centrifugal pumps suitable for maintaining flow at high temperatures usually do not perform well at temperatures where the viscosity exceeds 400 cSt at start-up
- Boiling (initial) point - if below the specified bulk outlet temperature range, the system must be pressurized
- Flash point and autoignition temperature[3] - the higher, the safer to operate
- Low to high boilers generation rates determine top off rates - high low-boiler formation, the higher top off rate and cost
- Price of the heat transfer fluid or oil

The thermal stability of a heat transfer fluid or oil is important but the heat transfer system design and operation must complement it for satisfactory service.

[2] MARLOTHERM Newsletter No. 15 *Exclusion of Oxygen from Organic Heat Transfer Fluids* covers this subject in detail.

[3] High boiling points, low vapor pressures and high flash points are almost always synonymous, but the autoignition temperatures may not be high. The reverse is also true, some low boiling point, high vapor pressure and low flash point products, may have high autoignition temperatures.

Availability and Service

SASOL offers a comprehensive range of high performance heat transfer fluids under the MARLOTHERM® and ILEXAN® trade names. The MARLOTHERM products cover the temperature range from -70 to 360 °C (-94 to 680 °F). ILEXAN products are for special applications. Detailed information is available on request. SASOL has more than 30 years of experience in the field of heat transfer technology. This know-how is available to you, should you as our customer have any questions or problems. Whether you have questions about the choice of a heat transfer medium for a certain application, system design, troubleshooting, safety issues or specification problems, our experts are here to help you. Just contact us!

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