

ICHEME SYMPOSIUM SERIES NO. 141

ABNORMAL OCCURRENCE: IRON REDUCTION

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An abnormal occurrence during a telescoped iron reduction resulted in over-pressurisation of a reactor and ejection of the contents. The telescoped reduction / acetylation is highly exothermic and the nitro body is charged in a controlled manner and at such a rate to balance the available vessel cooling capacity. When the addition was first started, heat was evolved in the normal manner and there was no indication of any abnormal occurrence. When the addition was complete, the batch self-heated, at an increasing rate, to boil and the reactor over-pressurised with the result that a considerable portion of the batch was ejected from the vessel.

Keywords: heat flow calorimetry, iron reduction, aromatic amine

INTRODUCTION

The reduction of aromatic nitro bodies by iron and mineral acid is a well known process operated by many chemical manufacturers on a commercial scale. The reduction is highly energetic and usually involves a controlled addition of the substrate to the reaction mixture.

In the present process, the reduction was carried out in the presence of an anhydride and the reduction product, an aromatic amine, was converted in situ to the corresponding acetylamino species.

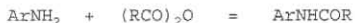
Prior to the abnormal occurrence, the process had been carried out for a number of years without any incident. Immediately prior to the incident a new, finer, grade of iron was introduced.

PROCESS

The process involves the reduction of an aromatic species:



The intermediate aromatic amino species is converted in situ to the corresponding acetylamino compound:



Overall, the reaction can be written as:



HAZARD ASSESSMENT

As part of the routine hazard assessment, the process was examined in a power compensation heat flow calorimeter. Figure 1 is the raw data output and shows the addition rate of the aromatic nitro body together with the corresponding power output profile for the process carried out at 10°C. It can be seen that the addition was carried out over four hours and that the evolved process power output was immediate with little indication of any accumulation of reagents having occurred.

Figure 2 is obtained from the raw data by correction for the change in the overall heat transfer coefficient of the system. It can readily be seen that the reaction power output profile follows an almost ideal pattern. When the addition is started there is an immediate response and the exotherm levels out at about 5 to 6 Watts. This amount of heat energy is maintained throughout the addition and only returns to zero when the addition is complete. Analysis shows that over 97% of the process power output occurs during the addition period.

On the basis of the experimental data we were able to state what the process vessel cooling requirement would be for a given scale of operation and for a given addition time of the nitro species. The process was then operated on the small pilot plant scale, without incident, for a number of years.

ABNORMAL OCCURRENCE

On the day of the abnormal occurrence, the addition of the aromatic nitro species had been carried out as usual, ie over four hours to the batch at 0 to 5°C. The addition was started with the batch at about 5°C and was accompanied by an initial temperature spike of about 5 to 10K before the batch temperature was brought under control by the vessel cooling system, see figure 3. Accordingly it was assumed that the reaction was progressing in the normal manner.

The addition was complete after four hours, and in accordance with the given operating procedure, the batch was sampled for end of reaction and allowed to warm to room temperature. Analysis showed that this batch had only about 30% conversion to the amino species and about 70% of the nitro body remained unreacted. When the batch was re-examined, the batch was found to have warmed / self-heated to about 33°C. It should be noted that the boiling point of the batch is about 40°C. In view of the obvious self-heating which was now apparent, cooling was applied and the batch

temperature fell to about 30°C. Cooling was still applied to the batch when further exothermic activity led to the batch temperature increasing rapidly to boil. At this stage, the rate of self-heating was very fast and the condenser started to log. The system continued to self-heat at an increasing rate and the reactor over-pressurised and much of the batch was ejected from the reactor.

An investigation into the cause of the abnormal occurrence was carried out.

HAZARD INVESTIGATION

The original heat flow calorimeter experiment was repeated using the same materials as used in the incident batch. Figure 4 shows the rate of addition of the nitro body to the batch and the resultant power output profile from carrying out the addition at 10°C. The power output trace shows that when the addition was started it was accompanied by an exotherm. This is normal behaviour. However, after about 30 minutes the amount of evolved process energy decreased suddenly and no further process energy was evolved throughout the addition period. The batch was then agitated at 10°C for a further 12 hour period when suddenly a very strong exotherm was found to occur. Analysis of the heat flow process power output trace showed that 70 to 80% of the total process power output occurred in the second exotherm period.

Following the heat flow calorimeter experiment, the result of which were in accordance with the incident batch, we looked for an explanation as to why the reaction has suddenly stopped part way through the addition. The incident batch was the first batch in a new campaign which was to consist of several batches. The supplier of iron had advised us of a change to the specification of iron and now the material was supplied in a finer, ie larger surface area, grade.

In order to determine the effect of the change in grade of iron, the heat flow calorimeter experiment was repeated using old grade iron. The power output trace was found to be identical to the original power output trace, ie figure 1 in which there was no indication of any accumulation of materials.

The new grade was examined further and perhaps due to the greater activity of the finely divided material the surface of the iron was found to be oxidised to an extent of about 75%. This is in line with the amount of accumulation which resulted from its use in the reductive acetylation process.

FUTURE PROCESSING

Process Hazards Section, Blackley were very concerned not to allow a repeat of the incident. It had been shown that the reductive acetylation could stop partway through the addition and then without warning could suddenly and rapidly react to cause over-pressurisation of the reactor and ejection of the batch. A new processing method had to be established.

Aliquot addition of the aromatic nitro species with analysis of the batch was proposed. Figure 6 pertains to the aliquot addition of the nitro body and gives the resultant process power output profile. It can be seen that following each addition, there is an immediate exotherm which is complete within about 10 to 30 minutes. It is proposed therefore that the aliquot addition is repeated for the plant scale process and that analysis is carried out to ensure that the batch is free from accumulated reagents before making any new aliquot charge.

The revised process has now been operated successfully.

FIGURE 1

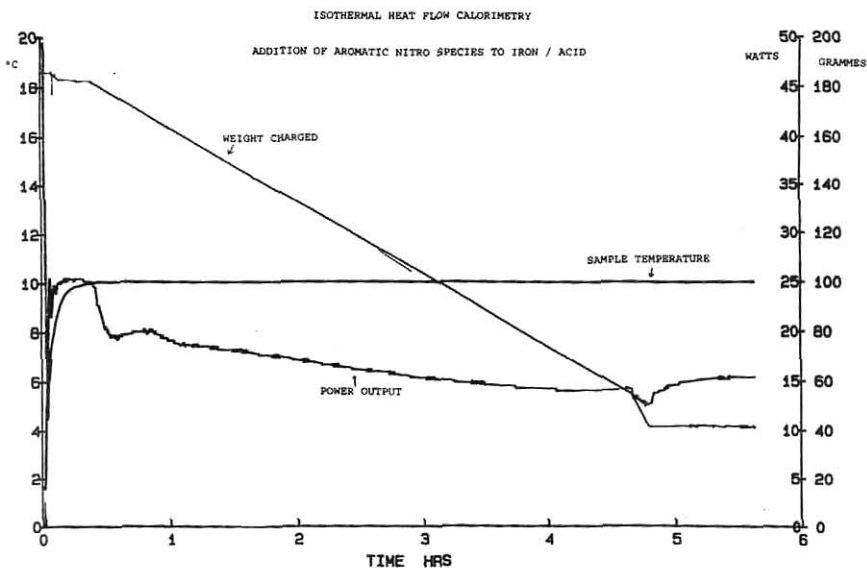
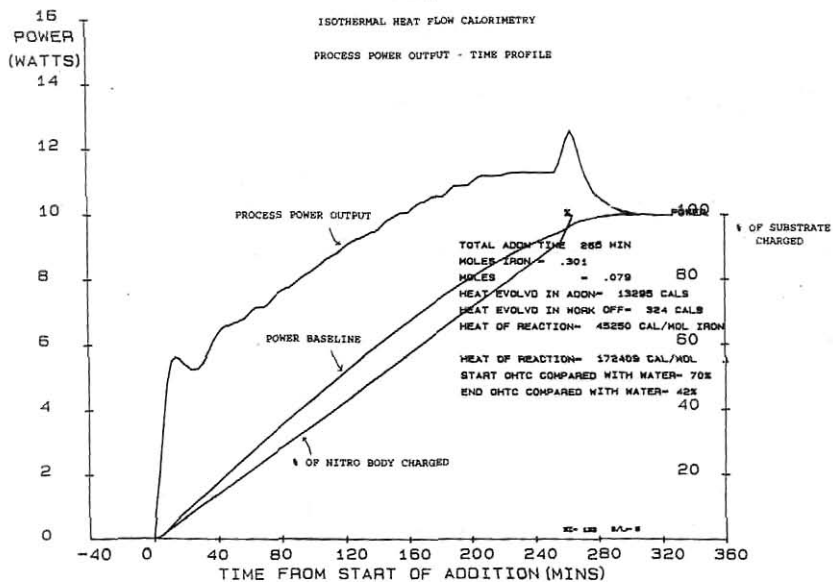


FIGURE 2



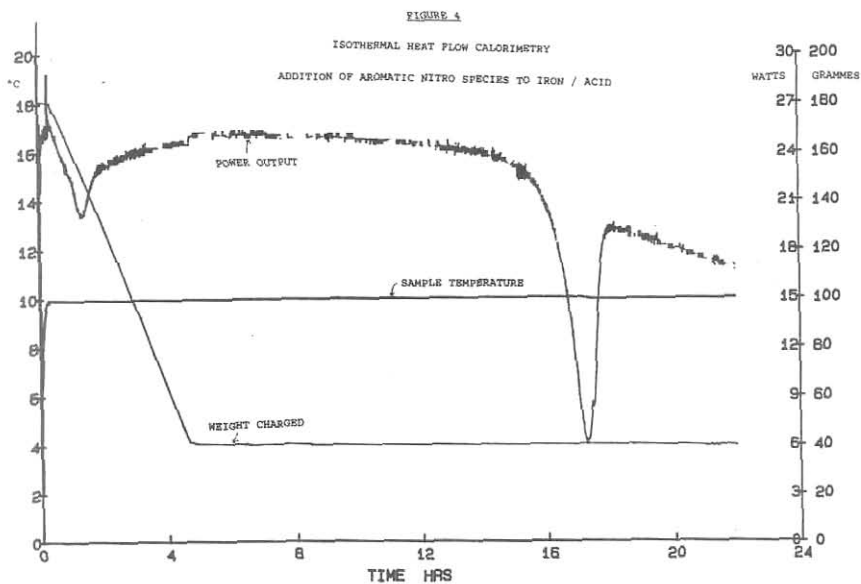
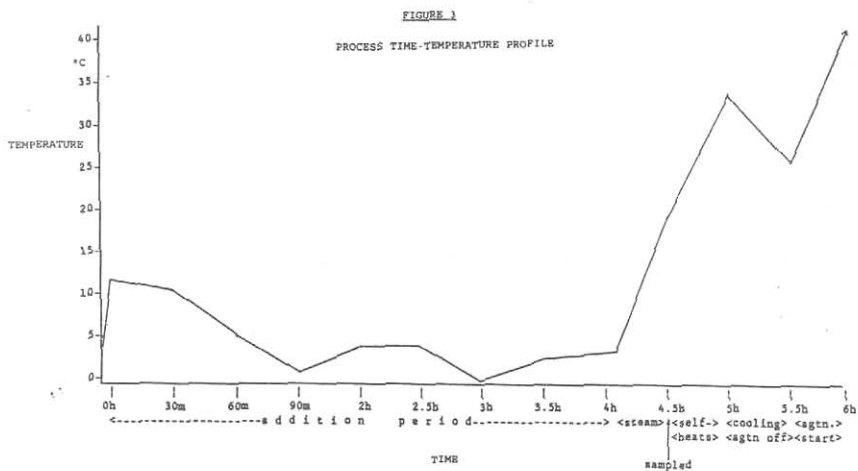


FIGURE 5

