**A STRATEGY FOR PROCESS SAFETY IN THE FINE CHEMICAL AND SPECIALITY CHEMICAL INDUSTRIES**

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The process safety needs of the fine chemical and speciality chemical industries are identified by consideration of the characteristics of their manufacturing activity (e.g. batch chemical reactors, multi-process plants, diverse chemical reactions). A strategy for process safety is described that establishes and maintains safe manufacturing practices.

Key words: Process Safety, Chemical Reactivity, Batch Reactors.

## 1. INTRODUCTION

Manufacturing in the fine chemical and speciality chemical industries involves the processing of reactive chemicals, flammable liquids, vapours, gases and powders. The safety record of the chemical industry is good but uncontrolled fires, explosions and chemical reactions can result in hazardous situations.

A strategy is required that ensures that the chemical manufacturing activities are carried out safely. The objective of the strategy is to establish and maintain safe manufacturing practices in a manner that is compatible with the plant design, the operating conditions, production demands, commercial requirements and economic factors.

In simplistic terms, chemical manufacturing involves raw material storage, chemical reactions and isolation of the product, drying, product preparation (e.g. milling, tabletting) and product storage and packaging. Features common to many operating units are: (a) batch or semi-batch operations, (b) multi-purpose plant, (c) plant configurations that can be readily modified, (d) a wide range of chemical reactions and (e) short production runs requiring quick response times. The strategy and procedures must be compatible with this modus operandi and in particular they must produce valid decisions in a short time scale.

Conveniently, albeit crudely, sources of hazard can be grouped as follows:-

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(1) General hazards of the workplace.
(2) Health hazards, toxicity.
(3) Hazards associated with operations not specific to a particular process, e.g. electrical equipment, welding etc.
(4) Hazards associated with chemical reactivity - chemical reaction hazards.
(5) Hazards associated with flammable materials and plant operations in specific processes/plants - operational hazards.

This paper is concerned primarily with (4) and (5) but these process hazards must not be considered in isolation, due attention must be given to statutory requirements, "good practices" etc. for all sources of hazard and the appropriate techniques of HAZOP and HAZAN (1) used for each.

A successful strategy leads to the allocation of realistic responsibilities and the establishment of procedures that lead to effective safety measures in the most practical manner.

## 2. ORGANISATION - FUNCTIONAL RESPONSIBILITIES

The most appropriate organisation and allocation of functional responsibilities depends very much on the size and infrastructure of the company.

In a large company, plant design and construction, process development, production and hazard evaluation may well be carried out by personnel from departments with different functional responsibilities (e.g. engineering, research/process development, manufacturing, and safety departments). Specialists in one or more of these areas may be available "in house". In a small company individual managers may have responsibility for more than one of these areas and may not have readily available specialist support. Experience of the process prior to manufacture will also differ. In a large company processes are often developed ab initio within the company. Toll or contract manufacturers, in contrast, receive process details in complete or near complete form and are expected to start full scale manufacture with minimum delay.

Responsibility for process safety can be allocated in the way that is compatible with existing infrastructures. Whichever organisation is used however it is essential that responsibilities are allocated and procedures established for the following key stages:-

(A) Chemical Reaction Hazards

- definition of process chemistry/operating conditions
- investigation of potential chemical reaction hazards
- selection and specification of safety measures
- implementation and maintenance of safety measures.

(B) Operational Hazards

- identification and characterisation of flammability of materials under plant operating conditions
- identification of ignition sources
- selection and specification of safety measures
- implementation and maintenance of safety measures.

The procedures must be applicable to hazard assessments carried out (a) during initial (research) development work, (b) prior to transfer to pilot plant scale, (c) before full scale manufacturing is established and (d) when modifications to the process/plant are undertaken.

## 3. EVALUATION OF CHEMICAL REACTION HAZARDS

Essentially chemical reaction hazards are associated with loss of control of exothermic reactions, gas evolution and/or decomposition phenomena. Each of these must be considered under the operating conditions present during each stage of manufacture.

### 3.1 Process Definition

The degree of safety achieved from a hazard assessment is directly related to the range of process operating conditions and plant design features considered in its preparation. It is important therefore that the process definition be sufficient to produce the desired level of safe operation.

Four levels of process definition can be identified.

#### Level 1: Process Definition with Fixed Parameters

Process descriptions, particularly at early stages of development, often include specific values for such parameters as temperature, reactant concentrations, time, etc. The hazard assessment can only *cover a process operating with these fixed values.*

It will not consider variations in the process conditions that would be allowed to occur in full scale operation and not be considered to be abnormal (e.g. small changes in temperature, concentration, batch hold times). Project definition at this level will rarely produce a hazard assessment giving an acceptable level of safety.

#### Level 2: Process Definition Including Normal Variations in Operating Parameters

This level of process definition recognises that in actual operation the process conditions will vary. It defines the range of values over which each parameter will be permitted to change without corrective action being taken, i.e. the process as normally operated.

Certain of these variations are well recognised, e.g. the temperature of a batch varying by plus or minus 10°C. Others are less well recognised and incidents have occurred because the significance of variations in basic parameters that are an accepted part of the manufacture are not included in the process definition and consequently not covered by the hazard evaluation. For example, the hold time at elevated temperature for analysis of product quality that is normally one hour extending to twelve hours at weekends. This is a situation in which "side reactions" virtually dormant over one hour at the elevated temperature can accelerate exponentially to a dangerous level in the increased time.

Hazard assessment based on level 2 process definition should adequately protect a process operating normally.

Level 3:
Process Definition Including Non-Specific Fault Conditions

Certain failure situations, although not common, are known to occur in chemical processing. Examples are agitator failure, loss of cooling, fracture of an internal coil. These are not specific to individual processes and the effect of them can be included in the hazard assessment without additional detailed process definition.

Unless the plant design is such as to eliminate them then the effect of such failures on process stability and the consequences of any subsequent runaway situation has to be included in the hazard evaluation.

Level 4:
Process Definition Including All Conceivable Abnormal Situations

It is possible to postulate a large number of abnormal conditions that could conceivably cause exothermic activity. Examples are: contamination of the batch by a reactive chemical used in a neighbouring process, variations in raw material quality, the possibility of a general fire overheating the reactor. Unconstrained, this approach can lead to an open-ended commitment to testing.

The techniques of Hazard and Operability that can provide guidance as to the probability and consequence of any abnormal situation are a means of determining the additional abnormal situations that need to be considered in the hazard assessment.

It is considered that Level 3 is the minimum standard that leads to an acceptable level of safety in the majority of processes.

The process/plant definition should include:

(a) Definition of the process/plant conditions including all known/expected variations in the process parameters (e.g. temperature ranges, concentration variations, hold times, etc.).

(b) details of operations (e.g. cooling, agitation, pumping, etc.) that are not protected by high integrity trips.

Where necessary this assessment should be expanded to cover the maloperations, etc., that Hazard and Operability Studies indicate could realistically occur in the process.

## 3.2 Characterisation of the Process

In summary characterisation of the process requires:-

- *identification of detonation/deflagration that precludes manufacture in standard chemical plants*
- early identification of the possibility of exothermic reaction and guidance as to temperatures at which it could become uncontrolled
- data on the rate and magnitude of exothermic reactions and gas evolution under full scale conditions
- sensitivity of the "normal" process to changes in process/operating conditions.

Techniques now exist for the systematic quantification of potential chemical reaction hazards. Small scale tests (e.g. DSC, DTA) can be used for the quick screening of a process, the runaway reaction can be characterised by adiabatic calorimetry and the "normal" process can be simulated in Heat Flow Calorimetry. The details of these techniques and the interpretation and application of the data are to be discussed in contributions to this symposium by Nolan, Dixon - Jackson, Lambert and Amery, Rogers and Maddison. No one technique will provide a comprehensive hazard assessment but a suitable combination of the available techniques can ensure this (2).

## 3.3 Selection of Safety Measures

Safe operation can be based on:

(A) Process control that prevents conditions being attained under which uncontrolled exothermic reaction will be initiated.
or
(B) Process control to minimise the probability of a runaway reaction combined with protective measures should such a reaction occur. The options for protective measures are:

(1) Process control + containment.
(2) Process control + reactor venting.
(3) Process control + crash cooling/drown out.
(4) Process control + reaction inhibition.

The most appropriate safety measure depends on process detail - including toxicity of products, magnitude and rate of the runaway *parameters and the practicality of implementing and maintaining the* safety measures.

Critical technical considerations for each are:

### Process Control

- definition of minimum temperature at which uncontrolled exotherm will start under plant conditions.
- safety margin between operating temperatures and exotherm temperature.
- monitoring and control systems to maintain temperature in the safe region.

- maintenance of temperature should agitation or cooling fail - e.g. stop feed reactant, use solvent that boils at safe temperature. - control sources of risk external to process - e.g. addition of wrong materials.
- specification of lower temperature limit to prevent accumulaton.
- reaction of two phase systems to agitation failure.

Process Control and Reactor Venting

- definition of worst case - i.e. conditions leading to maximum rate of exothermic activity.
- establishment of "kinetics" of the runaway reaction.
- nature of discharge material - gas, liquids, solids.
- methods for calculating reactor vent area and discharge system for the vented materials.
- safe discharge area - flammable and toxic hazards - dump tanks.

Process Control and Crash Cooling/Drown Out

- rate of temperature rise/heat generation after runaway detected.
- time to hazardous pressure.
- availability of compatible cooling medium.
- relative thermal capacities of reaction mass and cooling medium.
- plant design/operation to intermix reaction mass and cooling medium and stop temperature rise before maximum permissible pressure is attained.

Process Control and Reaction Inhibition

- availability of compatible reaction inhibitor.
- time to hazardous pressure.
- inhibitor efficiency.
- plant design and operation to intermix reaction mass and inhibitor and stop temperature rise before maximum permissible pressure is attained.

In addition to the technical considerations, the selection of the appropriate basis for safe operation must take account of:

(a) acceptability to the engineering and manufacturing functions with respect to their compatibility with the design construction, operation, maintenance and economic requirements of the process.

(b) the essential features of the safety measures must be understood by the manufacturing personnel.

(c) the safety measures must be fully implemented and maintained.

(d) the boundaries of the safety evaluation and the effect of changes in plant construction or process operation.

## 4. EVALUATION OF OPERATIONAL HAZARDS

Operational hazards are those arising from the use of flammable materials (liquids, gases, vapours, and powders) in chemical manufacturing. A fire or explosion can occur if such materials come into contact with an ignition source. Examples of incidents at different stages of the manufacturing cycle are:

(a) vapour explosion on solvent storage tanks initiated by an electrostatic discharge.
(b) *vapour/dust explosion during addition of reactants to a reactor* initiated by static electricity.
(c) vapour explosion in batch reactor due to presence of pyrophoric catalyst.
(d) vapour explosion in isolation centrifuge initiated by mechanical friction.
(e) decomposition and fire in a fluid bed dryer due to abnormally high air temperature.
(f) dust explosion in a dust filter collector due to the entry of smouldering material ignited in an upstream mill.
(g) fire in powder storage silo due to exothermic decomposition.

To eliminate such hazards each stage of manufacture must be considered in terms of:

(1) Identification and charactersation of flammable materials.

(2) Identification of potential ignition sources.

(3) Selection, design and installation of the most appropriate safety measures.

### 4.1 Identification and Characterisation of Flammable Materials

Flammability characteristics of liquids, vapours and gases are well known. The majority of organic powders are also combustible. They form flammable dust clouds when admixed with air in certain proportions. Ignition of such clouds can result in a flash fire or dust explosion.

Each material must be examined to establish whether or not it is combustible/flammable in bulk or when dispersed in air, to determine its sensitivity to ignition, and to indicate the consequences of ignition, e.g. fire, explosion, rapid decomposition.

Tests for characterising materials with respect to the above are well established (3). The interpretation of the date and its application to chemical plants will be discussed in the contributions by Lloyd, Beever, Lunn and Moore.

## 4.2 Identification of Ignition Sources

In chemical plants handling flammable materials, ignition sources such as flames, burning material, cigarettes, matches, lighters etc., are controlled by general fire regulations. In addition to this procedures/regulations should exist to avoid ignition of hazards associated with welding/cutting operations, electrical equipment, exposed heated surfaces and lightning.

The operational hazard evaluation of a specific process/plant is concerned with auto-ignition, mechanical friction, thermite reaction, static electricity, spontaneous combustion, thermal decomposition, pyrophoric catalysts and any other ignition sources intrinsic to the process and plant operation. A detailed discussion of ignition sources

is to be presented by Lloyd, it is only necessary to indicate here that an essential part of the hazard evaluation procedure is a formal analytical system (e.g. HAZOP) to identify all sources of ignition.

## 4.3 Selection of Safety Measures

Safety can be achieved by one or more of the following:

(1) Avoidance of flammable atmosphere. Use of inert gas or operating outside the flammability limits.
(2) Avoidance of all ignition sources.
(3) Containment of fire and explosion.
(4) Explosion venting.
(5) Explosion suppression.

Critical technical considerations for each are:

### Avoidance of Flammable Atmospheres

- Can fuel concentrations be maintained outside flammability limits at all times including start up and shut down.
- Is the material dependent on atmospheric oxygen for combustion and/or decomposition.
- Can system be sealed to prevent ingress of air.
- Can ingress of air be avoided when reactants are added, e.g. air entrained in powders.

### Avoidance of All Ignition Sources

- Can all ignition sources be identified.
- Is the sensitivity to ignition by these sources known for all the materials in the process.
- Can all ignition sources be eliminated under normal and abnormal conditions.

Containment of Explosion/Decomposition

- Can maximum pressure developed in explosion/decomposition be predicted
- Can all interconnected components withstand the maximum pressure.
- Can system be mechanically separated into discrete volumes to prevent pressure piling.
- Can system be sealed at high pressures.
- Can process operations (e.g. addition of powder) be carried out with a pressure sealed system.

Explosion Venting

- Can maximum rates of pressure rise under process conditione be established.
- Can adequate relief areas be provided relevant to process conditions.
- Can a safe discharge area be provided for flammable/toxic products.

Explosion Suppression

- Is pressure arising from combustion the sole source of pressure. Supressant systems cannot control pressure resulting from gas evolution.
- Are the combustion characteristics of the process materials such that the suppressant can effectively stop flame propagation.
- Are the suppressant chemicals compatible with the process chemicals.

In addition to the above technical considerations, the selection of the most appropriate safety measures must take account of constraints imposed by process/plant details, operability, maintenance, cost and product output and quality.

## 5. PROCEDURES TO IMPLEMENT THE STRATEGY

Implementation of the strategy requires procedures that can be applied to the establishment of a process and routine manufacture, and that can take account of process/plant modifications.

### 5.1 Procedure for Establishment of Manufacturing/Routine Manufacture

The key stages in the procedure are shown in Figure 1 - initiation, evaluation, implementation and monitoring. Each of these must take place as the process proceeds from early development to full scale manufacture. Typically a hazard assessment will be carried out to assess the initial chemistry and then at the pilot plant and full scale production stages. The contents of the review at each stage is shown in Figure 2.

The individual and functional responsibilities incorporated in the procedure will depend on the size and infrastructure of the company. Whatever the detailed organisation there must be allocation of responsibility for each stage of the procedure.

Use of this procedure in chemical manufacturing (dyestuffs, pigments, speciality chemicals, pharmaceutical and plant protection products) has produced a manufacturing situation in which uncontrolled incidents have been virtually eliminated. With minimal effort, it has produced a clearly defined and acceptable set of safety measures for each process that can be readily implemented and controlled by the manufacturing personnel.

## 5.2 Procedure for Control of Process/Plant Modifications

Uncontrolled modifications to process or plant can lead to incidents. Examples are:

(a) an increase in hold time at elevated temperature leading to an uncontrolled exothermic reaction.
(b) a change from a stainless steel to a mild steel still producing a high rate decomposition because mild steel was a catalyst for the reaction.
(c) a change from a stainless steel to a plastic lined reactor leading to an electrostatically initiated vapour explosion.

It is not possible to produce a generally applicable check list of "significant" modifications. Serious incidents have been caused by relatively small changes in process conditions and/or plant construction.

Each modification must be recognised as having possible consequences with respect to manufacturing safety and evaluated in this light. Process specifications and the hazard assessments based on them have boundaries. If the modification moves operating conditions outside the limits considered in the hazard assessment then a hazardous situation may develop that has not been identified in the initial assessment.

A procedure that requires the process/plant to be re-evaluated fully after each modification is impracticable. In many cases the time scale of manufacturing will not permit this. A procedure is required whereby the effect of change can be evaluated rigorously and quickly by people close to the point of production. The following procedure has been used effectively:-

(1) Production personnel identify modifications to process/plant.
(2) Production personnel assess the effect of the modification on the safety of the process by consideration of the hazard assessment for the original process/plant.
(3) If the modification does not invalidate the basis for safe operation then manufacturing is continued,
(4) If there is any uncertainty with regard to (3) and the modification may lead to conditions not considered in the original hazard assessment then production personnel initiate a new hazard evaluation.

## 6. CONCLUSIONS

The evaluation of process hazards and the specification of realistic and practical measures that ensure manufacturing safety can be achieved by use of the strategy and outline procedures described in this paper. Procedural details will depend on the infrastructure of the company but the essential stages of initiation, evaluation, implementation and monitoring are applicable to both large and small companies.

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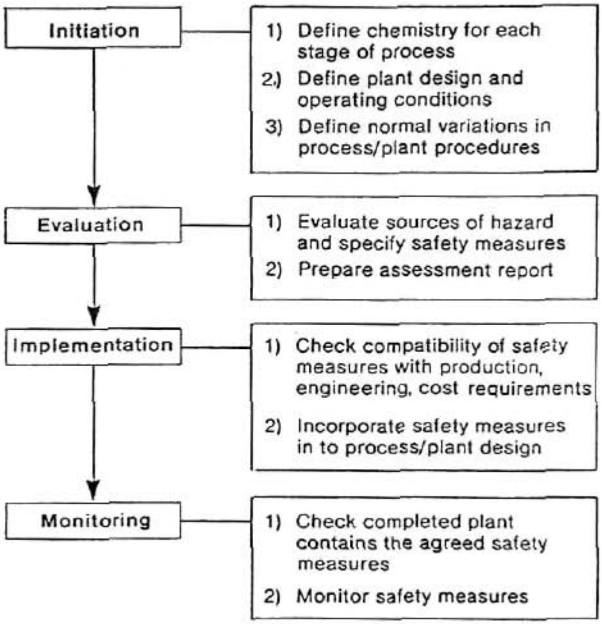


Fig 1. ASSESSMENT PROCEDURE

| | |
|---|---|
| **1. Initial Chemistry** | (a) Characterisation of materials/process<br>(b) Suitability of production |
| **2. Pilot Plant :** | a) Chemical reaction hazards<br>b) Influence of plant on hazard<br>c) Definition of safe procedures |
| **3 Full Scale Production :** | a) Re-evaluation of chemical reaction hazards<br>b) Effect of expected variations in process conditions<br>c) Hazards from plant operations<br>d) Definition of safe procedures<br>e) Interaction of technical safety with engineering, production, economic and commercial aspects of process. |

Fig 2 **STAGES IN ASSESSMENT PROCEDURE**