



CONTENTS

From the Secretary General's Desk	1
Introducing the new Governor	2
ESD ignitions, a manufacturer's experience	3
Influence of the European Track & Trace regulation on the security of usage and storage of civil explosives	4
Minimum Burning Pressure Test for Ammonium Nitrate Emulsions	6
Safe Treatment of Organic Contaminated Spent Acids	8
Compatibility of Ammonium Nitrate Systems with Sodium Salts	13
Safety considerations for the addition of organic additives when prilling Ammonium Nitrate	20
Ammonium nitrate emulsions, suspensions and gels explosion risk and risk controls for road transport	22
Concerns with the use of hollow pipes in explosives plants	30
Chance is a fine thing	32
IMESAFR Training	37

QUARTER 3 September 2016

SAFEX NEWSLETTER no.58

While **SAFEX International** selects the authors of articles in this Newsletter with care, the views expressed are those of the authors and do not necessarily represent the official position of **SAFEX International**. Furthermore, the authors and **SAFEX International** cannot accept any liability for consequences arising (whether directly or indirectly) from the use of any advice given or opinions expressed in this Newsletter

FROM THE SECRETARY GENERAL'S DESK

Three quarters through the year and another change of season is upon us. The Southern hemisphere is approaching Summer and the North, Winter—these changes are a constant in the lifecycle of man and we are used to it. Change out there, however, isn't constant, and life, technology and business as we knew it is changing at an ever rapid pace. The industry moved from NG to water based explosives over the period of 160 years, computers moved from vacuum tube systems to the smart phones in less than half that time. The speed of change is exponential. What changes does the industry anticipate in the next few years? What can be developed to make explosive rock breaking more safe and effective? 3D printing offers a vast potential in printing of many materials—what about explosives and detonators? How can the cost of production be driven down using energetic printing techniques whilst maintaining a high safety culture at all times? All these questions will be answered over the next 10 years for those prepared to risk innovation and hold SHE dear to their organisations.

Three incidents have been reported since the last Newsletter, the latest unfortunately resulted in two fatalities. SAFEX's condolences goes out to the families of the individuals and the Management Team dealing with the incident:

IN09-16 – RDX Explosion in Australia.

IN 10-16- A Gear Pump Explosion in Chile.

IN 11-16- Plant Explosion

Please learn from these and other incidents – **not repeating the errors of the past saves lives and business!!**

The deadline for submitting the draft papers for the plenary sessions is past and the Convenors thank the presenters for their efforts and being on time. The Plenary Session programmes will be communicated in due course after



CONGRESS XIX

NEXT CONGRESS
15-20 May 2017 at the
Scandic Grand Marina
Hotel

the Editing Teams completed their work on the papers.

On the eLearning front the good news is that the Spanish version of the BoS Module will be launched early in October .SAFEX thanks Enrique Barraincúa from MAXAM for doing most of the work on this module .The Russian translation is progressing well and work on the Incident Investigation Module is nearing completion.

Arrangements for the Congress in Helsinki are progressing well and a Brief on the proposed detailed programmes will be issued in October. After this documentation for registration and hotel bookings will be communicated to all SAFEX Member Contacts.

IMESAFR will also be conducting a training course in the week prior to the Congress ,at the Scandic Grand Marina Hotel .The course will cover their software ,that assists in assessing the overall risk of explosives operations-their bulletin is included in the Newsletter. Bookings are to be made directly with them.

In this Newsletter SAFEX welcomes Mike Powell from Incitec Pivot to the Board of Governors. He is replacing Steve Dawson who served in this position since 2011. SAFEX thanks Steve for his dedicated input and wish him all the best in his future ventures.

The Chairman and myself successfully reached out to several CEO's and senior executives over the last six months to update them and get commitment for future SAFEX initiatives and getting guidance as to what these companies expect of this organisation. This input will serve to assist in SAFEX's strategy to become a better serving industry organisation.

I have received a large number of articles and all of excellent quality for this Newsletter and ask for similar response for the last Newsletter of 2016 in December.

INTRODUCING THE NEW GOVERNOR –MIKE POWELL

Mike Powell BA(Env) MSc (OHS) PGCert(Law)



**Vice President Heath Safety & Environment
Incitec Pivot Limited**

Mike Joined IPL in 2012 as the Group Vice President HSE and since then has also joined the Global Manufacturing Leadership Team (2014) and Australian Manufacturing Team (2016).

Mike has 20 years' experience in senior leadership/executive team roles driving change and improvement with 10+ years at this level in global, multi business complex organisations like :

- Chemicals Manufacturing: Explosives and Fertilisers
- Defence: Manufacturing (aircraft, ships, land vehicles, munitions), Through life service
- Nuclear Life Cycle: Power, Reprocessing, Decommissioning and Waste Management

Prior to IPL Mike held senior HSE roles with BAE Systems plc (Defence Manufacturing & Services), British Nuclear Fuels plc (Power, Reprocessing & Decommissioning) and NUKEM Nuclear Limited (Nuclear Decommissioning and safety Services).

ESD ignitions, a manufacturer's experience by

**C. Guymon, Ph.D. Safety Management Services,
Inc.**

J. Shaver, Ph.D. Special Devices, Incorporated

INTRODUCTION:

Electrostatic discharge (ESD) is sometimes incorrectly accepted as the primary ignition source of an accidental ignition of an energetic material without identifying the two requirements for an ESD event as outlined in NFPA 77 (2014): (1) locations of where charge can separate and accumulate, and (2) assessment of the ignition hazards in the location of charge accumulation. Unfortunately, the misassignment and premature acceptance of ESD as the ignition source may be used to justify implementation of controls that create other potential hazards and a false sense of security.

Several years ago, a company reported that an electro-explosive device ignited during a visual inspection process in a workstation. Fortunately, the Technician's injuries were not severe. Company investigators quickly concluded the mishap was an ESD ignition and immediately installed wrist-straps at the workstation. Two days later, the mishap was repeated at the same inspection workstation. Fortunately, the Technician was not harmed. The investigation team took a more detailed and deliberate examination of both mishaps and discovered the workstation electrical connections were recently modified leaving an electrical fixture in the workstation ungrounded and live (220v).

ESD is unlikely to present a significant hazard when production facilities and manufacturing equipment are grounded and bonded properly. Locations of charge accumulation is thereby eliminated or significantly reduced. ESD is unlikely to present a significant hazard when energetic materials are transferred in approved containers where charge separation scenarios are limited and charge accumulation is also limited. Similarly, ESD is unlikely to present a significant hazard when energetic materials are completely contained (Faraday shield) and unexposed within the finished article. ESD is more likely to present a potential ignition hazard when explosive process controls (e.g., SAFEX Good Explosives Practice Series, Managing Electrostatic Discharges (ESD) in the Manufacture of Explosives) are ignored, bypassed or missing thus facilitating accumulation of electrostatic charges in areas where ignition sensitive material are processed. The NFPA 77 and SAFEX guidelines provide additional understanding and a sound approach to prevent ESD hazards in an explosive manufacturing environment.

BACKGROUND:

The SDI engineering team noted that mishaps involving pyrotechnic materials and articles before 2001 were too

frequently connected to ESD without a factual basis. Upon further examination of the mishap history, the engineers determined that process safety engineering and procedural controls were often bypassed or ignored when events likely connected to ESD occurred (e.g., sweeping spilled material with a broom, experimenting with unproven process controls, undocumented process changes).

The engineering team implemented a fact-based, data-driven approach to safety, quality and productivity improvements. The process improvements included augmentations to ESD controls, removal of non-value added ESD controls, and, the implementation of CCTV to monitor manufacturing operations and provide opportunity to re-examine mishaps. Process improvements had immediate results where mishaps connected with ESD decreased dramatically. The SDI engineering team continues to refine process controls and has confidence that lessons learned and guidelines recommended by SAFEX, NFPA, and others, can minimize the likelihood of unplanned ignitions.

One of the resources the SDI team examined for ESD controls was the electrostatic energy controls and measurement instruments applied to the production of electronic components. The electronics industry recognizes three main test models for ESD; the human body model (HBM), the charged device model (CDM), and the machine model (MM). The HBM simulates ESD due to discharge from human beings and people are considered a principal source of ESD in the electronics industry. The HBM is a commonly used model to describe an ESD event in the electronics industry. CDM simulates the discharge of a charged device when it comes in contact with a conductive material. The MM represents an ESD from an object to an article. Any production tool or equipment (machine motion) could potentially present an ESD threat.

ESD – Human Body Model (HBM)

When people walk/move they generate electrostatic energy and generally discharge the electrostatic energy generated to ground without issue. HBM ESD events have fast rise times and fast rise time pulses are required to accurately simulate a HBM discharge event.

ESD Test – Charged Device Model (CDM)

CDM simulates an article charged either directly by triboelectric effect or electrostatic induction. A static charge stored on an article discharges to the outside environment. This test may be used to simulate conditions in manufacturing environments (e.g., article sliding down a transfer tube or chute, article being handled on a track). CDM current measurements are likely to be higher than HBM currents because there is no current limiting resistor in the path to limit the discharge.

ESD Test – Machine Model (MM)

The MM is designed to simulate production equipment discharging through a device to ground. The amount of charge can be significantly greater than that of a smaller device or a human body discharge depending on the capacitance of the machine. Failure modes in MM testing can be similar to those in HBM testing which are primarily related to prevention of charge accumulation.

ESD Hazards – Testing

ESD testing is frequently used to evaluate the ignition hazards in areas of charge accumulation. Two common tests include minimum ignition energy (MIE) testing with a spark in a 20-liter sphere to evaluate dust ignition characteristics, and Method 1032 of MIL-STD-1751A to determine the energy threshold required to ignite explosives by ESD. Ignition tests can also include documenting the power and energy required for igniting articles for a given ESD model (three described above) to properly evaluate the associated risk of ignition of that article. Processing conditions should be closely reproduced or included in the risk analysis to accurately assess the initiation risk. A qualified person should be consulted to examine potential ESD hazards in the production environment.

CONCLUSION

ESD should not be the auto-default root cause when examining mishaps involving explosive substances and articles prior to evaluating (1) locations of where charge can separate and accumulate, and (2) assessment of the ignition hazards in the location of charge accumulation. Better understanding of ESD charge accumulation and ignition hazards has resulted in significant risk reduction as well as cost savings from proper implementation of ESD safeguards.

Charge accumulation near energetics is most likely when the energetic substance is moving or under other conditions where there is significant contact and separation with solids, liquids, or gases. When the energetic is enclosed in a properly grounded package or article, charge separation and accumulation is less likely as stated in the US Department of Defense Contractor Safety Manual, C6.4.2, Static Electricity Hazards:

“ESD does not present a substantial hazard during the handling of most bulk explosive substances if the explosives are in approved containers. It also does not present a hazard near explosives totally contained and unexposed within loaded articles. It is not possible to prevent the generation of static electricity entirely. Elimination of potential ESD hazards requires proper grounding to dissipate static charges before they accumulate to danger-

ous levels.”

When considering production and handling of explosive substances and articles, the potential for ESD hazards should be given proper examination by qualified persons. The emphasis should be fact-based, data-driven engineering and administrative process controls to reduce potential ESD risk factors.

REFERENCES:

SAFEX Good Explosives Practice Series, Managing Electrostatic Discharges (ESD) in the Manufacture of Explosives, www.safex.org

NFPA 77 Recommended Practice on Static Electricity, www.nfpa.org

DOD Contractor’s Safety Manual for Ammunition and Explosives 4145.26, March 13, 2008

Influence of the European Track & Trace regulation on the security of usage and storage of civil explosives

By

Frank Hirthammer.

Security in the life cycle of explosives is nowadays more important than ever before. Terror attacks all over the world enforced the EU to decide a Commission Directive for the identification and traceability of Explosives that set a series of requirements for involved manufacturers, distributors and end users. The challenge was to find and implement a track and trace system for all concerned European companies by 15th April 2015. Hence, countries worldwide follow this example and implement similar regulations.

But what are the advantages of such a solution? Tracking enables to record data about the movement of a product along the whole supply chain. Tracing is the ability of operators, authorities and final customers, to access all the tracking information associated with the given product in order to understand its properties and the path taken for it to arrive at the location monitored. Herewith processes become more transparent and loss of material or information more unlikely. Track & Trace is nothing new and used in several business and private sectors. It is used e.g. for postal services, in food industry and pharmaceutical industry. So compared to other industries Track & Trace of civil explosives had a late start, but with the implementation of the Commission Directives 2008/43/EG and 2012/4/EC, the EU was a pioneer in its industry.

Implementation of EU-directives

The EU-directive itself required as a first step the identification of each explosive since April 5th, 2013. The second step however, had to be realized from April 5th, 2015 on. It demanded, that each company that deals or uses explosives, is required to use a system to guarantee gapless traceability. To ensure the information exchange, each company has to name a contact person, who is available twenty-four-seven. This person must have the ability to supply the relevant information. The necessary tracking and tracing information has to be stored for at least ten years after making use of the explosives. Furthermore it has to be protected against accidental or intentional destruction and modification. Unfortunately these are only corner points and specified the general requirements for a Track & Trace solution. On initiative of the FEEM (Federation of European Explosives Manufacturers) manufacturers and software companies developed a Guidance Note, which was the precondition to develop the needed software for the European market.



Registration of explosives into TTE-Track & Trace software before blasting

Experiences with and influences of Track & Trace software

Approximately one and a half years of practice made the usage of Track & Trace software being part of normal and daily business of European companies. The aim – to fulfill the European Directive is no longer regarded as mayor reason for the application of Track & Trace. Additional benefits given from this system outweigh the negatives, so that the use of the tracking software delivers comfort and support.

Production control is one of the advantages. Users can now receive exact proof up to individual items and precise accounting within the warehouse. Explosives of different types and quantities relating to corresponding logistic processes can be handled easily and fast without manual records. All kinds of material and record data e.g. dates, times, comments, permits and editors can be managed by the electronic stock book and thus the company quality assurance may be improved. If requested, all steps can be logged and evaluated. Neither searches for items, nor the whereabouts of a delivery have to be extensively investigated anymore. It is possible to perform searches in different company sites at once and receive an immediate overview about all items on stock. Digital and printed reports and structured overviews of the stock book shall facilitate one's work and give an outline of the shelf life and the history of all products. Inventories do now require very little time and the recorded error rate decreased, due to the possibility of scanning pallets, boxes and items.

The intuitive operator guidance of the software reduces errors within the operation. Furthermore a company's own compliance rules can be integrated into single processes. Documentation and analyses can afterwards be provided to the management. Herewith companies receive an exact evaluation of their business operation and can adapt and optimize their processes to avoid future errors. This also affects expired or about to expire explosives, which can be displayed as such before usage or simultaneous in an overview function.

In case of errors at blasting, fault detection could be improved by exact allocation of used explosives to batch, manufacturer, production date and special warehousing comments, which can be added in the software.

These examples show that not only has the integration of the EU regulation became manageable but also security and transparency in product life cycles of explosives were increased. Furthermore companies using Track & Trace software can profit from several features to optimize processes businesses and fill so far existing gaps in production, handling and warehousing of civil explosives.

The Minimum Burning Test for Ammonium Nitrate Emulsions

by

Dr.Noel Hsu

Introduction

In the SAFEX Newsletter No. 56, a brief history of Test Series 8 for ammonium nitrate emulsions (ANE) was provided. The paper also described that one of the prescribed tests – the Koenen Test – is not suitable for ANEs, which due to their higher water content are very insensitive and have shown to give false positives, i.e. they fail the test. The research into ANEs that are subjected to the Koenen test has shown that the extended time required for the ANEs to react results in a weakening of the steel tube containing the product. Thus the observed failure of the tube is not only due to the reactivity of the ANE being tested (the intent of the test) but also due to the weakening of the steel tube. This leaves the explosives industry with a UN testing regime for ANEs in which one test has been deemed unsuitable.

At the 48th session of the UN Subcommittee of Experts on the Transport of Dangerous Goods (SCETDG) the expert from Canada proposed the Minimum Burning Pressure (MBP) test as an alternate to the Koenen Test, and by default, to the Vented Pipe Test, which in effect is a scaled-up Koenen Test.

This article describes the MBP test as it is currently carried out and gives an overview of the discussions at the UNSCETDG on Test Series 8.

Minimum Burning Pressure

For many explosives, the initial stages of combustion are endothermic and not self-propagating. For thermally ignited ammonium nitrate based explosives (ANE) it is well established that the initial stage of combustion is endothermic¹. Even though the subsequent stages are generally exothermic, they would not react unless the pressure is sufficiently high. Therefore for such explosives there is a low-pressure limit below which stable combustion becomes impossible. This is the so-called Minimum Burning Pressure (MBP). The MBP is being

used by some manufacturers as a basis of safety for many associated manufacture, transport, and handling processes. In Canada the MBP is also used in the Guidelines for bulk emulsion pumping.

The Minimum Burning Pressure Test

Two major accidents, in 1975 and 1988 related to the pumping of ANEs, led to the development of the Minimum Burning Pressure (MBP) test. In the 1990s the Canadian Explosives Research Laboratory (CERL) partnered with CIL/ICI/ORICA and after years of research developed the MBP test, which is now being routinely run by CERL. The history of development of the MBP test is described in more detail in Newsletter No. 56.

The research by CERL has been published in many journals and show that for a wide variety of commercial emulsion products, the MBP test is consistent and repeatable using the testing methodology described. Their research also shows that the major factor controlling the MBP for ANEs appears to be its water content, accepting that there are other variables such as the other formulation ingredients that need to be considered.

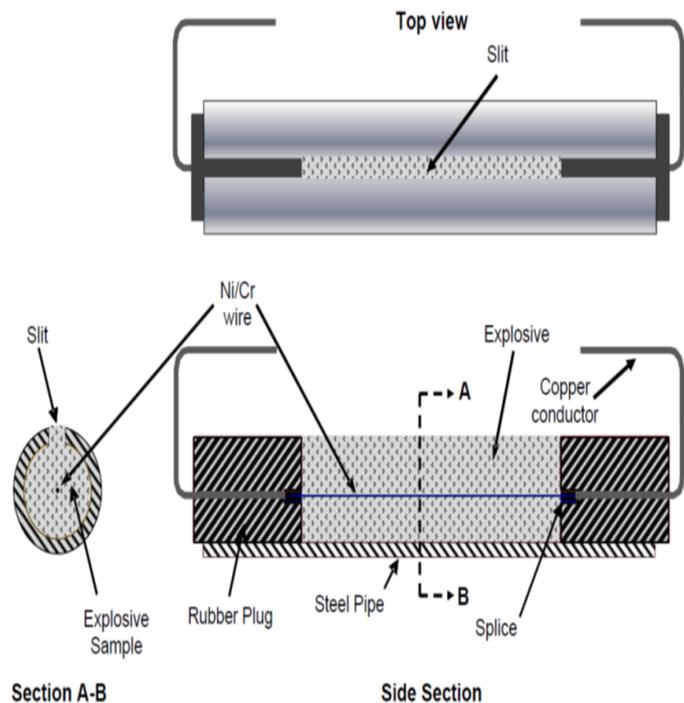


Figure 1. Steel tube that holds the ANE sample

The ends of the steel tube are closed off with neoprene stoppers once the Ni/Cr (60/16) wire of diameter 0.51mm and nominal resistance $5.5\Omega\text{m}^{-1}$ (at 20°C) has been introduced into the steel pipe as shown. The Ni/Cr wire has both ends spliced onto 50cm lengths of 14 AWG solid copper wire and bent as shown to ensure that the Ni/Cr wire is straight along

1. Richard Turcotte, Phillip Lightfoot, Christopher Badeen, Marie Vachon, David Jones, and Sek Kwan Chan, Propellants, Explosives, Pyrotechnics 30 (2005), No. 2

2. <http://www.unece.org/trans/main/dgdb/dgsubc3/c32015.html>

the axis of the pipe.

The assembled pipe is introduced into a pressure vessel (minimum volume 4L and operating pressure of 20.8 MPa/3000psig) and held horizontally with the slit facing up. The pressure vessel should be installed in a protected room and be capable of remote operation.

The Ni/Cr wire is connected to a constant power supply capable of delivering a constant current up to 20A. A data acquisition source such as an oscilloscope is used to capture the pressure transducer signal and ignition wire current.

Test Procedure

The vessel is remotely pressurized to the required test pressure and held to ensure that there are no leaks. An educated guess is used for the test pressure if the sample MBP is not known. The initial pressurization is to a value higher than the target pressure. Once it has been established that no leaks are present, the pressure is adjusted to the desired value.

The data acquisition system is started and a 10.5A current is passed through the Ni/Cr wire. The current should stay on for a few seconds until the sample ignites and melts the Ni/Cr wire, at which point the power is turned off.

If the ANE sample burns completely, the result is a 'go'. The test is repeated with a lower pressure. If the sample does not burn the result is a 'no go' and the pressure should be increased for the next test. Examples of a 'go' and 'no go' are shown in Figure 2.



Figure 2. ANE samples that show a 'go' and 'no go' result

The trace from the pressure transducer can also be used as evidence of whether the sample has undergone sustained combustion (see Figure 3.)

The steps above are repeated while gradually decreasing the pressure increments (or decrements) until the MBP has been determined to the desired degree of precision. A minimum of 12 tests using this 'up-and-down' methodology should be performed. The MBP should be quoted as the mean between the

initial pressure of the highest 'no-go' event and that of the lowest 'go' event (Figure 4).

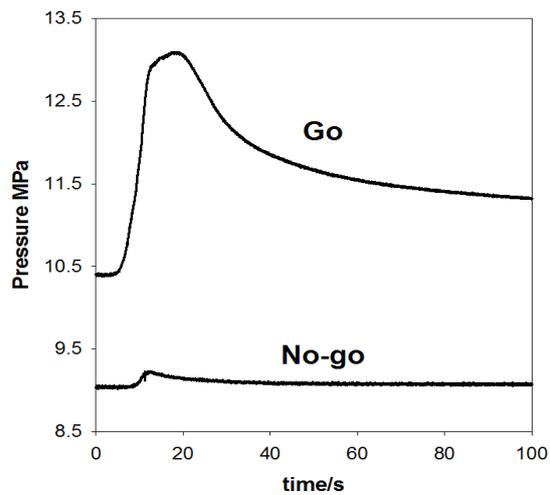


Figure 3. Pressure traces for 'go' and 'no go' samples

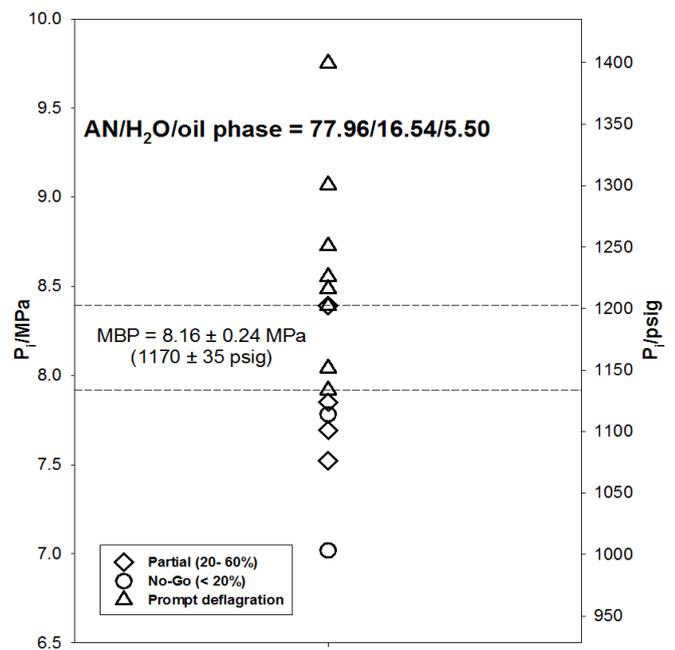


Figure 4. Typical MBP result for an ANE

Current Status

At the June 2016 session of the UN Subcommittee of Experts on the Transport of Dangerous Goods, the Explosives Working Group discussed the MBP test as a potential alternate test to the Koenen Test for ANEs. The expert from the UK did not consider the Koenen test as suitable for emulsion ANEs and proposed *to have the Koenen test applicable for suspensions or gels, and the MBP test applicable for emulsions due to their much higher water content and other factors*³. The expert from the USA believed that this could be a favourable path pending further discussion at the informal correspondence group, which Canada is leading; the group consists of seven competent

authorities and four NGOs.

Concluding remarks

As discussed in Newsletter No. 56 ANEs have been manufactured and transported for over three decades, and although there are accidental explosions with ANEs, there is sufficient doubt as to whether these substances actually caused the explosions, or in one case, to whether it is a bona fide UN3375 substance. Their relatively inert behavior is largely attributed to their high water content.

The application of a test, developed in the 1950s with very sensitive substances, to relatively inert ANEs has shown to be problematic. However, there is presently no directly substitutable test and yet the explosives industry needs to test and classify product on an ongoing basis. The MBP test provides an alternate method, as proposed by the expert from the UK and supported by the US expert, for emulsion ANEs and gives the competent authority and industry time to develop a test that takes into account the relatively inert nature of ANEs.

3.<http://www.unece.org/fileadmin/DAM/trans/doc/2016/dgac10c3/UN-SCETDG-49-INF66e.pdf>

Safe Treatment of Organic Contaminated Spent Acids

by

Dr. Hansjuergen Winterbauer

Director Development / Patents

PLINKE GmbH

Introduction

Organic compounds, even in small quantities, can cause huge problems and create safety risks during treatment of spent acid from several production/nitration processes. This is well known from production of explosives and propellants: The received nitration spent acids contain dissolved sensitive organic compounds, but also more stable organics are not risk free. For both cases safety related process considerations and related solutions are described. Treatment of spent acids from different nitration processes can be executed in the same plant. Depending on the organic compounds, operational conditions and treatment units have to be adapted.

Treatment of spent acid containing sensitive organic compounds

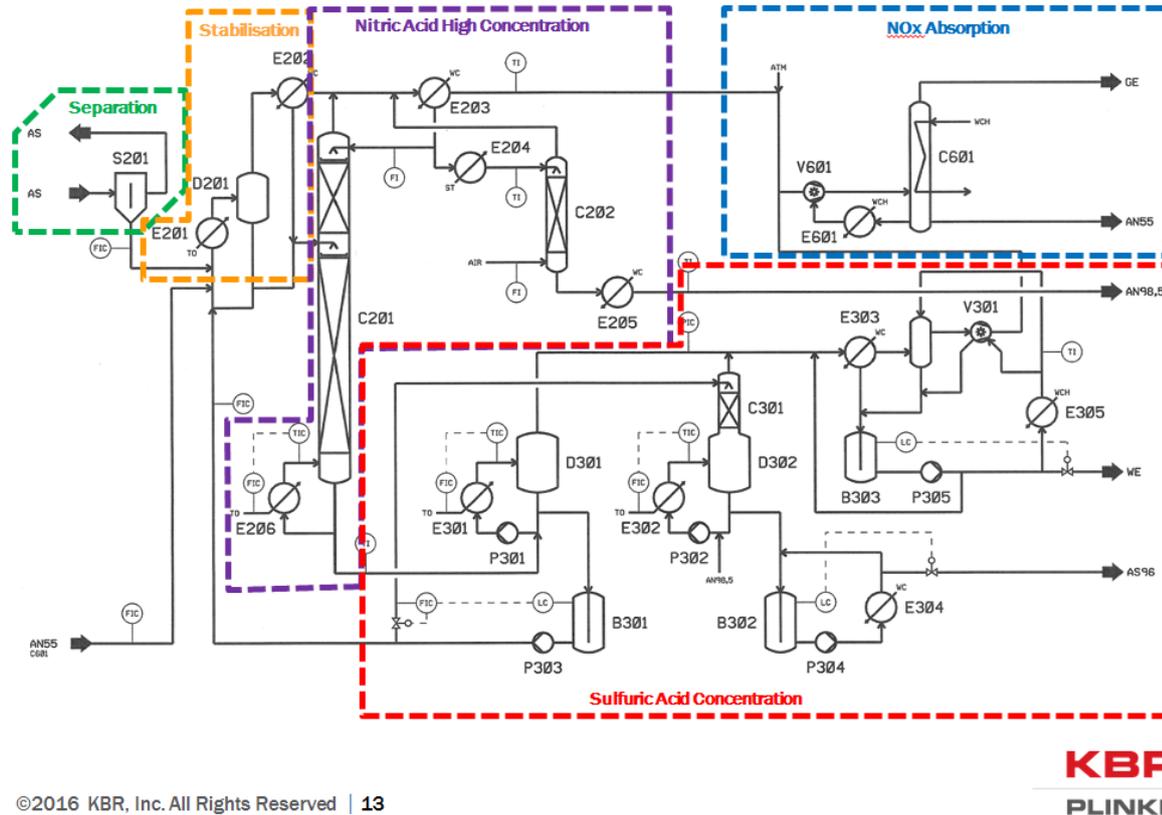
Spent acid from the production of nitroglycerine shall be described here as an example for nitration spent acids with sensitive organic compounds to demonstrate the particularities, which have to be considered. The spent acid consists of sulfuric acid, nitric acid, nitrous acid, water and a certain amount of dissolved nitroglycerin and other organic compounds generated during nitration reaction. The following main safety risks have been determined in the past:

- 1) Due to temperature variations in the spent acid tank and in the transfer pipeline, dissolved nitroglycerine can separate and undissolved material might enter the spent acid treatment plant.
- 2) During decomposition of the organics the decomposition energy and the developed gas have to be dissipated safely.
- 3) Accelerating effects caused by other impurities in the spent acid have to be considered.

A suitable treatment process considering these safety aspects is shown on figure 1.

To avoid that non-dissolved organic oil enters the spent acid treatment plant, the spent acid is circulated through a separator (S102 in figure1). The spent acid from the tank is introduced in the middle of the separator. Internals within the separator improve droplet accumulation and separation of undissolved organic matters. The part of the spent acid, which is fed to the treatment plant, leaves the separator at the bottom. It is sent by gravity flow to the stabilization unit. The remaining spent acid leaves the separator at the upper part and is recycled to the tank. In case undissolved organic oil is present, it will float after separation and will therefore be recycled to the tank together with circulating spent acid. The tank has to be equipped with a suitable separation system to remove organics floating due to temperature variations.

Spent Acid Recovery Process



©2016 KBR, Inc. All Rights Reserved | 13

KBR
PLINKE

Figure 1: Process Flow Diagram for Spent Acid Treatment

The spent acid from separation is treated in the stabilization unit by liquid phase decomposition of dissolved organic compounds. The stabilization unit consists of a heat exchanger (E201), a flash evaporator D201 and a condenser E202.

Within the system sulfuric acid of about 70 wt.-% H_2SO_4 is circulating, moved by thermo-syphon generated within the heat exchanger. Operational temperature has to be sufficient to decompose the organic compounds. About 160 °C is sufficient for most of explosives including Nitroglycerine, which is present in this example. The amount of circulating sulfuric acid is about 10 to 20 times the amount of spent acid, which enters the system by gravity flow. The organic dissolved in spent acid is immediately distributed in the huge surplus of circulating sulfuric acid. Also the temperature immediately equalizes to the temperature of the circulating acid. Thereby the organic decomposes and transfers the decomposition energy to the huge surplus of sulfuric acid. The acid is thereby heated up. Then the acid is further heated by indirect heating and flashed into the evaporator. In the evaporator, developed gas and circulating acid are separated. Surplus energy is dissipated by water and nitric acid evaporation.

Figure 2 shows a stabilization unit in operation. You can see the gas development by decomposition. This also causes a certain foam level within the evaporator, which has to be considered in advance for the design of the system.



Figure 2: Stabilization unit in operation

The evaporated water and nitric acid are condensed in condenser E202 and sent to the nitric acid high concentration step. The decomposition gases, which normally contain a certain amount of NO_x gas, are sent to the NO_x -Absorption for purification and recovery of nitric acid.

The surplus of sulfuric acid entering the system with the spent acid, which is now virtually free of sensitive organic compounds, is sent to the nitric acid high concentration step.

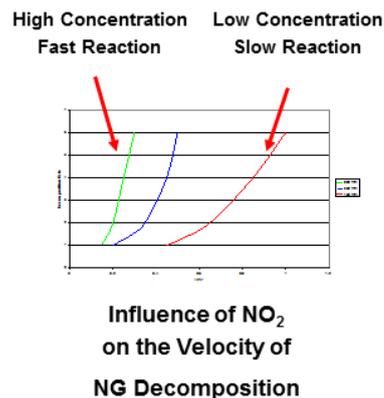
Accelerating effects caused by other impurities in the spent acid also have to be considered in the design of the stabilization unit. Catalytic effects of by-products can be used to increase the decomposition velocity. The influence of some by-products on decomposition velocity for nitroglycerine is shown of figure 3.

Accelerating Effects on Decomposition

Increasing the velocity of decomposition by making use of catalytic effects of decomposition by-products



➤	HNO₃		Increase of velocity
➤	NO₂		Increase of velocity
➤	O₂		Increase of velocity
➤	H₂O		Increase of velocity
➤	NO		no influence



©2016 KBR, Inc. All Rights Reserved | 16

KBR
PLINKE

Figure 3: Accelerating effects on decomposition of nitroglycerine

While the presence of HNO₃, NO₂, O₂ and even H₂O increases the decomposition velocity of nitroglycerine, the amount of NO present in the system seems to have no impact. Therefore, adding additional nitric acid, e.g. weak nitric acid from NO_x absorption, improves the performance of the stabilization unit.

After stabilization the spent acid is free of sensible organic compounds. All further acid concentration steps can be safely operated. Therefore these process steps are described here only briefly.

In the Nitric Acid High Concentration unit the nitric acid is separated from sulfuric acid, concentrated up to 99 % HNO₃, freed from dissolved NO_x by bleaching and sent to concentrated nitric acid storage.

The separated sulfuric acid leaving the Nitric Acid High Concentration is concentrated up to 96 % H₂SO₄ in the Sulfuric Acid Concentration unit at vacuum conditions and is sent to concentrated sulfuric acid storage.

The effluent gases from all process units are treated in the NO_x Absorption Unit recovering weak nitric acid, which is recycled to stabilization.

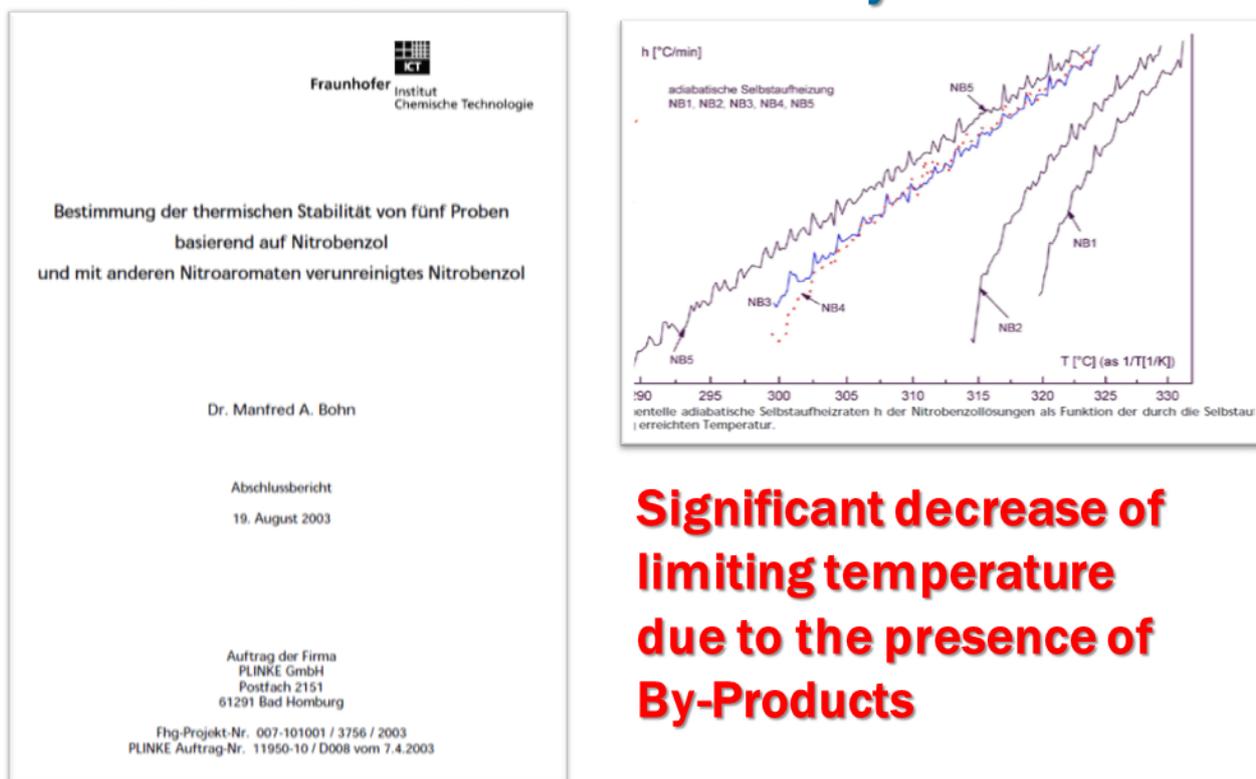
Treatment of spent acid containing stable organic compounds

In case stable organic compounds are present in the spent acid, treatment has to be continued in the Sulfuric Acid Concentration unit. Even stable organic compounds in spent acids can cause problems and safety risks during spent acid treatment, but also in other plants, when treated acids with remaining organic compound are recycled. Especially in case organic compounds are only partly decomposed during spent acid treatment, unpredictable risks may be created.

Figure 4 shows the drastic decrease of limiting temperature due to the presence of reaction by-products in the production of nitrobenzene.

Sample NB1 is for pure nitrobenzene, which is stable up to 320 °C. Depending on type and amount of by-products, the limiting temperature, where the substances start to decompose independently, can drastically decrease. E.g. a quite small amount of picric acid in sample NB5 decreases the limiting temperature by more than 10 %.

Determination of Thermal Stability of Nitrobenzene and Influence of By-Products



Significant decrease of limiting temperature due to the presence of By-Products

KBR
PLINKE

©2016 KBR, Inc. All Rights Reserved | 24

Figure 4: Decrease of limiting temperature due to the presence of by-products in the production of nitrobenzene.

To decompose stable organic contaminants, high sulfuric acid temperature and addition of nitric acid or other oxidizers are required. In past times the spent acids have been reconcentrated in kettles at atmospheric conditions and temperatures up to 320 °C. At these conditions all organic contaminants had been decomposed. Due to economic and environmental reasons this technology is replaced by alternative technologies.

Spent acid treatment temperature is restricted due to the corrosion behavior of available materials of construction. E.g. Tantalum, which is most popularly applied for heat exchangers in sulfuric acid treatment, can only be used up to 190 °C operational temperature at sulfuric acid concentration higher than 94 % H₂SO₄. Temperature of 190 °C is not sufficient to decompose most types of stable organic compounds.

Alternative materials of construction nowadays allow treatment at temperatures up to 250 °C, where most organic compounds can be safely destructed. For that purpose a thermal oil heated hot temperature process has been developed. The process combines sulfuric acid high concentration and purification by thermal treatment.

This process is applied e.g. in the production of methyl-ethyl-ketone at atmospheric conditions and sulfuric acid product concentration up to 85 % H₂SO₄. For several nitration processes e.g. production of polyurethane pre-products and lacquers, the process is operated at vacuum conditions and product acid concentration up to 96 % sulfuric acid.



Figure 5: Thermal oil heated heat exchanger for sulfuric acid high concentration

Figure 5 shows a thermal oil heated heat exchanger for sulfuric acid high concentration and treatment at 250 °C.

The sulfuric acid is normally concentrated at vacuum of approx. 80 mbar_a up to 85 wt.-% H₂SO₄ using a steam heated tantalum heat exchanger. Then the high concentration step follows with final acid concentration up to wt.-% 96 H₂SO₄. In that step the acid is mixed with hot circulating acid. Additionally concentrated nitric acid as oxidizer is added to the circulating acid before entering the circulation pump P302. Then the acid is superheated to 250 °C using special hot thermal oil heated heat exchanger E302. The acid is high concentrated up to 96 wt.-% H₂SO₄ by flash evaporation into evaporator D302. The principle is similar to the stabilization unit as the released decomposition energy is absorbed by the circulating acid.

Operating at hot acid temperature and injection of small amounts of nitric acid for oxidation ensures that stable organic compounds resulting from nitration process are

decomposed and a very pure sulfuric acid with min. 96 wt.-% H₂SO₄ product is achieved. The organic content of the product sulfuric acid can be reduced below 300 ppm TOC.

Summary

Organic compounds, even in small quantities, can cause huge problems and create safety risks during treatment of spent acids. This is not only related to sensitive organic compounds since stable organics are not risk free. Nowadays suitable solutions are available for both cases. Spent acids can be treated in a safe and reliable way. When all safety related process requirements are considered, treatment and concentration of spent acids from different nitration processes can be combined in a single plant.

Compatibility of Ammonium Nitrate Systems with Sodium Salts

by

S. Singh, R. Turcotte, S. Goldthorp, C. Badeen
Canadian Explosives Research Laboratory
(CanmetCERL), Ottawa, ON, Canada

© Her Majesty the Queen in Right of Canada, as represented by the Minister of Natural Resources, 2016.

The contents of this report may be based on work in progress or may contain speculative comments by the authors. Readers are cautioned to rely on their own judgment in assessing the correctness of the contents. CanmetCERL does not warrant the quality, accuracy or completeness of the contents and is not responsible for any errors or omissions, or any technical inaccuracies. CanmetCERL disclaims liability for any injury, damage, or other loss resulting from any use of or reliance on the report or its contents.

1. Introduction

Soon after the invention of dynamite by Alfred Nobel towards the end of the 19th century, the inclusion of ammonium nitrate (AN) and sodium nitrate (SN) as oxidizer ingredients in NG-based dynamites became popular. Also,

the first attempts to use AN as a main explosive ingredient started. However, for many years there were considerable difficulties to initiate steady detonations in these types of explosives. Also the processing and end use of AN proved very difficult due to its very hygroscopic nature and its high solubility in water. It is only in the early 1950s that AN became available in the form of porous prills and its use in conjunction with fuel oil as a blasting explosive was investigated by several surface mines [1]. This was so successful that it started the ANFO "revolution" which caused a rapid dynamite replacement in many applications. Still today, ANFO dominates the commercial blasting industry but due to its low water resistance and its inherent low density, it could not constitute a strict dynamite replacement especially for small diameter boreholes.

The ANFO limitations were first addressed in 1956 by Melvin A. Cook in the USA who then invented a new water resistant explosive based on AN: the slurry explosive. It consisted of AN, generally combined with another oxidizer such as SN, aluminum powder, water, and a gelling agent (guar gum). This explosive was found to be extremely safe and could be made to be detonator sensitive through the use of chemical sensitizers or density modifiers. These inventions gave rise to the bulk explosive loading concept, which accelerated blasting operations. Soon after the slurry became popular, a different class called "Water Gel" was developed. It contained a cross-linking agent that forms chemical bonds after the product is loaded [3].

Soon after the slurry became popular in blasting applications, another water-based AN system was invented: the emulsion explosive (1961). It consisted of microscopic droplets of a liquid oxidizer solution surrounded by a continuous oil phase. The first stable and practically useful emulsion blasting explosive was developed by Harold F. Bluhm in USA (1969) [2]. However, the successful commercialization of this type of explosive did not really happen before the beginning of the 1980s. In these emulsions, the liquid oxidizer phase usually consists mostly of AN with various other oxidizing salts such as SN, calcium nitrate and sodium perchlorate.

Emulsion explosives rely on the presence of small voids that become "hot-spots" upon initiation by a detonator or a booster charge. These were initially provided by blending glass or phenolic microspheres into the product. A much cheaper technology based on the production of gas microbubbles in the emulsion quickly developed. It consists of injecting a "gassing solution" into the emulsion explosive as it is pumped down into the borehole. Several different "gassing" processes have been developed. One of them, based on the nitrite/ammonium reaction producing nitrogen gas bubbles [3], has been and is still very popular. In this case, a solution containing sodium nitrite (SNi) as well as other ingredients has often been used [4, 5].

Nowadays, ANFO, emulsion explosives, and their blends form the vast majority of blasting explosives being used worldwide. This generation of explosives is inherently

much safer than the earlier ones but accidents still happen during manufacture and use of these explosives. One of the reasons for several of these accidents is that AN itself and AN-based systems are incompatible with a large number of substances [6]. This often causes uncontrollable runaway reactions or increases the probability of high-speed deflagrations. When large quantities are involved both these reactions can lead to large scale detonations.

As discussed above, both SNi (NaNO_2) and SN (NaNO_3) are often incorporated in AN-based systems (slurries and emulsions for instance). In the case of SNi, several anecdotes have been shared with the authors concerning accidental ignitions and fires caused by contact of SNi with various AN-based systems. To the authors' knowledge, no such effect of SN on the stability of AN and the safety of processes involving AN-based systems has been reported through the literature. Only one study reported by Yeager [7] claims that both SN and SNi cause significant destabilization of AN. This result was obtained using the well-known small-scale cook-off bomb test (SSCB) [8] which uses as much as 15-20g of sample material heated in a closed stainless steel bomb. In this work, it was noted that both salts very significantly reduced the onset temperature for runaway of AN but that the reactions obtained with the AN/SNi system were much more severe than with the AN/SN system. It was also stated that traditional small-scale tests such as DSC lacked the ability to detect the hazard potential of these two systems.

In the present work, various calorimetric methods such as DSC, Accelerating Rate Calorimetry (ARC), and Heat-Flow Calorimetry (HFC) were used to study the effect of both SN and SNi on the stability of AN. A Minimum Burning Pressure [9] test was also used to gain information on the safety of introducing SN in emulsion explosives.

2. Experimental

2.1 Chemicals

AN (ACS reagent grade, 95% min. purity, Alfa Aesar) was dried overnight at 70°C in an explosion-proof oven to promote bulk water loss while minimizing dissociation of the salt to HNO_3 and NH_3 . After drying, the resulting white crystals were stored in a desiccator under argon atmosphere since it is well known that ammonium nitrate is very hygroscopic. All tests were performed using the same batch of dried AN. SN ($\geq 99\%$ purity, Sigma Aldrich) was dried at 105°C and similarly stored under argon before use. SNi ($> 99\%$ purity, J.T. Baker) was used as received. Drying using high temperatures was not attempted to avoid degradation of the pure sample.

All emulsions investigated in this study were prepared in-house using procedures and ingredients already described in details elsewhere [9, 10]. Several emulsion systems were prepared by adjusting ingredients systematically. To closely replicate manufacturing and handling conditions of

emulsion products, MBP testing was performed on freshly manufactured product.

2.2 Calorimetry

A TA Instrument 2910 DSC with associated analysis software was used for the thermal study of AN, SN, SNI and the binary mixtures AN/SN and AN/SNI. The DSC was calibrated for temperature and heat flow using standard methods [11, 12]. The samples were heated at $5\text{ }^{\circ}\text{C min}^{-1}$ under a purge of nitrogen gas at a rate of 50 mL min^{-1} . These samples were encapsulated into hermetically sealed aluminum vessels having an internal volume of approximately 30 mL and pressure capability of 0.2 MPa (2 atm). This volume permitted the introduction of one to five milligrams of the pure salt or the mixture to be tested; however, pressure buildup from decomposition gases often ruptured the aluminum cold weld of the vessels. Various methods were attempted to achieve manipulations at milligram scale. The most reproducible one involved adding the appropriate mass of components directly to the DSC vessel. The samples were prepared in the dry state under ambient conditions with less than 40% relative humidity. This appeared to minimize adsorbed moisture since the samples did not show any drift when weighing on an ultra-microbalance having a precision of $\pm 0.00001\text{ mg}$. When known amounts of water were required, a microdroplet of distilled deionized water was first syringed into an empty sample vessel and allowed to evaporate under ambient conditions while on a microbalance until the appropriate weight was obtained. Then, the correct proportions of dry powders were immediately added and the vessel was quickly sealed. The AN/salt mixture was referred to as 'humid' when used as received with the water content between approximately 1 to 3 mass % and the individual crystals were still free flowing. Mixtures containing approximately 10 mass % of water were also produced and investigated. These are referred to as "wetted" and, in all these cases, all the crystals were observed to lightly adhere and form a single mass. All mixtures were tested at least in duplicate.

Accelerating rate calorimetry (ARC) measurements were performed using an instrument originally manufactured by A.D. Little Inc. The mixtures were prepared by first placing the AN at the bottom of a cylindrical titanium vessel. The SN or SNI were then added on top of the AN in the vessel. Experiments were performed from $30\text{ }^{\circ}\text{C}$ to an upper temperature of $350\text{ }^{\circ}\text{C}$, with the ARC instrument manifold closed. The standard ARC procedure of "heat-wait-search" ($5\text{ }^{\circ}\text{C}$ step size; $0.02\text{ }^{\circ}\text{C min}^{-1}$ threshold self-heating rate) was used [13]. In order to perform measurements in humid atmosphere, an unsealed glass capillary containing 40 mg of distilled water was inserted into the 1 mL ARC vessels containing the mixture samples. With this set-up, the relative humidity inside each ARC vessel varied as a function of temperature: 100 % up to $260\text{ }^{\circ}\text{C}$, down to 65 % at $300\text{ }^{\circ}\text{C}$.

A Setaram C80 Calvet heat flux calorimeter (HFC) was also used for larger scale thermal stability testing of AN/SNI. In this calorimeter the sample size is typically 100 times larger than using DSC. A 3D arrangement of thermopiles surrounds the sample and allows very small temperature excursions to be detected when using a very slow ramp rate (i.e., $0.1\text{--}0.3\text{ }^{\circ}\text{C min}^{-1}$). These quasi-adiabatic conditions with the larger sample size enable self-heating effects to be detected if a reaction is sufficiently exothermic.

The C-80 calorimeter was calibrated by the manufacturer for heat flow measurements using a joule effect probe. This calibration was verified at CERL using well known standards for temperature and enthalpy [11, 142]. The samples were contained in a quartz liner tightly fitted into a 10 mL stainless steel cell equipped with a pressure transducer, flushed with dry air.

The C-80 calorimeter can also be equipped with various reaction cells designed to simulate different process conditions. One of them called "Safety Reaction cell" can be used to measure enthalpy changes evolved when two substances are immediately put into contact with each other. In this case the two substances are first held in independent concentric top and bottom glass ampoules within the closed cell. This arrangement can then be introduced in the calorimeter and equilibrated at a given temperature. Once equilibrium has been achieved, a metallic plunger can be pushed down towards the cell and used to break the bottom of the top ampoule, thus allowing the top substance to fall into the bottom ampoule, and make contact with the second substance. In the present work, this Safety Reaction cell has been used to characterize the AN/SNI reaction at an isothermal temperature of $50\text{ }^{\circ}\text{C}$.

2.3 Minimum Burning Pressure

Back in the 1970s, it was found that, following local ignition in water-based explosives, there is a minimum pressure required for combustion to propagate [14]. The latter is usually referred to as the 'Minimum Burning Pressure' (MBP) of the explosive. In the last few years, a research program at the Canadian Explosives Research Laboratory (CanmetCERL) has been focused on the development of a validated measurement protocol for realistic MBP measurements. In this test, the sample is contained in a steel cylindrical cell. A small diameter Ni/Cr wire is held along the axis of the cell. This cell arrangement is introduced in a high-pressure vessel and the Ni/Cr wire is connected to feedthrough electrodes connected to a current source. The vessel is pressurised at a given initial pressure and the sample is ignited by passing a high electric current through the Ni/Cr wire. Several such tests are repeated at various initial pressures until one can define the minimum pressure required for full combustion of the sample. The detailed testing protocol has already been described elsewhere [15].

3. Results

3.1 Calorimetry

3.1.1 DSC

The DSC heat flow curves for pure samples of AN, SN, and SNI are shown in Fig. 1. As it is well known, AN is seen to undergo distinct crystal phase transitions as a function of temperature. Above room temperature, it is

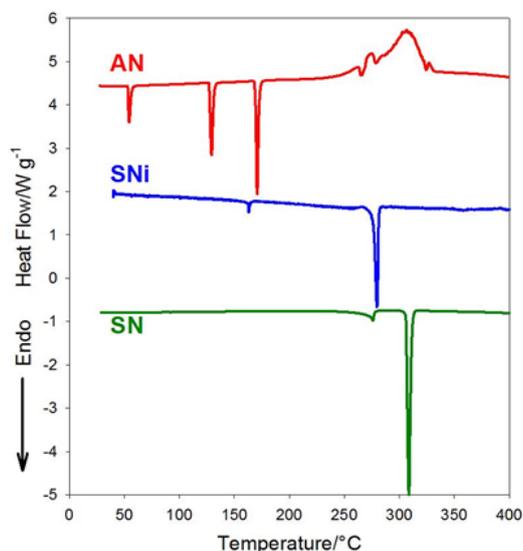


Fig. 1 DSC thermograms for pure AN, SN, and SNI

generally recognized that solid-solid transitions would occur at 32, 84, and 125 °C. In Fig. 1, the 32 and 84 °C transition are replaced by a single transition in the 50-55 °C range. This is known to happen when AN is very dry [16], in which case the phase III (α -rhombohedral) is suppressed so that the IV \leftrightarrow III transition at 32 °C and the III \leftrightarrow II transition at 84°C are replaced by a single IV \leftrightarrow II transition around 50-55°C. The melting of AN is observed by another endotherm around 170 °C, while the AN thermal decomposition appears as a broad exothermic structure between 230 and 340°C. The observed thermal behaviour of SN was as expected, with a known solid-solid phase transition around 275°C [17] and melting at 308°C. Similarly the thermal curve for SNI displays a solid-solid phase transition at about 164°C [18] and a melting endotherm in the 270-280°C range. In both the SN and SNI cases, no indication of exothermic decomposition was observed up to 500 °C.

The DSC results for 60/40 mixtures of AN/SN are shown in Fig. 2. The two cases for which the SN was used as received (humid) and wetted with excess water were tested. It can be seen that for both cases the onset temperature for thermal decomposition of AN remained approximately unchanged while the enthalpy was considerably reduced. It should also be observed that, in both cases, the AN melting endotherm disappeared while the endotherms related to the AN solid-solid phase transitions either disappeared or were modified by the presence of SN.

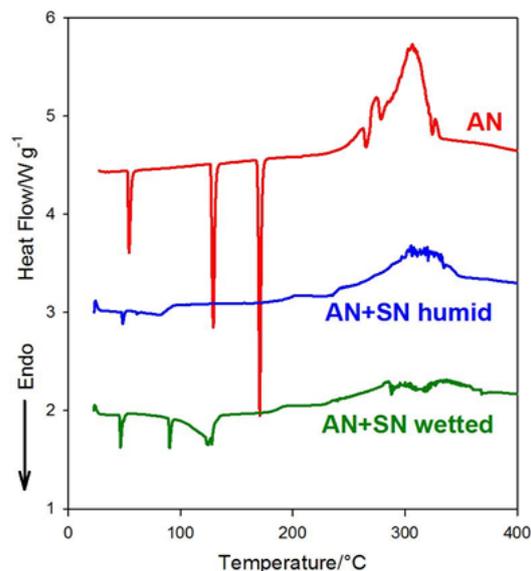


Fig. 2 DSC thermograms for pure AN, AN/SN humid (60/40), and AN/SN wetted (60/40)

The DSC results for the same two cases (humid and wetted) but for 60/40 mixtures of AN/SNI are compared with pure AN in Fig. 3. It can be observed that the introduction of as received SNI decreases the onset temperature of the exotherm from 230 °C to nearly room temperature. One can also see a large increase in exotherm enthalpy. As excess water is added this low temperature exotherm (peak temperature of 95 °C) is still present but over a smaller temperature range and higher onset temperature (about 60 °C). The enthalpy is also seen to be reduced.

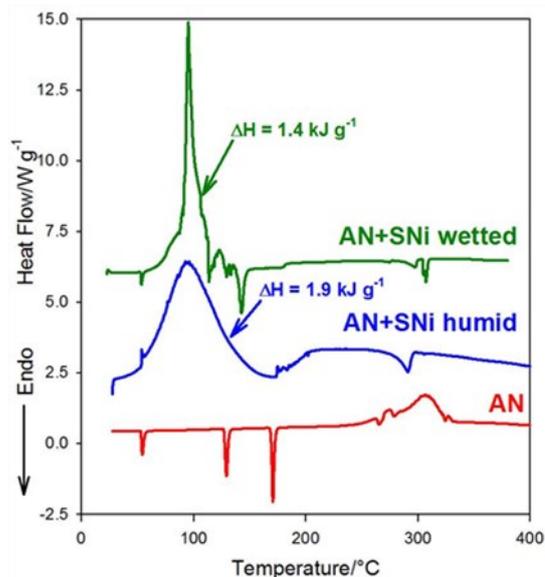


Fig. 3 DSC thermograms for pure AN, AN/SNI humid (60/40), and AN/SNI wetted (60/40)

3.1.2 ARC

Since no AN/SN incompatibility could be observed in the above DSC experiments on milligram samples, the ARC technique was selected to perform a larger scale experiment under adiabatic conditions. The sensitivity was further improved by selecting a small and light sample vessel with relatively large sample mass (600-700 mg), thus minimizing the thermal inertia (so-called phi factor [19]).

A typical result for a 50/50 mixture of AN/SN (690 mg) under high relative humidity is shown in Fig. 4, where it is compared to that of pure AN (630 mg) under the same conditions. It can be first observed that, for both the pure AN and the 50/50 mixture, no exotherms have evolved at temperatures lower than their final runaway exotherms above 200 °C. Also, the onset temperature for the 50/50 mixture is well above that of pure AN while the acceleration of the self-heating rate is slower for the mixture. This is more a characteristic of a dilution effect of the SN rather than an incompatibility.

Since very energetic reactions at low temperatures had been observed for 60/40 mixtures of AN/SNi, it was decided to use the ARC technique to test a mixture with much lower SNi content. A typical result for a 97/3 mixture of AN/SNi under high relative humidity is shown in Fig. 5, where the sample self-heating rate and the pressure are plotted as a function of sample

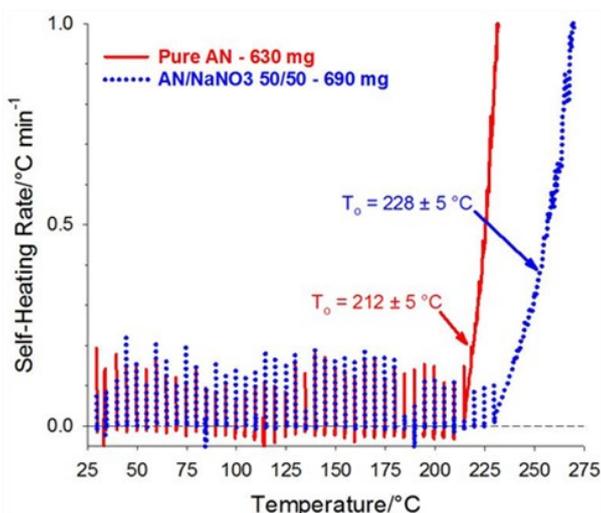


Fig. 4 ARC result for pure AN and AN/SN 50/50 under high relative humidity

temperature. It can be observed that a first small exothermic reaction took place around 50 °C. Corresponding to a small increase in the self-heating

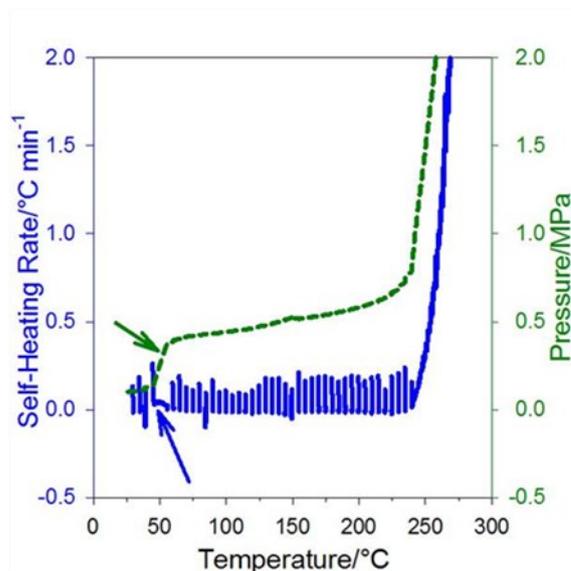


Fig. 5 Result of an ARC high relative humidity experiment on a 97/3 mixture of AN/SNi

rate at this temperature, a significant increase in pressure is also observed. This small reaction probably left a large

proportion of the AN sample relatively wet since the measured onset temperature for runaway was about 240°C, which is significantly higher than normally observed for dry AN under equivalent conditions. In much larger industrial inventories, the observed low temperature exotherm may lead to a runaway behaviour.

3.1.3 HFC

In a first set of experiments, 50/50 mixtures of AN/SNi were investigated. Fig. 6 shows a typical result as compared with a measurement on pure AN. The AN/SNi sample had a total mass of 138 mg and was heated in a closed high-pressure cell from 30 to 300 °C at a rate of 0.1 °C min⁻¹. The sample of AN had a mass of 96 mg and was heated over the same temperature range at a rate of 0.3 °C min⁻¹. It can be first observed that the sample of AN was relatively humid as the IVàIII and the IIIàII phase transitions at 32 °C and 84°C, respectively, are clearly visible and that no IVàIII transition in the 50-55°C range is present. A large decomposition exotherm is also observed in the temperature range from 200 to 270°C. This onset temperature is appreciably lower than that obtained in the DSC (Fig.1) and this is due to the combined effect of the much lower heating rate and the higher sensitivity of the HFC technique. As observed in the DSC, this exothermic structure has completely disappeared in the case of the AN/SNi mixture and is replaced by another strong exothermic structure at much lower temperature, in the 50 to 90°C range.

One isothermal experiment using the Safety Reaction cell was performed (Fig. 7). In this case, 168 mg of AN was loaded in the bottom ampoule while 142 mg of SNI was inserted in the top one. This arrangement was inserted into the calorimeter and equilibrated at 50°C (onset

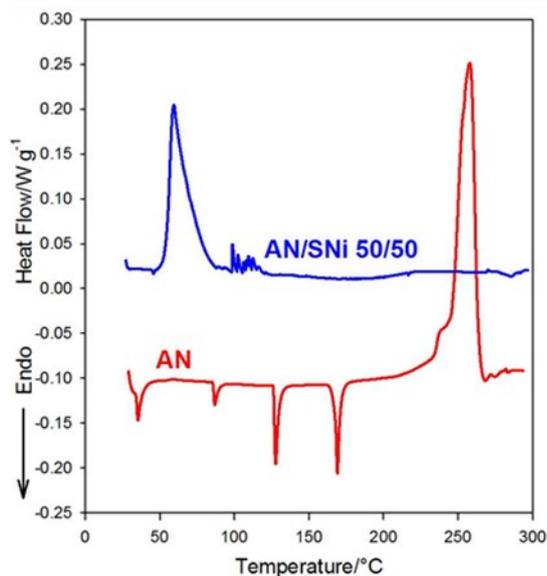


Fig. 6 HFC results for pure AN (96 mg) and a 50/50 mixture of AN/SNI (138 mg)

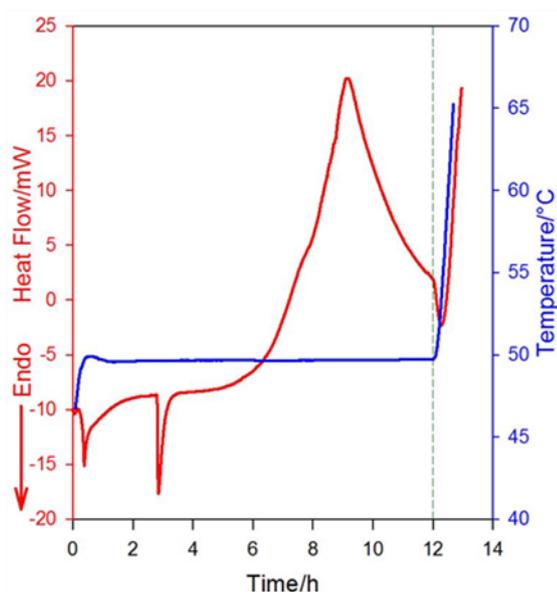


Fig. 7 Result of isothermal (50°C) HFC experiment using the Safety Reaction cell

temperature observed in previous experiment (Fig. 6)). After equilibrium was reached, the bottom of the top ampoule was ruptured so that the SNI was allowed to fall onto the AN. This resulted in a first endotherm. After about 3 hours a second endotherm is observed, which corresponds to the IVall solid-solid phase transition. After an induction time of about 5 hours, a very wide exothermic structure was observed to take place until the end of the 12 h isothermal time period set in the calorimeter software. Unfortunately, this time period was too short and the complete

exotherm could not be captured. Due to time constraints, this experiment could not be repeated. Nonetheless, a very energetic reaction was observed within a relatively short induction time close to typical storage temperatures.

3.2 MBP

Throughout the research program on MBP at CanmetCERL, MBP measurements were performed on a large variety of emulsion formulations. Selected measurements are presented in Fig. 8. The behaviour of two types of formulations is illustrated: (i) formulations containing only AN in their oxidizer phase (with and without AN prills) and (ii) formulations containing both AN and SN (9 to 11 mass %) in their oxidizer phase (with and without AN prills). It is seen that for these two series of emulsion, the MBP correlates approximately linearly with the water content. So, in general, emulsions having high water content have high MBP values. Also, the presence of AN as prills rather than dissolved in the oxidizer solution does not appear to have much effect on the resulting MBP value. However, it can be observed that the correlation line for the AN/SN emulsion has a much lower slope than that of the all AN emulsions. This means that the presence of SN in the formulation tends to reduce the MBP quite significantly. For example, if we compare the MBP values of the all AN emulsion E6 (8.2 MPa) to that of the AN/SN formula E2 (5.3 MPa), which nearly have the same water content and similar oil phase, the presence of SN appears to cause a 35% reduction in MBP value. As described earlier, SNI

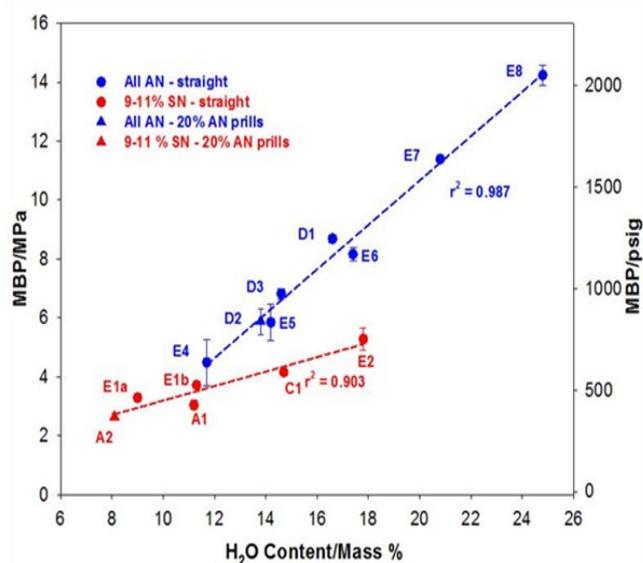


Fig. 8 Correlation of MBP with water content for selected all AN and AN/SN emulsions

in solution is often used as the main ingredient of some gas-ging solutions for emulsion sensitization. In the present work, the effect of SNI on the MBP of emulsions could not be investigated. When in contact with the ammonium ions, the nitrites quickly produce nitrogen gas bubbles [3] which

tend to diffuse out of a small unconfined sample of emulsion. Therefore, in the time scale required to prepare a small batch of emulsion and then perform the MBP testing, no SNI was still present as nitrite in the sample.

4. Conclusions

The DSC results obtained in the present work for the AN/SN mixtures are in agreement with those reported by Yeager [7]. No reduction of AN thermal stability could be evidenced in these tests. However, the DSC results obtained for the AN/SNI mixtures are in disagreement as, in the present work, a very important reduction in thermal stability was observed while no effect was reported by Yeager. This cannot be explained as no details are given in ref. [7] on the physical conditions that were used to perform these DSC tests.

Ref. [7] also claims that in SSCB tests, SN was observed to lower the onset temperature for runaway of AN significantly. In the present DSC work, no sign of such lowering could be observed. Even in larger scale ARC experiments no evidence of incompatibility could be obtained. This disagreement brings some doubt on a possible AN destabilization caused by the presence of SN. More experiments at even larger scale would be required to obtain confirmation.

The HFC experiments confirm the thermal instability of the AN/SNI system. Due to the low onset temperature close to room temperature, SNI could represent a major hazard when used in processes involving AN. The isothermal experiment at 50 °C using the Safety Reaction cell demonstrates that, close to room temperature, contact of SNI with AN leads to very energetic exothermic reactions soon after the chemicals have been put into contact.

The ARC experiment on AN/SNI reported here demonstrates that thermal instabilities can be induced close to room temperature even with small proportions of SNI in contact with AN (3 mass %). In a small sample such as used in the ARC experiment (600mg) this is not sufficient to push the system to run away, however this may represent a hazard in larger masses of AN.

While the presence of SN with AN does not appear to affect the thermal stability of AN, its presence as an ingredient in emulsion explosives seems to promote self-sustained combustion at lower pressure. This could increase the level of hazard for the associated pumping processes with emulsions containing SN.

Acknowledgement

The authors would like to thank Dr. Miao Yao of Nanjing University of Science and Technology and Dr. Wassila Benaissa of SOLVAY Corporate Research & Innovation for their assistance with some of the DSC and HFC experiments.

References

- [1] *Forensic Investigation of Explosions*, Second Edition, International Forensic Science and Investigation Series, Ed. Beveridge, A., CRC Press, Taylor & Francis Group, 2012.
- [2] Persson, P.-A., Holmberg, R., and Lee, J., *Rock Blasting and Explosives Engineering*, CRC Press, 1994.
- [3] Melane, P., *Kinetics Reactions of Ammonium Nitrate-Sodium Nitrite Reaction and Ammonium Nitrate Emulsion Explosives*, M. Sc. Thesis, University of Cape Town, Department of Chemistry, February 2010.
- [4] Alilovic, I., and Reckzin, E., *Method of gassing emulsion explosives and explosives produced thereby*, Patent US 6855219 B2, February 15, 2005 (<http://www.google.com/patents/US6855219>).
- [5] Nguyen, A.D., *Chemically gassed emulsion explosive*, patent US 4997494 A, March 5, 1991 (<http://www.google.com/patents/US4997494>).
- [6] Lightfoot, P., "Hazardous Contaminants of Ammonium Nitrate", *Research Notes from CERL*, SAFEX Newsletter No. 36, pp. 7-11, March 2011.
- [7] Yeager, K., "Hazards of AN Formulations Employing Sodium Nitrite and Nitrate", *Proceedings of the Twenty-fifth Annual Conference on Explosives and Blasting Technique*, International Society of Explosives Engineers, Vol. 1, pp. 387-395.
- [8] Pakulak, J.M., and Cragin, S., *Calibration of Super Small-Scale Cook-Off Bomb Test (SSCB) for Predicting the Severity of the Cook-Off Reaction*, Naval Weapons Center, China Lake, CA, NWC TP 6414, July 1983.
- [9] Goldthorp, S.; Turcotte, R.; Badeen, C.M.; Chan, S.K., Minimum Pressure for Sustained Combustion in AN-based Emulsions, *Proceedings of the 35th International Pyrotechnics Seminar*, July 13-18, 2008, Fort Collins, Colorado, USA.
- [10] Turcotte, R.; Goldthorp, S.; Badeen, C.; Chan, S.K., Hot-wire Ignition of AN-based Emulsions, *Propellants Explos. Pyrotech* **2008**, 33, 472-481.
- [11] ASTM E 968-02, *Standard Practice for Heat Flow Calibration of Differential Scanning Calorimeters*, American Society for Testing and Materials, West Conshohocken, PA., USA.
- [12] ASTM E967-03, *Standard Practice for Temperature Calibration of Differential Scanning Calorimeters and Differential Thermal Analyzers*, American Society for Testing and Materials, West Conshohocken, PA., USA.
- [13] ASTM Standard E1981-98 (2004), *Standard Guide for Assessing the Thermal Stability of Materials by Methods of Accelerating Rate Calorimetry*, West Conshohocken, PA., USA.

- [14] Chan, S.K., and Kirchnerova, J., "Ignition and Combustion Characteristics of Water-gel Explosives", *18th Explosives Safety Seminar*, US DoD, September 12-14, 1978.
- [15] Turcotte, R., Goldthorp, S., Badeen, C.M., Johnson, C., Feng, H., Chan, S.K., "Influence of Physical Characteristics and Ingredients on the Minimum Burning Pressure of Ammonium Nitrate Emulsions", *Propellants Explos. Pyrotech.* **2010**, 35, 233-230.
- [16] Wu, H.B., Chan, M.N., Chan, C.K., FTIR Characterization of Polymorphic Transformation of Ammonium Nitrate, *Aerosol Sci. Technol.* **2007** 41, 581-588.
- [17] Steinitz, M.O., Pink, D.A., Clancy, J.P., MacDonald, A.N., Swainson, I., "Sodium Nitrate - a Difficult Discontinuous Phase Transition", *Can. J. Phys.* **2004** 82, 1097-1107.
- [18] House, J.E., and Goerne, J., "Thermal studies on the phase transitions in sodium nitrite", *Thermochim. Acta*, **1993**, 215, 297-301.
- [19] Townsend, D.I., and Tou, J.C., "Thermal Hazard Evaluation by an Accelerating Rate Calorimeter",

high strength solution for the production of explosives grade prill.

1.Additive composition

An organic additive is capable of initiating a decomposition or burning of ammonium nitrate. The precautions and assumption on design is that the additive is present only in a small concentration (typically 0.1% m/m) and is well mixed. It is also an assumption for safety of the system that the additive supplied is homogeneous and consistent.

It is very difficult for a prill manufacturing plant to ensure that the additive is consistent. This is the responsibility of the manufacturer of the additive. The additive may be manufactured at a facility with other materials present which are not compatible with AN. In any case, the dangers of contamination should be discussed with the manufacturer. An obligation to ensure a safety barrier for changes in composition is maintained by inserting clauses in supply contracts or even visits to the manufacturing facility.

When a new additive is considered for use it is recommended that stability tests, such as ARC tests are performed with the additive mixed at a higher rate than the operational value, perhaps 4 times the operational value. These tests are detailed in the references. [6]. The result of this testing determining the value of the temperature at which decomposition will commence. This should not deviate by a large degree from the temperature for pure AN. A typical minimum value would be 210 °C.

Excessive recycle is a danger as organic additive can concentrate in recycle loops.

If any test shows a low decomposition temperature, this additive should be not considered for use.

Ultimately there is a statistical spread with test results and any low value decomposition temperature should be considered as a negative result.

2.Engineering issues design and flowsheet of addition

There are a number of engineering design issues to consider when an organic additive is used on an ammonium nitrate prilling plant.

- Ensure temperatures do not exceed the decomposition point. Recommended much lower at around 150°C.
- Ensure the additive is added at the correct rate and then mixed well and prilled rapidly
- Ensure there is no potential for accumulation of additive when the plant is not operational

Safety considerations for the addition of organic additives when prilling Ammonium Nitrate

by
Ron Peddie

The manufacturing process for the production Porous Prilled Ammonium Nitrate (PPAN) normally involves the addition of a small amount of organic additive to a relatively high strength ammonium nitrate (AN) solution. Although this process is usually safe, there are dangers inherent in the process.

The use of an organic additive in such high strength ammonium nitrate solutions has led to a number of major explosions [1] [2] [3]:

- 1963 at OULU in Finland
- 1999 at Joplin Missouri USA
- 2014 at Mejillones Chile

As well as these major incidents, there are a number of decompositions and unexpected reactions reported [4] [5]. There are also, probably, a large number of incidents not reported in a public forum.

This paper looks at the engineering, operational problems and dangers of adding an organic additive to a

- Ensure there is no potential for the additive (or other contaminants) to accumulate in the recycle system of the plant

2.1. Design of steam heating in the prilling section

In a low density plant the highest concentration used is about 97% AN with a fudge (fog) point of about 150° C. There is no need for the steam used in the jackets to exceed this temperature. A common mistake is to think that once the plant is operational that the jackets need to transfer heat to the solution. This is not true, when the plant is operational the Ammonium nitrate is supplying all its own heat and the jackets are not required to transfer heat. So there is just a requirement for heating on start up. This would imply a steam pressure of 4 Bar (60 psi) or less. It is also likely that a special let down station will be needed for this steam. The evaporator needs higher pressure steam and relies on different protection mechanisms or layers.

It is desirable to have a de-superheating station, but the most important point is that the steam pressure is lowered. If you compare the 150°C temperature of the jackets with the 210°C minimum temperature for the decomposition, a substantial margin of safety can be built into the system and the plant will have no other consequence.

2.2. Design of mixing of the additive

The additive should be mixed completely and rapidly into the ammonium nitrate solution. The standard chemical engineering design methods of mixing design for equipment are used to check this.

In tanks there must be sufficient agitation.

In lines the velocities of mixing must be sufficiently high.

The additive should be filtered before addition. It is always possible that contamination could occur in the make-up tanks. There are also some reports of agglomeration of material in the additive addition system. [4]. The filter used for this should be quite robust and unable to be bypassed. In some instances, baskets are placed on the inlet lines to tanks. This type of filter is of dubious reliability.

2.3. Safety precautions for addition for an organic additive.

The system should be engineered such that the organic additive addition is stopped automatically when ANS flow stops and not able to be started before ANS is flowing in the prilling lines. This can be achieved by linking the opening of the additive valve to a permissive temperature in the prilling section.

The instrumentation of the mixing system should ensure correct dosage

The system should shut down if it sees errors. These include too high an addition rate, lack of agitation or no ANS present.

To achieve these conditions at all times a well-constructed addition and mixing system is required.

As there is a large consequence for an error, the instrumentation must be assessed as critical - SIL (safety integrity level) rated. In existing plant where SIL rating is not possible the general precautions should follow the logic above.

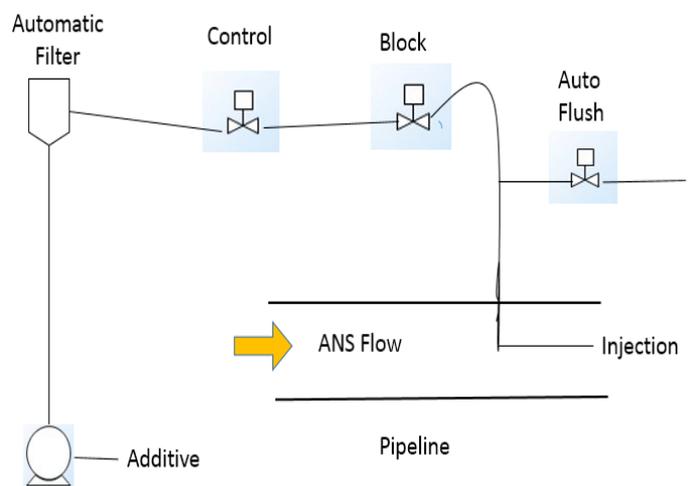


Figure 1 Suggested layout for injection of an organic additive

The instrumentation precautions should be backed up by clear and consistent operational policies and instructions.

2.4 . Avoidance of accumulation of organic additive

Tests have consistently shown the level of organic additive in recycle loops is far higher than in general production, typically 2 – 3 times higher. The reason for this is not known but it can be speculated that the organic additive preferentially sticks to the dust captured in the scrubbers. For this reason, it is recommended that the rate of recycle be limited to say 10% of the total plant flow.

It is also recommended that line velocities be kept high enough to ensure the line is full and the velocity is high enough to keep the line clear by “self-cleaning”. If a line is running at very low velocities, there are two potential separation mechanisms

coming into play. Any organic material in vapour coming off the material can accumulate on the top of a pipe. Any products separating can accumulate in the bottom of a pipe.

It is desirable that plants are set up for complete cleaning with water on shutdown and that all pipes and vessels are easily inspected for accumulation.

3. Operational issues

It is also important is that the that operational staff be trained in these critical issues. The main action being to ensure complete clean out of pipes tanks on shutdown. As part of training and instruction the dangers of addition should be explained. It should also be emphasised that there must be no build-up of organic material in these systems.

As additive material arrives at the prilling plant there should be a system of checks:

- Correct name.
- Record batch numbers.
- Analysis to show colour is consistent and perhaps to show no chloride present (Chloride is the most likely and one of the most potent contaminants).

The prilling plant should also record which batch is used.

4. Safety guidelines in operating instructions

The operating instructions should have guidance on the signs of decomposition. This is not just for additive areas but for all areas:

- If there is any indication of decomposition, we know this does not necessarily mean yellow gas, the gas can be white, but there may still be a smell of NO_x.
- If a high temperature alarm is initiated this must trigger a shut down and be investigated.
- If there is evidence of unexplained contamination in the plant, for instance coloured solution.
- If there is loss of control of a critical system such as steam temperature controller or pH, control even if the plant can continue to operated.

A clear instruction for response and reporting are essential. Operators should report any of these conditions as a high significance incident.

5. Conclusion

The use of an organic additive in the production of ammonium nitrate is useful and provides many properties of prill to the great advantage for the whole explosives and mining industry. While there are risks in the manufacturing plant, if these risks are understood and acted on these can be minimised

A well-engineered and controlled system will reduce risk of this addition to an acceptable level.

6. References

- [1] H. Kiiski, "Mixing explosion in an An /CAN plant Oulu Finland 9.1.63," in *ANNA conference 2004*, St Louis Mo. USA, 2004.
- [2] Private-correspondence, "Accident in a head house Oct 16 1999," Joplin Mo, 2000.
- [3] ENAEX, "Explosion in Mejillones (Chile)," in *SAFEX incident database [Record N°20478]*, 2014.
- [4] L. Clark, "Prill Tower Organic problem," in *ANNA Conference proceedings*, Augusta GA USA, 2005.
- [5] J. H. Im, "An decomposition in a hot melt line," in *ANNA conference proceeding*, Jasper AB , 2105.
- [6] R Turcotte et al. "Physical factors affecting the stability of Ammonium Nitrate solutions (ANS)," in *ANNA proceedings*, London On Canada, 2006.

Ammonium nitrate emulsions, suspensions and gels

(ANEs)

explosion risk and risk controls for road transport

by

Dr Peter Drygala – Principal Adviser Explosives and Dangerous Goods

Dangerous Goods and Petroleum Safety Branch, Department of Mines and Petroleum in Western Australia

(The Hazmat conference presentation for 4 May 2016 in Melbourne was based on many aspects of this paper, which has not been published as yet)

Summary

The explosion-insensitivity of ANEs under most conditions, combined with the regulator's demands for ANEs to pass the rigorous UN Test Series 8, has resulted in the development of intermediates for explosives, which can be classified as Division 5.1, non-explosive dangerous goods. This development has been of great benefit for public safety and mines safety, because it allows the transport, storage and handling of explosion-insensitive intermediates, which are only changed into explo-

sives at the very last opportunity by a mobile processing unit (MPU) at the blast hole.

ANEs are explosion-insensitive to intense heat and direct flame as long as the decomposition gases can escape freely. Under unconfined conditions the combustion and decomposition of ANEs will proceed quietly, and cease as soon as the heat or flame source is removed.

Notwithstanding the remarkable explosion-insensitivity and safety of ANEs, an explosion hazard arises when ANEs are transported in steel tanks with inadequate pressure-relief devices and are engulfed in an intense vehicle fire. It is recommended that steel tanks should be fitted with pressure-relief devices that are as large as practicable. It should be feasible for the complete manhole to be designed to act as a free vent so decomposition gases can escape at any pressure above atmospheric. It is important for Australia to develop national guidance for pressure-relief devices for steel tankers with ANE.

Three full-scale fire tests with aluminium tanks have demonstrated that fire engulfment causes holes and cracks to appear which allow the ANE to flow into the fire and decompose quietly. This is strong evidence of the greater safety of aluminium tanks and any other type of tank material that does not unduly confine the ANE in fire situations.

This paper describes practical ways to minimise the risk of vehicle fires and prevent explosions when transporting ANEs, and the actions to take in response to an emergency.

Introduction

Ammonium nitrate emulsions, suspensions and gels (ANEs) are precursor substances for conversion into bulk explosives in a mobile processing unit (MPU) and are classified as Division 5.1 dangerous goods conforming to UN 3375 – *ammonium nitrate emulsion or suspension or gel, intermediate blasting explosive*.

Ammonium nitrate is the world's cheapest form of explosive energy and Australia's globally competitive explosives industry has been a world leader in harnessing this energy. ANEs are a big and growing part of this industry, which uses almost 3 million tonnes of ammonium-nitrate-containing explosives per annum.

It has taken many decades of technical improvements to get to today's advanced ANEs. For nearly 100 years the emphasis was on water-proofing hygroscopic ammonium nitrate when part of gelignite explosives. Paradoxically, to get the best out of ammonium nitrate it had to be converted into water-based ANEs, overturning the old adage of "Keep your powder dry" that had dominated the thinking in the explosives industry until 1959.

Today's latest ammonium nitrate emulsion explosives that are derived from ANEs represent the pinnacle of a 150-year pursuit in improving the safety of explosives and explosives technology, which started with Alfred

Nobel's inventions of the blasting cap (1864) and dynamite (1866).

The ANEs are converted by MPUs into a range of water-resistant explosives that are the safest and most versatile mining explosives ever made. They come in a wide range of relative bulk strengths in order to match the hardness of the rock, allowing up to three times the explosive energy to be pumped or augured into a blast hole, compared to ammonium nitrate fuel oil (ANFO). They can be designed for open-cut or underground mines, for hard or soft rock, for non-reactive ground or reactive ground, or for normal or hot ground.

Timeline of important inventions leading up to today's ANE derived explosives

1864	Alfred Nobel invents the blasting cap to start the slow phase-out of black powder
1866	Alfred Nobel invents dynamite
1876	Alfred Nobel invents gelignite
1900s – 1980s	Use of ammonium nitrate containing gelignite cartridge explosives, such as <i>AN Gelignite '60'</i> (containing 64% AN; 27% NG)
1956	The United States (US) mining industry discovers ANFO, the first ammonium nitrate bulk explosive
1960s	Suspension-ANEs are introduced simultaneously in the US and in Australia.

They were called water slurries or water gels. Suspension-ANEs are set into a gel shortly after pumping into blast holes by the cross-linking of thickeners, such as guar gum. They are used as bulk explosive for wet-hole applications and only become explosives once all components are mixed at the blast hole.

Suspension-ANEs are saturated solutions of ammonium nitrate (AN) with suspended, solid AN. They may contain other nitrates and soluble fuels, such as sugar or insoluble fuels, such as aluminium powder. They often contain sensitising agents such as suspended TNT or soluble hexamine nitrate/methylamine nitrate. They are further sensitised by the formation of dispersed gas bubbles.

1980s **Emulsion-ANEs** are introduced to make bulk and packaged explosives.

They replace most of the suspension-ANEs and further reduce the need for packaged explosives except as primers for bulk explosives. Emulsion-ANEs are viscous, water-in-oil emulsions made up of countless, micron-sized (1 to 15 microns) droplets of aqueous super-saturated ammonium nitrate solution evenly dispersed in an oil matrix, stabilised with

proprietary emulsifiers. They do not require sensitizing agents and are sensitized by glass micro-balloons or nitrogen bubbles.

The secret for the success of emulsions derives from the tiny size of the droplets, which allows for intimate surface contact between the two liquid phases. The small droplet size enables stable super-saturated AN-droplets and high viscosity.

1989 ICI closes the last plant in Australia for the manufacture of packaged nitro-glycerine blasting explosives

How regulators classify and test ANEs to make sure they are explosion insensitive

The risk associated with the transport of ANEs is much reduced by ensuring that the material is explosion-insensitive and is correctly classified. The testing regime for the classification constitutes an important risk control measure.

The *United Nations Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria*¹, Part 1 provides classification procedures, test methods and criteria relating to explosives of Class 1. Before 2001, Test Series 2 was used to ensure that ANEs were sufficiently insensitive to be excluded from Class 1. On the basis of Test Series 2 they were usually (e.g. in Australia) put into UN 3139 or UN 1479 – oxidising liquid and oxidising solid, respectively, of Division 5.1.

No common classification existed internationally and some countries placed them into Division 1.5D while some left them un-classified as “non-dangerous goods” because the United Nations Manual of Tests and Criteria (UNMTC) did not contain any test that could compel regulators to classify them.

In 2001, international uniformity to the classification of ANEs was achieved by the UN Committee of Experts on the Transport of Dangerous Goods with the introduction of a specific UN entry of UN 3375 – *ammonium nitrate emulsion or suspension or gel, intermediate for blasting explosives* (Division 5.1 oxidising agents) in the 12th edition of the *UN Recommendations on the Transport of Dangerous Goods*.

Still, regulators were not satisfied and demanded a new, more appropriate and rigorous testing regime than Test Series 2 to make sure that ANEs were really very explosion-insensitive.

Hence, in 2003, Test Series 8 was first published in the 4th edition of the UNMTC to address the following concerns:

The large bulk quantities of potentially explosive ANEs carried in tanks carry an unusually large risk during transport. Test Series 2 was designed to suit smaller loads with explosives in cardboard packaging. Since these potentially explosive substances would be transported in large

tanks without the usual “Explosives” signs and onerous safety requirements for Class 1 explosive, it was decided to apply more rigorous testing criteria which are more suitable for substances with a lower velocity of detonation.

The only difference, albeit a critical difference, between the ANE precursor and the sensitised 1.1D explosive is a change in density (through the introduction of countless nitrogen bubbles or glass micro-balloons).

The more rigorous Test Series 8 was developed:

To make sure that only thermally stable ANEs are allowed to be transported in order to exclude substances that are “too dangerous to transport” from the UN 3375 entry

To require a more stringent shock test than the UN gap test 2 (a) from Test Series 2. Therefore the ANE gap test 8 (b) was introduced. It is derived from the identical shock test from Test Series 7 developed by the US Defence Department for Extremely Insensitive Detonating Substances (*test 7 (b): EIDS gap test*) belonging to Division 1.6 explosives. This shock test applies four times more shock energy to the test substance and features a much larger diameter. The larger diameter (73 mm instead of 44 mm) and shorter length (280 mm instead of 400 mm) of the steel pipe makes the propagation of the detonation from the booster through the test substance much more likely and is therefore more suitable for explosives with a lower critical diameter.

Overview of all eight Test Series for classifying Class 1 explosives for the purposes of putting Test Series 8 into context:

Test Series 1 determines if a substance has explosives properties.

Test Series 2 determines if a substance is too insensitive for inclusion in Class 1 and was the testing used until Test Series 8 to exclude ANEs from Class 1.

Test Series 3 determines if a substance is thermally stable and not too dangerous to transport in the form in which it was tested.

Test Series 4 determines if an article or packaged substance is too dangerous for transport.

Test Series 5 determines if a substance may be assigned to Division 5.1.

Test Series 6 assigns a substance or article to Division 1.1; 1.2; 1.3 or 1.4 or excludes it from Class 1.

Test Series 7 determines if an article may be assigned to Division 1.6.

Test Series 8 to determine if an ANE is insensitive enough for inclusion in Division 5.1 and to evaluate the suitability for transport in tanks.

Test Series 2 demonstrates that a substance is too insensitive for inclusion into Class 1, because it gives no explosions (negative results) in any of the tests:

UN gap test Type 2 (a) - To determine if a detonation shock wave is propagated by the test substance with a 50 mm gap between the 160 g booster and test substance;

UN Koenen test Type 2 (b) - To determine whether the substance detonates when heated under strong confinement - orifice vent of the steel tube is set at 2 mm;

Time/pressure test Type 2 (c) – To determine the effect of ignition under confinement;

Test Series 8 demonstrates that a precursor substance is too insensitive for inclusion into Class 1 and must be classified as UN 3375 of Division 5.1 (oxidising agent):

Test 8 (a) – Thermal Stability Test for ANE;

Test 8 (b) – ANE Gap Test is a test to determine the sensitivity to intense shock using nearly twice the sample volume of UN gap test 2 (a) and a 1,100 g booster;

Test 8 (c) – Koenen test is a small-scale test (approximately 40 g) to determine the sensitivity when heated under confinement;

Test 8 (d) – Vented pipe test is a large-scale test (approximately 60 kg) to determine the sensitivity when heated under confinement to determine the suitability for transport in portable tanks;

Tests 8 (a), (b) and (c) are used for classification into UN 3375. Test 8 (d) is only required for the transport in portable tanks, which are mainly used for sea transport.

Containment systems for the transport of ANEs in

Australia

The transport of Class 1 explosives on public roads has reduced significantly, as a direct result of MPUs being responsible for the manufacture of nearly all bulk explosives at mine sites, and is now estimated to be only about 1% of the total explosives used at mine sites. This is a huge improvement for public safety, as well as for mining safety and was the result of regulators and the explosives industry driving the development of ANE precursors that are sufficiently insensitive to pass Test Series 8 and be safely classified into UN 3375.

ANEs are explosion-insensitive to intense heat and direct flame as long as the decomposition gases can escape freely. Containment tank material which does not unduly confine ANEs in fire situations minimises the risk of explosions.

Containment systems for the transport of ANEs must be constructed in accordance with a design that is approved by state and territory jurisdictions. This is achieved on a national basis by approvals given by CAP comprising the state and territory jurisdictions⁷. Such design approvals are an important risk control measure.

The following describes the four types of approved transport methods:



Mobile processing units (MPUs) are mainly found on mine sites and are specially designed to blend various sensitisers into the ANEs to convert them into Class 1 explosives. MPUs are approved under explosives legislation rather than by CAP. ANEs are stored at mine sites in large storage tanks from which they are transferred to MPUs.

MPUs have the dual purpose of transporting ANEs, ammonium nitrate prill, diesel fuel and sensitising agents in separate steel or aluminium compartments and then converting the ANEs into Class 1 explosives at the blast hole. They are permitted on public roads when transporting non-Class 1 dangerous goods intermediates.



Composite intermediate bulk containers (CIBCs) consist of a rigid inner plastic container and an outer protective rigid steel-mesh casing conforming to the Intermediate Bulk



Multimodal portable tanks or isotainers are internationally approved tanks with pressure-relief devices. They are twist-locked onto road and rail platforms, and carry about 20 kilolitres of product. For sea transport, it is an international requirement to use portable tanks.



History of accidental explosions of ANEs

The road-transport accident record of ANE is still unblemished after many years of transport – there has not been an accidental explosion during road or rail transport.

Despite the inherent explosion insensitivity of ANEs, explosions involving ANEs are not unknown, two examples of which are the MPU explosion in Norway in 2013 and the Porgera mine explosion of ANE storage tanks in 1994.

MPU explosion in Norway

An explosion of an MPU took place on a mine site in Norway on 17 December 2013. The MPU was loaded with 5,000 kg of ammonium nitrate and 8,000 kg of ANE in separate 6,600 litre aluminium tanks when an electrical fault caused a vehicle fire during the loading of a blast hole. It is not known whether the ammonium nitrate or the ANE or both were responsible for the explosion.

The fire burned for about 2.5 hours before exploding. The explosion was a detonation involving the energy equivalent to 500 – 1,000 kg of TNT. This is a low explosives yield and illustrates that most of the approximately 13 tonnes of potentially explosive material either decomposed before the explosion, or did not react in the explosion.²

Porgera gold mine explosion of ANE storage tanks

ANEs are capable of devastating detonation reactions. This was clearly indicated by the explosion which happened at the Porgera gold mine in New Guinea on 2 August 1994.

A detonation took place in storage tanks holding a total of approximately 90 tonnes of ANE. The detonation followed a primary explosion, involving the

pumping and manufacture of packaged explosives, which killed 11 employees. This first explosion caused a severe fire of the diesel fuel stored in close proximity to the ANE tanks with burning diesel engulfing the tanks because of the unfortunate location of diesel and emulsion in a single, banded compound. The bigger second explosion occurred after the external diesel fire had impinged on the emulsion tank for 1.15 hours. There were no further casualties as survivors from the first explosion had evacuated the area³.

What is the explosion risk of ANEs during road transport?

The following explosion behaviour summarises the experience gained from the use and explosion testing of ANEs:

ANEs are insensitive to friction, impact and sparks

The shock sensitivity of these mixtures is approximately four times lower than for a low-density, Division 5.1, ammonium nitrate prill on the borderline of being a Class 1 explosive and passes Test Series 2 as being too insensitive for Class 1. Even the most energetic traffic collision will not result in an explosion.

ANEs will not sustain combustion if unconfined

Combustion and decomposition of ANEs results from direct and indirect flame impingement, but ceases as soon as the external flame is removed. There seems to be sufficient evidence that flame impingement on ANEs in unconfined conditions, such as direct flame impingement on IBCs, will not result in an explosion.

ANEs are hazardous when heated under confinement

Heating under strong confinement in a tank is the most hazardous aspect of ANE's explosive properties and such confinement is to be avoided by the correct selection of the tank and its pressure relief devices.

The heat resistance of ANEs is higher than for solid ammonium nitrate, because an explosion is less likely to happen until much of the water has been driven off by the heat, allowing more time for evacuation.

However, the thermal conductivity of ANEs is relatively low and this explains why it is possible that in a strong fire, under strong confinement in a tank with insufficient venting, localised high temperatures can result in a violent decomposition and pressure explosion, while much of the remainder of ANE is unaffected by the heat.

The only realistic road-transport explosion-accident scenario arises when a large vehicle fire decomposes the ANE in a metal tank in an explosive reaction. An explosion can occur if the tank confines the reaction gases to such an extent that they overcome the pressure relief capacity of the pressure relief valve.

This hazardous aspect of tank transport can be closely examined by the explosion behaviour of ANEs in the vented pipe test and in particular in the full-scale fire tests in Kuosanen in Sweden.

The vented pipe test 8 (d)

The vented pipe test 8 (d) is meant to ensure the suitability of the ANEs for the transport in tanks. The utility of this test has been criticised on the basis that it is very difficult to perform in practical terms and requires a very remote location suitable for the release of large volumes of toxic nitrogen oxide decomposition gases and with a 2 km range, where the potential impact of red hot shrapnel (only if the vented pipe fragments and if the ANE explodes and does not pass the test) will not be an unacceptable bushfire risk.

It has also been argued that the test is not representative of a fire impinging on a real tank vehicle because of the disproportionately large venting capacity and the 10 mm thickness of the mild steel (compared to 3 to 5 mm for a real tank on a road vehicle).

The large venting capacity offered by the 78 mm diameter vent in relation to approximately 60 kg of ANE test substance is not matched by the much smaller relative venting capacity in a road tank vehicle. An Australian ANE steel tank vehicle can carry 37,000 kg: if one assuming the most ideal vent, where the complete man-hole of 600 mm diameter acts as a free vent, then the relative venting capacity of the vented pipe test in mm of vent diameter per kg of ANE is approximately 80 times larger than in the best-vented tank vehicle.

On the positive side, the vented pipe test routinely demonstrates that ANEs, in the presence of sufficient venting capacity, are remarkably explosion insensitive when subjected to intense heat – the ANE in the vented pipe is heated to approximately 800°C for 30 minutes without an explosion while giving off large quantities of decomposition gases.

Regulators and the explosive industry are aware of the shortcomings of the vented pipe test. The Canadian Explosives Research Laboratory, with the assistance of the explosive industry, has been working on the minimum burning pressure (MBP) test for over twenty years. Some industry experts now regard it as a practical alternative for the vented pipe test and the Koenen test 8 (c) in regard to ANEs. The MBP value of an ANE is the minimum pressure required before the ANE can undergo self-sustaining decomposition or deflagration when subjected to heating. The MBP test will be discussed by the UN Explosives Working Group this year.

Full-scale fire tests in Kuosanen

Swedish and Norwegian Government authorities conducted two full-scale fire tests in Kuosanen⁶ in 2007 on an insulated aluminium as well as an uninsulated stainless steel road transport tank, each containing 6,000 kg of ANEs. The tests demonstrated that the particular steel tank, but not the aluminium tank, experienced a violent 10 bar pressure explosion after only eight minutes, because the decomposition gases could not

adequately vent. The pressure explosion produced two large tank fragments of 43 kg and 116 kg, which were propelled a distance of 76 m and 92 m, respectively. The explosion also propelled a significant amount of unreacted ANE into the surroundings. Unreacted ANE remained in the tank.

The steel test tank featured a pressure relieve valve, which was designed to actuate only at and above 2.5 bar allowing only 15 seconds of venting before the explosion. Venting occurred through a very small 25 mm diameter vent with a low venting capacity of approximately 0.0042 mm/kg, similar to some Australian ANE tank vehicles.

The test confirmed the result of two previous full-scale tests on aluminium tanks, which demonstrated that the heating of aluminium tanks allows the formation of large holes and significant cracks, removing the confinement and preventing an explosion. Subsequent to the appearance of holes and cracks, emulsion oozed on to the fire from the cracked tank and burned quietly, but only while it was still supported by the burning of the external fuel.

The experiment used a high fuel loading measured as the amount of fuel per mass unit of ANE. 400 L of diesel fuel and eight truck tyres confined in a small steel basin placed one metre below the ANE tank seems high for 6,000 kg. To obtain such an extreme fire impingement in a real-life scenario would be rare and represents the worst case scenario.

The experiment points out what is most likely to occur with worst-case fire impingement on a 4 mm thick stainless steel tank with an inadequate and unsuitable pressure-relief device.

This one-off experiment cannot exclude the possibility that other similar experiment, under slightly different conditions, will



Photo of the stainless steel tank before the fire test



Photo of ruptured stainless steel tank after the fire test – note the unreacted ANE on the ground, which was

Conclusions regarding a potential explosion in tankers and portable tanks

It is not possible to judge the likelihood of an explosion in a large fire with certainty, because of the lack of experience (and lack of information) on near-miss tank vehicle fires.

By contrast, the transport of solid ammonium nitrate (AN) experiences many near-miss incidents – there are more near-miss incidents of this type than there are explosions.

Currently there is uncertainty of how Australia's steel tankers and the international steel portable tanks (mainly used at sea) will perform in a strong vehicle fire under worst-case conditions. There is a lack of knowledge of how well prevailing pressure relief valves allow decomposition gases to escape from a steel tank.

There is currently no national standard for the design requirements specifically suited for ANEs. Hence there is no guidance for pressure-relief devices for ANE steel tanker vehicles.

The specification for pressure-relief devices for portable tanks in the Special Tank Provision TP32 in the *UN Recommendation on the Transport of Dangerous Goods Model Regulations* is unsuitable to allow adequate venting.

On the strength of three full-scale fire tests, it seems that aluminium is a good material to transport ANEs. Other non-confining materials may potentially be even more suitable than aluminium.

Notwithstanding the lack of accidental explosions of ANE in road and rail tank vehicles and portable tanks, and considering the current uncertainty of how metal tanks would perform in a strong vehicle fire, it is recommended that emergency responders plan for the possibility of an explosion, especially in the case of steel tanker vehicles and steel portable tanks.

Recommendation for pressure-relief devices for steel tanks:

Steel tanks require the largest practical venting capacity and should allow immediate venting at any pressure above atmospheric pressure. We do not know whether the vent can be made large enough to totally prevent an explosion, but it should be practical to convert the complete manhole (some 600 mm in diameter) into a free vent without a minimum bursting pressure. At the very least, in an emergency the biggest practical vent will buy time for evacuation.

There is an urgent need for Australia to develop a national guidance for the specifications for adequate pressure-relief devices in ANE tank vehicles.

There is also a need for Australia to seek amendments to the Special Tank Provision TP32 of the *UN Recommendations on the Transport of Dangerous Goods Model Regulations* to introduce suitable specifications for pressure-relief devices for portable tanks.

Safety measures to prevent a vehicle fire

A vehicle fire can be initiated by various causes including electrical or mechanical faults, a tyre fire or a vehicle collision or roll-over. These are all issues which offer the transporter many opportunities for further practical risk mitigation controls, which should include minimisation of driver fatigue. Transporters need to regularly review their safety management systems and those of their subcontractors to ensure that the risk of a fire is minimised and they comply with the requirements of the *Australian Code for the Transport of Dangerous Goods by Road and Rail (ADG7.4)*⁴.

The transport of ANEs in MPUs primarily needs to comply with the Australian Explosives Industry Safety Group (AEISG) Code of Practice for *Mobile Processing Units*⁵.

Potential causes of fires include:

traffic collisions and single vehicle crashes

Any issues contributing to such accidents need to be addressed. It will require close attention to the roadworthiness of the vehicles, especially tyres and brakes, as well as the driver's health and fitness, and measures to avoid driver fatigue.

poor vehicle maintenance

Wheel fires are usually caused by seized bearings, "dragging" brakes and overheating tyres. Electrical faults and failed fuel lines may also lead to fires.

Bushfires

The bushfire risk at some mine sites may need to be considered for suitable parking locations of MPUs.

Safety measures to minimise the adverse consequence of a fire

Transporters need to provide the driver with the ability to fight small vehicle fires in an effective way by making sure:

fire extinguishers are fit for purpose and meet the minimum requirements of Table 12.1 of ADG7.4

vehicles loaded with tanks or portable tanks have a 10B dry powder extinguisher in the cabin and either one 60B dry powder extinguisher or two 30B dry powder extinguishers for each trailer, maintained in accordance with Australian Standard AS 1851 *Routine service of fire protection systems and equipment*

the driver has been trained and is competent in the use of fire extinguishers and emergency response procedures for ammonium nitrate

the vehicle's cabin contains the required emergency information inside a special emergency information holder, as prescribed in Chapter 11 of ADG7.4

the required emergency information consists of an emergency procedure guide (EPG) for a vehicle fire and a separate EPG to address spills and fires involving ANEs

the driver understands the need to evacuate to a safe distance in the case of a fire that is not able to be controlled with a fire extinguisher. If the fire involves only the trailer, and it safe to do so, the driver should unhitch it and drive the prime mover to safety.

Notwithstanding the mandatory minimum requirements for dry powder extinguishers, this type of extinguisher is not as effective against a tyre fire as water-based foams, but the foams are unsuitable for electrical fires. A number of new vehicle-mounted fire protection systems are now on the market.⁸

Emergency response

Transporters need to regularly review their procedures and practice their emergency response. Good communication between transporter, driver and emergency services is essential for a fast and effective response.

If there is an accident or fire, the Emergency Information Panel (EIP), transport document and EPG provide critical information to emergency services. The EIP must list the telephone number of a competent emergency advisor, whose service is available at all hours.

Emergency services have a difficult decision to make whether to fight a fire or withdraw to a safe distance from a potential explosion.

SAA/SNZ HB 76:2010 *Dangerous Goods – Initial Emergency Response Guide* contains the required EPG. *Guide 51 – Ammonium Nitrate Emulsion, Gel or Suspension (UN 3375)* recommends, in the case of a large fire, an initial evacuation distance of at least 1,000 m in all directions and to be completely protected against a detonation explosion, an evacuation distance of 1,600 m is required.

Fires will produce toxic decomposition gases and can be fought with flooding quantities of water, delivered as fine spray. Hazchem Code is "1Y".

Spills of ANE, without a fire, do not present a respiratory hazard to persons. Spills are too viscous to flow outwards and can be shovelled into containers for disposal without respiratory protection. Skin contact should be avoided by wearing overalls, gloves and boots. ANEs are eye irritants and goggles should be worn. It is toxic by ingestion.

References:

1. United Nations Manual of Tests and Criteria (UNMTC) regarding the Transport of Dangerous Goods, 6th revised edition, 2015: viewed 27 April 2016 <<http://www.unece.org/trans/areas-of-work/dangerous-goods/legal-instruments-and-recommendations/un-manual-of-tests-and-criteria/rev6-files.html>>
2. Norwegian Directorate for Civil Protection, 2013. Explosion accident during Mobile Production of Bulk Explosives, Report by DBSs project committee on the follow up of the accident in Drevja on the 17th December 2013: viewed 27 April 2016 <[http://www.dsb.no/Global/Publikasjoner/2015/Rapport/Explosion Accident during Mobile Production of Bulk Explosives.pdf](http://www.dsb.no/Global/Publikasjoner/2015/Rapport/Explosion%20Accident%20during%20Mobile%20Production%20of%20Bulk%20Explosives.pdf)>
3. Sen, G.C. and Downs, G., 2008. An approach to addressing explosive related accidents by implementing strategic training: viewed 27 April 2016 <<http://ro.uow.edu.au/cgi/viewcontent.cgi?article=1027&context=coal>>
4. Australian Code for the Transport of Dangerous Goods by Road and Rail (ADG7.4): viewed 27 April 2016 <<http://www.ntc.gov.au/heavy-vehicles/safety/australian-dangerous-goods-code/>>
5. The Australian Explosives Industry Safety Group (AEISG) codes of practice are freely available at <http://www.aeisg.org.au/index.php/cop.html>
6. Kalström, H., Brobäck, K., van Dam, L., Folkesson, B., Heino, P., Johansen, A., Nilimaa, F., and Vestre, J.H., 2007. Full-scale Fire Test of ANE Matrix in Aluminium and Stainless Steel Tanks, Report by Kimit AB, Räddningsverket, Skanexplo, Forcit, DSB og Orica, (2007).
7. Link to the Competent Authorities Panel https://infrastructure.gov.au/transport/australia/dangerous/competent_authorities.aspx
8. <http://quitfire.com/> just one example of a commercially available water-based foam fire-fighting system for mounting on vehicles to fight tyre fires

CONCERNS WITH USE OF HOLLOW PIPES IN EXPLOSIVE PLANTS

BY

R.K.GUHA

Solar Industries India Ltd.

I was recently going through some old Safex Alerts and one which caught my notice was SSA04-09 from TITANO-BEL on detection of cracks on the rotor of a progressive cavity pump. This was in use in emulsion explosives. A similar incident had happened in one of the major explosive plants in India. It is reported that in this case it was a rotor of an acrison blender and also was in contact with emulsion explosives. This turned out to be a hollow rotor which had developed a crack and was removed for welding. The knowledge that it was a hollow rotor was not known to plant/maintenance personnel and it was in use for nearly 12 years. The rotor was suitably cleaned with diesel and sent for flame passing before it could be sent for welding of the crack.

During flame passing there was a small explosion and the rotor split into two over a length of about 30 cms. Apparently it appears that explosive may have penetrated in the hollow section through the crack, which could not be properly decontaminated, resulting in the explosion.

This brings us to the serious question about the use of hollow sections in plants where there is a likelihood of its being in contact with explosives and if at all it is required then a proper decontamination procedure should be put place.

At Solar a review of the decontamination procedure has been done and is presented here for the benefit of SAFEX community.

Before decontamination of any process part or equipment, it is extremely important to know for sure that the relevant part is hollow or solid. For this, the history of the relevant part equipment should be known – may be from the drawing as received from the manufacturer or earlier experience during any repairs done on it. The common practice of hearing the sound on tapping the relevant part with a metal generally gives correct clues to indicate whether it is solid or hollow.

For solid parts in contact with Oxidizer Blend(OB) or AN melt, the procedure is to wash the part thoroughly with water and visually inspect that it is free of contaminant. For hollow part, however, the washing should be done

more vigorously with water(if necessary hot water may be used) and checking to be done either by monitoring pH or by detecting for nitrate ion using diphenylamine solution in Sulphuric acid which will turn blue indicating presence of nitrate ion.

For solid parts in contact with Fuel blends, the procedure is to wash part thoroughly with hot water mixed with Soap solution and visually inspect that the part is free of any contaminant. For hollow parts, however, the same needs to be done and the detection is done for presence of oily material in the wash water.

No heat treatment by burning in Burning station or flame passing when the equipment part cannot be removed from the plant, is considered necessary in both the above cases.

For equipment parts which are solid and in contact with emulsion matrix / gassed matrix or slurries, decontamination is done by first physically removing all visible matrix /gel using cotton piece. If required, rod covered with cloth piece soaked in diesel may be used. Dry it using a fresh cotton cloth. Ensure it is completely dry and then burn it in Burning station or apply flame from a safe distance(> 1.5 meters) behind a shield.

For equipment parts which have hollow sections which may be in contact with Emulsion matrix / gassed matrix or gel, same procedure is followed but with an additional precaution of provision of a vent in the hollow section before it is allowed for heat treatment. The vent if not available may be made manually beforehand by making a cut or hole with running water.

Procedure for Decontamination of Process part/equipment prior to removal from process areas for repair, storage or disposal

- Identify the part /equipment of the Plant which is required to be decontaminated.
- Identify the explosive(s) / hazardous chemicals which has contaminated the part/equipment.
- The equipment shall either be decontaminated in situ or transferred to a special decontamination area for treatment, the later should be preferred option.
- Personnel involved in the decontamination shall have knowledge related to the hazards of all potential contaminants and be very clear of the decontamination procedure. He should have access to MSDS of the potential contaminants.
- Issue Clearance Certificate for removal of the part/equipment.
- Carry the part/equipment to a designated place, if required, for decontamination. Care should be taken to divert the wash water through to the relevant effluent treatment system.
- Check and ensure removal of contaminants, taking into consideration any enclosed spaces where contaminants may be trapped.
- The part/equipment should be tagged with a Material

Decontamination Certificate to confirm its decontamination status. **It shall be attached to the part. Untagged material shall not be transferred from process areas.**

- If flame passing is required to be done on the part/equipment then a Clearance certificate along with a Fire permit shall be issued after the part/equipment has been decontaminated as far as reasonably practicable.
- Flame passing shall be done by a competent person from a distance of at least 1.5 meters and the relevant equipment should be subjected to flame for a period sufficient to ensure the contaminants are burnt/ exposed to the

As an example we give below a table below gives a brief guideline to the procedure which can be used for decontamination of various equipments in contact with explosives in emulsion/slurryplants.

Procedure for decontamination of Process equipments & part of m/c for hot work.

S.No	Plants	Types of Equipment	Decontamination procedure
A	Emulsion/ Slurry	Equipment which are SOLID(Not containing any hollow part) and in contact with OB/AN Melt	Wash generously with water/ hot water and check visually for any contamination. If none found, it can be called decontaminated.
		1. OB reactors & storage tank (Agitator shaft)	
B	Emulsion/ Slurry	Equipment which are HOLLOW including jacketed equipments & pipeline and in contact with OB/AN Melt	1. Make sure that the jacketed equipment /pipeline is open from both ends. 2.Wash generously with water/ hot water and check for presence of Nitrate ion/ acidity till pH is that of normal water.
		1. All pipelines (Jacketed/Non jacketed)	
		2. OB Basket filters	
		3. OB reactors & storage tank (steam coils)	
C C	Emulsion/ Slurry	Equipment which are SOLID (Not containing any hollow part) and	Purge with steam & then with Nirma water and check visually for any contamination
		1. FB reactors & storage tank (Agitator shaft)	
D	Emulsion/ Slurry	Equipment which are HOLLOW and in contact with OIL/FB	Purge with steam & then with Nirma water and check visually for any contamination
		1. All pipelines (Jacketed/Non jacketed)	
		2. FB Basket filters	
		3. FB reactors & storage tank (steam coils)	
		4. FB reactor, storage steam coil	
E	Emulsion/ Slurry	Equipment which are SOLID(Not containing any hollow part) and	1. Physically remove the matrix / gel using cloth with rod. 2. Also apply cloth soaked with diesel over the equipment 3. Wipe with dry cloth. 4. Ensure it is completely dry. 5. Burn in Burning station
		1. Jet mixer	
		2. Feeder/ Blender screw and Auger	
		3. Jet mixer jacket- Not to be sent for hot work	
		4. KP m/c film folder (Emulsion & slurry plant)	
		5. KP m/c Extruder (Canopy, screw, barrel, nozzle- Emulsion & slurry)	
		6. Chain conveyer/Cooling bath	
		7. . Jet mixer jacket- Not to be sent for hot work artridge collection tray (Emulsion slurry)	
8. Gluing m/c (conveyer shaft, flap, pressing rod)			

	Emulsion/ Slurry	Equipment which are HOLLOW and in contact with Matrix/Gassed matrix.	
F		1. All pipelines (Jacketed/Non jacketed)	1. Physically remove matrix /gel using cloth with rod. 2. clean using cloth soaked in with diesel. 3. Wipe with dry cloth. 4 Ensure it is completely dry. 5. if the equipment has no vents , then make hole/cut in running water with water in the pipe/jacket. 6. Burn in Burning station
		2. Matrix line& bend after product pump (Not to be sent for hotwork)	
		3. Hot conveyer belt drum (Hollow, shaft, side plate)	
		4. Box conveyer drum	
		5. Tote bin hand wheel	
		6. Bend after product pump (Not to be sent for hot work)	

CHANCE IS A FINE THING

By

Tony Rowe



I have become old. I'm too slow to be a car guard and too short for a speed bump. My hair has turned white and my teeth have all fallen out. Sticky-spare ribs are no longer a menu item. Gnawing and biting are things of the past, a nasty suck being the best I can manage these days. Nothing works anymore and nobody listens.

It is not easy getting old, I can no longer tie my own shoelaces or put on socks, but despite all the physical changes, the same accidents that plagued my misspent youth are continuing to happen. Things continue to go bang unexpectedly, shrapnel still flies and the pyro's still manage to produce a tissue devouring thermal pulse. Did you know that skin begins to burn at temperatures under 50 degrees Centigrade? Amazing and painful at the same time! As before, some lives are lost, some are changed forever, and just a few experience lasting psychological trauma. Few survivors remain wholly untouched.

These days it has become a tenet of the explosives & chemical industries that all accidents must be reported, but contrary to what you may believe, accidents are not inevitable. They can be prevented. Prevention comes via the adoption and strict implementation of safe procedures. With the possible exception of 'reflex actions' **all** acts carried out by persons (whether safe or unsafe) are learned acts. Every single act is therefore either (a) self-motivated, (b) gained from experience or (c) taught in a classroom environment by a competent instructor. However, within the warm embrace of the explosives industry it is understood that learning about safety only via the somewhat flawed medium of experience can have life changing consequences, not only because the novice may be involved with energetic materials, but because the necessary knowledge is so wide ranging. Within the explosives industry the classroom environment is therefore the preferred model.

With all of that in mind, today's article is going to concentrate on acts that are '**self motivated.**'

About 50 years ago when I was just a little bit younger I would watch an American series on the TV. It had a Western theme

and was called Maverick. I think it starred James Garner. Anyway, luck was his companion and gambling was his game. Week after week, Brett Maverick, (James Garner) the main character in the show, would get into trouble. Somehow he always managed to beat the odds and would emerge - just as the credits began to roll – with his wounds healed, his clothing spotless, his skin glowing and ready for the next adventure.

Thinking about it now triggers images of a man in a white ruffled shirt and black string tie; a black cowboy hat tilted back on his head. It is an image that prompts the question, “Are you a gambler like Brett?” If you said no then your tongue has probably just turned black. Stick it out so that we all can see. There, I told you, black as soot.

We all gamble. We gamble each time we carry a mug full of coffee across into the lounge. We gamble that (a) we won't spill any and (b) that even if we do, we can clean it up before our partner notices. Some of us might chug-down milk or juice straight from the carton or container or perhaps drink cool-drink directly from the bottle. We know that we shouldn't, but we trust to luck not to get caught, but hey, even if we are, the downside's not that bad, but there is another position to gambling. This particular viewpoint is not about coffee or juice, milk or pop. It's not a harmless flutter on the horses or a few coins fed into a slot machine either. This is the less acceptable face of gambling and it is all about risk. It's the great roulette wheel of life. When you lose, you lose big time. In this game the croupier wears a black cloak and carries a scythe and the term “you bet your life” is true.

Throughout human history there have been those willing to take great risks. Fred Flintstone, Flash Gordon, The Lone Ranger, Hernan Cortez, Conan, Captain Pugwash, John McClane, Chuck Norris and James T Kirk to name, but a few. Then there were the early explorers who perhaps seated on a log paddled out into the great unknown. How many failed to make it is unclear, but some certainly did and a lucky few found fertile ground and hopefully even flourished. There were those who chose to taste the great red fruit of the tomato plant and others who tried a few death-cap mushrooms. Tomatoes it transpired were OK, death-cap mushroomsWell.

We are clearly hardwired to take risks, it's in our DNA. When we look at DNA under the microscope, the gambling element so associated with risk is that little squiggly green bit about a third of the way down the double helix. The risk-taking section of my own DNA helix is incredibly small and quite strangely so is another portion of my anatomy. To tell the truth there are two of them. They never get much of a mention, but I am very attached to

them both. They're my ears - well actually, the sticky-out cartilaginous bits of my ears. My ears are so tiny. Perhaps the two things are genetically linked, an anomaly which explains my great age although some say that my wiring is also faulty.

Now, I don't want to preach about risk. What I want to discuss is at-risk behaviour.

At-risk behaviour is a lifestyle activity that places the sufferer at an increased risk of contracting a particular condition, illness or injury. It can be a terminal disease with no certain cure. Rock salt and pigeon dung poultices have been tried on volunteers as have ice-cold baths and electro-convulsive therapy. Despite vigorous and prolonged applications of such treatments, both singly and in array, positive results have thus far proven difficult to verify. Worse, the begging and screaming that accompanies such therapy can be extremely wearing.

The ailment itself you see focusses upon unnecessary risk. Sometimes the behaviour endangers only the person engaged in the particular activity, but other at-risk behaviours can also threaten the lives and well-being of those caught up in the activity itself or, in some cases who through chance, fate or just plain bad luck, happen to be close by. Simply put, at one end of the spectrum we have the person who refuses to wear hearing protection whilst at the other end sits the driver of a (filled to capacity) 747 passenger plane who is either falling down drunk or high on drugs.

There are so many at-risk behaviours that it is impossible to list them all, but as Forest Gump once said “Stupid is what Stupid does,” but if there are risk behaviours then it probably follows that there will also be anti-risk behaviours.

There are and a few of them are built in, but others clearly have to be learned. Now I hope it is clear that it is impossible to avoid risk entirely so as stated in the opening paragraph we must either be taught or learn from experience. Learning from experience is definitely not a good idea, but whatever the learning mechanism, we learn to guesstimate the level of risk for any given situation and then take whatever steps that we deem necessary to reduce it. A lack of such experience probably explains why adolescents have become notorious for indulging in a wide range of at-risk behaviours. Motorbikes, cars, lakes, rivers and oceans, drugs and excess alcohol all take their toll of our inexperienced youth. You see, the methodology of risk-assessment carried forward within our DNA and engraved on our genes is not really that effective or accurate. We don't know how best to carry out a proper evaluation and so all of us, on a daily basis, both underestimate and overestimate risk. This is because there are a gazillion factors which can influence not only the decision, but also its outcome. Exactly how much risk each person is willing to take on any particular occasion varies therefore not only with the individual, but also on a range of other circumstances.

For many, risk is a vital part of the gambling experience. For some people it is the seasoning on the meal, the hot spice, the distilled essence, but it is the element of physical risk that provides the motivation.

So what is risk? Risk is about exposure to actual physical danger and the real possibility that something bad will happen. Incredibly, people deliberately go in search of risk. For instance, they will often drive fast and recklessly, the additional recklessness enhancing the experience, but just sometimes the need for risk is more subtle. Some drivers refuse to wear their seatbelts and will go on to drive at speed whilst simultaneously texting on a cellphone. They will even take risks for others. Look around you. Is that an unsecured child or baby plonked there onto the front passenger seat of that car?

There are those who drink and drive, take drugs and drive or fail to stop appropriately. I've even seen risk-takers driving around a traffic circle the wrong way or even reversing into oncoming traffic because they missed their turn instead of just going around again. Why? Have their lives become so jaded or their arrogance and conceit grown so tall that no-one else matters? Has life become so much about ego, arrogance and conceit that all that remains is Me, Me and only Me. Some folk will stand on railway tracks taking selfies and one-day wonder at what just hit them. In such cases the wondering bit tends to be all too brief and the after action cleanup long and unpleasant.

Other sufferers will run across major highways at rush hour, jump off buildings or skateboard down long concrete staircases. Is it for the adrenaline surge or simply bragging rights? There is no apparent gain and no financial reward whatsoever. Perhaps mountain climbers, base jumpers and guys who jump out of planes without parachutes understand this endless quest for more and more risk. The behavior isn't necessarily imaginative, but it is repetitive.

It is an attitude that is not the sole reserve of the young. I recently had a guy come to replace some tiles on my roof. When he arrived he had no safety gear beyond the belt that was holding up his trousers. He nevertheless climbed up onto the roof using an unsecured and rickety old ladder and proceeded, using a couple of old screwdrivers, to pull out and replace half a dozen or so damaged tiles. Bear in mind that he was working on a steeply sloping and possibly slippery surface a mere fifteen meters above the ground. A strong wind was gusting and a hint of curry from the Indian sub-continent added a little extra spice. Far, far below and ready to break his fall or perhaps his neck lay a brick

driveway. There was no medical team on site nor anyone locally who was trained in any sort of resuscitative techniques. I did, however, possess a large box that had once contained waterproof Elastoplast and thus bore a big red cross on its lid. I also came across a first aid manual, circa 1917. It had a chapter devoted to the bandaging of both bullet wounds and bayonet stick injuries and yet another on gas attacks. No worries then mate!

I have to confess that despite my extensive preparations my heart was in my mouth all the time he was up there. I was beyond rational thought, but I bravely readied the garden hose - to wash away any blood - and tore some old curtains into strips for bandages. I even put some water on to boil. I thought that might be for when babies are born, but I didn't know if he was pregnant or not. He looked a bit like he could be.

To keep it brief when he returned to terra-firma, I asked him if he thought what he was doing was safe. He said that he had been doing this job for thirty years and had never had a fall. He needed to work quickly and move on to the next job as soon as possible. There was no time for securing ladders or tying and untying a safety harness. Time was money. He was wholly unrepentant and his attitude became increasingly aggressive as I continued to question his methods and motivation. Experience had apparently convinced him that what he was doing was entirely safe. He could cram lots of small jobs into his working day whilst maintaining a low inventory of tools and equipment. Hard to fault his rationale, but then we humans can usually find some sort of justification for our actions, however reprehensible they may be

From my perspective, skydiving off a roof is simply not worth the risk, but then I don't like heights. If I had been up there I would have been at great pains to secure myself against a possible slip or fall. I would have also have tied off my ladders, top and bottom. You see, I don't want to die, or worse, end up as a Cabbage Patch Kid sucking up puree for the rest of a horribly miserable life.

What do you think, was the guy right or wrong, after all it was his life that was being placed at risk wasn't it or is it simply a judgement call?

The pastime itself is called gambling. It is seen by many as entertainment and is usually played at casino's, or at racetracks, but more often at home. It is a form of escapism as it can help some people (temporarily at least) to escape from life's little problems. There are even gambling websites where the punter can play a game of his or her choice. The problem is, that just like hard drugs, gambling can be addictive. Lots of small wins makes us feel invulnerable and this helps boost our ego. Worse, it creates further impulsivity, a serious condition in which people act without thought or assessment and which all too often they win. Most of the time the gains are trivial, but just sometimes the losses exceed all expectations.

So do you think things through or are you the impulsive type, acting instantly without thought? If so then for you there are no consequences, nothing to go wrong.

Perhaps we just lost a small sum playing a one-armed bandit or the local Lotto or maybe the guy we just cut up on the highway simply didn't for once drag out that .45 calibre Thompson sub-machine gun he keeps under his seat, but just sometimes when the stakes are higher, we may have to be cut out of a car wreck leaving an arm, a leg or a life behind. Sometimes, Old Sausage, we lose.

There is though another form of at-risk behavior. It's called "The Calculated Risk."

There is a world of difference between a gamble and a calculated risk.

In the "calculated risk scenario," the issue is removed entirely from the realms of 'reckless decision making.' Any exposure to actual physical danger is delayed until all the options available have been carefully considered and all possible negative outcomes best mitigated against. It cannot guarantee that things will turn out as hoped, but it certainly encourages personnel to investigate and evaluate the whole range of potentially accessible options and the process at least helps to minimise loss.

What are the odds of you surviving the year? I cannot say, but it is almost certain, some of you reading this article will not see Christmas. You can though improve your chances massively by avoiding impulsive actions, by thinking more clearly and understanding the rules of unforeseen consequences much better than you do right now.

Safety is always the first thing to be compromised. It is always safety that is lost first. It's just so easy to let go and so with that simple thought in the forefront of your mind, can you justify the things you did today? The rules you ignored, the shortcuts you took, the safety features you overrode? What about that chair on the table business? Using stacked furniture to reach the light, the fan or the projector. Yeah I know, you were just trying to get the job done? What about that long cellphone conversation you had on the highway. There were cars whizzing by on both sides as you chatted away and what about the texts you typed and sent off immediately afterwards? Then there were those few extra beers you had at work on Fri-

SAFEX BOARD OF GOVERNORS

Chairman: John Rathbun (Austin International)

Governors: Enrique Barraincúa (MAXAM);

Claude Modoux (Poudrierie d'Aubonne);

Andy Begg (Individual Associate);

Terry Bridgewater (Chemring Group);

Aleksandr Chernilovskiy (Azot Vzryv);

Mike Powell (incitec Pivot);

Rahul Guha (Solar Industries);

Thierry Rouse (Groupe EPC);

Edmundo Jimenez (ENAEX);

Noel Hsu (Orica);

Colin Wilson (AELMS)

ARTICLES FOR NEWSLETTER

This is a reminder that through the Newsletters we share knowledge in the areas of Safety, Health, Environment and Security pertaining to the Explosives Industry. SAFEX thus call on all members to submit articles on these subjects within their own companies and countries. **The deadline for articles for the September Newsletter is 30 November 2016 and I look forward to your support .**

SAFEX thanks the following authors for their invaluable support:

- Dr.C. Guymon, Safety Management Services, Inc.
- Dr.J. Shaver, Special Devices, Incorporated.
- Frank Hirthammer, TTE Europe ,GMBH.
- Dr.Hansjuergen Winterbauer ,PLINKE ,GMBH.
- S. Singh, Canadian Explosives Research Laboratory (CanmetCERL), Ottawa, ON, Canada.
- R. Turcotte, Canadian Explosives Research Laboratory (CanmetCERL), Ottawa, ON, Canada.
- S. Goldthorp, Canadian Explosives Research Laboratory (CanmetCERL), Ottawa, ON, Canada.
- C. Badeen, Canadian Explosives Research Laboratory (CanmetCERL), Ottawa, ON, Canada.
- Ron Peddie ,Peddie Engineering.
- Dr Peter Drygala – Principal Adviser Explosives and Dangerous Good.
- Rahul Guha ,Solar Explosives.
- Tony Rowe , Retired AELMS.

Your Contact:

Dr Pieter S J Halliday

Secretary General, SAFEX International

Home office

49 Market Street, Johannesburg North, 2188 Randburg. South Africa

(Tel): +27 11 704 1743 | Mobile (Tel): +27 82 556 5351 | (Fax): +27 11 704 1743 |

(E-mail): secretariat@safex-international.org

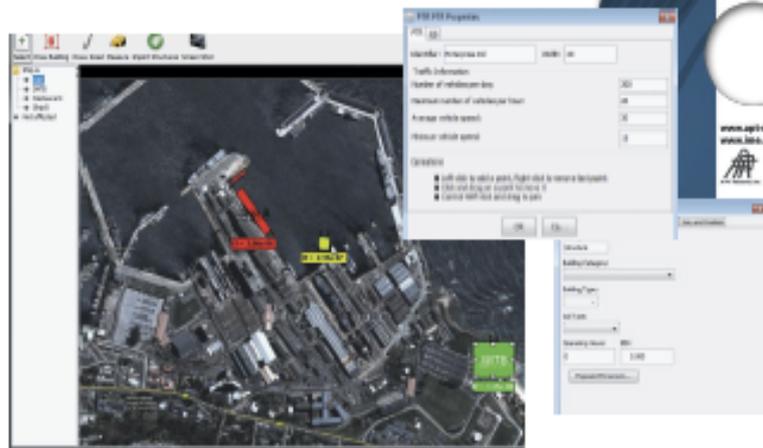
IMESA FR

Institute of Makers of Explosives Safety Analysis for Risk

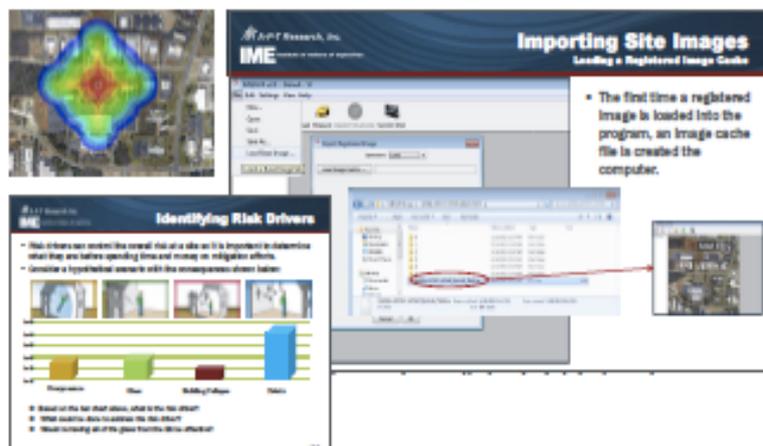
What is IMESA FR?

Institute of Makers of Explosives (IME) Safety Analysis for Risk (IMESA FR) is a software program developed through a joint effort by IME and APT to provide a more comprehensive assessment of the overall risk of explosives operations than the current method of American Table of Distances siting.

IMESA FR is a risk assessment tool used to calculate risk to personnel from explosives facilities. This software not only calculates Quantity Distances (QD) based on the American Table of Distances and other QD regulations, it can determine a level of safety based upon risk.



IMESA FR uses the donor structure and activity, the structure of the exposed sites, and duration of exposed personnel to determine a level of safety. The program provides users with the ability to work in metric or imperial measures, and allows users to import maps or drawings of their site to assist with visualizing facility layouts and results.



IMESA FR Training

Presented over three days with eight hours of mixed lecture and discussion for a total of 24 classroom hours. A competency test will be given upon completion of this course, and attendees will be credited with 2.0 Continuing Education Units (CEU).

Registration Information

Dean Nichols
256.327.3373

imesafrtraining@
apt-research.com

Schedule

- November 15-17, Huntsville, AL
- November 28-30, 2016, Ottawa, ON (CEAEC Conference)
- January 26-28, Orlando (ISEE Conference)
- May 12-14, 2017, Scandic Grand Marina Hotel in Helsinki, Finland

Cost

IMESA FR v2.0 Training: US\$1800

IMESA FR v2.0 Software:

- Standard Price: US\$1500
- IME member: US\$750

Upgrade IMESA FR v2.0:

- Non IME member: US\$750
- IME member: US\$375

For more info, visit
www.apt-research.com/training