Phase-Change Materials for Vaccine Cold Chain Applications

Summary Report

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For more information on PATH's work in vaccine and pharmaceutical technologies, visit: http://sites.path.org/vpt/.

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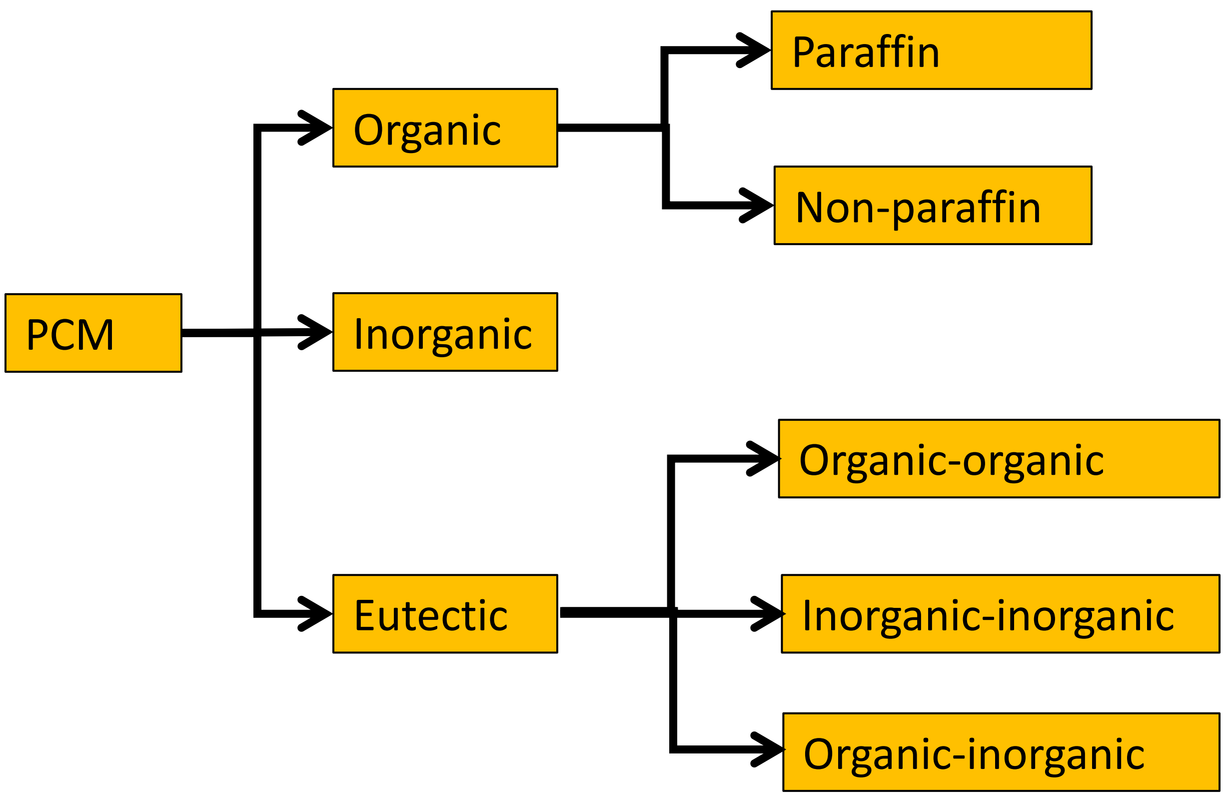
Acronyms

CCE	cold chain equipment
HDPE	high-density polyethylene
HIPS	high-impact polystyrene
PCM	phase-change material
PEG	polyethylene glycol
PP	polypropylene
PQS	Performance, Quality and Safety
PVC	polyvinyl chloride
SDS	safety data sheets
WHO	World Health Organization

Introduction

When selecting phase-change materials (PCMs), it is important to understand the interactions of the PCMs with the materials with which they may come into contact. PCMs may change the mechanical properties of the material, and a material may impact the phase-change properties (e.g., melting point or latent heat) of the PCM. In this study, we investigated the impact of PCMs on the mechanical and visible properties of materials commonly used in vaccine cold chain equipment (CCE), including refrigerators, cold boxes, and carriers. The materials tested included polypropylene (PP), polyvinyl chloride (PVC), high-density polyethylene (HDPE), high-impact polystyrene (HIPS), copper, aluminum, mild steel, polyisocyanurate foam, polyurethane foam, enamel appliance paint, and PVC-insulated copper wire. PCMs were classified according to the scheme shown in the figure below. The phase-change materials investigated included water, salt hydrates, paraffins, organic non-paraffins, and a nominal eutectic. Table 1 (see page 9) summarizes the material testing data. We also evaluated the potential hazards to human and environmental health of the PCMs based on information from their safety data sheets (SDS) as well as the useful product life of the PCMs and disposal considerations. Table 2 (see page 10) summarizes the results of the hazards, disposal, and useful product life research.



PCM classification schemes

For the salt hydrate, non-paraffin organic fatty acid ester, and eutectic categories for which we tested only one PCM, we tried to identify additional PCMs in the category and obtain information on human and environmental hazards, product life, and disposal, though these additional PCMs were not tested for material compatibility. We were not able to identify additional PCMs in the eutectic category within the relevant melting point range, and as discussed in the following paragraph, the E0 eutectic that we did test may not be a true eutectic system.

We have learned in recent discussions with the manufacturer of the E0 eutectic PCM (PCM Products, Hertfordshire, UK) that E0 consists of water, biocide, nucleating agent, and a stabilizer. It is therefore unlikely that E0 meets the technical definition of a eutectic system, and we could not get the manufacturer to explicitly confirm that E0 is a eutectic PCM. PCM Products could not provide data on the phase-change cycling stability of their PCMs (E0, A6, and S8).

Key points based on literature search and materials compatibility testing

- PP, HDPE, and PVC tensile properties are affected by PCMs.
    - HDPE and PP are weakened by the paraffin and fatty acid ester-based PureTemp® 8 PCMs. PVC is stiffened by soaking in all PCMs tested.
    - Particular care must be taken in designing CCE with HDPE and PP with organic PCMs to reduce the risk of PCM leakage. Thin HDPE or PP plastic film containers should not be used for primary containment of organic PCMs in CCE. Primary container seams should be robust to continue to function after weakening by PCMs.
- HIPS was drastically weakened by PureTemp 8 PCM. Fatty acid ester-based PCMs should not be used in CCE containing HIPS.
- Aluminum, copper, and mild steel tensile properties are affected by most PCMs.
    - Certain PCMs will corrode these metals and their use together should either be avoided or further engineering steps taken to protect the metals from corrosion. For example, coatings could be applied to the metals to protect them from the PCMs, or corrosion inhibitors added to the PCMs if the corrosion inhibitors did not negatively impact PCM performance.
    - Specific combinations where corrosion or a weakening of the metal were seen were:
        - All PCMs except A6, RT3HC, and OM06P with mild steel.
        - PlusICE® E0 with aluminum.
        - PlusICE S8 with copper.
- Polyisocyanurate and polyurethane foams are affected by most PCMs.
    - The greatest effect on polyisocyanurate was increased yield stress, which should not significantly impact CCE performance.
    - The greatest effects on polyurethane were increased stiffness and yield stress, which should not significantly impact CCE performance.
    - Polyethylene glycol (PEG) 400 is strongly absorbed by and degrades polyurethane.
- Enamel appliance paint is softened by continuous contact with most PCMs.
- PVC-insulated copper conductor wire is generally not affected by contact with PCMs. Some PCMs will corrode exposed copper conductor.

- The useful life of PCMs used within their design specifications should generally exceed World Health Organization (WHO) Performance, Quality and Safety (PQS) requirements for cold chain equipment. Some salt hydrate PCMs do not have a sufficiently long usable life.
- While hazards to human health and the environment from PCMs are generally low, PCMs should be disposed of properly, in accordance with local regulations and manufacturer recommendations. Generally speaking, PCM liquid at ambient temperatures should not be disposed into dumps, landfills, on the ground, or into ground or surface waters.

Compatibility

To evaluate the impacts of PCMs on different materials, samples of the materials were soaked in PCM for short and long periods of time and then tested for changes in tensile (plastics and metals), flexural (HIPS) or compressive (foams) properties. For the short-term test, samples were immersed for 14 to 26 days. For the long-term test, plastic and metal samples were immersed between 91 and 105 days. The long-term foam samples were immersed between 101 and 140 days. If a significant change in one or more properties compared to the baseline sample or published values was observed, the PCM was noted as having a significant impact on the material in Table 1. A change was significant if the average property value plus or minus the standard deviation fell outside the standard deviation of baseline sample values. Samples on which observable corrosion occurred were also marked as being significantly impacted by the PCM, even if no significant change in material properties occurred, under the assumption that continued exposure would eventually measurably impact material properties, or the corrosion was confined to the surface and was removing the material without impacting the properties of the material underneath.

Plastics

Plastics are well known both for absorbing chemicals they come into contact with and for releasing some of their chemical constituents, most notably plasticizers. It is therefore not surprising that most PCMs had a significant effect on the mechanical properties of the plastics with which they were in contact. The impact varied by plastic and PCM. The greatest impacts were by the paraffin PCMs (A6, RT3HC, and OM06P) and the non-paraffin organic PCM PureTemp 8 on PP, HDPE and HIPS. The stiffness (Young's modulus), the stress at which the PP and HDPE undergo permanent deformation (yield stress), and the highest stress they will sustain (ultimate tensile strength) were significantly reduced. In the case of HDPE in contact with the paraffins for the short-term test, the reduction in stiffness was 44% to 49%, the reduction in yield stress was 24% to 28%, and the reduction in ultimate tensile strength was 15% to 18%. In the long-term test, the reduction in stiffness was 31% to 43%, the reduction in yield stress was 5% to 9%, and the reduction in ultimate tensile strength was 5% to 8%. Reductions in these properties for HDPE with PureTemp 8 were about half the short-term values above for the paraffins in the short-term test. In the long-term test for HDPE for PureTemp 8, the reduction in stiffness was 43%, the reduction in yield stress was 20%, and the reduction in ultimate tensile strength was 13%. When flexed by hand, the short-term test HIPS samples soaked in PureTemp 8 broke easily. Untreated HIPS, by contrast, would bend slightly when flexed and return to its original shape. HIPS was not put through long-term testing. Based on these results, fatty acid ester-based PCMs should not be used in CCE containing HIPS.

The changes in material properties for the PP in contact with the organic PCMs were much smaller than for HDPE in the short-term test. In the long-term test in the paraffins, the Young's modulus of PP was reduced from 16% to 44%, the yield stress was reduced from 14% to 35%, and ultimate tensile strength was reduced from 10% to 14%. For PureTemp 8, the Young's modulus, yield stress, and ultimate tensile strength were reduced by 17%, 12%, and 6%, respectively. Appropriate engineering judgement should be exercised if PP and HDPE are used with organic PCMs. For example, containers made of HDPE and PP in direct, constant contact may need to be designed with thicker walls to avoid container failure.

The yield stress and ultimate tensile strength of PVC were not significantly impacted by any of the PCMs in either the short- or long-term test. The significant impact on PVC was a stiffening of the material (increase in Young's modulus) caused by the majority of PCMs. This could be an effect of the plasticizer leaching from the PVC, but further studies would be required to validate this hypothesis. The increase in Young's modulus ranged from 5% to 34% in the short-term test, with A6 and E0 having the greatest effect. In the long-term test, Young's modulus increased by 30% to 44%. Depending on the application, the stiffening of a plastic may be relatively unimportant, and so for practical purposes, PVC is the plastic least affected by the PCMs in this study. The applications to CCE are limited; however, because WHO PQS requirements forbid the use of chlorinated plastics in CCE, PVC is still used in some CCE in the form of insulation for electrical wires. The resistance of PVC to degradation by PCMs is beneficial in the event that a PCM leaks onto electrical wires.

Metals

In general, metal material properties were not impacted by contact with PCMs. A6, RT3HC, OM06P, S8, and E0 caused a 14% to 36% reduction in stiffness of copper in both the short- and long-term tests. There were four PCM-metal combinations in which the PCM had a significant impact on the metals' yield stress and ultimate tensile strength. For copper, the S8 PCM caused visible corrosion and reduced the yield stress by 3% and ultimate tensile strength by 4% in the short-term test. In the long-term test, S8 reduced the yield stress and ultimate tensile strength of copper by 20% and 17%, respectively. Aluminum reacted significantly with E0 and reduced the yield stress by 22%, the ultimate tensile strength by 23% in the short-term test. In the long-term test, E0 reduced the yield stress and ultimate tensile strength of aluminum by 7% and 8%, respectively. The stress at which mild steel would break was not significantly affected by any of the PCMs during the short- or long-term test. Values for yield stress and stiffness could not be determined from the data in the short-term test. In the long term, yield stress values for steel were not significantly different from published data, and Young's modulus was reduced by 23% to 55% by all PCMs except for the paraffins.

Besides the PCMs noted in the above paragraph, negative impacts on copper, aluminum, and mild steel in contact with PCMs are unlikely. For the PCM-metal combinations above for which there was an impact on the metal, sustained direct contact between the PCM and the metal should be avoided.

Foam

For the polyurethane foam, increases in compressive modulus for samples soaked in the organic PCMs (except PEG 400) and S8 became more significant, with the increases ranging from 21% to 74%. The decrease in compressive modulus seen for PEG 400 in the short-term test disappeared in the long-term test, as did the increase for distilled water. Consistent increases in yield stress of 17% to 48% were seen for the paraffin, S8, and E0 PCMs. Triacetin showed a 22% increase in yield stress in the long-term test that did not occur in the short-term test. The large change in mass of the polyurethane foam soaked in PEG 400 and the decrease in volume of the foam sample in both the long- and short-term tests indicated that PEG 400 penetrated deeply into the foam and affected its structure.

The compressional properties of polyisocyanurate were not significantly affected in both long- and short-term tests by any of the PCMs except for A6. A6 increased the yield stress by 23% in both tests. All of the organic PCMs increased the yield stress in the long-term test by 15% to 36%. Polyisocyanurate is less affected by the PCMs than the polyurethane foam.

Under normal circumstances, the PCMs will not be in contact with the foam insulation of the CCE, so foam-PCM compatibility issues are not likely to be very important. In the event that the PCM primary container leaks and the PCM contacts the foam, most PCMs in this study did not decrease the mechanical properties of the foams. The effects of the PCMs were generally an increase in the stiffness and yield stress of the foams.

The exception was PEG 400 with polyurethane. PEG 400 was absorbed by the polyurethane and damaged the structure of the foam, resulting in a decrease in the volume of the foam samples. The decrease in volume of the foam penetrated by PEG 400 could deform the walls of the CCE. We did not test the effect of PCMs on foam thermal properties, but given that foams rely on the non-convecting gas in their cells for insulation and that liquids typically conduct heat better than gases, we would expect the insulation properties of foams to be decreased substantially by PCMs that penetrate deeply into the foam. Given the porous nature of foams and the potential impact on insulation properties, sustained contact with any liquid PCM is not recommended.

Electrical wire and painted steel

Samples of mild steel were painted with enamel appliance paint and the painted portion immersed in the PCMs. With the exception of A6 and RT3HC, all of the PCMs softened the paint. E0 and distilled water caused the paint to bubble from the surface of the steel. The damage to the appliance paint is not surprising, as the paint is not designed for continual immersion in liquids. Given that PCMs would have to leak out of their primary containment and sit in continuous contact with enamel appliance paint to damage the paint, the risk posed to these painted surfaces is minimal.

PVC-insulated copper hookup wire was also immersed in the PCMs. PVC-insulated wire was chosen for the test because PVC is widely used for insulation in electrical wiring. The PVC insulation did not show visible changes, consistent with the PVC samples that were tested for their mechanical properties after immersion. The exposed copper for the S8, E0, and PureTemp 8 was discolored after immersion. In the long-term samples soaked in S8, the exposed copper wire had nearly corroded away. Corrosion rates of the copper wire may be affected if electrical current is running through the wire when the wire is in contact with the PCMs. Given that PCMs would have to leak out of their primary containment and sit in contact with exposed copper to cause damage, the risk posed to PVC-insulated electrical wire is minimal.

Human health

Based on a review of the SDS for each PCM, the health hazards posed by the PCMs are minimal. The worst of the health hazards are the potential serious eye irritation due to getting S8 salt hydrate into an eye, or the potential for fatal complications from aspirating the paraffin PCMs if one were to ingest them. Considering that these health hazards could occur only if the PCMs leak out of their primary containment, the risk posed is very low. Furthermore, these hazards are similar to the health hazards posed by other chemicals that are likely to be widely present in the settings where the PCMs are used. For example, gasoline poses the same aspiration hazard as the paraffin PCMs.

Environmental impacts

Based on a review of the SDS for each PCM, none of the PCMs examined in this study posed significant hazards to the environment, with the exception of CrodaTherm™ 5, which is toxic to some aquatic life. According to the SDS, all of the PCMs were biodegradable and none were environmentally persistent, bioaccumulative, or contained toxic chemicals. While releases of the PCMs into the environment should be avoided (especially the release of CrodaTherm 5 into drains, waterways, or the soil), sustained negative environmental impacts were not indicated from our analysis.

Life span

PCM manufacturers estimate the useful life span of their products by cycling them through the phase change repeatedly and testing the PCM for changes in thermodynamic properties, such as thermal conductivity, latent heat of phase change, and melting/freezing point temperatures. The reported values are the minimum number of cycles after which no significant change in thermodynamic properties is observed. PCMs may be able to sustain more useful phase-change cycles than the minimum numbers reported by the manufacturers.

The organic PCMs are very stable and should maintain their performance for at least 5,000 phase-change cycles. Assuming that the PCMs are cycled once per day, 5,000 cycles translates to a useful life of at least 14 years, well beyond the PQS-required life spans of vaccine carriers and cold boxes (5 years) and vaccine refrigerators (10 years).

Salt hydrate PCMs may have shorter useful life spans than organic PCMs. The primary cause of decreased performance of salt hydrate PCMs over repeated phase-change cycles is the separation of the water from the hydrated salt due to density differences. The phase separation that occurs during the dehydration reaction phase change can be reduced by adding stabilizers to thicken the PCM or by proper design of the PCM containment. The relatively low minimal cycling life (1,000 cycles) of the C7 may be due to the phase separation issue.

Useful life span estimates assume that PCM has been used as specified. Contamination of the PCM, evaporation of liquid components, or exposure of the PCM to temperatures outside their specified design range can damage PCMs. If the PCMs are properly contained and kept within their specified temperature range, their useful life should be similar to that reported by the manufacturers.

Disposal considerations

When the CCE containing a PCM reaches the end of its useful life, disposal of the CCE and its PCM becomes an important issue. The PCMs in CCE are held in containers of plastic or metal, and as long as the containers are intact, the PCM should not enter the environment. Over time, however, these materials will degrade, and the ambient conditions of many disposal locations for CCE (e.g., open-air landfills or other outdoor areas) will speed the degradation of the container material or facilitate puncturing of the container. Therefore, it would be ideal if PCMs were drained from CCE at the end of their useful life for proper disposal.

Legal disposal methods for the PCMs will depend on the local and national regulations of the locations in which they are used. None of the PCMs in this study are sufficiently hazardous to require disposal in a hazardous waste facility in the United States. Since the PCMs have melting points between 0°C and 10°C, they generally exist as liquids and should not be disposed of in a landfill, as solid waste landfills are not intended for liquid wastes. Incineration is appropriate for the paraffin PCMs. Some non-paraffin organic PCMs may be disposed to a municipal wastewater treatment plant through the sewer system if allowed by relevant regulations. PCMs in some newer PCM technologies (not examined in this study) are impregnated into solid material such as wood fiber. If these impregnated PCMs are used in CCE, it may be appropriate to treat them as solid waste.

Outside of nations where waste handling facilities and regulations are well developed, PCM disposal becomes more complicated. CCE-containing PCMs may be discarded on the open ground, left idle in facilities, or disposed into landfills. Ideal disposal methods may not be possible in low-resource settings. As these PCMs, with the exception of CrodaTherm 5, are not particularly hazardous to human health or the environment, the potential impact of improperly disposed PCM from CCE on human health and the environment is low and should not dissuade use of PCM in CCE given the potential benefits. Establishment of a CCE recycling program for all CCE products, not just those containing PCMs, would be ideal.

Table 1. Material compatibility testing results.

Manufacturer/ supplier	Product line	PCM	Category	Subcategory	Type	Impact on material								
						Plastic				Metal			Foam	
						PP	PVC	HDPE	HIPS[4]	Copper	Aluminum	Steel	Polyisocyanurate	Polyurethane
		Water	Inorganic	NA	NA	Min	Sig	Sig	Min	Min[1]	Sig	Sig	Min	Min
PCM Products	PlusICE	S8		Salt hydrate	NA	Min[1]	Sig	Sig	Min	Sig	Sig	Sig	Min	Sig
PCM Products	PlusICE	E0	Eutectic[3]	Inorganic-inorganic	Water based	Min[1]	Sig	Sig	Min	Sig	Sig	Sig	Min	Sig
PCM Products	PlusICE	A6	Organic	Paraffin	NA	Sig	Sig	Sig	Min	Sig	Min[1]	Min	Sig	Sig
RGEES	NA	OM06P		Paraffin	NA	Sig	Sig	Sig	Min	Sig	Min[1]	Min	Sig	Sig
Rubitherm	NA	RT3HC		Paraffin	NA	Sig	Sig	Sig	Min	Sig	Min	Min	Sig	Sig
Entropy Solutions	PureTemp	PureTemp 8		Non-paraffin	Fatty acid ester	Sig	Sig	Sig	Sig	Sig	Min[1]	Sig	Sig	Sig
ChemWorld	NA	PEG 400		Non-paraffin	Polyethylene glycol	Sig	Sig	Sig	Min	Sig	Min[1]	Sig	Sig	Sig[2]
SigmaAldrich	NA	Triacetin		Non-paraffin	Fatty acid ester	Sig	Sig	Min	Min	Sig	Min	Sig	Sig	Sig
Climator	ClimSel™	C7	Inorganic	Salt hydrate	NA	Not tested								
Croda	CrodaTherm	CrodaTherm 5	Organic	Non-paraffin	Fatty acid ester	Not tested								
Croda	CrodaTherm	CrodaTherm 6.5		Non-paraffin	Fatty acid ester	Not tested								

Impact on material codes

Code	Meaning
Minimal (Min)	Minimal impact on material properties compared to baseline in long-term tests. Average value ± standard deviation falls within baseline standard deviation. Minimum-impact PCM-material combinations are highlighted in green. For HIPS, minimal impact designates no visually observable difference when sample was flexed by hand compared to an untreated sample.
Significant (Sig)	Significant impact on material properties compared to baseline in long-term tests. Average value ± standard deviation falls outside baseline standard deviation. Use of material-PCM combination may require additional engineering measures to mitigate impacts on material properties. Significant-impact PCM-material combinations highlighted in yellow. For HIPS, significant impact designates visually observable difference when sample was flexed by hand compared to an untreated sample.

Notes

NA - Not applicable

1. Significant changes were observed in the short-term test.
2. Rating based on absorption of PCM by polyurethane foam and short-term test results.
3. PCM Products markets E0 as a eutectic PCM. The manufacturer states that E0 consists of water, biocide, nucleating agent, and a stabilizer. The manufacturer would not confirm that the components of E0 form a eutectic system, and it is not likely to be a true eutectic given the stated components.
4. HIPS results are based solely on short-term, qualitative testing. Quantitative tensile testing of short-term and long-term tested HIPS samples might yield further "Significant" classifications for PCMs in addition to PureTemp 8.

Table 2. Human health and environmental hazards, disposal considerations, and useful life.

Manufacturer/ supplier	Product line	PCM	Category	Subcategory	Type	Human health hazards	Environmental hazards	Disposal considerations[1]	Useful life[2]	
									Phase-change cycles[3]	Years[4]
		Water	Inorganic	NA	NA	None	None	None	Infinite	Infinite
PCM Products	PlusICE	S8		Salt hydrate	NA	Causes serious eye irritation.	None	None	Unknown[5]	Unknown[5]
PCM Products	PlusICE	E0	Eutectic[6]	Inorganic-inorganic	Water based	May cause allergic reaction.	None	None	Unknown[5]	Unknown[5]
PCM Products	PlusICE	A6	Organic	Paraffin	NA	May be fatal if swallowed and enters airways.	None	Transfer to a suitable container and arrange for collection by specialized disposal company. Incineration on land.	Unknown[5]	Unknown[5]
RGEES	NA	OM06P		Paraffin	NA	May be fatal if swallowed and enters airways.	None	May be disposed of as nonhazardous waste.	>5,000	14
Rubitherm	NA	RT3HC		Paraffin	NA	May be fatal if swallowed and enters airways.	None	The product can be incinerated in accordance with local regulations.	>10,000	27
Entropy Solutions	PureTemp	PureTemp 8		Non-paraffin	Fatty acid ester	None	No data available.	All waste must be handled in accordance with local, state, and federal regulations.	>10,000	27
ChemWorld	NA	PEG 400		Non-paraffin	Polyethylene glycol	None	No data available.	No information available.	Unknown[5]	Unknown[5]
SigmaAldrich	NA	Triacetin		Non-paraffin	Fatty acid ester	None	None	Offer surplus and nonrecyclable solutions to a licensed disposal company.	Unknown[5]	Unknown[5]
Climator	ClimSel™	C7	Inorganic	Salt hydrate	NA	Safety data sheet is not available.			1,000	3
Croda	CrodaTherm	CrodaTherm 5	Organic	Non-paraffin	Fatty acid ester	None	Very toxic to aquatic life.	Dispose of in accordance with local regulations. The product should not be allowed to enter drains, water courses, or the soil.	Unknown[5]	Unknown[5]
Croda	CrodaTherm	CrodaTherm™ 6.5		Non-paraffin	Fatty acid ester	None	None	Dispose of in accordance with local regulations.	Unknown[5]	Unknown[5]

Color codes: Green, minimal concerns; yellow, some concerns; red, not suitable for CCE.

Notes

1. Disposal considerations based on human health hazards, environmental hazards, and biodegradability information from the PCM SDS. Additional local, regional, or national disposal regulations may apply.
2. Useful life estimates assume that PCMs are kept within their normal operating conditions and not used outside of their normal temperature and pressure range, exposed to excessive light, or have their composition changed through contamination or removal of components (e.g., solvent evaporation).
3. Cycling life of PCMs are minimums based on testing showing no degradation in properties. Actually, useful cycling life is likely longer.
4. Cycling life assuming one cycle per day.
5. Published data or data from the manufacturer could not be located.
6. PCM Products markets E0 as a eutectic PCM. The manufacturer states that E0 consists of water, biocide, nucleating agent, and a stabilizer. The manufacturer would not confirm that the components of E0 form a eutectic system, and it is not likely to be a true eutectic given the stated components.