RUNAWAY REACTION DURING PRODUCTION OF AN AZO DYE INTERMEDIATE.

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On Sunday 9th June 1996 a violent runaway reaction occurred in a 2.3 m^3 Pfaudler reactor creating a high pressure that led to rupture of the vessel: consequential damage to equipment and buildings was very significant. This paper provides explanations of how and why this accident occurred. At the time of the incident a diazonium ion was being produced for subsequent decomposition to form a phenol. The process had been carried out many hundreds of times before without incident. A combination of isothermal and adiabatic calorimetry was subsequently used to study the thermochemistry of both the desired synthesis reaction, and the undesired decomposition reaction. Plant simulation studies based on this experimental data were then used as an aid to analysing and understanding the events leading up to the accident. In due course the plant was rebuilt and production resumed: some of the strategies used to reduce both the hazards and risks associated with renewed production are discussed. A summary of the overall business impact of the accident is presented.

Keywords: reactor, exotherm, runaway, decomposition, diazonium, adiabatic, calorimetry, business impact

INTRODUCTION

HOLLIDAY DYES AND CHEMICALS

The Holliday company began in 1830 when Read Holliday established a factory in Huddersfield producing ammonia from coal tar waste residues. This was followed in 1856 with the production of magenta and other dyestuffs. L. B. Hollidays were soon in the forefront of the British dye industry and were involved in the formation of the Society of Dyers and Colourists (SDC), and later the British Dyestuff Corporation (which subsequently became ICI in 1926.) New factories were built in 1916 on the current site on Leeds road to manufacture explosives and colourants as part of the war effort. Post war expansion in the 20s and 30s into new higher technology markets, such as fluorescents and transfer-printing dyes, followed. In 1987 L. B. Holliday became the cornerstone of Holliday Chemical Holdings (HCH) who were themselves eventually acquired by Yule Catto in 1998. Since then however, declining markets, severe Eastern competition and escalating site running costs have lead to difficult times and in November 2000 Yule Catto announced the phased closure of the HDC site in Huddersfield.

Over the years Hollidays established a reputation as a quality supplier of dyestuff and chemical intermediates traditionally based on anthraquinone and naphthalene. The diverse molecular structures of the Holliday products necessitated many types of batch and semi-batch reactions including chlorination, hydrochlorination, sulphonation, nitration, cyanation, amination and diazotisation. It was the last of these reactions classes that led to the runaway exotherm that is the subject of this paper.

PRODUCTION OF THE SUBSTITUTED PHENOL

For reasons of commercial sensitivity, full details of the particular chemistry of the reaction that was taking place when this incident occurred cannot be provided. However Figure 1 indicates that an aromatic amine was reacted with a mixture of sulphuric acid and nitrosonium hydrogen sulphate (Nitrosyl Sulphuric Acid, or NSA) to produce the diazonium ion that was then decomposed to form the phenol. It is worth mentioning that this process had been operated over several years, with more than 100 batches per year being made, without incident. All the diazotisations were carried out in a dedicated 2270 litre Pfaudler model AH glass lined reactor. The process equipment was simple in concept and is illustrated in Figure 2.

DETAILS OF THE INCIDENT

The accident was associated with the decomposition stage of the diazo compound that is shown in Figure 1. The graph shown in figure 3 is the actual temperature trace for batch 123 with which the accident was associated. The chart runs from right to left: for clarity a variety of important data have been superimposed on the chart.

We are initially concerned with the first stage of the process that starts with the addition of the amine to be diazotised into 100% sulphuric acid (monhydrate) to give a solution. Typically this takes about 4 hours. Once in solution, and cooled to the correct temperature, NSA is added over 5 hours whilst maintaining the temperature between 30°C and 40°C. At the end of the addition diazotisation is complete.

For batch 123 there were some differences from the norm. During the addition of the amine the temperature rose to about 48°C. When the addition was complete the batch was cooled back to ~ 35°C and the NSA addition started, see point A in figure 3. (Note that the NSA was delivered in drums, there being 4 drums per batch. These were charged individually to a head tank and then run into the reactor contents: an orifice plate in the reactor feed line restricted the maximum flow rate of NSA. The capacity of the head tank was only slightly in excess of one drum.) After a short period the batch had cooled to 30°C, point B. Further addition of NSA took the temperature up to 50°C, point C. The NSA feed was then suspended and the batch temperature was brought down with unintentional over cooling. NSA addition was resumed at 25°C, point D. The batch temperature fell slowly (as a consequence of the cold NSA) to ~ 21°C, point E, and then rose continuously with the last recorded temperature showing 60°C at point F. Shortly after this temperature a massive over pressurisation of the vessel occurred resulting in the pan lid and head gear being blown off the vessel with devastating consequences. The agitator was left on the mezzanine roof but the pan lid itself travelled approximately 150 metres before landing and smashing into an office wall. The main body of the reactor was driven off its mounts and down through the concrete floor below. It would have travelled further but for a steel structure beneath the floor impeding its progress. Thankfully nobody was injured in the incident which happened at 9.30 am on a Sunday morning when site activities were at a minimum. A short video taken a few hours later captures the devastation of the unit, surrounding vessels and equipment.

UNDERSTANDING WHAT WENT WRONG

The simulation in the laboratory of an accident in which a major process vessel has ruptured because of overpressure should not be undertaken lightly. Even on the laboratory scale the hazards from an explosion may be very significant, and a rigorous risk assessment is required before experiments can be started.

The plant in question relied heavily on manual control systems, and data recording was rudimentary. Despite this, the limited process information considered during the early stages of accident investigation indicated clearly that reactor temperature control had been erratic and that eventually the temperature in the reactor had risen out of control. A high pressure had been generated: a relatively small portion of this could be attributed directly to the vapour pressure of the reaction mixture present. The major component of the pressure was therefore due to non-condensable gas production. Such instability of diazonium salts is well documented[1, 2].

THE THERMOCHEMICAL DATA

The thermochemistry of the reactions taking place was examined using the facilities at Hazard Evaluation Laboratory with a combination of isothermal and adiabatic calorimetry. The former was primarily used to study the desired process under operating conditions at, or close to, those that were normally intended. The latter was used to simulate loss of cooling and to understand the severity of the decomposition exotherm(s) that could occur: by working with test cells with a low thermal mass (low ϕ factor) the behaviour of large scale plant can be accurately reproduced.[3]

Isothermal calorimetry

Isothermal calorimetry studies on the production of the diazonium ion were made in the one litre SIMULAR reaction calorimeter[4]. The final stage of this procedure involved the pumped addition of Nitrosyl Sulphuric Acid (NSA) into the remainder of the reaction mixture. In the laboratory this was carried out at temperatures of 50°C, 40°C and 30°C: these temperatures were selected to cover the range of extremes of temperature permitted during plant operations. At some stages of these additions the feed was suspended so as to enable the enthalpy accumulation to be inferred corresponding to intermediate times during the feed addition. Enthalpy accumulation was also calculated when each feed stage was terminated. At 30°C ~ 80% of the reaction enthalpy was released after cessation of the feed: analogous figures at 40°C and 50°C were ~ 28% and ~ 17%. The history of a typical two-stage experiment at 40°C and 30°C is shown in Figure 4.

Adiabatic calorimetry

Adiabatic experiments were made in the PHI TEC II calorimeter[5] in magnetically agitated, low phi factor glass test cells. In the first test the desired diazonium salt was prepared under normal conditions in the laboratory and then charged to the test cell. The test cell was open to the pressure containment vessel in which the calorimeter was housed: this vessel was purged with nitrogen and then initially pressurised to 7 bara so as to minimise evaporative losses from the sample. A heat-wait-search procedure was then started with ~ 5°C steps starting from 30°C. A weak exotherm in excess of the chosen onset threshold of $0.04^{\circ}\mathrm{C\,min^{-1}}$ was first detected at 43.35°C. However this was not sustained and after ~ 45 minutes when the sample temperature was 44.25 the self-heat rate fell below the termination threshold and the heat-wait search was resumed. This exotherm could have been the result of a small amount of residual activity from the diazonium salt preparation stage, or the earliest phases of decomposition. At 56.33°C a second exotherm was detected. This was sustained over a period of ~ 150 minutes with the final stages of the exotherm becoming very violent. A maximum temperature of 301.2°C was reached with a corresponding pressure of 16.6 bara. This is illustrated in figure 5. If the test had been conducted in the sealed cell mode, then, at a test cell fill level of ~ 70%, the final pressure in the cell head space would have been several hundred bara. The kinetics of the decomposition reaction are not simple. In figure 6 the self-heat rate is plotted as a function of temperature: the exotherm accelerates to a peak self-heat rate of ~ 100°Cmin^{-1} at 141°C, then subsides briefly before reaching a maximum self-heat rate in excess of 2100°Cmin^{-1}. This self-heat rate is, of course well in excess of that at which true adiabatic conditions can be maintained.

In another adiabatic experiment starting at 30°C nitrosyl sulphuric acid was injected into the reaction mixture prepared after dissolving the amine in the monohydrate. Note that 30°C was the lowest reaction temperature permitted in the HDC process instructions. The resultant exotherm is illustrated in figure 7. The initial exotherm is the direct consequence of the desired reaction, i.e. the formation of the diazonium salt. However the temperature that is reached is sufficient to trigger the violent decomposition exotherm that follows within less than 10 minutes of the start of the experiment. What is even more clear than before is the fact that the decomposition reaction itself involves two stages, see figure 8. The first peak in self-heat rate of 882°Cmin^{-1} occurs at ~150°C and the second of 2700°Cmin^{-1} at 255°C. These figures are in excellent qualitative, and quantitative, agreement with the analogous data shown in figure 6 which it should be recalled is for the decomposition of the diazonium compound when prepared under normal conditions.

SIMULATION

Process simulation was carried out by Dr Alan Wright of BatchCAD Consulting. The main objectives and purposes were to:

- Provide a better understanding of the chemistry and its interaction with process operation, with a view to simulating the possible causes of the incident.
- Provide a simulation and development tool to aid in the design of the process as it was to be re-built.

Using the BatchCAD RATE program the rate constants, and reaction orders, in power law kinetic models for both the diazotisation reaction and the subsequent decomposition reaction were evaluated by curve fitting the model predictions to both the isothermal and adiabatic calorimetry data. For the diazotisation step a model with first order rate dependence on the amine concentration and second order rate dependence on NSA concentration fitted the data best. The Arrhenius constants were evaluated using the isothermal calorimetry data (reaction power output, reaction enthalpy and reactant accumulation) at 30°C, 40°C and 50°C. The model thus developed generated good data fits to all of the experimental results. Enthalpy and rate parameters for the reaction of the water formed during the diazotisation with the monohydrate were determined using a combination of literature and experimental data. The decomposition reaction was modelled using both the adiabatic calorimetry data in figure 5 as well as isothermal data gathered at 110°C. The complete reaction model predictions were then tested for the combined synthesis and decomposition reaction data shown in Figure 7: the overall agreement was reasonable and generated a good measure of confidence in the efficacy of the model and the validity of simulation studies.

A reactor model for a Pfaudler AH series 500 gallon (2270 litre) reactor with water cooling, as being used by HCH at the time of the incident, was developed using the BatchCAD REACTION program. This included information on the physical dimensions of the vessel, the jacket service fluids, the reactor control system and the reactor heat transfer capability. Best estimates of cooling water temperature (which was not logged) and overall heat transfer coefficient were based on experience and those portions of Figure 3 (together with some sections of the temperature trace from earlier in the batch) when reactor cooling was applied fully. On this basis the overall heat transfer coefficient was ~ between 210 and 280 $Wm^{-2}K^{-1}$.

The process charge and feed conditions on the day of the incident were included in the model with estimated NSA feed rates and operation of a safety trip on feed rates if the reactant temperature was outside the 25°C to 36°C range. There was good plant evidence that the reactor agitation system had functioned normally throughout the batch reaction and this assumption was made in the plant model.

A number of causes of the incident were possible including accumulation of unreacted NSA and inadvertent heat input to the reactor, e.g. from a passing steam valve. Reduction of heat transfer capacity due to fouling was possible but this, of course, was already allowed for in that the overall heat transfer coefficient was estimated from the plant data. Many simulations were carried out with the recorded temperature profile of Figure 3 being used as the set point in the simulator feedback controller that was used to regulate the coolant flow. Using these techniques the simulation showed that an addition of 60% of the NSA could have been made in 2 hour 15 minutes for an overall heat transfer coefficient of 210 $Wm^{-2}K^{-1}$. For a value of 280 $Wm^{-2}K^{-1}$,70% of the NSA could have been added in this same time, or 100% could have been added in 3 hours 30 minutes.

CONCLUSIONS

The combination of laboratory based experimental studies in isothermal and adiabatic calorimeters, and computer simulation of plant behaviour, gave vital insights into the possible causes of the incident. These can be summarised as follows:

1. The reported addition of 75% of the NSA over 2 hours and 15 minutes would have resulted in an accumulation of ~ 30% of unreacted NSA within the reactor.
2. This accumulation alone could not account for the severity of the thermal runaway that took place.
3. The temperature on plant rose from ~ 21°C to ~ 60°C over a period of ~1 hour. This rate of temperature rise could not be reproduced without an additional heat input to the reactor.

4. A constant heat input to the reactor of ~ 34kW throughout this period would have been required, in addition to the reaction enthalpy release, in order for the simulation studies to reproduce the plant runaway.
5. Application of steam to the reactor jacket could have produced a heat input of this magnitude. Thus a steam valve that was inadvertently left open, or a badly leaking steam valve, could have been a contributory cause of the incident.
6. Some other source of additional heat, e.g. resulting from the ingress of water cannot be ruled out.

Some general observations can also be made:

- Operating a semi-batch reactor below the specified temperature range can greatly increase the accumulation of unreacted feed, and hence the potential for a runaway reaction.
- Increased reactant accumulation will raise the Maximum Temperature of the Synthesis Reaction (MTSR) and as a consequence reduce the Time to Maximum Rate (TMR) for any subsequent exotherm, e.g. the decomposition reaction in this case.
- A small additional heat input to a reactor can dramatically reduce the TMR at the end of a semi-batch feed. For example, in the system studied, with the reactor at 35°C and the NSA feed over 5 hours, the TMR at the end of the batch was just over 10 hours. With an additional heat input of only 5 kW to the reactor this falls to ~ 3.5 hours.

THE NEW PLANT

There was an urgent need to resume plant production as soon as possible but neither Hollidays nor the HSE would have allowed re-installation of the original facility. At the time Hollidays were looking at the feasibility of continuous, rather than batch, processing technology in relation to other products. After some small scale trial studies in which a small amount of product was produced it was decided to continue to use a semi-batch process similar to the original one. However the original design would be modified extensively so as to eliminate or reduce hazards where possible and reduce the risks associated with those that remained. Important inputs into the new plant design were the thermochemistry studies and simulations referred to earlier sections.

Safety features for the new plant included:

- Computer control, and data logging, with soft and hard-wired trips and interlocks.
- Prevention of the possibility of a rapid NSA dump charge by pump metering and drum charging.
- Reactor weight monitoring and control via the use of load cells.
- Header tank weight monitoring and control via the use of load cells for accurate NSA weight charge.

A pressure relief vent on the reactor would not be an appropriate basis of safety for coping with any potential runaway reaction and consequent over-pressurisation. The relief line would have to be sized in accordance with the DIERS principles, as outlined the HSE “Workbook for chemical reactor relief system sizing”[6], and, because of the very high rates of pressurisation, would be impossibly large. A far better policy was to devise a process design that would not allow an exothermic decomposition runaway to occur. This was achieved by ensuring that if temperature control was not within defined limits then the contents of the vessel would be dumped before any exotherm could develop into a hazardous event. This was achieved by having a special Pfaudler reactor manufactured with 2 bottom outlets of sufficient capacity to permit rapid dumping of the contents into an appropriately sized quench tank. This revised plant layout is shown in Figure 9. General aspects of the design of such a system, and specification of the necessary amount of quench fluid to be present, are discussed in an HSE Contract Research Report CRR 100/1996,[7]. Pressure relief vent sizing could then be specified to cope with other specific, and less arduous, maloperations: this resulted in an acceptable pressure relief line size of 150 mm.

BUSINESS IMPACT

When a catastrophic event such as this accident occurs there is inevitably a major impact on the company’s business. This usually extends far beyond the product stream involved and is only revealed long after the damage to the plant and the fabric of the building have been assessed and catalogued. Some of the major costs associated with this accident are summarised below:

- Cost of new installation: £1.0 M
- Business interruption: £1.1 M
- Re-instatement of surrounding plant/buildings: £0.5 M
- Fines and costs: £0.1 M

However there were many other factors too that are more difficult to quantify in purely financial terms. These include:

- Opportunities for competitors to increase their market share of the business.
- Existing customers now insisting on dual sourcing of their chemical feedstocks.
- Additional employee costs.
- Psychological impact on the workforce.
- Deleterious effect of morale.
- Implications, and extra costs, associated with other existing processes that could be candidates for a similar event.
- Preparation of the accident investigation and legal defence using the services of Hammond Suddards.
- Training and re-training of various types, including simulated on- and off-site crisis management (with Link Associates), improvement and strengthening or works emergency teams, accident investigation.

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Figure 1

Routine reaction

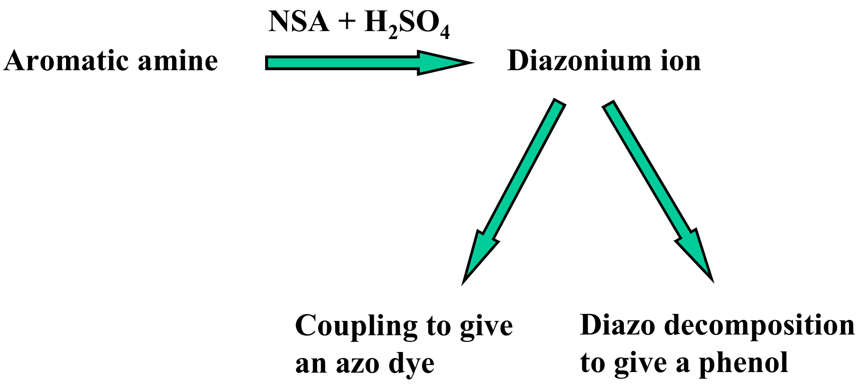

Figure 2

Original plant line diagram

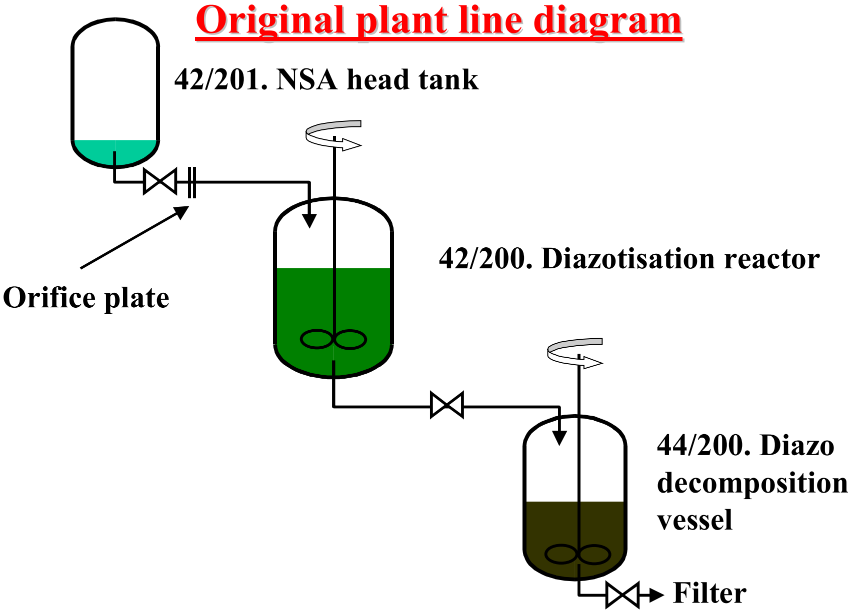

Figure 3

Temperature trace during the NSA addition

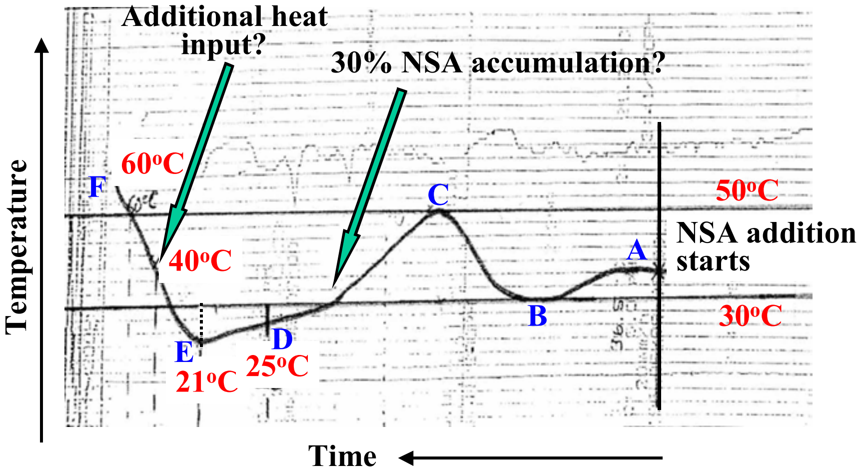

Figure 4. Isothermal calorimetry on the semi-batch addition of NSA at 30°C and 40°C

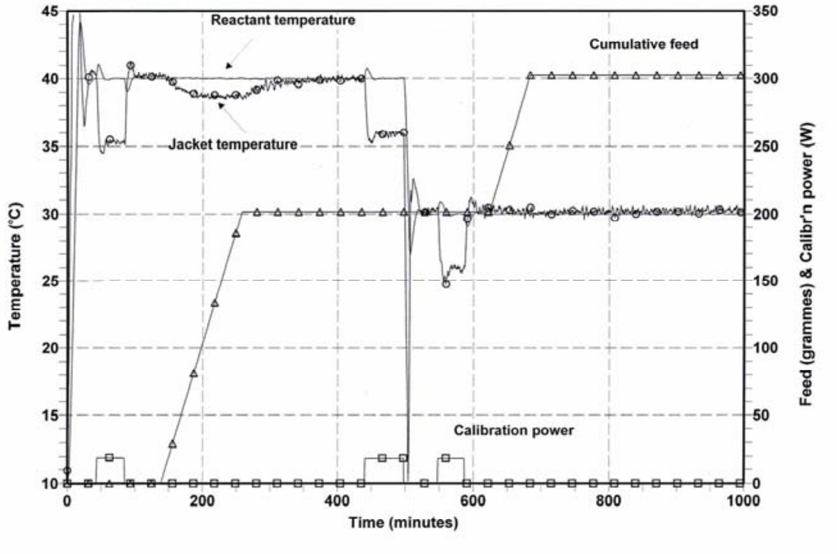

Figure 5. Decomposition exotherm for the diazonium ion: sample prepared externally in a automated reactor. Open cell test with 7 bara N_2 pressure

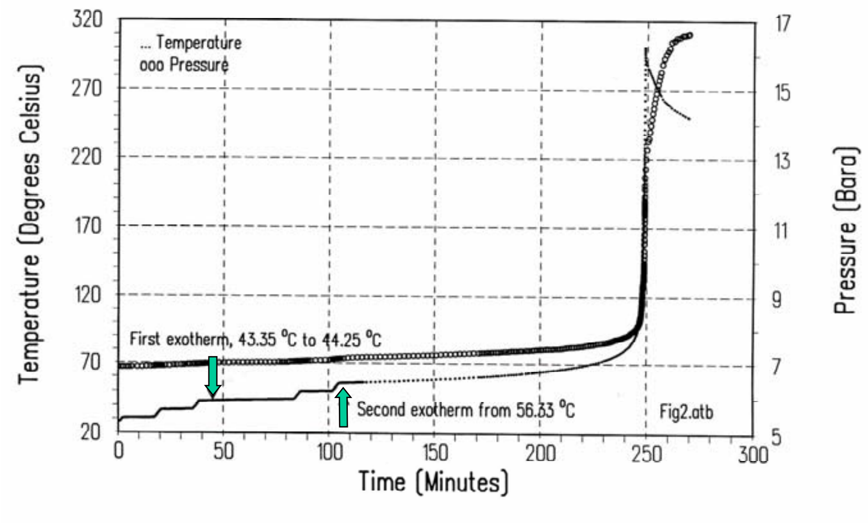

Figure 6. Decomposition exotherm for the diazonium ion: self heat rate versus temperature shows a two stage decomposition

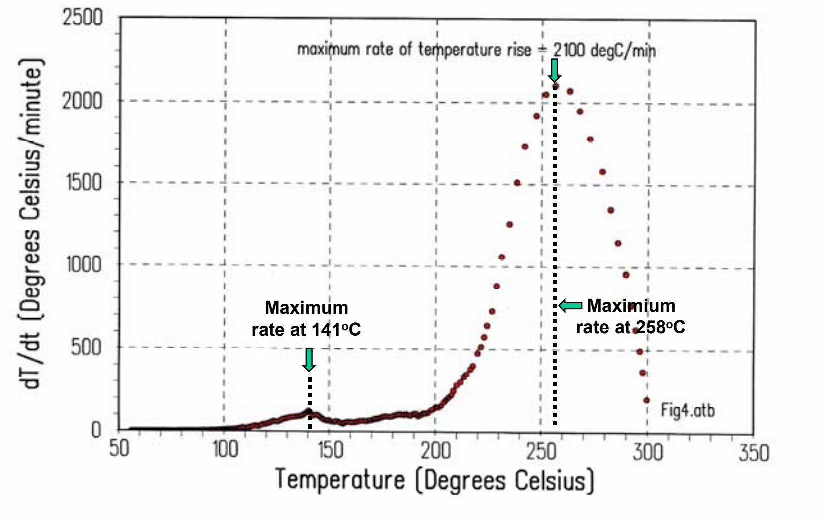

Figure 7. Exotherm for the synthesis reaction and the subsequent diazonium ion decomposition. Open cell test with 7 bara N_2 pressure. Runaway complete in ~ 10 minutes

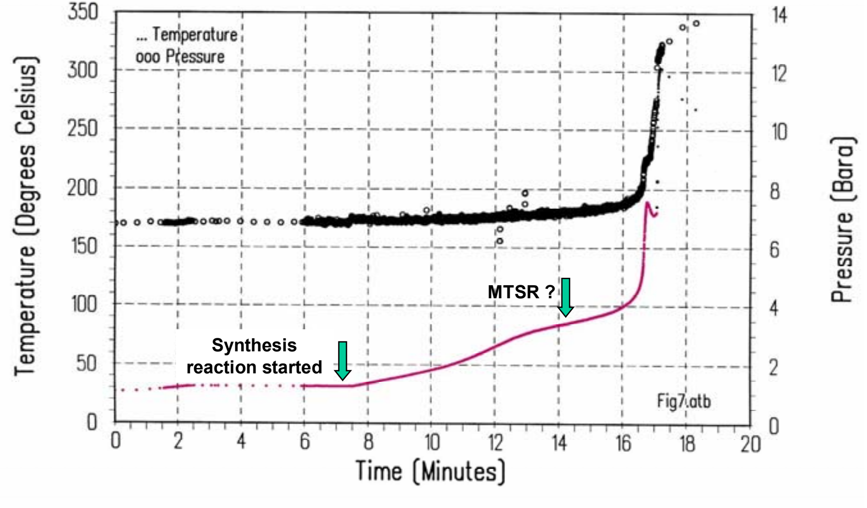

Figure 8. Exotherm for the synthesis reaction and the subsequent diazonium ion decomposition. Open cell test with 7 bara N_2 pressure

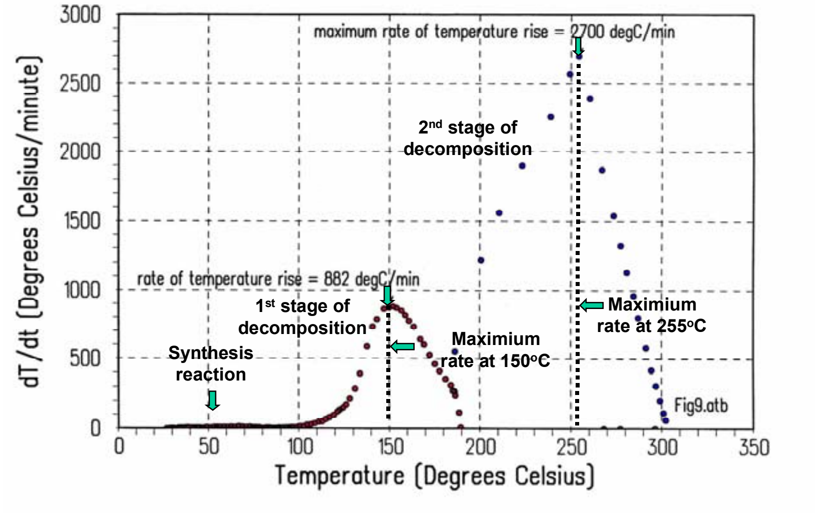

Figure 9

New plant line diagram