

Using Segregated HFEs as Heat Transfer Fluids

Avoiding problems in system design



By Phil E. Tuma

The majority of heat transfer fluids used at temperatures below -50°C suffer from regulatory or safety limitations. Regulations related to ozone depletion concerns have made it difficult to use chlorofluorocarbons (CFCs). Other chlorinated fluids such as trichloroethylene and methylene chloride have unfavorable toxicological properties. Many fluids designed to replace potentially toxic fluids are flammable or corrosive.^{1,2} Perfluorocarbon (PFC) fluids have been suggested as alternatives,³ but these fluids have long atmospheric lifetimes and high global

criteria often are indistinguishable from other chemical classes (e.g., hydrofluorocarbons [HFCs] and PFCs) from a global warming standpoint.

The HFEs that are the subject of this article are shown in Table 1 and include: $\text{C}_3\text{F}_7\text{OCH}_3$, $\text{C}_4\text{F}_9\text{OCH}_3$, $\text{C}_4\text{F}_9\text{OC}_2\text{H}_5$ and $\text{C}_3\text{F}_7\text{CF}(\text{OC}_2\text{H}_5)\text{CF}(\text{CF}_3)_2$. These HFEs not only possess the requisite performance properties,⁷ but because they are members of a class known as "segregated" HFEs, they also possess uniquely low GWPs.⁸ The term segregated refers to HFEs that possess a PFC segment separated or segregated from a fully hydro-

Fig. 1 shows the useful temperature range of each of these fluids. The lower limit is defined as the point at which viscosity reaches 30 centistokes (cSt). The upper limits shown are those imposed by the boiling point and the limits of thermal stability. Thermal stability limits often can be exceeded for systems exposing only a relatively small amount of the fluid vapor to the higher temperature.

Compatibility considerations

Table 2 shows the compatibility properties of HFEs. If kept dry, the fluids are inherently noncorrosive and may be used with all common metals. If the fluids are saturated or nearly saturated with water, corrosion rates on most metals will be similar to those on the same metal left in ambient air. Under these conditions, corrosion may be more rapid than in the same system filled with pure water because ionic contaminants (such as solder fluxes, residue, etc.) tend to concentrate in the aqueous phase where they are most soluble.

HFE fluids are inert to most common nonfluorinated polymers such as ethylene propylene, nitrile, silicone and polyurethane. The fluids do, however, have some solvency for many of the additives and plasticizers commonly added to the elastomeric forms of these polymers. Heavily plasticized elastomers may shrink or become brittle, whereas relatively pure elastomeric polymers perform well. For this reason, designers cannot generalize about the compatibility of various types of polymers, and must pay attention to the specific formulation. Table 2 shows some common polymers that work well with HFEs.

Toxicity

$\text{C}_4\text{F}_9\text{OCH}_3$ and $\text{C}_4\text{F}_9\text{OC}_2\text{H}_5$ exhibit very low acute toxicity. The American

Table 1. Physical Properties of Four Segregated HFEs (at 25°C , except where noted)

| | $\text{C}_3\text{F}_7\text{OCH}_3$ | $\text{C}_4\text{F}_9\text{OCH}_3$ | $\text{C}_4\text{F}_9\text{OC}_2\text{H}_5$ | $\text{C}_3\text{F}_7\text{CF}(\text{OC}_2\text{H}_5)\text{CF}(\text{CF}_3)_2$ |
|--|------------------------------------|------------------------------------|---|--|
| Boiling point, b.p. ($^{\circ}\text{C}$) | +34 | +61 | +76 | +130 |
| Pour point ($^{\circ}\text{C}$) | -126 | -135 | -138 | -100 |
| Vapor pressure (Pa/1,000) | 69.8 | 26.8 | 15.7 | 2.10 |
| Density (kg/m^3) | 1,400 | 1,510 | 1,420 | 1,610 |
| Coefficient of thermal expansion (1/K) | 0.0013 | 0.0018 | 0.0016 | 0.0013 |
| Kinematic viscosity (cSt) | 0.32 | 0.38 | 0.41 | 0.77 |
| Dynamic viscosity (cp) | 0.45 | 0.58 | 0.58 | 1.24 |
| Specific heat (J/kg-K) | 1,300 | 1,180 | 1,220 | 1,130 |
| Heat of vaporization at b.p. (kJ/kg) | 142 | 112 | 119 | 88.5 |
| Electrical resistivity (ohm-cm) | 10^8 | 10^8 | 10^8 | 10^8 |
| Dielectric strength (0.1-in. gap) | ~ 40 | ~ 40 | ~ 40 | ~ 40 |
| Atmosphere lifetime (years) | 4.7 | 4.1 | 0.8 | 2.5 |
| GWP (100-year integrated time horizon) | 400 | 320 | 55 | 210 |

warming potentials (GWPs); therefore, their use is inconsistent with a growing global trend to select chemicals with the lowest possible environmental impact.

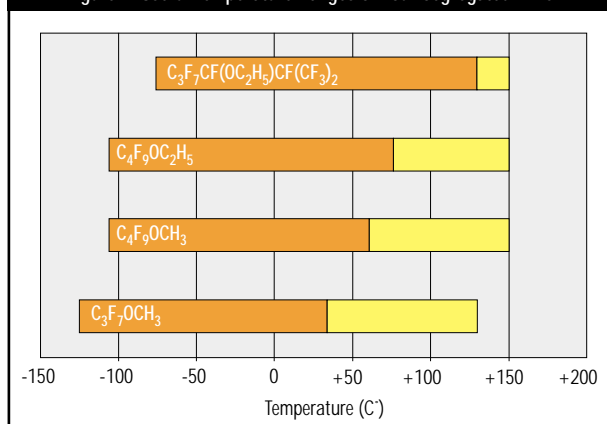
Hydrofluoroether (HFE) fluids have been suggested as alternatives to the aforementioned fluids. Although all are nonozone-depleting, their toxicological, compatibility and stability properties can vary widely.^{4,5,6} Those that satisfy toxicological, compatibility and stability

generated portion by an ether oxygen. Examples of this include the structures shown in Table 1 and discussed here. ($\text{C}_4\text{F}_9\text{OCH}_3$, $\text{C}_4\text{F}_9\text{OC}_2\text{H}_5$ and $\text{C}_7\text{F}_{15}\text{O}_2\text{H}_5$ are sold commercially as 3M Novec HFE-7100, HFE-7200 and HFE-7500, respectively. $\text{C}_3\text{F}_7\text{OCH}_3$ is currently under development by 3M.)

Heat transfer properties

Table 1 shows pertinent properties and

Figure 1. Useful Temperature Ranges of Four Segregated HFEs



Useful temperature range of four segregated HFEs. Yellow bars show the liquid range. Orange bars show the pumpable range, as dictated by thermal stability.

Industrial Hygiene Association (AIHA) set an 8-hour (hr.) worker exposure guideline of 750 parts per million per volume (ppmv) for $C_4F_9OCH_3$, based on the results of a 90-day inhalation study. This material is not a cardiac sensitizer — an agent that makes the heart tissue more sensitive to the effects of adrenaline, leading to arrhythmia — at

(g/m^3) (850 ppmv). The compound tested negative in the Ames mutagenicity test and was not a skin irritant. It has been corroborated that $C_3F_7OCH_3$ exhibits low acute and subacute toxicity. A 28-day inhalation study was conducted at 1,000 ppmv, 10,000 ppmv and 30,000 ppmv. The no adverse effect level (NOAEL) in this study was 1,000 ppmv.

>100,000 ppm, and is nonirritating to the skin and eyes.

Toxicity tests conducted by Sekiya and Misaki⁹ with $C_3F_7OCH_3$ resulted in an acute oral LD_{50} of >2,000 milligram per kilogram (mg/kg). Inhalation tests conducted six hours per day for seven days showed a no observable effect level (NOEL) of >7.0 grams per meters cubed

Toxicity tests conducted to date with $C_3F_7CF(OC_2H_5)CF(CF_3)_2$ indicate this compound exhibits a very low order of toxicity. For instance, the acute oral LD_{50} for this compound is greater than 2,000 mg/kg. It is not classified as an eye or skin irritant. The molecule tested negative in two mutagenicity screens: the Ames assay and the chromosomal aberration assay. In a 28-day feeding study, no adverse health effects were observed at a dosing level of 1,000 mg/kg body weight.

Thermal stability considerations

When used below their boiling points, these HFE fluids should never require replacement. Their lifetimes, within the decomposition limits shown in Fig. 1, depend largely upon the amount of time spent at that temperature and the amount of water present. In applications where HFE fluids are used above their boiling points, a long lifetime can be expected if the system is kept dry. Thermal decomposition can be detected with test kits commonly used with refrigeration system lubricants.

It sometimes is possible to exceed the temperature limitations indicated in Fig. 1. For example, in some applications, the pump is turned off while a relatively brief high-temperature operation is performed on some subportion of the system. If the system is plumbed properly, it is possible to maintain only a small amount of superheated vapor in this portion.

Not only is the amount of fluid represented by this vapor a small percentage of the overall system, but the kinetics of thermal decomposition are different in this vapor. It has been shown experimentally, for example, that $C_4F_9OCH_3$ can be used in such an application safely and without corrosion at 275°C¹⁰, well above common steam sterilization temperatures.

System design and component selection

Figure 2 depicts a typical heat transfer system. The numbers at the beginning of each paragraph refer to a numbered section in Fig. 2. When designing a system, each component must be considered. It is important to note that:

1. HFE fluids are highly wetting liquids with low surface tensions and contact angles on most surfaces. This makes them difficult to seal. Welded or brazed

Table 2. Compatibility¹ with Segregated HFEs

| Metals | | |
|---------------------------------|-----------------------|-----------------------------------|
| Copper | Iron | Zinc |
| Stainless steel | Titanium | Aluminum |
| Hard polymers | | |
| Polyethylene | Polypropylene | Phenolic |
| ABS | Nylon | Ryton |
| Polyvinylchloride (PVC) | Polycarbonate (Lexan) | Polyetheretherketone (PEEK) |
| Acrylic (Plexiglas) | Rulon | Thermoplastics |
| PTFE (Teflon) | Polysulfone | Epoxies |
| Elastomers ¹ | | |
| Nitrile | Silicone | Ethylene propylene (EP or EPDM) |
| Butyl | Fluorocarbon | Stillman SR721-80 |
| Stillman SR634-70 | Stillman TH1387 | Parker EPR 540-80 |
| Bay Seal Co. B0612-70 | Natural rubber | Jackson Flex. Prods. EPR E3450-80 |
| Fluorosilicone | Polysulfide | Parker EPR E515-80 |
| Chloroprene | Polyurethane | Newman EPDM 2107 |
| Polyacrylate | Styrene butadiene | International Seal E480 |
| Hoses | | |
| Tygon C-544-A I.B. polyurethane | | TFE |
| Tygon 3370 I.B. silicone | | Parker Parflex 550 |
| Flexfab 5521 silicone | | Aeroquip FC373 |
| Nalgene 290 PUR polyurethane | | TFE, PFA |

¹Compatibility depends upon the specific formulation. The specific compounds shown have performed well in extraction studies.

joints and compression or sanitary fittings are preferable to pipe threads.

2. When pipe threads must be used, they should be sealed with epoxy, Leak Lock, Locktite 290 or some other compatible sealant. TFE or Teflon tape generally does not work well, and the binders used in common TFE-based paste sealants often are soluble in HFE fluids.

3. Although hard TFE O-rings and gaskets perform well, expanded TFE gaskets or fibrous gaskets do not. HFE fluids may wick or diffuse through these materials.

4. Valves with “packed” shaft seals or those designed for water service are prone to leakage and should be avoided. Bellows valves (which use only static seals) or those designed for high-pressure refrigerant or chemical service are preferable.

5. The elastomers present in quick disconnects are particularly sensitive to shrinking or embrittlement resulting from plasticizer extraction. Quick disconnects for these fluids should be purchased from original equipment manufacturers (OEMs) that have experience with these fluids.

6. Conventional pumps with inexpensive shaft seals designed for water or oil service are prone to leakage. Ceramic shaft seals will perform well if properly designed for such fluids, but magnetically coupled or canned pumps are preferable.

7. Because these fluids are volatile and have a large affinity for dissolved gas, pump suction lines should be as short and as unobstructed as possible to prevent cavitation or spontaneous degassing, a phenomenon commonly confused with cavitation. Whenever possible, place the pump below the reservoir that feeds it.

8. The critical heat flux of HFE fluids is similar to that of PFC fluids. For a heated horizontal wire in a saturated quiescent pool boiling experiment,¹¹ the critical heat flux was found to be 16 watts per cm² (W/cm²) to 20 W/cm², roughly 25 percent that of water. Therefore, off-the-shelf immersion heaters, which often are designed for water service, should be used with caution. To avoid thermal decomposition, surface heat fluxes should be kept below about 10 W/cm². Although considerably higher heat fluxes are practical in forced convection situa-

tions, an interlock should be used to shut the heater off if the hottest, most downstream surface of the heater exceeds the fluid’s boiling point by 50°C or more. Regardless of heat flux, a similar interlock should be used to shut the heater off if a “no flow” condition develops. (For a given geometry and flow condition, the critical heat flux is the point at which boiling is no longer sustainable. A stable, insulating vapor blanket forms on the heated surface. If this surface is an electric resistance heater, the surface temperature will rise abruptly to very high levels.)

9. Filters should be sintered metal, metal screen, polyethylene or polypropylene. TFE filter media are not recommended because they may swell, making the filter ineffective.

10. As they can with elastomeric seals, HFE fluids can extract plasticizers from elastomeric hoses. Because the mass of hose in a system is generally quite large, hoses can be a significant source of contamination that can cause system problems such as fluid discoloration, odor, static discharge and component coating or clogging. For this reason, hoses must not be heavily plasticized. For low-temperature applications, TFE or corrugated stainless hoses may be used.

11. Although systems usually can be sealed without danger of pump cavitation, it often is desirable to add a vacuum break valve that opens at a prescribed vacuum level. The air that enters a system through such a valve during cool-down can be significant. The moisture that enters with this air will condense if the system temperature is below the dewpoint of the air. This moisture can cause corrosion if it contacts metal components.

To avoid this problem, the air entry path can be equipped with a common desiccant cartridge containing silica gel or a molecular sieve. If located on the fluid side of the vacuum break, the desiccant also will remove water that is dissolved in the fluid. A silica gel cartridge also can be placed in the liquid loop.

The amount of water dissolved in the fluid may be monitored by measuring the relative humidity in the headspace of the reservoir with a suitable hygrometer. If the fluid is well agitated, the relative humidity will be equal to the percent saturation of the fluid. Typical

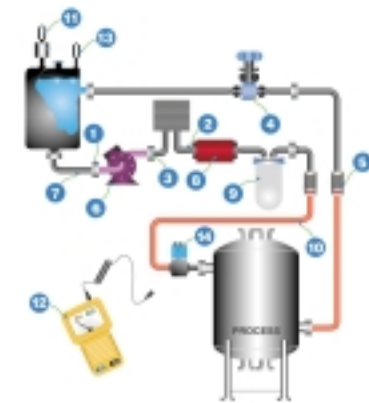


Figure 2. A schematic of a typical heat transfer system. Numbers refer to points discussed in the “System design and component selection” section of the text.

water saturation levels for HFEs are 40 parts per million per weight (ppmw) to 100 ppmw. A measurement of 100 percent indicates a separate water phase.

12. Leaked fluid evaporates quickly and leaves no residue. Ordinary halogen leak detectors will detect HFE leaks that might otherwise be hard to find.

13. The solubility of air in HFE fluids is typically 50 volume percent — 1 liter of fluid will hold 500 ml of air at standard temperature and pressure — well below the boiling point. As the temperature of a vented heat transfer system is increased, the solubility of air decreases. The air that leaves the system as a result of this decrease will be nearly saturated with fluid vapor. This evaporative fluid loss mechanism can lead to high fluid losses over many thermal cycles.¹² To avoid this problem, operators should use a valve designed to maintain a positive pressure within the system.

14. As mentioned earlier, the temperature limits shown in Fig. 1 often can be exceeded only if the vapor is exposed to such temperatures. A practical way of doing this is shown here for a steam-sterilized reactor cooling application. If one of the liquid lines enters the reactor from the bottom and another from the top, a solenoid valve on the top line can be closed before sterilization. As the fluid within the jacket boils, its vapor displaces liquid from the jacket, leaving only superheated vapor behind. If both lines enter from the bottom, no solenoid valve is needed. If both enter from the top, more complicated techniques must be used.

Case Histories

Minnesota Mining and Manufacturing

At St. Paul, Minn.-based Minnesota Mining and Manufacturing Co., one of the fine chemical plants uses a system containing roughly 530 gallons of $C_4F_9OCH_3$ in a large distributed network that is used to cool jacketed formulation tanks. The system uses two cascaded screw compressors operating with refrigerants 23 and 22. The system provides 17 tons of cooling at $-75^\circ C$. CFC-11 once was used as the heat transfer fluid, but corporate environmental policies would not tolerate the losses associated with normal operation and maintenance. $C_4F_9OCH_3$ was chosen primarily because it is not subject to regulations for transport or use. Its nonflammability and favorable toxicological profile were important considerations for the serviceability of the system. Because the system was designed to use CFC-11, no elastomer retrofit was needed.

Mayekawa Manufacturing Co. Ltd. (MYCOM Co.)

More than 1,000,000 metric tons of tires are used in Japan each year. Disposal of these tires is a problem familiar to all developed nations. Mayekawa Manufacturing Co. Ltd. (MYCOM Co.), Tokyo, Japan, has a system that permits tire recycling. A two-stage refrigeration cycle uses ammonia on the high side and ethane on the low side to achieve more than 47 kilowatt-capacity (13 tons) at suction temperatures as low as $-100^\circ C$. This system is used to chill $C_4F_9OCH_3$, which then is used to cool air to $-87^\circ C$. The chilled air is passed over incoming tires, which, when cooled, are milled into a powder that is suitable for recycling.

The environmental goals of this system could not be met with conventional high-pressure HCFC or HFC refrigeration systems. Ammonia and ethane are certainly more environmentally benign, but their use in a conventional direct-expansion system would pose safety challenges. However, use of low-pressure secondary refrigerant or "brine" systems greatly reduces the primary refrigerant charges and allows the refrigerants to be located away from personnel and machinery. HFE was chosen as a brine not only for its low-temperature properties but also because it is nonflammable, nonozone-depleting, and has a low toxicity and a low GWP. The finished system is considered cheaper and friendlier to the environment than liquid nitrogen systems the company had used previously.

DuPont Pharmaceuticals

A blend of $C_4F_9OC_2H_5$ and $C_3F_7CF(OC_2H_5)CF(CF_3)_2$ is used at Wilmington, Del.-based DuPont Pharmaceuticals to optimize the fluid performance from $-80^\circ C$ to $100^\circ C$. Twenty liters of the blend are used in a Julabo model FP90-SP chiller to control a set of 0.5-L to 5-L scale reactors. Because HFE blends behave ideally, the composition, viscosity and boiling point of the mixture can be monitored via density measurements made with a simple hygrometer.

Lyophilization Technology

$C_3F_7CF(OC_2H_5)CF(CF_3)_2$ was installed in a 2-square-foot Hull Model 2FS8C pilot-scale lyophilizer at Lyophilization Technology, Ivyland, Pa. Although more volatile HFEs might perform more proficiently, $C_3F_7CF(OC_2H_5)CF(CF_3)_2$ was used because its $130^\circ C$ boiling point is above common steam sterilization temperatures. Three distinct tests were run: shelf temperature uniformity, cooldown rate and heatup rate. Comparisons were made to the TCE data from Reference 1. These data were measured on the same lyophilizer.

Shelf uniformity results at various temperatures between $-50^\circ C$ and $+50^\circ C$ showed that HFE shelf temperature ranges were, on average, about $0.17^\circ C$ higher than TCE. The controlled cooldown rate ($0.5^\circ C/\text{minute}$) for HFE between $20^\circ C$ and $5^\circ C$ was $0.53^\circ C/\text{min}$. Between $+5^\circ C$ and $-25^\circ C$ it was $0.48^\circ C/\text{min}$. The maximum warm-up rate for HFE from $-50^\circ C$ to $+50^\circ C$ was, at $0.65^\circ C/\text{min}$, very similar to TCE. The maximum cool-down rate between $20^\circ C$ and $-50^\circ C$ was $0.87^\circ C/\text{min}$, 27 percent lower than TCE.

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