

# Peroxy bleaches

## Part 1. Background and techniques for hazard evaluation

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### Abstract

Fabric laundering is now a sophisticated chemical process involving a variety of operations including bleaching. The chemistry of peroxy bleaches is described including the use of novel organic compounds to provide effective bleaching at the lower temperatures of modern wash cycles. The instability of peroxy compounds is illustrated using cameo case histories to relate theory and practice. Techniques available for determining their thermochemistry are summarised. A model is provided for hazard and risk assessment of development projects in general (particularly those involving new molecules, processes or formulations) from ideas phase through exploratory laboratory investigations to pilot plant scale-up and eventual manufacture and commercial exploitation. This paper is a prelude to Part 2, which describes the determination of thermodynamic and kinetic properties of peroxy bleaches and discusses the implication of the results in terms of precautions for their safe storage and incorporation into detergent formulations during processing.

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### 1. Introduction

The science of detergency is discussed elsewhere [1,2]. References to laundering date back to 2500 BC when soap was used in washing around the River Tigris and Euphrates (now southern Iraq) [3]. Since these early days, there have been many advances including the development of synthetic detergents, washing machines, and more complex and sophisticated product formulations and washing regimes. Washing products contain an array of ingredients, each designed to perform a specific function in enhancing detergency and meeting ever-demanding customer expectations. Typically, fabric-washing powders contain

- ca 30% surfactant. These are usually anionic such as alkylbenzene sulphonates, alcohol sulphates and sulphonates, and/or non-ionic compounds such as alcohol ethoxylates to aid removal of fatty soils from substrates;

- ca 40% ‘builder’ to soften the water by removal of  $\text{Ca}^{++}$  and  $\text{Mg}^{++}$  ions. Examples include sodium tripolyphosphates, zeolites [4];
- low levels of additives such as enzymes (e.g. protease, lipase, or amylase to digest proteins and fats); anti-redeposition aids such as sodium carboxymethyl cellulose [5] to prevent removed soil from adhering to fabric; fluorescers to enhance whiteness; perfumes to provide specific odour cues such as ‘freshness’;
- ca 20% bleaches to assist stain removal by lightening or whitening the substrate through chemical degradation of coloured soils.

This paper concentrates on the function and safety of bleach materials in fabric-washing formulations.

### 2. Background

There is historic evidence of chemical bleaching of cloth prior to 300 BC using soda ash from burnt seaweed followed by treatment with soured milk to neutralise the fabric and finishing with exposure to sunlight [4]. Nowadays, common detergent

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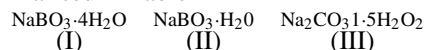
bleaches are either chlorine (e.g. in the form of hypochlorite, dichlorocyanuric acid) or peroxy compounds (e.g. percarbonate, perborate). Peroxy bleaches are more extensively used than chlorine bleaches in fabric-washing products because of the difficulty of incorporating chlorine bleaches into formulations during processing, and because of their health hazards, ability to cause fibre damage, and malodour [6,7]. Also, there is concern that organic matter in the waste-water may become chlorinated and produce dangerous organic chlorine compounds [8]. Peroxy bleaches contain the O–O linkage, and during the washing process they deliver active oxygen usually in the form of triplet/single oxygen. This destroys conjugated double bonds (via epoxidation and subsequent hydrolysis to the 1,2-glycols) in those molecules that are responsible for colour [9].

The power/activity of a peroxy bleach is expressed by its active oxygen content (AO) where

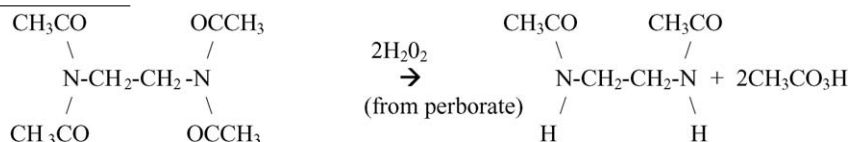
$$\text{AO}(\%) = \frac{\text{number of active oxygen atoms} \times 16 \times 100}{\text{molecular weight of material}}$$

The higher the AO value the greater the bleach potential. Also, comparison of the theoretical AO value with that obtained by potassium permanganate titration under acidic conditions provides a simple means for determining the purity of the sample [10].

Globally, the most common peroxy bleaches are salts such as sodium perborate tetrahydrate (I), sodium perborate monohydrate (II), and sodium carbonate perhydrate (III), commonly referred to as sodium percarbonate. Their AO values are summarised in Table 1



Sodium perborate tetrahydrate is the most widely used bleach for fabric detergency [11,12] but the development of more concentrated formulations has seen a growth in demand for the



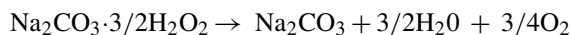
### TAED

monohydrate because of its higher AO content and faster dissolution in water [11]. However, perborates may be converted in to phytotoxic boron in the aquatic environment. Concern has been expressed about their subsequent deposition on to agricultural land from sewage treatment plants or when effluent water is used for irrigation where they could cause damage to crops and soil [13]. This provided impetus for the search for boron-free bleaches such as percarbonates and organic peroxy compounds.

Table 1  
Active oxygen (AO) content for inorganic peroxy compounds

Compound	AO (%)
Sodium perborate tetrahydrate	10.5
Sodium perborate monohydrate	16
Sodium carbonate perhydrate	14

Sodium percarbonate has a respectable AO content and dissolution rate [10], but is less widely used because of its lower storage stability. Under vacuum at 360–410 K it decomposes thus [14,15]

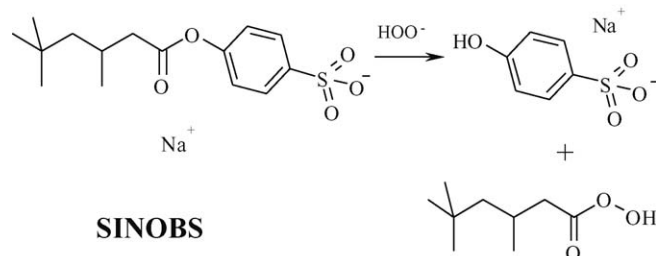


This reaction is catalysed by water, heat, and the presence of organics and metal ions.

Usually the rate of loss of oxygen is so small that it poses no significant effect on quality of the percarbonate. During bulk storage, however, the rate of heat rise may exceed the rate at which heat is dissipated to surroundings, which may lead to self-accelerating decomposition. Packaged percarbonate has a characteristic temperature above which decomposition takes place, i.e. the self-accelerating decomposition temperature (SADT). This temperature generally decreases with increasing packaging size and varies with the stacking arrangement. For 25 kg of percarbonate the SADT is 76 °C, whereas for 1 tonne big bags it is ca 50 °C. Also, when formulating with percarbonates the latter must be added slowly to organic material with good mixing to avoid deterioration of product quality and even fire or explosion as a result of the presence of percarbonate-rich pockets. Each type of formulation requires an individual hazard assessment. The value of studying self-heating hazards has been discussed elsewhere [16].

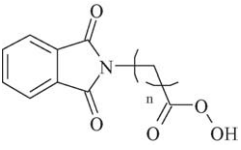
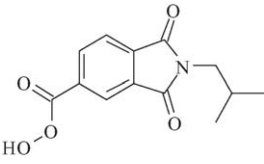
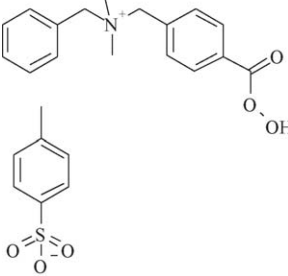
All three peroxy salts above show good bleaching at ca 70 °C although their effectiveness declines with decrease in washing temperature. To overcome this, bleach activators such as tetracetylene diamine (TAED) are added. The bleach activator reacts in situ with the salt to produce peracid. This, because of its higher oxidation potential than perborate (hydrogen peroxide), results in a superior cool-water bleach which is less aggressive towards fabric dyes.

General trends are towards cold-water washing to save energy, reduce costs, and cause less fibre damage, and in parts of the world including the USA and Japan, often washing machines are not equipped with heaters [17]. Therefore, organic peroxy activators possessing facile leaving groups to increase the rate of perhydrolysis have been described to enhance bleaching at low temperatures, e.g. sodium isononyl oxybenzene sulphonate (SINOBS) [10,18]



### SINOBS

Table 2  
Selected novel organic peroxy bleaches studied

Structure	Chemical name
	$x = 3$ , <i>n</i> -Phthalimidoperbutanoic acid (PAP3); $x = 5$ , <i>n</i> -phthalimidoperhexanoic acid (PAP5); $x = 7$ , <i>n</i> -phthalimidoperoctanoic acid (PAP7)
	4-Percarboxy isobutyl trimellitimide (PIBTA—a branched PAP5 derivative)
	$\alpha$ -( <i>N,N</i> -dimethyl- <i>N</i> -benzylammonium)-4-peroxytoluic acid tosylate (DMBAPTAT)

Alternatively, peracids can be incorporated directly into the detergent formulations although with current systems this presents technical problems due to their instability during processing and formulation. To overcome such difficulties a selection of novel organic peroxy acids (Table 2) have been prepared and evaluated [19,20] for their bleaching potential in fabric-washing powders. For example, formulations containing 16% sodium perborate and 5% TAED can be replaced with products containing only 4% phthalimidoalkanoic peracid (PAP) 5 to achieve good bleaching. Furthermore, the pH of the wash solution can be modified to increase overall cleaning efficacy or 'detergency'.

PAPs are unstable in the presence of water and metal ions, which may lead to exothermic decomposition. Samples evaluated in the present studies include dry powder, wet cake, and granules comprising polymer, sequestrant and either amine oxide or sodium alkane sulphonate, stabilised with varying amounts of boric acid.

The cationic moiety in DMBAPTAT (Table 2) was incorporated to increase the affinity of the bleach molecule for the negative surface of cotton and thereby enhance substantivity and hence efficacy.

### 3. Hazards of peroxy compounds during manufacture, storage, transport and use

In order to ensure the safe use of peroxy compounds during their manufacture, bulk storage, post-dosing during processing into detergent formulations, subsequent transportation and final use by the consumer, it is crucial to fully understand the chemistry involved in the various unit operations. The haz-

ardous properties, which differ with structure, concentration, purity, and temperature, include mammalian and aquatic toxicity, physicochemical properties, chemical reactivity, flammability, and explosivity.

Generally, the basic hazardous properties and causes of incidents when dealing with peroxides and peroxy salts are attributable to

- their exothermic decomposition to oxygen and water and subsequent temperature rise;
- pressurisation as a result of liberation of oxygen;
- catalytic decomposition due to the presence of impurities and water ingress;
- formation of explosive mixtures with organic materials and spontaneous 'runaway' reactions with reducing agents (e.g. between perborates and non-ionic);
- oxygen-enriched atmospheres [21].

Serious accidents with peroxides, peracids or oxidisers have been encountered as exemplified by the following case histories.

Explosions have occurred because self-decomposition is highly exothermic. This decomposition is greatly accelerated by increasing temperature and/or the presence of contaminants [22].

Steam was seen rising from a bulk storage silo containing 80 tonnes of percarbonate [23]. Investigation showed the silo, transfer system, and an interconnecting silo were all very hot. The percarbonate in the silo completely decomposed liberating large volumes of oxygen and steam and leaving concrete-like residues of sodium carbonate. The practice of receiving and storing bulk supplies of percarbonate was replaced by delivery of 1 tonne bags. Key controls were introduced to

- limit moisture pick-up;
- avoid contamination;
- monitor temperature in day bins and ensure temperature is below SADT;
- control loading of big bags into day bin and avoid unnecessary and prolonged exposure to air;
- rotate stock ('first in' 'first out');
- add percarbonate to organic material not vice versa.

One analysis of incidents (Table 3) suggests a relatively high percentage of accidents involving hydrogen peroxide are caused

Table 3  
Causes of hydrogen peroxide accidents world-wide (some incidents fall into more than one category)

Cause	Percent
Spillage	38
Rapid decomposition	36
Fire	34
Pressure burst	13
Runaway reaction	12
H <sub>2</sub> O <sub>2</sub> /organic vapour phase explosion	14
Condensed phase explosion	5

by over-pressurisation due to inadequate care, house-keeping and lack of venting [24].

Although the rate of isothermal decomposition of commercial hydrogen peroxide is well below 1% per year the amount of oxygen evolved can be considerable. A screw-capped Winchester bottle containing 35% hydrogen peroxide solution exploded after 2 years due to internal pressure from liberated oxygen [25].

Fire and explosion hazards of hydrogen peroxide have also been discussed by Merrifield [26]. It is to be appreciated that hazards can arise even with using low concentrations of peroxy compounds (e.g. as may be encountered in detergent formulations and hence a need to establish the stability of formulated products).

Hydrogen peroxide was being used to bleach a surfactant in a continuous process when a thin layer of enriched hydrogen peroxide solution concentrated at the bottom of the tank during the shutdown procedure. An explosion and fire occurred which fortunately resulted in no injuries but required the plant to be completely rebuilt [27].

Dilute aqueous hydrogen peroxide is generally considered safe to handle provided simple precautions are taken. Nevertheless, an explosion occurred during pre-treatment of waste-water with dilute hydrogen peroxide. An explosion also occurred during an experimental oxidation of an amine using dilute hydrogen peroxide solution. The explanation in both examples is production of unstable byproducts, which exploded following separation and concentration [28].

The importance of hazard assessment at the early stage of a project can be illustrated by many examples [22] but the following case history involving the bleach precursor SINOBS is particularly apt [29–31].

Rashes, rhinitis, conjunctivitis and wheezing were noted in several detergent workers involved in a 12–18 month development programme on SINOBS. Delayed contact hypersensitivity to SINOBS was probably responsible for some of the rashes. One employee then developed asthma from an estimated exposure of between 0.02 and 1.0 µg of SINOBS. This patient did not smoke and had no pets or other relevant domestic exposures but skin prick tests gave positive immediate reactions to a range of common allergens. Upon return to work after three weeks' absence there was a slight recurrence of his symptoms and he again ceased work for a fortnight. Inhalation challenge tests with nebulised SINOBS solutions gave late asthmatic reactions that were dose-related. The mechanism by which sensitisation is induced differs from that of Aspirin, a compound of some structural similarity to SINOBS. When SINOBS was eventually registered as a new substance on ELINCS under the regulations governing marketing of new chemicals it had to be classified as a skin sensitiser, a danger to health by prolonged exposure through inhalation, toxic if swallowed, and a skin and eye irritant. Such classification has serious implications for the

labelling of product formulations containing such ingredients and hence their customer appeal.

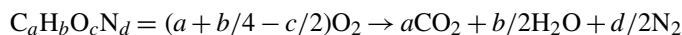
Clearly, innovation projects involving novel moieties must include a structured programme to establish hazardous properties and devise appropriate controls to avoid accidents at any phase of the product development. Typical stages in bringing a new chemical process or product to successful commercial exploitation are summarised in Fig. 1 [after 22].

A simple desktop evaluation of hazard potential is performed at the initial exploratory stage, which is then followed up by practical laboratory studies. Once these hazard data have been gathered and analysed risk assessments are made at each stage. A formal hazard evaluation, such as a Hazard and Operability study or 'HAZOP' [32], is usually conducted at the process stage taking account of detailed handling during manufacture, storage, transportation, subsequent processing, storage and distribution of formulated product, and by end user, anticipating possible misuse by the consumer. Selected safety data required before full commercial launch are illustrated by Table 4 [22].

### 3.1. 'Desk top' evaluation of hazard potential

An early phase in the process depicted in Fig. 1 is to conduct a 'desk top' review of hazards. This entails consideration of the properties of all raw materials, solvents, catalysts, impurities, side reactions, products, and byproducts, and comparisons with known related problematic chemicals. This paper-study reviews data already available in the literature including databases. It includes information on unusual or hazardous reactions or accidents, supplier's preliminary safety data sheets, Bretherick's Handbook of Reactive Chemical Hazards, the Institution of Chemical Engineers' Accident database, etc. Using only the molecular structure, the 'CHETAH' computer programme can be used to predict both thermochemical properties and certain reactive chemical hazards and thereby identify potential energetic substances [33]. It is a conservative screening tool for use during the initial stages of hazard assessment.

Of particular relevance to peroxy bleaches is the calculation of theoretical oxygen balance. This corresponds to the difference between the oxygen content of the molecule and that which is required to fully oxidise the carbon, hydrogen and other oxidisable elements to carbon dioxide, water and other oxidation products. Product oxidation occurs thus [34]



$$\text{Oxygen balance} = \frac{-1600 \times (2a + b/2 - c)}{\text{molecular weight of material}}$$

The greater the inherent oxygen content of the compound the less that is needed from external sources such as the atmosphere to facilitate complete combustion and pressure build-up. Since any nitrogen atoms present are liberated as the gaseous element in an explosive decomposition they are not considered as oxidisable. However, they do add to the pressure build-up and contribute to the hazard potential.

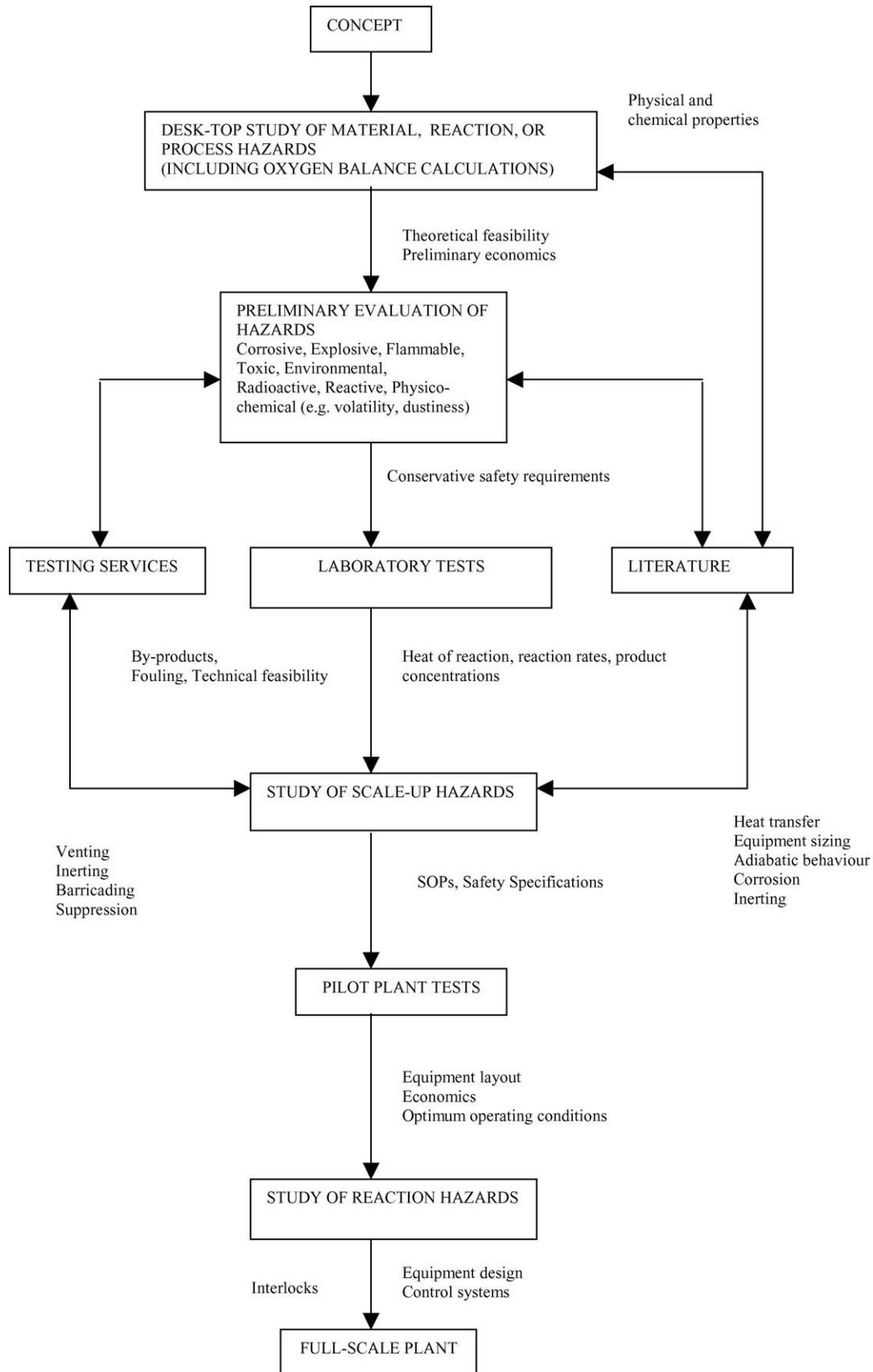


Fig. 1. Hazard and risk assessment during process development.

Table 4  
Examples of typical safety data for hazardous materials

Name of chemical	
Other names	
Uses	
General description of hazards	
General description of precaution	
Characteristics: evaluate as appropriate under all process and in-use conditions	
Formula (chemical structure: empirical formula)	
Composition/purity (identity of contaminants), physical state, appearance, other relevant details	
Concentration, odour, detectable concentration, taste	
Physical characteristics	
Molecular weight	Particle size: size distribution
Vapour density	Foaming/emulsification characteristics
Specific gravity	Critical temperature/pressure
Melting point	Expansion coefficient
Boiling point	Surface tension
Solubility/miscibility with water	Joule-Thompson effect
Viscosity	Caking properties
Corrosivity	
Contamination (incompatibility), oxidising or reducing properties; dangerous reactions	
Flammability	
Flash point	Vapour pressure
Fire point	Dielectric constant
Flammable limits (LEL and UEL)	Electrical resistivity
Auto-ignition temperature	Electrical group
Spontaneous heating	Explosion properties of dust, aerosol, mist, vapour
Toxic thermal degradation products	
Reactivity (instability)	
Acceleration rate calorimetry	Drop weight test
Differential thermal analysis	Thermal decomposition test
Impact test	Influence test
Stability (air, heat, light, moisture)	Self-acceleration test
Lead block test	Card gap test (under confinement)
Explosion propagation test with detonation	JANAF
	Critical diameter
	Pyrophoricity
Toxicity	Ecotoxicity
Toxic hazard rating	Chemical oxygen demand
Hygiene standard	Biological oxygen demand
Lethal concentration (e.g. LC <sub>50</sub> )	Biodegradation
Lethal dose (e.g. LD <sub>50</sub> )	Toxicity to fish (e.g. EC <sub>50</sub> and NOEL) daphnia, zebra danios, trout
NOEL (28 days)	Toxicity to algae
Eye/mucous membrane irritation	
Skin irritation and sensitisation	
Respiratory irritation and sensitization	
Mutagenicity	
Teratogenicity	
Carcinogenicity	

Materials are classed for explosion hazard according to Table 5. The oxygen balance should not be considered in isolation but in conjunction with other information such as the presence, or absence of reactive groups. Common sense should

prevail since, e.g. sodium bicarbonate has an oxygen balance of +28.6 whereas that of glyceryl trinitrate is +4. Clearly, the former is not an explosive whereas the latter is. Similarly, the oxygen balance of oxalic acid is -18 but it is not an explosive.

Table 5  
Classification of explosivity hazard based on oxygen balance values

Oxygen balance limits	Explosivity hazard rating
Greater than +240 or less than -160	Low
+240 to +120 or -160 to -80	Medium
-80 to +120	High

### 3.2. Laboratory studies

Bench-scale determinations of kinetic and thermodynamic properties are most frequently achieved using a selection of the following techniques, which we summarise in Table 6 to indicate the type of data that can be obtained with each.



Table 6  
Summary of experimental calorimetry techniques

	DSC/DTA	ARC	Isothermal reaction calorimetry	Dewar calorimetry	Isothermal micro-calorimetry	VSP	PHI-TEC
Basic information derived	$\Delta$ power (DSC)/ $\Delta$ temp (DTA) vs. temperature	Temperature/ pressure vs. time	Power vs. temperature	Temperature vs. time	Power vs. temperature	Temperature/ pressure vs. time	Temperature/ pressure vs. time
Thermal data							
Energy content	√√	√	√ (1)	X	X	√	√
Onset temperature (process design)	√	√√	√	√√	√√	√	√√
Onset temperature (bulk storage or transport)	√	√	√	√√	√√	√	√
Time to maximum rate	√ (1)	√√	√ (1)	√√	√ (1)	√	√
Vent sizes							
Vessel, flow and system characterisation	X	X	X	X	X	√√	√√
Hardware							
Stirring	X	Optiona	√	√	X	√	√
Remote addition	X	X	√	√	X	X	√

√/√, wide applicability, including solids; X, not applicable; √, applicable with limitations; (1), possible if isothermal kinetics are valid.

### 3.2.1. Differential scanning calorimetry (DSC)

DSC is one of the most useful reactive hazards screening tools, the basis of which is to monitor the change in enthalpy accompanying a chemical reaction. It measures the energy necessary to maintain both sample and reference at the same temperature and can be used to determine the enthalpy and temperature range of the desired reaction as well as undesirable reactions such as thermal degradation that occurs at high temperatures.

### 3.2.2. Differential thermal analysis (DTA)

Thermogravimetry (TG) is often coupled with DSC to quantify the weight loss resulting from such decompositions and the temperature for the onset of decomposition can be determined.

### 3.2.3. Adiabatic rate calorimetry (ARC)

The ARC monitors a sample as it undergoes thermal decomposition due to self-heating and is of particular value because of the number of thermal parameters derived from a single experimental run with a small amount of test material.

### 3.2.4. Thermal activity monitor (TAM)

TAM is a non-destructive, non-invasive, flexible and highly-sensitive microcalorimeter detecting changes of  $1-3 \times 10^3 \mu\text{W/g}$ . Kinetic parameters such as order of reaction ( $n$ ) and rate of decomposition ( $k$ ) can be derived from the Arrhenius rate law and when linked to the ARC enables additional kinetic data to be obtained. Such investigations should be performed on representative samples, and the effects of water, rust, packaging materials, etc. established. It is difficult to ensure that the small-scale tests, e.g. on mg quantities of development samples in DSC are representative of bulk material eventually used at marketing. Also, results from experimentally-determined values are influenced by the rate of heating and results need interpretation with care.

### 3.2.5. Dewar calorimetry

This simple, cheap technique has been used for many years to assess runaway reactions. However, a disadvantage at the research phase of development is the need for relatively large samples (ca 200 g).

### 3.2.6. Vent sizing packages (VSP)

This technique combines the evaluation of runaway parameters with vent sizing under emergency conditions. It uses a heat-wait-search technique to detect an exotherm that is followed adiabatically.

### 3.2.7. PHI-TEC

This computerised adiabatic calorimeter is designed to simulate the thermal behaviour or larger scale uncontrolled, runaway chemical reactions.

## 4. Summary

This paper described the function of bleaches in fabric-washing products and their hazardous properties. The merits of organic peroxy bleach compounds were discussed. By reference to a model, readers are reminded of a need to establish a comprehensive safety programme for any new development to assist its safe transition from laboratory to production and distribution. As part of such a programme the importance of establishing the thermodynamic and kinetic properties of new, potentially-unstable materials such as peroxy bleaches is emphasised. The data that may be derived from various calorimetry techniques are summarised. ARC and isothermal micro calorimetry are most appropriate for establishing the thermochemistry of peroxy bleaches using small sample sizes. Part 2 describes the application of these techniques in studies of a series of selected peroxy compounds, and it discusses

results in terms of implications for hazard classifications, risk assessments and recommendations for their safe use in industry.

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