AMMONIUM NITRATE STABILITY

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At ICI, our range of compound fertilizers is based on ammonium nitrate and, therefore, in recent years we have been doing research work on the thermal stability of compound fertilizers based on ammonium nitrate as well as the safety problems that arise during the manufacture and distribution of straight ammonium nitrate fertilizer itself. For the discussion to be useful I think it is essential to clearly differentiate between the thermal instability problems associated with compound fertilizers that contain ammonium nitrate and the safety aspects that arise during the manufacture, storage, and distribution of fertilizer ammonium nitrate.

The article by A. Parker and myself (1) is mainly concerned with the thermal instability of compound fertilizers. This is a subject which has not received a great deal of attention in research work. In recent years, the safety aspects of compound fertilizers based on ammonium nitrate has caused as much concern to the international fertilizer industry as any of the incidents involving fertilizer ammonium nitrate itself.

Aspects of thermal instability

There are five aspects of thermal instability of compound fertilizers which should be considered separately since a formulation which shows one form of instability may or may not be inert in other respects.

The first one, Type A, is fuse-type reactions. This will be discussed in detail later.

Type B is spontaneous decomposition at high temperatures. This occurs in all fertilizers based on ammonium nitrate and chloride if the whole mass of fertilizer is raised to a high temperature. This type of decomposition results from the acidity that develops when these fertilizers are held above about 115°C and is characterized by an induction period whose duration depends on the temperature and presence or absence of components which buffer the system and prevent acidity from developing. If inorganic fertilizers are kept below 115°C this type of decomposition is avoided.

Type C is self-heating and mainly concerns fertilizers which can become acidic and contain organic impurities. Free acidity may develop from superphosphate in fertilizers and the subsequent oxidation of any organic matter can cause a self-heating problem. Several papers in the past have indicated how these problems can be overcome, in particular the mixing of organic matter with any fertilizer containing ammonium nitrate should be avoided.

Type D and E instability, i.e., explosibility and oxidizing ability only become important at levels of about 80% ammonium nitrate and above, when the properties of such fertilizers approach those of pure ammonium nitrate. In general the wide range of N-P-K fertilizers are not susceptible to this type of hazard, but it is necessary to test for this type of instability before a project to market a new ammonium nitrate based fertilizer has progressed very far.

Fuse-type reactions

In recent years, in the United States, Germany, and Holland, hazardous incidents have occurred in which several thousand tons of compound fertilizer based on ammonium nitrate have decomposed resulting in large clouds of toxic gases sweeping across the countryside and causing considerable concern to the local population. Even more recently, as you may recall, the S.S. Sophocles carrying 6,000 ton of compound fertilizer sank in the Atlantic. We consider that these incidents were due to what we term fuse-type or "cigar-burning" reactions which have not been properly understood, to date, by the fertilizer industry. A fuse-type reaction is a specific form of exothermic decomposition, which can self-propagate throughout a mass of material, and requires the presence of an oxidizing chemical and a reducing or catalytic agent. In compound fertilizers ammonium nitrate acts as the oxidizing agent and potassium chloride, which is present in fertilizers, provides the chloride ion which catalyzes the ammonium nitrate decomposition.

Figures 1 and 2 indicate what we mean by cigar-burning of fertilizers. Figure 1 shows two compound

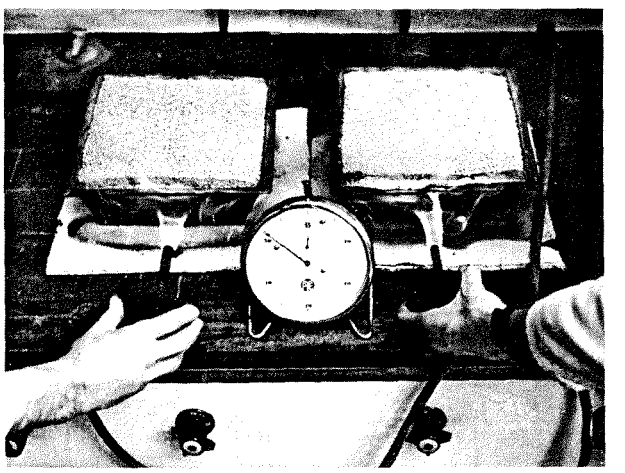

Figure 1. Cigar burning on a laboratory scale; initiation stage.

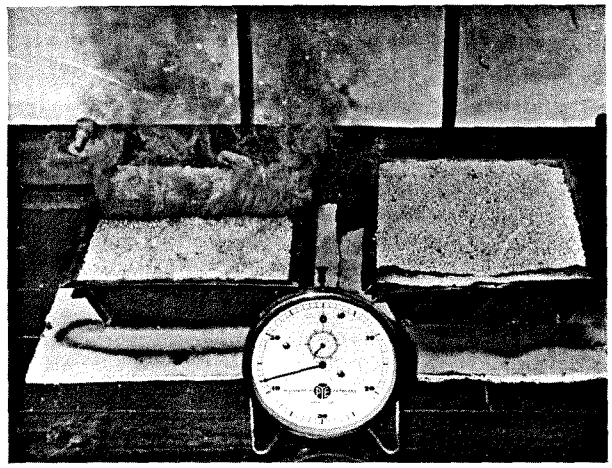

Figure 2. Cigar burning of N-P-K fertilizer containing water insoluble phosphate (left-hand tray) and nonburning formulation (right-hand tray).

fertilizers being heated. In actual fact, the left-hand one contains about 35% while the right-hand side one contains about 50% ammonium nitrate. While heat is applied both fertilizers decompose. Figure 2 shows that when the source of heat is removed the fertilizer on the right-hand side, despite its high ammonium nitrate content, stops decomposing. The one on the left side though, once initiated continues to burn like a fuse despite the fact that the source of heat has been removed. You can see that fertilizers such as this present a problem to the industry since if accidental initiation occurs due to any source of heat, for example hot metal from a welding operation, the decomposition will not be restricted to the local area of initiation but could result in the whole store of fertilizer decomposing. It is this kind of thermal instability that caused the incidents in the United States, Germany, and Holland previously referred to.

Test procedure

We described a test procedure (1) for showing whether any fertilizer is, or is not, a cigar-burner. Using this procedure a manufacturer can go through the materials he produces and see if any are susceptible to this type of hazard. Figure 3 shows the principle of the test method. Decomposition is initiated by buried electric light bulbs or hot metal ball-bearings. Putting thermocouples in different positions in the velocity zone allows the rate of burning of the fertilizer to be determined. In other tests we have also measured the rate of decomposition in the vertical direction where the hot decomposition gases cause channelling and a faster reaction.

Figure 4 shows the actual apparatus employed at ICI. I should point out that we think it is always necessary to work behind a sandbag barricade when very hot metal is being added to fertilizers containing ammonium nitrate.

Liability to fuse-type reactions

Figure 5 shows the results we have obtained in a study of fertilizers based on ammonium nitrate, potassium chloride, and ammonium phosphate. The zone of fertilizer compositions that are liable to cigar-burn is shown by the shaded area. This shows that liability to cigar-burning is not simply proportional to ammonium nitrate content, but the susceptible formulations are restricted to a well-defined area bounded on one side by the ammonium nitrate-potassium chloride edge of the graph. You can see that if sufficient ammonium phosphate is present you get right out of the cigar-burning range and get rid of this particular hazard.

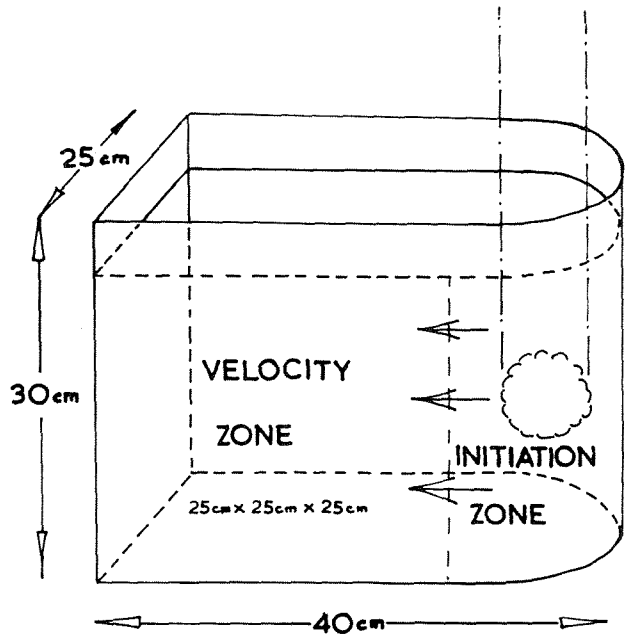

Figure 3. Standard test vessel for cigar burning ability and front velocity.

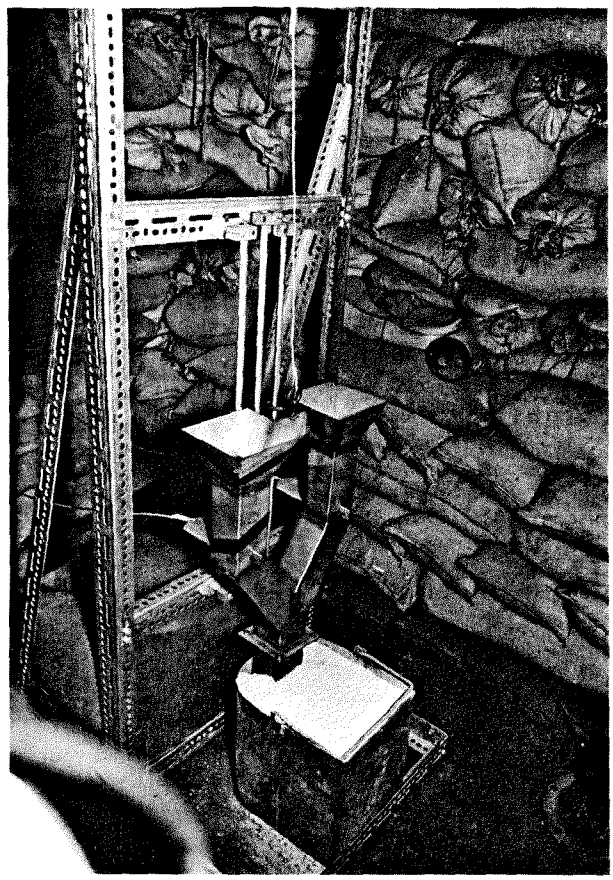

Figure 4. Test procedure: initiation rig in charging position.

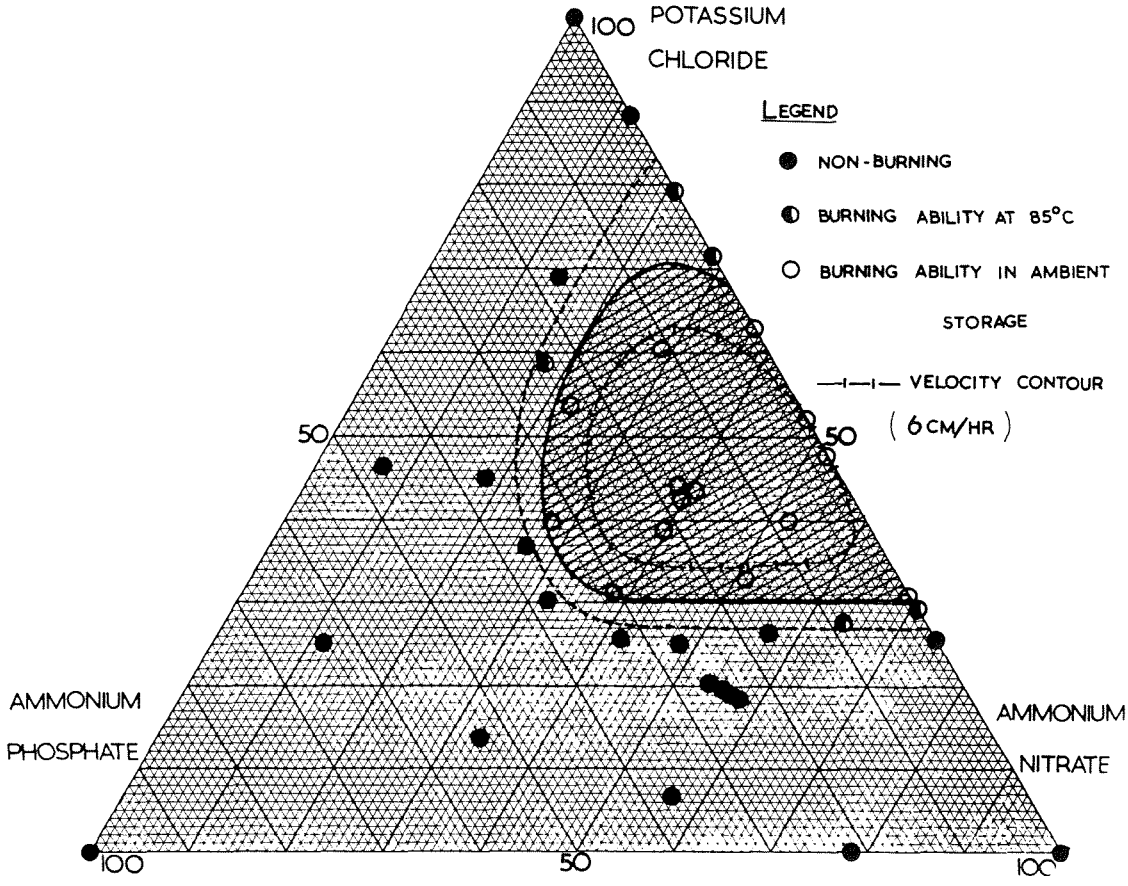

Figure 5. Cigar burning ability of N-P-K fertilizers based on ammonium nitrate, potassium chloride, and ammonium phosphate.

We have also carried out some work on other formulations including some containing ammonium sulphate and some in which the ammonium phosphate is replaced by calcium phosphates. Some details of this work are given in our paper (1).

Porous structure

Basically what we have shown is that for cigar-burning to occur an ammonium nitrate content is necessary, a chloride content is necessary and, thirdly, the fertilizer must possess a rigid porous structure at the temperatures (200 to 500°C) involved in cigar-burning. Not all fertilizer formulations containing ammonium nitrate and a chloride have a suitable structure and, therefore, not all of them are subject to cigar-burning. As shown in Figure 5, the presence of water soluble phosphates only results in a small range of N-P-K formulations capable of cigar-burning. Addition of ammonium sulphate or water insoluble phosphates results in more rapid rates of burning and a wider area capable of cigar-burning.

LITERATURE CITED

1. Parker, A. B., and N. Watchorn, "Self-Propagating Decomposition in Inorganic Fertilizer Containing Ammonium Nitrate," J. Sci. Food Agriculture (June, 1965).

DISCUSSION

GRAHAM—Tennessee Valley Authority. I read your excellent paper very recently and noted that you said that it was very difficult if not impossible to put this out with a jet of water.

WATCHORN: Yes, if you try to penetrate a bulk store of compound fertilizer, particularly one that is decomposing, with water, what generally happens is that a crust forms on the top and the water does not get down to the rest of the material. Now cigar-burning is a chloride catalyzed decomposition of ammonium nitrate and does not require air or oxygen for its propagation so it will continue below the surface and will not be put out very easily. Remember, this is not like normal burning, oxygen is not required, there are no flames, the main hazard arises from the toxic gases evolved from the chloride catalysed decomposition.

In our paper we recommend that if you have a fertilizer that is a cigar-burner, you try and change the materials used so that you take the formulation outside the cigar-burning zone. If this cannot be done and you have to manufacture a cigar-burner, we recommend that it not be stored in bulk but in bags with gaps left between stacks of bags. In this way a cigar-burning incident can be restricted to the small tonnage in each stack. Since no flames are involved, this fuse type of reaction cannot jump across even a small air gap and this is a practical way of limiting the effect of any accidental local initiation of a cigar-burning formulation.

Anonymous: Is this a self-accelerating process? Does the reaction accelerate as time goes on?

WATCHORN: This is not easy to answer for all formulations, however, in fertilizers based on ammonium phosphate we did not find any tendency to accelerate. At one stage we were worried about this. We wondered whether, at the pressures that could be envisaged in a large bulk store, some acceleration of the reaction might occur. In our paper we mention that we did do burning tests in vented bombs where the escape of the decomposition gases was restricted. This work did not suggest that any accelerated reactions would occur under the low pressure conditions likely to occur in normal land storage nor did it suggest that at these relatively low pressures a non-burner would become capable of sustained burning.

SWAN—Sohio Chemical: Is this type of behavior possible in true compound fertilizers or blended fertilizers? Are dry blended fertilizers made from three separate components subject to this type of thermal instability?

WATCHORN: Both true compound fertilizers and blended fertilizers are subject to cigar-burning and, in general, the area of compositions which are capable of undergoing this self-sustaining decomposition are similar. In the marginal regions however, on the border of the cigar-burning area, some differences will occur. Because a blend obviously has a different structure to a compound fertilizer of the same analysis some difference can be expected. In a blend the chloride and ammonium nitrate are in less intimate contact, therefore, in the case of marginal burners, there will be occasions in which the blend will not cigar-burn but the equivalent compound fertilizer would.