

SESSION THREE - DISCUSSION

EXPLOSIONS ANALYSES OF ACTUAL INCIDENTS

INVESTIGATION INTO THE CAUSE OF AN EXPLOSION DURING THE DRYING OF POROUS NITROCELLULOSE POWDER.

By J.W. Hartgerink (Technological Laboratory TNO, P.O. Box 45, Rijswijk, The Netherlands).

Mr K.N. Palmer (Building Research Establishment, Borehamwood):

Was the operative provided with antistatic clothing and footwear? If so, would not the aluminium rim have been grounded as soon as he touched it?

Dr Pasman:

The operative did not wear antistatic clothing or shoes.

Dr D. Rae (Safety in Mines Research Establishment, Buxton):

In considering the ignition of the powder by friction, was the presence of steel clamps, aluminium lid and container, and the fact that the powder itself could act as the oxygen carrying agent in a thermite type reaction, taken into account? Were the BAM tests done only with impact of non-reactive metals?

Dr Pasman:

Before we arrived at the electrostatic spark theory we considered the possibility of initiation by friction, in particular by sparks between aluminium and corroded steel. Therefore besides the standardised trials with the BAM friction apparatus we also performed trials in the same apparatus where propellant was rubbed between a metal plate of aluminium and a stift of steel.

Even after addition of 5% of rust (and also 10% of KNO<sub>3</sub>) to the ground propellant, the sample did not ignite.

Mr M Kneale (Lankro Chemicals Ltd):

Were the bolts in fact mild steel?

Dr Pasman:

Yes, they were, but as they were used very often, the bolts were well greased.

Dr N. Gibson (I.C.I., Organics Division):

The use of non-conducting non-metallic elements in plant such as the rubber gasket, increases the risk of the plant becoming insulated from earth, particularly if an earth/bonding device is not correctly applied. It would appear that this incident would not have occurred if a conducting rubber gasket had been used. With vapours and sensitive dust clouds we would recommend the maximum possible use of conducting non-metallic materials and minimise the use of non-conducting materials.

ANALYSIS OF A BATCH PROCESS EXPLOSION.

By P.D. Bloore (Albright and Wilson Ltd, Technical Development Dept, Industrial Chemicals Division, P.O. Box 3, Oldbury, Warley B69 4LN).

(In Dr Bloore's absence)

Mr H.A. Duxbury (I.C.I., Plastics Division, Welwyn Garden City):

I found Dr Bloore's paper very interesting, and in particular his application of Boyle's approach to vent sizing for exothermic batch reactors. I do not wish to comment on the first part of the paper except to observe that I found it an interesting account of the explosion and of the author's investigations into the behaviour of this unusually complex three-phase system. This was followed by the application of Boyle's approach to vent sizing. We in I.C.I., Plastics Division, have also made some use of this approach, and I have a number of comments which may be of interest, as detailed below.

(1) On page 141, equation (4),  $R = c.e.^{aT}$  is described as the Arrhenius equation, and I believe from memory that this follows Boyle. The usual Arrhenius equation is, I think,  $R = c.c.^{-E/RT}$  which is not the same, although in many cases the difference may well be unimportant.

More important, although this equation was (again following Boyle I think) considered suitable in this application for representing the effect of temperature on conversion rate, our experience shows that this is by no means always the case, and it can lead to serious error. In other cases, of course, it is applicable.

(2) Equation (8), page 142, is a heat balance, following Boyle's approach. While reasonable in most cases probably, the equation neglects any latent heat effects, and can lead to serious error if applied to a reactor with a relatively large gas space where considerable evaporation may occur during the reaction.

(3) In the Appendix, page 148, I think Dr Bloore's use of "conservative" may mislead some readers. In this context, I understand Dr Bloore's "more conservative" as meaning that the predicted size is smaller, i.e. less safe.

(4) Following Boyle's approach, Dr Bloore has considered both steady state gas venting and liquid venting. Our current approach in I.C.I. Plastics Division, is to assume that a two-phase gas/liquid mixture is vented. This leads to a larger vent size.

I would welcome any comments on these points.

Mr W.W. Russell (Monsanto Company, St. Louis, Missouri):

Dr J. Huff, Dow Chemical Co., U.S.A. presented a paper on two-phase (liq-gas) venting of reactors at the AIChE Meeting in Philadelphia last November. I believe he concluded from the two-phase model that larger vents are needed than predicted either by Boyle's liquid phase model or the gas phase model of venting.

THE HAZARD OF GAS PHASE OXIDATION IN LIQUID PHASE AIR OXIDATION PROCESSES.  
By J.M. Alexander (I.C.I. Ltd, Petrochemicals Division, Billingham).

Mr P.H. Fogg (BP Chemicals Int. Ltd, Hedon, Yorks):

Had the team considered any other means of ignition for the vapour phase reaction? Was it possible that particles of catalyst were being deposited in the air line and were causing premature vapour phase reaction?

Mr Alexander:

No, I don't think so. The air lines concerned were very long, and I think we are fairly confident that the ignition was due to the process and not something extraneous.

Mr Fogg:

Surely the free radicle mechanism postulated for vapour phase ignition would also apply in a laboratory auto-ignition test, and laboratory devised auto-ignition temperatures should therefore be directly applicable to the full scale reactors?

Mr Alexander:

No, this is not the case, liquid phase oxidation is not likely to initiate in a normal auto-ignition test when the liquid is introduced into the test apparatus. A catalyst or hydroperoxide is required to be present before the liquid phase reaction occurs. It would be very difficult to test the free radical hypothesis. However, it would be possible to test the more empirical supposition that a liquid phase oxidation reaction is necessary in the liquid phase/gas phase interface before an ignition is possible in the gas phase. The cumene oxidation process could be used as a model. Cumene hydroperoxide is produced without intermediates, except for free radicals, by bubbling air through cumene containing cumene hydroperoxide as a catalyst. Auto-ignition measurements could be made for a range of cumene hydroperoxide compositions using a large excess of liquid. This auto-ignition temperature may well be a good indication of the initiation of a gas phase reaction via the liquid phase. To check the auto-ignition temperature is not due to cumene hydroperoxide auto-ignition, the same experiments could be repeated with a few hundred ppm of phenol. Phenol suppresses the liquid phase reaction so one would get two sets of auto-ignition temperatures, with and without liquid phase oxidation. One would expect the phenol suppressed results to give higher temperatures.

Dr G.W. Stewart (Burmah Oil Trading Ltd, Bromborough):

Does the sludge which separates out in the base of the reactor and air inlet tube, after a shutdown period, exhibit an appreciable peroxide value? My thoughts on this are that if relatively high concentrations of hydroperoxides and peroxides were to form in the base of the reaction, then on reheating for commencement of the autoxidation a highly exothermic decomposition would occur which could cause severe damage to the adjacent surfaces of the plant.

Mr Alexander:

The solids were analysed and found to be peroxide free. I think we can be confident that they were inert.

Dr E. Hutton (Laporte Industries Ltd):

Re organic peroxides, at the temperatures which we are discussing, i.e. 125-150°C., the half life of many organic peroxides are short, for example, cyclohexanone peroxide half life is between 1 and 15 minutes. We are not therefore with these compounds, likely to build up any significant quantities unless the peroxides present do have longer than general half lifetimes.

Mr Alexander:

Some peroxides are more stable than others.

Dr Hutton:

There has been experience with some types of organic peroxides of boil-off accompanied by evolution of vapours below their self ignition temperatures. Subsequently these vapours ignited on the absence of sources of ignition. Although no definitive evidence is available it is surmised that ignition is due to the formation or carriage of free radicals into the gas phase and the interaction of these with air to raise the temperature above the auto-ignition point.

Mr H.A. Duxbury (I.C.I., Plastics Division, Welwyn Garden City):

Cyclohexyl hydroperoxide is reasonably stable. I believe I am right in saying that it will last for several days, in KA solution at least. Each of the above comments relates to reaction in the absence of trace metals and catalysts: The stability is discussed in "Organics Peroxides", E.G.E. Hawkins, E. & F. Spon Ltd., London, 1961.

Dr G.W. Stewart, (Burmah Oil Trading Ltd, Bromborough):

Would it be possible to test your hypothesis, on the size of the air bubbles being the cause of the trouble, by introducing air into a process through large holes in a sparge pipe and thus producing larger air bubbles?

Mr Alexander:

The agitation from the air bubbling through an open pipe is sufficiently good to prevent gas phase ignition from occurring. The original cyclohexane oxidation process worked quite satisfactorily in this way. Ignition only occurs when the agitation is so bad that a large air bubble is formed which cannot easily break away from the air inlet line. However, higher oxygen levels would occur in the off-gases due to reduced rate of oxygen uptake.

Dr I.E. Eastham (Rohm & Haas (UK) Ltd, Jarrow):

It is interesting that Dr Gagan suspects aldehydes as the source of auto-ignition in his petroleum oxidation incident. We have recently had an incident where we suspect styrene decomposed in contact with a surface at or about 180°C. Our tests suggest Benzaldehyde could have formed. If however only styrene had been involved could Mr Alexander have foreseen an air oxidation reaction causing ignition below auto-ignition temperature?

Mr Alexander:

No, I don't think I would have foreseen this. I would have expected styrene vapour to behave in a normal way, i.e. auto-ignition at the temperature expected. If we knew liquid decomposition products were formed which would oxidise rapidly in the liquid phase, then it would be possible to predict an ignition at an unusually low temperature.

Dr B.J. Tyler (Dept of Chemistry, U.M.I.S.T.):

Do you investigate near misses as well as failures?

Mr Alexander:

Yes we do. But we have to recognise that a near miss has occurred.

A LIQUID PHASE OXIDATION INCIDENT.

By K. Gagan (Dr J. H. Burgoyne & Partners).

Mr M. Kneale (Lankro Chemicals Ltd):

Did you mean to imply that you would be happy about a stabilised flame at a bifurcation within the reactor, say in the space above the liquid? Would not a failure of the pipe then lead to a major fire?

Dr Gagan:

No, not inevitably. Although flame stabilisation at the upstream bifurcation of the air supply pipework appears to be a probability should ignition occur within the sparger system, the likelihood of disaster would be very much greater with the bifurcation outside the reactor shell because the hot pipework experiences the full working pressure. A bifurcation within the reactor experiences a pressure of only a few pounds per square inch which may well not cause failure even at red heat. However, if failure should occur, air would discharge directly into the reactor, probably above the liquid level. This would be a very dangerous circumstance and could lead to a major catastrophe. The American experience however seems to be that, when flames become stabilised within the pipework inside an L.P.O. reactor, carbon deposition occurs and plant conditions quickly change to indicate that something out of the ordinary is occurring.

Mr Alexander:

If you have a stabilised flame inside the air line inside the vapour space then the air line can weaken, burst and let air into the vapour space of the vessel. One would then expect a vapour space fire fed by fresh air and flammable vapour from the liquid surface. The vessel would then be likely to overheat, burst under process pressure and cause an extensive fire in the plant. If the stabilised flame were inside an air line which was submerged in the liquid, and the air line ruptured, air would come out of the open end and normal oxidation would occur, except for a higher oxygen level in the off gas due to the larger bubbles and the reduced path length of the bubble.

Mr A.H. Searson (Esso Engineering Services Ltd, New Malden):

Presumably piping configurations other than the bifurcation described could create a stagnant zone in which flame stabilisation could occur (such as non-flowing branch connections)?

Dr Gagan:

A branched configuration of the air supply pipework seems to be a prerequisite for flame stabilisation. At least two branches in parallel both connected to the sparger matrix are required for the flash-back mechanism to work: an ignition at one extremity of the parallel flow system reverses the flow in that branch whilst augmenting the flow in the other branch(es). Such transitory behaviour enables the flame to reach the point of division of the air pipework where it stabilises.

Mr J.A. Dukes (U.K.A.E.A., Reactor Group, Springfields, Preston):

Fig. 1. of Dr Gagan's paper describes a vessel operating at 180°C. and 50 atm. pressure with a 60-ton inventory of butane. One wonders how the Design Engineers can have involved the operators of the plant in a highly exothermic process with this quantity of material at risk on a single batch? If the concept of "stored energy" had been used this ought to have caused great anxiety about this scale of operations.

Dr Gagan:

By 'stored energy' I understand : maximum available energy, not only physically contained, but also latently present and realisable on combustion with the surrounding atmosphere. I can only agree with Mr Dukes in the light of what has been learnt since the plant in question was erected in 1965. A retrospective judgement of the design engineers would be too harsh however especially since the rate of energy release, which is the important practical criterion, would have been limited, and was limited in the event, by the size of pipework adopted. Nevertheless my present view is that in new plant, control rooms and all other staff areas should be constructed to withstand the likely blast pressure as dictated by the stored energy equivalent of, and distances of separation from, the plant in question. Consideration should perhaps be given to existing plant in order to adequately protect employees.