Two explosions inside a polymer plant

23rd November 2009

Andrézieux-Bouthéon (Loire)

France

Chemical engineering manufacture
Explosion
Incompatible substances
Risks assessment
Organisation / procedures
Victims / injuries

THE FACILITIES INVOLVED

The site:

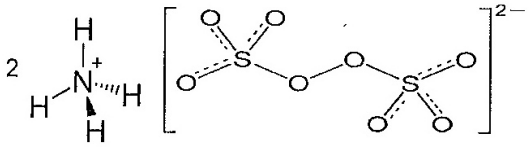
The plant, rated upper-tier Seveso, had been located within an industrial park isolated from all residential uses since 2004. The facility was producing acrylamide copolymers used as flocculants in water treatment processes.

Photo credit : DREAL Rhône-Alpes

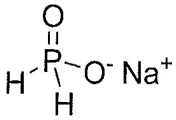
The specific unit involved in the accident:

The accident occurred in a workshop assigned to the manufacture of a dispersant. The laboratory associated with this workshop was testing the site's production of various liquids and contained a number of temporary reagent storage tanks, along with solid catalysts packaged in 25 kg bags. Quantities had to be adjusted for each synthesis run.

The synthesis of polyacrylamides necessitated, among other things, a polymerisation initiator: ammonium persulphate ($2(NH_4)S_2O_8$), a strong oxidiser, had been chosen for this particular synthesis.



The polymerisation catalyst used here was sodium hypophosphite ($NaPO_2H_2$), itself a powerful reducing agent.



These 2 substances, which combined to cause the accident, are both available in white powdery form and display a regular intermediate particle size distribution, making them impossible to distinguish.

According to the supplier's technical specifications, the persulphate anion is the most powerful oxidiser in the peroxygen family. Moreover, this document stipulated that under certain circumstances, hydrolysis of this anion may lead to both the bisulphate anion and hydrogen peroxide, whose oxidation kinetics are faster than persulphate. This document ("FMC: Technical Information on Persulphates") listed several recommendations, namely:

- Persulphates are oxidisers requiring special care during all transport and use;
- Aqueous solutions containing ammonium persulphate are more likely to decompose than the same compound in solid form, and storage above 25°C accelerates i ts decomposition;
- Humidity significantly lowers the decomposition temperature;
- Impurities, metals, humidity and other contaminants are capable of triggering or stimulating decomposition.

Hypophosphorous acid also acts as a powerful reducing agent. Its metal salts are highly soluble, while its composition is capable of producing phosphoric acid and phosphonate as well as hydrogen and phosphine, both of which are colourless, odourless and flammable gases.

THE ACCIDENT, ITS CHRONOLOGY, EFFECTS AND CONSEQUENCES

The accident:

Shift 1:

During the morning of 23rd November, a technician was preparing the raw materials needed to run a synthesis. At the end of the formulation stage, around 10:30 am, he was left with a 10 to 15 kg bag of sodium hypophosphite that, around 11 am, he mistakenly began pouring into a tank reserved for the temporary storage of ammonium persulphate. He recognised the error after pouring, by his account, 2 to 3 kg of hypophosphite; aware that these 2 products (oxidiser and reducing agent) were incompatible, he duly informed his superior.

The supervisor decided to separate the products as much as possible, in isolating the 2 stockpiles and using them up quickly. A film several cm thick was scraped from the tank surface and the powder removed was placed in a plastic bag (2-3 kg of sodium hypophosphite + a little ammonium persulphate). The remaining persulphate tank contents were deposited into a new barrel marked as holding approx. 15 kg of persulphate (PSA) mixed with a small amount of sodium hypophosphite (SHP). Around noon, the technician was isolating these products in one of the building zones, but a workshop colleague asked him to return the products to the shop. A shift change occurred at 5:30 pm.

Shift 2:

Around 5:40 pm, another technician poured the barrel contents (15 kg PSA + small quantity of SHP) into a dissolution tank. An explosion inside the barrel ensued, slightly injuring both the technician and one of his fellow workers. One would resume work the next day, the other sustained a fractured thumb and arm struck by the barrel following the blast. A portion of the workshop was secured. The supervisor of this 2nd shift called back the 2 employees from the earlier shift. Upon returning to the shop, one of them explained what had taken place to the chemical engineer in charge of safety training for both these products. The technician then grabbed the bag containing the mix (2-3 kg of SHP + trace amount

of PSA) for observation with the engineer, when at 6:15 pm the bag exploded just as it was being placed on the pallet again. The technician and engineer were both seriously injured, the former to his hands, the latter to his face (despite wearing protective glasses). The bag containing pure sodium hypophosphite (i.e. not poured into the tank when the technician realised his error) was probably also hit by projections and was burning when fire-fighters arrived on the scene. This combustion was extinguished by workshop staff.

Consequences of this accident:

The two successive explosions injured four, two of whom seriously.


Photo credit : SDIS 42


Photo credit : SDIS 42

Fire-fighter response, evacuation of the injured

The European scale of industrial accidents:

By applying the rating rules applicable to the 18 parameters of the scale officially adopted in February 1994 by the Member States' Competent Authority Committee for implementing the "SEVESO" Directive on handling hazardous substances, and in light of information available, this accident can be characterised by the four following indices:

Of the 2 substances involved in the accident, ammonium persulphate is assigned a Seveso threshold of 200 tonnes. Since the quantity of substance released was in the order of 15 kg, the index relative to dangerous materials released is scored a "1" (see Parameter Q1).

The accident injured four, two of whom seriously, placing the index relative to human and social consequences at a "2" (Parameter H4).

The accident did not result in any direct or indirect environmental impacts, nor were any economic consequences reported; the two corresponding indices were therefore scored "0".

The parameters composing these indices and their corresponding rating protocol are available at the following Website: http://www.aria.developpement-durable.gouv.fr.

THE ORIGIN, CAUSES AND CIRCUMSTANCES SURROUNDING THIS ACCIDENT

The explosions were directly caused by the accidental mix of sodium hypophosphite and ammonium persulphate. The 1st explosion in the barrel occurred after 7 hours of contact between the hypophosphite and persulphate powders. Handling of the bag 30 mins. later led to the 2nd explosion, following a total contact time of 7 hours, 30 mins.

A departmental memorandum indicating the operating protocol to follow in case of an accidental mix of products had been drafted subsequent to a previous accidental mix in February 2006 that caused an explosion without consequences. In the present instance, the operator did point out an incompatibility between the 2 products used, though the finding was only mentioned for soluble products showing a risk of explosion or violent reaction. A bibliographic research conducted by the Classified Facilities Inspectorate failed to reveal for either product a property of spontaneous combustion during powder-to-powder contact. For both products to react when in this form, an external energy input seemed necessary (handling and shocks: bag placed on the pallet, etc.). Moreover, the presence of water accelerated the process. Lastly, the remaining hypophosphite bag, which had likely been contaminated, ignited spontaneously following explosion of the (SHP + PSA) bag.

ACTIONS TAKEN

A formal notification issued in the subsequent weeks by the Prefecture imposed full compliance with all procedures announced as part of the company's safety management system.

The plant operator implemented a number of remedial measures, namely:

In the short term:

- weighing of ammonium persulphate and sodium hypophosphite in 2 laboratories outside the workshop;
- revised mix designs and associated checklists in order to remove the "bag bottoms";
- in each laboratory, products stored temporarily in their respective tank tagged by a specific colour were to remain in their original enclosed packaging.

In the longer term:

- replacement of ammonium persulphate by the less reactive potassium persulphate, after testing the behaviour of the new mix;
- implementation of a process dedicated to diluting sodium hypophosphite in order to allow for direct distribution of products in solution inside the liquid workshop.

Study of mix behaviour

The operator carried out tests on a few grams of the sodium hypophosphite / ammonium persulphate mix. In the laboratory, these tests demonstrated the critical importance of contact time between the 2 products in dry powder form. When mixed and stirred immediately after being poured into a beaker, the products do not detonate, yet they do explode after several hours of contact. This testing campaign confirmed the hypotheses adopted on the day of the accident regarding product behaviour, though the exact process could not be explained. In light of this observation and as stated during deliberations of the Workplace Safety and Hygiene Committee meeting on the accident, the company requested a specialised subcontractor to conduct a study on the reactivity of these 2 powders. Based on differential scanning calorimetry (DSC) analyses, this study tested the sensitivity of SHP-PSA mixes in various proportions and with variable maturation times to both friction and shocks; released in October 2010, its main conclusions were as follows:

- the key influence of maturation time on mix sensitivity, with very strong incompatibility of the 2 ingredients, and increasing reactivity vs. maturation time from 0 to 5 hours then decreasing thereafter;
- accelerated onset of the reaction in the presence of water;
- the need for external energy input.

Given the properties of both ingredient products and their degree of oxidation, an oxidation-reduction reaction was suspected, along with the existence of an autocatalytic phenomenon, which might explain the influence of maturation time.

During the accident, shocks provided the necessary energy input: barrel handling for the first explosion, bag placement on the pallet for the second.

Management of accidental mixes

The plant operator clarified facility procedures for handling accidental mixes of incompatible products, by emphasising that such a mix can never be treated like waste.

LESSONS LEARNT

The accident occurred subsequent to the accidental mix of 2 incompatible products and an underestimation of the hazard induced by placing these substances in contact with one another.

The chemical behaviour of a dry mix of ammonium persulphate and sodium hypophosphite powders, which had been poorly identified in the bibliography, was not adequately anticipated by the company, even though product incompatibility in soluble form had been acknowledged and recalled in operating procedures. The ammonium persulphate supplier's technical specifications mentioned the risks of decomposition and projection, yet without indicating the conditions under which such phenomena could arise.

Measures introduced by the operator were insufficient to ensure compliance, under all circumstances, with procedures designed for the company's safety management system (operating protocol to follow in case of an accidental product mix).

Reactions between solids are indeed rare. The risk had been partially identified since the decision was made to separate the products; despite being trained in chemical risks, the staff did not properly assess the magnitude of the risk incurred when these 2 solid substances were placed in contact, even after the first explosion in the barrel.

Effective knowledge of both physicochemical and toxicological characteristics of each substance introduced on-site, whether manufactured or stored, is not sufficient to avoid all danger. Regardless of the physical state of the substances involved (solution, powder, etc.), 2 incompatible products entering into contact can generate a hazardous chemical reaction should the technicians not be fully aware of the potential for an accident, no matter how limited, and not proceed in strict compliance with established procedure.