Thermal stability of dry detergent formulation containing sodium percarbonate

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Dry laundry detergent formulations, powders and unit doses, contain sodium percarbonate at high weight concentrations. Sodium percarbonate is a key cleaning and stain removal technology delivering unbeaten removal of bleachable stains, at affordable cost; however incorporation of this ingredient into detergent formulations poses severe stability problems to be solved. Sodium percarbonate is an unstable chemical ingredient, which, naturally, over ageing decomposes generating initially hydrogen peroxide and in the end water plus molecular oxygen. This decomposition reaction is exothermic and autocatalytic. In order to preserve the chemical stability over ageing of dry detergents and to exclude the risk of thermal runaway during product supply chain, the formulation composition should be accurately designed and the storage conditions and the product purity should be carefully controlled. In this paper, we describe the key features of sodium percarbonate decomposition reactions in detergents and we critically discuss the applicability and the validity of the commonly used thermal runaway models (Semenov, Frank Kamenetski and Thomas) to study runaway risks of detergent formulations.

1. Introduction

Commercial dry laundry detergent formulations contain high weight fraction of sodium percarbonate (>10 % w/w). This ingredient is used to provide bleachable stain removal, at affordable cost and unbeatable performance. While sodium percarbonate is a critical technology for detergency, its chemical stability is a key challenge to address to formulate detergents. This issue is becoming bigger and bigger in view of the compaction trend that is undergoing into detergent industry.

1.1 Sodium percarbonate decomposition reaction

Sodium percarbonate (SPC) is an adduct formed between sodium carbonate and hydrogen peroxide (Na₂CO₃·1.5H₂O₂) and it decomposes over storage following the overall stoichiometry described in the reaction below:

\[ \text{Na}_2\text{CO}_3 \cdot 1.5\text{H}_2\text{O}_2 \rightarrow \text{Na}_2\text{CO}_3 + 1.5\text{H}_2\text{O} + 0.75\text{O}_2 \]  

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This reaction is exothermic (>600 J/g for pure SPC) and irreversible, however if the detergent matrix is properly formulated and stored in proper conditions, this is extremely slow.

SPS chemical decomposition has been studied, for pure dry raw material and in presence of liquid water, by Galwey et al. (1979 and 1982). They found that the decomposition mechanisms are very different: through intra-crystalline solid state reaction for the dry case and, in the case of presence of liquid water, through heterogeneous dissolution of peroxide followed by radicalic decomposition of hydrogen peroxide catalyzed by metal impurities in the liquid state, as described in reaction (2) and (3):

\[ \text{Na}_2\text{CO}_3 + 1.5\text{H}_2\text{O}_2(\text{s}) \rightarrow \text{Na}_2\text{CO}_3(\text{s}) + 1.5\text{H}_2\text{O}_2(\text{l}) \] (2)

\[ 1.5\text{H}_2\text{O}_2(\text{l}) \rightarrow 1.5\text{H}_2\text{O}(\text{l}) + 0.75\text{O}_2(\text{g}) \] (3)

Where, reaction (3) just describes the overall stoichiometry of a multistep radicalic decomposition reaction (see for example, Gozzo, 2001).

While the pure SPC/water system has been, at least qualitatively, understood, very little is known so far on more complex matrixes like a full commercial detergent is. In these systems, on top of SPC and some water, several other ingredients are present, which either can be oxidized or per-hydrolyzed by hydrogen peroxide or have the ability to bind water somehow, reducing its activity and thus its ability to extract and dissolve peroxide from SPC crystals.

SPC decomposition has also been object of calorimetric studies. For example, Lunghi et al. (1996) used DSC and heat flow calorimetry to follow dry sodium percarbonate decomposition and they derived a first order Arrhenius decomposition model to describe reaction rate:

\[ R = K_0 \exp(-E_a/RT) \cdot c \] (4)

Where R is the reaction rate, c is the SPC concentration and \( K_0 \) and \( E_a \) are the Arrhenius model parameters.

Johansson et al (2007) used isothermal calorimetry to follow decomposition of SPC in presence of zeolite, a common detergent ingredient, in air and at different relative humidity values. They showed that the heat flux results are in good accordance to the reaction rates as estimated from analytical results for SPC residual levels and that both zeolite addition and air humidity increase the decomposition rate of SPC. Johansson et al (2007) did not attempt to make a reaction model for this, albeit simple, system, however, the heat flow curve are indicative of a complex kinetics path, which cannot be described by either an order single decomposition reaction, or by a simple autocatalytic model. In fact, in the case of low relative humidity, they found that rate of reaction is monotonically increasing over several days at 30 °C, thus showing evidence of autocatalysis. On the contrary, at high relative humidity, reaction rate decreases, in a complicated way, with time, with no evidence of autocatalysis. The low humidity autocatalysis can be qualitatively explained by the model postulated by Galwey et al (1982) as by decomposing SPS, water is generated thus enhancing the rate of
heterogeneous dissolution of peroxide. This effect is important when water is scarcely available (low relative humidity), not important at high water activity (high relative humidity).

1.2 Thermal runaway models
The first thermal runaway model was developed by Semenov in 1928 (see Semenov, 1959); this assumes an isothermal system, heating up through a zero order Arrhenius kinetics and cooling through Newtonian natural convection. Frank-Kamenetskii model, developed in 1939, (see for example: Frank-Kamenetskii 1969) assumes that the cooling is controlled by thermal conduction in the bulk of the product, thus leading to a non isothermal system. Thomas model (1954) studies the generalized case when both internal and external heat transfer resistances are important (Biot number ≈ 1). All these models essentially predict thermal runaway by linear stability analysis of a single energy balance equation. Balakotaiah et al. (1994) presented a unified criterion to extend the above results to a network of n order parallel and serial reactions. Tseng et al. (2006) analyzed the case of methyl ethyl ketone peroxide decomposition, which comprise an autocatalytic step and establish runaway criterion by explicit simulation of the mass and energy balance equations. Li et al. (2005) analyzed the case of a simple autocatalytic reaction and pointed out that only isothermal calorimetry allow to safely distinguish between autocatalysis and n order reaction by separating the time concentration depletion effect and the temperature effect. In all these cases, one needs the heat generation kinetics, which can be obtained through isothermal calorimetry. Using these data, different single reaction kinetics models can be used to fit the experimental data.

In this paper we examine a dry detergent model system and we assess its thermal decomposition behavior to critically review the suitability of the above cited models to predict runaway conditions.

2. Materials and methods

2.1 Materials
We used, as dry detergent model system, a 30 % in weight active SPC prototype, formulated with tetraacetylthlenediamine (TAED, a peroxide activator) and a spray dried granule containing, among other ingredients, zeolite and anionic surfactants. This product was tested as produced and also artificially aged in a relative humidity controlled oven, to rapidly simulate real ageing.

2.2 Methods
We measured heat generation from the product using 2 isothermal calorimeters, a TAM III, and a TAM air, equipped respectively with a 4 ml and a 20 ml glass ampoule calorimeter. Both instruments are manufactured from TA Instruments. Using these calorimeters, heat evolution was followed up to 5 days at 30, 40, 50 and 60 °C.
3. Results and discussion

3.1 Calorimetric analysis results
As first step, we measured thermal activity (TAM) at 30, 40, 50 and 60 °C up to 5 days (fig. 1).

Fig. 1 Thermal activity (TAM) at 30 (●), 40 (■), 50 (▲) and 60 (●) °C, measured via isothermal calorimetry using a TAM III with 4 ml closed glass ampoule

The results, at all temperatures, show an initial autocatalytic stage, which lasts up to 1 day, and a subsequent plateau or very slow decay, which last up to 4 days. This is incompatible with a simple one stage autocatalytic reaction, like:

\[ A + X \rightarrow B + 2X \]  

(5)

A, B and X are chemical species. In fact, a single reaction would have only one characteristic time scale. Furthermore, we assessed the change in thermal activity of samples, after artificially accelerated ageing, by storing them at 32 °C and 80 % RH in a sealed commercial pack (Fig. 2).

Fig. 2 Thermal activity (TAM) at 40 °C of product fresh (●), aged for 1 week (■) and 2 weeks (▲) at 32 °C/ 80 % RH, measured via isothermal calorimetry using a TAM III with 4 ml closed glass ampoule
The ageing process affects mainly the characteristic time of autocatalytic stage and the absolute values of the thermal activity. Specifically, the longer the ageing, the shorter is the autocatalytic stage length; this can be explained assuming autocatalysis happens during ageing rather than in an instrument. In order to verify if water pick up can be the reason of absolute increase in thermal activity, we measured the thermal activity (Fig. 3) of samples produced with different water contents, by varying spray drying conditions. Water activity was measured through equilibrium relative humidity (e RH), using a Hygrolab 3 ex Rotronic.

![Graph showing TAM activity after 24 hours at 40 °C](image)

*Fig. 3 Thermal activity (TAM) after 24 hours at 40 °C of products produced at different water activity (e RH), measured via isothermal calorimetry using a TAM III with 4 ml closed glass ampoule*

Indeed, the water activity change is capable of explaining changes in absolute thermal activity, specifically the higher the water activity, the higher the thermal activity. All the results shown so far are compatible with a non radicalic mechanism, where the water provides autocatalysis by dissolving SPC crystals. In order to assess if radical decomposition could be present, we tested thermal activity at 40 °C of one sample using two different calorimeters with different ampoule size (a 4 ml ampoule for the TAM II and a 20 ml ampoule for the TAM AIR). Results are shown in the table 1.

<table>
<thead>
<tr>
<th>TAM Air (20 ml ampoule)</th>
<th>TAM III (4 ml ampoule)</th>
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<tr>
<td>15 μw/g</td>
<td>30 μw/g</td>
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Table 1 Thermal activity at 40 °C after 24 hours in a closed ampoule

This result seems to indicate the existence of a sample border effect which is, often encountered with radical reactions (see, for example, Christian et al., 2000). Even though we did not run any specific experiment, we would expect that this border effect is also dependant on the ampoule material.

3.2 Results interpretation and discussion

The objective of this isothermal calorimetry study was to evaluate the suitability of the generally accepted runaway models (Semenov, Frank-Kamenetskii, Thomas) to study the runaway risk of dry detergents. To this end, we believe that our results prove that:
• Thermal activity of detergents depends on water activity, which changes over ageing, because of water pick from outside through diffusion through the package

• A simple autocatalytic model, as described in eq. (5) is not capable of quantitatively describing the kinetics of SPC decomposition and heat generation

• Isothermal calorimetry results are sample size dependant. Thus we expect that using this to scale up heat generation in container of big size is not straightforward.

Given all of the above, we believe that the runaway models previously mentioned are not correctly predicting the runaway conditions of dry detergents and that we would need a more complex model, coupling heat transfer and SPC decomposition with water and radical generation, diffusion and quenching and using a more detailed decomposition kinetics pathway of SPC. Said this, we can still use a zero order Frank-Kamenetskii model to calculate runaway, using the highest TAM value recorded during in small ampoule isothermal calorimetry experiments, however this would result in unnecessarily high safety factors.

References

Johansson C., Pekonen P., Forstrom D., The long term stability of sodium percarbonate in presence of zeolite as measured by heat flow calorimetry