

Committee of Experts on the Transport of Dangerous Goods and on the Globally Harmonized System of Classification and Labelling of Chemicals

Sub-Committee of Experts on the Globally Harmonized
System of Classification and Labelling of Chemicals

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Updating of the Globally Harmonized System

of Classification and Labelling of Chemicals (GHS): Physical hazards

Self-acceleration decomposition temperature (SADT)

Transmitted by the expert from China

The use of a self-accelerating decomposition temperature (SADT) less than or equal to 75 °C for a 50 kg package as the threshold for the classification of self-reactive substances and mixtures is worth to deliberate.

Introduction

1. In chapter 2.8 (section 2.8.2) of the Globally Harmonized System of Classification and Labelling of Chemicals (GHS) (Rev.3), a SADT less than or equal 75°C for a 50 kg package is used as the threshold for the classification of self-reactive substances and mixtures. The same criteria are used in the UN Recommendations on the Transport of Dangerous Goods - Model Regulations.
2. We have written a letter to the Dangerous Goods and Special Cargoes Section to ask the reason and basis of the temperature of 55°C for temperature control and the temperature of 75 °C for classification as self-reactive.
3. Mr. O. Kervella replied to our letter as follows: “The temperature of 55°C for temperature control has been chosen because it is assumed that the temperature of the immediate surroundings of a package does not exceed 55°C during transport and that this temperature could only prevail during a relatively short time in a 24 hour period. And the temperature of 75°C for classification as self-reactive is the result of a compromise. It was finally agreed to fix a SADT limit of 75°C for the definition of self-reactive substances, but to retain in the dangerous goods list those which had a SADT value above 75°C.”
4. It was proved our guess: the threshold of self-reactive substances and mixtures in the GHS was based on transportation, but other situations were not considered, like the process of production. But GHS address potential exposures to all potentially hazardous chemicals in all types of use situations, including production, storage, transport, workplace use, consumer use, and presence in the environment.
5. During the process of production, some substances and mixtures do not belong to self-reactive substances and mixtures according to the classification threshold. We have analyzed accidents occurring during storage and production and find out that they occurred because chemicals had taken place self-reactive. During the process of production, ambient temperatures above 100°C are frequently reached. But according to GHS, there is no need to take account of control temperature if the substances and mixtures do not have self-

reactive properties. In fact, during the production and use the ambient temperature shall be controlled below the SADT.

Proposal

6. Considering the process of production, it is proposed to enhance the SADT threshold of self-reactive substances and mixtures appropriately.

Annex

Nitration residues accident in England Hickson and Welch corporation in 1992

1. In 1992, England Hickson & Welch corporation, an accident involving nitration residues occurred and resulted in 5 deaths. The capacity of the vessel was 45,500 liters, and it had never cleaned since it was installed 30 years before. The residues were not analyzed and were mistakenly taken as being a thermally stable tar. In order to soften it the operators applied steam to the bottom battery. It was suggested that the heating temperature should not exceed 90°C. The day when the explosion happened, the vessel's temperature gauge in the control room was reported to be reading 48°C, while actually the thermocouple was not extended into the residue (because of misestimating the amount of residue). Local temperatures went up to 165°C (steam temperature) and the high temperature caused decomposition and dash out of the nitration residues.

Pesticide explosion accident of American BPS on May 18, 1997

2. On May 18, 1997, a serious explosion and fire accident occurred at a plant of the second unit of BPS at West Helena, Arkansas. EPA and OSHA established a Joint Chemical Accident Investigation Team (JCAIT), this group participated in a simulation experiment at Tifton industry control center on May 18, 1998 hold by MFC (the MicroFlow Company). The simulation experiment was intended to establish the simulation temperature range of the compressor system at the time when the BPS accident happened. After experiment and analysis, JCAIT estimated that the temperature of the outlet pipe connecting the two compressor in the warehouse was more than 149°C, while the decomposition temperature of azinphos-methyl (AZM) is about 100°C. With the raise in temperature between 170°C and 180°C, a strong exothermic reaction took place and the product almost decompose instantaneously. JCAIT considered that the accident could have been caused by a big bag of pesticide azinphos-methyl (AZM) which was placed on or near the hot vent-pipe of the compressor, which resulted in thermal decomposition of AZM, the release of flammable gases and lead to a devastating explosion.

Ammonium nitrate explosion accident of France AZF chemical plant on September 21, 2001

3. At about 9:20 on September 21, 2001, an explosion occurred at the AZF chemical plant (of Total Fina Elf Petrochemical Group) in Toulouse (France). The explosion site was a warehouse in which were stored about 300t of highly flammable and extremely unstable ammonium nitrate.

4. The nature of ammonium nitrate is unstable, easily decomposed when heated. The decomposition reaction is rather complex since the products vary depending on the temperature. At 110°C the decomposition reaction is: $\text{NH}_4\text{NO}_3 = \text{HNO}_3 + \text{NH}_3$

5. If heated to higher temperature suddenly, or being knocked fiercely, an explosive decomposition will take place: $2\text{NH}_4\text{NO}_3 = 2\text{N}_2\uparrow + \text{O}_2\uparrow + 4\text{H}_2\text{O}$

6. It was reported that self-accelerating decomposition temperature (SADT) for the massive pile of ammonium nitrate was 200.3°C.

7. When the accident happened, the exploded warehouse stored about 390t~450t ammonium nitrate. Ammonium nitrate is a granular product, such accumulation is more likely to result in poor heat dissipation that lead to local overheating and decomposition. If the ammonium nitrate is mixed with impurities, it will further promote the decomposition reaction, eventually leading to the thermal explosion reaction of ammonium nitrate.

Explosion accident of First chemical company in October 13, 2002

8. On October 13, 2002, a fire explosion accident occurred in America first chemical company (FCC) plant located in Mississippi Pascal. In normal circumstances, the exploded No.1 distillation column should run in a vacuum environment to promote the completion of the separation process. Operating temperature of the bottom was about 176.7°C, top of the tower was about room temperature and heat was supplied by two steam heated regenerators.

9. On September 22, the operator isolated the heat source of the distillation tower that considered to be relatively minor at that time (such as tower that being refluxed including the No.1 distillation tower). In the next 5 days, all the valves on the steam line were off, but after the accident, through review on DCS information, it was found that bottom temperature was not dropped below 148.9°C. If the distillation tower was not heated, the temperature should have dropped to room temperature.

10. On September 29, the steam boiler of the plant stopped for maintenance as planned. Temperature of No.1 distillation tower was cooled to about room temperature. Maintenance of the boiler ended at about October 5, after boiler started, material temperature in No.1 nitrotoluene tower raised continuously, to the morning, the bottom material temperature had up to around 212.8°C. The higher the distillation tower bottom temperature, the more likely the vaporization of certain substances which will reach the top of the distillation column and accumulated on the exhaust plate. The heated MNT can decompose and release considerable heat, when MNT was heated to decompose for a few days later, the accumulated heat caused MNT's runaway reactions finally lead to an explosive reaction.

“7·28” Explosion accident of Sheyang County, Yancheng City, Jiangsu Province, yancheng fuyuan chemical plant Co. Ltd. Linhai subsidiary company on July 28, 2006

11. At 8:45 on July 28, 2006, Yancheng City, Jiangsu Province, Yancheng fuyuan chemical plant Co., Ltd. Linhai subsidiary company, No.1 workshop happened chlorination reactive tower explosion accident. At 15:10 on July 27, 2006, the material was fed for the first time into the column kettle of the chlorination reactive tower. At 17:20 inject heat conducting oil for heating-up. At 19:10, temperature of the column kettle rise to 130°C, then began to pass chlorine gas into the column kettle of chlorination reactive tower. At 20:15, operators find there was no condensate water in the condenser, then stopped to pass chlorine gas into the column kettle and turned off the heat-conducting oil valve. At 4:20 on 28, there was still no condensate water in the condenser, under this situation they began to pass chlorine gas and opened the valve of conducting oil to continue heating. At 7:00, stopped heating. At 8:00, the bottom temperature was 220℃, temperature of the top column was 43°C. At 8:40, chlorination reactive tower exploded. Under the situation of there was no condense water in the condenser and no product in the top of tower they did not stop working, instead they continue heating up in error, resulting in material (2,4-dinitrofluorobenzene) exposed to high temperature for a long time and eventually leading to the decomposition explosion.