

**Proc. 448: Safety Aspects of Blended and Granulated Compound Fertilisers
Based on Ammonium Nitrate,**
by: K D Shah and D C Thompson.

Discussion following the presentation of the paper:

Bob Milborne *Kemira Agro UK Ltd, Ince, UK:*

I'll restrict myself to two questions and both these relate to decomposition of fertilisers. The first point is to do with your comments about ammonium sulphate sensitising self-sustaining decomposition (SSD). We know about the effects of copper and other contaminants but in general terms we would challenge your statement, and we have some experience. At Ince we had a particular B-type product which was borderline class B and we reformulated this to include sulphur about 7% SO₃. Based on trough tests this product did not show this self-sustaining property and that was true whether we used calcium sulphate or ammonium sulphate as the sulphur source. The only problem we did note resulted from an experiment in which we increased the ammonium sulphate content to as much as possible; I think we got up to about 18% SO₃. In this case there was some self-sustaining decomposition, but you can easily explain that from the triangular diagram. Because what is actually happening is that you depress the quantity of ammonium nitrate required, and if you look on the triangular diagram you then find yourself in the danger zone, which has got nothing to do with the fact that it's ammonium sulphate, rather it's the ammonium nitrate content which is changing. We produce quite a number of products at Ince now containing ammonium sulphate and none of them has this self-sustaining property, so I would ask you to try and convince us of this statement you make!

David Thompson:

I don't have an acetate of this graph (Figure 7, page 38) from Proceeding N^o 124 by Perbal to the Fertiliser Society, I hope that you can see it if I hold it up. You saw the graph that Kish showed earlier which was the ammonium nitrate, potash, phosphate triangle. This graph I show now is the ammonium nitrate, potash, ammonium sulphate triangle and you can see the area of self-sustaining decomposition determined by Perbal; our tests show that that is substantially correct. Also you find that with sulphate when you do get cigar burning it tends to have a higher velocity. If I can just emphasise, as Kish mentioned, that you will find that some blended fertilisers with ammonium sulphate present are non-burners and some of them are burners, depending upon where you are in the diagram. It's not possible to have any generalisations.

Bob Milborne *Kemira Agro UK Ltd, Ince, UK:*

This is true. Taking the original formulation, when we tested it in the trough, it was actually better than we would have expected from the chart. It's a different experience but it's a practical one.

David Thompson:

The answer is always to test it.

Bob Milborne *Kemira Agro UK Ltd, Ince, UK:*

Yes, you have to test it - we agree! My second question is also to do with decomposition, in terms of granulation operations. You have mentioned this hazard being particular bad when a drier stops rotating. In this case the fact that the product has self-sustaining properties is perhaps less important as a heat source is still present of course. Surely in that case there are other important factors such as the initiation temperature and the rate of formation of toxic gases, etc. It can be the case for grades containing a lot of ammonium nitrate that melting and fume-off occurs at a low temperature and they will give off relatively large volumes of gas. Such products are not usually self-sustaining in nature. But from a process point of view don't you think they are more hazardous than products which are Class B but have a higher initiation temperature and produce relatively low volumes of gas, or are you more concerned about the composition of the gases being evolved in terms of their toxicity?

Kish Shah:

I don't think we should over-play self-sustaining decomposition products in terms of hazard. What you are saying is quite correct. If there is heat and there is a large quantity of pre-heated material then a Class C would be equally as hazardous as a Class B. It could even be more so in terms of its potential to release toxic fumes, as you rightly say. So for that reason I did not put down that hazard as only being associated if it's self-sustaining. It's a general hazard for all NPK fertilisers which we must be aware of. Thank you for making that point.

Pan Orphanides, *Consultant, Greece:*

According to your experience which are the best additives for use in ammonium nitrate, prilled or granular, to increase its thermal stability, while at the same time not making it too hygroscopic?

David Thompson:

There isn't one! There is no known additive to my mind that will satisfy all of your requirements. Remember in the end of course that the fertiliser has to be readily available to the crops, otherwise we could talk about water-proofing the outside to prevent moisture-uptake for bulk handling. Personally, we have been handling desiccated ammonium nitrate now for over 35 years, using magnesium nitrate. The advantage of the desiccant, for those who aren't familiar with it, is that the breakdown due to thermal cycling is totally eliminated. However as Pan suggests, you will have a lower vapour pressure above a desiccated material. As I said in the presentation the best way to prevent moisture pick-up is to keep the doors of the store closed; if you have a bulk store with no doors open and not letting moisture in, the desiccated material is as good as an undesiccated material. There are various organic coatings which can be applied to the surface of the fertiliser prill or granule which will reduce the rate at which moisture pick-up takes place, but they are only reducing the rate, they don't prevent it.

Pan Orphanides, *Consultant, Greece:*

I accept that you can do in your own storage but you cannot control it on the way to the farmer, where the product is transported in bulk, whether or not it should be, and stored in places which you cannot control by closing doors. Returning to

your remark that there is no answer to the problem, I think as a desiccant aluminium sulphate combined with calcium sulphate is a much better able to fight thermal instability, thermal decomposition and hygroscopicity.

Another question I have concerns the production of ammonium nitrate. In the melt phase during the concentration, many people are afraid of possible decomposition due to the acidic condition of the melt produced inside the concentrator and are introducing an excess of ammonia to be on the safe side. The result is that you get a lot of ammonia in the vapours which you condense and you have to strip it back again. How can we de-mystify this? Do we need to run a pH high regime during the concentration phase or can we safely apply acidic conditions and then adjust the pH?

Kish Shah:

If you are concentrating the solution using what is widely used in the industry, - a falling film evaporator - what we have found is that independent of the pH of the starting solution the final solution usually ends up only lightly acidic. If there is excess acid vapour it comes off, or if there is excess ammonia that comes off. At that temperature and that residence time you usually end up with a slightly acidic ammonium nitrate melt and the amount of ammonia required to ammoniate that in a separate vessel is a very tiny amount so there is no need to over-ammoniate it. That has been our experience and we are able to control it fairly well. You don't have to measure the pH after the evaporation to add the ammonia; it's something you get a good feel for your plant and you know how much to put in. I would not over-ammoniate, that is not healthy and you might end up with prills which are not good quality. Over-ammoniation could lead to prills with shell structure.

Roger Dyson, Kemira Agro UK, Ince, UK:

One point you make in your paper that didn't come out of the presentations and which I would like to address is that there is a misconception that formulations made by a compound complex method and which show SSD properties are not always burners when made as blends. In other words a blend made to a formulation that would be as SSD as a complex fertiliser will still burn.

Kish Shah:

There is no hard and fast rule - you can't predict that in all cases that will be the situation. Some grades made as granulated products which 'cigar burn' they may not necessarily do so when blended, and that's why the testing is important. We have come across formulations which when granulated would cigar burn but when blended would not.

David Thompson:

But just to emphasise that the word is 'may' there is no rule that could be used to predict. If you wanted to be on the same side assume that the granulated diagrams such as in Perbal hold true for blends and you are playing on the safe side. I don't think we have got any examples where a granulated material is a non-burner and a blend is a burner.

Roger Dyson, Kemira Agro UK, Ince, UK:

We must remember that many blenders add additives at this stage and that can be the real problem as against the actual formulation.

Don Martin, Hydro Agri (UK) Ltd, Immingham, UK:

I see the point that we are getting at, but I think we must remember that what we are doing is a particular test using a particular piece of equipment and it is that which is determining whether the product is Class B or Class C. Our experience is that broadly we have not found any SSD blends. Generally speaking a blend will pass this test when the granulated equivalent won't, although most cases are on the SSD borderline. But that is using that test and that test might not be representative of what would happen in the real situation.

David Heather, Fertiliser Manufacturers Association, UK:

I was going to ask the same question as Roger, but I was going to put it the other way round. My understanding is that blends do exhibit characteristics in that context and I think Don has drawn that out, but I was also going to make an observation on what David was saying about the lack of reporting of incidents. I think perhaps that in itself is an answer. The reason why they are not reported is that they don't happen so much now and the ones that do happen are far less headline-grabbing than those in the past. If you take Kish's recent paper on ammonium nitrate safety itself, the figures in there, and I may get some of them slightly wrong but there were I think over a thousand fatalities in the 40 years up to the 1960s, there have been about 30 fatalities since then, so that would explain why there has not been so much reporting of incidents. Fertiliser with ammonium nitrate is a much safer product than it used to be and I don't think we want to lose sight of that as a particular factor with regard to the product we deal with. The other things is I think the incidents that you seem to be referring to David tended to be more in the process stage rather than as the title reads "Safe handling and storage of granulated and blended compounds" once they have been made, so would you perhaps agree that the greatest risk of something happening is during the processing stage rather than afterwards?

David Thompson:

If you look at the numbers given in the paper, there were seven incidents during manufacture which were decomposition plus four explosions - that's eleven, four during maintenance and eleven during storage and transport. Of course that is looking back over the last 40 years, but over that 40-year period the same number in distribution and storage and transport as there were on the plant.

David Heather, Fertiliser Manufacturers Association, UK:

But the point I would make is that there have been fewer major incidents recently. It's also a consequence of better reporting that the lesser incidents are now included in the statistics, quite rightly, but it is probable that if you actually look back at what happened 40 years ago there were at least as many of the smaller incidents.

The Chairman thanked the speakers.