

HOLDING PHASE INCIDENT IN A VESSEL CONTAINING 1200 L JOINT-FILLER

BIRGITTE RASMUSSEN

Risk Analysis Group, Systems Analysis Department, Risø National Laboratory, DK-4000 Roskilde (Denmark)

(Received January 7, 1988; accepted in revised form July 10, 1988)

Summary

A holding phase incident that had occurred in a vessel containing a reaction mixture composed of chlorinated paraffins, lead dioxide, manganese dioxide, carbon black and silane has been investigated. A reconstruction of the incident was carried out on a laboratory scale. The mixture is thermally unstable, its viscosity high and its thermal conductivity low. The appearance of a hot zone in the mixture is therefore a safety problem. The reaction mixture was analysed by use of four thermal stability tests. An initial temperature of about 90°C and a reaction enthalpy of about 3650 J/g in the temperature range 90–500°C were found. As the maximum normal process temperature is 60°C, this yielded a rather low safety margin of about 30°C. Normally, a safety margin of at least 50–60°C is recommended.

1. Introduction

An important aspect of safety analysis is identification of chemical hazards in the chemical industry. Unwanted chemical reactions are especially dangerous if a sudden release of energy or a toxic release occurs. The consequences to humans, environment, and equipment can be very serious.

Many batch, semibatch, or continuous processes are exothermic. Uncontrolled reactions may develop during chemical processing or under holding/storage conditions. Even slightly exothermic reactions may become dangerous if they are capable of initiating an exothermic decomposition at some higher temperature.

A quantification of exothermic reactions with respect to initial temperature, induction time, magnitude and rate of heat release is therefore necessary in the chemical industry. The necessary data can be determined by use of methods of thermal analysis that are a related group of techniques whereby the dependence on temperature of certain physical properties of a substance/mixture is measured.

The safe operation temperature is affected by a number of factors. Often a

safety margin of about 50°C is specified to be the acceptable difference between the maximum anticipated process temperature and the minimum detected initial temperature. The initial temperature recorded for a particular material will depend on a number of experimental parameters, which can include sample size, construction material of sample container, sample heating rate, thermal inertia, and endothermic effects [1].

This paper presents results from a study entitled "Unwanted chemical reactions in the chemical process industry" [2]. Here a detailed study was performed of an incident that occurred at a Danish process unit. The study comprised an investigation of the causes of the incident and a testing of the thermal stability of the reaction mixture by use of thermal stability tests. This batch reactor incident was chosen first because it was known to the author and second because it is representative of the type of incidents and accidents that have frequently taken place in the chemical industry, namely runaway and exothermic reactions.

2. The incident

The incident occurred in the joint-filler section of Sadofoss A/S, a Danish company. Other Sadofoss products are adhesives and paints. On Sunday, the 9th of January 1983 at 7:30 p.m. a batch reactor containing 1200 l reaction mixture ready for preparing a joint-filler got out of control. The batch was left (without stirring) on the previous Friday afternoon for further processing on the following Monday. This led to a violent generation of toxic gases probably containing HCl and Cl₂. The neighbours were warned by the police and by Danmarks Radio (Danish broadcasting service). People were requested to stay indoors because of the toxic release. After about two hours the alarm was called off [3]. Seventy-one people were brought to the hospital for observation for possible chlorine poisoning. However, no one was seriously injured [4].

2.1 The process

The joint-filler in question is a two-component filler. One component is a mercaptan polymer with an average molecular weight of about 400 g/mol. The other, the oxidizer, is a mixture of chlorinated paraffins and the oxides MnO₂ and PbO₂. The chlorinated paraffins are a C₈-C₁₂ mixture containing 56% chlorine. The chlorinated paraffins are not a stoichiometric product. In order to make the oxidation simple and reproducible it is carried out in two steps [3]:

Step 1: The chlorinated paraffins and the oxides are mixed in a 1200 l batch reactor (the incident batch).

Step 2: The oxidation of the mercaptans is carried out when use of the joint-filler is required.

2.2 The reaction mixture

The substances are added one by one while the mixture is stirred and at last the mixture is ground in a bead mill until the degree of dispersion desired is reached. During the grinding process the temperature is not allowed to exceed 50°C.

The reaction mixture, on a weight per cent base, is composed of [5]:

| | |
|--|--------|
| Chlorinated paraffins (with inhibitor) | :29.3% |
| Chlorinated paraffins (with inhibitor) | :23.5% |
| Carbon black | : 1.5% |
| Lead dioxide | :33.4% |
| Manganese dioxide | : 5.9% |
| Silane (surface activator) | : 0.5% |

One per cent inhibitor is added to the chlorinated paraffins. In the absence of inhibitor, chlorinated paraffins are very unstable. The inhibitor is epoxidized soya bean oil which can react with HCl. Two types of chlorinated paraffins with different viscosities and two types of manganese dioxide with different particle sizes are used in the process. The density of the mixture is about 2 g/cm³.

The raw materials used were all parts of larger lots. Materials from these lots had previously been used in other productions without problems.

2.3 Possible unwanted chemical reactions

The mixture of chlorinated paraffins (CP), PbO₂ and MnO₂ is a chemically unstable system. The unwanted reaction course may have been:

1. CP → CP + HCl
2. 2 PbO₂ → 2 PbO + O₂
3. 2 MnO₂ → 2 MnO + O₂
4. PbO₂ + 4 HCl → PbCl₂ + Cl₂ + 2 H₂O
5. MnO₂ + 4 HCl → MnCl₂ + Cl₂ + 2 H₂O
6. CP + O₂ → CO₂ + HCl + H₂O
7. CP + Cl₂ → CP + HCl
8. C + PbO₂ → CO₂ + Pb
9. C + MnO₂ → CO₂ + Mn

The key reaction must be no. 1. Chlorinated paraffins are thermally unstable and a decomposition reaction may occur. If the chlorinated paraffins are destabilized, small quantities of HCl will be formed. Free HCl can develop if all of the inhibitor is used. HCl reacts with PbO₂ (PbO₂ is more reactive than MnO₂). Reaction 4 is exothermic and starts at about 90–100°C. The reaction between MnO₂ and HCl begins at a higher temperature and a higher concentration of HCl. At 300°C PbO₂ begins to decompose (reaction 2); at this temperature reaction 6 is also possible. Under these conditions the reaction course can be self-accelerating and a violent exothermic reaction course can take place.

A contributing factor could have been a heterogeneity in the distribution of oxides in the reaction mixture. A local higher than average concentration of oxidisers could have acted as a priming composition in the reaction mixture.

3. Reproduction of the incident

The purpose of the first part of the experimental work was to investigate the unwanted chemical reaction course. The laboratory work comprised:

- reproduction of the incident on a laboratory scale;
- investigation of contributory causes.

The experimental equipment chosen consisted of a heater placed in the center of a small well-isolated container without stirring. A point supply of heat and lack of stirring were chosen because one of the causes was believed to be a hot spot. The temperature was measured in the center, T_c , and at the outside wall, T_w . As a safety precaution the experiments were carried out outdoors.

3.1 *Reproduction of the incident on a laboratory scale*

The purpose of this experiment was to investigate if it was possible to accomplish on laboratory scale a reaction course which could be representative for the incident. The reaction mass was about 5 kg. The substances were mixed in accordance with the plant procedure and afterwards the mixture was ground. The energy supply was set to about 110 J/s. After a heating period of 0.5 h the first whitish gas evolution was observed. T_c was registered as 90°C. Indicator paper showed the reaction with the gas to be acidic.

After 2.5 h a seething sound was observed and T_c was 157°C. After 3.75 h T_c had risen to 206°C upon which the heat supply was switched off to investigate if a self-accelerating reaction course was running. In the subsequent half-hour T_c dropped (170°C).

The energy supply was increased to about 170 J/s. During the succeeding 40 min, T_c increased to 220°C and a growing evolution of whitish gas was observed.

In the next half minute a sudden increase of T_c to above 300°C was observed. A violent evolution of whitish gas was seen (a plume about 1–2 m high and 2–3 m wide in the wind direction). The power was switched off as quickly as possible. We attempted, without success, to stop the reaction with solid carbon dioxide.

About 50 min later an exothermic reaction still continued but with reduced evolution of gases.

During this experiment the temperatures T_c and T_w were measured. The difference between T_c and T_w varied from 60°C to 120°C. The distance between “wall” and “center” was 4–5 cm.

The reaction product was a grey clinker in which the thermometer and the heating coil were firmly cemented. The clinker was analysed for Pb(II) (PbO,

PbCl₂), and Mn(II) (MnO, MnCl₂) content. The result was 6.5% Pb(II) and 19.9% Mn(II) by weight.

Originally the reaction mixture contained 33.4% PbO₂ and 11.8% MnO₂. Compared to the content in the clinker this could indicate that MnO₂ is more reactive than PbO₂, the opposite of what was expected.

An explanation could be that PbO₂ was reduced by carbon (reaction no. 8) and that metallic lead was formed which, when molten, would gravitate to the bottom of the clinker mass because of its high density. Perhaps this caused a heterogeneity in the clinker.

The conclusion from this experiment is that the reaction mixture is thermally unstable and that a self-accelerating reaction course is possible if the system is thermally initiated. The reaction mixture is viscous and the thermal conductivity low.

3.2 Contributing factors

The reaction mass was reduced to 1 kg. Two experiments were performed and in their light the following conclusions can be stated:

The degree of dispersion: A non-ground reaction mixture was heated. Poor dispersion and heterogeneity in the distribution of oxides have a thermally destabilizing effect on the reaction mixture. (Among other things the aim of the grinding process is to coat the oxides effectively. Two factors can complicate the coating process: 1) the diameter of the oxide, i.e. small particles are more reactive and more difficult to coat effectively, and 2) formation of oxide agglomerates makes the oxides more reactive and more difficult to coat.)

Local overheating: A brief strong heating of the reaction mixture produced an acid gas evolution in about half a minute. If the reaction mixture is allowed to cool down a previous strong heating has either no or only little effect on the thermal stability of the reaction mixture.

3.3 Effect of iron impurities

For the chlorinated paraffins in question the thermal stability was clearly reduced if a small amount of water-free FeCl₃ was added. This is in accordance with [6].

The importance of FeCl₃-impurities in connection with the reaction mixture is that FeCl₃ can be formed by a reaction between Fe and Cl₂, (the reaction vessel is made of steel, and Cl₂ can be formed by decomposition reactions 4 and 5). Iron impurities can also be introduced as corrosion products.

4. Heat generation and conduction

Heat supply is necessary to initiate the thermal degradation of the reaction mixture. It is hypothesized that a thermal initiation of the reaction mixture occurred in the bead mill when the mixture was ground. The mixture was prob-

ably overheated by friction resulting in a hot zone being transferred to the holding vessel. Without stirring this hot zone became fatal and the incident occurred.

In a bead mill the disruptive forces are imposed by rotating discs creating circulating flow patterns within a mixture of steel particles, paste and solid particles (in this case MnO_2 and PbO_2). An agglomerate caught between two relatively large steel particles moving at different velocities is subject to considerable shear stress.

Large amounts of mechanical energy are needed to mix heavy plastic masses. The energy supplied disappears mainly as heat, which ordinarily must be removed to avoid damaging the machine or the material. The heat removal (i.e. the heat loss to the surroundings and the heat in the output flow) is manually controlled by reading the temperature and regulation of the flow.

From the experimental work it was learned that the thermal conductivity of the reaction mixture is low. This indicates that if a hot zone has developed, the heat will stay in that zone and perhaps initiate an exothermic reaction. The presence of a hot zone can therefore be a safety problem.

The heat removal from the surface is the only cooling capacity during the holding phase in the vessel. If an exothermic reaction is running during the holding phase we have a similar heat transfer problem as with exothermic batch reactions where an incident can be initiated by agitator stop. In this situation it is well-known that the surface cooling capacity is not sufficient.

5. Thermal stability tests

The reaction mixture was analysed by Differential Scanning Calorimetry (DSC), Differential Thermal Analysis (DTA), Thermogravimetric Analysis (TGA), and Thermal Activity Monitoring (TAM). The principles of the methods are described in the literature (see e.g. [7] and [10–12]).

5.1 Equipment

- DSC : Mettler TA3000 System composed of a TC10A TA Processor and a DSC20 Measuring Cell.
- DTA : Du Pont 900 Differential Thermal Analyzer.
- TGA : Du Pont 950 Thermogravimetric Analyzer (N_2 -atmosphere).
- TAM : LKB Multichannel Microcalorimeter.

5.2 Results

Differential Scanning Calorimetry:

The reaction mixture and the chlorinated paraffins alone were tested (Fig. 1).

The thermogram for the chlorinated paraffins shows that an exothermic

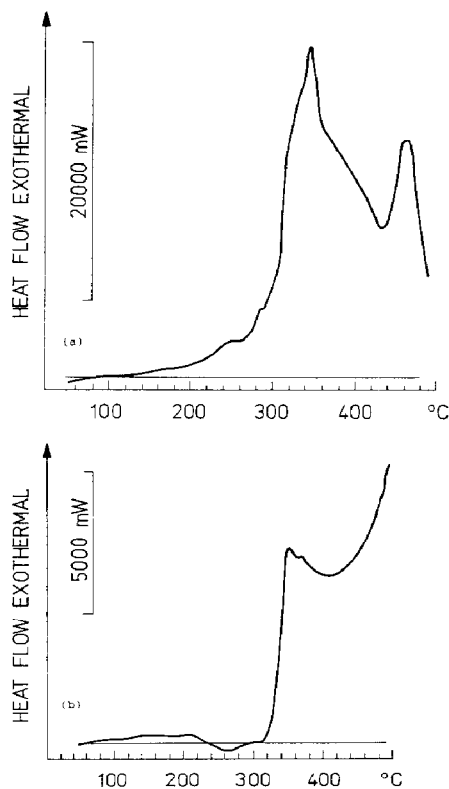


Fig. 1. DSC-thermograms (heating rate $10^{\circ}\text{C}/\text{min.}$), (a) reaction mixture, (b) chlorinated paraffins.

reaction starts at about 310°C with a marked heat generation. This indicates that the thermal degradation of the chlorinated paraffins is an important element in obtaining thermal stability of the reaction mixture.

In the thermogram for the reaction mixture, a peak can be seen that corresponds to the peak in the thermogram for the chlorinated paraffins. At this peak the heat generation for the reaction mixture is about four times larger than for the chlorinated paraffins. The contributing exothermic reaction is probably a decomposition of PbO_2 which makes an oxidation of the chlorinated paraffins possible (reaction no 6.).

The exothermic reaction enthalpy for the reaction mixture was found to be about 3650 J/g for the temperature range in question. According to [8] reaction energies of $3500\text{--}4000\text{ J/g}$ can be hazardous.

For the reaction mixture an initial decomposition temperature of $90\text{--}100^{\circ}\text{C}$ was found. As the maximum normal process temperature is 60°C this yields a low safety margin of about $30\text{--}40^{\circ}\text{C}$. According to [9] a safety margin of at least 50°C is recommended if a DSC-test with a heating rate of $10^{\circ}\text{C}/\text{min}$ has been carried out.

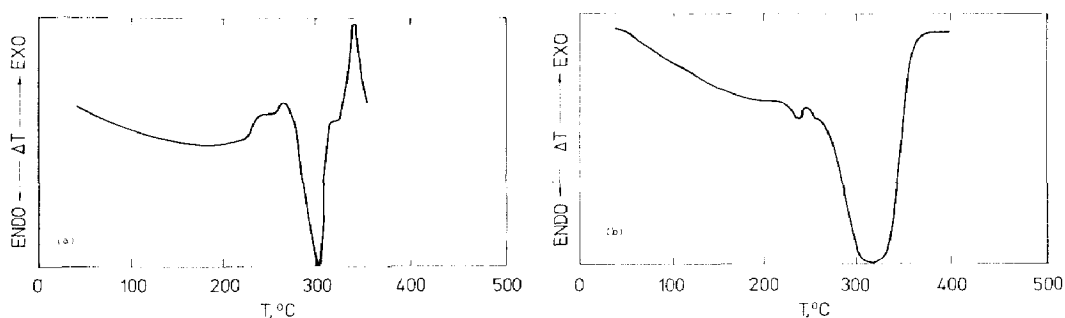


Fig. 2. DTA-thermograms (heating rate $10^{\circ}\text{C}/\text{min.}$), (a) reaction mixture, (b) chlorinated paraffins.

Differential Thermal Analysis:

By use of DTA it was possible to identify an exothermic reaction starting at about 300°C (Fig. 2). On the basis of this DTA-test the potential hazard was not identified because an exothermic reaction course starting at about 300°C would not have been considered to be a safety problem. This is about 240°C above the maximum normal process temperature, which seemingly gives a very high safety margin.

As seen in Fig. 2 the DTA-experiment shows an endothermic reaction course below 300°C while the DSC-experiment shows an alternation between endo- and exothermic reactions. Contrary to the DSC-test, the DTA-test was carried out in an open vessel and the evaporation of the chlorinated paraffins could probably be the predominant process and mask an exothermic reaction course.

Thermogravimetric Analysis:

By use of TGA a weight loss of about 45% was registered below 300°C . The weight loss is probably due to evaporation and thermal decomposition of the chlorinated paraffins.

Thermal Activity Monitor:

Six experiments were carried out at four different temperatures (25, 37, 50 and 77.6°C). On the basis of the TAM-experiments, the activation energy was estimated to about 70 kJ. According to [13], this is a low value which means that the reaction mixture is relatively temperature-insensitive at low temperatures.

6. Conclusions

For the incident in question it was possible to carry out a qualitative assessment of its course and causes. The weak point is the determination of the initiation mechanism.

6.1 *The incident*

- a) The reaction mixture is thermally unstable and hazardous. If the mixture is thermally initiated a self-accelerating exothermic reaction will proceed. Some of the reaction products are gases probably containing HCl and Cl₂.
- b) The reaction mixture is a poor conductor of heat, and there is no heat convection because the mixture is highly viscous. Without stirring, the temperature distribution in the mass will remain uneven.
- c) The heat removal from the surface is the only basis for cooling. Without stirring, this is insufficient if an exothermic reaction is running.
- d) The reaction mixture is relatively temperature-insensitive at low temperatures as the activation energy is low.

6.2 *Contributing factors*

- a) Poor dispersion and heterogeneity in the distribution of oxides have a thermally destabilizing effect on the reaction mixture. An effective coating of the oxides is important for attaining thermal stability.
- b) The thermal stability of the chlorinated paraffins is clearly reduced if small amounts of FeCl₃ are added. The reaction vessel is made of steel. FeCl₃ can be formed by a reaction upon heating between iron and chlorine.

6.3 *The missing link*

The missing link is the initiation factor. The hypothesis has been that a thermal initiation occurred in the bead mill and that a hot zone was transferred to the vessel. It has not been possible to verify this. During the process no temperatures above 55°C were read. But this does not exclude the possibility that a hot zone was developed which was not noticed.

6.4 *Safety recommendations*

- Installation of thermocouples which continuously measure the temperature in the bead mill and in the vessel.
- Installation of temperature alarms.
- Reduction of the maximum process temperature to about 50°C.
- Reduction of the batch size.
- Stirring the reaction mixture continuously during holding periods.

References

- 1 J.L. Cronin and P.F. Nolan, The comparative sensitivity of test methods for determining initial exotherm temperatures in thermal decompositions of single substances, *J. Hazardous Materials*, 14 (1987) 293-307.
- 2 B. Rasmussen, Unwanted chemical reactions in the chemical process industry, Ph.D. Thesis, Risø-M-2631. Risø National Laboratory, July 1987, 116 pp.
- 3 O. Bostrup, Uheld på Sadofoss i Fredensborg/Incident occurred at "Sadofoss". *Dansk kemi*, 64 (1983) 25. (In Danish).
- 4 H.C. Høgh, Ild i kemikaliekar/Fire in tank with chemicals. *Brandværn*, 4 (1983) 30-31 (In Danish).
- 5 Process concept from Sadofoss A/S. (In Danish).
- 6 W.J. McGill and L. de Kock, Effect of iron impurities on the thermal stability of chlorinated paraffins, *South Afr. J. Sci.*, 73 (1977) 210-20.
- 7 J.L. McNaughton and C.T. Mortimer, Differential Scanning Calorimetry. (Reprinted from "IRS: Physical Chemistry Series 2, Vol. 10" with permission of the publisher Butterworths, London) The Perkin-Elmer Corporation, Norwalk, 1975.
- 8 T. Grewer and E. Duch, Thermochemistry of exothermic decomposition reactions. 4th International Symposium on Loss Prevention and Safety Promotion in the Process Industry, Vol. III. *Int. Chem. Symp. Series*, No. 82 1983.
- 9 R.C. Duval, Thermochemical Hazard Evaluation. *Chemical Process Hazard Review*, ACS Symposium Series 274, American Chemical Society Washington, DC, 1985, pp. 57-68.
- 10 W.W. Wendtlandt, Thermal methods of analysis. *Chemical Analysis*, Vol. 19. John Wiley & Sons, 1964.
- 11 J. Suurkuusk and I. Wadsö, Use of isothermal microcalorimetry for the characterization of thermal power occurring in technically important materials and products. CHEMPOR' 85. 4th International Chemical Engineering Conference, April, 1985.
- 12 J. Suurkuusk and I. Wadsö, A multichannel microcalorimetry system, *Chem. Scripta*, 20 (1982) 155-163.
- 13 O. Levelspiel, *Chemical Reaction Engineering*, John Wiley & Sons, Inc., 1972, 578 pp.