Safety & Health News

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SAFETY AND HEALTH DIVISION
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John F. Murphy and Dennis C. Hendershot, Editors

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Improving Reactive Hazard Management

John F. Murphy, PE

It has been nearly eight years since the U. S. Chemical Safety and Hazard Investigation Board (CSB) issued the results of its hazard investigation into reactive chemical incidents with the report entitled *Improving Reactive Hazard Management*. The investigation reported that over a twenty year period there were 167 serious incidents that involved chemical reactivity in the United States resulting in 108 fatalities. These numbers do not include the many incidents that are not reported. Some things have been done to decrease the occurrence of reactive chemical incidents, but reactive chemical incidents continue to occur with regularity. I count 12 serious reactive chemical incident investigations completed by the CSB since the completion of the hazard investigation. This is just the tip of the iceberg. Many reactive chemical incidents are not reported and the CSB can only investigate a small fraction of the process safety incidents that are reported. According to the CSB web site only 60% of the recommendations from the CSB report have been closed. The most important closed recommendations are the inclusion of the definition of reactive chemical incidents in the EPA Risk Management Plan (RMP) regulation and the completion of the Essential Practices for Managing Chemical Reactivity Hazards concept book by The Center for Chemical Process Safety (CCPS). This book is publically available on the OSHA web site. Recommendations to improve the OSHA PSM standard regarding reactive hazards are still open, although industry should improve reactive hazard management because it is good business and the right thing to do, not just because the regulations require compliance.

The CSB found that over 90% of the reactive chemical incidents that occur are the result of known chemical hazards documented in publically available literature. We know that even eight years later, people who need to know about reactive hazards are not getting the information they need. One recent incident investigation has resulted in another significant recommendation by the CSB regarding the management of reactive chemicals.

> "On December 19, 2007, four people were killed and 13 others were transported to the hospital when an explosion occurred at T2 Laboratories Inc. during the production of a gasoline additive called methylcyclopentadienyl manganese tricarbonyl"

The following recommendations were offered by the CSB.

American Institute of Chemical Engineers

- Work with the Accreditation Board for Engineering and Technology, Inc. to add reactive hazard awareness to baccalaureate chemical engineering curricula requirements.
- Inform all student members about the Process Safety Certificate Program and encourage program participation.

Accreditation Board for Engineering and Technology, Inc.

- Work with the American Institute of Chemical Engineers to add reactive hazard awareness to baccalaureate chemical engineering curricula requirements.

AIChE is actively working with ABET to adopt these recommendations. By including reactive hazard awareness in the undergraduate chemical engineering curriculum, there is a better chance that future chemical engineers will identify reactive hazards before they become incidents.

The CCPS Reactivity Management Round Table (RMR), which began with a meeting organized by CSB to address the management of reactive hazards, was initiated by CCPS in 2003. The RMR had 100 members with about 40 active members when it was initially organized. Over the years active participation in the RMR has decreased. I was at the last meeting in San Antonio where there were only about ten members of the RMR present. I interpret this lack of support a sign of complacency by the industry on the reactivity management issue. The RMR continues to work on the reactive chemical issue. With support from the RMR, the National Oceanic and Atmospheric Administration (NOAA) has done an excellent job keeping its Chemical Reactivity Worksheet on its web site current. The Chemical Reactivity Worksheet is a free program that can be used to find out the about the reactivity of substances or mixtures of substances. The data base contains reactivity information for more than 5,000 common hazardous materials.

The most exciting project supported by the RMR is the Reactivity Evaluation Software Tool (REST) which is presently under development. The primary objective of REST is to assist all users, especially small to medium size companies, to identify chemical reactivity hazards associated with their chemical processing and support operations. Once the tool is available, the challenge is to get people who need it to use it. REST should be available to users by the end of 2010. CCPS is also offering to the industry basic training on process safety including managing reactive hazards in its new training course entitled Process Safety Boot Camp.

There are tools to manage reactive hazards; we just need to use them!

To all Safety and Health Division Members and Supporters

Peter Lodal, AIChE Safety and Health Division Chair

I hope this issue of the newsletter finds all of you well. As I write this, I have just returned from the 6th Global Congress on Process Safety in San Antonio, and several things stick in my mind; the wide variety of interests and expertise on display at the four parallel sessions, the quality of the information being presented from across the globe, and most vividly (and somewhat depressingly), the amount of work still in front of us as a profession. As I am fond of telling my employees, “there are things that ought to keep you up at night, but running out of work is not one of them.” From dust, to reactive hazards, fires and explosions, safety instrumented systems, and current and future regulatory issues (including the interplay between process safety and chemical plant security), there is still much to be done.

As the chemical and process industries face ever increasing public and regulatory scrutiny, we as professional process safety practitioners must remain engaged, producing technically accurate information that is as easy to understand and use as possible. The Global Congress is an excellent forum for showcasing such contributions. I encourage each of you to look for opportunities to share

your insights and expertise with the broader community, either by submitting a proposal for the 7th Global Congress in Chicago next March, or one of the many other excellent information sharing venues. In doing so, you will help to ensure the long-term health of the chemical and process industries worldwide.

Some Highlights from the Chairman's Report Presented at the DCHAS March 2010 Executive Committee Meeting

Stefan Wawzyniecki, CIH, CHM, University of Connecticut
2010 Chair, ACS Division of Chemical Health & Safety

2010 is well under way, and, as Chair, I am seeing first what my predecessors experienced before me - that DHAS is a respected Division both within ACS and outside the Society. In these first few weeks, the contacts I've made, and the people who have contacted me, indicate that we as a Division have that priceless attribute known as Integrity. I take no credit for what we all know is a group effort. Here are some recent highlights of DCHAS accomplishments:

The DCHAS Booth at the March 2010 ACS Meeting in San Francisco. From left to right: Ralph Stuart, Al Hazari, Patricia Schumann and Soo-Ying Lee. Photo courtesy of Larry Doemeny.

- The DCHAS Web Site (http://www.dchas.org/) has been much improved for our membership; and fulfills that part of our Strategic Planning workshop goal for providing members with access to information related to our expertise. The goal for the year is to continue this improvement.
- We are continuing to work to increase participation at ACS regional meetings and investigating other means to make participation in program activities easier. Since 2002 we have provided over a dozen workshops and half a dozen technical sessions at ACS Regional Meetings.
- Another goal is to apply the over-used "sustainability" to our Programming efforts.

You can download the complete minutes from the March Executive Committee meeting from the DCHAS web site:

http://www.dchas.org/index.php?option=com_rokdownloads&view=folder&Itemid=30&id=172

Bill Doyle Award for the Best Paper at the 2009 Loss Prevention Symposium

The Bill Doyle Award was presented to Scott Davis for his paper "Lessons Learned from the 2006 Facility Explosion in Danvers, MA" (co-authored with Olav Roald Hansen). A webcast of the paper is available at:

http://aiche.confex.com/aiche/s09/webprogram/Session8711.html

Here is the paper abstract:

Scott Davis receives the Bill Doyle Award for the best paper at the 2009 Loss Prevention Symposium from 2010 Loss Prevention Symposium Chair Ron Wiley.

On November 22, 2006 the largest explosion in the history of Massachusetts occurred in Danvers, MA at approximately 2:46 am. The explosion and resulting fire occurred at an ink and paint manufacturing facility. The facility was unoccupied when the explosion occurred. The blast destroyed the facility and caused significant damage to the surrounding property and structures. It was reported that approximately 17 to 19 structures were damaged beyond repair as a result of the blast wave and that community damage was the worst witnessed in the 10-year history of the CSB. Approximately a dozen individuals sustained minor injuries and no fatalities were reported as a result of the incident. The paper presents a detailed analysis into the potential causes and lessons learned from the Danvers explosion. This paper will present analyses that contradict proposed scenarios into the cause and origin of the explosion and discuss other potential causes not considered by other investigative groups. These analyses include results from ground-penetrating radar and soil gas sampling in the area surrounding the facility. In addition, the CFD tool FLACS was utilized in the present investigation to simulate the chain of events leading to the explosion and included: (1) evaluating various leak scenarios by modeling the dispersion and mixing of gases and vapors within the facility, (2) evaluating potential ignition sources of the combustible fuel-air mixtures within the facility and (3) evaluating the explosion itself by comparing the resulting over-pressures of the combusting fuel-air cloud with the structural response of the facility and the observed far field blast damage. Based on the results of our detailed analysis, various methods for mitigating this and future explosions are discussed.

2009 Process Plant Safety Symposium Best Paper Award

The award for the best paper at the 2009 Process Plant Safety Symposium was presented to Tim Overton for the paper "Lessons Learned from Corrosion Under Insulation". A webcast of the paper is available at:

http://aiche.confex.com/aiche/s09/webprogram/Paper145311.html

Here is the paper abstract:

Mechanical Integrity programs have been an essential element of process safety programs in the chemical and petroleum industries for decades. This is an area where considerable materials have been published regarding industry best practices for inspection and maintenance – including excellent advice on inspection for "corrosion under insulation". However, The Dow Chemical Company experienced a significant near miss event at one facility recently caused by lapses in understanding by local personnel of corrosion under insulation causes or inadequate leveraging of learnings from plants of similar design. This paper seeks to explain the circumstances behind this event and the key lessons learned such that other companies can avoid similar occurrences.

2009 Process Plant Safety Symposium Chair John Champion presents the award for the best paper at the symposium to Tim Overton

7th Global Congress on Process Safety - Call For Papers Now Open

The 7th Global Congress on Process Safety (GCPS) will be held on March 13-16, 2011, in Chicago. The Call For Papers is now open at:

http://www.aiche.org/Conferences/Specialty/GCPS.aspx

The deadline for submitting abstracts is September 15, 2010.

The GCPS is the largest gathering of process safety professionals in the world, and is organized by the Center for Chemical Process Safety (CCPS) and the AIChE Safety & Health Division. This annual event — the primary forum for practitioners to share practical and technological advances in all aspects of process safety — is comprised of the coordinated sessions of the 26th CCPS International Conference, the 45th Loss Prevention Symposium (LPS), and the 13th Process Plant Safety Symposium (PPSS). In 2011, the 7th Global Congress on Process Safety focuses on Inherently Safer Design (ISD) — an approach to process safety that focuses on eliminating or reducing hazards. As a concept and philosophy, Inherently Safer Design serves as part of an

iterative decision-making process aimed at risk reduction. ISD is ongoing and continuous throughout the lifecycle of a material or process and across the entire footprint of the process — from supply, to processing, through final material disposition.

The abstract deadline is September 15, 2010. The currently proposed sessions for the 2011 GCPS include:

Loss Prevention Symposium:

- Combustible Dust Hazards, chaired by Walter L. Frank and John E. Going
- Fires, Explosions and Reactive Chemicals, chaired by Erdem A. Ural and John Murphy
- Impact of Sustainability Efforts On Loss Prevention, chaired by Frank H. (Hank) Gurry and Henry L. Febo
- Risk Assessment – Consequence Modeling and QRA, chaired by Kathleen A. Kas and Cheryl Grounds

Process Plant Safety Symposium:

- Facility Siting – for Existing Operations and Their Permanent, Temporary and Tent Structures
- Inherent Process Safety – Experience Applying the Discipline in Operating Facilities
- Layer of Protection Analysis (LOPA) – Case Studies and Application Experience
- Management of Change – the Most Difficult PSM Challenge
- Management of Combustible Dust Hazards
- Mechanical Integrity – Critical Line of Defense
- OSHA's National Emphasis Programs for Refineries and Chemical Plants – Experiences and Challenges
- Process Safety Culture – Impact of the Baker Panel Report to BP
- Risk Assessment – Assessing Risk and Retiring Recommendations in On-Going Operations
- Things Every Plant Engineer Should Know about Process Safety

Center for Chemical Process Safety International Conference:

- Advancements in Application of Risk Assessment Techniques, chaired by John Wincek and Robert F. Wasileski III
- Application of Process Safety Principles, chaired by Revonda Tew and Don Connolley
- Emerging Issues in Global Process Safety – Impact On Industry From Recent Accidents, chaired by
- Shakeel Kadri and Steve Arendt
- Integrating Reliability with Mechanical Integrity Programs, chaired by Randal L. Montgomery and Brook Vickery
- Lessons Learned From Facility Siting Studies, chaired by Don Connolley and Robert Fischer
- Lifecycle Management of Independent Protection Layers, chaired by Robert F. Wasileski III and Jeff Fox
- New Relief System Solutions, chaired by Sara Saxena and Steve Meszaros
- Process Safety Knowledge, Competence, and Human Performance, chaired by Jeff Fox and Steve Meszaros
- Reinvigorating and Evolving Process Safety Implementation, chaired by Steve Arendt and Shakeel Kadri

Pictures from the March 2010 Global Congress on Process Safety

The 11a (Loss Prevention) Programming Committee met before the Loss Prevention Symposium

Attendance was great at the opening session of the Global Congress on Process Safety

Roxy Schneider of CCPS welcomes attendees to the Global Congress

Global Congress Chair and 2009 Safety and Health Division Chair Kathy Pearson at the opening session

Past Safety and Health Division Chair Bob Benedetti and long time active member Tom Pratt

Jack McCavit was the speaker at the Safety And Health Division Dinner

Pictures from the March 2010 Global Congress on Process Safety

Division Chair Pete Lodal was master of ceremonies at the Division dinner

The Division dinner at a great Mexican restaurant in San Antonio was sold out

2010 First Vice Chair Cheryl Grounds at the Division dinner

Pete Lodal presents a plaque recognizing Kathy Pearson's service as 2009 Division Chair

Roxy Schneider of CCPS and *Process Safety Progress* co-editor Joe Louvar

Phil Myers and Jack Chosnak at the Safety and Health Division dinner

PAPERS OF INTEREST

Thanks to Stan Grossel for providing the following list of recent papers which might be of interest to Division members.

1. "Thermal Stability at Elevated Pressure - An Investigation Using Differential Scanning Calorimetry" by Priestley, I. J. G. et al, *IChemE Symp. Ser*. No. 154, Paper 59 (2008).

During laboratory scale development of a new chemical process which is to be operated at elevated pressure a material was found to undergo an unexpected thermal decomposition. Initial DSC testing had indicated that melting appeared to be a prerequisite for decomposition and based upon this and the fact that melting points are elevated at increased pressures the material had been expected to be thermally stable under the proposed operating conditions. The unexpected thermal decomposition resulted in a more extensive investigation into the thermal stability of the material being performed. Work was carried out primarily at adiabatic pressure in order to obtain an understanding of the mode of the decomposition. The work was then extended to pressures of up to 30 bar and although this gave us a further insight into the decomposition it failed to simulate the process conditions which could reach 600 bar. A collaboration with the University of Aberdeen has enabled DSC measurements to be carried out at 500 bar confirming predictions about the melting point behavior, but also giving an unexpected view of the thermal decomposition. A second collaboration with the University of Huddersfield provided a further insight into the thermal decomposition of the material.

2. "Dewar Scale-up for Reactive Chemical Waste Handling" by Vechot, L. and Hare, J., *IChemE Symp. Ser. No.154*, Paper 57 (2008).

The use of non-pressurised Dewar flasks had been proposed by some parts of the chemical waste treatment industry to determine the exothermic reaction incompatibility of mixtures. Temperature rises of between 6-10°C in the Dewar vessel over a period of 10 minutes has been suggested by industry as criteria to indicate an exothermic reaction of concern. A literature review of the specific heat losses from Dewar flasks and large-scale vessels is compared to specific heat losses of Dewar flasks measured experimentally. Typical values of thermal characteristics of large-scale vessels used in the waste industries have also been assessed. The specific heat loss in the Dewar flask and large-scale vessels are very different. Scale-up limits of four types of Dewar have been calculated for different values of overall heat transfer coefficients for large-scale vessels. Thermal behavior of exothermic reactions in a Dewar flask has been compared to that predicted in large vessels using reaction kinetics and heat transfer models. For fast and highly energetic reactions the reaction energy release rate can be significant compared to the heat losses and the Dewar flask can detect runaway reactions. However, for low energy reactions or reactions with long induction time, the heat losses can be significant compared to the heat release rate and the Dewar test can then miss exotherms or give non-conservative results. It appears that the 6-10°C criterion proposed by the waste treatment industry might be observed when the heat losses do not have a significant importance compared to the reaction heat release rate. However, the reaction completion time at large scale would be shorter than at the Dewar scale. In some cases, 10 minutes might be sufficient to detect the exotherm but not the runaway reaction. The test should therefore be run to reaction completion in order to fully detect exotherms. Reliable conclusions about the scale-up of Dewar data can be obtained when the chemical reaction kinetics are well known. Unfortunately, this is not generally the case in the waste treatment industry. So, unless the specific heat loss of the Dewar has been shown to be less than large-scale vessels, this method in isolation is likely to be unreliable for scale-up to large vessels.

3. "Sizing of Safety Valves Using ANYSIS CFX-Flo" by Moncalvo, D. et al, *Chem. Eng. Technol*., Vol. 32, No. 2, pp.247-251 (2009).

This work discusses the effect of the degree of fineness of the flow volume discretization and that of the turbulence model on the accuracy of reproduction of air mass flow rates in two safety valves using the CFD software ANYSIS Flo®. Calculations show that the degree of fineness of discretization is the decisive factor affecting the exactness of the calculations and that the best reproduction is achieved with grids where at least two cells are built on the smallest edge. The selection of the turbulence model has by far in comparison a lower impact; however, the best accuracy is obtained using the standard model and the SST modification of Menter.

4. "Influence of the Liquid Phase Physical Properties on the Void Fraction at the Inlet of a Full-Lift Safety Valve" by Moncalvo, D. and Friedel, L., *Chem. Eng. Technol*., Vol. 32, pp.273-282 (2009).

This work studies the influence of the physical properties of a liquid on the void fraction at the inlet of a corner valve resembling a full-lift safety valve. The test media are mixtures of air and aqueous solutions of glycerin. Our own measurements evince a reduction in the void fraction when the relative weight of glycerin in the solution is increased. If the effects of density, viscosity, and surface tension on the void fraction are accounted for by increasing the relative weight of glycerin in the solution, it results that the observed reduction of the void fraction is primarily a consequence of the enhancement of viscosity. On the other hand, the increment of the liquid density is responsible for a modest increase in the void fraction and the effect of the reduction in the surface tension is almost negligible. The enhancement of either the density or the viscosity of the liquid phase increases the relative velocity of the gas in the two-phase mixture, and, therefore, the slip. The impact of the liquid properties on the void fraction in co-current vertical pipe flows is similar to that at the inlet of the corner valve. Among the most common correlations for pipe flows, the formulation of Rouhani and the homogeneous void fraction accurately reproduce the void fraction at the inlet of the valve only for two-phase flows with liquids of low viscosity. A new void fraction correlation is proposed here, which reproduces all measurements very well and correctly predicts the impact of the liquid phase properties. Despite numerical coefficients, which can be fitted to additional sets of measurements, the structure of the new correlation is also applicable outside the range of two-phase flows for which it has been explicitly validated.

5. "Advanced Kinetics-Based Simulation of Time to Maximum Rate Under Adiabatic Conditions" by Roduit, B. et al, *J. Thermal Analysis and Calorimetry*, Vol. 93, pp. 163-173 (2008).

An adiabatic calorimeter is very often used for the investigation of runaway of exothermic reactions. However, the ideal adiabatic environment is a theoretical state which during laboratory scale testing cannot be obtained, but may only be approached. Deviation from the fully adiabatic state comes from (i) the thermal inertia of the test system or heat lost into the sample container, and (ii) the loss of heat from the container itself to the environment that reflects the 'operational adiabaticity' of the instrument. In addition to adiabatic testing, advanced kinetic approach based on the kinetic parameters determined from DSC data performed under different heating rates can be applied. It enables to simulate what may happen on a large scale by testing and up-scaling results obtained with a small amount of the sample. The present study describes the method of the evaluation of kinetic parameters of the coupling reaction of aniline with cyanamide in water/HCl from the DSC signals measured in non-isothermal experiments carried out with the rates of 0.5-8°K per minute. The reaction rate and reaction progress in adiabatic conditions were predicted after introducing the kinetic description of the reaction into the heat balance equations.

It enabled to calculate the thermal safety diagram depicting the runaway time as a function of the process temperature. The influence of thermal inertia of the system, expressed as the factor, on the reaction course in concentrated and diluted reactant solutions was determined and discussed.

6. "Evaluation of Runaway Reaction for Dicumyl Peroxide in a Batch Reactor by DSC and VSP2" by Wu, S-H et al, *J. Loss Prev. Process Ind*., Vol. 22, pp. 721-727 (2009).

Benzoyl peroxide (DCPO) is usually employed as an initiator for polymerization, a source of free radicals, a hardener, and a linking agent. In Asia, due to is unstably reactive nature, DCPO has caused many thermal explosions and runaway reaction incidents in the manufacturing process. This study was conducted to elucidate its essentially hazardous characteristics. To analyze the runaway behavior of DCPO in a batch reactor, thermokinetic parameters, such as heat of decomposition (?Hd), exothermic onset temperature (To), maximum temperature rise (dT/dt)max, maximum pressure rise (dP/dt)max, and self-heating rate, were measured via DSC and the VSP2. Meanwhile, adiabatic thermal runaway phenomena were then thoroughly investigated by VSP2. The thermokinetics of DCPO mixed with acids or bases were determined by DSC/VSP2, and the experimental data were compared with kinetics based curve fitting of thermal safety software (TSS). Results from curve fitting indicated that all of the above mentioned acids and bases could induce exothermic reactions at even an earlier stage of the experiments. To diminish the degree of hazard, hazard information must be provided to the manufacturing process.

7. "2-Methylpyridine-N-Oxidation Runaway Studies" by Saenz, L. et al, J. Loss Prev, Process Ind., Vol. 22, pp. 839-843 (2009).

Calorimetry has been used in order to identify the runaway behavior of 2-methypyridene-N-oxidation (2-picoline-N-oxidation). Experiments were performed in an Automatic Pressure Tracking Adiabatic Calorimeter (APTAC), employing 2-methylpyridine-N-oxide (2-picoline-N-oxide) with or without catalyst, 2-methylpyridine-N-oxide, hydrogen peroxide, 2-methylpyridine (2-picoline) and catalyst, and 2-methylpyrididine, hydrogen peroxide, and catalyst. Approximately 16.5 g of aqueous solutions were used in 100 ml closed glass cells, in all but one measurement. Measurements were performed isothermally or employing the Heat-Wait-Search (HWS) technique. During reaction runaway, any excess of hydrogen peroxide and the produced 2-methyl-pyridine-N-oxide decompose releasing non-condensable gases and raising the pressure. It was found that the reaction runaway is condition sensitive. Catalyst, the presence of 2 icoline and/or its N-oxide, affect hydrogen peroxide and/or 2-picoline-N-oxide decomposition rates. Further research accompanied by analytical measurements of the gas and liquid phase would provide indications in regard to the decomposition mechanisms followed in those cases.

8. "A Simple, Explicit Formula for the Critical Pressure of Homogeneous Two-Phase Nozzle Flows" by Moncalvo, D. and Friedel, L., J. Loss Prev. Process Ind., Vol. 23, pp. 178-182 (2010).

The critical pressure ratio of the homogeneous two-phase nozzle flow model known as the Omega method is expressed as a function of the Omega Parameter as the exact numerical solution of a transcendental equation. A well fitting, easy to use, explicit approximation for flashing and non-flashing flows is presented here. The validation against the exact numerical solution proves that this new formula is better fitting than the other ones in the technical literature for both single and two-component flows.

9. "Reactive Chemicals Emergency Response and Post-event Calorimetric Testing" by Frurip, D. et al, *Process Safety Progress*, Vol. 29, No, 1, pp. 2-10 (March 2010).

A serious upset in process conditions may result in a reactive chemicals incident. In such an emergency, procedures must be implemented to prevent injuries, mitigate the event and minimize proper6ty loss and/or environmental release as dictated by the required Emergency Plan. This article describes the process the Dow Chemical Company uses for engaging reactive chemicals experts in an emergency situation. In order to be effective, the reactive chemicals expert must have or be provided with in-depth knowledge of the process streams and raw materials involved. The information is crucial for understanding what is happening, what might happen in the immediate future, and what can be done to successfully mitigate the reactive chemicals incident. Following the incident, calorimetric experiments are typically performed to confirm or refute the hypotheses of what caused the event; additionally, the experiments provide information as to reactive chemicals hazards that may potentially still exist in the process streams. The aforementioned process will be illustrated by describing an actual event. Useful methods are described and recommended for (a) characterizing and storing reactive chemicals, and (b) responding and mitigating safety incidents with reactive chemicals. The role of a reactive chemicals "expert" during and after a plant emergency is important and potentially critical to the safe handling of an ongoing event and also in determining the root cause of the incident.

10. "Study on the Reaction Mechanism and Kinetics of the Thermal Decomposition of Nitroethane" by Wang, Q., Ng, D., and Mannan, S. M., *Ind. Eng. Chem. Res*., Vol. 48, pp. 8745-8751 (2009).

Despite many theoretical and experimental advances in understanding the macroscopic properties of energetic materials, much work remains to be done to understand their microscale mechanism. In this work, the reaction mechanism and kinetics of thermal decomposition of nitroethane were studied by density functional theory (DFT) calculations, APTAC measurements, and gas chromatography analysis. The APTAC results were used to determine Arrhenius parameters of A=1013.5±0.2 and Ea=46.2±0.5 kcal/mol. The decomposition includes three initial steps: concerted molecular elimination of HONO, nitro-nitrite isomerization, and rupture of C-NO2. Following these initial reactions, a detailed mechanism that consists of 23 elementary steps was proposed. Numerical simulations of the proposed mechanism reproduce reasonably well the distributions of major products over the temperature range. It was found that the relative concentrations of NO and C2H4 depend on the reaction temperatures. Combining theoretical and experimental studies, it is concluded that elimination of HONO is predominant at low temperature and dissociation of C-NO2 becomes significant at high temperature.

11. "A Little Knowledge is a Dangerous Thing-Unexpected Reaction Case Studies Make the Case for Technical Discipline" by Brennan, J. and Kiihne, C. M., *J. Loss Prev. Proc. Ind*., Vol. 22, No. 6, pp. 757-763 (November 2009).

The old saying, "what you don't know can't hurt you," implies that ignorance is bliss. "A little knowledge is a dangerous thing," may be closer to the truth; however, it is not the little that we know that is dangerous, but that which is not known. By design, the processes used in the chemical industry are reactive, and the intended reaction receives much scrutiny. However, other reactions occur, often unexpectedly, and possibly with severe consequences. The lessons we learn from these reactions must drive the improvement of our process development and technology management processes and the culture that shapes those processes, a culture of Technical Discipline. Technical Discipline, analogous to Operating Discipline in the manufacturing organization, is a culture committed to fully identifying and characterizing chemical and reaction hazards, and properly documenting and communicating these hazards to

create a permanent knowledge and understanding within the organization operating that process. A culture of Technical Discipline will reveal reaction hazards that might otherwise remain unknown until being unveiled in a dramatic and unexpected fashion. Until you fully identify and characterize the hazards of the materials you handle in your processes….what you don't know can hurt you.

12. "Thermal Behavior of Aqueous Solutions of Hydroxylamine During Isothermal and Isoperibolic Decomposition in a Closed System" by Papadaki, M. I. and Pontiki, E., *J. Chem. Eng. Data,* Vol. 54, pp. 2616-2621 (2009).

Hydroxylamine (HA) has been independently involved in several tragic accidents, which incurred numerous fatalities and injuries. Following these incidents, adiabatic calorimetry and computational chemistry research was conducted, suggesting potential reaction pathways of HA decomposition, but the mechanism of HA behavior still has not been completely understood. In the present work, the thermal decomposition of HA was studied via isothermal and isoperibolic calorimetric measurements in a glass and in a metal reactor, respectively. Identification of stable intermediates, like ammonia, nitrates, or nitrites during the course of the reaction did not provide any conclusive results. The calorimetric measurements presented here show condition-dependent endothermic and exothermic reaction steps that are consistent with previous findings of computational chemistry. These finding corroborate previously reported results, according to which the NH2- moiety may trigger reaction runaway.

13. "Thermal Risk Assessment and Rankings for Reaction Hazards in Process Safety" by Wang, Q. and Rogers, W. J., *J. Therm. Anal. Calorim*., Vol. 98, pp. 225-233 (2009).

Reaction hazards remain the most serious concern in the chemical industry in spite of continual research and attention devoted to them. Many commercial calorimeters, such as DSC are useful screening tools for thermal risk assessment of reaction hazards. Some important thermodynamic and kinetic parameters, including onset temperature, adiabatic time to maximum rate, and maximum adiabatic temperature are analyzed in this paper. A kinetic-based model under adiabatic conditions was developed, and the adiabatic time to maximum rate was estimated. Correlations between onset temperature (To) and activation energy (Ea) and between onset temperature (To) and adiabatic time to maximum rate (TMRad) were found and were illustrated by some examples from the previous literature. Based on the heat of reaction and the adiabatic time to maximum rate, a thermal risk index (TRI) was defined to represent the thermal risk of a specific reaction hazard relative to di-tert-butyl peroxide (DTBP), and the results of this index were consistent with those of the reaction hazard index (RHI). The correlations and the thermal risk index method could be used as a preliminary thermal risk assessment for reaction hazards.

14. "Triple Sections of Thermal Decomposition for Lauroyl Peroide by TGA-FTIR" by You, M-L et al, Paper presented at the NATAS 37th Annual Conference on September 20-23, 2009 at Lubbock, TX.

Thermogravimetric analyzer-Fourier transform infrared spectrometer (TGA-FTIR) technique can be used to evaluate thermal decomposition for organic peroxides. Gases evolved from the sample of interest during the TGA were transferred from the furnace by a purge gas to the flow cell of an FTIR. The intensity of the infrared spectra of evolved gases, such as CO2, was measured as a function of time and displayed as a chromatogram. This study enabled us to identify the gases which are lost and associate them with a specific TGA-FTIR curve with triple sections. Different heating rates were analyzed and mass loss was elucidated. This can greatly

aid in understanding the lauroyl peroxide (LPO) decomposition mechanism and detailed kinetic parameters.

15. "Runaway Reaction of Methyl Ethyl Ketone Peroxide Mixed with H3PO4 or H2SO4 by TAM III Tests" by Su, T-S et al, Paper presented at the NATAS 37th Annual Conference on September 20-23, 2009 at Lubbock, TX.

Methyl ethyl ketone peroxide (MEKPO) is a very intrinsically unstable substance that can induce self-decomposition even under normal atmospheric condition. During storage, MEKPO can release an enormous amount of heat if the temperature is higher than the recommended storage temperature, due to the self-accelerating reaction having been ignited. In this study, MEKPO combined with inorganic acids of H3PO4 6N or H2SO4 6N was tested by the thermal activity monitor TAM III under three isothermal conditions of 70, 80, and 90°C to evaluate the basic kinetic parameters and safety parameter of time to maximum rate (TMR), which is derived from the time and temperature during isothermal tests. The results of this study indicate that the degree of hazard of MEKPO could increase when combined with H3PO4 6N or H2SO4 6N compared with pure MEKPO. This study established an important guiding principle for related manufacturing processes worldwide.

16. "Runaway Reaction of Lauroyl Peroxide with Nitric Acid by DSC" by You, M-L et al, Paper presented at the NATAS 37th Annual Conference on September 20-23, 2009 at Lubbock, TX.

Mixing lauroyl peroxide (LPO) with nitric acid, we used DSC to assess the kinetic parameters, such as exothermic onset temperature (To), heat of decomposition (?Hd), frequency factor (A), and other safety parameters. When LPO was contaminated with nitric acid (HNO3), we found the explosive 1-nitrododecane. Obvious compounds produced were sensitive and hazardous chemicals. Concentrations reaching 1N to 12N HNO3 emitted a large amount of heat. This study, combined with a curve-fitting method, elucidated the unsafe characteristics and thermally sensitive structure of LPO to help prevent runaway reactions, fires, and explosions in the process environment. According to the findings of this study and the concept of inherently safer design, LPO runaway reactions could be adequately prevented in the relevant plants.

2010 AIChE Safety and Health Division Election Results

Chair	Peter Lodal
1st Vice Chair	Cheryl Grounds
2nd Vice Chair	Dave Hermann
Directors	Mike Moosemiller and Amy Theis

Kathy Pearson is now the nominating committee chair, and in this capacity, has requested candidates for the 2011 election. If you are interested in running for election as a division officer, please contact Kathy at Katherine.Pearson@bp.com.

2010 ACS DIVISION OF CHEMICAL HEALTH AND SAFETY OFFICERS AND COMMITTEE CHAIRS

Visit the DCHAS web site at http://www.dchas.org/

Chair (2010)
Stefan Wawzyniecki
Dept EH&S Unit 4097
University of Connecticut
3102 Horsebarn Hill Road
Storrs, CT 06269-4097
(860)486-1110
stefan.w@uconn.edu

Chair-Elect; Audit Committee Chair; (2011 Chair)
Ken Fivizzani
kfivizzani@wowway.com

Immediate Past Chair; Nominating Committee (2008 Chair)
Russell W. Phifer
WC Environmental, LLC
PO Box 1718
West Chester, PA 19380
(W) 610-696-9220
(H) 610-869-0119
(F) 610-344-7519
rphifer@wcenvironmental.com

Treasurer (2009)
Neal Langerman
Advanced Chemical Safety
7563 Convoy Court
San Diego, CA 92111
(W) 858-874-5577
(F) 858-874-8239
neal@chemical-safety.com

Secretary (2009); Web site and E-mail Administrator
Ralph Stuart
University of Vermont
667 Spear St.
Burlington, VT 05405
rstuart@uvm.edu

JCHAS Editor and Alternate Councilor
Harry J. Elston
Editor, Chemical Health and Safety
Midwest Chemical Safety
9380 Wandering Trails Lane
Dawson, IL 62520
(W) 217 971-6047
(F) 217 364 9626
helston@bigfoot.com

Councilor (2010)
George H. Wahl, Jr.
Box 8204, Department of Chemistry
North Carolina State University
Raleigh, NC 27695-8204
(W) 919-515-2941
(F) 919-515-2545
george_wahl@ncsu.edu

Alternate Councilor (2011)
Frankie Wood-Black
Trihydro
fwblack@cableone.net

Member-at-Large (2010)

Bill Galdenzi
Environmental Health & Safety
Boehringer-Ingelheim Pharmaceuticals Inc.
bill.galdenzi@boehringer-ingelheim.com

Training and Workshops Coordinator
Russell W. Phifer
WC Environmental, LLC
PO Box 1718
West Chester, PA 19380
(W) 610-696-9220
(H) 610-869-0119
(F) 610-344-7519
rphifer@glasmesh.com

Awards
Douglas Walters
Environmental and Chemical Safety Educational Institute
6807 Breezewood Rd.
Raleigh, NC 27607
919-851-1465
waltersdb@earthlink.net

Social Chair
Pat Schumann
Safety Specialist (contract)
Sanofi-Aventis
520-403-8228(cell)
Patricia-EXT.Schumann@sanofi-aventis.com

Program Co-Chair
Linda Stroud
Science & Safety Consulting Services
2808 Rue Sans Famille
Raleigh, NC 27607
lmstroud@sciencesafetyconsulting.com

Program Co-Chair
Debbie M. Decker
Environmental Health and Safety
University of California, Davis
1 Shields Ave.
Davis, CA 95616
530-754-7964 (office)
530-752-1493 (EH&S main office)
530-752-4527 (FAX)
dmdecker@ucdavis.edu

Regional Meeting Coordinator
Vicki A. Stanavitch
Instructor of Biology and Chemistry, Laboratory Supervisor
Keystone College
One College Green
La Plume, PA 18440
vicki.stanavitch@keystone.edu

Archives; Speaker's Bureau
James Kaufman, Chair
The Laboratory Safety Institute
192 Worcester Road
Natick, MA 01760-2252
(W) 508-647-1900
(F) 508-647-0062
labsafe@aol.com

Membership
RJ Wolcik
Strem Chemicals,Inc. Newburyport, MA

2010 AICHE SAFETY AND HEALTH DIVISION OFFICERS

www.shdiv.aiche.org

Chair
Peter N. Lodal
Eastman Chemical Company
Tennessee Division – Bldg 18
P. O. Box 511
Kingsport, TN 37662
423-229-2675
423-229-3949 (FAX)
pnlodal@eastman.com

First Vice-Chair
Cheryl A. Grounds
BP Exploration & Production, Inc.
501 Westlake Park Boulevard
Houston, TX 77079-2696
281-366-4740
281-366-7969 (FAX)
cheryl.grounds@bp.com

Second Vice-Chair
David D. Herrmann
DuPont Company
1007 Market Street (B7246)
Wilmington, DE 19898
302-774-1766
302-773-6508
david.d.herrmann@usa.dupont.com

Past Chair
Katherine Pearson
Katherine.Pearson@bp.com

Secretary-Treasurer
Albert Ness
Process Safety Technology Leader
Engineering Solutions
The Dow Chemical Company
3100 State Road
Croydon, PA 19021
215-785-7567
215-785-7077 (FAX)
aness@dow.com

Director (2008 – 2010)
Dr. Brian R. Dunbobbin
Air Products & Chemicals, Inc.
7201 Hamilton Boulevard
Allentown, PA 18195-1501
610-481-6736
610-481-7157 (FAX)
dunbobbr@apci.com

Director (2008 – 2010)
Brian D. Kelly
Bririsk Consulting Ltd.
121 Royal Bay NW
Calgary AB T3G 5J6
403-375-0709
403-375-0710 (FAX)
kellybd@telus.net

Director (2009 – 2011)
Dr. Daniel A. Crowl
Michigan Technological University
203 Chem Sci & Eng. Bld
1400 Townsend Drive
Houghton MI 49931-1295
906-482-7144
906-487-3213 (FAX)
crowl@mtu.edu

Director (2009 – 2011)
Henry Febo
FM Global
P.O. Box 9102
1151 Boston-Providence Tpke
Norwood, MA 02062
781-255-4771
henry.febo@fmglobal.com

Director (2010 – 2012)
Mike Moosemiller
Baker Engineering and Risk Consultants, Inc.
MMoosemiller@BakerRisk.com

Director (2010 – 2012)
Amy Theis
Fauske & Associates, LLC
Theis@Fauske.com

AIChE Liaison to Division
Felicia Guglielmo
American Institute of Chemical Engineers
Three Park Avenue
New York, NY 10016-5991
646-495-7329
646-495-8882
felig@aiche.org

Center for Chemical Process Safety Liaison to Division
Roxy Schneider
Center for Chemical Process Safety
American Institute of Chemical Engineers
Three Park Avenue
New York, NY 10016-5991
646-495-1372
roxys@aiche.org

Chemical Technology Operating Council Liaison to Division
Stephen Smith
American Institute of Chemical Engineers
Three Park Avenue
New York, NY 10016-5991
646-495-7335
646-495-8883 (FAX)
steps@aiche.org

Webmaster
Emil H. Groth
Michigan Technological University
Minerals & Materials Building, Room 727
Houghton, MI 49931
906-487-2079
906-487-2782 (FAX)
ehgroth@mtu.edu

Process Safety Progress Editor
Ronald J. Willey
Northeastern University
Dept. of Chemical Engineering, 342 SN
360 Huntington Ave
Boston, MA 02026
617-373-3962
617-373-2205 (FAX)
r.willey@neu.edu

Process Safety Progress Editor
Joseph F. Louvar
Wayne State University
Department of Chemical Engineering
5050 Anthony Wayne Road
Detroit, Michigan 48202-9988
313-577-9358
313-577-3810 (FAX)
jlouvar@ameritech.net

Newsletter Editors
John F. Murphy
hamjfm@embarqmail.com

Dennis C. Hendershot
d.c.hendershot@att.net