THE GENERAL PRINCIPLES OF INTERMEDIATE STORAGE DURING EXPLOSIVES MANUFACTURE DURING THE PROCESSING OF ENERGETIC MATERIALS

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1. INTRODUCTION

Safe storage of explosives products or semi-products is highly dependent on the stability of the product. At the outset one needs to distinguish between physical stability as opposed to chemical stability. Physical stability relates to products which for instance are in the form of gels or emulsions. For this discussion we will be focussing on chemical stability and more specifically on the intermediate storage of nitrate esters (e.g. PETN, NC, NG, EGDN) and related products.

Various important lessons can be learnt from past accidents and incidents, including those which may be categorized as “near misses” an analysis of accident causes can indicate what problems might again arise in the future and the steps that should be taken to try to prevent any re-occurrence. As far as explosives events are concerned the causes of such incident/accidents occur on a number of levels.
At the first would be the energetic stimulus which initiated the explosives material, secondly, the immediate or proximate cause of the accident, i.e. the sequence of events which resulted in exposure of explosives to the stimulus; and thirdly, the underlying causes e.g. organizational deficiencies, oversights, etc. which may have allowed the sequence of events to occur in the first place.

2. DECOMPOSTION/RUNAWAY CHEMICAL REACTION

There have been numerous cases of explosives events/incidents at manufacturing sites caused by runaway chemical reaction during process operations.
Some reasons for such decomposition could be due to heat, the presence of a chemical such as nitric acid, UV rays, friction leading to heat, moisture or strong alkalis (destroying agents) causing hydrolysis, other contaminants such as in the case of azides copper, mixing the product with other explosives products such as in the case of PETN being mixed with DNT, TNT, etc.

The proximate causes for such events include but not confined to:

- addition of incorrect proportions of reactants
- addition of reactants in incorrect sequence,
- addition of contaminants to process equipment,
- inadequate mixing or over agitation of the reactants,
- failure to control process temperatures and;
- failure to adequately stabilize materials prone to spontaneous decomposition.

For each of these broad proximate causes it is normally possible to identify a number of sub-causes, such as;

- failure of process equipment including instrumentation,
- poor training
- frequent staff changes
- poorly written operating instructions (OI's)
- failure to follow instructions,
- poor or slack supervision
- failure to apply sound good explosives practice (GEP) or basis of safety (BoS) principles,
- confusion as to the clear allocation of areas of responsibility and accountability etc.

DEFINITION*: A *runaway reaction, also known in the explosives industry as a "fume off", can simplistically be described as follows:

An explosives material may for whatever reason start decomposing. e.g. Organic matter in solution or in contact with HNO_3 tends to be oxidised. As it decomposes there will be a heat rise which in itself will exacerbate the rate of decomposition. The explosives material will decompose and release copious amounts of NO_x (normally NO_2). This will act as a strong auto-catalyser and will speed up the decomposition rate leading to a violent, uncontrollable reaction which could lead to a detonation.

UNCONTROLLED DECOMPOSITION IN A PETN NITRATOR

DETONATION WITH NO_X EVOLUTON

Nitric acid tends to oxidise organic matter that is present either as a solid or in solution. This happens particularly when the temperature is increased or the concentration of the acid is reduced. This tendency reaches maximum potential when the acid strength is within the range 60-70% HNO_3. The system is then regarded as unstable, as decomposition sets in rapidly and accelerates. This vigorous reaction is accompanied by the evolution of brown fumes, (hence process often termed 'fume-off').

Note; the reason for the instability has often been incorrectly attributed to the fact that diluted nitric acid has a better oxidation power than a concentrated acid. What in fact happens is that hydrolysis induced in the weaker acids having less than 75% HNO_3, initially produces a product which is more easily oxidised than the initial product.

The mechanism appears to be as follows-

Initially the hydrolytic action converts the nitrate to an alcohol and HNO_3. The alcohol is then readily oxidised by the HNO_3 to an aldehyde, which in turn is further oxidised.

$$R\ CH_2\ ONO_2 + H_2O \rightleftharpoons R\ CH_2\ OH + HNO_3 \quad \text{(hydrolysis)}$$

$$R\ CH_2\ OH + HNO_3 \rightleftharpoons R\ CH\ O + H_2O + HNO_2 \quad \text{(oxidation)}$$

The HNO_2 so formed, initiates a direct attack on the nitrate group with the formation of an intermediate nitrosonium compound.

$$R\ CH_2\ ONO_2 + HNO_2 \rightleftharpoons R\ CH_2\ ONO + HNO_3$$

Since organic nitrates are more unstable than the nitric esters. Oxidation by the nitric acid then follows and completes the reaction.

$$R\ CH_2\ ONO + HNO_3 \rightleftharpoons R\ CH\ O + 2HNO_2$$

The accelerating effect of HNO_2 is evident as it is also a product of its own catalytic action with the nitric esters. As more HNO_2 is formed the reaction proceeds, causing further decomposition of the products formed. The progressive liberation of heat in this process also contributes to the rapid decay of the organic compound.
Acid compositions having strengths less that 60% HNO_3 are normally too weak to oxidise even the products of the intermediate decomposition reactions.

3. SOME EXAMPLES OF SOME THESE DECOMPOSITION INCIDENTS.

Biasutti reports in the "History of accidents in the Explosives industry" that up to 1984 some 22 accidents had occurred where during the ***INTERMEDIATE STORAGE OF NG SPENT ACID.*** *The spent acid carries with it a certain amount of un-dissolved NG, which may well have been the source of these accidents. In this regard many accidents are thought to have been caused by the self-decomposition of the NG dissolved in the acid during this intermediate storage (before stabilisation or de-nitration). In two of these accidents the spent acid storage tanks burst from overpressure, due to poor venting.*

It is a well known fact that in NG refuse acid has "free" NG to the level of 0.1% and the NG is soluble at a level of 2.55 to 3.00%. Upon the ***INTERMEDIATE STORAGE OF NG REFUSE ACID*** *prior to de-nitration of the refuse acid, the solubility of NG decreases at a rate of 0.1%/2^{O}C and may result in free NG being present. This can be mitigated by the addition of 3% H_2O. This increases the solubility of NG up to a level of about 4%.*
When the water content of the refuse acid however increases to 18-20%, the acid becomes unstable and a fume off can occur due to the oxidation of the NG by the nitric acid.

An explosion occurred in the de-nitration tower whilst de-nitrating PETN spent acid. After investigation it was found that the spent acid had contained large quantities of PETN dissolved and present as solids. This was due to a torn screen at the filtration section of the batch process plant. Following the incident some 24 hours later the ***PETN SPENT ACID BEING KEPT IN INTERMEDIATE STORAGE*** *also decomposed with a rise in temperature and evolution of NO_x gas. The decomposition fortunately did not result in a detonation.*

An expense magazine containing 300kg of ***NITROCOTTON (****most of it dry) exploded when nobody was in or near it. Extensive damage was caused to other buildings. The exact cause of the accident was not ascertained but it was determined that the most likely cause was due to occluded residual acidity left after stabilisation, leading to decomposition and then to spontaneous combustion/explosion.*

An explosion occurred during the **PASSIVE STORAGE OF DERELICT AMMUNITION** *awaiting disposal on an open site. The 20 mm ammunition concerned was known to be in an extremely bad condition and many of the shells were heavily rusted. The exact reason for the explosion was not found but the most likely explanation was that sensitive copper azide had been produced in one shell and that the high temperatures on the day of the incident caused movement of some part of the detonator which ignited the sensitive copper azide and fired the detonator.*

SILICON DISPERSIONS *are used to produce pyrotechnic compounds. It is well known that silicon reacts with water and has the potential for* **PRODUCING HYDROGEN GAS.**

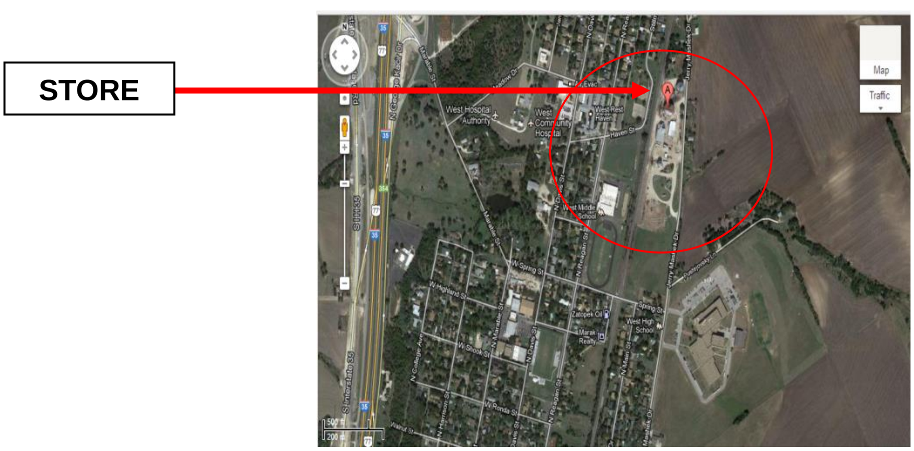
The reaction is given as: $2Si + O_2 + 2H_2O \rightarrow 2SiO_2 + 2H_2 \uparrow$

At a plant where a pyrotechnic mixture was being prepared, it was reported that the silicon slurry tank temperature was very high and that hydrogen had been released .It was found that the material had been held ***IN STORAGE*** *in the vessel for an excessive length of time. The plant shut down and all staff and electrical equipment isolated*
Note: H_2 + air gas mixtures can support deflagration in the concentration range 4 %-75 % (volume hydrogen fuel basis)

A fire followed by an explosion (some 250kg) demolished a building used for melting and casting Pentolite. A steam line had been left on during a break to melt a small quantity of ***PENTOLITE WHILE IN STORAGE IN THE MELTER.*** *It was also suspected that a small amount of contaminant such as sulphur could have been present.*

A slow decomposition of NPP propellant occurred during the INTERMEDIATE process of coating with TEGDM (triethyleneglycol dimethacrylate). The decomposition was probably due to inefficient mixing, allowing hot spots to form as the exothermic polymerisation reaction progressed.

(2013) West Fertilizer Company; A fertilizer company in west Texas caught fire. Around 20 minutes later fertiliser grade ***AMMONIUM NITRATE STORED*** *there exploded levelling roughly 80 homes and a middle school. 133 residents of a nearby nursing home were trapped in the ruins. In all, 15 were killed, and about 200 injured. There were reports that the facility had stored more ammonium nitrate than it was allowed to, without regulation by the Department of Homeland Security.*

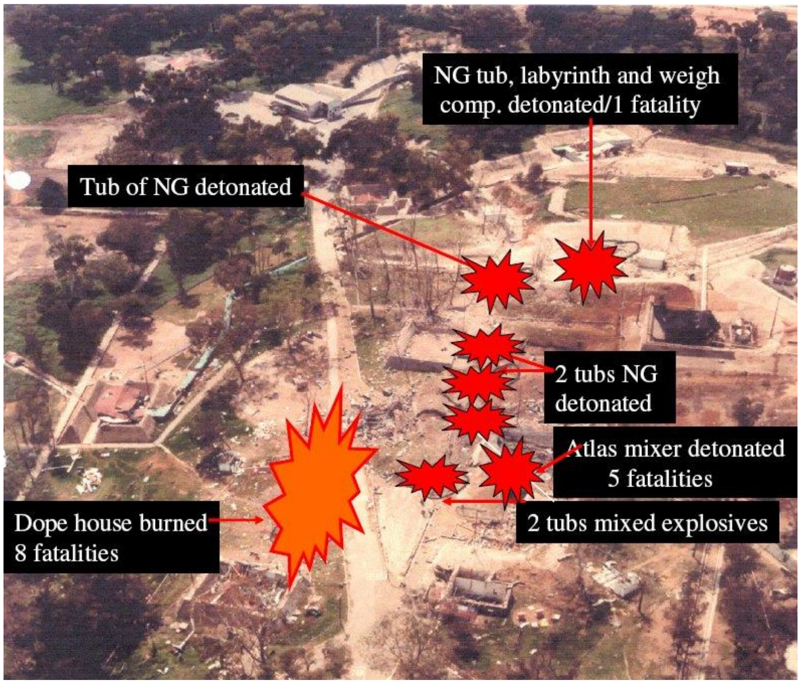


SURROUNDS AND
WEST FERTILIZER COMPANY SITE CIRCLED

SITE BEFORE **SITE AFTER**

*An explosion wrecked a magazine at a quarry. Corroded **DETONATORS BEING STORED** there were later recovered from the remains of the demolished building.*

CORRODED DETONATORS



An initial explosion in a NG tub in one building, caused one fatality.
*But because **NG tubs were left between buildings** (presumably because it was convenient), each was triggered in an explosive chain **by sympathetic detonations** and ultimately by a fireball.*
The result was a further <u>13 fatalities</u>, turning a tragedy into a disaster.

4. PETN INCIDENTS

There have been many incidents on PETN plants where the mixing ratios or temperatures of reaction have been out of control and serious fume offs or even detonations have occurred.

BELOW ARE HIGHLIGHTED THREE SPECIFIC INCIDENTS FROM A NUMBER OF INCIDENTS THAT HAVE OCCURRED OVER THE YEARS.

FROM THESE THERE ARE **TAKE HOME LESSONS** AS ALL.THE INCIDENTS SPECIFICALLY INVOLVE THE **INTERMEDIATE STORAGE OF PETN** PRIOR TO STABILISATION.

MANY OF THESE ARE APPLICABLE TO THE MANUFACTURING OPERATIONS OF MANY OTHER TYPES OF EXPLOSIVES.

4.1. THE BACKGROUND

To manufacture PETN using a batch process, the following steps normally take place;

NITRATION (Y 1) Step 1 Pentaerythritol+ di-pentaerythritol + nitric acid → PETN + PETN refuse acid

FILTRATION (Y1) Step 2 water washed > then washed with a soda solution (3.0%) >then water washed (Vacuum applied at each point)

Step 3 PETN (63kg) scooped into rubber bags (21kg each)

INTERMEDIATE (Y14) STORAGE Step 4 Bags removed to magazine and stored/stacked in a clockwise direction Bags to be stored for <72 hour

STABILISATION (Y3) Step 5 Recrystallization and neutralisation of occluded acid in presence of sodium carbonate

STORAGE Step 7 Wet (10%) stabilised

FINAL USE Step 8 Dry PETN prior to use in products such as detonating cord and boosters

NOTE: *AT SOMERSET WEST FACTORY (SWF), LORENA (EXPLO BRAZIL) AND AT MODDERFONTEIN THE PROCESSES ARE/WERE VERY SIMILAR*

4.2. WHAT HAPPENED?

BUILDING	TIME	DAY	DATE	SEQUENCE OF EVENTS
MAGAZINE 307 (LORENA)	**22h30**	**SUNDAY**	**8/11/1987**	**29te CAUGHT FIRE 24te BURNT REMAINING 5te DETONATED**

MAGAZINE AFTER DETONATION

MAGAZINE Y14 SWF	**01h20**	**SUNDAY**	**20/11/1989**	**500kg CAUGHT FIRE 300kg DETONATED**

Y14 AFTER DETONATION
NOTE MAGAZINE BELOW GROUND

BUILDING NEXT DOOR 30M AWAY

ROOF OF BUILDING 50M AWAY

MAGAZINE PE2 MDF	02h40	SATURDAY	16/04/1994	670kg CAUGHT FIRE 250kg DETONATED

PE02 NOTE THE DESTRUCTION OF MOUND

4.3. WHY DID IT HAPPEN? THE COMMON THREAD

- Some materials stored in the magazine were acidic (both externally and occluded)
- In some cases the materials were highly acidic with added contaminants e.g. recovered “save-all” material
- The material had been stored for longer periods than specified either verbally or as per the operating instructions (OI’s)
- Specifications

- SWF NOT > 96 HOURS
- MDF NOT > 72 HOURS
- LORENA NOT SPECIFIED

- The method of storage was not specified in OI'S and only ad hoc tests were done on PETN prior to storage.
- In all three cases the findings were that the PETN had chemically decomposed in to the presence of "high" acidity. It was highly likely that this decomposition was autocatalytic leading to elevated temperatures, fire and finally detonation.
- In all three cases "crude" PETN was stored together with other products such as material recovered from the "save alls" (labyrinths).
- IN THE CASE OF LORENA SOME MATERIAL HAD BEEN STORED IN THE MAGAZINE FOR MORE THAN **A YEAR!**

4.4. SOMERSET WEST FACTORY (SWF)

At Y14 rotation of stocks was not recorded. The procedure was informal. Stock in the magazine was not recorded.
At Y14 bags of product had been moved around to make space.
OI's for nitration at y1 were not absolutely clear and were open to interpretation.
At Y1 the crude PETN had not been washed free of external HNO_3 (channelling)
There was no on plant check for residual acidity
The Na_2CO_3 solution was under-strength. The set of OI'S detailing the make-up of this solution were poorly written.
The plant had been working under pressure with many staffing changes 10 different workers had accessed Y14 the previous week.
There had been a mechanical failure of plant at Y3 stabiliser, thus no material could be processed.
No contingency plans were made in the OI'S for such an event.
At times materials were moved from Y1 directly to Y3 eliminating the storage step at Y14. These actions lead to the potential and the high likelihood of older material remaining in Y14, thus being in storage for longer than specified.

4.5. WHAT LESSONS WERE LEARNT

- OI's need to explicit detailed and updated regularly
- stock rotation was critical and had to controlled (colour coding was introduced to avoid exceeding specified storage times)
- operators had to be fully conversant with OI'S and needed to be retrained (and re-passed out) at regular intervals
- areas of responsibilities needed to be clearly defined
- and tasks in those operational areas needed to be clearly defined
- plant checks for important parameters are critical to the safety process.
- working under pressure creates situations where safety is often compromised.

- OI's must include contingency plans as well as recovery (from an incident) protocols.
- eliminate unnecessary (nice to have) steps in explosives manufacturing processes.
- consider redundancy installations on plants that from a safety point of view, are critical to the flow of operations.
- Critically examine and review the findings from all incident investigations to ensure that the root cause has been established.

SWF took 25 mitigating steps to avoid a re-occurrence of the Y14 incident. Despite this on the 14/8/1990 at Y14, THERE WAS ANOTHER INCIDENT WHERE 2 BAGS OF PETN "FUMED OFF"! THIS WAS DURING THE MANUFACTURE OF "SUPER FINE GRADE" PETN. A FURTHER 6 "NEW" ISSUES WERE HIGHLIGTHED DURING THE SUBSEQUENT INVESTIGATION

4.6. ANDTHEN!!!!!!!!

A FINAL DECISION WAS TAKEN TO ELIMINATE THE STEP OF STORAGE OF NON-STABILISED PETN AT Y14 AND IN ADDITION, THE MITIGATING STEPS IN THE OTHER AREAS WERE IMPLEMENTED BEFORE FURTHER PRODUCTION TOOK PLACE.

5. IN CLOSING.

IN FACT, DO NOT EVER ASSUME THAT THE CAUSE OF AN INCIDENT IS NECESSARILY THE MOST OBVIOUS ONE.

6. ACKNOWLEDGMENTS.

7. AEL Mining Services, NIXT (RSA)

8. REFERENCES.

AEL Archives, AEL Basis of Safety documents, EIDAS, HSE Web Communities, SWF PETN Technical Manual.