INCIDENT DURING NITRATION IN A BATCH REACTOR

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During routine production of a nitro diazo species a serious thermal incident occurred. Due to agitation stoppage a slow deflagration was initiated, downward, in the mass which was being nitrated. On restarting the agitator dangerously high mass temperatures were encountered.
(Key words: chemical reaction hazards, exotherms, slow deflagration, heat of reaction, heat of decomposition).
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INTRODUCTION

The process in question was a batch nitration at ca 20°C over 8 hours using Mixed Acid (100% HNO_3/100% H_2SO_4 50/50 w/w) of an aromatic cyclic-diazo intermediate. The product, a nitro diazo, had been produced without serious incident for many years. The process had to be fully investigated by RC1 (1) and DSC (2). The heat of reaction would give an adiabatic temperature rise of +66°C. There was no evidence of accumulation at any stage. The mass was thermally unstable, with Time to Maximum Rates under adiabatic conditions (TMRad) as follows:

TMRad	T°C
3 hours	70°C
17.7 days	30°C

A full Process Risk Analysis had been carried out and all the actions and recommendations resulting were fully implemented on the computer controlled plant.

The reaction mass was a viscous slurry at the early stages of the nitration.

It was known that excess mixed acid (at the +5% level or above) i.e. beyond that required for completion of the reaction reduced the thermal stability (TMRad) of the mass by about a factor of two.

1. The Incident

The batch production records were all complete and intact. Both the measure vessel containing the mixed acid and the reactor itself were on load cells and automatically recorded.

The sequence of events was follows:

NITRO DIAZO INCIDENT

9 - 11/12

9/12 2330 Reactor charged as normal waiting transfer of Diazo

10/12 1857 Transfer completed of Diazo

2031 Mixed Acid addition started. T = 17.7°C.

11/12 *0040 Agitator warning light. Agitator stopped.

0041 Addition of Mixed Acid stopped. 30% added. Cooling off T = 22.6°C.

0135 Agitator Restarted T = 23°C.

0138 Programme Reset.

*0145 Alarm Temperature High T = 27°C. SSS + emergency cooling. (SSS = Software Safety State).

0201 Tmax reached T = 34.9°C.

0255 T = 30°C.

0330 T = 22°C. Restart addition.

* These events triggered alarms and hard-copy warnings.

In essence an oil level warning light on the agitator gear-box caused the operator to halt production until the fault had been rectified following a pre-set procedure.

On restart the temperature was found to be + 12°C hotter than when the reactor was shut down.

2. Possible Causes

The following possible causes of the overheating were considered.

- Thermometry failure/malfunction

Dual independent thermometry with error checking was in use. Routine servicing and maintenance before and after showed no sign of malfunction.

- Accidental heating by the temperature control system

The system could supply cooling only i.e. there was no mechanism in place to supply heat to the heat transfer oil.

- Accumulation of unreacted mixed acid due to physical causes or changes in the chemical nature of the reaction mass

Repeat RC1 work on current samples showed instantaneous reaction with no accumulation; in addition the reaction proceeded as normal both before and after the interruption. In order to effect a 12°C temperature rise on accumulation of ca 18% of the total heat of reaction (+66°C) would be required at the 30% addition stage for an instantaneous reaction this did not appear possible.

- Leakage of Mixed Acid into the reactor once the agitator had halted

The load cells showed no drop or gain in weight for the reactor or measure vessel over the entire hold programme. Two independent block valves and the flow control valve would have had to pass about 11% of the mass contained in the measure vessel to effect a temperature rise of +12°C.

- Leakage and exothermic reaction of gear-box oil or heat transfer oil into reactor

Inspection after the incident showed that gear-box oil could not physically enter the reactor and that the heat transfer system was intact and uncontaminated.

- Ingress of other substances (water etc) to reactor

There were only three other pipe branches to the reactor. The ventilation system, the over-pressure relief and the raw materials inlet. Inspection showed that only the ventilation system was open. Chemical analysis showed no ingress of water had occurred and in addition no weight gain was recorded on the reactor.

- Thermal decomposition of the mass on removal of cooling (adiabatic conditions)

At the maximum measured temperature of 34°C the TMRad would be ca 12 days. Repeat DSC work showed no change in the thermal stability over time. The decomposition would be isomorphic and temperature should not change during the hold period.

3. Laboratory Investigations

A series of tests were carried out on the reaction mass in a 250ml Dewar Flask (3) at 20-22°C, to establish whether slow deflagration could be induced in the mass.

The deflagration rate was measured on 3 vertically displaced thermocouples in the Dewar. (See Fig. 2).

Two methods were used to induce slow deflagration

(a) addition of large local excess of mixed acid

(b) insertion of a B19 "Cold-finger" adapted to accept hot oil from a thermostatically controlled circulator. The immersion depth was 0.5 cm.

In this case deflagration refers to a decomposition band which moves vertically through the mass evolving gas and locally raising temperatures in the band. As opposed to a decomposition which occurs isomorphically (see Fig 1.). In Fig 1. the deflagration is shown moving vertically upwards as opposed to what happened in this particular case where the deflagrating band moved vertically downwards.

The following observations were made:

The reaction mass can deflagrate vertically downwards, slowly.

The slow deflagration can be initiated by a large local excess of nitrating agent (mixed acid) at the 30% nitration stage at which the incident occured.

The deflagration can be halted by the application of agitation to the still mass.

On the 100% nitrated mass, deflagration can be instigated by a hot-oil temperature of 120°C. Tests at oil temperatures of 100° and 110°C failed to initiate deflagration on this mass.

The rate of deflagration was measured at 0.25 m/hour in the 100% nitrated mass.

The temperature in the deflagration band was measured at 240°C.

4. Conclusions

1. The incident was probably caused by a local small excess of mixed acid. This local excess occurred due to agitation stoppage. Nitration and/or local decomposition in the area of the excess initiated a slow (ca. 0.25 m/hour) deflagration in the mass.

2. Calculation shows that ca. 3 to 5% of the mass had deflagrated when the restart of agitation quenched the deflagration. This assumes that 3-5% of the mass was at ca. 240°C due to deflagration and when mixed, raised the total mass by +12°C. This value fits very well with the incident duration and the measured rate of deflagration.

3. The consequences of a slow deflagration are:-

i) Total loss of product
ii) A final pressure in a sealed system with a mass to head-space volume ratio of one to one in excess of 30 bar due to gas evolution.
iii) In an open system > 30 l/kg of gases would be evolved with foaming.

iv) The final mass would be at ca. 240°C and contain unknown organic decomposition products and char which could block transfer lines.

4. If agitation is restarted at an inappropriate time then a violent decomposition could ensue. For example a delay of 1 hour gave a temperature rise of +12°C a delay of 5 hours could give a temperature rise of +60° or a final mass temperature of 80°C with a TMRad measured in minutes.

At this stage some 1.25 vertical meters of the mass would be decomposed.

5. Recommendations

1. Good agitation is required during the mixed acid addition.

2. The agitation must be monitored at all times by a direct method (not electric current to motor or rotation of shaft alone).

3. In the event of an agitation failure at any time after nitration has commenced a drown-out must be commenced immediately.

4. In any alarm or emergency shut-down situation the mixed acid addition must be halted before the agitator is stopped (e.g. low oil in agitator gear box alarm).

5. Further work is necessary to identify the likelihood of deflagration in other nitrations.

The following references give a general guide to the techniques outlined in the text.

References

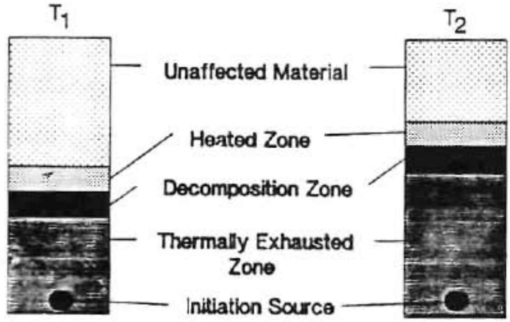
1. K Dixon-Jackson "Heat Flow Calorimetry - Application and Techniques" Hazards X I.Chem E. Symp. Series No. 115 ISBN 0 85295 2422.

2. K Dixon-Jackson "Use of DSC in Assessment of Chemical Reaction Hazards" Chemical Reaction Hazards Dec. 1989 IBC Technical Services Ltd. 57-61 Mortimer Street, London W1N 7TD.

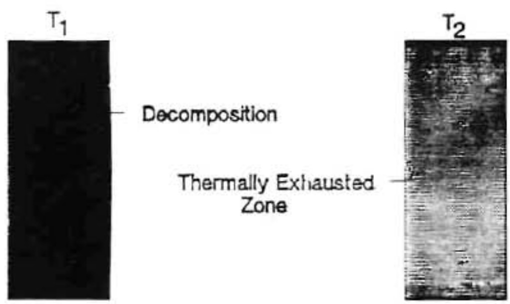
3. R L Rogers "The Use of Dewar Calorimetry in the Assessment of Chemical reaction Hazards". Hazards X I. Chem E Symp. Series No. 115 ISBN 085292 2422.

FIG 1 DEFLAGRATION, DECOMPOSITION & FIRE

1. Deflagration



2. Decomposition



3. Fire

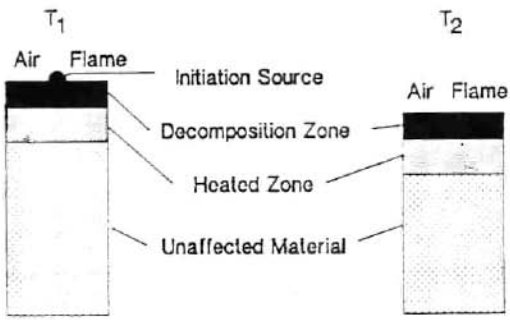
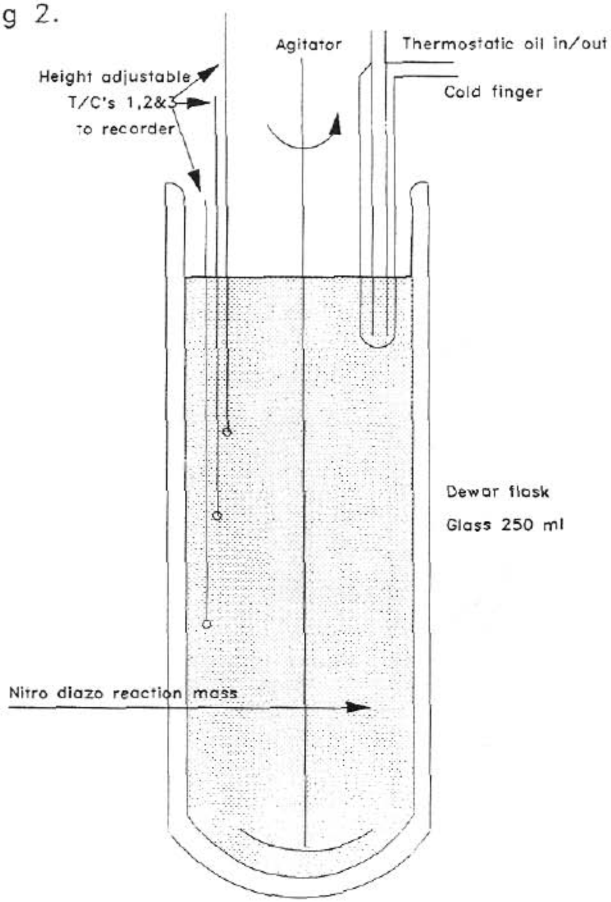


Fig 2.


Agitator
Thermostatic oil in/out
Height adjustable
T/C's 1,2&3
to recorder
Cold finger
Dewar flask
Glass 250 ml
Nitro diazo reaction mass