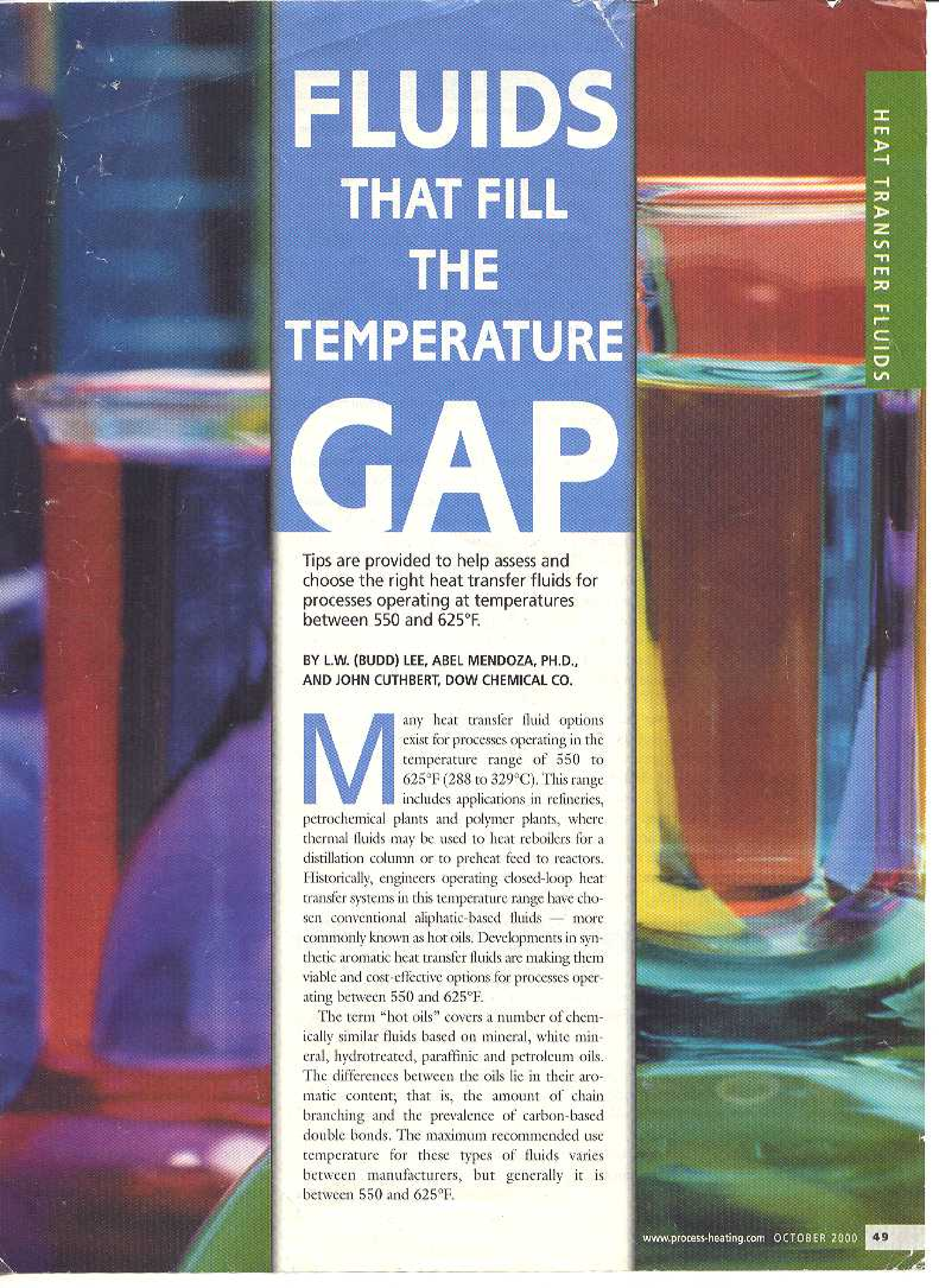

FLUIDS THAT FILL THE TEMPERATURE GAP

Tips are provided to help assess and choose the right heat transfer fluids for processes operating at temperatures between 550 and 625°F.

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Many heat transfer fluid options exist for processes operating in the temperature range of 550 to 625°F (288 to 329°C). This range includes applications in refineries, petrochemical plants and polymer plants, where thermal fluids may be used to heat reboilers for a distillation column or to preheat feed to reactors. Historically, engineers operating closed-loop heat transfer systems in this temperature range have chosen conventional aliphatic-based fluids — more commonly known as hot oils. Developments in synthetic aromatic heat transfer fluids are making them viable and cost-effective options for processes operating between 550 and 625°F.

The term "hot oils" covers a number of chemically similar fluids based on mineral, white mineral, hydrotreated, paraffinic and petroleum oils. The differences between the oils lie in their aromatic content; that is, the amount of chain branching and the prevalence of carbon-based double bonds. The maximum recommended use temperature for these types of fluids varies between manufacturers, but generally it is between 550 and 625°F.

TABLE 1. SATURATED LIQUID PHYSICAL PROPERTIES

(Film Coefficient Calculations Based on 1' Pipe, 7 ft/sec)

	Synthetic Organic Fluid 1			Synthetic Organic Fluid 2		
	77°F (25°C)	302°F (150°C)	599°F (315°C)	77°F (25°C)	302°F (150°C)	599°F (315°C)
Viscosity (cP)	3.478	0.453	0.177	16.45	0.96	0.22
Heat Capacity (BTU/lb-°F)	0.399	0.492	0.609	0.389	0.486	0.614
Density (lb/ft^3)	60.03	54.13	46.32	59.85	54.19	45.65
Thermal Conductivity (BTU/hr-ft^2-°F)	0.0702	0.0603	0.0455	0.0706	0.0631	0.0531
Vapor Pressure (psia)	0.00	0.47	35.05	0.00	0.05	11.34
Reynolds Number	15,014	103,903	227,404	3,164	49,144	177,721
Film Coefficient (BTU/hr-ft^2-°F)	161	417	508	87	302	501

Tables 1 and 2 show a comparison of film coefficients and physical properties for several synthetic organic fluids and hot oils.

Hot oils have high boiling points that allow them to be used in low-pressure or nonpressurized systems. How-ever, when used at these high temperatures in liquid-phase heat transfer systems, hot oils typically experience relatively high rates of thermal degradation. This can lead to costly and excessive fluid replacement and system operation problems.

Synthetic organic heat transfer fluids and silicone-based fluids have long been recognized as having superior thermal stability compared with hot oils at all use temperatures. Thermal stability is a measure of how much a fluid will degrade at a given temperature. In effect, it serves as an accurate indication of the operating cost for a heat transfer system. The more stable the fluid, the less makeup will be required and the less expensive the system will be to operate.

Silicone-based fluids are suitable for processes requiring fluids to be used either at very low temperatures (e.g., less than -20°F [-29°C]) or high temperatures (e.g., greater than 650°F [343°C]). They especially are suitable for pharmaceutical processes requiring an operating range of -148 to 500°F (-100 to 260°C). Not surprisingly, they are not widely used in the range normally consigned to hot oils.

Synthetic organic heat transfer fluids are based primarily on various types of aromatic compounds. These fluids include eutectic mixtures of diphenyl oxide and diphenyl (DPO/DP), alkylated aromatics of various descriptions, and di- and tri-aryl compounds. Here, the maximum recommended use temperatures vary rather dramatically, depending entirely on the fluid's aromatic chemistry, but can extend as high as 750°F (399°C). Typically, however, they have not been chosen for the 550 to 625°F range because of vapor pressure concerns and/or initial cost.

Developments in synthetic organic heat transfer fluids have produced fluids based on alkylated aromatics that combine the thermal stability expected of synthetic organic fluids with low vapor pressures, which reduces the need for system pressurization. These features, combined with a maximum use temperature of 625°F, are what make these fluids viable and practical alternatives for liquid-phase heat transfer systems required to operate in the 550 to 625°F range.

EXAMINING PHYSICAL PROPERTIES

In addition to good thermal stability, the physical properties of synthetic organic fluids result in high heat transfer coefficients as well as good low temperature pumpability, with a vapor pressure near or below atmospheric pressure. Another benefit of synthetic aromatic fluids, when compared with hot oils, is improved heat transfer performance. The lower viscosity and greater density associated with synthetic organic fluids generally result in higher values for the film coefficient at a given flow rate and temperature.

Film coefficient is a calculated value used to determine the rate at which a fluid will transfer heat in a given flow situation. The greater the film coefficient, the faster heat is transferred from the fluid to a surface. Larger film coefficients can result in less surface area needed to transfer a given amount of heat. This can reduce capital costs for a heat transfer system.

Tables 1 and 2 show a comparison of film coefficients and physical properties for several synthetic organic fluids and hot oils. The film coefficients were calculated from the Seider-Tate equation.

As the results demonstrate, the lowest film coefficient for the listed synthetic organic fluids at approximately

HOT SHEET

KEY BENEFIT

Synthetic organic heat transfer fluids capable of operating in the 550 to 625°F range provide:

- Good thermal stability.
- High heat transfer coefficient.
- Low temperature pumpability.
- Vapor pressure near or below atmospheric pressure.

This alternative to hot oils results in less fluid degradation and fouling.

EQUIPMENT COVERED

Hot oils; synthetic organic heat transfer fluids; silicone-based heat transfer fluids; heat transfer systems

INDUSTRIES SERVED

Chemicals/petrochemicals; electronics; finishing; food processing; packaging; pharmaceuticals; plastics/rubber; pulp/paper; textiles

TABLE 2. SATURATED LIQUID PHYSICAL PROPERTIES

(Film Coefficient Calculations Based on 1" Pipe, 7 ft/sec)

	Hot Oil 1			Hot Oil 2		
	77°F (25°C)	302°F (150°C)	599°F (315°C)	77°F (25°C)	302°F (150°C)	599°F (315°C)
Viscosity (cP)	65.69	2.02	0.48	71.20	1.97	0.43
Heat Capacity (BTU/lb-°F)	0.460	0.558	0.687	0.435	0.550	0.701
Density (lb/ft³)	53.27	48.02	41.06	53.21	47.91	40.29
Thermal Conductivity (BTU/hr-ft²-°F)	0.0824	0.0786	0.0736	0.0697	0.0598	0.0468
Vapor Pressure (psia)	0.00	0.01	1.39	0.00	0.02	2.32
Reynolds Number	705	20,684	73,968	650	21,157	81,836
Film Coefficient (BTU/hr-ft²-°F)	49	235	415	41	197	321

As the results in tables 1 and 2 indicate, the heat transfer capability of synthetic organic fluids at the lowest film coefficient is 20% greater than hot oils at their highest film coefficient.

600°F (316°C) is 501 BTU/hr-ft²-°F while the highest film coefficient for the two hot oils listed is 415 BTU/hr-ft²-°F. For this flow rate and temperature, the heat transfer capability of the synthetic organic fluid is more than 20% greater than that of the hot oils.

FILM COEFFICIENT COUNTS

One factor often overlooked when comparing fluids is the film coefficient effect on fluid performance in the heater. In a liquid-phase heating system, the fluid is subjected to the highest temperatures in the heater. Most comparisons of heat transfer fluids examine fluid properties and degradation rates at the bulk fluid temperature as it exits the heater. But, another temperature also should be considered: the calculated maximum film temperature in the heater.

For a gas- or oil-fired heater, the maximum film temperature is calculated according to API Standard 530 from the following equation.

Assuming $t_c = 0$:

$$\Delta T_f = \frac{q_m}{h_i}\left(\frac{D_o}{D_i - 2t_c}\right)$$

Where:

ΔT_f is the maximum film temperature increase

q_m is the maximum heat flux

h_i is the film coefficient

D_o is the outside tube diameter

D_i is the inside tube diameter

t_c is the coke thickness

Because coke thickness is assumed to be 0 for a new heater, the equation can be reduced to:

$$\Delta T_f = \frac{q_m}{h_i}\left(\frac{D_o}{D_i}\right)$$

The value for maximum heat flux (q_m) depends on the heater's rating, the radiant section's surface area and the geometry of the tubes inside the heater. It is derived from the average heat flux multiplied by the circumferential heat flux factor (F_c). This factor also comes from API 530.

For the sake of comparison, a 10 million BTU/hr heater with a 4" dia. vertical helical coil was evaluated. Tube spacing has a significant effect on the maximum film temperature rise, so a tightly packed coil and a coil with 3" between the coils were compared. Assume the heater follows industry guidelines and is designed for an average heat flux of 10,000 BTU/hr-ft². To determine the maximum heat flux for this heater, average heat flux was multiplied by the flux factor (F_c). For a tightly packed coil, the flux factor (F_c) from API 530 was 3.2, so the maximum heat flux (q_m) equals 32,000 BTU/hr-ft². For the coil with 3" spacing between coils, the flux factor (F_c) was 1.75 and the maximum heat flux (q_m) equals 17,500 BTU/hr-ft².

Spacing between the tubes in a heater may increase its overall size, but it greatly reduces the maximum heat flux across the tubes. For a nominal 4" schedule 80 tube, the outside and inside tube diameter factor (D_o/D_i) is 1.18. The maximum film temperature rise can be calculated by:

Case 1

$$\Delta T_f = \frac{32{,}000}{h_i}(1.18)$$

Case 2

$$\Delta T_f = \frac{17{,}500}{h_i}(1.18)$$

Table 3 shows the calculation results comparing the maximum film temperature rise of the four fluids at 600°F (316°C) with a flow rate of 7 ft/sec. The results demonstrate the film coefficient's

TABLE 3. COMPARISON OF FILM TEMPERATURE RISES IN A 10 MILLION BTU/HR FIRED HEATER

	Case 1 (q_m = 32,000 BTU/hr-ft²)			Case 2 (q_m = 17,500 BTU/hr-ft²)		
	h_i (BTU/hr-ft²-°F)	ΔT_{film} (°F)	Film Temperature (°F)	h_i (BTU/hr-ft²-°F)	ΔT_{film} (°F)	Film Temperature (°F)
Synthetic Organic Fluid 1	389	97.1	697.1	389	53.1	653.1
Synthetic Organic Fluid 2	383	98.6	698.6	383	53.9	653.9
Hot Oil 1	317	119.1	719.1	317	65.1	665.1
Hot Oil 2	246	153.5	753.5	246	83.9	683.9

Film coefficient has a dramatic impact on the film temperature to which a fluid is exposed in a heater.

dramatic impact on the film temperature to which the fluid is exposed in a heater.

The lower heat transfer coefficients of hot oils can result in a film-temperature increase as much as 50% higher than for synthetic organic fluids at the same bulk temperature and flow rate. In effect, the less stable hot oils are exposed to higher film temperatures than synthetic organic fluids in heat transfer systems operating at comparable temperatures. Synthetic organic fluids are subjected to less thermal stress. This reduced thermal stress, coupled with the synthetic organic fluids' greater thermal stability, can extend the operating life of the fluid in the heat transfer system, resulting in less downtime and better operating efficiency.

As table 3 also makes clear, allowing spacing between the heater coils in the radiant section of the heater has a significant impact on the maximum film temperature to which the fluid is exposed. This also extends the fluid's useful life.

GAUGING THERMAL STABILITY

While a fluid's physical properties have a significant impact on the system's initial design, the thermal stability of a fluid will have a profound impact on the system's overall operating cost.

How is thermal stability measured? Most suppliers use some variation of the same test method. A small amount of fluid is placed inside a small-diameter (1") carbon or stainless steel tube, which then is sealed under a nitrogen atmosphere. The sealed tube is placed in a temperature-controlled oven for a predetermined period of time, then removed from the oven and opened. The degraded fluid is analyzed by whatever method the experimenter chooses.

To bring some standardization to this procedure, a group of thermal fluid suppliers has worked on a test standard under the auspices of the Deutsches Institut für Normung (DIN) in

TABLE 4. RELATIVE THERMAL STABILITY OF THERMAL FLUIDS TESTED PER DIN 51528 500 HR AT 625°F (329°C)

(Values Are All Relative to Synthetic Organic Fluid 2)

	Gas + Low Boilers* (wt%)	High Boilers + Nonvolatile Residue* (wt%)	Total Degradation (wt%)
Synthetic Organic Fluid 2	1	1	1
Hot Oil 1	4.5	6.1	5.1
Hot Oil 2	4.6	8.2	6.0

*For simplicity, these data have been combined.

Hot oils exhibited five to six times higher thermal degradation rates than the synthetic organic heat transfer fluid that was tested, an alkylated aromatic-based fluid.

Germany. DIN standard 51528 specifies test conditions and analytical procedures to be used in the measurement of the heat transfer fluid's thermal stability. The thermal stability data for the fluids presented in these cases were measured using DIN 51528.

In this test, Synthetic Organic Fluid 2, an alkylated aromatic-based fluid, and two hot oils were measured for thermal stability. Table 4 lists the test results. Depending on the hot oil manufacturer, the maximum fluid bulk temperatures are between 600 and 620°F (316 and 327°C). For all the hot oils tested, 625°F was within the limitations on maximum film temperature. For the alkylated aromatic-based fluid, 625°F was the maximum recommended bulk temperature.

To gauge the economic impact of these results on the economics of a system, consider the temperature-volume profile in table 5. This profile assumes that the film temperature rise from Case 2 for Synthetic Organic Fluid 2 is the same for all fluids, which is a conservative assumption. Using thermal stability data developed for the alkylated aromatic-based heat transfer fluid, the following system degradation rate can be predicted:

- Total system degradation rate (wt%/yr): 2
- Total low boiler generation (wt%/yr): 1.4
- Total high boiler generation, including nonvolatile residue (wt%/yr): 0.6

Assuming that Arrhenius's Law applies to hot oils and that the slopes of the Arrhenius equations for all the fluids are approximately equal (the first assumption being perfectly valid while the second is slightly conservative), then it is possible to conclude that hot oils would undergo five to six times the thermal degradation under similar operating conditions.

The temperature-volume profile in table 5 assumes that the film temperature rise would be the same for all fluids in a given heater. However, as discussed, this is not a valid assumption. Holding all other temperatures constant and using the film temperature rises from Case 2 for the hot oils creates a much higher degradation rate. Using the film temperature for Hot Oil 1 (665°F [352°C]) creates an estimated system degradation rate of 2.86 wt%/yr for Synthetic Organic Fluid 2; using the film temperature for Hot Oil 2 (683°F [362°C]) creates an estimated system degradation rate of 5.7 wt%/yr for Synthetic Organic Fluid 2. Therefore, based on the relative stability data in table 4, the hot oils would see degradation rates five to six times higher.

TIPS ON SYSTEM CONVERSION

Comparisons will prove helpful in designing a new system. But, what can be done if you already have a hot oil system operating in this temperature range and you are not satisfied with the degradation rate or the fluid performance?

TABLE 5. TEMPERATURE-VOLUME PROFILE USING FILM TEMPERATURE RISE FOR SYNTHETIC ORGANIC FLUID 2

System Segment	Temperature (°F)	Volume %
Heater Film	653.9	1
Bulk Temperature At Heater Exit	600	33
Bulk Temperature At Heater Inlet	550	33
Expansion Tank	300	33

Using a synthetic organic heat transfer fluid with good thermal stability has a significant impact on the heat transfer system.

Most systems designed to operate with hot oils can be converted to a synthetic organic fluid; however, it may not be as simple as draining the old hot oil and putting in the new fluid. The differences in physical properties may require changes to pump impeller size or the placement of a back-pressure device in the pump discharge.

Relief valves should be checked to determine if any changes are necessary. Heat exchangers and process vessels are of less concern because the heat transfer properties of the synthetic organic fluids should provide better performance. In most cases, gaskets, valves and piping that are compatible with hot oils also should be compatible with synthetic organic fluids.

If the system is heavily fouled with sludge and degraded oil, chemical cleaning may be necessary before introducing a new fluid. In addition, if a nitrogen-inerting system is not present on the expansion tank, it should be added. Thermal fluids should be kept free of oxygen. Oxygen contamination in a high-temperature heat transfer system will increase the rate of sludge formation and greatly reduce fluid life. **PH**

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Please note: The conclusions in this article are based upon the research and opinions of the authors. Any person interested in utilizing newer synthetic organic heat transfer fluids should independently determine the appropriateness of using such fluids for the intended application. Neither the authors nor Dow Chemical Co. warrants such fluids in any specific application.

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