

Heat packs: applications in abundance

Silvana Cardoso and Mansel Rogerson says there's more to heat packs than simply warming the red wine

A BOTTLE of red wine can be warmed conveniently by wrapping around it a heat pack. This is a plastic jacket filled with a transparent liquid. When a metallic disc inside the jacket is pressed, the liquid gradually becomes solid and warm. But how does a heat pack work? And, can we extend its application beyond the simple warming of red wine?

Inside a heat pack is an aqueous solution of sodium acetate. Figure 1 shows a sequence of photographs illustrating the crystallisation process in a heat pack. By flexing the metal disc in the top left corner of the pack, the solution is made to crystallise and release latent heat. The crystals grow from the trigger site in all directions where liquid is available. Very rapidly a network of solid is formed throughout the pack. This phase-change releases heat and, as a result, the temperature of the solid-liquid mixture rises to a maximum of 54°C, the melting temperature of the solution. Eventually, as heat is transferred to the surroundings, the temperature of the heat pack gradually decreases.

Before being used again, the pack needs to be regenerated. Regeneration is accomplished by simply melting the crystals and allowing them to cool. The simplest and safest method is by boiling the pack in water until all the crystals are melted. When the solution is completely liquid, it is allowed to cool below its freezing temperature. It is then ready to

be activated again. This process of melting and activating may be repeated hundreds of times.

A sodium acetate solution has two unusual properties that make it ideal for use in heat packs. First, it has a relatively large latent heat of crystallisation, of 125 kJ/kg. This means that a typical pack of 300 ml can heat up a bottle of red wine from an initial temperature of 12°C to approximately 22°C. Secondly, the solution exists as a metastable, subcooled liquid at room temperature. After the crystals have been melted during regeneration, the liquid remains remarkably resistant to crystallisation at temperatures well below its freezing point.

At present, portable heat packs are only used for simple applications such as warming drinks or soothing muscle aches. The reason for this limited range of applications is that the operation of such heat packs is not very reliable. The problem lies in the fact that small vibrations of a heat pack containing the metal trigger can set off the crystallisation process, making the pack unavailable when it is needed. So, although the sodium solution itself is very stable, it becomes prone to inadvertent crystallisation when it has a metal trigger immersed in it. In order to be able to improve the operation of heat packs and significantly extend their range of applications, we need to understand firstly how the metal trigger works to solidify a sodium acetate solution.

thermodynamics and the metallic trigger

Consider the process of solidification at the molecular level. Molecules in the liquid collide and stick together to form solid clusters. These clusters may then grow by further molecular attachment or by collision and attachment to other clusters (Figure 2). The clusters may also shrink by molecular detachment or by breaking up into smaller clusters. For nucleation, the size of the cluster is of major importance. Below a critical size, the cluster may persist suspended in solution but will not grow rapidly to solidify the entire body of liquid, whereas as soon as a cluster of critical size is formed then continuous growth occurs very rapidly. A cluster of critical size is called an 'incipient nucleus'.

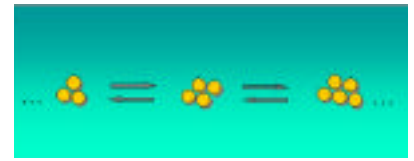


Figure 2: Growth and shrinkage of a cluster

Thermodynamics tells us that there are only a few ways in which such a solution may be made to solidify. Either the temperature, pressure or concentration must be altered or a catalyst, such as a seed crystal, added.

Let us look in detail at the metallic trigger used in commercial heat packs. This trigger consists of a flexible stainless steel disc about 20 mm in diameter, as shown in Figure 3. The disc has a pattern of indentations on its surface. The processes of stamping and stressing the metal to form these indentations also produce cracks around the edges of each indentation. The disc has one slightly concave and one slightly convex face. These faces may be reversed by a flexing action with our fingers.

In normal use, the disc is immersed in the sodium acetate solution within the heat pack. Flexing the disc between the fingers triggers solidification, whereupon solid crystals grow from the indentations on the disc.

During the regeneration procedure, the disc is heated with the crystals. After the solution cools, the disc will trigger solidification again when flexed. The disc does not need to be flexed from one conformation to the other in order to trigger solidification. It only needs to be flexed slightly in either direction.

In light of the physical observations described above, we speculated that such a metallic disc initiates solidification by releasing minute crystals of solid sodium acetate trihydrate into the solution when the disc is flexed. These crystals would reside in the sub-micron cracks on the



Figure 3. Photograph of the metallic disc used currently in heat packs

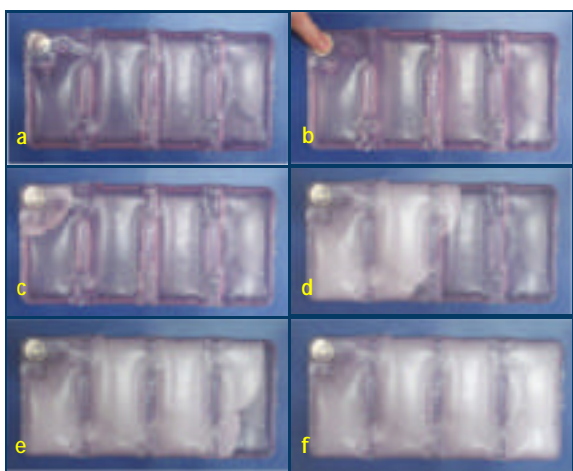


Figure 1: Sequence of photographs illustrating the onset and development of crystallisation in a heat pack: (a) the supercooled solution and metal trigger; (b) the metallic trigger is flexed: the solidification front at times (c) 3 s, (d) 5 s and (e) 6 s after triggering; and (f) the solution is completely solidified 7 s after triggering

Figure 4: Schematic of the triggering mechanism (left) Crack in the surface of an active disc containing a crystal (centre) Crystal is ejected when disc is flexed, causing solidification (right) Crystal survives at high regeneration temperature

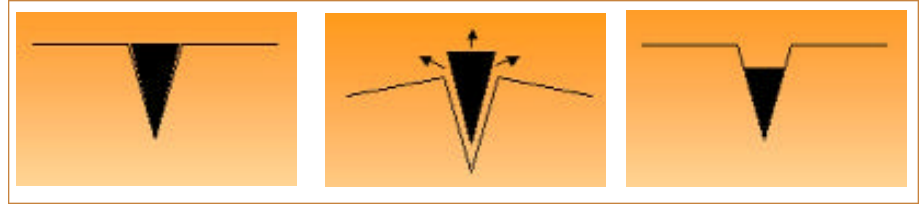
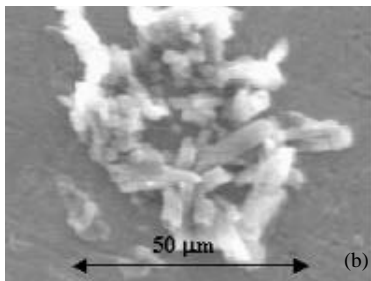
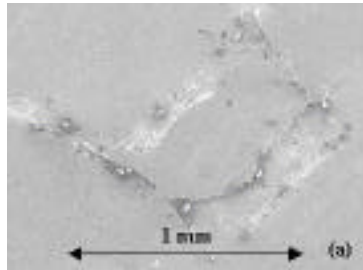


Figure 5: Scanning electron microscope images of cracks and crystals on the surface of an active disc (a) before flexing and (b) after flexing. a) Cracks and particles surrounding one of the 20 indentation marks. (b) Cluster of crystals in an indentation on the surface



discs surface and so wouldn't normally cause crystallisation prior to flexing. The interactions between the stainless steel and the crystals can effectively raise their melting point, such that they do not melt during the regeneration procedure. The minute crystals then grow in the cracks during the cooling process. These events are illustrated in Figure 4. We tested this hypothesis theoretically and experimentally.

Classical nucleation theory was used to investigate the behaviour of crystals residing in cracks on the metallic disc's surface during heating and cooling. We found that such crystals are able to survive in the cracks at regeneration temperatures of the order of 85°C, and that when the solution is cooled below the melting temperature such crystals grow to the mouth of the crack but not beyond. These crystals will only be able to grow out of the crack and induce

solidification of the whole solution surrounding the disc when the temperature is sufficiently low.

Experimentally, we could not look directly into a crack on a disc. Direct observation of what is believed to be such seed crystals was made on a disc, only after flexing it, using a scanning electron microscope (Figure 5). We therefore carried out a range of experiments to gather indirect evidence to test our hypothesis. Our experiments on the activation and de-activation of a disc showed that: the cracks on the surface of a disc are crucial to its activity; a disc may be de-activated by flexing it a large number of times in hot solution or hot water; and a disc may be re-activated by making the solution in which it is immersed solidify. This experimental evidence supported our hypothesis and refuted alternative mechanisms. We concluded that minute crystals of sodium acetate are indeed contained in the cracks of an active disc. Some of these crystals are ejected from the cracks each time the disc is flexed. In hot solution or water, the ejected crystals melt, and if all seeds are released from a disc in this manner, it becomes inactive. To re-activate it, new seed crystals need to lodge in the cracks of the disc. This is achieved by making a solution solidify around the disc, eg by putting the heat pack in a deep freezer.

We also showed experimentally that at a sufficiently low temperature of -17°C, a solution containing a metallic disc solidifies without flexing the disc. A solution in which no disc is immersed does not solidify at this temperature. These observations are supported by the theory, which suggests that as the temperature decreases, the critical radius above which a crystal can grow spontaneously out of the mouth of the crack decreases. At -17°C, the critical radius has a maximum value of 1.75 nm. Thus, if the mouth of a crack containing a crystal is larger than approximately 1.75 nm, solidification should occur in the presence of the disc but not in its absence.

a new reliable trigger

We can now understand why the metallic trigger is unreliable; when a heat pack is vibrated one of the small seed crystals

inside the cracks on the surface of the disc may be accidentally released into the sodium acetate solution, thereby triggering crystallisation. In order to design a reliable trigger, a new different mechanism had to be chosen.

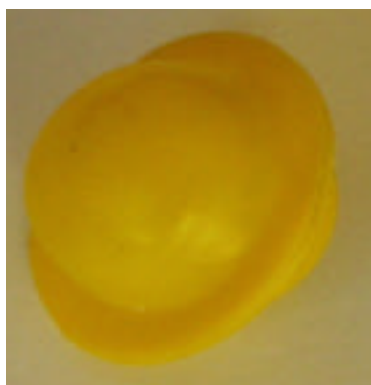
Our work on the design of a new trigger began with the determination of the pressure and temperature conditions under which the probability of an incipient nucleus in an aqueous solution of sodium acetate growing beyond the critical size becomes appreciable and nucleation occurs spontaneously.

A set of carefully controlled laboratory experiments was carried out to determine the nucleation temperature of a heat-pack sodium acetate solution, at atmospheric pressure. We then used classical nucleation theory to predict theoretically the rate of nucleation in a sodium acetate solution as a function of temperature and pressure. Using our theoretical results for high pressure and our experimental measurements at atmospheric pressure, we derived an equation for the nucleation temperature as a function of pressure.

Our new trigger uses a system that produces the temperature and pressure changes necessary to set off crystallisation in a subcooled solution of sodium acetate. A prototype of the new trigger has been tested and has been shown to be 100% reliable. A photograph of this trigger is shown in Figure 6. The trigger works by gently squeezing it between one's fingers. We estimate that the manufacturing costs for this new trigger would be very low, of the same order of magnitude as the presently available metallic trigger.

We are now at a position where the properties of sodium acetate may be fully explored and used to the benefit of our society. Our new trigger can be used reliably in medical, architectural and home developments. This new trigger may also be used in inducing crystallisation in other subcooled solutions, besides that of sodium acetate. ■

Figure 6: Photograph of the new trigger developed at Cambridge



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