

Chemical Reaction Hazards

DIN No	TD5/001	Issue Date	2 October 2000
Open Government Status	Fully Open	Review Date	30 November 2003

INSPECTION OF CHEMICAL REACTION SYSTEMS

by A M Jones

CONTENTS

Summary
Q1: Do the chemical reactions pose a known hazard?
Q2: How are the potential hazards identified?
Q3: What are the chemical reaction hazards?
Q4: What methods were used to assess the chemical reaction hazard?
Q5: Who carried out this assessment?
Q6: How can the process be made safer?
Q7: What inherent safety measures were considered?
Q8: What preventive measures were considered?
Q9: What protective measures were considered?
Q10: Will the protective measures work?
Q11: What precautions are taken during plant maintenance?
Q12: What are the procedures for plant modifications?
Q13: What are the preferred safety measures?
References
Further References Since This DIN Was Written

Summary

This DIN is intended to act as a check-list of main questions Inspectors may wish to ask during visits to chemical manufacturers. It covers chemical reaction hazards only, other flammable and toxic hazards of the materials used are not included.

Q1: Do the chemical reactions pose a known hazard?

A: All chemical reactions should be considered hazardous until proved otherwise. Of the reported incidents, polymerisation reactions are by far the most numerous, followed by nitration, sulphonation, and hydrolysis reactions. Due to the number of polymerisation reactions involving phenol-formaldehyde resin production the British Plastics Federation published "Guidelines for the safe production of phenolic resins" (this is no longer in print, but should be available at Area Libraries). Other reactions involved in known incidents are

given in general terms in reference 1 and, more specifically, in reference 2. However, just because a reaction is not listed, does not mean that it is safe.

Q2: How are the potential hazards identified?

A: It is as equally important to consider the design and operation of a process plant as the intrinsic thermochemical hazards. Systematic procedures (eg Hazop) should be used to identify hazards. Where appropriate, their likelihood can be quantified using techniques such as Hazan, fault tree analysis, etc.

Q3: What are the chemical reaction hazards?

A: Chemical reaction hazards arise from: thermally initiated decomposition (of reactants, intermediates and products); rapid exothermic reaction; rapid gas evolution; and can occur at any time during a chemical process if not properly controlled.

Q4: What methods were used to assess the chemical reaction hazard?

A: The main methods include: literature data and calculations; basic screening tests, eg. differential scanning calorimetry (DSC), ICI 10g sealed tube test, etc; isothermal calorimetry, to characterise the reaction under normal (non-runaway) conditions; adiabatic calorimetry, to characterise the run-away reaction; specific tests, to generate data for vent sizing calculations. See reference 1 for details of these methods and their interpretation.

Q5: Who carried out this assessment?

A: The majority of the tests can only be carried out in specially designed equipment, and by people who have experience in the use of the equipment and interpretation of the results. There are a number of commercial organisations who will provide this service (see OC 431/15).

Q6: How can the process be made safer?

A: The process can be made safer by providing: inherent safety measures; preventive measures; protective measures. Although absolute inherent safety is the preferred option, it is rare in practice, but the principle can be used to reduce the need for further preventive/protective measures.

Q7: What inherent safety measures were considered?

A: Measures to be considered include: semi-batch, as opposed to "all in" batch, operation where the reactants are metered in and there is some control of the rate of reaction; process intensification - minimising the inventory of hazardous chemicals; limit the size of charge vessels to prevent overcharging of chemicals; use a solvent or heating medium whose boiling point and maximum temperature, respectively, are below the temperature at which the reaction mixture can decompose exothermically; containment of the runaway reaction (this may also be considered to be a protective measure).

Q8: What preventive measures were considered?

A: The use of preventive measures requires the early identification of process hazards and the conditions under which they can occur. This allows the specification of boundary conditions, or an envelope within which the process must be maintained if it is to operate safely, and the provision of measures to ensure that the process remains within the envelope. The safe process envelope is defined by several parameters, these are:

temperature/ pressure	the minimum and/or maximum temperatures/ pressures of the desired reaction should be defined;
additions	it is important that the correct chemical is added at the correct time and at the correct rate;
agitation	unreacted material can accumulate or separate into different phases if the agitator fails;
scrubbing system and vents	the rate of vapour/gas evolution under normal and abnormal conditions should be defined to ensure these systems are adequate;
safe time	the maximum time any reaction mass can be held at elevated temperatures without it going to run-away should be determined;
personnel	operators should be well trained and be provided with well defined instructions (which should include non-standard situations);
instrumentation and control	is required to monitor key parameters and, when required, take corrective action.

Q9: What protective measures were considered?

A: Protective measures are rarely used on their own, some preventive measures are usually included to reduce the demand on the protective system. Protective measures include: emergency relief venting; crash cooling; dumping; reaction inhibition.

Q10: Will the protective measures work?

A: A knowledge of the reaction kinetics is essential when designing protection systems to ensure that their operation is sufficiently quick, effective and can be used without introducing further danger. As examples: the speed at which a valve responds to either introduce an inhibitor, or dump a reactors contents, must be such as to ensure the reaction is stopped, or the contents are dumped, before there is reaction run-away in the reactor; an explosion relief and any downstream equipment and ducting should be designed to cope with the rate of reactant release which could be emitted as gas/vapour, liquid, solid or any combination of these.

Q11: What precautions are taken during plant maintenance?

A: Efficient and regular planned preventive maintenance ensures a smoothly running plant, and is also an important way of preventing process maloperation. However, maintenance can itself be hazardous if not carried out properly. To ensure the safety of the maintenance team, others working in the vicinity of the

plant and the recommissioning team, a formal system, normally a permit to work system, should be set up and operated.

Q12: What are the procedures for plant modifications?

A: No process or plant modifications should be carried out until the hazards have been reassessed. This may result in a full re-appraisal of the process thermochemistry and hazard assessment. Often relatively simple tests or calculations will be sufficient. It is important that all process/plant changes are recorded.

Q13: What are the preferred safety measures?

A: Preventive measures are preferred to protective measures. However, whatever safety measures are chosen, it is important that they make the plant safe under the full range of operating conditions and credible maloperations and remain effective after plant modifications.

References

1. Barton, J. A. and Rogers, R. L., 1993, Chemical Reaction Hazards, I chem E.
2. Bretherick, L., 1990, Handbook of Reactive Chemical Hazards, fourth edition, Butterworths, London.

Further References Since This DIN Was Written

3. Reference 1 is now available in a second edition (1995), which includes care histories and an update of the legislation, ISBN 0 85295 341 0.
4. Reference 2 is now available as a 6th edition, and is also on disc. The reference is Bretherick's handbook of reactive Chemical Hazards, Urban, P G and Pitt, M.J., ISBN 075063605X 6th ed Butterworth-Heinemann, 1999, 2 volumes.
5. Chemical Reaction Hazards and the risk of Thermal Runaway, HSE Free leaflet INDG 254.
6. Etchells J and Wilday J, Workbook for Chemical Reactor Relief System Sizing, HSE CRR 136, ISBN 0 7176 1389 5, HSE Books.
7. Designing and Operating Safe Chemical Reaction Procedures, HSG 143, HSE Books.

J C Etchells
August 2000