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Space engineering — Thermal design handbook

Part 10: Phase — Change Capacitor

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European Foreword

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It is highlighted that this technical report does not contain any requirement but only collection of data or descriptions and guidelines about how to organize and perform the work in support of EN 16603-31.

This Technical report (TR 17603-31-10:2021) originates from ECSS-E-HB-31-01 Part 10A.

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This document has been developed to cover specifically space systems and has therefore precedence over any TR covering the same scope but with a wider domain of applicability (e.g.: aerospace).

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1 Scope

Solid-liquid phase-change materials (PCM) are a favoured approach to spacecraft passive thermal control for incident orbital heat fluxes or when there are wide fluctuations in onboard equipment.

The PCM thermal control system consists of a container which is filled with a substance capable of undergoing a phase-change. When there is an the increase in surface temperature of spacecraft the PCM absorbs the excess heat by melting. If there is a temperature decrease, then the PCM can provide heat by solidifying.

Many types of PCM systems are used in spacecrafts for different types of thermal transfer control.

Characteristics and performance of phase control materials are described in this Part. Existing PCM systems are also described.

The Thermal design handbook is published in 16 Parts

TR 17603-31-01	Thermal design handbook – Part 1: View factors
TR 17603-31-02	Thermal design handbook – Part 2: Holes, Grooves and Cavities
TR 17603-31-03	Thermal design handbook – Part 3: Spacecraft Surface Temperature
TR 17603-31-04	Thermal design handbook – Part 4: Conductive Heat Transfer
TR 17603-31-05	Thermal design handbook – Part 5: Structural Materials: Metallic and Composite
TR 17603-31-06	Thermal design handbook – Part 6: Thermal Control Surfaces
TR 17603-31-07	Thermal design handbook – Part 7: Insulations
TR 17603-31-08	Thermal design handbook – Part 8: Heat Pipes
TR 17603-31-09	Thermal design handbook – Part 9: Radiators
TR 17603-31-10	Thermal design handbook – Part 10: Phase – Change Capacitors
TR 17603-31-11	Thermal design handbook – Part 11: Electrical Heating
TR 17603-31-12	Thermal design handbook – Part 12: Louvers
TR 17603-31-13	Thermal design handbook – Part 13: Fluid Loops
TR 17603-31-14	Thermal design handbook – Part 14: Cryogenic Cooling
TR 17603-31-15	Thermal design handbook – Part 15: Existing Satellites
TR 17603-31-16	Thermal design handbook – Part 16: Thermal Protection System

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2 References

EN Reference	Reference in text	Title
EN 16601-00-01	ECSS-S-ST-00-01	ECSS System - Glossary of terms
TR 17603-30-06	ECSS-E-HB-31-01 Part 6	Thermal design handbook – Part 6: Thermal Control Surfaces
TR 17603-30-11	ECSS-E-HB-31-01 Part 11	Thermal design handbook – Part 11: Electrical Heating

All other references made to publications in this Part are listed, alphabetically, in the **Bibliography**.

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3 Terms, definitions and symbols

3.1 Terms and definitions

For the purpose of this Standard, the terms and definitions given in ECSS-S-ST-00-01 apply.

3.2 Abbreviated terms

The following abbreviated terms are defined and used within this Standard.

ATC	air traffic control (aerosat)
B & K	Brennan & Kroliczek
GfW	Gessellschaft für Weltraumforschung
HEPP	heat pipe experiment package
HLS	
IHPE	international heat pipe experiment
IKE	institut für kernenenergetik (university of Stuttgart)
LDEF	long duration exposure facility
MEK	methyl-ethyl ketone
MLI	multilayer insulation
PCM	phase-change material
SINDA	systems improved numerical differencing analyzer
SS	stainless steel
SSM	second surface mirror
S day	stoichiometric day, see clause 8.5
TIG	tungsten-inert gas
TIROS	television and infra-red observation satellite

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TOC	tag open cup
TCC	tag closed cup
TPHP	transporter heat pipe

Other Symbols, mainly used to define the geometry of the configuration, are introduced when required.

3.3 Symbols

A	cross-sectional area, [m^2]
E	modulus of elasticity, [Pa]
E_{max}	maximum energy stored in the PCM device, [J]
L	thickness of the PCM device, one-dimensional model, [m]
M	mass, [kg]
Q	heat transfer rate, [W]
T	temperature, [K]
T_M	melting (or freezing) temperature, [K]
T_0	temperature of the components being controlled, [K]
T_R	reference temperature, [K]
ΔT	excursion temperature, [K], $\Delta T = T_0 - T_M$
c	specific heat, [J.kg^{-1}.K^{-1}]
h_f	heat of fusion, [J.kg^{-1}]
h_t	heat of transition, [J.kg^{-1}]
k	thermal conductivity, [W.m^{-1}.K^{-1}]
p_v	vapor pressure, [Pa]
q_0	heat flux to the PCM device, one-dimensional model, [W.m^{-2}]
q_R	heat flux from the PCM device to the heat sink, one-dimensional model, [W.m^{-2}]
$s(t)$	interface position, measured from $x = 0$, one-

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	dimensional model, [m]
t	time, [d], [h], [min], [s]
t_{max}	time for complete melting, [h]
t_{90}	time for melting 90% of the volume of the PCM, [h]
x	geometrical coordinate, one-dimensional model, [m]
α	thermal diffusivity, [$m^2.s^{-1}$], $\alpha = k/\rho c$
β	thermal expansion coefficient, volumetric (unless otherwise stated), [K^{-1}]
μ	dynamic viscosity, [Pa.s]
ρ	density, [$kg.m^{-3}$]
σ	surface tension, [$N.m^{-1}$]
σ_{ult}	ultimate tensile strength, [pa]
χ	isothermal compressibility, [Pa^{-1}]

Subscripts

C	Container
F	Filler
PCM	Phase-Change Material
T	Total
l	Liquid
s	Solid

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4 Introduction

Solid-liquid phase-change materials (PCM) present an attractive approach to spacecraft passive thermal control when the incident orbital heat fluxes or the onboard equipment heat dissipation fluctuate widely.

Basically the PCM thermal control system consists of a container which is filled with a substance capable of undergoing a phase-change. When the temperature of the spacecraft surface increases, either because external radiation or inner heat dissipation, the PCM will absorb the excess heat through melting, and will restore it through solidification when the temperature decreases again. Because of the obvious electrical analogy this thermal control system is also called PCM capacitor.

To control the temperature of a cyclically operating equipment, the PCM cell is normally sandwiched between the equipment and the heat sink.

When the PCM system aims at absorbing the abnormal heat dissipation peaks of an equipment which somehow the excess heat to a sink, the cell is placed in contact with the equipment, without interfering in the normal heat patch between equipment and heat sink.

For achieving the thermal control of solitary equipment, the PCM capacitor may be used as the sole heat sink, provided that the heat transferred during the heating period does not exceed that required to completely melt the material.

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5 PC working materials

5.1 General

The ideal PCM would have the following characteristics:

1. Melting point within the allowed temperature range of the thermally controlled component. In general between 260 K and 315 K.
2. High heat of fusion. This property defines the available energy storage and may be important either on a mass basis or on a volume basis.
3. Reversible solid-to-liquid transition. The chemical composition of the solid and liquid phases should be the same.
4. High thermal conductivity. This property is necessary to reduce thermal gradients. Unfortunately most PCM are very poor thermal conductors, so that fillers are used to increase the conductivity of the system.
5. High specific heat and high density.
6. Long term reliability during repeated cycling.
7. Low volume change during phase transition.
8. Low vapor pressure.
9. Non-toxic.
10. Non-corrosive. Compatible with structural materials.
11. No tendency to supercooling.
12. Availability and reasonable cost.

Relevant physical characteristics of phase-changing system are discussed, from a general point of view, in the following pages.

5.1.1 Supercooling

Supercooling is the process of cooling a liquid below the solid-liquid equilibrium temperature without formation of the solid phase. Supercooling when only one phase is present is called one-phase supercooling. Supercooling in the presence of both solid and liquid, or two-phase supercooling, depends upon the particular material and the environment surrounding it. The best way to reduce supercooling is to ensure that the original crystalline material has not been completely molten In such a case the seeds which are present in the melt tend to nucleate the solid phase when heat is removed. Nucleating catalysts are available for many materials.

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Several PCMs have been tested under repeated heating and freezing cycles by DONIER SYSTEM. The main purpose of these tests has been the detection of eventual supercooling phenomena. Among the tested materials, the normal paraffins did not show any supercooling tendency. This result is also confirmed by the available literature. However, according to investigations carried out by Bentilla, Sterrett & Karre (1966) [5], contamination of the paraffins with water leads to supercooling of the molten substance down to 283 K. Care should therefore be taken to prevent this contamination.

5.1.1.1 Experimental investigations

An experimental investigation has been performed by DORNIER SYSTEM with the aim of finding out the variables having any influence on the supercooling behavior of the PCM; namely: total number of cycles, cooling rate, and type of container.

In these experiments, the temperature of the test chamber was alternatively increased and decreased at constant steps within a range of 240 to 320 K. The results are summarized in Table 5-1, and Figure 5-1 and Figure 5-2.

The temperature history of both the PCM inside the containers and the honey comb packages was measured by means of copper-constant thermocouples, and continuously recorded. The test points were located in the center of the container.

5.1.1.2 Results

Water and paraffins did not show any tendency to supercooling during freezing, not even at the maximum realizable cooling rate of $2x10^{-2}$ $K.s^{-1}$.

Acetic acid showed supercooling of different orders of magnitude. It could not be determined whether or not supercooling is a function of cooling rate. Supercooling was also independent, at least not noticeably dependent, on the number of cells constituting the container. If however, Al-chips were added to facilitate heterogeneous nucleation, supercooling was reduced during the first cycles, although it augmented when the test time increased.

Supercooling of disodium hydroxide heptahydrate amounted to 3-3,5 K regardless of cooling rate and number of temperature cycles.

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Table 5-1: Supercooling Tests

PCM	Container	Number of Cycles	FIRST CYCLE		Maximum Supercooling	Comments
			Plateau Temperature [K]	Supercooling		
DODECANE	Aluminium Cell. Honeycomb adhesive-bonded to end plate.	146	265	NO	NO	
TETRADECANE	Aluminium Cell. Honeycomb adhesive-bonded to end plate.	50	280	NO	NO	Slightly ascending temperature.
HEXADECANE	Test tube without honeycomb.	50	293	NO	NO	
	Aluminium Cell. Honeycomb adhesive-bonded to end plate.	70	300	ΔT =9,5 K	ΔT = 10 K	
ACETIC ACID	Neck flash with splinters.	70	301	NO	ΔT = 6,5 K	Normal supercooling: ΔT= 5 K
	Aluminium Cell. Honeycomb inserted (not adhered).	23	299	ΔT = 1,5 K	ΔT = 5 K	
DISODIUM HYDROXIDE HEPTAHYDRATE	Neck flash with splinters.	36 22	286,5 287	ΔT = 3,5 K ΔT = 2,5 K	ΔT = 3,5 K ΔT = 3 K	No plateau temperature during heating-up.
DISTILLED WATER	Aluminium Cell. Honeycomb adhesive-bonded to end plate.	85	274	NO	NO	

NOTE From DORNIER SYSTEM (1971) [9].

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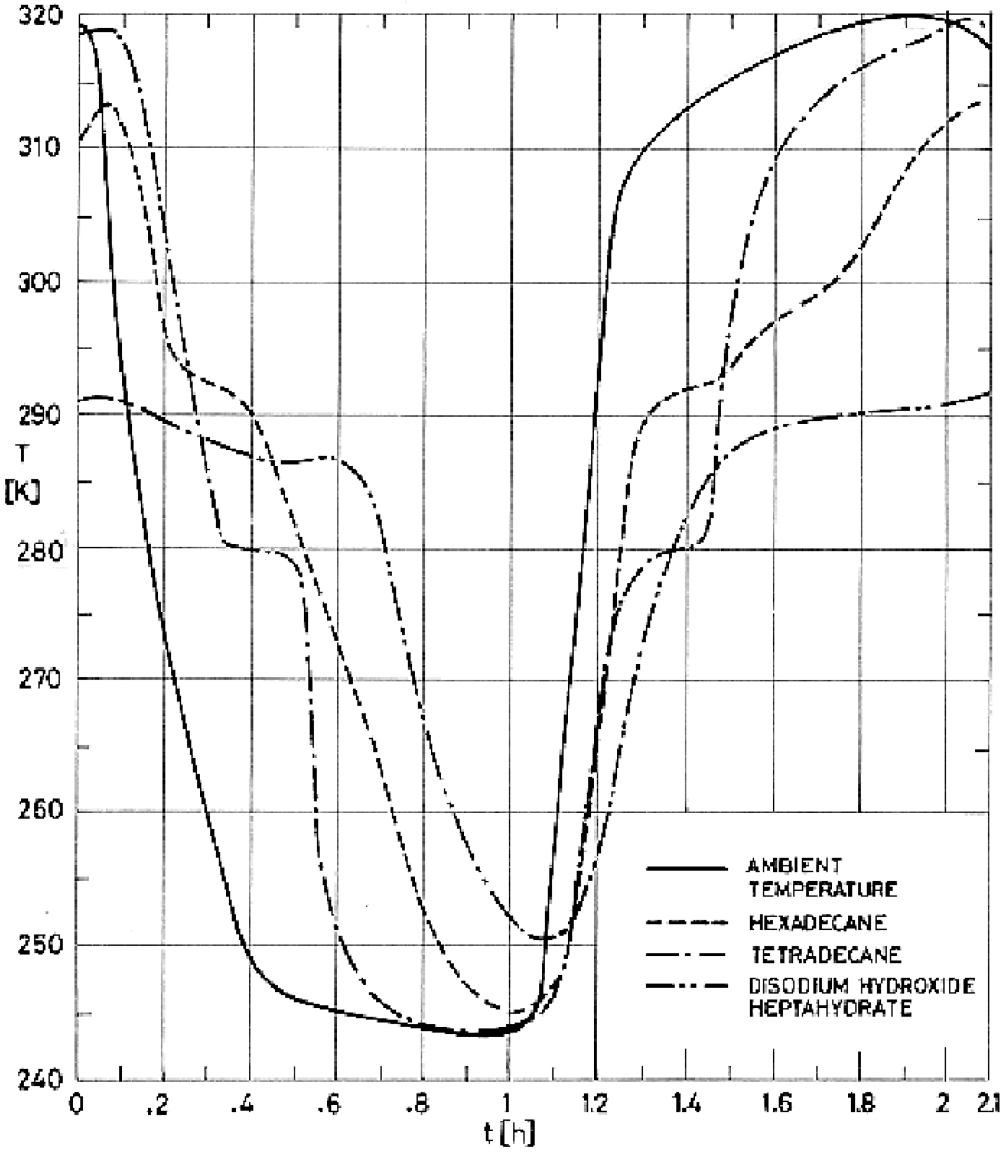

Note: non-si units are used in this figure

Figure 5-1: Temperature, *T*, vs. time, *t*, curves for heating and cooling of several PCMs. From DORNIER SYSTEM (1971) [9].

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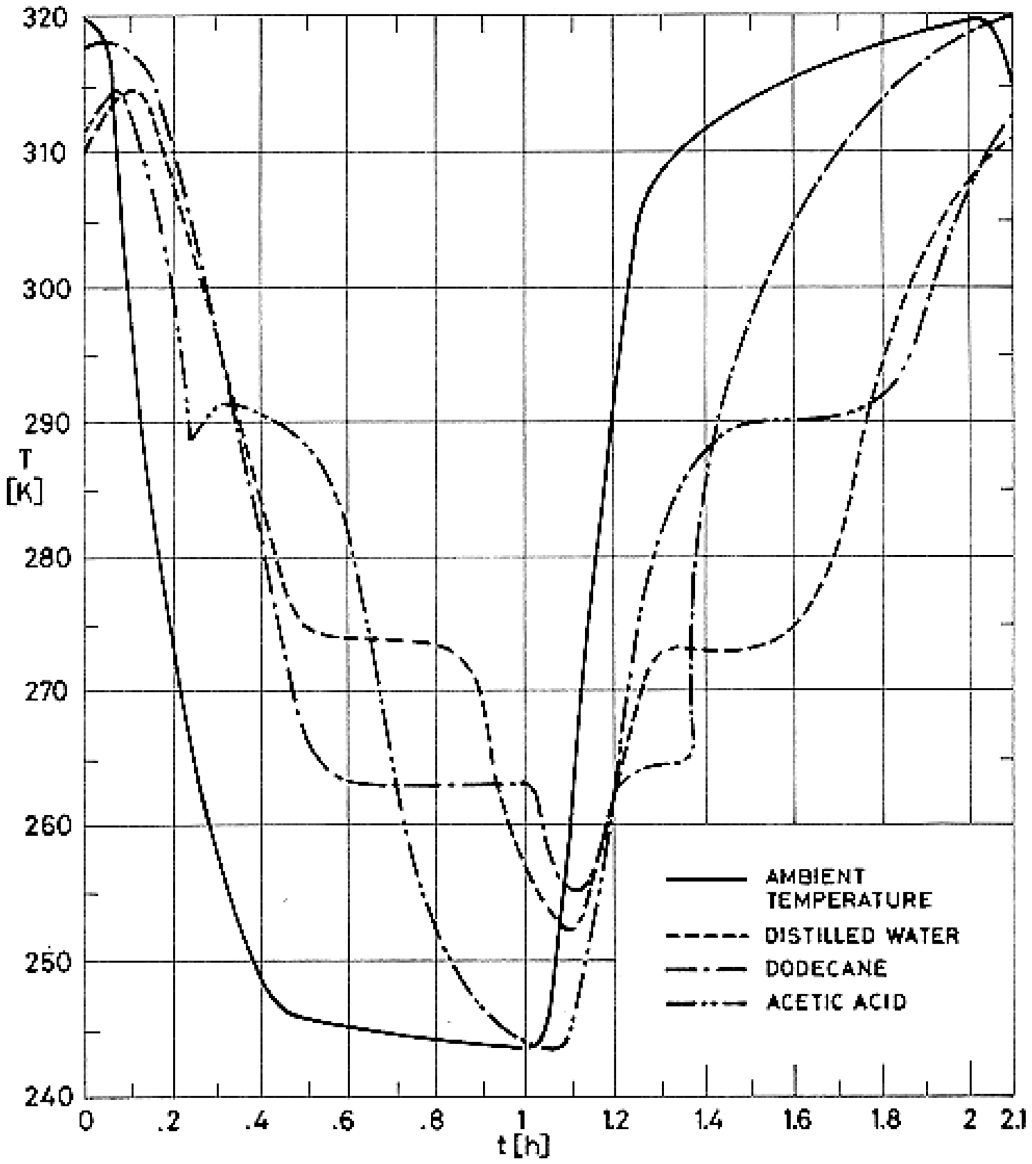

Note: non-si units are used in this figure

Figure 5-2: Temperature, *T*, vs. time, *t*, curves for heating and cooling of several PCMs. From DORNIER SYSTEM (1971) [9].

5.1.2 Nucleation

Nucleation is the formation of the first crystals capable of spontaneous growth into large crystals in an unstable liquid phase. These first crystals are called nuclei.

Homogeneous nucleation occurs when the nuclei may be generated spontaneously from the liquid itself at the onset of freezing. The rates of formation and dissociation do not depend on the presence or absence of surfaces, such as container walls or foreign particles.

Heterogeneous nucleation occurs when the nuclei are formed on solid particles already in the system or at the container walls. Supercooling (see clause 5.1.1) can be considerably reduced or even eliminated when heterogeneous nucleation is present.

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5.1.3 The effect of gravity on melting and freezing of the pcm

Gravitational forces between molecules are comparatively small relative to intermolecular or interatomic forces; for example, the ratio between gravitational and intermolecular forces between two molecules of carbon dioxide is of the order of 10^{-30}.

Since phase-change is controlled by intermolecular forces, the rate of melting or freezing should be the same under microgravity as it is under normal gravity conditions, provided that thermal and solutal fields are the same.

However, phase change happens to be indirectly influenced by gravity through the following effects:

1. Convection in the liquid phase which propagates nuclei and enhances heat transfer, and
2. thermal contact conductance between the heated (or cooled) wall and the PCM.

1. Convection can be induced by volume forces and/or by surface forces.

   When the density gradient (due to thermal, solutal, or other effects) is not aligned with the body force (gravitational) vector, flow immediately results no matter how small the gradient. On the other hand, when the density gradient is parallel to but opposed to the body force, the fluid remains in a state of unstable equilibrium until a critical density gradient (more precisely, a critical Grashof number) is exceeded. The Grashof number gives the ratio of buoyancy to viscous forces.

   Convection from the interfaces is produced by surface tractions due to surface tension gradients (which again can be due to thermal, solutal, or other effects). If the temperature gradient is parallel to the undisturbed interface, flow immediately results no matter how small the gradient. When the temperature gradient is normal to the undisturbed interface, convection appears provided that a critical Marangoni number is exceeded. This Marangoni number is defined as the ratio of surface tension gradient forces to viscous forces.

   A priori information on which type of convection prevails under given circumstances can be obtained from an order of magnitude analysis (Napolitano (1981) [19]). Nevertheless, convection is presumably negligible for most PCM capacitors because of the low temperature gradients (associated to the high thermal conductances usually required) and of the reduced characteristics lengths of the enclosures when a metallic filler is used (see clause 6.2).

   Convection due to shrinkage forces associated to phase change is normally small when solid and liquid densities are not too different.

2. Gravity presses the denser phase against the lower wall of the container.

   At the onset of the cool down the liquid remains in contact with the lower wall, be it cooled or heated, while the upper part of the cell is empty because of the void (ullage) which is usually provided for safe operation at high temperatures when using rigid containers (see clause 6.1). Thence, the temperature of the cooled wall is expected to be lower when the device is cooled from above (poor thermal conductance), that when cooled from below.

   As soon as the cool down progresses, the solid, which is assumed to be denser than the liquid, makes contact with the lower wall enhancing the heat transfer to it, because the solid phase has normally a higher thermal conductivity than the liquid.

   Reliable cooling data of PCM cells are not easily found in the literature since cooling is difficult to control precisely. Data reported in Figure 8-36b, Clause 8.5, do not support the above prediction, rather the average wall temperature is higher (not smaller) when the solid is pressed by gravity against the cooled wall. Notice, however that according to Table 5-9, clause 5.3, liquid 1-Heptene is more conductive than the solid.

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During heat up, the insulation is similar. Since the frozen PCM is usually denser than the liquid, the solid falls to the bottom of the cell. When heating up from below, the solid PCM remains close to the heated face, with a thin liquid layer amid them, whereas when heated from above a void space or, at most, a thick gap filled with the liquid appears between the heated face and the solid PCM. Thence, the heated wall temperature is expected to be higher when the device is heated from above than when it is heated from below. This effect has been observed experimentally, see for instance, in clause 8.3 the tests corresponding to Figure 8-14. Melting time is barely affected by the orientation of the gravity vector.

Metallic fillers (see clause 6.2) have the two-fold effect of increasing the thermal contact conductance between container and PCM, and of impeding liquid motion. Migration of the liquid by capillary pumping toward selected parts of the container can be achieved by varying the cross sectional area of the filler cells as in the PCM device shown in clause 8.4.

5.1.4 Bubble formation

Bubbles can affect PCM operation in several ways: the thermal conductivity will be altered; bubbles in the liquid phase will cause stirring actions; small bubbles in the solid phase can take up some of the volume shrinkage, thereby avoiding the formation of large cavities.

There are several types of bubbles likely to occur during PCM performance under microgravity: PCM vapor bubbles, cavities or voids from volume shrinkage, and gas bubbles.

The most persistent bubbles seem to be those formed by dissolved gases. During solidification, dissolved gases can be rejected just as any other solute at the solid-liquid interface. During the reverse process of melting, bubbles previously overgrown in the solid can be liberated. In an one-g field, bubbles would be more likely to float to the top and coalesce. Under microgravity, bubbles would be trapped in the frozen solid.

In order to reduce the amount of dissolved gases it is suggested to boil the PCM in liquid form under reduced pressure. Another method would be to purge the liquid with a less soluble gas.

5.2 Possible candidates

Possible PCM candidates have been classified as follows:

— Paraffins. Table 5-2.

— Non-Paraffin Organics. Table 5-3.

— Salt Hydrates. Table 5-4.

— Metallic. Table 5-5.

— Fused Salt Eutectics. Table 5-6.

— Miscellaneous. Table 5-7.

— Solid-Solid. Table 5-8.

In each table, the PCMs are arranged in order of increasing melting temperatures.

Data given in this preliminary list deal only with chemical formula, melting temperature, heat of fusion, and density.

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All the PCMs that either are dangerous, have undesirable freezing behavior, or that, according to several authors, do not show sufficient merit, have been excluded from these tables.

Table 5-2: PARAFFINS

Name	Chemical Formula	Melting Temperature [K]	Heat of Fusion, $h_f x10^{-3}$ [J.kg^{-1}]	Density, ρ [kg.m^{-3}]
2,4-Dimethylpentane	C_7H_{16}	153,8	67	673 (293 K)
1-Heptane	C_7H_{14}	154		697 (293 K)
n-Heptane	C_7H_{16}	182,4	129	684 (293 K)
n-Dodecane	$C_{12}H_{26}$	263,4	141	749 (293 K)
n-Tridecane	$C_{13}H_{28}$	267,5	215	756 (293 K)
n-Tetradecane	$C_{14}H_{30}$	278,9	228 [b]	763 (293 K)
n-Pentadecane	$C_{15}H_{32}$	283	205 [b]	768 (293 K)
n-Hexadecane	$C_{16}H_{34}$	291,2	237 [b]	773 (293 K)
n-Heptadecane	$C_{17}H_{36}$	295	213 [b]	778 (293 K)
n-Octadecane	$C_{18}H_{38}$	301,2	243 [b]	777 (301 K)
n-Nonadecane	$C_{19}H_{40}$	305,1	171	777 (305 K)
n-Eicosane	$C_{20}H_{42}$	309,8	247	789 (293 K)
n-Heneicosane	$C_{21}H_{44}$	313,5	161	792 (293 K)
n- Docosane	$C_{22}H_{46}$	317,4	158	794 (293 K)
n-Tricosane	$C_{23}H_{48}$	320,6	129	778 (321 K)
n-Tetracosane	$C_{24}H_{50}$	323,9	162	766 (343 K)
n-Pentacosane	$C_{25}H_{52}$	326,7	164	769 [b]
Paraffin Wax		327,6 [b]	146 [b]	880 [b]
n-Hexacosane	$C_{26}H_{54}$	329,4	256 [b]	803 (293 K)
n-Heptacosane	$C_{27}H_{56}$	332,5	159	805 (293 K)
n-Octacosane	$C_{28}H_{58}$	334,4	164	807 (293 K)
n-Nonacosane	$C_{29}H_{60}$	336,7		
n-Triacontane	$C_{30}H_{62}$	338,8	240 [b]	763 (373 K)
n-Hentriacontane	$C_{31}H_{64}$	340,9	251 [b]	775 (351 K)
n-Dotriacontane	$C_{32}H_{66}$	342,7		811 (293 K)
n-Tritriacontane	$C_{33}H_{68}$	344,2 [b]		812 (293 K)

NOTE COMMENTS: All paraffins are chemically inert and stable below 773 K. They exhibit negligible supercooling and low volume change on melting. Many are commercially available at reasonable cost. No-Toxic. Non-Corrosive.

[a] All data in this table, unless otherwise stated, are from Weast (1976) [25]. Most of these data supersede those previously given by Hale, Hoover & O'Neill (1971) [13].

[b] From Hale, Hoover & O'Neill (1971) [13].

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Table 5-3: NON-PARAFFIN ORGANICS [a]

Name	Chemical Formula	Melting Temperature [K]	Heat of Fusion, $h_f x10^{-3}$[J.kg^{-1}]	Density, ρ [kg.m^{-3}]
1-Chloropropane	C_3H_7Cl	150,2 [b]	84 [c]	891 (293 K) [b]
Methyl Ethyl Ketone	C_4H_8O	186,6 [b]	111 [d]	805 (293 K) [b]
Ethyl Acetate	$C_4H_8O_2$	189,4 [b]	118 [d]	900 (293 K) [b]
Methyl Propyl Ketone	$C_5H_{10}O$	195,2 [b]	104 [d]	809 (293 K) [b]
Ethyl Myristate	$C_{16}H_{32}O_2$	285,3 [b]	184	857 (298 K)
Acetic Acid	C_2H_4O2	289,8	187	1050 (293 K)
Polyethylene Glycol 600	$HO(C_2H_4O)_nH$	293-298	146	1100 (293 K)
d-Lactic Acid	$C_3H_6O_3$	299	184	1249 (288 K)
Diphenyloxide	$(C_6H_5)_2O$	301		1073 (293 K)
Methyl Palmitate	$C_{17}H_{34}O_2$	302	205	
1-3 Methyl Pentacosane	$C_{26}H_{54}$	302	197	
Camphenilone	$C_9H_{14}O$	312	205	
Docasil Bromide	$C_{22}H_{45}Br$	313	201	
Caprylone	$C_{15}H_{30}O$	313	259	
Heptadecanone	$C_{17}H_{34}O$	314	201	
1-Cyclohexylo-octadecane	$C_{24}H_{48}$	314	218	
4-Heptadecanone	$C_{17}H_{34}O$	314	197	
8-Heptadecanone	$C_{17}H_{34}O$	315	201	
Cyanamide	HNCNH	317	209	1073 (291 K)
Methyl Eicosanate	$C_{21}H_{42}O_2$	318	230	1282 (293 K)
Elaidic Acid	$C_{18}H_{34}O_2$	320	218	851 (352 K)
3-Heptadecanone	$C_{17}H_{34}O$	321	218	805 (321 K) [b]
2-Heptadecanone	$C_{17}H_{34}O$	321	218	
Oxazoline Wax-ES-254		323		
9-Heptadecanone	$C_{17}H_{34}O$	324	213	
Methyl Behenate	$C_{23}H_{46}O_2$	325	234	
Ethyl Lignocerate	$C_{26}H_{52}O_2$	327	218	
Hypophosphoric Acid	$H_4P_2O_6$	328	213	
Trymyristin	$C_{57}H_{110}O_6$	329	191	862 (353 K)
	$C_{45}H_{86}O_6$	306-330	201-213	885 (333 K) [b]

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Name	Chemical Formula	Melting Temperature [K]	Heat of Fusion, $h_f x10^{-3}$[J.kg^{-1}]	Density, ρ [kg.m^{-3}]
Myristic Acid	$C_{14}H_{28}O_2$	331	199	858 (333 K)
Ethyl Cerotate	$C_{28}H_{56}O_2$	333	226	
Heptadecanoic Acid	$C_{17}H_{34}O_2$	342,6	199	847 (342 K)
Oxazoline Wax-TS-970		347		
Acetamide	C_2H_5ON	354	241	1159 (293 K) [b]

NOTE COMMENTS: Most of these materials are flammable. Many of the long-chain acids exhibit polymorphism (two or more crystalline forms). The flash point is usually low. Impurities may greatly affect melting point. Elevated temperatures decompose many of these compounds.

[a] All data in this table, unless otherwise stated, are from Weast (1976) [25]. Most of these data supersede those previously given by Hale, Hoover & O'Neill (1971) [13].

[b] From Weast (1976) [25].

[c] From Bledjian, Burden & Hanna (1979) [6].

[d] From Keville (1976) [15].

Table 5-4: SALT HYDRATES

Name	Chemical Formula	Melting Temperature [K]	Heat of Fusion, $h_f x10^{-3}$ [J.kg^{-1}]	Density, ρ [kg.m^{-3}]
Calcium Chloride Hexahydrate	$CaCl_2.6H_2O$	302,6	170	
Lithium Nitrate Trihydrate	$LiNO_3.3H_2O$	303,03	296	1550 (solid)
Sodium Hydrogen Phosphate Dodecahydrate	$Na_2HPO_4.12H_2O$	309	280	1520 (293 K)
Ferric Cloride Hexahydrate	$FeCl_3.6H_2O$	310	226	
Ferric Nitrate Enneahydrate	$Fe(NO_3)_3.9H_2O$	320,4		1684 (293 K)
Magnesium Sulfate Heptahydrate	$MgSO_4.7H_2O$	321,6	202	
Sodium	$Na_2S_2O_3.5H_2O$	322	200	1690 (solid)

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Name	Chemical Formula	Melting Temperature [K]	Heat of Fusion, $h_f x10^{-3}$ [J.kg^{-1}]	Density, ρ [kg.m^{-3}]
Thiosulfate Pentahydrate				
Lithium Acetate Dihydrate	$LiC_2H_3O_2.2H_2O$	331	251-377	
Magnesium Chloride Tetrahydrate	$MgCl_2.4H_2O$	331	178	
Sodium Hydroxide Monohydrate	$NaOH.H_2O$	337,5	272	1720
Barium Hydroxide Octahydrate	$Ba(OH)_2.8H_2O$	351	301	2180
Aluminium Potassium Sulfate Dodecahydrate	$AlK(SO_4)_2.12H_2O$	364	184	
Magnesium Chloride Hexahydrate	$MgCl_2.6H_2O$	390	167	1560

NOTE COMMENTS: Corrosive. Small volume change upon melting. Supercooling to a marked extent, which can be minimized with suitable nucleating agents. Most of the materials tested have incongruent melting points and subsequent lack of easy reversibility.

From Hale, Hoover & O'Neill (1971) [13].

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Table 5-5: METALLIC

Name	Chemical Formula	Melting Temperature [K]	Heat of Fusion, $h_f x10^{-3}$ [J.kg^{-1}]	Density, ρ [kg.m^{-3}]
Gallium-Gallium-Antimony Eutectic	Very Small Amounts of GaSb in Ga Matrix	303		
Gallium	Ga	303,2	80,3	5903 (298 K)
Cerrolow Eutectic [a]	49 Bi + 21 In + 18 Pb + 12 Sn	331	90,9	8800 (293 K)
Cerrobend Eutectic [a]	50 Bi + 26,7 Pb + 13,3 Sn + 10 Cd	343	32,6	9400 (solid)
Bismuth-Lead-Indium Eutectic	52 Bi + 26 Pb + 22 In	343	29	8000-10000
Bismuth-Lead-Tin Eutectic	52,2 Bi + 32 Pb + 15,8 Sn	369		
Bismuth-Lead Eutectic	55,5 Bi + 44,5 Pb	398		10460

[a] Cerrolow and Cerrobend are registered trademarks of CERRO Co., New York, N.Y.

NOTE COMMENTS: Low volume change on melting. These materials are of interest when the volume is a consideration. High thermal conductivity, filler not required.

From Hale, Hoover & O'Neill (1971) [13].

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Table 5-6: FUSED SALT EUTECTICS

Name	Chemical Formula	Melting Temperature [K]	Heat of Fusion, $h_f x10^{-3}$ [J.kg^{-1}]	Density, ρ [kg.m^{-3}]
	31 Na_2SO_4 + 13 NaCl + 16 KCl + 40 H_2O	277	234	
	32 Na_2SO_4 + 14 NaCl +12NH_4Cl + 42 H_2O	284		
	37 Na_2SO_4 + 17 NaCl + 46 H_2O	291		
	25 Na_2SO_4 + 21 $MgSO_4$ + 54 H_2O	294-297		
	19 Na_2SO_4 + 17 $MgSO_4$ + 64 H_2O	294-297		
	21 Na_2SO_4 + 19 $MgSO_4$ + 60 H_2O	294-297		
	20 $LiNO_3$ + 61 NH_4NO_3 + 19 $AgNO_3$	325		
	79 $AlCl_3$ + 17 NaCl + 4 $ZrCl_2$	341	234	
	66 $AlCl_3$ + 20 NaCl + 14 KCl	343	209	
	24 $LiNO_3$ + 71 NH_4NO_3 + 5 NH_4Cl	359		
	60 $AlCl_3$ + 26 NaCl + 14 KCl	366	213	
	66 $AlCl_3$ + 34 NaCl	366	201	
HTS [a]	40 $NaNO_2$ + 7 $NaNO_3$ + 53 KNO_3	415		

[a] Registered Trademark of E.I. duPOINT DE NEMOURS Co., Inc.

NOTE COMMENTS: Components can be varied using several eutectics to allow a choice of values for the malting point and heat of fusion. The variations in melting temperatures reported by different investigators are due to the influence of moisture during preparation. These materials are corrosive. From Hale, Hoover & O'Neill (1971) [13].

Table 5-7: MISCELLANEOUS

Name	Chemical Formula	Melting Temperature [K]	Heat of Fusion, $h_f x10^{-3}$ [J.kg^{-1}]	Density, ρ [kg.m^{-3}]
Water	H_2O	273,2	333,4	999,8 (273,2 K)
TRANSIT HEET SERIES [a]		222-505	230-301	1600

[a] Registered Trademark of ROYAL INDUSTRIES, Santa Ana, Cal.

NOTE From Hale, Hoover & O'Neill (1971) [13].

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Table 5-8: SOLID-SOLID

Name	Temperature [K]		Heat of Fusion, $h_f x10^{-3}$ [J.kg^{-1}]	Heat of Transition, $h_t x10^{-3}$ [J.kg^{-1}]	Density, ρ [kg.m^{-3}]	Molar Mass
	Melting	Transition				
Diaminopentaerythritol	352-357	341	31,7	184		105,14
2-Amino-2-Methyl-1,3-Propanediol	354-357	351	32	264		135,12
2-Methyl-2-Nitro-1,3-Propanediol		352		201		
Trimethylolethane		354	46	192		
2-Hydroxymethil-2-Methyl-1,3-Propanediol	470	354		192	1160	
Monoaminopentaerythritol		359		192		
Tris (Hydroxymethil) Acetic Acid		397		205		
2-Amino-2-Hydroxymethyl-1,3-Propanediol		404		285		
2,2-bis (Hydroxymethyl) Propionic Acid	411-419	425	25	289		121,14
Pentaerythritol	425-428	457	26,8	301		134,13
	531		37,2			136,15

NOTE COMMENTS: Soft, waxy solids that can be extruded under considerably less pressure than ordinary crystals. They have unusually high vapor pressures for solid. Volume changes are in the range of 10 to 50%. Supercooling is not an inherent property of solid state transitions. Transition temperatures are fairly high.
From Hale, Hoover & O'Neill (1971) [13].

5.3 Selected candidates

Data concerning several selected PCM candidates are presented in the following. All of these PCMs have reasonably large heat of fusion and, according to literature searches, their characteristics seem to be attractive. Several among them have been used in existing systems (see clause 8).

The candidates are listed as follows:

— Paraffins Table 5-9.
— Non-Paraffin Organics Table 5-12.
— Salt Hydrates Table 5-17.
— Metallic and Miscellaneous Table 5-18.

Information given in these tables includes: chemical formula, density, specificheat, surface tension, thermal conductivity, thermal diffusivity, vapor pressure, viscosity, melting and boiling temperature, heat of fusion, thermal expansion coefficient (and isothermal compressibility) volume change on melting, flash point, autoignition temperature, supercooling, cost and compatibility.

Above *Italics* were used to indicate properties whose temperature dependence is given graphically in Figure 5-3 to Figure 5-6, Clause 5.3, for a limited number of PCMs.

Costs per unit mass have been deduced from price quotations by the producers, for containers of given volume. High purity products are sold in small amounts. The fact that the cost is quoted indicates that the product is commercially available to the stated purity and, thence, the producer should be contacted.

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Table 5-9: PARAFFINS

NAME	SYNONYMS	CHEMICAL FORMULA
2,4-DIMETHYL-PENTANE, see Table 5-10		C_7H_{16}
1-HEPTENE, see Table 5-10	α-HEPTYLENE	C_7H_{14}
n- HEPTANE, see Table 5-10		C_7H_{16}
n-DODECANE, see Table 5-10		$C_{12}H_{26}$
n-TETRADECANE, see Table 5-11		$C_{14}H_{30}$
n-HEXADECANE, see Table 5-11	CETANE	$C_{16}H_{34}$
n-OCTADECANE, see Table 5-11		$C_{18}H_{38}$
n-EICOSANE, see Table 5-11		$C_{20}H_{42}$

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Table 5-10: PARAFFINS

NAME	2,4-DIMETHYL-PENTANE	1-HEPTENE	n- HEPTANE	n-DODECANE
SYNONYMS		α-HEPTYLENE		
CHEMICAL FORMULA	C_7H_{16}	C_7H_{14}	C_7H_{16}	$C_{12}H_{26}$
MOLAR MASS	100,21	98,19	100,21	170,34
DENSITY, ρ [kg.m^{-3}]	673(293 K)[a]	697(293 K)[a]	684(293 K)[a]	749(293 K)[a]
SPECIFIC HEAT, cx10^{-3} [J.kg^{-1}.K^{-1}]		1,800 [l b] 1,214 [s]		2,2 (298 K) [l c] 1,62 (250K) [s]
SURFACE TENSION, σx10^{2} [N.m^{-1}]	1,815 (293 K) [d] 1,766 (298K)	2,042 (293 K) [e] 1,993 (298K)	2,030 (293 K) [d] 1,980 (298K)	2,491 (298 K) [d]
THERMAL CONDUCTIVITY, k [W.m^{-1}.K^{-1}]		0,104 [l b] 0,06 [s]	0,129 (293 K) [e]	0,15 [c]
THERMAL DIFFUSIVITY, αx10^{8} [m^2.s^{-1}]				
VAPOR PRESSURE, p_v [Pa]	133 (225 K) [a] 13332 (298,5 K)	50662 (344 K) [b]	35370 (338 K) [f]	133 (320,8 K) [a] 13332 (419,2 K)
VISCOSITY, μx10^{3} [Pa.s]	0,375 (288 K) [d] 0,360 (293 K)	0,35 (293 K) [e] 0,34 (298 K)	0,4412 (288 K) [d] 0,3967 (298 K)	2,26 (273 K) [c]
MELTING TEMPERATURE [K]	153,8 [a]	154 [a]	182,4 [a]	263,4 [c]
BOILING TEMPERATURE [K]	353,5 [a]	366,6 [a]	371,4 [a]	489,3 [c]
LATENT HEAT OF FUSION, h_fx10^{-5} [J.kg^{-1}]	0,67 [a]	1,29 [a]	1,41 [a]	2,15 [a]
COEFF. OF THERMAL EXPANSION, β [K^{-1}]				
VOLUME CHANGE ON MELTING				Less than +10% [c]
FLASH POINT [K]	260,9 [d]		272,0 (TOC) [d,g]	346,9 (TCC) [d,h]
AUTOIGNITION TEMPERATURE [K]				
SUPERCOOLING	ΔT = 15 K [b]	ΔT = 5 K to 8 K [b]	ΔT = 5 K [f]	

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NAME		2,4-DIMETHYL-PENTANE	1-HEPTENE	n- HEPTANE	n-DODECANE
COST (Purity, %)	MERCK (1981) [18] [DM.kg^{-1}]	42500 (≥ 99,5%)	2400 (98%)	110 (≥ 99%) 41800 (≥ 99,7%)	660 (99%) 38200 (≥ 99,5%)
	FLUKA (1978) [11] [SF.kg^{-1}]	650 (≥ 99%) 8600 (≥ 99,5%)	470 (~99%)	19 (≥ 99%) 2700 (≥ 99,7%)	220 (~99%) 4900 (≥ 99,5%)
COMPATIBILITY		COMPATIBLE WITH: Al and Al/SS couple. [b]		COMPATIBLE WITH: Al, SS, Mg, Al/SS couple, and Mg/SS couple. [f]	
COMMENTS		Organic solvent. [d]		Organic solvent, volatile, flammable. Unpleasant sensory effects may develop after breathing air. Containing more than 2x10^{-3} kg.m^{-3}. Flammability limits in air 1,10%–6,70%v. Min. ignition temperature in air 496 K. [d,i]	Organic solvent, liquid, colorless, flammability limits in air at 298 K 0,61%–4,7% v. [d]
		Generally nontoxic. Toxicity varies with the volatility for all paraffin hydrocarbons. Exposed to flame or heat can react with oxidizing materials.			

[l] Liquid.

[s] Solid.

All data in this table, unless otherwise stated, are from Hale, Hoover & O'Neill (1971) [13].

[a] From Weast (1976) [25].

[b] From Bledjian, Burden & Hanna (1979) [6].

[c] From DORNIER SYSTEM (1971) [9].

[d] From Riddick & Bunger (1970) [21].

[e] From Vargaftik (1975) [24].

[f] From Keville (1976) [15].

[g] Tag Open Cup flash point tester.

[h] Tag Closed Cup flash point tester.

[i] From Windholz (1976) [27].

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Table 5-11: PARAFFINS

NAME		n-TETRADECANE	n-HEXADECANE	n-OCTADECANE	n-EICOSANE
SYNONYMS			CETANE		
CHEMICAL FORMULA		$C_{14}H_{30}$	$C_{16}H_{34}$	$C_{18}H_{38}$	$C_{20}H_{42}$
MOLAR MASS		198,38	226,45	254,51	282,54
DENSITY, ρ [kg.m^{-3}]		763 (293 K) [a]	773 (293 K) [a]	777 (301 K) [a]	798 (293 K) [a]
SPECIFIC HEAT, cx10^{-3} [J.kg^{-1}.K^{-1}]		2,07 (278,9 K) [l] 1,56 (250 K) [s]	2,21 (298 K) [l c] 1,52 (250 K) [s]	2,16 [s]	2,01 [l] 2,21 [s]
SURFACE TENSION, σx10^{2} [N.m^{-1}]		2,743 (283 K)	2,747 (293 K)	2,745 (303 K)	2,90 (293 K) [e]
THERMAL CONDUCTIVITY k [W.m^{-1}.K^{-1}]		0,15	0,15 (289,8 K)	0,15 (301,2 K)	0,15
THERMAL DIFFUSIVITY, αx10^{8} [m^{2}.s^{-1}]			8,7		
VAPOR PRESSURE, p_v [Pa]		133 (349,4 K) [a] 13332 (451,5 K)	133 (378,3 K) [a] 13332 (481,5 K)	133 (392,6 K) [a] 13332 (509 K)	133 (471,2 K)
VISCOSITY, μx10^{3} [Pa.s]		2,92 (283 K) [c]	3,454 (293 K)	3,060 (313 K) [e]	4,29 (311 K)
MELTING TEMPERATURE [K]		278,9 [a]	291,2 [a]	301,2	309,8
BOILING TEMPERATURE [K]		525,6	560 [c]	591,1	616 [a]
LATENT HEAT OF FUSION, h_fx10^{-5} [J.kg^{-1}]		2,28	2,37	2,43	2,47
COEFF. OF THERMAL EXPANSION, β [K^{-1}]					3x10^{-4}
VOLUME CHANGE ON MELTING		Less than +10% [c]	Of the order of +8% [c]		
FLASH POINT [K]					
AUTOIGNITION TEMPERATURE [K]					
SUPERCOOLING		NONE OBSERVED	NEGLIGIBLE	NEGLIGIBLE	NONE OBSERVED
COST	MERCK (1981) [18]	37500 (≥ 99,5%)	540 (99%) 37 00 (≥ 99%)	650 (98%) 36800 (≥ 99,3%)	1400 (98%)

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NAME		n-TETRADECANE	n-HEXADECANE	n-OCTADECANE	n-EICOSANE
(Purity, %)	[DM.kg^{-1}]				
	FLUKA (1978) [11] [SF.kg^{-1}]	260 (≥ 99%) 5100 (≥ 99,5%)	210 (≥ 99%)	200 (≥ 98%) 640 (≥ 99%)	480 (≥ 97%)
COMPATIBILITY		Noncorrosive to most structural materials			Compatible with most structural materials, noncorrosive.
COMMENTS		Liquid, colorless.		Crystal, colorless.	White, waxy solid.
		Generally nontoxic. Toxicity varies with the volatility for ell paraffin hydrocarbons. Exposed to flame or heat can react with oxidizing materials.			

[l] Liquid.

[s] Solid.

All data in this table, unless otherwise stated, are from Hale, Hoover & O'Neill (1971) [13].

[a] From Weast (1976) [25].

[c] From DORNIER SYSTEM (1971) [9].

[e] From Vargaftik (1975) [24].

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Table 5-12: NON-PARAFFIN ORGANICS

NAME	SYNONYMS	CHEMICAL FORMULA
1-CHLORO-PROPANE, see Table 5-13	n-PROPYL CHLORIDE	$CH_3CH_2CH_2Cl$
METHYL ETHYL KETONE, see Table 5-13	2-BUTANONE, ETHYL METHYL KETONE	$CH_3CH_2COCH_3$
ETHYL ACETATE, see Table 5-13	ACETIC ACID ETHYL ESTER, ACETICETHER, VINEGAR NAPHTHA	$CH_3CO_2CH_2CH_3$
METHYL PROPYL KETONE, see Table 5-13	2- PENTANONE, ETHYL ACETONE	$CH_3CH_2CH_2COCH_3$
OXAZOLINE WAX-ES-254, see Table 5-14		
TRISREARIN, see Table 5-14	GLYCEROL TRIOCTADECA-NOATE, GLICEROL TRISTEARATE, STEARIN	$C_{57}H_{111}O_6$
MYRISTIC ACID, see Table 5-14	TETRADECA-NOIC ACID	$C_{13}H_{27}COOH$
STEARIC ACID, see Table 5-14	OCTADECANOIC ACID	$C_{17}H_{35}COOH$
ACETIC ACID, see Table 5-15	VINEGAR, GLACIAR ACETIC, ETHANOICOR METHANE CARBOXYLIC ACID	CH_3COOH
POLYETHYLENE GLYCOL 600, see Table 5-15	α-HYDRO-ω-HYDROXYPOLY(Oxy-1,2-ETHANEDIYL), CARBOWAX, NYCOLINE, MACROGOL, PLURACOL E, POLY G, POLYGLYCOL E, SOLBASE, PEG	$HO(C_2H_4O)nH$
ELAIDIC ACID, see Table 5-15	9-OCTADECENOIC ACID (trans)	$C_{17}H_{33}COOH$
OXAZOLINE WAX-TS-970, see Table 5-16		
ACETAMIDE, see Table 5-16	ACETIC ACID AMIDE, ETHANAMIDE	CH_3CONH_2
METHYL FUMARATE, see Table 5-16		$(CHCO_2CH_3)_2$

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Table 5-13: NON-PARAFFIN ORGANICS

NAME	1-CHLORO-PROPANE	METHYL ETHYL KETONE	ETHYL ACETATE	METHYL PROPYL KETONE
SYNONYMS	n-PROPYL CHLORIDE	2-BUTANONE, ETHYL METHYL KETONE	ACETIC ACID ETHYL ESTER, ACETIC ETHER, VINEGAR NAPHTHA	2- PENTANONE, ETHYL ACETONE
CHEMICAL FORMULA	$CH_3CH_2CH_2Cl$	$CH_3CH_2COCH_3$	$CH_3CO_2CH_2CH_3$	$CH_3CH_2CH_2COCH_3$
MOLAR MASS	78,54	72,12	88,12	86,14
DENSITY, ρ [kg.m^{-3}]	891 (293 K) [a]	805 (293 K) [a]	900 (293 K) [a]	809 (293 K) [a]
SPECIFIC HEAT, cx10^{-3} [J.kg^{-1}.K^{-1}]				
SURFACE TENSION, σx10^{2} [N.m^{-1}]	2,178 (293 K) [b] 2,048 (303 K)	2,69 (273 K) [b] 2,397 (297,8 K)	2,375 (293 K) [b] 2,255 (303 K)	
THERMAL CONDUCTIVITY, k [W.m^{-1}.K^{-1}]			0,0092 (273 K) [c] 0,0166 (373 K)	
THERMAL DIFFUSIVITY, αx10^{8} [m^2.s^{-1}]				
VAPOR PRESSURE, p_v [Pa]	133 (204,7 K) [a] 13332 (270,5 K)	65568 (338 K) [d]	68701 (338 K) [d]	21025 (338 K) [d]
VISCOSITY, μx10^{3} [Pa.s]	0,372 (288 K) [b] 0,318 (303 K)	0,423 (288 K) [b] 0,365 (303 K)	0,473 (288 K) [b] 0,400 (303 K)	
MELTING TEMPERATURE [K]	150,2 [a]	186,6 [a]	189,4 [a]	195,2 [a]
BOILING TEMPERATURE [K] [e]	319,6 [a]	352,6 [a]	350,1 [a]	375 [a]
LATENT HEAT OF FUSION, h_fx10^{-5} [J.kg^{-1}]	0,84 [f]	1,11 [d]	1,18 [d]	1,04 [d]
COEFF. OF THERMAL EXPANSION, β [K^{-1}]				
VOLUME CHANGE ON MELTING				
FLASH POINT [K]		272,0 (TCC) [b,g]	268,7 (TCC) [b,g]	
AUTOIGNITION TEMPERATURE [K]				

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NAME		1-CHLORO-PROPANE	METHYL ETHYL KETONE	ETHYL ACETATE	METHYL PROPYL KETONE
SUPERCOOLING		ΔT = 5 K [f]	ΔT = 11 K [d]		
COST (Purity, %)	MERCK (1981) [18] [DM.kg^{-1}]	520 (98%)	58 (99%) 35500 (≥ 99,5%)	66 (99%) 86 (≥ 99,8%)	140 (98%)
	FLUKA (1978) [11] [SF.kg^{-1}]	89 (>98%)	10 (≥ 99,5%)	12 (≥ 99,5%)	61 (>98%)
COMPATIBILITY		Incompatible with: Al/SS couple. [f]	Compatible with: Al, SS, Mg and Mg/SS couple. Incompatible with Al/SS couple. [d]	Compatible with: Al, SS, Mg, Al/SS couple and Mg/SS couple. [d]	
COMMENTS		Organic solvent. Colorless liquid. Relatively safe. Flammability limits in air are 2,60% and 11,10% v, the latter value at elevated temperature. [b,h]	Organic solvent. Flammable. Acetone-like odor, low hazard with normal handling. Low toxicity. Irritation prevented below 0,59x10^{-3} kg.m^{-3} in air. Flammability limits in air 2,05%–11,00% v. Minimum ignitium temperature in air 778 K. [b,h]	Organic solvent. Clear, volatile, flammable liquid, fruity odor, pleasant taste when diluted. Ignition temperature 700 K. Explosive limits in air 2,2%–11,5% v. Slowly decompose by moisture, then acquires an acid reaction. [b,h]	Organic solvent. Colorless liquid. [h]

NOTE All data in this table, unless otherwise stated, are from Hale, Hoover & O'Neill (1971) [13].

[a] From Weast (1976) [25].

[b] From Riddick & Bunger (1970) [21].

[c] From Vargaftik (1975) [24].

[d] From Keville (1976) [15].

[e] Measured at a pressure of about 10^5 Pa, unless otherwise indicated.

[f] From Bledjian, Burden & Hana (1979) [6].

[g] Tag Closed Cup flash point tester.

[h] From Windholz (1976) [27].

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Table 5-14: NON-PARAFFIN ORGANICS

NAME	OXAZOLINE WAX-ES-254	TRISTEARIN	MYRISTIC ACID	STEARIC ACID
SYNONYMS		GLYCEROL TRIOCTADECANOATE, GLICEROL TRISTEARATE, STEARIN	TETRADECANOIC ACID	OCTADECANOIC ACID
CHEMICAL FORMULA		$C_{57}H_{111}O_6$	$C_{13}H_{27}COOH$	$C_{17}H_{35}COOH$
MOLAR MASS	723	891,46	228,37	284,47
DENSITY, ρ [kg.m^{-3}]		862 (353 K)	858 (333 K)	847 (342 K)
SPECIFIC HEAT, cx10^{-3} [J.kg^{-1}.K^{-1}]			2,26 [l] 1,59 [s]	
SURFACE TENSION, σx10^{2} [N.m^{-1}]				3,93 (358 K)
THERMAL CONDUCTIVITY, k [W.m^{-1}.K^{-1}]	APPEARS TO BE QUITE LOW			
THERMAL DIFFUSIVITY, αx10^{8} [m^2.s^{-1}]	ESTIMATED VERY LOW			
VAPOR PRESSURE, p_v [Pa]		133 (378,4 K)	133 (415 K) [a] 13332 (523,5 K)	133 (446,7 K) [a] 13332 (564 K)
VISCOSITY, μx10^{3} [Pa.s]		18,5 (348 K)		11,6 (343 K)
MELTING TEMPERATURE [K]	323	329	331	342,6
BOILING TEMPERATURE [K] [e]			523,6 (1,33x10^{4} Pa) [a]	505 (2x10^{3} Pa) [a]
LATENT HEAT OF FUSION, h_fx10^{-5} [J.kg^{-1}]	ESTIMATED LARGE	1,91	1,99	1,99
COEFF. OF THERMAL EXPANSION, β [K^{-1}]				8,1x10^{-10}
VOLUME CHANGE ON MELTING				
FLASH POINT [K]				469
AUTOIGNITION				668

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