HarsNet: A EUROPEAN "THEMATIC NETWORK" ON HAZARD ASSESSMENT OF HIGHLY REACTIVE SYSTEMS

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HarsNet is a "Thematic **Net**work" on **Ha**zard Assessment of Highly **R**eactive **S**ystems. It is a four-year European Community programme involving 31 partners. Its purpose is to make available to Small and Medium Sized Enterprises (SMEs) the best available advice for assessing and controlling the hazards of exothermic reactions.

Keywords: reactions, hazards, batch, semi-batch, exothermic, self-heating, runaway, thermal stability, assessment.

INTRODUCTION

Your reaction to the title of this paper may be *HarsWhat?* And anyway what on earth is a "Thematic Network?" The latter question is relatively easy to answer. It is a phrase dreamt up by the European Commission to describe a grouping of organisations with a shared common interest that they foster and develop for the benefit of the whole European Community. Many "Thematic Networks" have already been set up within the Member States. *HarsNet* (project BET2-0572) is the "Thematic Network" that is concerned with the hazards of exothermic reactions in batch and semi-batch processes. Funding for *HarsNet* comes in part from the "Industrial and Materials Technologies Programme" of the European Commission via contract number BRRT-CT98-5066. Partners also provide a defined fraction of the project costs themselves. *HarsNet* started on 1st October 1998 and will continue for a period of four years. It is a co-operative rather than regulatory project.

The *HarsNet* coordinator is Professor Rosa Nomen of the Institut Quimic de Sarri× at the Universitat de Ramon Llull in Barcelona, Spain. She has the responsibility of controlling the network, co-ordinating the activities of all the partners, and reporting to the European Commission in Brussels. The *HarsNet* partners are listed in Appendix 1. There is a broad cross section of chemical producers, research groups and consultancies nearly all of whom have extensive experience in assessing the hazards of exothermic chemical reactions. Those without such experience have other qualities they bring to the network such as control system specification and design: this will be needed, for instance, for the early on-line detection of runaway reactions. This is the type of topic that might develop into a research project loosely associated with *HarsNet.*

HSE PUBLICATIONS

Think about some of the most serious chemical incidents in recent years. Recollection of the details of them will probably reveal that exothermic reaction hazards at some point played a significant role in many of them, see for example 1 - 4. Statistics produced by the HSE reveal that a reported exothermic runaway incident in a batch or semi-batch reactor occurs in the UK

approximately every two weeks, 5. A similar situation may well exist in other European partner countries though detailed statistics are not so readily available as for the UK. The subject of exothermic reaction hazards is therefore seen to be a real problem which needs to be addressed. HSE concerns in this area and the activities of *HarsNet* are, to a large extent, complimentary. HSE have already produced a number of publications and a guidance booklet is in preparation. These include:

1. A training video, entitled "Control of Exothermic Chemical Reactions", 6. This has been included in the IChemE training package "Control of Exothermic Chemical Reactions", 7, which also includes reference 8 and details of some case histories. The HSE were also involved in the production of these latter items.

2. A free (12 page) leaflet entitled "Chemical Reaction Hazards and the Risk of Thermal runaway", 9.

3. A "Workbook for Chemical Reactor Relief System Sizing", 10. This gives information on methods available for sizing emergency pressure relief systems for liquid phase chemical reactors.

In the UK employers are required to make a suitable and sufficient assessment of the risks to the health and safety of employees and others affected by their activities. Employers with 5 or more employees should also record the significant findings of the risk assessment. The free leaflet gives general guidance on the steps necessary in order to carry out such assessments for chemical reaction processes, the types of questions that should be addressed, and where further information can be obtained, e.g. in reference 8.

Any chemical process goes through various lifecycle stages, from the initial concept to the final decommissioning. An idealised life cycle, specific to chemical reaction hazards, is given in figure 1: more generalised guidance is given in IEC 61508, 11. It is important that, as the process develops, safety is considered continuously throughout the process lifecycle. This enables an appropriate basis of safety to be developed, updated and maintained. Where possible the hazards should be avoided, or at least minimised by inherently safer design and this can be done most effectively at the early stages of process development. The forthcoming guidance booklet emphasises this approach and gives information on how the hazards may be assessed, avoided if reasonably practical, and controlled. Where appropriate , further sources of information are given. For information on relief system sizing, the reader is referred to the workbook, although a brief overview of this complex technical area is given.

The information in the leaflet and draft guidance booklet have been made available to *HarsNet* by the HSE as part of the initial data gathering exercise that the network is carrying out.

THE OBJECTIVES OF *HarsNet*

Many large companies in the chemical and pharmaceutical industries have, over a long period of time, developed significant in-house expertise for assessing exothermic reaction hazards. Equipment has been purchased, experts recruited, training given and a methodology developed and defined. Similar teams and equipment have also been gathered in some

research institutes, university departments and consultancies. However, in many small and medium sized enterprises (SMEs) there is no analogous equipment or service. *HarsNet* activities are aimed at companies who find themselves in this situation. Our goal is to collect the accumulated "wisdom" of the *HarsNet* partners and to distil this into a single concise summary of recommendations for the approaches that should be used for the reaction hazard assessment procedure that we recommend. In due course this document will be written for non-experts in user friendly language. A wide variety of other sources of free information will be made readily available through the *HarsNet* website. The main topics with which *HarsNet* will be concerned are:

- Evaluation of methods used for the prediction of thermochemical properties and thermal stability of chemical compounds.
- Calorimetry, thermal analysis and other experimental techniques that can be used to assess the stability, or thermal hazard potential of reaction mixtures, isolated intermediates, reaction products and by-products.
- Methods for the thermokinetic analysis of calorimetry and thermal analysis data which have applications within the scope of the network.
- Criteria for developing intinsically safer chemical reaction processes.
- Specifying "worst credible maloperations" and the experiments which can be used to simulate these in the laboratory.
- Developing criteria for the thermal stability, sensitivity and safe design of batch and semi-batch chemical reaction processes. This will include some aspects of numerical simulation of the dynamic behaviour of reactors.

HarsNet activities can conveniently be grouped into a number of headings.

The *HarsNet* forum

This an internal activity that takes place continually between the partners via either e-mail or the secure partners area of the website, ***HarsWeb.*** Every six months the partners also gather for a two-day meeting. The partners share freely their experience and knowledge

HarsGuide

The *HarsNet* partners have all completed a detailed questionnaire about the way in which they assess reaction hazards. The questionnaire split the life of a chemical process into the 6 process life cycle stages illustrated in Figure 1:

- The earliest conceptual stages of process development prior to laboratory work starting.
- Discovery chemistry on the very small scale.
- Laboratory scale process development, optimisation and production.
- Pilot scale production.
- Industrial scale production.
- Process or hardware changes to an existing mature plant.

Partners answered detailed questions about the process development stages at which they first started to consider/use the following:

- The concept of inherent safety.
- Material Safety Data Sheets (MSDSs).
- Control of Substances Hazardous to Health (COSHH).

- Reference textbooks.
- Various databases and software packages (e.g. for physical property data, thermodynamic properties, ignition properties, accident data, enthalpy release estimation, etc.).
- Types of testing equipment (e.g. thermogravimetric analysis (TGA), differential thermal analysis (DTA), differential scanning calorimetry (DSC), other thermal screening methods, automated laboratory reactors, isothermal calorimeters, isoperibolic calorimeters, high phi factor adiabatic calorimeters, low phi factor calorimeters, powder flammability tests, gas/vapour flammability tests, etc.).
- The choice of what samples to test (e.g. reagent grade materials, plant grade samples, raw materials, isolated intermediates, products, by-products, waste products, intended recipes at intended conditions, wrong recipes at intended conditions, wrong recipes at unintended conditions, etc.)
- Who defines the worst credible maloperations? Is Quantitative Risk Assessment (QRA) used to decide what is credible? Or professional judgement?
- Who defines the basis of safety and is it written down clearly?
- There were further questions about the concepts of time to maximum rate (TMR), temperature of no return (TNR), self accelerating decomposition temperature (SADT) and maximum temperature of the synthesis reaction (MTSR).
- Methods used to ensure that the basis of safe operation is maintained, (e.g. the use of high integrity trips or interlocks, emergency cooling, in situ or external emergency quenching, total containment, pressure relief (possibly in combination with a dump tank, quench tank, gas scrubbing system, flare, incineration, etc.) inhibition, etc.)

From the detailed answers we have been able to build up a picture of the overall reaction hazard assessment process used by approximately 25 highly experienced organisations. We also have indications of the features and tactics of process design commonly used to control exothermic reaction hazards within a selected group of chemical producers throughout Europe. On the basis of this, and additional discussion, we are currently in the process of preparing *HarsGuide*, our own internal working document, that summarises the consensus amongst the partners about the most appropriate protocol for reaction hazard assessment and control.

HarsMeth will be one of the main documents with which we will communicate with SMEs. In due course it should be available via our website. This will be written for graduate level scientists and engineers, particularly in SMEs, who have little or no experience in assessing reaction hazards. It will define the structured methodology they can use to assess their exothermic reaction hazards, the types of equipment available, their main uses, the information they can be used to generate and the interpretation of this data. It will also explain how relatively cheap, simple and commonly available equipment can be used in the preliminary stages of reaction hazard assessment.

HarsBase is a collection of information resources which are useful in the context of exothermic reaction hazard assessment. This compilation is already extensive and includes books, papers, conference proceedings, journals, equipment manufacturers, consultancy companies, and perhaps most important of all a large set of internet addresses. Some of *HarsBase* is already available via links on the *HarsNet* website, *HarsWeb* .

HarsWeb is that part of the *HarsNet* activities that is to do with our website. The website is one of the main vehicles through which the partners are communicating with the process industries and letting them know what we are doing. The website address is **http://www.harsnet.de**. The Webmaster (Dr Klaus Peter Zeyer of the Max Planck Institute in Magdeburg) can be contacted via e-mail from the website. A mirror website is currently maintained by the Institut Quimic de Sarri×, Barcelona at **http://harsnet.iqs.url.es**: the two sites provide a continuous backup to each other in the event of problems with the local server. For instance during the summer of 1999 the Spanish site went off line for a period of ~ two weeks when computer cabling was damaged during building works! At that time it was the only website we had. The home page of the website is illustrated in figure 2.

HarsEdu will address the question of the provision of appropriate education relating to exothermic reactions and the hazards associated with them. This will include the *HarsNet* partners views about what should be taught at undergraduate level in chemical engineering and applied chemistry degree courses. It will also consider Continuing Professional Development (CPD) for all grades of staff, something in which the Institution of Chemical Engineers has played a leading role over many years, 12. The possibility of new multimedia presentations as part of such training will be considered.

HarsRes will be concerned with the definition of the new research projects that are required to support the activities and aims of *HarsNet* and to improve the knowledge base concerning exothermic reaction hazards.

PLENARY MEETINGS

Plenary meetings, at which all partners are expected to be represented, are held every six months. The purpose of these is critically to review the work that the partners have done in the previous six months, to measure progress against specified deliverables (targets, duties and dates by which they should be completed) and to plan work assignments for the coming six months. Regular progress reports are submitted by the *HarsNet* co-ordinator to the scientific case officer within the European Commission.

EXCHANGES OF PERSONNEL

Within the framework of *HarsNet* short secondments of individuals will take place between the partners. These will be at engineer/scientist level and will probably primarily involve younger staff. The exchanges are intended to expose staff to new and different working environments and to different ranges of testing equipment and methodologies.

NATIONAL MEETINGS

HarsNet will not achieve its objectives unless it is able to communicate effectively with the process industries in general, and SMEs in particular. As we have discussed earlier, a primary means of communication is via the website. In addition a National forum will be held in many of the member states during each of the four years of the *HarsNet* project. The first UK national forum was held on 10th June 1999 and was attended by 47 industrial representatives. Five formal presentations were made and there was a feedback session to allow the participants to say whether the proposed *HarsNet* activities were likely to be useful to them. In addition there was the opportunity to say what new but related activities the participants would like to see *HarsNet* adopting. Our plans are to hold the second UK forum in the Manchester area sometime near the middle of 2000.

The views expressed in this paper are those of the authors and are not necessarily those of the Health and Safety Executive.

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APPENDIX 1: *HarsNet* partners are:

Institut Quimic de Sarria, Spain (Co-ordinator)
Institut fur Makromolekulare Chemie, Germany
Stazione sperimentale per I Combustibili, Italy
Irradiare, Portugal
Universite de Haute-Alsace, France
National Technical University of Athens, Greece
Health and Safety Executive/Health and Safety Laboratory, UK
Universita di Messina, Italy
Technische Universitat Berlin, Germany
Institut fur Systemdynamik und Regelungstechnik, Germany
EC Joint research centre, ISPRA, Italy
Erkimia S. A., Spain
BASF Aktiengesellschaft, Germany
Solvay Quimica S. L., Spain
Solvay, Belgium
DSM, Holland
Sanofi Chemie, France
Hazard Evaluation Laboratory, UK
H. Lundbeck A/S, Denmark
Swiss Institute for the Promotion of Safety and Security, Switzerland
Esteve Quimica S. A., Spain

CHEMI SpA, Italy
Dow Benelux, Holland
Dow Chemical, USA
Dow Deutschland, Germany
Ciba Specialty Chemicals (UK) Ltd., UK
Inburex GmbH, Germany
Segibo Srl., Italy

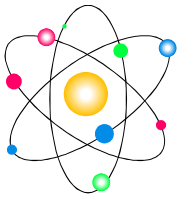
Guest partners are: TNO Institute of Environmental Sciences, Holland
Direccio General de Consum i Seguretat Industrial, Spain
European Process Safety Centre, UK
Instituto Superiore per la prevenzione e la sicurezza del Lavoro

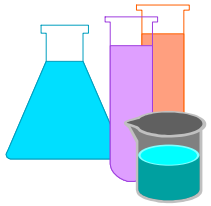
FIGURE CAPTIONS:

Figure 1: the idealised life cycle of chemical process development.

Figure 2: the home page of the *HarsNet* website

FIGURE 1: SAFE PROCESS DEVELOPMENT



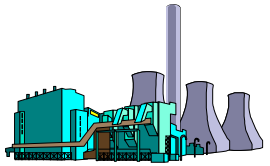


Small scale chemistry in the laboratory

Larger scale chemistry

Pilot plant

Design office



Synthetic organic chemistry ideas

Desktop screening, databases, calculations

Discovery research and multiple experiments

Automated laboratory reactors. Process optimisation

Pilot plant studies

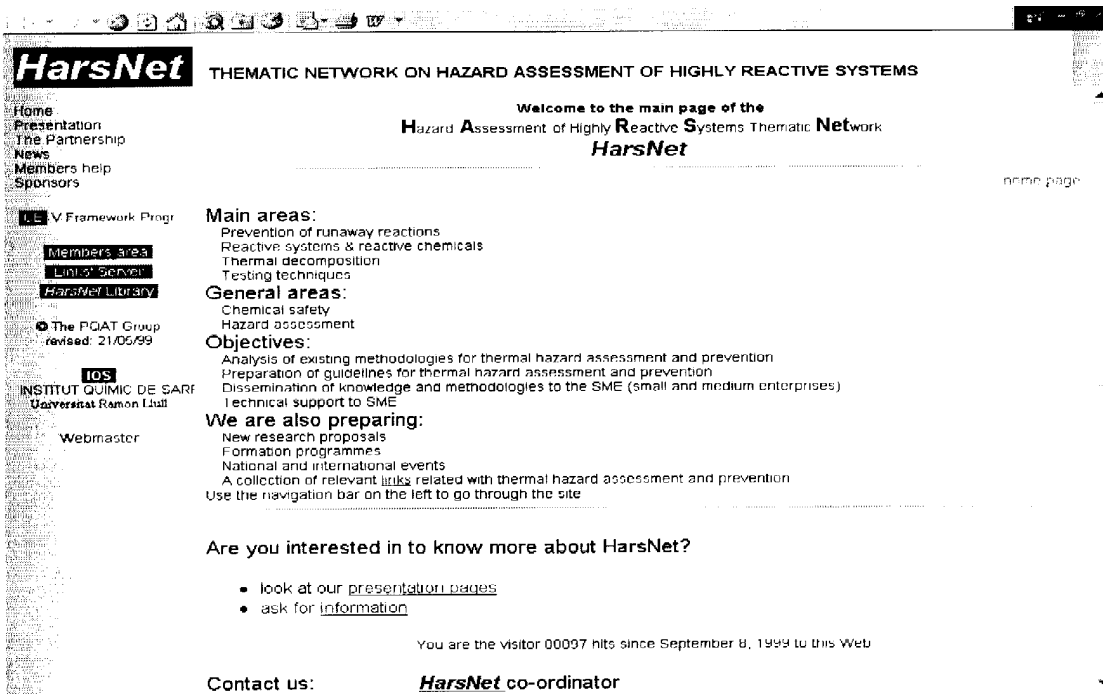
Scale up and design

Industrial production. Debottlenecking. Optimisation of mature processes. Retrofits.

CHEMICAL PROCESS LIFE CYCLE

	1	2	3	4	5	6
Desktop studies	Micro and mini scale reactors	Automated calorimeters and reactors	Kinetics, modelling, simulation	Adiabatic calorimeters	HAZOP, HAZAN, HAZID	Design reappraisal, relief systems, dump or quench tanks.etc

Move from the earliest phases of research and development through to full scale production in a confident, safe and cost effective manner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Universitat Ramon Llull
Webmaster
Welcome to the main page of the
Hazard Assessment of Highly Reactive Systems Thematic Network
HarsNet
Main areas:
Prevention of runaway reactions
Reactive systems & reactive chemicals
Thermal decomposition
Testing techniques
General areas:
Chemical safety
Hazard assessment
Objectives:
Analysis of existing methodologies for thermal hazard assessment and prevention
Preparation of guidelines for thermal hazard assessment and prevention
Dissemination of knowledge and methodologies to the SME (small and medium enterprises)
Technical support to SME
We are also preparing:
New research proposals
Formation programmes
National and international events
A collection of relevant links related with thermal hazard assessment and prevention
Use the navigation bar on the left to go through the site
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ask for information
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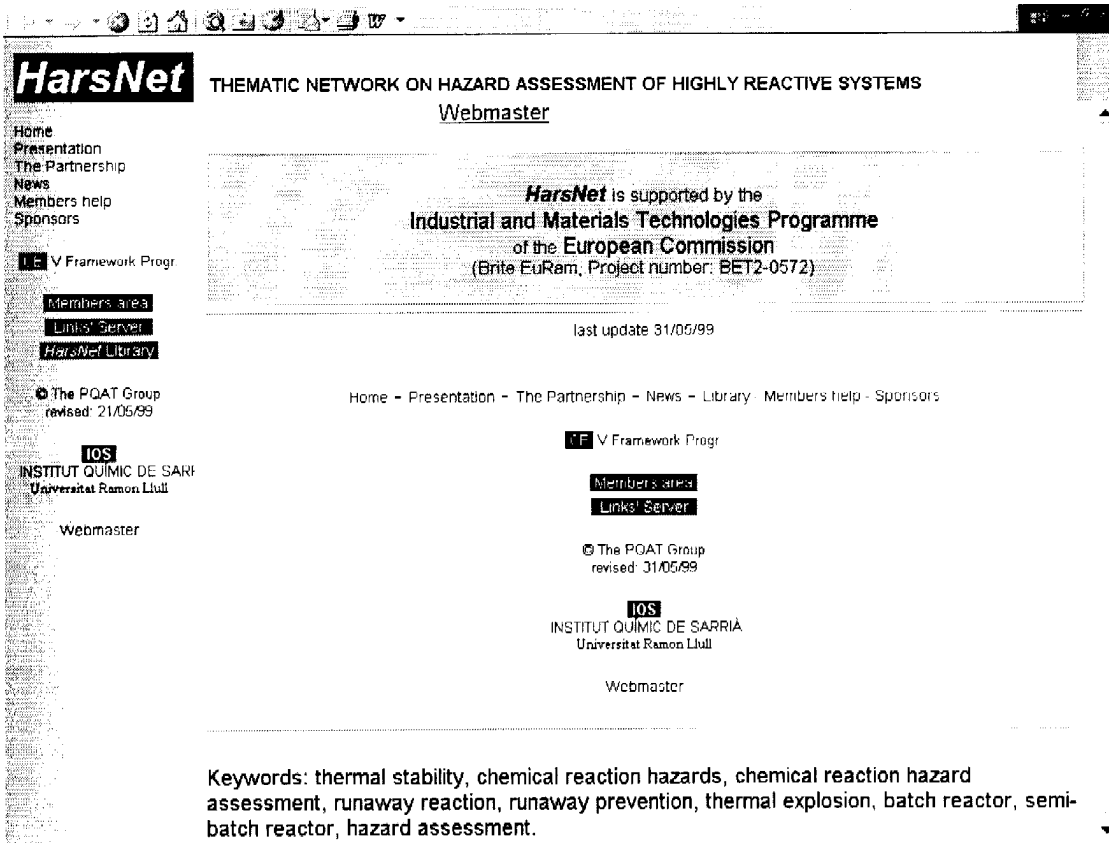
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of the European Commission
(Brite EuRam, Project number: BET2-0572)
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Keywords: thermal stability, chemical reaction hazards, chemical reaction hazard assessment, runaway reaction, runaway prevention, thermal explosion, batch reactor, semi-batch reactor, hazard assessment.