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

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SUMMARY OF PRESENTATION

- INTRODUCTION
- DECOMPOSITION/RUNAWAY REACTIONS
- SOME EXAMPLES OF DECOMPOSITION INCIDENTS FROM THE ARCHIVES
- PETN INCIDENTS SWF (Y14) AND OTHERS
  - THE BACKGROUND
  - WHAT HAPPENED
- WHY IT HAPPENED (THE COMMON THREAD)
- SWF
- LESSONS LEARNT
- AND THEN
- CLOSING
- ACKNOWLEDGEMENTS

INTRODUCTION

- Safe storage is highly dependent on the stability of the product.
- Physical stability as opposed to Chemical stability.
- Physical stability relates to products which for e.g. are in the form of gels or emulsions.
- 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.

Lessons can be learnt from past near misses accidents and incidents.

- 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.

INTRODUCTION CONT.

Causes of such incident/accidents occur on a number of levels.

- **Firstly** - the energetic stimulus initiating 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.

DECOMPOSITION

Many recorded cases of events/incidents at manufacturing sites caused by runaway chemical reaction during process operations

SOME CAUSES OF SUCH EVENTS

- Addition of incorrect proportions of reactants
- Addition of reactants in incorrect sequence,
- Addition of contaminants to process equipment,
- Inadequate mixing of reactants,
- Failure to control process temperatures
- Failure to stabilise material prone to spontaneous decomposition.

CAUSES FOR SUCH EVENTS CONT.

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

- As failure of process equipment
- Poor training
- Frequent staff changes
- Poorly written instructions
- Failure to follow instructions
- Lack of or slack supervision
- Unclear allocation of areas of responsibility

DEFINITION OF A RUNAWAY REACTION

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

The explosives material will for whatever reason start decomposing.

As it decomposes there will be a heat rise, which in itself, will exacerbate the rate of decomposition.

The explosives material decomposes and releases No_x ***(Normally*** NO_2***)***

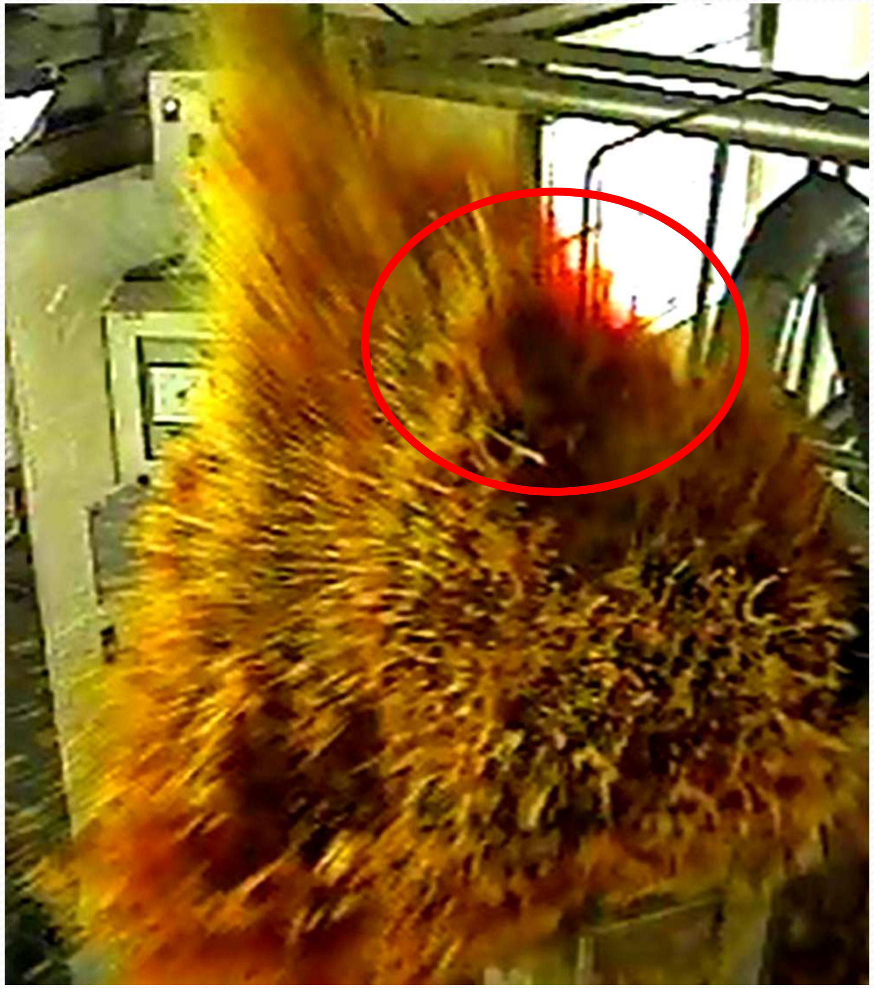
This acts as a strong autocatylser and speeds up the decomposition rate leading to a violent, uncontrollable reaction, which then could lead to an explosion.

REASONS FOR DECOMPOSITION

Could be due to:

- Heat,
- **The presence of a chemical such as nitric acid,**
- UV/IR 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 or TNT etc.

DECOMPOSITION AT A PETN NITRATOR



DETONATION WITH NO_X EVOLUTION

MECHANISM OF DECOMPOSITION

- 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.
- $R\,CH_2\,ONO_2 + H_2O \rightleftharpoons R\,CH_2\,OH + HNO_3$ (hydrolysis)
- $R\,CH_2\,OH + HNO_3 \rightleftharpoons R\,CH\,O + H_2O + HNO_2$ (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.

EXAMPLES
DRAWN FROM THE ARCHIVES

EXAMPLE	CAUSE	RESULT
INTERMEDIATE STORAGE OF NG SPENT ACID	*Water content of the refuse acid increases to 18 -20%- the acid becomes unstable*	*Fume off occurs due to the oxidation of the NG by the nitric acid.*
Biasutti ***INTERMEDIATE STORAGE OF NG SPENT ACID***	*Self-decomposition of the NG dissolved in the acid during this intermediate storage*	*Up to 1984 some 22 accidents had occurred*
PETN SPENT ACID BEING KEPT IN INTERMEDIATE STORAGE	*Spent acid had contained large quantities of PETN dissolved and present as solids*	*Decomposed with a rise in temperature and evolution of NO_x gas. No detonation.*
300kg NC with occluded acid held in storage	*Material self-decomposed*	*Expense magazine exploded with extensive damage caused to other buildings*

EXAMPLES
DRAWN FROM THE ARCHIVES

EXAMPLE	CAUSE	RESULT
Passive storage of derelict ammunition *awaiting disposal on an open site*	*20 mm ammunition concerned was known to be in an extremely bad condition and many of the shells were heavily rusted. sensitive copper azide had been produced*	*An explosion occurred*
Silicon dispersions in water held in storage	*Held in the vessel for an excessive length of time at an elevated temperature and pH* $2Si + O_2 + 2H_2O \rightarrow 2SiO_2 + 2H_2$	*Hydrogen evolution. H2 + air gas mixtures can support deflagration in the concentration range 4 %-75 % (volume hydrogen fuel basis)*

EXAMPLES DRAWN FROM THE ARCHIVES

EXAMPLE	CAUSE	RESULT
INTERMEDIATE process of coating NPP propellant with TEGDM (triethyleneglycol dimethacrylate).	*Inefficient mixing, allowed hot spots to form as the exothermic polymerisation reaction progressed.*	*Decomposition occurred*
Ammonium nitrate store caught fire at West Fertilizer Company	*After 20 minutes the fire caused an explosion*	*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.*
Corroded detonators being stored	*Decomposition of the azide took place*	Explosion and wrecked a quarry magazine
Pentolite steam line left on during a break to keep stored Pentolite molten	*Heat- decomposition together with the presence of possibly a small amount of contaminant such as sulphur*	A fire followed by an explosion(some 250kg) demolished the building

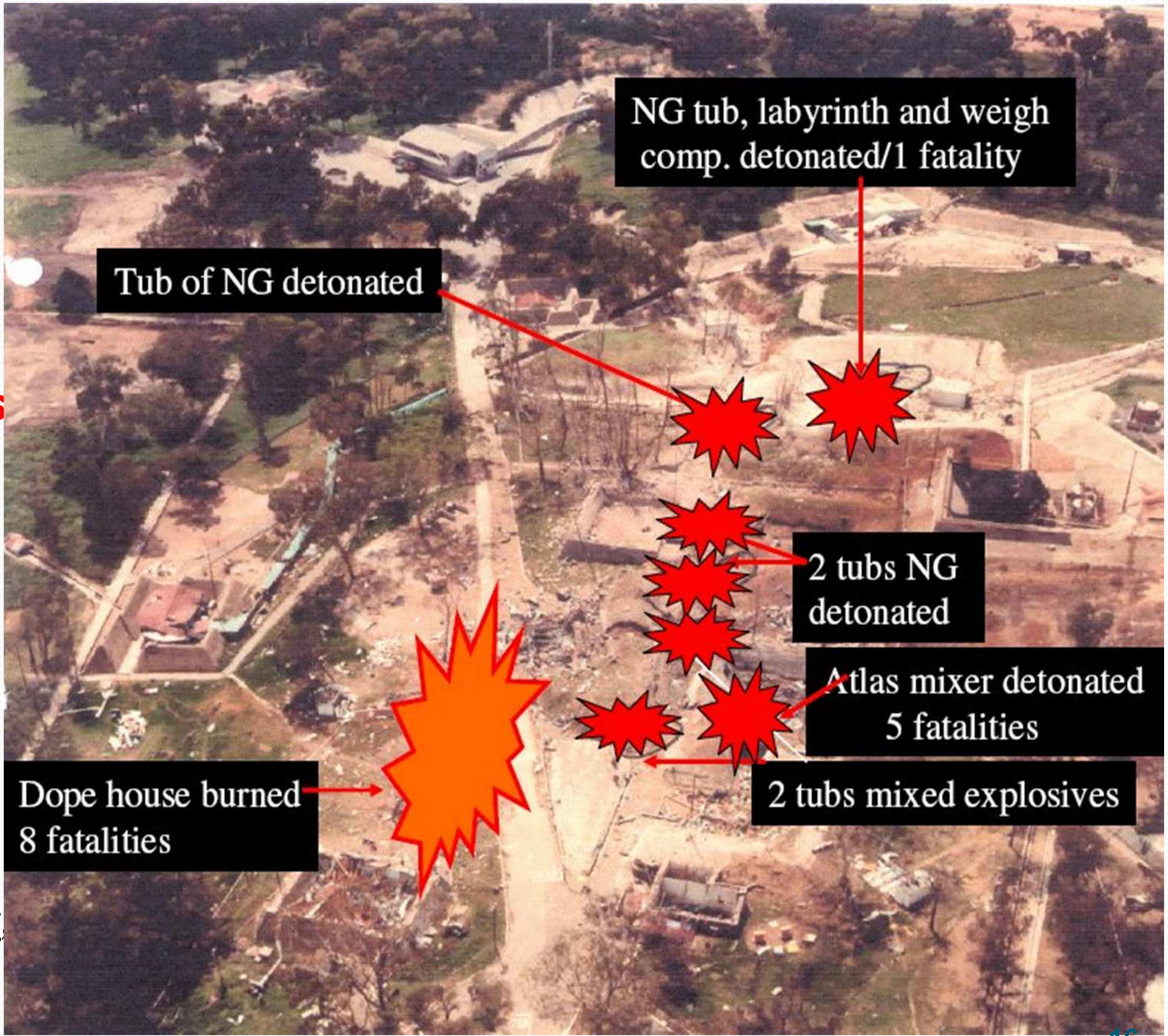
CORRODED DETONATORS

NG INTERMEDIATE STORAGE INCIDENT

Explosion in a NG tub in one building with one fatality.

NG tubs were left between buildings *(presumably because it was convenient), each was triggered in an explosive chain* ***by sympathetic detonations*** *– fireball*

Further <u>13 fatalities</u>, turning a tragedy into a disaster.



PETN INCIDENTS

- Three specific incidents from which there are take home lessons

- These incidents specifically involve **the intermediate storage of PETN prior to stabilisation**

PETN MANUFACTURE SWF

STEPS

Y1 NITRATION >

Y14 INTERMEDIATE STORAGE >

Y3 STABILISATION>

Y8 STORAGE>

Y4 DRYING>

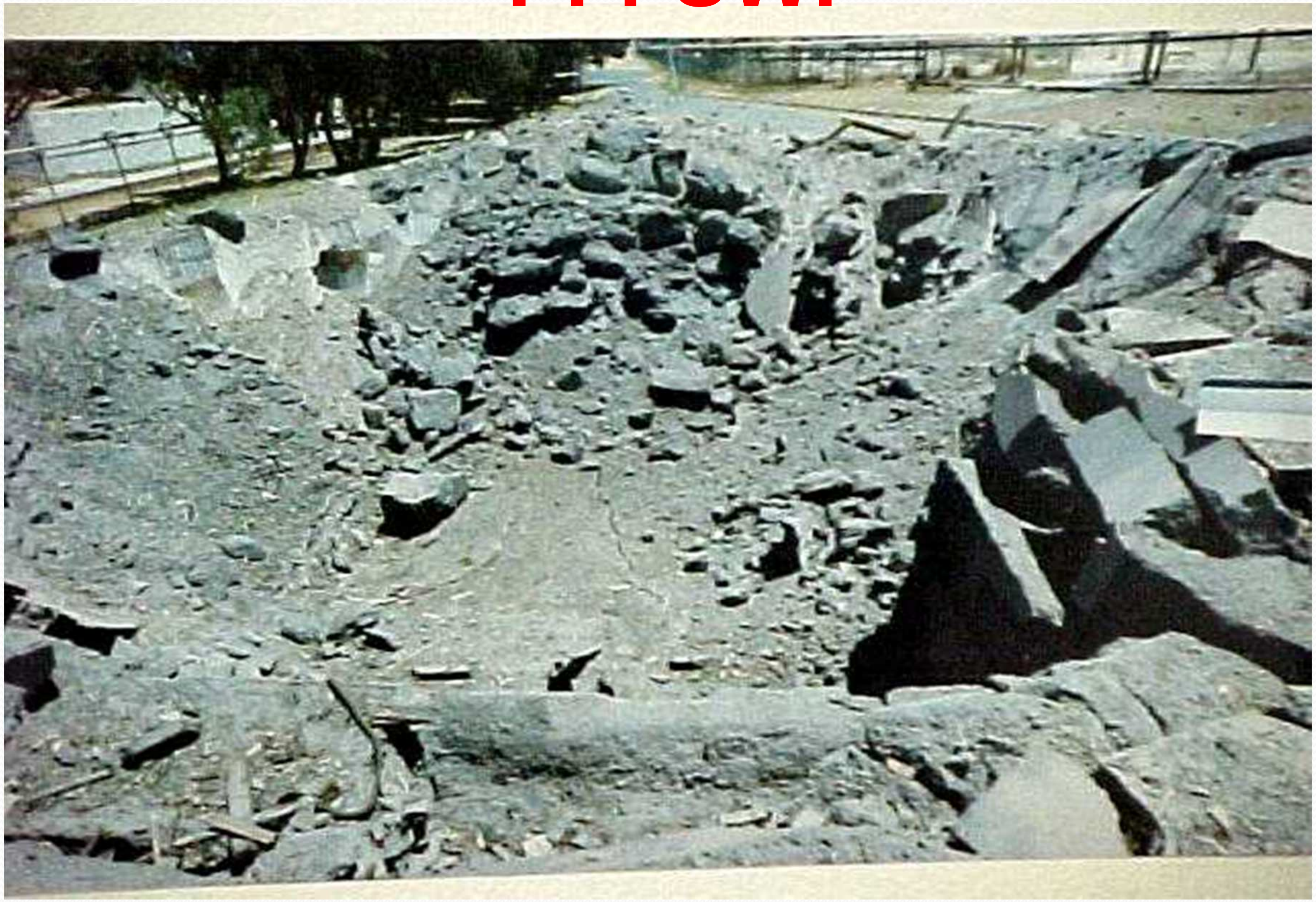
Y5 STORAGE

WHAT HAPPENED ?

LORENA 307	8-11-1987	SUNDAY 22h30	29 (te) → FIRE → 5 (te) DETONATION
SWF Y14	20-11-1989	SUNDAY 01h20	500 (kg) –FIRE some consumed DETONATION (300 (kg)
MDF PE2	16-04-1994	SATURDAY 02h40	670 (kg) → FIRE → 250 (kg) DETONATION

LORENA

Y14 SWF



Y1 NEXT DOOR TO Y14 (20m)

PE 02 MDF

WHY DID IT HAPPEN?

- Acidic PETN
- Long storage periods - rotational system poor
- Poor OI's / short cuts
- Verbal instruction system in place
- Product mix poor
- Plant working under pressure
- Mechanical failure at stabiliser

LESSONS LEARNT ?

Some key issues were that:

- OI’s must have regular updates and have sufficient detail
- Stock rotation is critical (colour codes)
- Training - no compromises
- Areas of responsibility and Definition of tasks are critical to ensure smooth operations and

There were another 26 mitigating measures taken

AND THEN ?

- All the mitigating measures were not enough
- On the 14 / 08 / 1990 there was a fume-off of another 2 bags of crude PETN

AND THEN?
ELIMINATE TO OBVIATE

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.

AND

NEVER ASSUME THAT THE CAUSE OF AN INCIDENT IS NECSSARILY THE MOST OBVIOUS ONE

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