

COMMISSIONING OF A PRODUCTION PLANT FOR HEXANITROSTILBENE

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Melt casts of TNT normally consist of long needle like crystals which tend to align themselves parallel to one another. The solid mass therefore contains extended planes of weakness and is thus prone to cracking along these planes. Obviously TNT would be more suitable as a carrier for RDX and HMX if it was not so brittle, and over the years much attention has been devoted to developing a means of preventing the growth of large crystals in TNT. The "creaming" of TNT is one such process. This involves the addition of fine seed crystals of TNT to the rapidly stirred TNT melt. The fine crystals act as sites for the growth of randomly orientated small crystals. The disadvantage of this method lies in the fact that addition of the fine crystals to the TNT thickens the melt and makes stirring difficult. As RDX/TNT slurries are usually operated at the highest practicable RDX content it is apparent that this method is not suitable for high energy RDX/TNT fillings.

Bofors in 1969 reported on a method for grain modification in TNT melt casts. This involved the inclusion of between 0.2 to 0.5% Hexanitrostilbene in the TNT. The mixture is then heated to 100°C, stirred until homogenous solution is obtained and then cooled and allowed to solidify. The material is then remelted without taking the temperature above 85°C. On this second cooling stage the TNT solidifies as a matrix of fine, randomly orientated crystals. It has been shown by M A Parry (references 1 and 2) that the active species which causes nucleation of the TNT is not HNS itself but the complex HNS(TNT). The disadvantage of having to melt the TNT twice in the presence of HNS before the HNS becomes effective as a nucleating agent is somewhat offset by the fact that the first melt can be done during manufacture of the composition at the explosives manufacturing factory, whilst the second melt is done at the filling factory.

Although HNS has attracted some attention as a high temperature resistant HE (m. pt (with decomposition) 596°K) in its own right, by far its greatest use in the UK is as a nucleating agent for nitramine/TNT fillings. It has been

manufactured in a very pure form at the Royal Ordnance Factory, Bridgwater since 1977. The Bridgwater process is based on the method of K G Shipp, first reported in 1964 (references 3 and 4), who obtained HNS in 42% yield by reacting TNT with sodium hypochlorite in a tetrahydrofuran (THF), methanol, water mixture as shown in Figure 1.

The reaction mechanism as proposed by Shipp and Kaplan (reference 5) is given at Figure 2.

The Shipp method was developed to a 5 kg pilot plant process at PERME, Waltham Abbey, England, before a production plant was installed at the Royal Ordnance Factory, Bridgwater, Somerset, England in 1977.

An outline of the present Bridgwater Production Process is shown at Figure 3.

During the long commissioning period, a number of problems were encountered and overcome. An account of the problems and the methods used to solve them now follows:

#### Problem 1

For economic reasons the plant was installed into an existing mounded building, originally designed for a different process. Because the building was really too low to house the gravity flow plant, solvent recovery lines had to be constructed below ground level. In cold weather, these low recovery lines tended to block up due to "salting out" of sodium sulphate by -product from the other liquors. Because of the fact that some of the lines were below ground level it was not possible to warm them to prevent "salting out". This problem was eliminated by using hydrochloric acid rather than sulphuric acid for the acidification stage. This change, however, could not be effected without first reviewing the materials of construction of the plant and changing the solvent recovery and storage vessels to polypropylene and installing glass stills and stripping columns.

These changes were found to be necessary because the by-products resulting after acidification with hydrochloric acid are much more corrosive to conventional materials of construction than the sulphuric acid by-products.

### Problem 2

The product cannot be purified by conventional recrystallisation methods as no suitable organic solvent exists for HNS. This increases the possibility of grit contamination in the final product and indeed this was found to be the case. Grit emanated from a number of sources, eg breakage of glassware in pipelines during construction, wind blown brickdust, drummed hypochlorite etc. Improvements were made to manufacturers' in line filter design, ie improved ribbon wound filter elements of US manufacture have been installed instead of the original ceramic ones and grit contamination of the product is now a rare phenomenon. A simple sedimentation and sieving process can be used to de-grit any contaminated batches.

### Problem 3

Because many side reactions occur and thus many hundreds of by-products are formed during the production of HNS by this method, the product is very heavily contaminated. A red oil clings to the HNS product after filtration from the mother liquors. No suitable organic solvent exists for HNS, so the product has to be purified by repeated washings on the filter beds. Acetone is used as the washing agent; followed by a final washing with water. Originally fitted membrane bucket filters were used, but this resulted in considerable loss of product (ca 50%) and a slow filtration cycle time of approx 8 days. The use of loose bag filters reduced the duration of filtration of the product from mother liquors to overnight retaining all the product.

### Problem 4

One bye product of the process is the lachrymatory gas chloropicrin. At one stage levels of chloropicrin of thirty times the threshold limit of  $0.7\text{mg/m}^3$  were recorded in the building. Improvements in fume extraction in the building and containment have virtually eliminated chloropicrin from the building atmosphere. Regular checks are still made as a matter of routine. The improvements in fume extraction consists of additional general building extraction, closed acidification and ageing vessels with ducting to outside, and closed filter vessels fitted with lip extraction so that air can be drawn across the top of the filter tubs.

Problem 5

Disposal of bottoms waste liquors from the solvent recovery stills is by pumping through activated charcoal packed column to factory effluent.

Problem 6

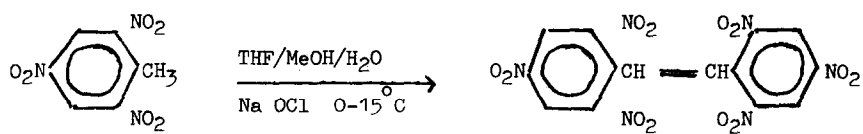
At the start of the commissioning period the yield of HNS based on TNT consumption was a reported consistent 33%. This was increased to an average 45% yield by the use of sodium carbonate/sodium bicarbonate buffer solution added to the reactants as they flowed from the reactor to the ageing vessel.

Conclusion

The present Bridgwater plant is capable of producing about 20 tonnes HNS per annum on a three shift basis. The average yield of HNS based on TNT consumption is 45%. The product is of high purity, average m. pt 319°C (Ca theoretical m. pt = 323°C). Recovery of THF solvent from the process is about 70%.

## REFERENCES

- 1 M A Parry and B W Thorpe, The Role of HNS in the Grain Modification of TNT J Crystal Growth, Vol 47, page 541-550, October 1979.
- 2 M A Parry, The Physical Properties of Cast TNT with Added HNS, Materials Research Laboratories, Defence Science and Technology Org, Melbourne 3032, Australia.
- 3 K G Shipp, Heat Resistant Explosives XVI, a New Synthesis of 2, 2 , 4, 4 , 6, 6 Hexanitrostilbene, HNS, 22 April 1964.
- 4 K G Shipp, J Org Chem, 29, 2620, 1964.
- 5 K G Shipp and L A Kaplan, J Org Chem, 31, 857, 1966.

SYNTHESIS OF HEXANITROSTILBENE

As reported by K G Shipp and L A Kaplan, *J Org Chem* 31, 857, 1966.

FIGURE 1

POSTULATED REACTION SEQUENCES IN THE SYNTHESIS  
OF HNS FROM TNT AND  $\text{NaOCl}$

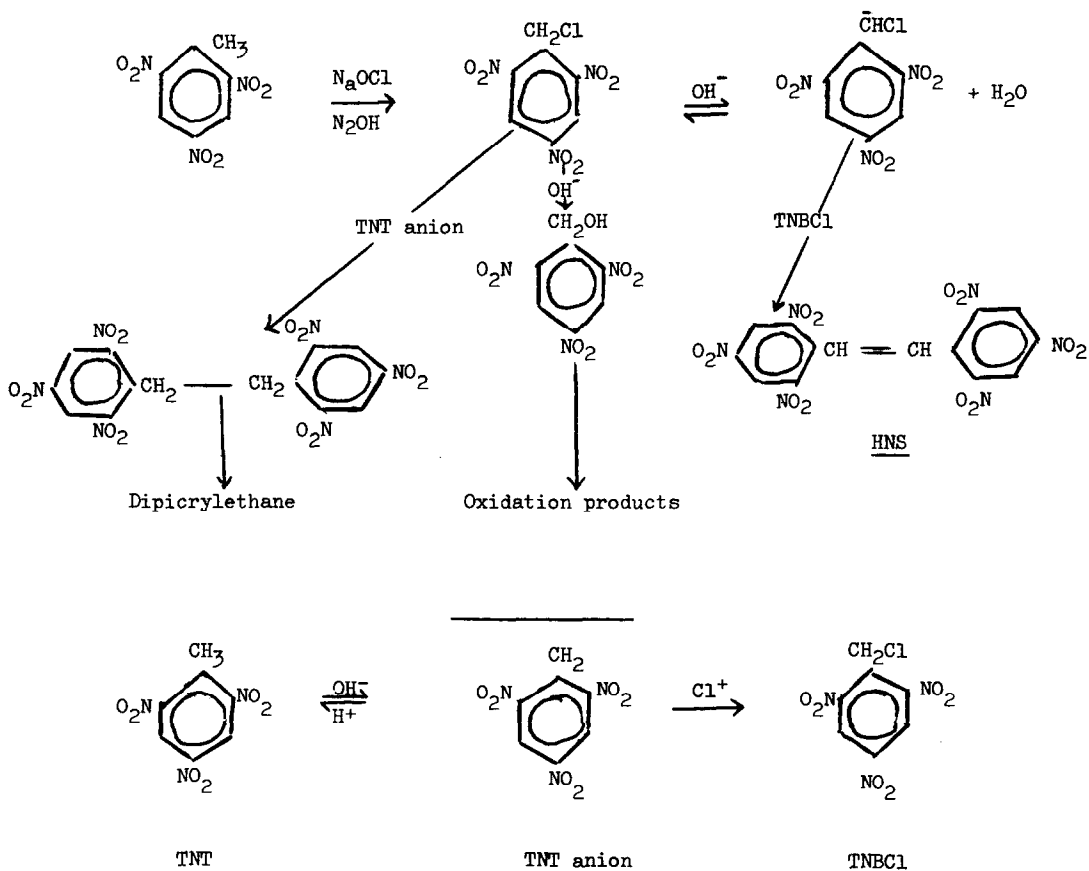


FIGURE 2

HEXANITROSTILBENE (HNS) PRODUCTION AT  
THE ROYAL ORDNANCE FACTORY BRIDGWATER

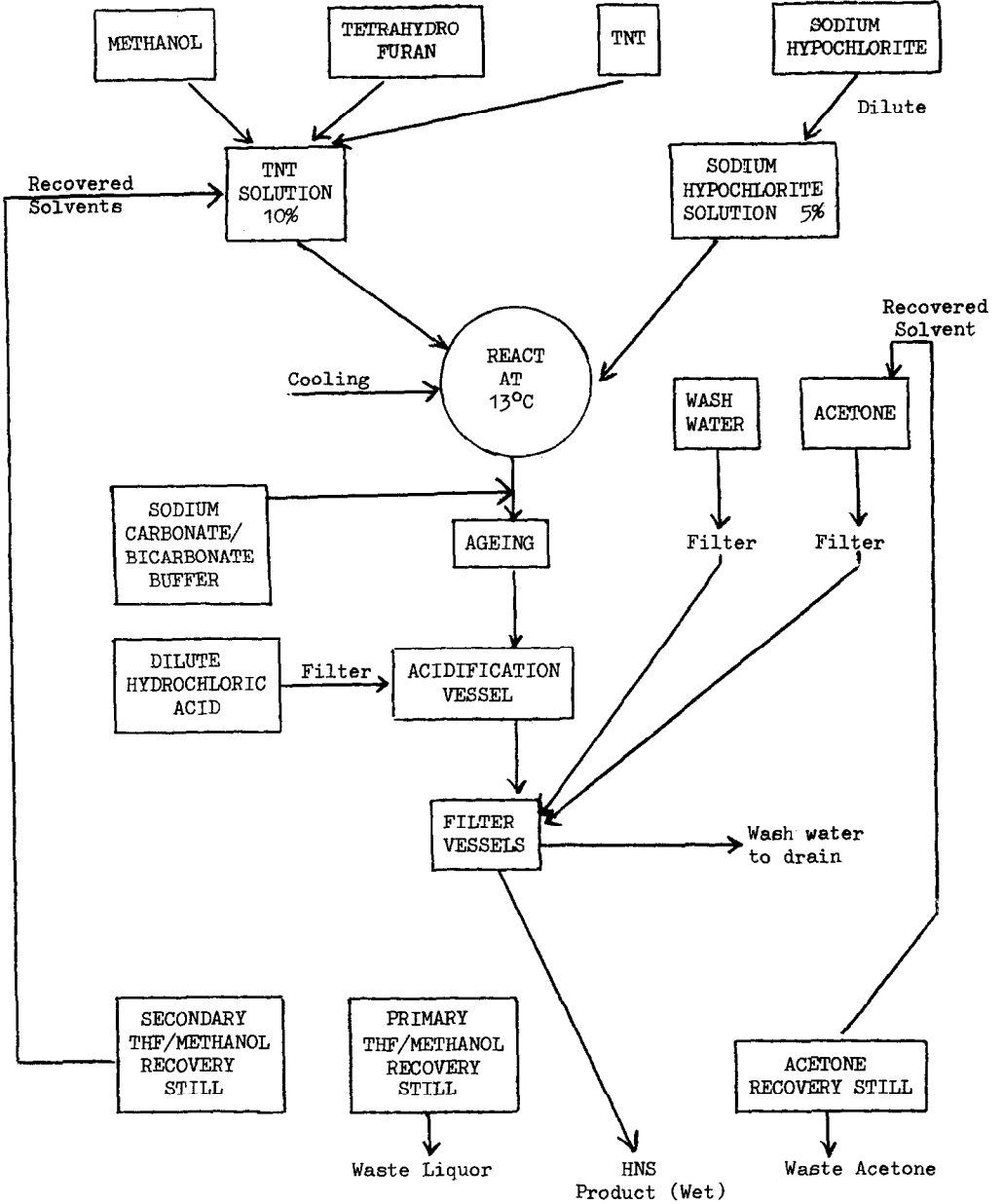


FIGURE 3