Heat Transfer Fluids and Systems for Process and Energy Applications

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Organic Fluids

5.1 INTRODUCTION

While the temperature range covered by water and gases for heat transfer theoretically accounts for all high-temperature requirements, neither of these media is suitable for many industrial applications. The problems with water (or steam) are related to the high vapor pressures at elevated temperatures and to a lesser extent the associated corrosion which necessitates extensive water treatment facilities. Gases suffer the drawback of very poor heat transfer rates (particularly at moderate or low pressures); this rules out their use except in special circumstances such as the nuclear industry or as products of combustion. Specially formulated organic fluids with reasonable heat transfer characteristics and low vapor pressures, sometimes termed <u>hot oils</u>, satisfy a relatively small but very important demand in the range 150 to 400°C.

At temperatures between 200 and 250°C, steam is still used very extensively and organic fluids normally only find favor if one of the following conditions prevails:

1. The user does not already possess a steam boiler.
2. Water contamination of a product must be avoided.
3. High-pressure equipment is a problem.
4. Very precise temperature control is required.

In the range 300 to 400°C organic fluids are almost universally accepted as the most suitable, although the choice at the upper end of this range is limited.

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Industrial applications of organic fluids are so widespread and cover so many fields of interest that comprehensive listing becomes impossible. Industries include textiles, chemical, petroleum, food, nuclear energy, plastics, rubbers, offshore oil and gas platforms, and many more. The major factors in selection may be high temperature, low pressure, cheaper system (than, for example, steam), accurate temperature control, and lower operating costs. Not all these items will apply in every case, nor will they all be realizable at the same time, but they include the overriding reasons for selection.

The total number of organic fluids commercially available is very large and selection can be a lengthy and tedious task. The situation is made worse by the often difficult (and very time consuming) task of obtaining the data required for evaluation from the various companies marketing these compounds.

5.2 OVERVIEW OF FLUID CHARACTERISTICS

5.2.1 Summary of Data

There are two basic types of fluids in common use, mineral oils and synthetic fluids. The former are marketed by the major oil companies and derived from thermal cracking of crude oil. Synthetic fluids are manufactured by petrochemical and chemical companies and consist primarily (with some exceptions) of components with an aromatic structure as the nucleus. These two fluid types compete with each other in the range subzero to 320°C, above which (up to about 400°C) only certain synthetics may be used. Selection between the two categories and within each category is based on a careful consideration of a number of parameters, the most important being:

- Maximum operating temperature
- Low-temperature behavior
- Safety aspects
- Fluid cost
- Heat transfer coefficient
- General engineering properties, such as corrosion, vapor pressure, pumping costs, etc.

These aspects are summarized in Table 5.1 for all the fluids currently available and specifically marketed for general heat transfer applications. Included in this table are the fluid trade names, chemical composition, the maximum temperature at which the fluid is stable, pour point, the flash point and autoignition temperatures as indicators of safety, the relative film transfer coefficients under forced convection, approximate cost, and vapor pressure at 250°C. Depending on their chemical nature, some fluids

TABLE 5.1 Summary of Characteristic Properties of Organic Fluids

Fluid name (usage)[e]	Chemical nature	Maximum temperature[a] (°C)	Pour point (°C)	Flash point[b] (°C)	Autoignition temperature (°C)	Cost[c] ($/kg)	Relative heat transfer rate[d]	Vapor pressure at 250°C (bar)
DP-DPO[f] (L&V)	26.5 wt % diphenyl 73.5 wt % diphenyl oxide Mol wt: 166	400 (420)	12	124	540	2.5	10	0.9
Breox HTF14 (L)	Polyalkylene glycol Mol wt: 900	260	-37	244	393	1.5	8.0	0.0
Caloria HT43 (L)	Paraffinic	316 (360)	-6	204	354	(1.1)	5.5	0.02
Chevron heat transfer oil 1 (L)	Paraffinic	288	-15	235	—	(1.0)	5.5	0.02
Chevron heat transfer oil 32 (L)	Paraffinic	340	-27	210	—	—	7.0	0.05
Chevron heat transfer oil 46 (L)	Paraffinic	340	-24	240	—	—	6.5	0.06
Diphyl (L&V)	See DP-DPO							
Diphyl DT (L)	Dimethyl-diphenyl oxides	330 (340)	-54	135	545	2.2	8.0	0.43

transfer oil 46 (L)	[illegible]	340	-24	240	—	—	6.5	0.06
Diphyl (L&V)	See DP-DPO							
Diphyl DT (L)	Dimethyl-diphenyl oxides	330 (340)	-54	135	545	2.2	8.0	0.43
Dowtherm A (L&V)	See DP-DPO							
Dowtherm G (L)	Di- and triaryl compounds Mol wt: 215	370	-28	157	>554	3.5	9.0	0.31
Dowtherm J (L&V)	Isomers of an alkylated aromatic Mol wt: 134	300	-73	63	430	2.0	12.0	4.3
Dowtherm LF (L)	Methylated diphenyl and diphenyl oxide mixture Mol wt: 176	315	-32	135	>548	4.8	12.0	0.69
Essotherm 500 or Humbletherm 500 (L)	Petroleum	315 (360)	-9.4	218	—	1.1	6.5	0.03
Gilotherm ADX 10 (L)	Alkylbenzenes	250 (280)	-80	136	375	—	8.5	0.56
Gilotherm ALD (L)	Alkylbenzenes	310 (340)	-30	180 FP	390	1.6	7.0	0.09

TABLE 5.1 (continued)

Fluid name (usage)[e]	Chemical nature	Maximum temperature[a] (°C)	Pour point (°C)	Flash point[b] (°C)	Autoignition temperature (°C)	Cost[c] ($/kg)	Relative heat transfer rate[d]	Vapor pressure at 250°C (bar)
Gilotherm D12 (L)	Aliphatic hydrocarbons Mol wt: 170	200	-70	—	265	—	10.5	1.35
Gilotherm DO (L&V)	See DP-DPO							
Gilotherm RD (L)	Alkylbenzenes	270	-55	125[FP]	395	1.7	8.0	0.43
Gilotherm TH (L)	Partially hydrogenated polyphenols	340 (370)	-25	190[FP]	400	3.7	8.0	0.06
Marlotherm L (L&V)	Mixture of iso-meric benzyl toluenes Mol wt: 182	350 (370)	-70	120	>500	2.1	8.5	0.41
Marlotherm S (L)	Mixture of dibenzyl toluenes Mol wt: 279	350 (370)	-35	190	>500	2.0	7.0	0.03
Mobiltherm Light (L)	Paraffinic	220 (250)	-34	121	—	1.1	8.5	0.72
Mobiltherm 594 (L)	Paraffinic	250 (280)	-50	128	—	1.1	9.0	0.40

(L)		(250)						
Mobiltherm 594 (L)	Paraffinic	250 (280)	-50	128	—	1.1	9.0	0.40
Mobiltherm 600 (L)	Paraffinic	315 (345)	-25	176	—	1.1	7.0	0.11
Mobiltherm 605 (L)	Paraffinic	320 (350)	-12	214	—	1.1	7.0	0.12
Santotherm (therminol) VP-1 (I&V)	See DP-DPO							
Santotherm (therminol) 44 (L)	Ester-based mixture Mol wt: 370	220 (245)	-62	207	375	4.0	7.5	0.05
Santotherm (therminol) 55 (L)	— Mol wt: 340	315 (335)	-29	180	357	1.0	6.5	0.15
Santotherm (therminol) 60 (L)	Polyaromatic mixture Mol wt: 250	315 (335)	-68	154	446	—	8.5	0.27
Santotherm (therminol) 66 (L)	Hydrogenated terphenyl Mol wt: 240	345 (375)	-28	178	390	2.5	7.0	0.11
Santotherm (therminol) 88 (L)	Mixed terphenyls Mol wt: 230	400 (435)	60/145	191	> 538	—	8.5	0.06

TABLE 5.1 (continued)

Fluid name (usage)[e]	Chemical nature	Maximum temperature[a] (°C)	Pour point (°C)	Flash point[b] (°C)	Autoignition temperature (°C)	Cost[c] ($/kg)	Relative heat transfer rate[d]	Vapor pressure at 250°C (bar)
Shell Thermia Oil B (L)	Paraffinic	320 (340)	-18	232	375	—	7.5	0.002
Shell Thermia Oil C (L)	Mineral oil	287 (316)	-15	227	—	—	5.0	0.02
Syltherm 800 (L)	Siloxane polymer Mol wt: 1000	400 (427)	-51[FP]	165	385	—	6.0	0.00
Thermex	See DP-DPO							
Texatherm 46 (L)	Paraffinic	300 (340)	-27	216	—	1.25	5.5	~0.02
Texatherm 320[g] (L)	Alkyl-based Mol wt: 325	320	-50	200	—	—	7.0	0.02
Transcal LT	Mineral oil	260	-46	160	310	1.25	8.0	0.11

Transcal LT (L)	Mineral oil	260	-46	160	310	1.25	8.0	0.11
Transcal N (L)	Mineral oil	320	-12	221	350	1.25	7.0	0.04
Transcal SA (L)	Hydrogenated terphenyl	345 (375)	-28	178	390	2.5	7.0	0.11
Ucon HTF 500 (L)	Polyalkylene glycol Mol wt: 900	260	-37	260	400	—	8.0	0.00

[a] Refers to bulk fluid temperature; figures in parentheses indicate maximum film temperatures where these are specified.
[b] Cleveland Open Cup (COC); FP indicates fire point.
[c] Very approximate 1983 prices (U.S. dollars) in Europe; figures in parentheses give prices in the United States, where the fluid is not sold in Europe.
[d] Forced-convection (turbulent flow) heat transfer parameter at approximately 250°C, relative to DP-DPO, which is defined as 10.
[e] Fluids usable only in the liquid phase are indicated by L; while those usable in both the liquid and the vapor phase are indicated by L&V.
[f] Sold under the following trade names: Diphyl, Dowtherm A, Gilotherm DO, Santotherm VP-1, Therminol VP-1, Thermex.
[g] Sold only in West Germany at present; also marketed as Texatherm HT.

are suitable only for liquid-phase applications (indicated by an L under the name) while others may also be used in the vapor phase (indicated by an L&V under the trade name. The significance of the temperature limitations is discussed in Section 5.5.2, the safety parameters in Section 5.9, and heat transfer aspects in Section 5.4. The cost information is intended as a guide only and applies in Europe, except for fluids available only in the United States. The cost will vary according to location, quantity required, and of course inflation. However, the relative costs should be fairly stable; this is indeed the main reason for their inclusion.

Detailed physical property data for all fluids are given in Appendix 2 and the salient features of each fluid are discussed in the following sections.

5.2.2 26.5 Diphenyl-73.5% Diphenyl Oxide (DP-DPO)

This is probably the best known heat transfer fluid, which is manufactured by a number of different companies and sold under a variety of trade names, including Dowtherm A, Santotherm VP-1, and Thermex. The mixture of 26.5% and 73.5% by weight of diphenyl and diphenyl oxide, respectively, abbreviated DP-DPO, is the eutectic composition, which freezes at 12°C and boils at 257.1°C. The vapor pressure curves of diphenyl and diphenyl oxide are so similar that the mixture may be considered as a single compound of molecular weight 166.0 [1].

This fluid may be used as liquid or vapor, up to a bulk temperature of about 400°C. It has a high heat transfer coefficient among organic fluids, although still much below water. There is a great deal of design and operating experience with the fluid, extending back over 50 years.

There are a number of drawbacks in using DP-DPO which must be carefully considered. At a cost of about $2.5 per kilogram, it is more than twice as expensive as mineral oils, although average for synthetic fluids. The relatively high (12°C) freezing point adds further to the cost of units, as this usually necessitates heat tracing. The DP-DPO vapors are quite unpleasant and uncomfortable to the eyes and skin, as well as being extremely toxic. This feature is to some extent accentuated by the fact that the fluid is quite volatile, so that any large spillage pose a considerable hazard. In hot climates, vapors are liberated in sufficient quantity even at atmospheric temperature to pose a toxic hazard. While good engineering practice normally ensures that the fluid presents no hazard, these aspects still have to be considered.

5.2.3 Breox HTF 14 [2]

This is a trade name of B.P. Chemicals and represents a polyalkylene glycol. It is basically produced only for the European market.

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The upper temperature limit of 260°C is quite low, but for applications below this value, it represents one of the safest fluids. The fluid has a number of unusual properties which may be used to advantage. It is an organic solvent and will therefore dissolve any waxes, resins, plasticizers, or petroleum sludge that may be in the system. If it is heated much above its upper limit (say above 315°C), it decomposes to form lighter compounds such as ketones, esters, and aldehydes rather than carbonizing. The rate of decomposition is normally quite low, so the light ends are easily vented. Hence on both these accounts, fouling of equipment is not likely.

Problems can arise with this fluid if its behavior with water is not fully understood. At ambient temperatures, water will dissolve in the organic and there is no problem. However, at temperatures much in excess of 55°C, the water forms a separate phase. If the water layer reaches the hot oil circuit, it will immediately boil, and this can be a serious problem. The source for water entry is normally the expansion tank; if this is blanketed by nitrogen, the problem is eliminated.

5.2.4 UCON 500 [3]

This is identical to Breox HTF 14, being also a polyalkylene glycol. It is a trade name of Union Carbide and is distributed principally for the U.S. market.

5.2.5 Mineral Oil Fluids

Mineral oils are petroleum-based, liquid-phase heat transfer fluids produced by the oil companies. The fluids included in this are Caloria HT 43 [4]; Chevron heat transfer oil 1, 32, and 46 [5]; Essotherm (or Humbletherm) 500 [6]; Mobiltherm Light, 594, 600, and 605 [7]; Shell Thermia Oil B and C [8]; Texaco Texatherm 46 and 320 [9]; Transcal LT and N [10]. These are among the cheapest fluids (typically $1.25 per kilogram) and are commonly (although by no means extensively) found on refinery-related processes and by weight account for about 80% of the organic fluids used in industry [11].

Mineral oils undergo deterioration by oxidation and thermal cracking. The oxidation produces insoluble compounds which settle out and interfere with heat transfer and increase viscosity. Overheating produces light components which lower the flash point, and carbon deposits which foul heat exchanger tubes. The presence of oxidation inhibitors and proper design can keep these problems in check.

5.2.6 Diphyl Fluids [12]

Bayer offers two fluids for high-temperature applications, Diphyl, which is DP-DPO, and Diphyl DT, a mixture of dimethyl-diphenyl oxides. The latter costs the same as DP-DPO, has a lower vapor pressure, and may be used up to 330°C.

5.2.7 Dowtherm Fluids [13]

The Dow Chemical company produces four synthetic fluids which can cover applications from below atmospheric temperature up to about 400°C. The highest temperature range is covered by Dowtherm A, chemically identical to the 26.5% diphenyl-73.5% diphenyl oxide mixture (DP-DPO). Dowtherm G, which is a little more expensive, can be used up to about 370°C, at which point its vapor pressure is only about 2.5 bar. It has the further advantage of a low pour point. It does have a very striking odor even at low concentrations, and is quite toxic. For temperatures up to 315°C, Dowtherm LF may be used. This costs almost $5 per kilogram, but may be used down to -30°C and has a very low vapor pressure. For temperatures down to -70°C, Dowtherm J may be used. Its upper temperature limit is 300°C and it may be used as a liquid or a vapor above 181°C.

In the United States Dowtherm HT is marketed as the fifth Dow fluid. This is essentially identical to Santotherm 66 (Therminol 66), being also a hydrogenated terphenyl.

5.2.8 Gilotherm Fluids [14]

Gilotherm fluids, of which there are six in the high-temperature range, are manufactured by Rhone-Poulenc. The DP-DPO mixture is sold as Gilotherm DO (except in the United States, where it is not marketed at present).

The high-temperature fluids are Gilotherm TH (maximum film temperature 370°C) and Gilotherm ALD (maximum film temperature 340°C). The low pour point, low vapor pressure, and reasonably high flash point associated with these two fluids makes them the most popular among the Gilotherm range [15]. The remaining fluids, going down to Gilotherm D12 with a minimum temperature of -70°C and maximum of 200°C, adequately cover the lower-temperature demand. As virtually all these fluids are based on benzene derivatives, careful attention to toxicity is paramount.

5.2.9 Marlotherm Fluids [16]

Chemische Werk Hüls manufactures Marlotherm S and Marlotherm L. These fluids have an upper limit of about 350°C and both may be pumped at subzero temperatures. Marlotherm L can be used in the liquid or vapor phase above 290°C. They are slightly cheaper than DP-DPO.

5.2.10 Santotherm (Therminol) Fluids [17]

Monsanto offers six fluids under the trade name of Santotherm in Europe and Therminol in the United States. The DP-DPO mixture is sold as Santotherm VP-1 (Therminol VP-1 in the United States).

Apart from Santotherm VP-1, the high-temperature fluid in this group is Santotherm 88, which has a maximum bulk temperature of 400°C. Its major drawback is that it cannot be pumped below 145°C and so in this respect resembles molten salts. The most popular fluid is Santotherm 66, with its high bulk temperature limit (345°C) combined with very good low-temperature properties and low vapor pressure. Monsanto have carried out some tests with various mixtures of Santotherm 66 and Santotherm VP-1 and can provide properties of mixtures. This combines the advantages of both fluids (low pour point and vapor pressure of Santotherm 66 and the higher stability of VP-1) to produce a fluid with intermediate properties (see Appendix 2). The low- to medium-temperature range, from 220 to 315°C, with pumping temperatures down to -50°C or less, is covered by Santotherm 44, 55, and 60.

5.2.11 Syltherm 800 [18]

Syltherm 800, a trade name of Dow Corning previously known as Q21162, is a modified polymer of dimethyl siloxane. It can be used from -40°C up to 400°C without the need for heat tracing, which makes it unique. It has a low vapor pressure and is neither very toxic nor unpleasant to handle.

The structure of the siloxane polymer is indicated in Fig. 5.1. Overheating of the fluid results in the rearrangement of the Si-O bonds, generating polysiloxane and lower molecular weight by-products which can be vented. Thus, under normal circumstances, overheating will not produce carbonaceous deposits, so the efficiency of heat transfer is not impaired. Problems can arise from contamination by any one of a variety of compounds, such as

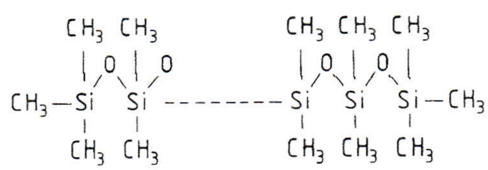

FIGURE 5.1 Dimethyl polysiloxane molecule (Syltherm 800).

water, air, acids, and bases, which results in high rates of volatile formation. Contamination by oxygen or any oxidizing agent can produce volatile oxidation products or in extreme cases can cause the polymer to gel. Attempts to keep the heating system airtight will of course trap any light-end materials generated and therefore alter the makeup of the fluid. For example, the flash point will be lowered. This is avoided by periodic venting of the light components.

5.2.12 Miscellaneous Fluids

In addition to the main fluids summarized in Table 5.1, there are a number of fluids which exhibit some interesting features and may become more widely used. A fluid which was once used as a heat transfer medium but is now used only as a solvent for oils, resins, and waxes is Tetralin [19]. This is 1,2,3,4-tetrahydronaphthalene ($C_{10}H_{12}$), and may be used as a liquid or as vapor (above 207°C). It has a freezing point of -31°C and may be used at temperatures up to 310°C. It costs approximately twice as much as DP-DPO, which may explain why it is no longer used.

The Kureha Chemical Industry Company of Japan [11] produces three heat transfer fluids under the general name KSK-oils, which are alkyl naphthalenes (hence similar to Tetralin) which are stable up to 320°C and have pour points ranging from -30 to -50°C. Two of these fluids are usable in the vapor phase, KSK-260 above 280°C and KSK-280 above 295°C.

Fluids currently used for cooling electrical equipment such as transformers may find wider application in the chemical and petrochemical field. An example is Midel 7131 [20], which is a mixture of esters obtained by reacting pentaerythritol (a tetra alcohol) with organic acids derived from vegetable origin. This fluid is claimed to be virtually nontoxic and has a fairly high flash point, very low vapor pressure, and good thermal stability up to about 300°C. Another set of fluids presenting a real alternative are halogenated hydrocarbons, an example being the Fluirinert liquids marketed by the 3M Company [21]. They are colorless, odorless, low in toxicity, and completely nonflammable. They are generally very dense and have low pour points and low viscosity; the major difference between the set of (at present) eight substances is their boiling point, which ranges from 56 to 215°C. They can be used in the liquid or vapor phase, the fluids most likely to find wider appeal being the high-boiling FC-70 or FC-43. There is one major drawback with these fluids: they are exceptionally expensive. The high-boiling fluids may cost 40 times as much as DP-DPO.

Another range of fluids, once quite common but now removed from the market, are chlorinated hydrocarbons, examples of which are Dowtherm E and Arochlor 1248. There have been a number of objections to the possible toxic effects of these compounds, but the major driving force for their removal probably came in the mid-1970s in relation to the possible threat