MANAGING HAZARDS AND RISKS IN FINE CHEMICAL AND PEROXYGEN OPERATIONS

P.G. Lambert, J. Phillips and R.J. Ward,
Fine Organics, Laporte Organics, Seal Sands, Middlesbrough, TS2 1UB, U.K.

The Organic Specialities Division of Laporte operates in two distinct areas: the Peroxygen Group manufactures organic peroxides, special catalysts and uses active oxygen for chemical synthesis. The Fine Chemicals Group manufactures intermediates and finished products for the pharmaceutical, agrochemical, food products, and associated speciality industries. There are considerable variations in the chemistry employed by both groups and the range of chemicals, reactions, hazards and their potential consequences also vary. This paper describes one part of the divisional management strategy relating to loss control. It uses, by way of illustration, three internal guidance procedures covering the risks and consequences of identified hazards in the manufacture of fine chemicals, organic peroxides and vapour phase explosion hazards.

Keywords: Loss Control, Chemical Reaction Hazards, Vapour Phase Explosions.

STRUCTURE

Laporte's five business divisions currently operate about 90 sites worldwide. The Corporate & Group Safety, Health and Environment (SHE) departments devise overall strategy, monitor company performance as well as providing training. They also create the tools for line managers to direct the safety, health, hazards & environment programmes in the areas under their control. A strong commitment therefore exists to line responsibility and authority in safety, health, hazards, and environment issues. A co-ordinator in each division supports line management, - collating and disseminating information for the Group or for the individual businesses.

The Organics Division manufactures at ten sites world-wide, with the Peroxygen Group having manufacturing operations in Germany (Peroxid Chemie), the USA (Aztec Peroxides), Australia and Brazil. The Group also has joint venture companies in Spain and South Africa, as well as storage facilities in Thailand, The Netherlands and France. The speciality Fine Chemicals Group has operations in the U.K. (Fine Organics), Canada (Raylo) and Italy (Laporte Organics Francis) and a new joint venture in India.

These businesses operate with different cultures and regulatory bodies, and face differing hazards, levels of operational complexity as well as rapid change. This has resulted in a strong divisional approach to the management of hazards and risks founded on the strategy of the company's Group SHE Department.

DIVISIONAL SAFETY, HEALTH, HAZARDS AND ENVIRONMENT PROGRAMME

The divisional Safety, Health, Hazards and Environment Programme was based on the model originally outlined by the International Loss Control Institute (I.L.C.I., now owned by D.N.V.) and the well established approach of POLICY, STANDARDS, PROCEDURES, AUDIT.

The Chief Executive has endorsed the Laporte Group's safety and environment policies. In addition, individual sites or businesses have their own policy, reflecting the needs of the business. It is therefore not necessary, or appropriate, for the division to have its own policy. However, it was appropriate to build on and interpret the company policy (or statements of intent) as a basis for the overall Programme.

To execute these *statements of intent* effectively, a number of agreed *objectives* were required based on sound *strategy*. To support the strategy, *standards* were also needed which would sustain our collective corporate memory and provide the tools to manage the risks and hazards in our businesses. The final two elements of the Programme are an *audit and monitoring plan* and the *identification of responsibilities* of site and divisional management.

The disciplines of loss control and high standards were given senior management support through a "profit through safety" initiative, introduced by the divisional Chairman.

The eleven statements of intent include several "givens" - such as compliance with local and national regulations, line management responsibility and the provision of training, procedures and overall suitability of manufacturing plant. In addition, we confirmed our stance on risk management and our commitment to operating an integrated S.H.H.E. programme at each site that could include other regulated activities, such as cGMP and quality.

Hazard, Consequence, and Risk Management.

Many of the key definitions adopted by our Programme will be familiar. *Hazards* are physical situations with the potential for harm. *Consequences* are the outcomes or potential outcomes from events. *Risk* is the likelihood of a specific undesired event occurring in a specified period and is reported as a *frequency* of an event occurring in a unit of time or as the *probability* of an event occurring during a specific operation. *Risk management* is the term applied to the whole process of risk identification, estimation, reduction and control.

Risk Management has at least five phases and, dependent on the particular process or project, work may be necessary in each phase. Normally, these stages are *Hazard Identification, Risk Estimation, Risk Evaluation, Implementation and Monitoring* and *Auditing*.

Many sources of hazards are associated with chemical processing. In simple terms, they can be defined as:

- general safety considerations ....working at heights, with machinery etc.,
- specialist operations......electricity, welding, radiation sources, etc.
- health hazards,
- environmental concerns.....emissions to air, waste, land, etc.,
- reactivity of chemicals,
- interaction of chemicals and the plant.....flammability, dusts etc.

To establish control and minimise loss, all of these issues need to be addressed. The large potential overlap between these general categories makes it critical to define the responsibilities and authority for the management of hazards.

By their nature, projects vary in complexity and in the degree of hazard involved. Potential environmental hazards and risks, for example, will dominate some projects; others may be primarily concerned with health risks associated with certain chemicals or with the risk of fire and explosion. A generic hazard management strategy has to accommodate these variations and provide the tools that line managers need, whatever circumstances apply. In Laporte's Organics Division, our approach is to consider the management of the risk as an integral part of the whole process or project, particularly since a number of activities may occur in parallel.

Our integrated hazards management strategy is known as the *Umbrella* approach. It provides protection to the company, its people and assets, and covers the range of hazards that we need to manage. To provide a comprehensive, fast and cost effective approach, we needed to develop guidelines and tools for the rapid assessment of hazards. Some of these tools are in the early stages of development, whilst others have been used effectively for many years.

The Umbrella Structure

The Umbrella structure is outlined below in figure 1. All its sections and subsections can be seen as ribs or supports to the shield provided by the umbrella. Failure in any one area lowers our overall protection.

A large number of Standards, Codes of Practice and Guidelines have been developed or adopted in Laporte. The terms of reference for these Guides, Codes and Standards are available to each site, and management is expected to apply them when required.

Figure 1 The Hazards Management Strategy

- A STANDARD is a technical specification for defining a system (plant, store, container, operating facility etc.) which is fit for its intended process.
- A GUIDELINE explains what, from the point of view of Laporte, is current good or best practice
- A CODE OF PRACTICE explains what, from the point of view of Laporte, is reasonably practicable.

A critical element is that each *process* or *project* should have a *basis of safety*. This is defined as the principle and methodology used to protect the business, people and assets from a known hazard. Examples are:

- Prevention (by avoiding the use),
- Minimise (by limiting the inventory),
- Render harmless (by treatment),
- Intrinsically safe (as a specific hazard does not exist),
- Emergency venting (to a safe location),
- Process control (via hardware, software, or human intervention),
- Elimination of ignition sources (by procedure, and equipment),
- Containment (by design).

Risk Criteria

The absolutely safe condition involves the lowest amount of energy and is therefore impossible to achieve in technological businesses. Processing chemicals necessarily increases the energy in a system and we therefore needed a definition of safety that recognises that it is not an absolute state. In this context, safety has been defined as a situation where the risk is no higher than the risk limit. At first sight, this definition seems to be of only partial use as it also raises other questions. However, this is the crux of the issue. It is difficult to obtain agreement on the risk limit, which is dependent on a large number of factors (such as perception, voluntary or involuntary, individual or societal). The risk limit, or tolerable risk, varies with the potential consequences. There are numerous examples of this principle in our everyday lives, for example whether we smoke, drive, climb mountains or simply eat certain types of food.

The Organics division uses consequence criteria to classify processes according to a basic scheme. This classification includes three classes which have been defined as having tolerable risk criteria, based on international guidance and best practice such as the Health and Safety Executive A.L.A.R.P. (as low as reasonably practical) methodology as shown in figure 2 below. The frequency of an event is defined as the demand rate of the system multiplied by the fractional dead time and is set at once in **X** years.

Class A includes processes where the simultaneous failure of the control and preventative system as well as the protective system would result in a major incident with a high probability of fatality, major environmental harm or considerable loss in terms of production, assets or business loss. Reliability is an essential characteristic of systems that may have these severe consequences.

Class B includes processes with a more limited potential for harm to the plant, environment or the business and where the probability of fatality is low - even if there was a simultaneous failure of the control/preventative system and the processes protective system.

Class C includes processes where simultaneous failure would mainly represent an inconvenience, such as a contained spillage, loss of minor equipment, or the momentary loss of production. This Class of process also includes systems that are adequately backed up by separate safety controls.

Reliability requirements for class A are ten times greater than for class B which in turn have a one hundred times greater requirement than class C.

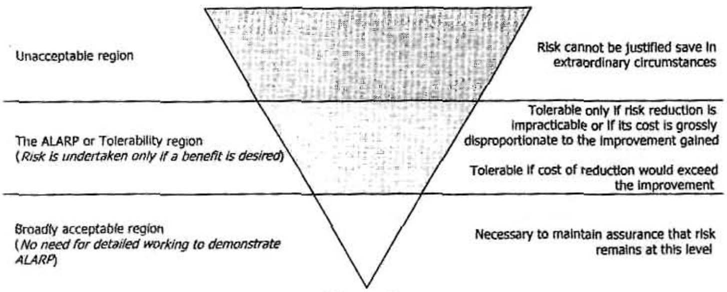

Figure 2

This basic system is currently under review. The aim is to have four classes, in line with the IEC 1508 (1) and DIN V 19 250 standards as in figure 3 below. The top tier reliability figures are likely to remain unaltered, and the fourth class is likely to fit between the current B and C classes.

The Risk Parameters are defined below:

Damage

D1	slight injury
D2	serious, irreversible injury of one or several persons Death of one person
D3	**death of several persons**
D4	catastrophe, very many casualties

Duration of Stay in the Hazard Area

S1	rare to more frequent stay
S2	**frequent to permanent stay**

Hazard Prevention

H1	possible under certain circumstances
H2	not possible

Probability of the Undesired Event

P1	Extremely Low Probability
P2	**Low Probability**
P3	Relatively High Probability

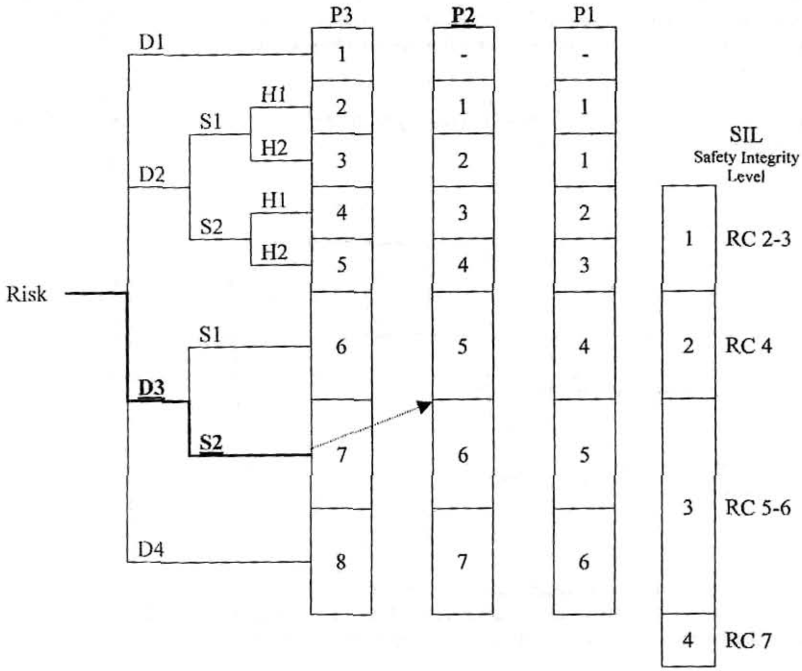

Figure 3 Risk Diagram and Requirement Classes

The purpose of the Standards, Codes and Guidance Notes is, at least in part, to help management to design, operate and maintain their processes with the *safety reliability* as defined above, whilst maintaining the *availability* of the plant to perform to the businesses' requirements.

SPECIFIC GUIDANCE NOTES

The remainder of this paper concentrates on three specific standards for the safe design of processes.

All three are important elements in the Umbrella system. They are (like all of the standards), based on the IDENTIFY, ASSESS, CONTROL, MONITOR principle. All the Standards or Guides are performance-based unless a prescriptive method is better suited, perhaps because there are only a limited number of ways to control a hazard.

We will examine the:

- handling and use of flammable gases and liquids.
- design of processes for organic peroxide manufacture.
- determination of chemical reaction hazards.

It is important to remember that these can rarely be taken as stand alone problems.

The Handling and Use of Flammable Gases and Liquids

Perhaps the most common hazard on the manufacturing plant for both fine chemicals and organic peroxide manufacture is the risk of fire and explosion associated with flammable gases and vapours.

The risk depends upon two factors:

- *the physical properties of the material*
- *the nature of the process*

To maintain a high standard at all our sites, a method of analysing and rating the explosive risk from a wide range of materials and processing operations has been developed by three Laporte personnel. The method was published in 1995.

Briefly, all of the common flammable solvents and gases have been categorised according to three physical properties, namely,

- *flammability rating* (the ratio of the flammable range divided by the lower explosive limit), *given as 0, 1, or 2*
- *minimum ignition energy rating* *given as 0, 1, or 2*
- *conductivity rating* *given as 0, 1, or 2*

Each material therefore has a rating that comprises three numbers. For example, Cyclohexane is coded 1,1,2 and hydrogen sulphide is coded 2,2,1.

This system provides five categories for assessing the explosive risks associated with materials using the coding outlined above:

- Very low risk materials coded 0,0,0
- Low risk materials coded 0,0,1 / 0,1,0 / 0,1,1
- Standard risk materials coded 1,0,0 / 1,1,0
- High risk materials coded 1,1,1 / 1,1,2 / 2,0,0
- Very high risk materials coded 2,1,* / 2,2,* where * is 0, 1 or 2

The range of operations occurring on the plant were also assessed and categorised as:

- Very low risk,
- Low risk,
- Medium risk,
- High risk,
- Very high risk

Each operation has its own risk rating. For example, centrifuge filtration is very high, and off gas scrubbing with hydrogen peroxide is medium. Examples are shown in figure 4 below.

	Operation	Rating
EXTRUSION	Open	**High**
	Closed	**Medium**
BULK STORAGE And TRANSFER	Storage tank	**Very Low**
	Tanker transfer to Storage	**Very Low**
	Transfer to closed operations	**Very Low**
	Transfer to open operations (see also Level 2)	**Low**
	Tank transfer to tanker	**Very Low**
VACUUM SYSTEMS, RELIEF SYSTEMS & DUCTS (downstream)	Centrifugal	**High**
	Ejectors	**Medium**
	Open	**Medium**
	Closed	**Low**
DUST COLLECTION	Open	**High**
	Closed	**Medium**

Figure 4 Unit Operation Risk Rating

Knowing both the material and the operation involved enables the site management to use a matrix, rating the material risk *vs.* the operational risk to establish the level of control required to maintain safe operation.

There are four operational levels of control and the option of a fifth requiring input from a specialist as shown in figure 5 below.

The four operational levels of control become more sophisticated as the overall risk increases. For example, Level 1 requires attention to a number of issues including earthing, anti-static protection and flow rates. Level 4 includes the use of continuous on-line oxygen monitors.

The transfer of hexane by pump to a closed vessel provides an example of the rating system. Hexane has a material rating of *1.1.2 (High Risk)* and the process has a *very low risk* process rating. This implies an Operational Standard of Level 1.

This system has been used throughout the division (and other parts of the company) for about three years and, whilst some sites have fine-tuned the system to their own needs, the overall guidance has operated well.

	PROCESS RATING				
MATERIAL RATING	Very Low Risk (level)	Low Risk (level)	Medium Risk (level)	High Risk (level)	Very High Risk (level)
Very Low Risk	1	1	1	1	1
Low Risk	1	1	1	2	2
Standard Risk	1	1	2	3	4
High Risk	1	2(*)	2	3	4
Very High Risk	2	3	3	4	5(')
Flammable Gases	2	3	4	5(')	5(')

(*) In general, Level 5 represents an unacceptable level of risk and expert advice should be sought.

(') Recommending inerting, for example, when crystallising from low conductivity liquids appears harsh, but localised areas with high charge densities can develop which can discharge to the vessel walls.

Figure 5 The matrix of material risk *vs.* operational risk

The Manufacture of Organic Peroxides

In very simple terms, organic peroxides are manufactured because they are unstable! There are seven basic types of organic peroxide (O.P.). The particular O.P. used as a catalyst or promoter depends on the physical characteristics and properties involved.

If the O.P. is stable under particular conditions then it will be unable to perform its function which, in turn, presents problems for the manufacture of such materials. Not only are the products unstable, but the manufacturing processes are often highly exothermic and use energetic, corrosive and toxic raw materials. The sequence of additions, reaction temperatures, quantities, agitation and processing methodologies are also often critical.

With seven sites manufacturing O.P.'s world-wide, it was important everyone understood the hazards and risks associated with these materials and that a common standard was in place for implementation by line management.

A Laporte standard was devised based on the knowledge and experience of the operations, safety, hazards and engineering staff. Internally, the standard is known as *OPTIMIST* (Organic Peroxide Testing Information Minimum Acceptable Safety Techniques).

The early versions of OPTIMIST were based on an *open* flowchart and checklist system that was found to be inappropriate, as the number of new products, was limited when compared with fine chemicals. A new *closed* system is based on the same principles, but results in a more focused approach.

Processes are categorised according to the energy in the system and the ease with which materials or mixtures that present a major hazard can be made. Each category has certain reliability and control requirements according to it risk and consequence. Once categorisation has been completed, process changes, engineering improvements or procedural changes can be initiated to change the category to a safer one, if that is possible or is required.

Category 1 processes are those that would result in a detonable reaction mixture if the quantities or sequence of addition were incorrect.

Category 2 processes are those with a product or intermediate with detonable properties.

Category 3 processes are those where a rapid thermal runaway could not be vented.

Category 4 processes are those where a rapid thermal runaway is possible but could be vented.

Category 5 processes are those where no rapid thermal runaway possibility exists.

An additional category exists where the reaction mixture or a product has detonable properties and the initiating stimuli are small. These sensitive systems cannot be operated safely and are not allowed; thus, the category is an "X".

A chart lists recommendations for each process category and has sections on:

- Detonable properties,
- Runaway reactions and kinetics,
- Fire and vapour phase explosions,
- Decomposition,
- Toxicology,
- Environment, and
- Pressure burst

A review of the available information about the process, the operating plant, the preventative and protective systems and a comparison with the required standard will show any areas for priority improvement.

Category 2 processes are the highest category processes that are allowed to be operated in our production plants. They correspond to the class A processes described earlier and are required to be operated with a very high levels of safety reliability and availability.

An example of the first part of a study is outlined in figure 6 below.

1 Condensed phase explosion

1.1 Formation of a detonable mixture if Hydrogen peroxide is present
Data: Triangular diagram

#	Identification	Assessment	HR	Control Measure	Remark
1	Wrong sequence of addition	If H_2O_2 is added before tert.-Butanol: detonable mixture possible.			
2	If order of addition is correct, the H_2O_2 excess has to be 4 times the required quantity to reach the detonable area				

1.2 Formation of an autodetonable mixture (e.g.: undiluted ketoperoxide)

#	Identification	Assessment	HR	Control Measure	Remark
3	Omission of diluent	N/A No diluent used			
4	Wrong raw material	Use of MIBK instead of TBA causes serious detonation hazard			
5	Wrong order	N/A			
6	Wrong quantities	N/A			

Figure 6 Example of an OPTIMIST study.

To check the OPTIMIST requirements against the reliability criteria, three Laporte sites performed independent quantitative risk assessments (QRA) on the safety shutdown system (SSS) in place for their Category 2 processes. The three sites were chosen because they had attempted to reach the reliability goal by slightly different means, mainly for geographical and historical reasons.

One SSS was based on a double PLC system, another on a single PLC with a hard-wired backup and the third system used a double PLC system with a hard-wired backup. The results varied by a factor of about 3 between the systems, but all three sites were within the criteria for Class A processes. This was a very acceptable result given the nature of QRA studies and proved that the standards were compatible.

The Manufacture of Fine Chemicals

The range of chemistry and products in the Fine Chemicals business means that a different approach is required for the identification and control of hazards. A closed classification system cannot be operated.

For the last eight years, an internal standard has operated which has met most of the company's requirements and which categorised processes primarily on the energy content of reactive mixtures and products. At a higher level, the rate of gas generation and pressurisation in an enclosed system was also taken into account.

With an increased knowledge base and with the availability of new techniques, the old method is being replaced with a standard called *COMPASS* (COMputerised Process Assessment Safety System). The aim is to easily categorise processes so that the appropriate safety techniques can be incorporated into operational design in a safe, but efficient manner.

COMPASS will be used to assess the hazards involved in a chemical process and is based upon the physical and chemical properties of the process components, along with historical data on similar processes.

COMPASS is essentially broken down into six sections

1. Basic Data
2. Desk Screening
3. Reaction Data
4. Thermal Screening
5. Undesired Reactions
6. Consequences

In the prototype version of the system, the first two sections listed above have been completed with test data being entered for around 50 chemicals. The remaining sections will be coded and tested over the course of the next two months. The system is being written in Microsoft Visual Basic 5.0 with the underlying data being stored in Microsoft Access tables. All database activity is controlled using SQL constructs.

A key feature of the system is that it should be flexible enough to allow use in several countries, using different languages. With this in mind, all on-screen text labels are stored in a system database and loaded when the system is run (they are not 'hard-coded'). This allows efficient translation to be carried out.

The programme can be accessed at four levels. For everyday use, the data input screens are supported by a complete help system, giving basic information and guidance. A computer-based tutorial system is included to allow the user to gain additional knowledge and experts can access a high-level knowledge system to carry out specialised assessments.

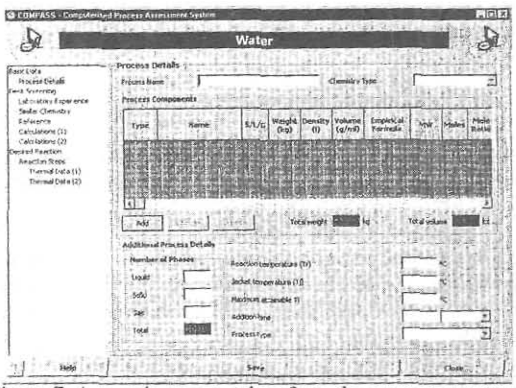

Figure 7. A sample screen, taken from the current prototype.

The database allows rapid access to the properties of a wide range of solvents and reagents. A variety of calculators has been built into the system that operate automatically (such as a molecular weight calculator, and an automatic oxygen balance calculation when the empirical formula is entered).

For desk screening, hyperlinks to standard texts such as Bretherick, the I. Chem. E. Accident Database and CHETAH® can be set up. Interrogation of the Corporate Memory is also required.

The system requests data on a wide range of variables and processes this information. Constant checks ensure that the data are self-consistent. From the entered data, the thermal properties of the chemical reaction are studied in order to generate the following key data:

- Heat of reaction,
- Rate of heat generation,
- Accumulation, which is a function of the reaction rate,
- The minimum temperature that a decomposition could be initiated,
- The maximum achievable temperature, and,
- The maximum temperature achievable for technical reasons.

The characterisation is based on the concepts of the desired reaction, undesired reaction, thermal runaway and the time to maximum rate established by the team at Ciba Geigy as well as other experts in the field.

The levels and reliability of the preventative and protective equipment for each process are set by internal standards. The preventative and protective systems increase on a scale from Class 1 to Class 5. No specific protection is necessary for class 1 but primary, secondary, tertiary and special measures are needed as the categories increase. These measures include duplication of temperature probes, automatic quench, secondary cooling, dual alarms and active or passive protection.

Reactions are classified according to the relative values of the reaction boiling point, the maximum temperature achievable in the runaway reaction and the temperature at which the time to maximum rate of reaction (and therefore heat evolution) under adiabatic conditions (TMR_{ad}) is 24 hours.

Class 1 reactions are those where the boiling point of the reaction mass is below the temperature where the TMR_{ad} = 24 hrs (hereafter called T_t) and the maximum theoretical heat release cannot raise the temperature of the reaction mass to its boiling point.

Class 2 reactions are those where the boiling point lies above T_t, but the maximum theoretical heat release cannot raise the temperature of the reaction mass to T_t.

Class 3 reactions are those where the maximum theoretical heat release can raise the temperature of the reaction mass to above its boiling point, but not to T_t.

Class 4 reactions are those where the maximum theoretical heat release can raise the temperature of the reaction mass to above its boiling point and also above T_t.

Class 5 reactions are those where the maximum theoretical heat release can raise the temperature of the reaction mass to above T_t, but not to its boiling point.

Neither Class 1 nor Class 2 reactions are safety critical. Simple control of temperature is all that is needed.

Class 3 reactions have a higher level of criticality in that the boiling point can be reached, with obvious consequences for the condenser capacity and release of V.O.C.'s.

Additional safeguards are required for Class 4 reactions where the loss of solvent may result in a temperature rise that could trigger the decomposition reaction. Here dual independent temperature probes may be required as well as indication of the performance of the condensers. Interruption of flow rates on loss of cooling will also be indicated.

Class 5 reactions need to be subject to the most rigorous analysis. Class 4 requirements will be needed together with automatic interruption of reagent addition on loss of cooling or loss of agitation. Quenching the reaction mass may also be required.

The original assessment system has been validated against the risk criteria using a QRA study. To date, only one process has been evaluated but the results were within the consequence criteria.

CONCLUSION

Risk management covers the whole business process and has been the subject of numerous books. In this paper, our aim has been to cover only one critical part of the risk management process, and to show the approach of Laporte and more specifically, its Organics division.

The integration of hazard management and the careful generic treatment of key problems have resulted in common high Standards, Guides and Codes of Practice at all manufacturing sites. A high level of awareness of the hazards and the tolerable residual risk results in cost effective controls or *PROFIT THROUGH SAFETY.*

ACKNOWLEDGEMENTS

The authors wish to acknowledge the contribution of colleagues within Laporte including, Dr F. Diem, Dr R. Band, Dr P. Bekk, Dr R. Owen and the late Dr N. F. Scilly all of whom wrote or contributed to specific standards.

REFERENCES

1. The International Electrochemical Commission IEC 1508
2. German national DIN standards.
3. H. L. Walmsley, 1992 Journal of Electrostatics, 27(1/2)
4. Scilly N. F., Owen R., Wilberforce J. K., 1995, A.C.S. forum, New Orleans.
5. Stöessel F.et al, 1997 Organic Process Research and Development, 1(6): 428, and references therein.
6. Lambert, P.G., 1993, Chemical reaction hazards. IBC symposium, London