Health and Safety Executive OC 431/15

Field Operations Division

To

Factory Inspectors

FCG Specialist Inspectors (Fire and Explosion)

EXOTHERMIC REACTIONS

This OC draws attention to the hazards associated with exothermic reactions and offers technical and practical guidance.

Reactive chemical hazards

1 All chemical reactions involve changes in energy, usually evident as heat. This is normally released during exothermic reactions (but occasionally, in endothermic reactions, may be absorbed into the products).

2 The main hazard associated with exothermic reactions is the release of heat at a rate too great to be dissipated to its surroundings. As a result the reaction mass heats up causing the reaction rate to increase, further accelerating the rate of heat production. Unless sufficient protective measures are provided this can lead to an explosion. Frequently the reaction giving rise to a runaway exotherm is not one which was intended, but is caused by process deviations. It is essential that occupiers assess the likely degree of risk involved in a particular operation and then plan and execute the operation in a way which will minimise the risks.

3 The underlying causes of many incidents which have involved unexpected violent reactions are:

(1) a basic lack of proper understanding by management of the process chemistry and thermochemistry;

(2) inadequate engineering design for heat transfer;

(3) inadequate control systems and safety back-up systems; and

(4) inadequate operational procedures, including training.

4 An understanding of the effects of simple physico-chemical factors on the kinetics of reaction systems is essential, especially the relationship of rate of reaction with concentration and the rise in temperature and pressure during the reaction. The concentration of each reactant can directly influence the speed of the reaction and the rate of heat release. Rates of chemical reactions generally increase exponentially with increase in temperature. As a rule of thumb, for most reactions an increase of 10^{o}C roughly doubles the reaction rate. Temperature control is thus vital, as an increase in temperature builds on itself very quickly, causing a runaway reaction to occur with very little time for correcting the situation.

5 A variety of laboratory techniques can be used to obtain data on the chemical and physical properties of reactants, intermediates and products and on the chemistry of the desired reaction and potential side reactions. The Association of the British Pharmaceutical Industry (ABPI) have developed a laboratory scheme for screening new products and processes. Details are given in the ABPI's booklet *Guidelines for Chemical Reaction Hazard Evaluation* (file 431).

6 The Chemical Reaction Hazards Centre, part of the Chemical Engineering Department at the South Bank Polytechnic, can provide advice to occupiers on:

(1) the establishment of hazard laboratories;

(2) the selection of appropriate assessment and testing procedures for specific thermal hazards;

(3) the assessment of hazards from thermal instability of materials including runaway potential, reactor control and vent sizing;

(4) the testing of new materials and reactions;

(5) the investigation of incidents.

The service provided by the Centre is particularly useful for companies which do not have the resources or expertise to test their own materials or adequately design a venting system. Other organisations can provide all or part of the above list of services (see Appendix for names and addresses).

7 The reactions which feature most frequently in runaway incidents are polymerisations, particularly phenol-formaldehyde condensations, nitration and sulphonation. Other reactions which have given rise to numerous incidents are Grignard reagent preparation, alkylation using Friedel-Crafts synthesis, amination, diazotisation, halogenation (chlorination and bromination), hydrolysis, oxidation and neutralisation (salt formation).

8 In view of the number of incidents with phenol-formaldehyde resin production, the British Plastics Federation (BPF) came forward with an exemplary approach to the problem in its publication *Guidelines for the safe production of phenolic resins*(file 303). Although the BPF document is specific to phenolic resins the general principles adopted could be used elsewhere.

Hazard identification

9 In order to deal with hazards it is first necessary to identify them, then decide how likely they are to occur, and how serious the consequences would be. A formal system should be used to study the plant, and identify and record process hazards. Hazard and operability studies (HAZOPs) can be used to identify hazards and hazard analysis (HAZAN) can be used to quantify the risks from these hazards. It is then necessary to decide what to do about the hazards in order to reduce the probability of a runaway occurring. The hazard assessment must take into account all foreseeable process deviations and the consequences of any unwanted reactions that might thus result. The process deviations would include, for example, reactants held at high temperature for an abnormally long time, incorrect addition sequence etc.

10 Where consequences are judged to be severe, or where the causes giving rise to the hazard are many or are inter-related, it is recommended that a fault-tree is constructed, showing the way in which various events or faults can give rise to a hazard. When constructed the tree can be used to see where the most likely causes of an incident lie, and where additional precautions can be introduced to minimise the risks. For the most rigorous examination it is necessary to allocate probabilities to each event in the fault-tree, allowing the total probability of the final event to be calculated. Clearly the probability assigned to each event in the fault-tree will need to be justified.

11 Where companies are not able to carry out such examinations of their processes alone, a consultant may be used. The Institution of Chemical Engineers (I Chem E) maintains a register of such consultants.

Adequate process control

12 Effective control is essential to minimise the hazards associated with particular reaction systems. To achieve such control it is necessary to assess potential hazards in the system. There are well known techniques available for such assessments as indicated in para 9.

13 Safe operation can be based on:

(1) process control that prevents conditions being attained under which uncontrolled exothermic reactions will be initiated, or

(2) process control to minimise the possibility of a runaway reaction, combined with protective measures should such a reaction occur.

14 The various options may be summarised as:

(1) process control + reactor venting;

(2) process control + containment;

(3) process control + crash cooling;

(4) process control + reaction inhibitions;

(5) process control only.

In practice there is likely to be a combination of these options. The most appropriate safety measures depend on process detail, type of industry, toxicity of products, magnitude and rate of the runaway parameters and the practicality of implementing and maintaining the safety measures. Options (2), (3), (4) and (5) imply the non-use of emergency venting which is discussed at para 17.

General precautions for exothermic reactions

15 The following check list may help in deciding what questions to ask occupiers:

(1) The thermo-chemical properties of the reaction should have been fully studied. As indicated above, experience has shown that nitrations, sulphonations, ethoxylations, acid neutralisations and polymerisations are particularly prone to uncontrolled exothermic reactions.

(2) The rate of a reaction may be controlled by limiting the rate at which reactants are brought together, or, where applicable, the rate of catalyst addition. This can be achieved by controlling, either volumetrically or gravimetrically, the addition of one or more of the reactants to the vessel at a predetermined rate.

(3) For immiscible liquids a reliable form of mixing should be provided. Normally this will be by a stirrer, but other means include jet mixing, fluid injection and sparging. Where a stirrer is used it should be provided with a stirrer failure alarm system. The rotation of the stirrer shaft, and not the motor, should be monitored since the shaft may become separated from the motor. Even if liquids are completely miscible means should be available to ensure adequate mixing. When efficient stirring is important for safe operation, monitoring of the motor load will also give warning of shaft failure, blade failure and high reactant viscosity. Where a mixing system other than a stirrer is used, an equivalent means of monitoring and alarm should be provided.

(4) Sufficient cooling capacity should be provided on the vessel for accurate control of the reaction temperature. The coolant should be provided from a reliable source. There should also be some visible indication of the flow of coolant and coolant failure alarms should be fitted, ideally at the coolant outlet. A back-up coolant supply may be necessary, particularly for reactions where constant cooling is essential.

(5) The vessel should be fitted with a high temperature indicator and alarm system. The feed to the vessel should be automatically cut off when a predetermined maximum safe temperature is reached. Alternatively, a rate of temperature increase indicator and alarm may give an earlier warning of potential runaway. Heating to the vessel should be automatically cut off when a predetermined maximum safe temperature or rate of temperature rise is reached, as should reactant feed to the vessel in the case of semi batch reactions. The temperature should be such that the cooling system has still sufficient reserve capacity to bring the reaction under control. A low temperature alarm should also be fitted if there is a danger of the reactants accumulating without reacting for some reason, ie to indicate a departure from normal process conditions. A temperature recorder should also be fitted in order to monitor the reaction. In some circumstances where

temperature measurement may not indicate an abnormal rise in pressure, a high pressure alarm and trip should be installed.

(6) If the vessel is heated, the provision of accurate and positive control of the heating medium to avoid over-heating should be checked. (Heating must be stopped when not required).

(7) For each reaction the maximum temperature attainable under the most adverse conditions arising from human, plant or instrument failure and also the maximum pressure generated should be determined. If this pressure exceeds the safe working pressure of the vessel a suitable vent and bursting disc/relief valve should be provided unless equivalent safeguards can be justified by other means. The vent should discharge to a suitably designed catchpot or should be so positioned that people working in the area and members of the public will not be in danger if the contents of the vessel are discharged. The vent duct should be as short and straight as practicable. The back pressure created by the duct should be taken into account in the vent design calculation. If the vent is connected to a catchpot, care should be taken to ensure that this vessel cannot be over-pressured when the contents of the reaction vessel are discharged into it. This type of calculation should be repeated whenever there is a wish to alter, including scaling-up, an existing reaction process. Inspectors are advised to note the implications of the Environmental Protection Act 1990.

(8) Care should be taken with the selection and training of operators. They should be aware of the significance of every stage of the process and the safety procedure to be followed. They should be trained to recognise abnormal conditions which may occur during the course of a reaction and the procedures to be followed to safeguard both themselves and others working in the area;

(9) Clear and precise process instruction sheets should be issued covering how the plant should be run normally and also:

(a) the hazards of the chemicals used and those deriving from the particular stages of the process, and

(b) the action to be taken in the event of predictable deviations, eg incorrect feeding of reactants, loss of agitation, loss of cooling water, abnormal temperature trace, delays in processing etc.

Inherently safe design

16 In some cases it may be possible to avoid or significantly reduce hazards and operating problems by a change in the plant design for example:

(1) lower inventory of hazardous materials in process at any one time;

(2) use of safer materials;

(3) less hazardous processing conditions;

(4) use of semi-batch plant rather than batch: In the former, the full charge of one reactant is added initially to a reactor and the other reactants are fed continuously over a period of time - only one reactant is present in large quantities at any one time. In the latter the full charges of all the reactants are added at the beginning of the reaction.

Where such improvements can be made, the plants are generally simpler with fewer opportunities for error. They are less dependant on additional safety systems which may fail and they respond more slowly to change.

To vent or not to vent

17 An occupier may have decided not to install an emergency relief vent for a potentially dangerous exothermic reaction, on the grounds that the alternative safety devices fitted are sufficiently reliable to prevent loss of control of the reaction. This may be acceptable provided that they can demonstrate that they

are able to do this, eg by using quantitive risk assessment.

18 The use of risk analysis techniques in determining the extent of plant protection for exothermic batch reactors can be accepted, providing that the technique is applied sufficiently rigorously. It is important that the consequences of loss of control are fully explored, and the decisions are properly documented.

19 If a company contend that they have arrived at a particular protection regime for a batch reactor, so that it is 'safe so far as is reasonably practicable', then they should be in a position to support their assertion by providing adequate documentary evidence. If it is contended that venting is not reasonably practicable then sound reasons for this should be clearly presented. The assessment should generally include:

(1) a hazard and operability study:

assessment of the process, operational and chemical hazards;

(2) a hazard analysis:

assessment of the consequences of a reactor failure including risk to operators, personnel in adjacent plant/building, the public, and any adjacent processes or storages (domino effect);

(3) a fault-tree analysis:

including quantification of failure probabilities and of the frequencies of worst-case events; and

(4) cost/benefit considerations for and against a vent system.

20 Inspectors should satisfy themselves that the company's rationale is sound. This may be done by checking that the company have done the appropriate tests and taken into account all the relevant parameters. HSE's knowledge and experience of the company's expertise are factors in deciding on the depth of assessment required.

1 It is accepted that venting is not a universal solution and may not necessarily be the safest option. For example, it may be inappropriate to vent a highly toxic material to atmosphere, and the use of catchpots and scrubbing systems can bring their own problems. The current view is that venting is generally to be preferred, and that where high-integrity control systems are used venting is still desirable as a long-stop.

Vent design

22 There is no simple guidance on the design of explosion relief vents for exothermic reactions. The Factory Insurance Association chart, which gives a plot of vent size as a function of reactor volume has no technical basis and was never intended as a design tool. There are a number of technically based design methods which can be applied to a limited range of reactions.

23 Work carried out by the Design Institute for Emergency Relief Systems (DIERS) in America represents the current state of the art but it has not been fully validated. Guidance on this has been published in a number of technical journals but, as yet, no design guide has been published.

24 A number of the consultancies listed at the Appendix offer services in vent sizing. In addition, a number of large companies have developed their own, in-house procedures based on a range of design methods. In cases of doubt, the FCG should be consulted.

25 When considering bursting disc/relief valve set pressure it is essential that the safe working pressure of the weakest part of the system is taken into account. This may well be a reactor vessel attachment eg glassware, rather than the vessel itself.

Request for information

26 The Chemical Manufacturing NIG would be grateful to receive detailed accounts of incidents involving exothermic reactions, information on any problems experienced, or details of circumstances where it has been accepted that emergency venting is not required.

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ASI headings

Chemical hazards: control systems: exothermic reactions: explosions.

APPENDIX

(paras 6 and 24)

ADDRESSES OF ORGANISATIONS ABLE TO PROVIDE ADVICE

AND CARRY OUT TESTING

Chemical Reaction Hazards Centre

Chemical Engineering Department

South Bank Polytechnic

Borough Road

London

SE1 0AA

Hazard Evaluation Laboratory Ltd

Fire Research Station Site

Melrose Avenue

Borehamwood

Hertfordshire

WD8 28L

Chilworth Technology Ltd

Beta House

Chilworth Research Centre

Southampton

SO1 7NS

Colombia Data Services Corporation

101 Garamonde Drive

Milton Keynes

MK8 8DD