Table II: Results of gaschromatographic analysis (Vol.-%)

No.	1	2	3	4	5a	5b	13	Accident
Methane	14,3	1,0	6,4	61/59	2,9	22	41	65
Ethane	0,2	< 0,1	0,1	1,2	< 0,1	0,8	10	0,6
Propane	< 0,1	< 0,1	0,1	0,8 ■	< 0,1	< 0,1	14	
Butane	< 0,1	1,2	0,8	0,5			5	
Methanol	0,9						1	3,5
Hydrogen	83	> 95	> 90	33	90	75	1,3	18
N_2	2,3	1,9	1,6	1,8		1,4		
O_2	< 0,1	0,1	0,1	0,1		< 0,05		
CO	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1	0,1		
CO_2	0,2	0,1	0,1	5,0/6,7	< 0,1	2,3	24	4,2

Nr.	6	7	8	9	10	11	12	13
Methane	5,5	35	25	3,4	4,2	4,4	13	
Hydrogen	90	46	64	98	97	92	73	
CO	< 0,05	0,05	0,05	0,05	< 0,05	< 0,05	0,05	
CO_2	0,3	0,7	0,25	0,4	0,07	0,05	0,25	

CASE STUDIES ON UNSTABLE SUBSTANCES

J Bond*

Three case studies are given to demonstrate various aspects of hazards that should be determined during the initial development of a process, from the research stage to plant operation. The need for a formal assessment of hazards at the research stage is proposed.

INTRODUCTION

The development of a product passes through five distinct stages:-

    Research
    Process development
    Process design
    Construction of plant
    Operation of plant

A sixth stage, that of demolition of the plant, may also be added if the whole history of the product and plant is considered.

At the research stage it is necessary to identify hazards that can reasonably be foreseen in the lifetime of the plant. Hazards may be associated with:-

    Flammability
    Explosability
    Toxicity
    Thermal and pressure conditions
    Environmental problems

*BP Chemicals Ltd, Belgrave House, 76 Buckingham Palace Road, Victoria, London, SW1W OSU

A systematic approach to the identification of hazards is required at the research stage for the same reason that operability studies are used at the design stage to identify hazards introduced by the design proposed. The research chemist has to consider what happens if there is more catalyst or less catalyst, more temperature or less temperature, in the reaction he proposes. Will the product of a reaction react with one of the raw materials? What unusual reactions may occur? The consequences of the unwanted reaction has to be assessed at an early stage. Possible by-products have also to be considered.

The great chemist Berthollet discovered potassium chlorate and after consultation with Lavoisier, proposed its use in gunpowder manufacture to replace potassium nitrate (BIASUTTI). A demonstration of the manufacture of the new powder was arranged in 1788 in front of a number of guests. The operation was nearly complete when the powder detonated and killed the assistant and the daughter of the French Government Commissioner of Explosives. The violent reaction of potassium chlorate with sulphur was not known at the time of the demonstration.

The following case histories also demonstrate the importance of assessing the hazards at the research stage.

EXPLOSION IN A HEAT EXCHANGER CAUSED BY COPPER ACETYLIDE

On Monday, 4 February 1974, maintenance work was in progress on a methanol product condenser when the shell of the exchanger ruptured emitting a blue green flame and a cloud of black smoke (figure 1). Seven men suffered minor burns.

The plant was on annual shutdown and the exchanger, a horizontal fixed tube sheet design of copper construction, was being prepared for inspection. The shell (process side) had been steamed out and had been open to atmosphere for a number of hours during the previous three days. The explosion occurred during removal of one of the water channels.

After the incident a black deposit was found in the shell side of the exchanger. This contained 9% cuprous acetylide in addition to cuprous oxide, copper metal and carbon. When dropped on to a hot plate, this material sparked in a manner similar to pure cuprous acetylide. It was concluded that the explosion was caused by copper acetylide decomposition.

Examination of the literature has shown that the following conditions favour acetylide formation in copper equipment.

1. The construction material has to contain more than 50% copper. The higher the copper content, the more easily the acetylide forms.

2. Formation is assisted by corrosion of the copper surface. Mineral acids, caustic solutions and ammoniacal solutions all encourage the formation of acetylide.

3. Moderate temperatures (10-50°C) are probably necessary for the formation of active material; decomposition can occur at any temperature, depending on activity.

4. The higher the concentration of acetylene present the greater the probability of active deposits of acetylide forming, but concentrations of a few ppm of acetylene can be sufficient.

These conditions were present in the exchanger. The source of acetylene was indentified as a minor process stream containing 300 ppm of acetylene which was used intermittently.

A procedure for deactivating copper acetylide deposits has been developed so that all copper equipment suspected of containing acetylide can be made safe. Vessels are treated with 5% hydrogen peroxide in water at 50-60°C followed by a 5% solution of sodium diethyl dithio-carbamate also at 50-60°C. Cleaning is then completed by flushing with methanol/water.

This incident is not an isolated case of an explosion caused by copper acetylide. We are aware of incidents in other companies which have been attributed to decomposition of this material.

COLLAPSE OF A TANK CONTAINING MONOETHANOLAMINE

A tank containing monoethanolamine was provided with a steam coil at the base to reduce the viscosity when pumping out the product. Most of the product had been pumped out of the tank. A short while later the steam coil was turned on to lower the viscosity of the remaining material prior to emptying the tank. When the operator returned to the tank he found the paint on the side of the tank was blistering due to heat. He turned the steam off the tank and called the foreman. In front of both of them, the tank started to implode.

This incident happened on the 14 October 1966. The investigation determined that a complex trisethanolamine iron (figure 2) was formed on the steam coil. This complex decomposed at 110°C when the steam was turned on and produced pyrophoric iron. The burning iron also ignited some monoethanolamine, producing carbon dioxide probably until all the oxygen in the atmosphere in the tank was consumed. It is not clear what sort of vent was fitted to the tank although it is probable that it was fitted with a flame arrester. Clearly the vent was blocked in some manner. The cooling down of the gases as well as some carbon dioxide dissolving in the remaining monoethanolamine caused the tank to implode.

The complex trisethanolamine iron is reported in the literature (DIXON and WILLIAMS).

RUPTURE OF A FEED HOPPER

On 4 July 1986 as a result of over pressure there was a rupture of a 1.8 m^3 feed hopper (figure 3) containing a hydrazide blowing agent. The hopper had been designed for handling a flammable powder delivered in

sacks. The bag was placed on the trap door and slit open with a knife. The trap door was then shut and the powder would fall into the hopper while the bag was retained on the door. The hopper was provided with a small vent which was connected to a dust extraction system and bag filter. To cater for a possible dust explosion three explosion suppression bottles containing a halon were provided. At the base of the silo there were two slowly rotating anti-bridging scrolls and a screw auger into a weigh hopper.

The rupture of the hopper caused extensive damage to the bag slitting device which was torn from the silo and displaced several feet. Cladding panels on the roof and side of the building were blown off. The explosion suppression device had been operated by a rise in temperature.

The investigation showed that there had not been a dust explosion. This was determined by the lack of halon pyrolysis products typically present after such an event. The 250 kg of powder in the hopper had been loaded one hour previously and there had been no further movement. Just prior to the rupture of the silo the auger had been started to weigh out a batch.

The hydrazide product had a decomposition temperature of about 150°C. On decomposition it gave off vast quantities of nitrogen and water. The decomposition reaction was exothermic. If there had been no venting of the hopper, the decomposition reaction would have generated a pressure of about 10 bar. The decomposition temperature was reduced by traces of other hydrazide products used in the hopper.

It was established that a decomposition of the hydrazide product had occurred, possibly initiated by friction of the auger against the wall of the tube to the weigh hopper. The decomposition was exothermic and initiated the explosion suppression system, which added to the volume of gas and caused the rupture of the hopper.

The designers of the hopper had been aware of possible dust explosion hazards and had provided explosion suppression equipment. They had not been aware of the possible decomposition of the product stored in the hopper.

DISCUSSION

Could the hazards identified in these three case histories be foreseen at the research or development stage? Some certainly could. It is important that at the research and development stage of a process, a search is made not only of the literature, but also of accident data banks, to establish what has happened to the chemical or equipment being considered. A logical procedure to identify all reasonable hazards should be carried out at this development stage.

CONCLUSIONS

During the research and development stages of a product, it is important to establish the physical properties of the product and possible byproducts, taking into account the likely uses and method of production. To establish the likely hazards a system of examining the reaction, the products and byproducts using an operability type approach, would be appropriate.
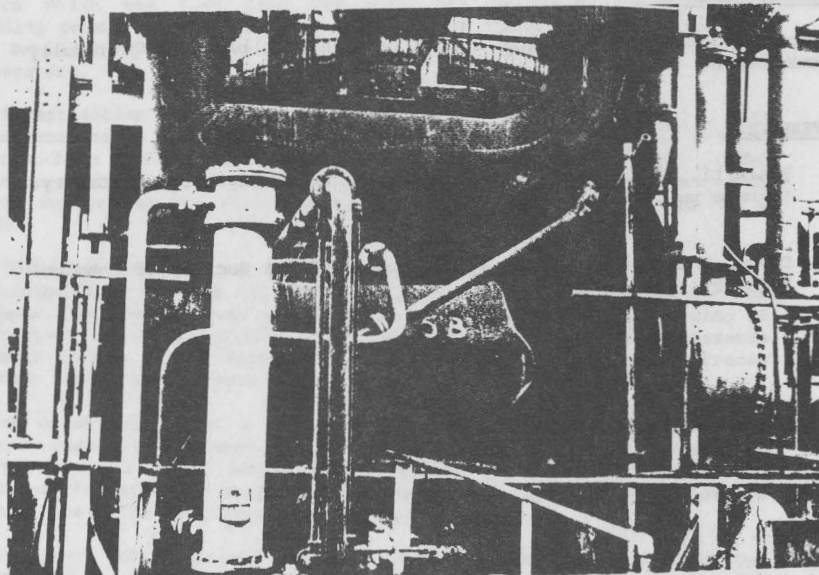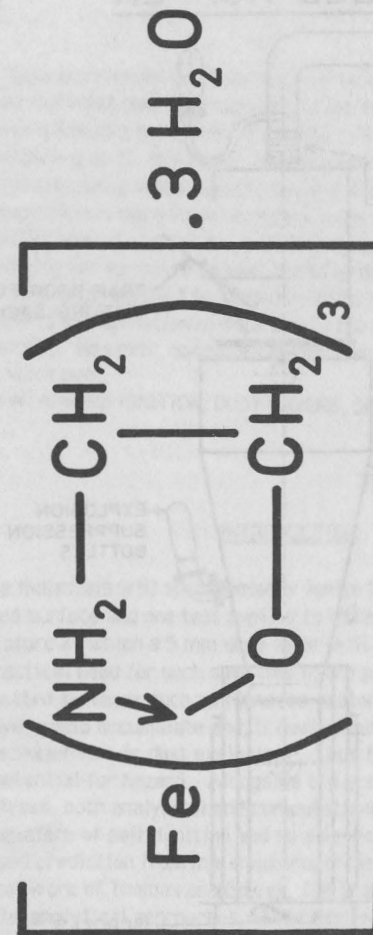
ACKNOWLEDGEMENTS

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1. Biasutti, G S, History of Accidents in the Explosives Industry. Private publication.

2. Dixon, B E and Williams, R A, Journal of the Society of Chemical Industry, 69, March 1950.

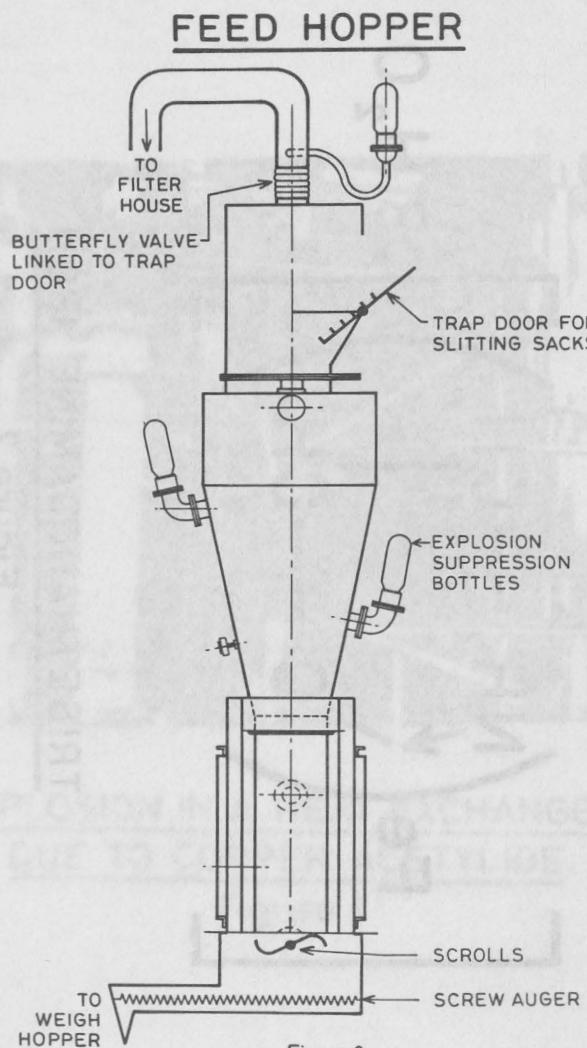## EXPLOSION IN A HEAT EXCHANGER
DUE TO COPPER ACETYLIDE
Figure 1

TRISETHANOLAMINE IRON
Figure 2

$$\left[Fe \overset{\curvearrowright}{\underset{O-CH_2}{NH_2-CH_2}} \right]_3 .3H_2O$$

FEED HOPPER

FEED HOPPER

TO
FILTER
HOUSE

BUTTERFLY VALVE
LINKED TO TRAP
DOOR

TRAP DOOR FOR
SLITTING SACKS

←EXPLOSION
SUPPRESSION
BOTTLES

SCROLLS

TO
WEIGH
HOPPER

SCREW AUGER

Figure 3

SPONTANEOUS IGNITIONS IN DUST LAYERS: COMPARISON OF EXPERIMENTAL AND
CALCULATED VALUES

B.J.Tyler[*] & D.K.Henderson[*]

A laboratory study has been made of ignitions in thin layers; the
test material used was sodium dithionite. Ignition temperatures
were measured for layers of 5 to 40 mm depth and for mixtures
containing up to 75% inert. Thermochemical and kinetic parameters
were measured independently to permit comparison with theory and
computations were made using the experimentally established
kinetic law. Comparisons with theory show the importance of
allowing for variation of heat transfer parameter at the cold
surface with depth of layer and confirm the use of the theory as a
guide to extrapolation of data and to the extinction of ignition upon
dilution. However, absolute comparisons of the critical parameter,
∂c, were poor.
SPONTANEOUS IGNITION, DUST LAYERS, SELF-HEATING

INTRODUCTION

Many flammable materials will spontaneously ignite if formed into a sufficiently deep
layer on a heated surface and one test applied to dusts is the determination of the
contact temperature at which a 5 mm deep layer will ignite (see for example Palmer
1973). The practical need for such data lies in the presence in most industrial
operations of heated surfaces such as furnaces, motor casings and steam pipes, on
which a dust layer could accumulate and, if heated sufficiently, ignite and form the
origin of a more major fire or dust explosion. Thus the practical test is a valuable
pointer to the potential for hazard. Alongside the practical tests there have been
theoretical analyses, both analytical and computational, which aim to identify the
controlling parameters of self-ignition and so allow extrapolation from limited
measurements and prediction from material properties. Examples of these approaches
are the analytical work of Thomas and Bowes, 1961, and the computations of Tyler and
Jones, 1981. The analytical approaches, of necessity, must simplify the problem. Thus
Thomas and Bowes assumed simple kinetic behaviour for the material, ignoring reactant
consumption, and adopted the Frank-Kamenetskii approximation for the temperature
dependence. Within these constraints their results predict a sharp boundary between
stability and ignition, with a critical ignition parameter, ∂c, obtained as a function of
the material properties, the temperature of the heated surface, the heat loss
characteristics from the upper surface of the layer and, of course, the layer thickness.

[*] Department of Chemistry, UMIST, P.O.Box 88, Manchester, M60 1QD