Hazards in Emulsion Explosives Manufacture and Handling

Understanding what they are and how to avoid them

by

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SAFEX Topical Papers Series
Paper No. 05/2008
Published: August 2008

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1. Introduction

Emulsion explosives, commonly called “emulsions”, are widely used for commercial blasting throughout the world, having replaced much of the nitro-glycerine and water gel based production. There are several reasons for the success of emulsions but one is the perceived lower level of hazard during their manufacture and handling.

Emulsion explosives consist of an aqueous phase of soluble oxidiser salts (mainly ammonium nitrate) dispersed using high shear mixing in an oil phase (usually paraffin oil based) with the help of an emulsifying agent. Their consistency can vary from almost liquid to stiff wax depending on the composition. They are usually processed at relatively high temperatures – often in excess of 95°C. The base emulsion has a relatively high density and this must be reduced to ensure it is detonable. Sensitisation is usually achieved by adding very
small hollow spheres (glass or plastic) or by chemically
gassing using a system based on sodium nitrite. Additional dry
materials such as ammonium nitrate and aluminium can be
added to the base emulsion to increase the available energy.
The process can be batch, continuous or a combination of
both. The product can be produced in bulk and packaged
forms depending on the application.

The replacement of nitro-glycerine production units by first
water gels and now emulsions has seen a significant change
in the philosophy of plant design and personnel exposure. A
typical NG line would be composed of several small separated
buildings each with a small number of personnel or even
remotely operated whereas an emulsion line may have all
operations and all personnel in a single building, the difference
being due to the balance between risk and consequence.

2. Incidents in the manufacture of emulsions
There have been many energetic incidents in the
manufacturing processes associated with emulsions. Many of
these incidents have been explosions resulting in major losses
of life. I believe this is partly because the materials and the
processes are thought to be “safe” and therefore (a) more
people can be exposed in a single building because the risk of
explosion is much smaller than with conventional explosives
and (b) less process safety control is necessary.

Even those explosions that have not resulted in such major
losses have very often had fatal or at least serious
consequences. This perception of emulsions being “safe” is
not just incorrect – it is also extremely dangerous for those
involved in working with them.

I will now try to explain why the perception is incorrect.
However, before I do so I would like to be clear about what I
mean when I refer to the term “explosion”. By explosion I
mean an energetic event that has the effect of an explosion. It
could be a detonation, a thermal explosion, a deflagration -
each is quite unique in its “scientific” characteristics and
sometimes it can be difficult even for an expert to distinguish between them by looking at the scene after an explosion. However, for the personnel working in the location of an “explosion” it really is not important whether the event was one thing or another – they may well be dead or seriously injured. Therefore I will be talking about explosions to cover all relevant energetic events.

3. Why do people believe emulsions are safe?
Emulsions are basically not sensitive in the same way that nitro-glycerine, PETN and lead azide etc are. They show no sensitivity to detonate when subjected to the normal levels of friction, impact, static and heat etc. found in a plant environment. Therefore it is assumed that not only are they safer – they are inherently safe. Here lies the problem. Are they safer? Yes. Are they safe? No - not if by “safe” we mean they will not detonate or explode in a fault condition in a plant environment.

The reason we have a problem is because the behaviour of emulsions in certain plant situations is not correctly understood by many of the people who handle them. To understand their behaviour we need to look at the materials that are used in emulsion processes, their properties and how they can interact with the process and equipment.

4. What materials are we talking about?
Based on industry experience of fires and explosions over the last few years, we need to consider three key materials widely used in emulsions and which have been involved in explosions.

1. Emulsions including sensitised emulsions (gassed or with micro-balloons) and non-sensitised matrix (base emulsion or precursor)
2. Ammonium nitrate (as a solution or solid)
3. Sodium nitrite for gassing (as a solution or solid) in combination with ammonium nitrate.
The common factor in these materials is ammonium nitrate and it is the properties of this material that are at the centre of the hazardous behaviour. Much has been written about the hazards of ammonium nitrate but it is sufficient here to say that if ammonium nitrate is heated under confinement it will decompose and depending on the exact conditions, may detonate.

(Other materials with their own specific hazards are also used including aluminium powder and sodium perchlorate. I will refer to these later.)

4.1 Emulsions

The simplest emulsions are those composed of ammonium nitrate, water, oil, and a surfactant. Other materials such as sodium nitrate or perchlorate, waxes, gas bubbles, micro-balloons etc can be added. These additives may slightly change thresholds for reaction but they do not change the basic hazard characteristics of the emulsion – they are relatively insensitive to friction, impact etc as mentioned earlier. However, all such emulsions are processed using equipment that operates by putting energy into the emulsion. This equipment may be a high energy mixer or a pump. Both basically move the emulsion by applying energy – pumps in particular move the emulsion by transferring their energy to the emulsion while high energy mixers operate by moving the emulsion at relatively high mixing speeds.

If for any reason the emulsion cannot flow and is replaced by fresh emulsion product, the energy still gets transferred into the emulsion. Because the emulsion cannot move as a mass, it heats up. This heat will eventually increase the temperature of the emulsion to the point where it loses water, continues to heat up, the ammonium nitrate starts to decompose releasing oxides of nitrogen, exothermic reaction starts and basically we have ANFO decomposing exothermically under confinement.
In effect the emulsion is “cooked-off” The consequences should not be surprising – it explodes. The chemistry may be much more complex than described but the cause and effect are simple - heat emulsion under confinement and it can explode.

This is typically what has happened when pumps have exploded. The pump runs dry or is operated against a blockage. In both cases there is no flow of emulsion, it heats up, decomposes and then explodes. A similar situation can arise in a high energy mixer if for any reason flow of product is not sufficient to dissipate the input energy. The time for these processes to occur depends on several factors – of course! It might be a few minutes, it might be closer to an hour or the incident may just fizzle out – we never know for sure just how it will behave, until it does.

However, the issue for us is that emulsions can and will explode if heated under confinement. This applies to all emulsions including:

- Ammonium nitrate only
- Ammonium nitrate, sodium nitrate or sodium perchlorate based
- Sensitised and unsensitised
- Bulk matrix

Some may behave in a slightly different manner to others but under the fault conditions that can occur in a plant they all will basically behave is the same way – they will heat up and explode. Some may be quicker than others. But by how much? It is not worth arguing about. It is this behaviour of emulsions that has caused so many fatalities in recent years.

This heating condition is not just associated with pumps and high energy mixers. It can apply to any situation where the emulsion is heated under confinement and where there is little or no dissipation of the heat. This can occur when emulsion in a pipeline is heated, or in a hopper, tank, silo etc. The heat can come from several sources, not just malfunctioning
mechanical and heating equipment including a fire, an over-heating bearing, a chemical reaction. The source is less important that the conditions at the time. If there is uncontrolled heating, confinement and no heat dissipation then explosion is likely.

To illustrate the situations where explosions have occurred here are some examples.

a. Two silos containing an estimated 75t of bulk matrix were subjected to fire after an explosion in a plant in New Guinea. The two tanks detonated after approximately 80 minutes causing massive damage to the entire plant area. The heat came from the fire.

b. A pump in a packaged emulsion plant exploded when it is believed the cartridging line blocked and the pump continued to operate. The heat came from the normal friction in the pump but operating with no flow.

c. A quantity of waste bulk matrix and ammonium nitrate exploded when a large quantity of sodium nitrite was accidentally added to it. The heat came from the exothermic reaction between the sodium nitrite and ammonium nitrate.

d. A bulk matrix transfer line exploded when a welder accidentally set fire to the grass underneath the pipe. The heat came from the fire.

e. A piston pump being used to push emulsion through a static mixer exploded killing 4 personnel. It is believed that the piston caused overheating of the product due to adiabatic compression of air pockets in the very viscous emulsion.

f. A bulk truck was seriously damaged when a matrix transfer pump was left running and eventually ran dry and exploded. The heat came from the friction in the pump.

g. Several very serious explosions are thought to have resulted from fault conditions developing in high energy mixers but due to the lack of information this cannot be confirmed.
h. This behaviour also applies to watergels. A watergel plant was destroyed by fire when an operator left a pump running over lunch break. It ran dry and caught fire – as did everything else in the building.

It should be clear now that emulsion can explode under fault conditions that can realistically arise in a plant, storage or use. It really does not matter if the emulsion is “sensitised” or not – the same sequence of events will take place. It will heat up – and it may explode; only the time period may be different.

4.2 Ammonium nitrate

Ammonium nitrate is classified as an oxidising agent but it takes very little to turn it into an explosive. Obviously, the addition of small quantities of fuels will convert it into a type of ANFO. However, pure ammonium nitrate detonates if it is in sufficient quantity, confined and exposed to heat. Also, small quantities of “impurities” can change the explosion characteristics of ammonium nitrate to the point where it can become a very sensitive explosive.

They can do this by acting as catalysts, which basically increase the rate of decomposition and/or reduce the temperature at which decomposition will start and/or they may chemically react with the ammonium nitrate to form an explosive compound. Organo-chloro compounds are examples of the former and sodium nitrite is an example of the latter.

In recent years there has been a large number of explosions involving ammonium nitrate

a. The warehouse in Toulouse when an estimated 250 te of ammonium nitrate apparently became contaminated, decomposed and detonated with devastating consequences

b. There have been numerous transport incidents where the ammonium nitrate became engulfed in fire and
subsequently detonated (but not every time, it should be said).

c. A tanker carrying ammonium nitrate solution exploded while parked at its on-site facility. The solution was thought to have been contaminated and have low pH.

d. The accidental addition of sodium nitrite to a tank of ammonium nitrate based solution caused a major fire in a plant in the Philippines

4.3 Sodium nitrite

Sodium nitrite is classed as an oxidising agent – similar to ammonium nitrate but in fact it is very incompatible with it. As mentioned earlier, sodium nitrite will react with ammonium nitrate to form an explosive compound – ammonium nitrite. Sodium nitrite solution is widely used in emulsions to sensitise them by reacting with other chemicals in the matrix to form gas bubbles. When used as a gassing agent, it is added in small, measured and controlled quantities and the small quantity of heat released during the reaction is quickly dissipated in the mass of emulsion. However, if it is added in excess there may be localised heating that could cause decomposition of the emulsion, as already described. If the emulsion is under confinement then this will increase the pressure, increase the reaction rate etc and eventually an explosion will occur. This has happened in a number of situations including:

a. A packaged emulsion plant where fortunately no-one was injured but the plant was basically wrecked

b. On a bulk site where 2 operators were less fortunate, being seriously injured by shrapnel from the blast in a waste bin where concentrated sodium nitrite solution waste had been added to emulsion and ammonium nitrate wastes.

So we can see from bitter experience that operations involving emulsions are not subject to the usual explosives hazards concerns - but they are subject to a range of other hazards
issues that have to be understood and preventative measures taken for their avoidance.

It should be stated that if nitro-glycerine explosives were exposed to the same fault conditions that we are referring to above then we would be very confident in expecting explosion to result. People experienced in nitro-glycerine technology would never consider processing or handling them in the ways employed for emulsions.

5. What measures can we take?

Let us now look at some of the measures that can be taken to avoid these hazards and minimise the potential consequences of incident.

The basic principles that should be adopted are the same as for all other explosives operations i.e. “Always expose the minimum number of personnel to the minimum amount of explosives, for the minimum period of time”. These principles are expanded as follows.

- **Minimum Inventory**
  The quantities of explosives and raw materials (including packaging) must always be kept as low as practical and appropriately separated. This includes the separation and segregation of waste.

- **Minimum Exposure**
  There should be as few people as practical involved in the process. In particular, non-related process people (i.e. support staff, office staffs, service waiters, etc) must be kept at appropriated safety distances)

- **Minimum Operations**
  Ideally there should either be only one operation per building or at least only one operation at a time per building.

- **Minimum Energy**
Whatever the process and very much related to the explosive being handled the amount of energy going in must be kept to a minimum.

6. What are the implications for a plant?

6.1 Plant process design
As with all explosives plants, the design and construction standards and conditions for safe operation of the plant should be determined by a formal and comprehensive Safety Study such as Hazard Study or Risk Assessment. The following issues should be amongst those derived from the Safety Study.

- **Pumps**
  - Where possible choose pumps that cannot not run against a blocked line e.g. low pressure self- stalling air pumps
  - For positive displacement pumps such as progressive cavity pumps (perhaps the most commonly used) ensure they are fitted with adequate safety devices to protect against dead-heading and dry running – basically protect against no-flow conditions. Safety devices include no-flow devices; high and low pressure trips, high temperature trips, thermo-fuses and bursting discs.
  - Ensure pumps are properly inspected and maintained.

- **High energy mixers**
  - Continuous mixers should be protected against no flow.
  - Batch mixers with mechanical stirring should be fitted with slipping clutch or other form of torque limiter.
• **Product mixers and hoppers**
  - Minimum capacity to take advantage of continuous operation to reduce inventories.

### 6.2 Plant layout

• Separate raw materials preparation, mixing/cartridging and packing into 3 buildings or areas to minimise personnel exposure to an incident

• Reduce the storage space for raw materials held in the process compartment to a minimum as they may add the effective explosives inventory in the event of an explosion. This is particularly the case with ammonium nitrate where it may be necessary by law to include a factored quantity for ammonium nitrate in the explosives inventory.

• Avoid multiple product operations running at the same time in the same compartment

• Clear and effective escape routes for all personnel are a priority. Emulsion rarely if ever just suddenly explodes in a fault condition – it is usually preceded by a period of heating and reaction with visible or audible signs that something is wrong. This should give personnel time to evacuate – but only if their escape route is always clear and they can access it without having to move towards the hazardous situation.
  - The presence of office and laboratory facilities inside the process building should be discouraged but if they are considered necessary then they should have their own escape door to the outside and personnel limited to the minimum required.
  - Personnel should not be blocked in by packaging equipment etc.
  - Escape doors should be fitted with “push open” doors that open outwards
- Emergency stop buttons and alarms should be located at emergency exits so that personnel can activate them as they exit the building.

- Fire engulfment of emulsion in any container that could provide containment has to be avoided by ensuring that:
  - All oil and fuel tanks are positioned such that any breach of the tank or associated pipe work will not allow the fuel to flow to a position underneath emulsion tanks, transfer pipelines etc.
  - All fuel tanks have sufficient secondary containment.

- In the event of a serious incident in a pump, mixer or other item of process equipment that results in fire it is vital that other high energy ingredients such as aluminium and ammonium nitrate cannot be added to the fire.
  - Hoppers and silos for the addition of other solid ingredients should not be located directly above critical items of process equipment such as mixers and pumps.
  - Emulsion silos and holding tanks should not be positioned directly above process modules and pumps.
  - Mezzanine floors should be positioned off-centre to process modules.

6.3 Raw materials handling

- Ammonium nitrate should be stored in conformance with the applicable regulatory requirements (these may involve applying quantity/distance considerations) and industry good practice guides. Ideally it should be stored in its own building/location but practical constraints may dictate that this is not possible. In such situations sodium and calcium nitrates may be stored in the same building but in separated areas - no
other materials should be stored with ammonium nitrate. Odd cans of lubricants, antifreeze and other chemicals etc must not be stored with ammonium nitrate. (There are also increasing security issues regarding the storage of ammonium nitrate that may need to be considered.)

- Sodium nitrite must be stored in its own unique store. It must be clearly labelled to avoid being confused with sodium nitrate where the latter is also used.
- Aluminium must be stored in its own store.
- Sodium perchlorate should be stored separately.

### 6.4 Waste management
Explosions and fires have arisen in the past when wastes have been mixed.

- Each waste should be kept in a unique container at all times.
- Unidentified wastes must not, under any circumstances, be mixed with other wastes
- Each waste should be disposed of by an approved method.

### 6.5 Formal systems and procedures
Robust safety systems and procedures have to be in place and complied with including:

- Maintenance schedules.
- Control of modifications - including process, equipment, operation and formulation.
- Materials management
- Waste management
- Safety devices.
• Design codes.
• Routine validation of all critical systems.

6.6 Training
As with all operations, the importance of training cannot be stressed too much.

• Knowledgeable design and technical personnel trained in the relevant hazards and control systems.
• Plant operators trained to understand the hazards, how they can arise and how they are controlled.

7. Conclusion
The development of emulsion technology gave the explosives industry the potential for a significant improvement in safety performance as measured by injuries and fatalities caused by explosion. This is due to emulsion products’ greater tolerance of friction, impact, electrostatic discharges, etc - the classic sources of accidental ignition.

However, the industry appears to have been slow to understand and manage the hazards caused by uncontrolled heating of these products (and intermediates/raw materials). The result has been several multiple fatality explosions. Clearly, this cannot be allowed to continue.

It is easy to avoid the types of incidents that we have seen. Producers must understand and avoid the uncontrolled heating of emulsions and ammonium nitrate by any source. It is that easy.

8. Acknowledgments
The author gratefully acknowledges inputs for finalising this Paper from: Frank Barker (Orica USA Inc), Paul Harrison (Orica Australia Pty Ltd) and the SAFEX Review Panel comprising Piet Halliday (African Explosives Ltd) and John Maher (Thales Australia).