

Safety & Health News

AIChEAMERICAN INSTITUTE OF
CHEMICAL ENGINEERSSAFETY AND HEALTH DIVISION
www.shdiv.aiche.org

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HAPPY BIRTHDAY AIChE

Dennis C. Hendershot

At the AIChE 2008 National Meeting in Philadelphia, AIChE celebrated its 100th anniversary. AIChE was founded in Philadelphia in 1908, and returned to the city to celebrate its 100th birthday. The meeting featured many sessions reflecting on the history of AIChE, including a session reviewing the history of AIChE activities in the area of safety, health, and loss prevention (Session #8 - A Century of Process Safety¹). Papers reviewed history and progress in safety in companies (DuPont and Air Products), government (OSHA), and AIChE (programming activities, the Safety and Health Division, the Center for Chemical Process Safety [CCPS], and Safety and Chemical Engineering Education [SACHE]). The June issue of *Process Safety Progress* will include papers given at that session.

Safety has always been an important consideration of all areas of engineering, and safety concerns were one of the factors which led to the formation of many professional engineering societies. For example, one of the first activities of the American Society of Mechanical Engineers (ASME), founded in 1880, was the issuance of its first standard, "Standard Method for Steam Boiler Trials," in 1884. In AIChE, safety activities began many years before the formation of the Safety and Health Division:

- The first "Safety in Air and Ammonia Plants" symposium was held in September 1957 at the AIChE Meeting in Baltimore, Maryland. This activity evolved into the annual "Safety in Ammonia Plants and Related Facilities" Symposium, which will be held for the 54th time, September 13th-17th, 2009 in Calgary, Canada.
- The first "Loss Prevention Symposium" was held at the AIChE National Meeting in Houston, Texas, in 1967.
- The Design Institute for Emergency Relief Systems (DIERS) was formed as an AIChE industry alliance in early 1976 by 29 companies to develop methods for design of emergency relief systems for runaway reactions, and continues to serve as an ongoing DIERS Users Group.
- The Safety and Health Division of AIChE was founded in 1979, and celebrates 30 years this year.
- In 1982, under the sponsorship of the Safety and Health Division, AIChE began publication of *Plant/Operations Progress*, subsequently renamed *Process Safety Progress*, as its primary journal devoted to safety, health, and loss prevention.

¹ <http://aiche.confex.com/aiche/2008/techprogram/S7099.HTM>

- In 1985, following the December 1984 Bhopal tragedy, CCPS was formed as an industry alliance by AIChE to promote process safety.
- One of the early efforts of CCPS was Safety and Chemical Engineering Education (SACHE), which provides resources for incorporating safety, health, and loss prevention into the undergraduate chemical engineering college education.
- The Process Plant Safety Symposium (PPSS) was first held in 1992, as a local event sponsored by the South Texas Section of AIChE in Houston. PPSS was subsequently incorporated into national AIChE Safety and Health Division programming.
- The Global Congress on Process Safety was first held in April 2005 in Atlanta, at the AIChE Spring National Meeting, combining the Loss Prevention Symposium, the CCPS Annual Conference, and the Process Plant Safety Symposium at a single location. The 5th Global Congress on Process Safety will be held in April 2009 in Tampa, Florida.

One thing that all of these activities have in common is the critical contribution of volunteers – both from individual engineers and volunteer contributions of time and money from industrial companies, consultants, educational institutions, governmental agencies, and others. Without these contributions, none of these activities would have been successful. But all contributors found that they received much more in return. Collectively, we are much smarter than any of us individually. We learn from interactions with our colleagues, and they learn from us. From my own experience working on many CCPS committees, when the committee product, usually a book, is complete, I did not have to read it. The book could just go on the shelf for future reference, because I already knew what was in the book. Everybody on the committee learned the contents through the process of developing and writing the book, and became an expert. In these days of increasing economic pressures, we need to continually remind ourselves of the value of these collaborative efforts, and make a strong effort to make sure they continue. They are essential to continued progress in safety in our industry.

Dennis Hendershot

SAFETY & HEALTH DIVISION UPDATE

Bob Johnson, 2008 Chair

Our Division's regular publication, *Process Safety Progress*, has been an invaluable resource for process safety professionals ever since starting out as *Plant/Operations Progress*. We are now turning over a new leaf with "*PSP*," as the editorship changes from one set of capable hands to another. Many thanks go to Dr. Daniel Crowl of Michigan Tech for his hard work and technical expertise the last five years as co-editor; congratulations go to Dr. Ronald Willey of Northeastern University as our new co-editor. Both thanks and congratulations go to Dr. Joseph Louvar, who will continue on as our other co-editor for the next five years. We can look forward to some changes in how *PSP* is managed, with more emphasis on electronic submission of articles in the future, but the combination of experience and enthusiasm that Joe Louvar and Ron Willey each bring will ensure *PSP* will continue its tradition of excellent articles and editorials.

I attended the 53rd annual "Safety in Ammonia and Related Facilities" conference this year in San Antonio, and was quite impressed with the programming, arrangements and content of the conference. The Ammonia Committee works autonomously from the rest of the Safety & Health

Division's programming committees, and has over many years developed this specialty conference into the premiere annual gathering of engineers and other company representatives from all over the world who are interested in ammonia plants and related facilities. Only about one-third of the over 300 attendees were from the United States. In addition to papers on topics such as facility siting and safety instrumented systems at ammonia plants, many of the presentations shared plant reliability lessons learned, including piping and equipment failure incidents. The call for papers for next September's conference in Calgary, Alberta is already open. If your job responsibilities relate to ammonia, urea, ammonium nitrate, etc., then you may want to plan on attending and maybe even making a presentation. See www.aiche.org/ammonia for more information.

Don't forget to take safety home with you, and protect your own family and property using some of the same management practices on a smaller scale as what you do at work. Regularly check your smoke detector batteries and GFCIs, keep vigilant for new hazards, think through and analyze each new job task, use the right tool or ladder for the job, and take care of the things you know need repairing or replacing. Have a safe and joyful holiday season.

Bob Johnson

CENTER FOR CHEMICAL PROCESS SAFETY UPDATE

CCPS China Training

The CCPS- China Section will be holding a training course "Pre-Startup Safety Review and Hazard Recognition" in Shanghai on March 11-12. The course will include translation into Chinese. Please share this information with your colleagues in China. You can find more information, including registration information, at:

http://www.aiche.org/March_2009_China_Training.aspx

Latin American Conference

CCPS, the Brazilian Chemical Industry Association (ABIQUM), and the Brazilian Association of Chemical Engineering (ABEQ), are coordinating to present the 2nd CCPS Latin American Process Safety Conference and Expo. This annual event is the major forum in Latin America for practitioners from the chemical and allied industries, academia, and government to share practical and technological advances in all aspects of process safety. The conference will take place in São Paulo, Brazil on October 21-23, 2009 and will be held in conjunction with ABIQUIM's Responsible Care® conference. The Call for Papers is open, with an Abstract Deadline of June 1, 2009. More information is available at:

<http://www.aiche.org/ccps/conferences/brazil2009.aspx>

New Books

CCPS books are available from Wiley, and all currently available books are listed at the following web site:

<http://www.wiley.com/WileyCDA/Section/id-350225.html>

CCPS has recently released two new books:

Inherently Safer Chemical Processes, 2nd Edition

Inherently Safer Chemical Processes presents a holistic approach to making the development, manufacture, and use of chemicals safer. Since the publication of the original concept book in 1996, there have been many developments on the concept of inherent safety. This new edition provides the latest knowledge so that engineers can derive maximum benefit from inherent safety

Guidelines for Chemical Transportation Safety, Security, and Risk Management, 2nd Edition

This book outlines current transportation risk analysis software programs and demonstrates risk assessment programs for land transport for consequences that may affect the public or the environment.

Join CCPS

Are you thinking about putting CCPS participation in your budget for 2009? Contact us at 646-495-1370 or ccps@aiiche.org for a dues quote and information about membership benefits.

CHEME CAR COMPETITION – INSPECTORS NEEDED

The ChemE Car competition is one of the highlights of the annual student conference, held in conjunction with the AIChE Annual Meeting each year. The 2009 Annual Meeting will be in Nashville, TN, November 8-13, 2009. To ensure safety in the competition, and also to teach students about the importance of considering safety in the design of any chemical process (including the ChemE car), students entering the competition are required to provide a safety analysis of their design, and the design must be reviewed by safety inspectors. We will need safety inspectors for the ChemE car competition, both at local competitions at various locations around the United States, and in Nashville in November 2009 at the final competition. The inspectors will review the safety analyses and the cars. Please consider volunteering to help with these inspections – it is a great opportunity to meet and talk with some great students about the interesting designs for their cars. If you are interested, please contact AIChE Volunteer and Member Support and Program Coordinator Felicia Guglielmi at felig@aiiche.org, and she will pass your information on to the appropriate person.

NATIONAL AIChE CHEM-E-CAR SAFETY COORDINATOR

Opportunity for AIChE committee position (with honorarium), February 2009. Duties to begin: Immediately.

The Student Chapters Committee of the American Institute of Chemical Engineers is looking for an individual to serve as National Chem-E-Car Safety Coordinator. The person assuming this position must have a demonstrated record in safety, particularly with respect to chemical handling. Participation in past Chem-E-Car regional competitions is a plus. The appointment for this position is normally January 1 through December 31. However, a multi-year commitment is encouraged.

The honorarium for this position is \$5,000 per year. AIChE will also provide free registration and a travel stipend for the Fall Annual Meeting — the site of the National Chem-E-Car Competition. There are two competition cycles in the Chem-E-Car program. The National Safety Coordinator is actively involved in both cycles. The first cycle occurs in February thru early May with the AIChE student regional competitions; attendance at these competitions by the National Safety Coordinator is optional. The second cycle occurs during the National Chem-E-Car Competition held during the Annual Meeting in November; attendance at the National Competition by the National Safety Coordinator is required. Most of the work is handled electronically, either by email, teleconference, or on SharePoint document sharing sites maintained by national AIChE.

Information and rules for the AIChE Chem-E-Car Competition can be found at:

<http://www.aiche.org/Students/Awards/ChemeCar.aspx>

The coordinator will receive ongoing support and collaboration from AIChE staff and the Student Chapters Committee. The general duties for this position are as follows:

1. Collaborate with AIChE staff and the National Chem-E Car rules committee on the following:
 - identify on-site inspectors and safety coordinators for regional and national competitions
 - identify and coach JSA reviewers for regional and national competitions.
 - ensure that the JSAs for national and regional competitions are collected and available for review to designated safety inspectors
 - monitor scheduling and location of national competition inspections
 - participate in rules revisions for the following year's competition
2. Review and update the safety rules, Job Safety Assessment Form (JSA) and vehicle inspector's checklist.
3. Assist and coordinate student team and adviser safety training with AIChE.
4. Work with Regional safety coordinators and inspectors to insure that they understand their duties and when these duties need to be performed.
5. Coordinate on-site orientation session for inspectors and on-site Chem-E-Car safety inspections at national competition.
6. Coordinate with the appointed student chapter host school(s) and the regional AIChE liaison on the organization of the Chem-E-Car chemical preparation area at the national competition.
7. Work with regional and national organizers to insure that all chemicals are received and stored safely, that on-site chemical handling by the student Chem-E-Car teams is done safely, that chemical disposal is done safely, and that all these activities meet all national and regional regulations.

8. Observe and assist with safety during the national competition – use this information to suggest future improvements in the program.

For information on this position and to apply, please contact:

Gordon Ellis
AIChE
3 Park Avenue, 19th Floor
New York, NY 10016
gorde@aiiche.org

5th GLOBAL CONGRESS ON PROCESS SAFETY

The 5th Global Congress on Process Safety will be held in Tampa, Florida, April 26-30, 2009. Registration for the 2009 Global Congress on Process Safety is now open, and more information is available at:

<http://www.aiiche.org/Conferences/Spring/GCPS/CFP.aspx>

The Center for Chemical Process Safety (CCPS), the Loss Prevention Symposium (LPS), and the Process Plant Safety Symposium (PPSS) are coordinating conferences again in 2009 to present the 5th Global Congress on Process Safety (GCPS). This annual event is the primary forum for practitioners from the chemical and allied industries, academia, and government to share practical and technological advances in all aspects of process safety. This GCPS will provide practitioners the necessary tools and information to address the next generation of process safety.

5th Global Congress on Process Safety

John Murphy, Global Congress Chair

43rd Annual Loss Prevention Symposium (LPS)

LPS Chair: Jean-Paul Lacoursiere
LPS Vice Chair: Ronald Wiley

Fires, Explosions and Reactive Chemicals

The analysis, prevention, protection and mitigation of fire, explosion, and reactivity hazards continue to be important to the loss prevention community. This session invites papers that identify, characterize, or offer design and operational guidance on fire, explosion and reactivity hazards.

Hazard Evaluations and Layer of Protection Analysis

Process hazard analyses (PHA's) and their extension into LOPAs and Safety Integrity Level (SIL) determinations continue to be central to loss prevention efforts. This session seeks original presentations related to identifying hazards, developing scenarios, determining the adequacy of

safeguards, and specifying the integrity of protection layers needed to meet risk goals in the context of team-based reviews.

Food and Consumer Products Process Hazards

The Food and Consumer Products area has significant hazards and risks from dust and flammable liquid explosions as well as from toxic releases. Moreover, the Montreal Protocol for the removal of Ozone Depleting Substances may result in the use of ammonia refrigerant with its associated risks. This session invites papers on the identification, prevention, control, and management of hazards and risks in the food and consumer products industries. Relevant knowledge extracted from analysis of incident databases is encouraged as well.

Audits, Inspection and Regulation

In the past few years, we have seen renewed emphasis on PSM through OSHA's National Emphasis Programs, and Homeland Security new Chemical Security's regulations. This session invites papers that discuss regulatory programs in the U.S. and internationally, and companies strategies for complying with them.

Consequence Modeling

Consequence modeling has evolved as a result of accident investigations. This session will review the state of the art in fire, explosion and toxic release modeling.

24th Annual CCPS International Conference

CCPS Conference Chair: Eric Freiburger
AIChE Global Congress Oversight: Roxy Schneider

Risk Criteria

The new CCPS Guidelines for Establishing Risk Criteria will be published in 2008. This session will include papers regarding the development and application of risk criteria to improve a company's risk profile. Topics may also include experience and examples with risk apportionment, international application of risk criteria, and business decision processes.

Process Safety Metrics and Culture

This session will feature presentations focusing on using the new CCPS Process Safety Metrics and other metrics to drive continual improvement in a company's process safety culture and in overall incident reduction performance. Emphasis will be placed on papers that describe actual experience with implementing metrics, tracking results, and making decisions based on these results.

Managing Organizational Change

Management of Change has long been recognized as a fundamental cornerstone of a process safety program. Through the years, most companies have evolved a mature system to manage technical changes -- equipment, materials, and technology -- in their facilities. In recent years, the effects of, and need to manage, changes to organizations have come to the fore. These types of changes include staffing (for instance due to career advancements, retirements or terminations) or staffing levels, creation or deletion of positions, position duties/job scope, shift durations, mergers and acquisitions, and maintaining competency and knowledge. Of particular interest are the management of change process used (if different from MoC for technical changes), the review techniques employed, authorization of organizational change, and experiences and lessons learned associated with organizational MoC

Transportation Risk

Transportation Risk Assessment (TRA) is an essential aspect of risk management. TRA manages transportation risks by considering hazards, routes, and impacts. This promotes the identification of major contributors to the risk and thus strategies for risk reduction. TRA includes consideration of toxic, flammability, explosivity, and security risks. This session will include papers that provide TRA examples and application experience, tools and methods, and risk management decisions made as a result of these assessments.

Auditing Process Safety

The 2nd Edition of the CCPS Guidelines for Auditing Process Safety Management Systems is currently being prepared. This session will include papers that address management systems for ensuring effective audit processes. Topics in this session may also include developing internal audit program; audit team independence, skills, and qualifications; tools to audit and to follow-up on items identified during an audit; auditing process safety culture; and auditing global operations.

Tools to Identify Hazards

Personnel involved with day-to-day plant operations maintain an important role in the hazard identification and risk assessment (HIRA) process. These individuals are often the first to identify hazardous process conditions in an operating environment. Papers submitted to this session should focus on tools and techniques for hazard identification and field evaluation. Subjects may include educational platforms, programs that raise awareness and improve understanding, and practical methods that can be readily implemented at the plant level.

Fire, Explosion & Quantitative Analysis

Fires and explosions result in the largest losses in process safety accidents. The increase sensitivity by industry, regulatory, and public sectors to recent events as well as challenging market conditions has caused industry to scrutinize their existing approaches and develop balance between consequence and risk methods. Papers submitted to this session will focus on new techniques, stories of applications, comparisons of methods, nuance of applications, etc. for both temporary and permanent facilities.

Implementing PSM Globally

In the last several years there have been numerous changes in technical and analytical methods, process safety management systems, regulations, globalization and consolidation, new and increased accountability to public and regulatory entities, and changing market conditions. Papers submitted to this session will focus on revisions to existing PSM systems and implementation of new systems in companies and sectors across the world. Issues for papers include, but not limited to, implementing and merging of different cultures, regulations, foreign owned companies, joint ventures, etc.

11th Process Plant Safety Symposium (PPSS)

Symposium Chair: John W. Champion

Symposium Co-Chair: Dr. Colin (Chip) S. Howat

Process Safety – From the Top-Down and Bottom-Up

The theme of this session is implementing Process Safety systems from two different perspectives: (1) what Senior Management needs from process safety and risk practitioners to effectively facilitate decision making and ensure ongoing process safety excellence and (2) what technical personnel

can do to best assess and then present what is needed for process safety to gain ongoing positive support of management and business leaders. Case histories, methods of analysis and assessment, approaches to presenting and “selling” general or specific process safety needs are solicited.

Safety Culture and Operating Discipline

This session welcomes abstracts focusing on the cultural aspects of a successful Process Safety program. Papers that present new and innovative ideas on corporate-wide and site-specific safety culture improvements, developing or improving operational discipline, and other approaches addressing the “human element” in operating safely will be considered.

Applications of Risk Analysis Techniques

Hazard identification and risk assessment continue to be a critical part of the process safety efforts in process plants. Papers highlighting methods, tools and examples of successful application or lessons learned from misapplication in a plant environment are desired.

Safety Instrumented Systems – Problems and Innovative New Solutions

The identification of Safety Instrumented Functions (SIFs) and the design and proper application of Safety Instrumented Systems (SIS) is an ongoing challenge for the process industries. This session invites papers featuring new and innovative ideas in the areas of Independent Protection Layer (IPL) identification, Safety Instrumented Function (SIF) identification, Safety Integrity Level (SIL) assignment, and SIS management systems.

Mechanical Integrity – State of the Art

This session solicits papers on the latest mechanical integrity concepts, practices and programs. All aspects of mechanical integrity are of interest, including equipment inspection, interlock testing, reliability initiatives, and overall system design. An additional area of focus is on the challenges of meeting the needs of a global organization, including language & cultural barriers, widely varied national regulations and availability of qualified resources.

Contractors and Their Impact on Process Safety

Contractors play a key role in many aspects of business in the chemical industry, including Process Safety. This session would welcome submissions on Process safety topics associated with engineering design, construction, operations support, and maintenance from the contractor and/or operating company’s perspective.

Joint Session: LPS, CCPS, and CCPS

Case Histories and Lessons Learned

Reviews of process safety incidents and near misses provide valuable learning opportunities. Papers dealing with incidents, near misses and the lessons learned are requested. This will be a joint session of PPSS with LPS and CCPS.

STUDENT AWARDS

The following student awards were presented by the AIChE Safety and Health Division and the SACHE Committee at the 2008 AIChE Student Conference, at the AIChE National Meeting in Philadelphia in November 2008. Congratulations to all of the award recipients.

SACHE Individual Safety Award - Walt Howard SACHE Award

Kaitlyn Kelly, University of Kansas (Advisor: Colin Howat)

SACHE Team Safety Award - Jack Wehman SACHE Award

Wesley Biddle, Andrew Kemmerling, Edward Ralph Soliz, Jr., Lamar University (Advisor: Carl Yaws)

Safety and Health Division Award - Ted Ventrone Award

Megan Benyshek, Kelsey Casad, Archie Meiseman, Oklahoma State University (Advisor: Rob Whiteley)

Safety and Health Division Award - Walt Silowka Award

Marklee C. Lockie, Craig A. Wiley, Tri-State University (Advisor: Majid Salim)

Safety and Health Division Award - Ephraim Scheier Award

Kaitlyn Kelly, University of Kansas (Advisor: Colin Howat)

ARTICLES AND PAPERS OF INTEREST

Thanks to Stan Grossel for providing the following list of papers potentially of interest to Division members:

1. "Thermal Evaluation of Multi-Walled Carbon Nanotubes with Sulfuric Acid by DSC" by Chang. C-W et al, Paper presented at the NATAS 2007 Conference, August 25-29, 2007 at Michigan State University.

Many concerns over unsafe or unknown properties of multi-walled nanotubes (MWNTs) have been raised. The thermal characteristics regarding stability would represent potential hazards during the production or utilization stage and could be determined by calorimetric tests for various thermokinetic parameters. Differential scanning calorimetry (DSC) was employed to evaluate the thermo-kinetic parameters for MWNTs at various compositions. Thermoanalytical curves showed that the average heat of decomposition of the MWNT samples in a manufacturing process was about 31,723.3 J/g, by identifying them as an inherently hazardous material. In this study, significant thermal activity occurred in the presence of sulfuric acid. From the DSC experiments, the purification process of MWNT could induce an unexpected reaction in the case of batch addition with reactants of sulfuric acid. The results can be applied for designing emergency relief systems and emergency response strategies during a perturbed or accident situation.

2. "Self-Accelerating Decomposition Temperature (SADT) Prediction of Methyl Ethyl Ketone Peroxide Using Various Calorimeters and Models" by Wu, W-H et al, Paper presented at the NATAS 2007 Conference, August 25-29, 2007, at Michigan State University.

As methyl ethyl ketone peroxide (MEKPO) possesses highly reactive and unstably exothermic features, it has caused many thermal explosions and runaway reaction accidents in manufacturing processes. To evaluate the self-accelerating decomposition temperature (SADT) of MEKPO in various storage vessels, it was proposed that thermokinetic parameters be determined by two approaches: DSC and vent sizing package 2 (VSP2). The thermokinetic parameters were, in turn, used to calculate and predict from theoretical equations based on the Semenov model. This study was aimed at predicting the SADT value of various storage vessels in Taiwan compared with the UN 25 kg package and the UN 0.51 L Dewar vessel. Important indexes, such as SADT, temperature of no return (T_{NR}), and time to maximum rate (TMR), are necessary and useful to ensure safe storage or transportation for self-reactive substances in the process industries.

3. "Thermal Decomposition of Hydrogen Peroxide in the Presence of Sulfuric Acid" by Wu, L-K et al, Paper presented at the NATAS 2007 Conference, August 25-29, 2007 at Michigan State University.

Hydrogen peroxide (H_2O_2) is widely employed as a reaction reagent in the chemical industry and semiconductor plants for cleaning of chips. By using DSC and the VSP2, this study focused on the thermal decomposition reaction of H_2O_2 mixed with sulfuric acid (H_2SO_4) with low (0.1, 0.5, and 1.0 N), and high concentrations (96 mass%), respectively. Thermokinetic data, such as onset temperature (T_o), heat of decomposition (ΔH), and pressure rise rate (dP/dt) were obtained and assessed from the DSC and VSP2 experiments. Comparisons of the reactivity of H_2O_2 mixed with H_2SO_4 , were assessed to corroborate the reaction of decomposition in these systems. From the reaction of thermal decomposition activity with different concentrations of H_2SO_4 , the experimental data of T_o , ΔH , and dP/dt were determined.

4. "Reactive Incompatibility of DTBP Mixed with Two Acid Solutions" by Lee, R-P et al, Paper presented at the NATAS 2007 Conference, August 25-29, 2007 at Michigan State University.

Organic peroxides are commonly employed as an inhibitor for polymerization, a source of free radicals, a hardener, and a linking agent. Due to its relatively weak oxygen-oxygen bond, di-tert-butyl peroxide (DTBP) has been categorized into a hazard classification of flammable type or Class III by the NFPA. The Transport of Dangerous Goods (TDG) document has published a warning against DTBP that it could potentially induce violent heat, explosion, fire, and self-ignition under certain circumstances. DTBP has been recommended as an international standard sample for estimating the performance of several isothermal calorimeters, such as glass test tube, DSC, and VSP2. In this study, we aimed to measure the precise temperature changes and heat flow in the above-mentioned instruments. However, some runaway incidents caused by DTBP have demonstrated that the reaction temperature could be as low as ambient temperature. The reactivity and hazardous incompatibility with sulfuric acid and hydrochloric acid of DTBP have not been evident and the runaway hazards involved in different processing conditions were clarified in this study by implementing the two calorimeters, as mentioned earlier. Acid-catalyzed characteristics and reaction hazards of DTBP were obtained, such as the time to maximum rate (TMR), heat of decomposition (ΔH), and exothermic onset temperature (T_o).

5. "Reaction Hazard Analysis for Cumene Hydroperoxide with Sodium Hydroxide" by Chou, Y-P et al, Paper presented at the NATAS Conference, August 25-29, 2007 at Michigan State University.

In Taiwan, organic peroxides have caused many serious explosions and fires, which were caused by thermal instability, chemical pollutants, and even mechanical shock. Cumene hydroperoxide (CHP) has been employed for producing phenol and dicumyl peroxide (DCPO). This study analyzed the thermal hazard of CHP with sodium hydroxide (NaOH) by DSC. The thermokinetic parameters were obtained, such as, exothermic onset temperature, peak temperature, and enthalpy. Through DSC, the experimental data were evaluated and then curve fitting was employed to obtain the kinetic parameters. Depending on the operating conditions, NaOH was one of the incompatible chemicals or catalysts for CHP. When CHP is mixed with NaOH, the onset temperature is induced earlier, and reactions become more complex than with CHP alone. After these data were assessed by curve fitting, the results showed that the activation energy (E_a) became lower and reaction was triggered more readily.

6. "Hazard Ratings for Organic Peroxides" by Duh, Y-S, Wu, X. H., and Kao, C-S, *Process Safety Progress*, Vol. 27. No. 2, pp. 89-99 (June 2008).

Nine commercially available organic peroxides were assessed with DSC and adiabatic calorimeters. These organic peroxides are cumene hydroperoxide (CHP), di-tert-butyl peroxide (DTBP), methyl ethyl ketone peroxide (MEKPO), tert-butyl hydroperoxide (TBHP), benzoyl peroxide (BPO), hydrogen peroxide, lauroyl peroxide (LPO), tert-butyl peroxybenzoate (TBPBZ), and dicumyl peroxide (DCPO). Exothermic onset temperatures, self-heat temperature and pressure rates, and heats of decomposition were measured and assessed. Adiabatic runaway reaction characteristics were determined by using ARC and VSP2 calorimeters. Incompatibility tests with several potential contaminants were made using DSC, VSP2, and a microcalorimeter. An incompatibility rating was developed using onset temperature, lowering of the onset temperature, heat of decomposition, maximum self-heat rate, adiabatic temperature rise, maximum pressure of decomposition, and maximum pressure rise rate, etc.

7. "Runaway Reaction of Non-Tempered Chemical Systems: Development of a Similarity Vent-Sizing Tool at Laboratory Scale" by Vechot, L. et al, *J. Loss Prev. Process Ind.*, Vol. 21, No. 4, pp. 359-366 (July 2008).

A new experimental "similarity" vent-sizing tool (A/V ratio) for non-tempered chemical systems was developed. It combines the advantages of both the DIERS method (laboratory scale) and UN method (less overconservative). This tool is based on the VSP2 adiabatic calorimeter. It uses a 0.1 liter test cell and allows blowdown experiments to be carried out in the $0.9 \times 10^{-3}/m < A/V < 4.0 \times 10^{-3}/m$ range. A simple additional setup allows for real-time vented mass measurements. Similarity limitations are discussed. Sizing experiments for an organic peroxide (cumene hydroperoxide 30% w/w) using both the "similarity tool" and the UN 10 liter reactor are compared. The similarity tool is on the safe side (0-50% oversizing). Heat losses are the main limits of the new tool.

8. "Safely Scale-up Processes and Accommodate Recipe Changes" by Theis, A. E., Burelbach, J. P. and Askonas, C. F., Paper presented at the AIChE 2008 Spring Meeting LPS Symposium, April 7-9, 2008, New Orleans, LA.

Thermal hazards screening can be quickly and cost-effectively performed to obtain the required data for safe scale-up of chemical processes and to accommodate changes to process recipes. Prior to scale-up, it is vital to identify safe temperature and pressure operating ranges, quantify the heat generated from a reaction, and the number of moles of gas generated. It is also prudent to determine the heat and gas generation rates in order to safely accommodate the reaction in the given process equipment. These rate data can also be used to verify the adequacy of the existing pressure relief system. PHA and HAZOP reviews identify credible upset scenarios, and data are required to address these issues. When a process recipe or batch size is changed, data are necessary to quantify the effect of the change on the above parameters. For modifications to existing processes, a management of change (MOC) review should occur. Data addressing issues resulting from these reviews are readily available by performing calorimetry experiments with the Advanced Reactive System Screening Tool (ARSST™) and examples of these applications are provided.

9. "Isothermal Decomposition of Hydroxylamine and Hydroxylamine Nitrate in Aqueous Solutions in the Temperature Range 353-433 K" by Liu, L., Rogers, W. J., and Mannan, M. S., Paper presented at the AIChE Spring 2008 Meeting LPS Symposium, April 7-9, 2008, New Orleans, LA.

Hydroxylamine (HA) and hydroxylamine nitrate (HAN) have been involved independently in several tragic accidents that incurred numerous fatalities and injuries. Following these incidents, adiabatic calorimetry and computational chemistry research was conducted on these compounds, suggesting potential reaction pathways of their decomposition, but the mechanism of their unstable behavior is still not completely understood. In the present work, isothermal decomposition tests have been performed accompanied with HPLC, ion chromatography, and UV analyses in the temperature range 353-400 K. Condition-dependent autocatalytic decompositions have been demonstrated for HA and HAN, and an intermediate formation has been observed that is most likely responsible for their autocatalytic behavior. These findings corroborate previously reported computational chemistry results.

10. "Evaluating Kinetic Parameters for Solid Substances Exhibiting Complex Self-Heating Behavior" by Morrison, D. and Ogle, R. A., paper presented at the AIChE 2008 Spring National Meeting LPS Symposium, April 7-9, 2008, New Orleans, LA.

Determining safe storage conditions for a self-heating material requires knowledge of the reaction kinetics governing its decomposition under potential storage conditions. Several thermal hazard analysis techniques are available, but most require kinetics analysis at a high temperature and microscale quantities. In contrast, isothermal calorimetry (i.e., isothermal oven tests) has proven to be a convenient method for conducting experiments with material quantities in the 0.1 to 1000 kilogram range at conditions more closely resembling the potential storage environment. The isothermal oven test protocol determines the critical temperature for several different sample sizes. The resulting data are then analyzed using the Frank-Kamenetskii variables to yield estimates for the activation energy and the pre-exponential factor. The classical Frank-Kamenetskii solution of the self-heating problem assumes that heat generation, described by zero order reaction kinetics, is balanced by heat loss from the self-heating body via

conduction at steady state. However, potential influences of other rate processes are neglected. In this paper we describe the decomposition behavior of two solid oxidizers, calcium hypochlorite and sodium percarbonate, that do not conform to the classical Frank-Kamenetski model. The two oxidizers exhibit complex self-heating behavior including temperature oscillations, particle agglomeration, gas generation, melting, and cavity growth within the self-heating body. Other investigators have extended the classical Frank-Kamenetski model to include factors such as multiple chemical reactions, solid melting, and gas evolution. The objective of this research task is to determine if the Frank-Kamenetski model, suitably modified to account for these complicating factors, can be applied to thermal ignition data for these solid oxidizers. The applicability of the modified Frank-Kamenetski model to these materials is discussed and compared with previously reported studies published in the literature.

11. "CRW 2.0: A Representative-Compound Approach to Functionality-Based Prediction of Reactive Chemical Hazards" by Johnson, L. E. and Farr, J. K., *Process Safety Progress*, Vol. 27, No. 3, pp. 212-218 (September 2008).

The NOAA Chemical Reactivity Worksheet (CRW) has produced a user-friendly, yet powerful method of qualitatively predicting reactive chemical hazards since its introduction in 1998, and has seen its use in spill response, storage management, and process safety for intentional chemistry. The CRW predicts reaction hazards based on a database of more than 6,000 common industrial chemicals, classified by major reactive groups, using a 43 x 43 matrix of organic and inorganic reaction groups, modified from the earlier "EPA method for determining the compatibility of hazardous mixtures." CRW output describes the hazards qualitatively; e.g., "spontaneous ignition of reactants or products due to reaction heat," or "combination liberates nonflammable nontoxic gas and may cause pressurization." The CRW also provides summaries of properties and special hazards for many of the compounds in the database. CRW 2.0, a new standalone version of the CRW, is due to be released later this year. Earlier versions of the CRW had a limited set of references and limited information about specific reactions, and this information could only be found in each compound's chemical profile, increasing search time for assessing reaction specifics, and providing little information that could be used to mitigate the chance of false-positives — the CRW is designed to be conservative in its predictions, and will indicate an incompatibility even if only a few reactions are found between two functional groups. Version 2.0 improves the database based on an extensive literature survey of potentially hazardous reactions for representative members of all 43 listed functional groups, with primary literature references available for many of the hazards predicted, and many errors and omissions corrected. This article describes the methodology for the literature search, rationale for changes to the operation of the database, extent of the new documentation, and the remaining design limitations of the product.

12. "Adiabatic Runaway Reaction, Blowdown, Quench, and Inhibition in Fire-Engulfed Vessels: An Experimental Study" by Waldren, S., Tee, D., and Ladlow, C. *Process Safety Progress*, Vol. 27, No. 3, pp. 225-229 (September 2008).

Two linked PHI-TEC adiabatic calorimeters were used to simulate a fire heating and runaway reaction scenario. This corresponded to plant-scale continuous flow reactors that are used for the production of acrylamide; two-phase venting from a fire-exposed "blocked-in" reactor into a dump tank containing water and a chemical inhibitor was simulated. After venting, continuous supplies of electrical power to both the reactor and the quench vessel were maintained so as to

simulate sustained fire exposure. The main purpose of the study was to determine whether this venting and continued fire exposure could induce any secondary decomposition reactions.

13. "Computation of Nozzle Flow Capacities for Superheated Steam, Subcooled Water, and Saturated Steam/Water Mixtures" by Westman, M. A., *J. Loss Prev. Proc. Ind.*, Vol. 21, No. 6, pp. 567-578 (November 2008).

A new computational tool models the discharge of steam, water, and saturated steam-water mixtures from safety relief valve nozzles, employing thermodynamic property formulas derived from the Helmholtz equation and programmed into spreadsheet-based software. The computational approach maps an isentropic process from initial conditions in a series of thermodynamic states at each of which the mass flux is computed. The user can identify the maximum mass flux from the generated mass-flux pressure graphical profile. The work describes other mass-flux predictive techniques commonly used in industry and then compares the results of the proposed method against those of the others. The data indicate a very high degree of correspondence between the proposed method and the Napier equation for saturated and superheated steam. The proposed method produces saturated-liquid results consistent with those of the other methods, particularly ASME VIII/1. For the relief of saturated liquid-vapor mixtures, the proposed method increasingly overpredicts maximum mass flux relative to the HEM-based ω -method for increasing pressures and qualities. In the low-quality range, for which there is experimental data to which to compare, the proposed method severely underpredicts measured results involving flows out of nozzles of lengths less than "relaxation" length, but for flows out of longer nozzles, the underprediction is significantly less. The proposed method's subcooled-water results compared to measured data also indicates large underpredictions for sub-relaxation lengths with improved results at generally greater degrees of subcooling at greater lengths. The proposed technique shows generally good agreement with other established predictive methods within demonstrated boundaries and has advantages in stand-alone capability and versatility.

14. "Reactions of Cumene Hydroperoxide Mixed with Sodium Hydroxide" by Hou, H-Y, Shu, C-M, and Tsai, T-L, *J. Hazardous Materials*, Vol. 152, pp. 1214-1219 (2008).

Decomposition of cumene hydroperoxide (CHP) was undertaken in a free radical chain reaction. The peroxy group is very reactive and unstable, while the remainder of the molecule is inert. CHP reacted with various concentrations of dilute sodium hydroxide as a catalyst to cleave at ambient and decomposition temperature. The products were verified by GC/MS, and were quantitatively analyzed by chromatography. CHP cleaved heterolytic with NaOH at 250°C, whose major product was dimethylphenyl carbinol (DMPC); however, the main products become acetophenone and α -methylstyrene by cleaved hemolytic pathway. The catalytic concentrations of NaOH significantly affected the branch ratios of DMPC under decomposition. Based on the experimental results, a radical cleavage mechanism was proposed. To sum up, the reaction parameters such as temperature, Lewis base, etc., could affect the incompatibilities and decomposition pathways for proper CHP cleavage process. In addition, exothermic onset temperature (T_o) and heat of decomposition (ΔH_d) of incompatible mixtures and CHP itself were studied by differential scanning calorimetry (DSC). Comparisons of T_o , ΔH_d , and peak power were assessed to corroborate the severity of thermal hazards. From the decay rate of CHP concentration, the reaction order was determined to be 0.5, and the Arrhenius parameters were measured as $E_a = 92.1$ kJ/mol and frequency factor $A = 2.42 \times 10^{10}$ /min.

15. "Effects of Acetone on Methyl Ethyl Ketone Peroxide Runaway Reaction" by Lin, Y-F et al., *J. Hazardous Materials*, Vol. 153, pp. 1071-1077 (2008).

Runaway reactions by methyl ethyl ketone peroxide (MEKPO) are an important issue in Asia, due to its unstable structure and extensive heat release during upset conditions. This study employed differential scanning calorimetry (DSC) to draw the experimental data for MEKPO 31 mass% and with acetone 99 mass% on three types of heating rate of 2, 4, and 10°C/min; the kinetic and safety parameters were then evaluated via curve fitting. Through the reproducible tests in each condition, the results show that acetone is not a contaminant, because it would increase the activation energy (E_a) and onset temperature (T_o) when combined with MEKPO, which differs from the hazard information of the material safety data sheet (MSDS).

16. "Studies on the Runaway Reaction of ABS Polymerization Process" by Hu, K-H, Kao, C-S, and Duh, Y-S, *J. Hazardous Materials*, Vol. 159, pp.24-34 (2008).

Taiwan has the largest acrylonitrile-butadiene-styrene (ABS) copolymer production in the world. Preventing of unexpected exothermic reactions and related emergency relief hazard is essential in the safety control of ABS emulsion polymerization. A VSP2 (Vent Sizing Package 2) apparatus is capable of studying both normal and abnormal conditions (e.g., cooling failure, mischarge, etc.) of industrial process. In this study, the scenarios were verified from the following abnormal conditions: loss of cooling, double charge of initiator, overcharge of monomer, without charge of solvent, and external fire. An external fire with constant heating will promote higher self-heat rate and this is recommended as the worst case scenario of emulsion polymerization with butadiene. Cooling failure coupled with bulk system of reactant was determined to be the credible worst case in ABS emulsion polymerization. Finally, the emergency vent sizing based on thermokinetics from VSP associated with the DIERS methodology were used for evaluating the vent sizing and compared to that of the industrial plants.

17. "Risk Evaluation on the Basis of Pressure Rate Measured by Automatic Pressure Tracking Adiabatic Calorimeter" by Iwata, Y. and Koseki, H., *J. Hazardous Materials*, Vol. 159, pp. 35-41 (2008).

An automatic pressure tracking adiabatic calorimeter (APTAC) has been employed to obtain the thermokinetic and vapor pressure data during runaway reactions. The APTAC is an adiabatic calorimeter with a large-scale sample mass and low thermal inertia, and is an extremely useful tool for assessing thermal hazards of reactive chemicals. The data obtained by the APTAC are important information for the design of the safe industrial process. The thermodynamic parameters and the gas production are discussed on the basis of the experimental data of various concentrations and weights of di-tert-butyl peroxide (DRBP)/toluene solution for the purpose of investigating the properties of the APTAC data. The thermal decomposition of DTBP was studied on the basis of the temperature data and the pressure data obtained by the APTAC. The activation energy and the frequency factor of DTBP are nearly constant and the same as the literature values in the concentrations between 20 and 60 wt%. The pressure rise due to gas production is important data for designing the relief vent of a reactor. The time history of the gas production was investigated with various weights and concentrations. The total gas production index, which had the vapor pressure correction, was 1.0 in the decomposition of DTBP.

18. "Rigorous Calculation of Critical Flow Conditions for Safety Devices" by Raimondi, L., *Process Safety and Environmental Protection* (Trans. IChemE), Vol. 85, Issue B4, pp. 277-288 (July 2007).

Sizing and verification of pressure relieving systems is an important topic in the design of plants in order to assure equipment and people protection against malfunctions and hazards. The calculation of the critical flow (choke) condition is analyzed with respect to existing calculation procedures (API and Omega methods) that implement approximate procedures and may not be extended to temperature/pressure regions near the thermodynamic critical point. These procedures may be replaced by a more rigorous calculation based on the evaluation of the local sonic velocity with equations of state. The method applies to systems composed of pure chemical components as well as to multi-component mixtures existing in the single phase and multi-phase regions. As a consequence of an exact calculation of the critical flow conditions, accurate values of the discharged flow rate may be obtained. Comparisons with calculations performed using the standard API RP 520 procedure and Omega method are presented.

19. "Study on Thermal Decomposition Characteristics of AIBN" by Li, X-R, Wang, X-L, and Kosecki, H., *J. Hazardous Materials*, Vol. 159, pp. 13-18 (2008).

It is found that the results such as observed in the DSC calorimeter, which shows the major thermal decomposition of a self-reactive material, lack the detail to reveal what happens at the initial stage of a reaction. The reaction at this stage is corresponding to the handling condition of storage or transportation, often possibly having the potential to be developed to a runaway reaction. This paper examined and compared the thermal behavior of AIBN at various working conditions in calorimeters and Dewar vessels. The mechanism that affects the initial reaction and self-heating behavior of the given material was clarified. Near its onset decomposition temperature, physical processes, such as sublimation or melting, interfered with the initial reaction of AIBN. The mutuality of the physical effect and the chemical reaction made AIBN behave differently under different measuring conditions, and as the result, quasi-autocatalysis or thermal decomposition possibly occurs in the same sample at the temperature range. The heat accumulation storage tests in two Dewar vessels presented completely different self-heating behaviors due to this mechanism and heat transfer capability of the vessels.

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