Organic Process Research & Development **2009,** *13,* 1388–1394

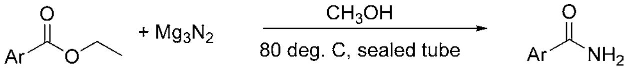
Safety Highlights

Safety Notables: Information from the Literature

This is the seventh annual literature overview on safety issues, which are of interest to process chemists and engineers, to appear in *Org. Process Res. Dev*. As in the previous years, this review will cover recent articles from the literature which address safety issues, common safety mistakes which seem to be repeated all too often, and major industrial accidents. This report was not intended to be all inclusive of the safety literature nor should the information presented be used to make decisions regarding safety without reading the full text of the appropriate article. The intent was to give a flavor of the issues facing other chemists and engineers and how they are solving these problems.

Chemical Safety Explosion Hazard

A safety letter appeared in the April 13, 2009 issue of *Chem. Eng. News* which alerted readers of a potential explosion hazard associated with the reagent magnesium nitride (Mg_3N_2). The author, Sheldon Crane, and his research team were using this compound for direct primary amide formation from esters according to a reported protocol (*Org. Lett.* **2008**, *10*, 3621).



The procedure was followed on at least two occasions without incident; however, when the reaction was scaled up, a violent explosion occurred. The explosion was strong enough to shatter the thick-walled Pyrex sealed tube and to sever the metal holding clamp. Fortunately, no one was injured. The published procedure calls for stirring in a room temperature water bath for one hour prior to heating to 80 °C. According to the authors of the *Org. Lett.* paper, a significant exotherm occurs during the formation of ammonia from magnesium nitride, and the water bath is used to control this exotherm. In the experiment that caused the explosion, the room temperature water bath technique was not employed and the resulting exotherm was not sufficiently controlled. Given the newly discovered potential hazard associated with the use of this reagent, the authors state that the published proceedure should be followed exactly as written and only on a scale comparable with those reported in the original paper. It is noted that extreme care should be used by anyone following this procedure in the future. A follow-up letter also appeared in *Chem. Eng. News* from Steven Ley, whose research group published the original *Org. Lett.* procedure (*Chem. Eng. News* **2009**, June 8, 4). Professor Ley expressed extreme concern that the accident had resulted. Despite having carried out over 200 magnesium nitride reactions in the past without incident, they did observe explosions in recent additional work when heterocyclic (indole and furan) esters were used as substrates. Steven Ley writes that, in view of these results, the procedure in the initial *Org. Lett.* paper should be followed with extreme care.

A follow-up letter on the safety aspect of this reaction was written by Gary Buske and published in a recent issue of *Chem. Eng. News* (*Chem. Eng. News* **2009**, July 13, 3). After a literature review and some calculation, he proposes that a safer way to run the reaction would be to add the magnesium nitride in small portions, or to dissolve/slurry the ester and magnesium nitride in an inert solvent such as toluene, diglyme, etc., and slowly add the methanol at a rate to control the reaction.

Laboratory Process Safety

Details of the recent fatal fire at UCLA involving *tert*-butyl lithium are extensively described by Jyllian Kemsley (*Chem. Eng. News* **2009**, *87*, 29−31). This article not only shows lab notebook entries, but also has a plethora of additional information and web links regarding the incident and associated safe handling practices.

Other tragic laboratory accidents involving chemicals have increased awareness about laboratory safety. A series of papers published this year in the *J. Chem. Health Saf.* attempt to address some of the issues of operating in a laboratory environment with chemicals.

One article by Neal Langerman (*J. Chem. Health Saf.* **2009**, March/April, 23) examines three incidents (hexane fire, reflux system failure and sodium fire) for their root and contributing causes and reviews the lessons learned. It also presents a section on incident prevention and a list of useful laboratory reference texts related to safety.

Another paper by the same author (*J. Chem. Health Saf.* **2009**, July/August, 22) advocates the use of the OSHA process safety management (PSM) approach to hazard recognition and assessment in laboratories and pilot plants. The article outlines the principles of PSM and how it can be applied to laboratories and pilot plants to minimize risk in these environments of frequent change.

In a related article, Joseph Zakzeski describes how a total quality management plan was developed and implemented at University of California Berkeley to improve general laboratory safety and augment existing safety plans (*J. Chem. Health Saf.* **2009**, May/June, 5).

Effective Emergency Shower and Eyewash Programs

When accidents do occur, emergency procedures and equipment are needed to minimize the effects of the accidental exposure to chemicals. In an article by Glen Ketchan and Vince McCleod, four take-home messages are discussed on the use of emergency showers and eye wash stations to provide the immediate decontamination often required in a laboratory accident (*Lab Manager* **2008**, September/October, 42). The four

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take home messages are (1) Speed to action - time to decontamination is critical in minimizing injury; (2) Duration - rinse the affected area for a sufficiently long time; (3) Access - maintain free and unimpeded access to emergency equipment; and (4) Equipment - use appropriate and maintained equipment. Advice is given on how to implement these points and what to look for in the emergency showers and eye wash stations in the lab you are working in.

Thermal Stability of Flavianic Acid Disodium Salt

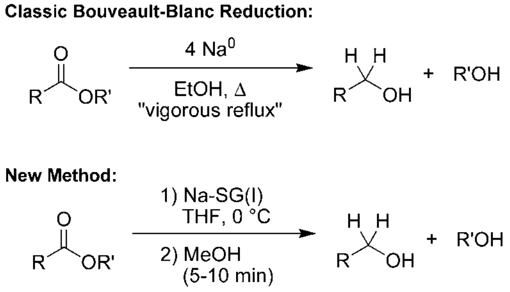
Flavianic acid disodium salt (a dinitro naphthyl sulfonate also known as naphthol yellow S) was involved in a spontaneous combustion incident during grinding in 2003. Fu and co-workers report on their investigation of the thermal stability of the sodium salt and the acid hydrate (*J. Loss Prev. Process Ind.* **2009**, *22*, 477). They attempted to use CHETAH to predict the stability of the two species, but were unable to get accurate estimates for the salt because the $-$ONa and $-SO_3Na$ groups are not available in CHETAH 7.3. The free acid hydrate is considered a high hazard in 5 of the 6 criteria. TG-DTA tests on the salt show an endotherm at 110 °C and a sharp exotherm at 375 °C. DSC test of the salt showed an exotherm at 371.9 °C. The PVT test of the salt give burst ratios of 9/10 and 1/7 for 1.0 mm and 9.0 mm orifices respectively. Four different particle size samples of the salt were tested by ARC (heat-wait-search and isothermal modes). There was little difference in the ARC results for the four different samples. The average onset for the exothermic decomposition was 294.70 °C in the HWS mode and 272.83 °C in the isothermal mode (both believed to be uncorrected). The onset occurred at a much lower temperature for the flavianic acid hydrate (160 °C). The C80 gave exothermic onsets of 149 and 211 °C for the acid hydrate and the salt respectively. They remind us that the ARC and C80 often give us much lower onset temperatures than the DSC (100−160 °C lower in this case). The lowest detected onsets were observed in the C80 tests in which the acid hydrate had onsets 62−134 °C lower than the disodium salt.

Conducting Process Hazard Analyses for Dust Handling Operations

According to Peter Stickles, et al. “three of the four deadliest incidents that have occurred since the U.S. Chemical Safety and Hazard Investigation Board (CSB; www.csb.gov) was created in 1998, have been dust explosions” (*Chem. Eng. Prog.* **2009**, *105* (2), 28). The CSB has been calling on the U.S. Congress to pass legislation requiring the U.S. Occupational Safety and Health Administration (OSHA) to better regulate workplaces that involve hazardous dusts. In 2007−2008 OSHA carried out a national emphasis program (NEP) about hazardous dusts. However, additional comprehensive legislation has not made it into law yet. Stickles and co-workers give an excellent overview of dust hazards and more importantly provide guidance to the reader how to use a checklist technique to begin carrying out process hazard analyses on operations involving hazardous dusts. They provide references to many critical standards and resources, give examples of checklists and matrices and links to free software to help get the reader started.

Improved Bouveault−Blanc Reductions

Before the advent of widely available hydride reagents, reduction of esters to primary alcohols was generally performed with alkali metals in ethanol, the Bouveault−Blanc reduction. Due to hazards associated with alkali metal handling and the vigorous reaction conditions (typically refluxing toluene or xylene), this process has been largely replaced by the use of metal hydrides such as lithium aluminum hydride (LAH) or sodium borohydride. A recent report describes an improvement upon the classic Bouveault−Blanc procedure that utilizes stabilized alkali metals, sodium in silica gel, to prepare primary alcohols from aliphatic esters in high yield (*J. Org. Chem.* **2009**, *74*, 2598).



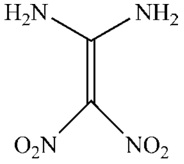
A mini-review of this new technology for the stabilization of sodium and other alkali metals, and their use in synthetic organic chemistry, was also published (*Manufact. Chem.* **2009**, *80*, 3 (April), 38).

Minimum Ignition Energy for Nano Titanium Powder and Nano Iron Powder

Nano materials continue to increase in acceptance for use in manufactured products and manufacturing. The attraction to these materials rests in the fact that their physical properties and reactivity can be drastically different from the same material with a larger particle size. Whenever these products are processed it is important to re-evaluate physical and reactivity parameters for the nano material and not rely on our past experience with the larger particle material. Wu and co-workers present the results of their minimum ignition energy tests for two nano metals, titanium and iron (*J. Loss Prev. Process Ind.* **2009**, *22*, 21). Among the nanoscale-powder manufacturing units in Taiwan, 100% have experienced dust explosions, highlighting the hazard of handling these materials. The authors used a 1.2 L Hartmann apparatus to test Ti powders with particle sizes of 45 μm, 20 μm, 8 μm, 3 μm, 100 nm, 75 and 35 nm. They tested Fe powders with particle sizes of 150 μm, 65 nm, 35 nm, and 15 nm. Each powder was tested at 7 spark energies and 6 concentrations. The lower limit of their test equipment was 1 mJ. The 8 μm, 20 μm, and 45 μm Fe powders had MIEs of 21.91, 18.73, and 21.91 mJ respectively. However, the 3 μm and all nanometer Fe powders had MIEs of 1 mJ or less. The 150 μm Fe powder failed to ignite at all concentrations and energy levels. However, all nano Fe samples had MIEs of 1 mJ or less.

Synthesis of Energetic Materials

Many readers of this review are looking for ways to lessen, or avoid all together, working with molecules that have hazardous thermal properties. However, scientists working to prepare novel propellants and explosives, such as Waldemar Trzcinski and colleagues, deal with the dangers and rigors of working with thermally unstable compounds on a daily basis. In one such example, the preparation and detonation properties of 1,1-diamino-2,2-dinitroethene (DADNE) (*J. Hazard. Mater.* **2008**, *157*, 605) is outlined in good detail. An additional report on the development of a recrystallization method for DADNE and on novel HPLC conditions to determine the purity of the desired molecule in a safe manner was also published (*J. Hazard. Mater.* **2009**, *162*, 1051).



DADNE

In a related article, Jalový and co-workers report the isolation and characterization of seven new salts of dinitromethane (DNM) (*Tetrahedron* **2009**, *65*, 7163). The materials were prepared by two new synthetic methods: (1) reaction of the organic base with DNM in ethyl acetate or (2) by ion exchange of sodium DNM and an organic base salt in water. ^{1}H and ^{13}C NMR chemical shifts, elemental analysis and IR data are given for all salts. Differential thermal analysis decomposition onsets are also provided for all salts and range from 98 °C for piperazinium bis(dinitromethanide) to 153 °C for acetamidium dinitromethanide. X-ray crystal structures are provided for three amidine analogues and the isolated yields for the salts ranged from 36% to 79%.

Reading these types of papers gives a solid background on the preparation of thermally energetic compounds. Hopefully, it can lead to insights into the proper amount of data required prior to synthesizing other potentially unstable targets on-scale.

Toxic Tips

William E. Luttrell continues to write reviews on organic molecules and the precautions which should be taken while working with these compounds. These molecular safety reviews appear in *J. Chem Health Saf.* and are a good addition to the MSDS which should be read prior to working with any new organic compound. Cyanogen bromide (*J. Chem Health Saf.* **2009**, July/August, 29) and acetaldehyde (*J. Chem Health Saf.* **2009**, September/October, 43) are two of the chemicals covered more recently.

Inherently Safer Technology

Trevor Kletz in his book on plant design (*Plant Design for Safety*; Hemisphere Publishing Corporation: New York, 1991) stated, “The essence of inherently safer approaches to plant design is the avoidance of hazards rather than their control by added-on protective equipment.” Trevor Kletz also proposed the five fundamental principles of inherent safety: minimization, substitution, attenuation, simplification, and limitation of effects. This year, as usual, many articles were published which discussed the principles of inherently safer design of chemical processes and process plants.

Valerio Cozzani et al. recently published an article on inherent safety key performance indicators for hydrogen storage systems (*J. Hazard. Mater.* **2008**, *159*, 554). With the growing increase in the use of hydrogen as an energy vector expected in the coming years, the need to store the hydrogen produced should increase as well. The results of the detailed studies concluded that the potential hazard is always lower for the innovative technologies proposed for hydrogen storage, as in metals or complex hydrides. The same authors expanded the scope of their research to the key performance indicators for inherent safety and its application to the hydrogen supply chain (*Process Saf. Prog.* **2009**, *28*, 156). In this work, a novel quantitative approach developed for the inherent safety assessment of process flow diagrams in early design stages is presented.

In a third article, the evaluation of an intensified continuous heat-exchanger reactor for inherently safer characteristics was reviewed. Benaïssa and co-workers used esterification of propionic anhydride by 2-butanol as a model reaction to evaluate a prototype heat exchanger/reactor called an open plate reactor (OPR) provided by Alfa Laval Vicarb (*J. Loss Prev. Process Ind.* **2008**, *21*, 528). The reaction occurs in the liquid phase, and the kinetic model is available for the reaction. The OPR is built like a multiplate heat exchanger in which the reaction mixture contacts poly(ether ether ketone) (PEEK). The total capacity of their system was 1.5 L. The OPR can be treated as a plug flow reactor and was modeled as series of 91 perfectly stirred tank reactors. A HAZOP was done for the apparatus and identified three scenarios as the most dangerous: no utility flow, no reactant flows, and stoppage of both the utility and reactant line. The runaway reaction was simulated for the system, and the process was found to be intrinsically safer because significant heat losses to the apparatus would reduce the adiabatic rise by 20−60 °C. Additionally, the reduced inventories in the reactor would minimize the consequences of a runaway.

Influence of Contamination on the Runaway Reaction of Hydrogen Peroxide

The decomposition of peroxides is well-known to be very sensitive to contamination, especially those of metals. Eto et al. studied the effect of contamination by a variety of metal salts (*J. Loss Prev. Process Ind.* **2009**, *22*, 15). Thirty-one different tests were run using a simple open-top glass vessel (83 mL) which prevented contact with metals of construction, allowed stirring to rapidly dissolve the salts, allowed substantial amounts of material to be used safely, and allowed direct visual observation of the reaction. As expected iron and copper were found to accelerate the decomposition, while nickel and potassium proved to be inert. While none of the anions were able to catalyze the decomposition, it was found that the anion did affect the rate with chloride accelerating the reaction and nitrate and sulfate decreasing the rate.

Mary Kay O’Conner Process Safety Center Symposium

A special issue of the *J. Hazard. Mater.* **2008**, *159*) was published which contained papers presented at the 2006 Annual

Symposium of the Mary Kay O'Conner Process Safety Center. The event was held in October 2006 near the campus of Texas A&M University in College Station, Texas. According to the forward written by M. Sam Mannan, the objectives of the symposium were the following:

(1) to provide the stakeholders with research reports and updates on the activities and programs of the Center
(2) to identify the complex problems facing the industry today, through the discussions and forum activities of the symposium, and bring the tremendous expertise and resources available at the Center to provide research and educational support to solve these problems
(3) to provide an independent and unbiased forum for the exchange of ideas and discussion among academia, industry, regulators and the general public

One contribution to the event was a study on thermal decomposition characteristics of 2,2′-azobis(isobutyronitrile) (AIBN). AIBN is used widely as a blowing agent and initiator. It is a typical self-reacting material, and as it is an azo compound, it belongs to Class 5 in the UN classification, having a risk for runaway due to its self-heating during storage or transportation. This paper (*J. Hazard. Mater.* **2008**, *157*, 13) examined and compared thermal behaviors of AIBN in various working conditions in calorimeters and Dewar vessels. The results indicate that the different storage conditions can have a large effect on the self-heating behaviour of AIBN and on its self-accelerating decomposition temperatures (SADT). It is implied, therefore, that only after all factors that influence self-heating are made clear can the determination of what may occur near the SADT of any azo compound be made.

Gregg Kiihne of BASF contributed a paper on root cause determination studies and improvement initiative results to find out 'What really went wrong?' in an accident or incident (*J. Hazard. Mater.* **2008**, *157*, 112). The paper discusses how many organizations do not determine what are the true root causes of incidents—the absence, deficiency, or neglect of the management systems that control human actions and equipment performance—stopping rather at the human error or equipment failures most closely related to the incident. Internally, over 1000 incident reports were reviewed, and a new program for the determination of root cause analysis was developed. The article outlines the development of this new process and the lessons learned.

A third contribution was a review of the U.S. Chemical Safety and Hazard Investigation Board's comprehensive investigation into the runaway chemical reaction at the MFG Chemical plant on April 12, 2004 (*J. Hazard. Mater.* **2008**, *157*, 2). This accident resulted in the uncontrolled release of a large quantity of highly toxic and flammable allyl alcohol and allyl chloride into the environment. The article outlines the incident that occurred, the factors that led to the incident, the pre-incident emergency planning, the emergency response, the key findings of the CSB investigation and the CSB recommendation. Of note in the article are the issues that surrounded the tolling arrangement between the end user and MFG. The authors state that there were flaws in the agreements and goes into detail on the responsibilities that toll manufacturers have in such relationships.

In a last example from the symposium, Russell Ogle and co-workers discussed the relationship between automation complexity and operator error (*J. Hazard. Mater.* **2008**, *157*, 135). It has been argued that manual operations provide too many opportunities for human error, and thus process automation should decrease the risk of accidents caused by operator error. Through the analysis of six separate explosions involving operator error in an automated process facility, the authors conclude that abnormal operating conditions can pose a serious threat to safe running of chemical process without regard for the level of automation. To run safely, the operator must have the information needed to diagnose the problem, must receive the information with adequate time to respond, and must have the appropriate skills and knowledge to implement the corrective action.

Borane as a Protective Group for Pyridine

Matthew Zajac published a report on the use of borane as a protecting group of pyridines and other heterocycles that contain nucleophilic nitrogens (*J. Org. Chem.* **2008**, *73*, 6889). Often, an *N*-oxide is employed to occupy the lone pair of the pyridine moiety, but as in the case described in this article, handling, removal and safety issues with *N*-oxides can limit their use on-scale. A detailed description on the thermal safety data of 2-chloropyridine *N*-oxide is given, and the use of borane as a protecting group in the scale-up synthesis of a vitronectin inhibitor is described.

An Unexpected Explosion

Alan Katrizky submitted a safety letter related to an unexpected explosion of the potassium salt 2,4,6-trinitroso-1,3,5-benzenetriol (*Chem. Eng. News* **2008**, October 6, 4). The compound was prepared according to the literature procedure of R. Benedikt (*Chem. Ber.* **1878**, *11*, 1374) which gave a decomposition onset of 130 °C. The material exploded spontaneously upon standing an hour and a half after preparation. Interestingly, analogous compounds are documented in *Bretherick's Handbook of Reactive Chemical Hazards* as being explosive and unstable. A response to the incident was posted by chemical safety expert Neal Langerman, who commented that nitroso compounds are generally energetic and frequently decompose. Also, he stated that several related compounds are known to be explosive, and that when working with such compounds synthetic chemistry should be conducted with appropriate controls to prevent an explosion and to limit the size of an energetic event, should one occur.

We are reminded of the importance to include appropriate warnings when one publishes work involving materials known to be hazardous. Similarly, one must exercise caution and diligently investigate stability data before preparing materials that may be energetic.

Continuous Flow/Microreactors

Continuous flow processing has become more popular over the past few years due to precise temperature control and superior mixing. The low reaction volumes are advantageous from a process safety perspective and also allow for material-sparing process development which can be fully automated, allowing for 24 hours a day operation if incorporated in an intelligent system. Finally, transfer of a continuous flow process from the laboratory to production scale is relatively easy because there is no need to reoptimize due to changes in thermal and mass transfer properties. The following is a sampling of the continuous flow literature that has appeared this year.

A general and efficient procedure for the conversion of esters into the corresponding hydroxamic acids with good yields and purities using a commercially available continuous flow reactor was published (*J. Org. Chem.* **2009**, *74*, 3540). After a program to optimize the reaction conditions, the protocol developed is quite general and works with aryl esters, alkylaryl esters, simple amino esters, Boc-protected amino esters, sulfonamide esters and heteroaryl esters. The protocol was also expanded to the first reported synthesis of the suberoylanilide hydroxamic acid (SAHA) by a continuous flow process.

Last year's review included a report by Steven Ley and co-workers on a fluorination method using DAST in a continuous flow microreactor (*Synlett* **2008**, *14*, 2111). In a continuation of that work, a full article was published this year on a series of fluorination methods including nucleophilic fluorination, electrophilic fluorination and trifluoromethylation facilitated using a modular flow reactor (*Tetrahedron* **2009**, *65*, 6611).

Greenness of Alternative Reaction Media

One of the major efforts of Green Chemistry is to replace toxic and hazardous substances with less hazardous, less volatile, nontoxic alternatives. In spite of much research effort, most organic solvents still used in chemistry are volatile and often hazardous both to humans and the environment. The solvent performances and ecological advantages and disadvantages of different solvent systems for a Diels−Alder reaction were published by Denise Reinhardt and co-workers (*Green Chem.* **2008**, *10*, 1170). Within this study, new potentially green solvent alternatives were examined for the Diels−Alder reaction between cyclopentadiene and methyl acrylate. These results were compared with a solvent-free version and with the standard organic solvents for this transformation. Several promising new solvents were found including $[C_6MIM][BF_4]$(1-hexyl-3-methylimidazolium tetrafluoroborate) and citric acid/*N*,*N*′-dimethyl urea. Several metrics to compare the relative greenness of these new solvents were discussed.

In a related article, Istvan Horvath gives a personal journey from solvent to solvent to demonstrate environmentally friendly solvents can be part of be solution of various chemical challenges (*Green Chem.* **2008**, *10*, 1024). He concludes that the development of solvent-free alternative processes is the best solution, especially when one of the components of the reaction is a liquid and can be used as the solvent in the reaction. However, if the solvents are crucial to a process, one should select from solvents that will have no or limited impact on health and the environment.

Trimethylsilyldiazomethane Fatalities

Trimethylsilyldiazomethane is described as a stable and safe substitute for hazardous diazomethane and is useful as a reagent for introducing a C_1 in chemical synthesis (*Organic Syntheses*; Wiley: New York, 1993, Collect.Vol. *8*, 612). Although this reagent is reported to be less volatile and energetically more stable than diazomethane itself, it is still an extremely dangerous chemical from a human toxicity point of view. There have been two reported fatalities from exposure to TMS-diazomethane since January of 2008 (http://www.canadaeast.com/front/article/666039).

Derek Lowe commented on these fatalities in a recent blog (http://pipeline.corante.com/archives/2009/01/23/the_real_hazards_of_the_lab.php). The problem with these sorts of reagents is that serious respiratory issues are not evident immediately. Diazomethane, phosgene, methyl bromide and others can actually take hours to kill a person, and for a good part of that time, the only symptoms might be a slight cough. These fatalities have also raised concerns over the availability and quality of Material Safety Data Sheets (MSDS). Several available sources significantly understate the hazards of these materials, and anyone who works with such volatile and damaging reagents needs to be fully aware of the potential hazards involved (http://pipeline.corante.com/archives/2009/05/19/tms_reagents_handle_with_care.php).

Proper Hood Operation

The laboratory hood is an important and often critical piece of equipment in many laboratories. However, biosafety cabinets, chemical fume hoods and laminar flow benches are easy to operate improperly and can be influenced by subtle factors in the lab environment. James Sigler wrote an article which outlines the sweet spot for effective hood use (*Lab Manager* **2009**, July/August, 24). Key factors include the operator properly interacting with the hood, having an environment in which the hood can be used properly, and last, the hood itself must be installed and working correctly. The author also comments on choosing a certification company for the hood in your facility. The key is that a good technician will arrive with a cart full of testing gear and not just a briefcase!

Before OSHA Comes Knocking

Since June 2007, OSHA has been implementing a national emphasis program (NEP) around process safety management (PSM) in the petrochemical industry which includes the detailed inspection of 81 refineries. The agency has announced its intent to expand the NEP to include the chemical industry. Steinway, et al. reviewed the findings made by OSHA during the detailed inspections of petrochemical facilities and discussed the trends (*Chem. Eng. Prog.* **2008**, *105*, 3, 28). During inspections of the first 20 facilities 516 citations were issued with penalties exceeding $2.7 million USD. The most common violations were related to operating procedures, process safety information pertaining to equipment, and process hazard analysis criteria. For the chemical industry, OSHA will focus on facilities that are considered Program 3 facilities under the EPA risk management program (RMP). On the basis of trends in the refinery inspections and informal statements made by OSHA the authors make a number of recommendations about how to best prepare for the inspections, e.g. chemical reactivity process safety information, identifying chemical reactivity hazards, and stability data for chemical storage.

Effective Investigations

After a 30-year career in industry, manufacturing and process safety, John Murphy worked as an investigator with the U.S. Chemical Safety and Hazards investigation Board (CSB). In a recent article, John describes what he has learned as an investigator (*Process Saf. Prog.* **2008**, *27*, 266). The article discusses his 10 keys to an effective incident investigation with examples from investigations in which he has participated.

Maintaining Safety during Corporate Transitions

Change in the chemical industry is a constant, and with the recent economic downturn, the rate of changes at chemical companies has increased. Layoffs, downsizing, site closures, retirements, reorganizations, and changes in ownerships present a real challenge from a safety perspective. Two articles appeared this year to address several of these concerns.

The first report was a discussion on the loss of corporate memory in the chemical industry and how it may cause accidents with the retirement of experienced staff (*ICIS Chem. Bus.* **2008**, October 3, 12). The article correctly states that there is a pattern of generic failures that is common to all of the recent incidents and, sadly, bears a remarkable similarity to lessons the industry should have learned in the past. The U.K. Health and Safety Executive has clearly communicated the need to raise the bar, collectively, on process safety management, leadership, and safety culture across the whole major hazard industry.

In a second article, Bob Alaimo describes the challenge of maintaining safety during a downsizing (*J. Chem. Health Saf.* **2009**, July/August, 42). The author states that the time preceding a layoff or a merger, when the rumors are flying, is a time when attention to safe work practices and safety awareness goes out the window. Once the downsizing begins the potential for bad things to happen increases. The reasons for these increases is outlined in the article. To limit these incidents the safety department staff should spend their time walking around in the work areas and laboratories, and facility directors need to speak with the on-site safety professionals as much as with the MBAs and CPAs during any downsizing event.

Safety of the Process Industries in the 21st Century

Knegtering and Pasman ask the question—why do we continue to have serious accidents for processes with known hazards in spite of the process safety and hazard analysis tools at our disposal today (*J. Loss Prev. Process Ind.* **2009**, *22*, 162). They examine three case studies of petrochemical explosions: Dutch Petroleum natural gas condensate in The Netherlands, BP America refinery in Texas, U.S.A., and the Buncefield oil storage and transfer depot in the U.K.. None of these accidents was caused by unknown physical or chemical process hazards. None occurred due to a single problem or failure. The authors state that the “bedding for having these accidents is mainly characterized by management quality and organization and human factors.” Process installations have become more complex and are being pushed to their operating limits. Process control equipment is more complex and is a larger distance from the manufacturing equipment. Large staff turnover, higher work load, job hopping, and outsourcing lead to additional oversights. They propose three focal points for the future. First an adequate process safety measurement system should be used, eliminating the use of personal accident rates as an indicator of the probability for a catastrophic event. Second, they highlight the need for evaluation and analysis and a continuous learning system. Third, a holistic approach toward control is needed, combining the safety culture with technical safety and hazard analysis methods.

Process Safety Accountability

An article on process safety accountability, which highlights the importance of establishing a good process safety culture, was scribed by Dennis Hendershot (*J.Chem. Health Saf.* **2008**, September/October, 35). The article highlights the fact that many organizations tend not to set goals for process safety performance, but the situation is changing with the advent of recently proposed process safety measures (http://www.aiche.org/ccps/knowledgebase/measurement.aspx).

Potent Pharmaceuticals in Contract Manufacturing Operations

The development of toxic and more potent APIs has grown over the past two decades. This growth has paralleled the use of contract manufacturing organizations (CMOs) to synthesize and formulate these potent molecules. Allan Alder and his colleagues at SafeBridge Consulting published a review this year on the methods for health-based risk assessments that are being implemented with increasing frequency in the pharmaceutical industry by drug innovators, CMOs and regulatory authorities (*Pharm. Outsour.* **2009**, July/August, 48). The article describes an approach to determine and calculate occupational exposure limits, acceptable surface limits and acceptable daily intakes for worker protection and patient safety. The appropriate use of these health-based risk assessments will assist both the innovator and the contractor to determine the adequacy of the controls, work practices and procedures for worker and product safety. A review of how a CMO handles these issues should be a part of the due diligence process done by the innovator before placing any work at a contract facility.

The Cost-Benefit Analysis of an Investment in Safety

Gavious and co-workers apply the theory of constraints to better evaluate the true cost-benefit of investment in safety (*J. Loss Prev. Process Ind.* **2009**, *22*, 434). Obviously the true cost of a safety incident has both direct costs and indirect costs. The direct costs can be easily tallied, but indirect costs are more difficult to assess. The authors propose a model to better account for indirect costs and use it to evaluate two accidents. Since the literature supports the observation that, as work load increases the probability of industrial accidents increases, then we should expect bottlenecks to have a greater number of incidents. This fact is important in assessing the cost-benefit of safety investment because indirect costs are higher if damage occurs at a bottleneck of a production process (capacity lost, scheduling upsets, and increased work in progress). The study should help management value the cost of investments in safety while ensuring that those resources are spent effectively.

The Need for Thermal Hazards Assessment

The Chemical Safety Board recently issued their final report into the fatal explosion that occurred at the T2 laboratories, Florida, in 2007. A thermal runaway resulted during the preparation of a gasoline additive, methylcyclopentadienylmanganese tricarbonyl (MCMT). The incident occurred during the preparation of the 175th batch of material, and the root cause was highlighted as T2 not recognizing the reaction hazard associated with the preparation of the MCMT. This incident, like many others in the past involving different companies, highlights the importance of thorough thermal hazard assessments of reactions. For the full report please go to http://www.chemsafety.gov. The report also includes a safety video describing the incident.

Learning from History

It is worth highlighting that this year marks the 25th anniversary (December 3, 1984) of the Bhopal incident that remains the world's worst chemical accident. During this incident many tons of toxic methyl isocyanate (MIC) were released into the atmosphere, and many thousands of people tragically died as a result. Many articles have been written on this tragedy, and without doubt many more will appear later this year (http://www.rsc.org/chemistryworld/News/2009/August/05080901.asp). Unconnected, but worth mentioning, is an incident at a Bayer Crop Science site in West Virginia, U.S.A., in 2008 that is still undergoing investigation by the U.S. Chemical Safety Board (http://www.csb.gov/newsroom/detail.aspx?nid=7). Although not involved in the incident, a 7-ton tank of methyl isocyanate narrowly escaped being struck by projectiles from the incident. Clearly, if this tank had been compromised, this disaster could have been on a much larger scale. Bhopal resulted in many companies moving to inherently safer processing options that negated the need to store large quantities of toxic materials. Bayer is actively addressing this issue, and learning from the past remains a constant challenge for us all.

Mining the Web for Safety Information

The following is a list of Web sites which the authors find useful for finding information on process safety and hazard analysis. If any readers have additions to this list we would be most interested in seeing them and perhaps including them in next year's review.

(1) ACS Green Chemistry Institute: www.acs.org/greenchemistry.

(2) Chemical Hazards Response Information System by the U.S. Coast Guard: http://www.chrismanual.com.

(3) Greener Educational Materials for Chemists at Oregon University: http://greenchem.uoregon.edu/gems.html.

(4) Standard system for the identification of the hazards of materials for emergency response: www.nfpa.org/aboutthecodes/AboutTheCodes.asp?DocNum=704.

(5) National Institute of Occupational Safety and Health pocket guide to chemical hazards: www.cdc.gov/niosh/npg.

(6) Safety videos from the U.S. Chemical Safety and Hazard Investigation Board: http://www.csb.gov/videoroom/videos.aspx?cid=1.

(7) U.K. Chemical Reaction Hazard Forum: http://www.crhf.org.uk.

(8) Chemical and Engineering New Safety Letters: http://pubs.acs.org/cen/safety/index.html.

(9) Center for Chemical Process Safety: http://www.aiche.org/ccps.

(10) European Process Safety Centre: http://www.epsc.org.

(11) International Process Safety Group: http://www2.icheme-ipsg.co.uk.

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