



Case study

Analysis of an accident at a solvent recovery plant**Valerio Cozzani^{a,*}, Giuliano Nardini^b, Luigi Petarca^b,
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Abstract

An accident in a plant for solvent recovery from solvent-contaminated wastes was examined. An experimental investigation of the accident was carried out using calorimetric and thermogravimetric techniques. The immediate cause of the accident was an unforeseen exothermic decomposition reaction. The main underlying cause of the accident was the absence of safety culture in the plant management, that resulted in the lack of a testing procedure to evaluate the thermal stability of the process feed. A simplified screening procedure based on differential scanning calorimetry was used in order to test the thermal stability of the nonvolatile fraction of the solvent-contaminated wastes present on the plant in order to be processed. More than 75% of the samples examined showed exothermal decomposition phenomena starting at temperatures higher than 100°C. These phenomena were common to solvent wastes that originated from a number of different industrial activities. Thus, the thermal instability of the process feed is one of the main problems in solvent recovery operations. Our analysis of the accident suggested that the safe operation of waste solvent recovery processes requires an accurate characterization of the thermal stability of the process feed. Process safety is also increased by an adequate emergency vent and an accurate control of operating temperature, that may be reduced operating under vacuum. Safety devices may also include a water supply for emergency quench. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Runaway reactions; Accident analysis; Process safety; Waste solvent recovery; Hazardous wastes treatment

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1. Introduction

The environmentally compatible disposal of wastes containing organic solvents is a relevant problem, in particular for small and medium enterprises (SME). Many industrial activities, as painting or coating of miscellaneous materials, produce waste solvents and solid or liquid wastes containing high quantities of solvents. Usually, the quantities of these wastes produced in SME do not justify the direct recovery or redistillation. Thus, waste solvents are usually disposed by way of companies that collect industrial wastes from different activities. However, the final destination of these wastes is problematic. Wastes containing relevant quantities of organic solvents are classified as 'hazardous wastes' and may be landfilled only at high costs in specific sites. The more common alternative to landfilling is incineration, but this solution has some drawbacks, both technical and environmental. Technical problems are related to the high viscosity and high solid content of waste solvents, that may cause difficulties in feeding the wastes to the burner. Environmental problems are due to the emissions of the process, in particular for the possible presence of metals (i.e. in the dyes and pigments that may be present in the solvents) or of chlorinated substances. Furthermore, in general, hazardous waste incineration plants are not well-accepted and the siting of these plants is problematic.

Therefore, the development of environmental-friendly processes, alternative to incineration and landfilling, is very important. In this perspective, the recovery of waste solvents by evaporation or distillation processes seems economically attractive and environmentally acceptable. In these processes, the solvents may be separated from the impurities by evaporation, and recovered for redistillation or reuse. The residue of the evaporation or distillation process is a solid fraction with a low, if any, solvent content. Nevertheless, even if solvent recovery plants are often better accepted than incineration plants, waste solvent redistillation may also be dangerous. Several hazards are present in these plants, such as the flammability of the solvents, the possible presence of oxidizing contaminants as peroxides in the waste solvents, and the thermal instability of the distillation residue. In particular, the hazards of the process are greatly enhanced if the composition of the feed material is not known and/or is not adequately tested. Among the major accidents that involved solvent recovery plants, several were caused by solvent decomposition or by the thermal decomposition of the distillation residue. This problem is of particular importance if the process feed is composed of waste solvents of unknown origin, as those collected from waste disposal companies. The relevant number of accidents that took place in solvent recovery or redistillation plants seems to indicate that the processes and the procedures for the safe recovery of waste solvents or solvent-contaminated wastes should still be optimized.

This paper is concerned with an accident that took place in a waste solvent recovery plant. The causes of the accident were investigated, and the methods to prevent similar accidents in these plants are discussed. Criteria to improve plant and process safety are also examined.

2. Description of the accident

2.1. Plant and process characteristics

The process involved in the accident was used for the treatment of wastes classified as ‘hazardous’ due to their high content of solvents. Process feed was composed of waste solvents from various industrial activities. Waste solvents were collected either directly from industrial plants or from intermediate waste selection and disposal sites. Thus, a wide range of different solvent wastes was fed to the process. No preliminary analysis was carried out before processing. In particular, the thermal stability of the materials fed to the process was not tested.

The aim of the process was the separation of the low-boiling point (liquid) fraction of wastes from high-boiling point (usually solid) impurities. The process was operated in batch. A scheme is shown in Fig. 1. Waste solvents were charged to a stirred tank (R1) at ambient temperature and pressure. The tank was blanketed with nitrogen. The temperature in the vessel was controlled circulating heating oil in an external jacket. The solvents were evaporated in the tank and condensed in a horizontal condenser (E1). Recovered liquid solvents were transferred by gravity to an intermediate storage tank (D1) before final storage in a tank park.

The inlet temperature of the heating oil in the R1 jacket was usually set at 180°C. Tank temperature progressively increased as a consequence of the evaporation of the different solvents present in the feed. The temperature in R1 during the final stage of the process usually reached 170–180°C. At the end of the process, the residue was discharged to a container (D2) at a temperature higher than 100°C.

Process variables measured online included R1 temperature (TI2), oil temperature at jacket inlet (TI3) and outlet (TICR1), level of intermediate storage tank D1 (LI1), and temperature of uncondensed gases leaving condenser E1 (TI11). Safety devices included bursting disks on tank R1 and tank D1.

The only gas-phase emissions of the process were originated by the venting lines of condenser E1 and tank D1. These passed through a water seal (D4) and were sent to an activated carbon fixed-bed adsorber before stack.

Recovered solvents were usually commercialized without further processing, to be used as raw materials in solvent redistillation processes or as washing liquids for industrial applications. The solid residue of the process is usually 10 to 20% of the initial batch weight and has a limited, if any, solvent content.

2.2. The accident

During the processing of a batch, tank R1 temperature progressively increased to about 147°C as a consequence of the evaporation of the different solvents. At that temperature, exothermic phenomena resulted in the sudden increase of R1 temperature to more than 200°C in less than 5 min. The temperature–time traces recorded during the accident are shown in Fig. 2. Unfortunately, the maximum temperature reached in tank

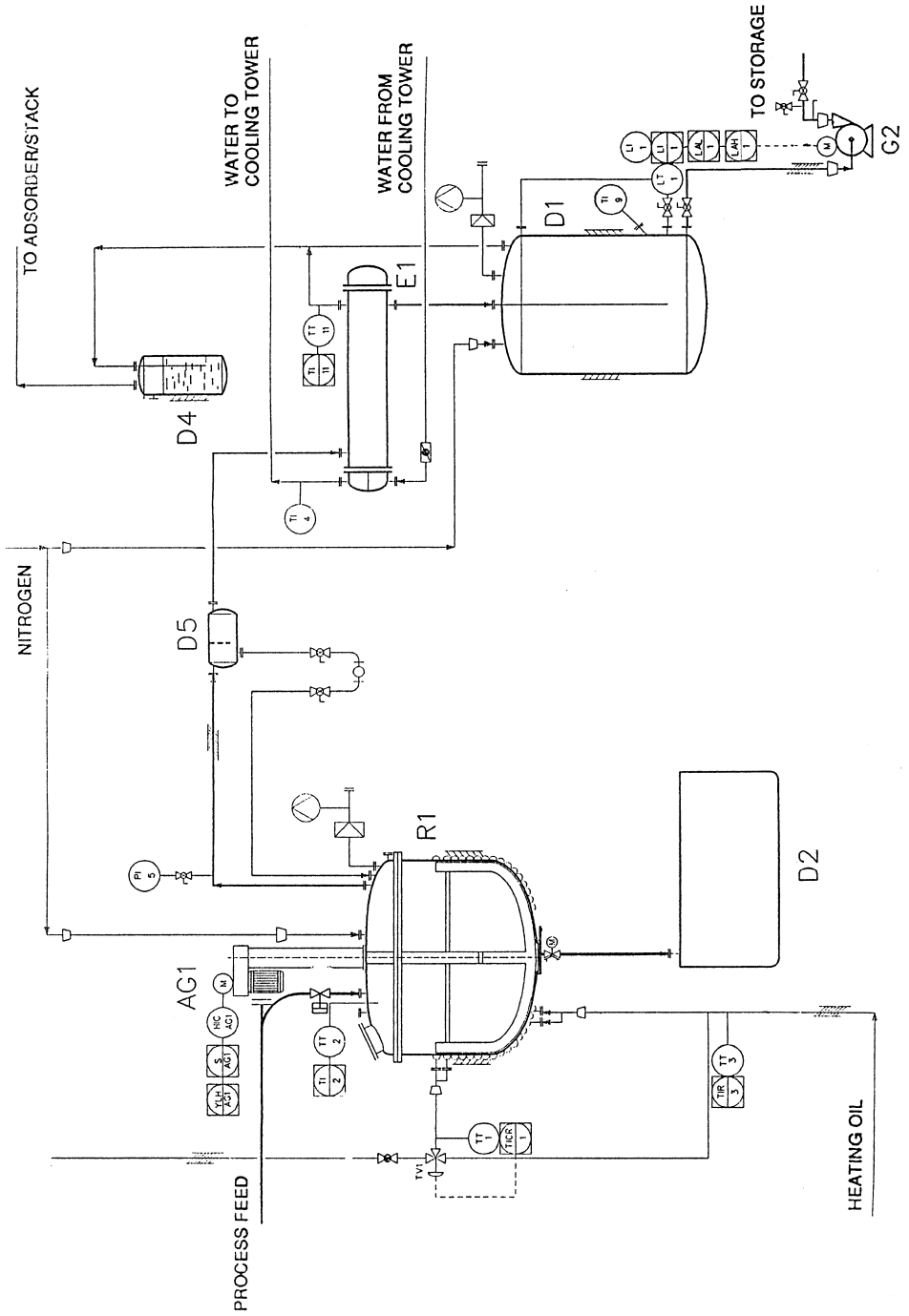


Fig. 1. Scheme of the plant section where the accident took place.

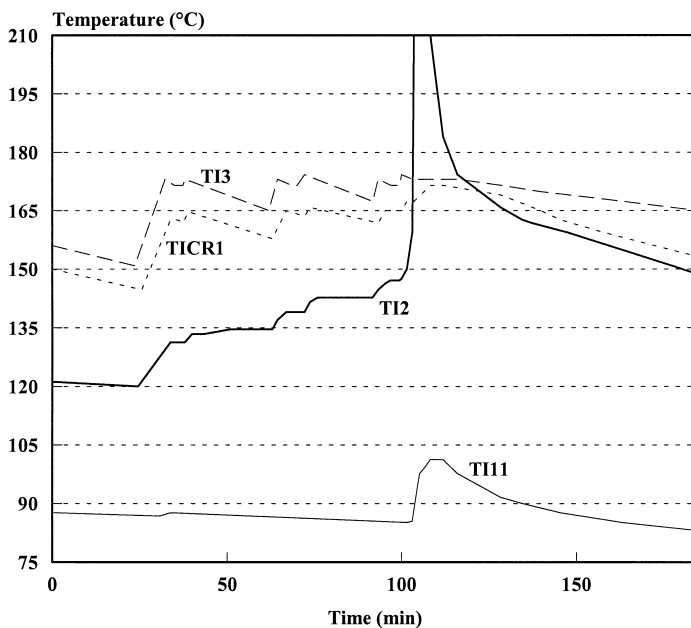


Fig. 2. Temperatures recorded during the processing of the batch that caused the accident.

R1 during the accident could not be determined, since the signal (TI2) went out of scale. However, the relevant increase of tank temperature resulted also in the relevant increase of the temperature of the uncondensed gases leaving condenser E1 through the venting line (TI11). The recorded level of tank D1 indicated that at the moment of the accident, about 300 kg of material was still in tank R1.

The exothermic reaction resulted in the pressurization of tank R1. The bursting disk ruptured at 1.45 bar, but the relief was not sufficient to stop pressure increase in the vessel. The tank had a project pressure of 3 bar and did not collapse; however, the bolted lid broke open. The gasket and the thermal insulation were blown to pieces. A vapour cloud, containing probably solvents and decomposition products, was released from tank R1 and ignited. A flash fire was started, that extinguished spontaneously without further consequences. Nobody was near to the tank at the moment of the accident, thus, no injuries to plant operators were recorded. A black smoke cloud of combustion products was formed and dispersed. The plant is sited in an industrial zone. The release did not affect neither resident population nor the employees present in the nearby buildings. No other consequences of the accident were reported.

Although the consequences of the accident were limited, it must be remarked that the effects could be more serious in larger plants. If larger quantities of vapour phase solvents and products of decomposition were released, larger areas could be affected by the flash fire and the cloud dispersion. Thus, even if the effects of this accident were limited, the lessons to be learnt may be important to prevent worst accidents in larger plants.

3. Experimental

3.1. Materials

A sample collected before processing from the batch that caused the accident was available. Other samples were collected from tank R1 and from tank D1 after the accident. These three samples were characterized using analytic and calorimetric techniques.

A relevant amount of drums containing wastes to be processed were present on the plant at the moment of the accident. Unfortunately, only in few cases data were available on the industrial activities that produced these wastes.

An experimental characterization of the waste solvents present on the plant was carried out using thermogravimetric and calorimetric techniques. Using the sampling procedure described below, 59 samples were collected from wastes coming from unknown industrial activities. Other six samples were collected from wastes coming from identified industrial activities (see Table 1).

3.2. Experimental techniques

The thermal stability of the samples was investigated using thermogravimetric (TG) analysis and differential scanning calorimetry (DSC).

TG runs were carried out in a Mettler TG-50 thermobalance using pure nitrogen as purge gas (100 ml/min) and constant heating rates of 10 or 20°C/min (0.167 or 0.333°C/s). Typical sample weights were of 20–30 mg.

DSC experimental data were obtained from a Mettler DSC 25 calorimeter, using a constant heating rate (10°C/min), pure nitrogen as a purge gas, and typical sample weights of 5–15 mg. DSC runs were carried out using crucibles with pierced lids ('open' crucibles). This was necessary to avoid excessive pressure build-up caused either by the presence of high quantities of low-boiling point solvents in the samples, and by decomposition reactions yielding gaseous products. Thus, an endothermic contribution due to evaporation phenomena may be present in the DSC data obtained for the samples examined.

Table 1
Results of the DSC and TG analysis of samples collected from wastes of different manufacturing activities

| Sample | Industrial activity | ΔH (J/g) | Temp. range (°C) | Weight loss (%) |
|--------|---|------------------|------------------|-----------------|
| 1 | moulding of plastic packings | 22.7 | 150–250 | 1.8% |
| 2 | paint and ink manufacturing | 66.4 | 150–250 | 6.3% |
| 3 | paint manufacturing | 19.5 | 150–250 | 3.2% |
| 4 | painting of plastic components | endothermic | 150–250 | 5.5% |
| 5 | painting of metallic components | endothermic | 150–250 | 5.1% |
| 6 | thermohardening plastic components production | 134.4 | 180–300 | 75.6% |

The stability of the solid residue of the samples was also investigated. The volatile fraction of the samples was evaporated heating the samples at 130°C for 30–60 min in the furnace of the TG analyzer. TG and DSC runs were carried out on the residue. The composition of the samples collected from the material that caused the accident and from tank D1 after the accident was investigated using gas-chromatographic (GC) and gas-chromatographic/mass-spectrometric (GC/MS) techniques. The results of GC runs were compared with available standards in order to identify the components. GC/MS data were used to verify and complete the results of GC analysis.

4. Results and discussion

4.1. Accident investigation

Fig. 3 shows the results of the TG analysis of a sample collected from the batch that caused the accident. The TG run was carried out in pure nitrogen using a heating rate of 20°C/min. It must be recalled that the temperature values of weight loss phenomena during constant heating rate TG runs are highly dependent on the heating rate used. The figure shows that the sample undergoes a relevant weight loss between 30 and 100°C, mainly due to the almost complete evaporation of the organic solvents. A slight weight loss (approximately 2% of initial sample weight) is present between 150 and 250°C. Tank R1 temperature was in this range when the accident took place. Further weight loss takes place at higher temperatures.

Stopping the TG run at 130°C, a black solid residue was observed in the crucible. A similar solid residue was obtained maintaining the sample 24 h in a dry air flow at ambient temperature.

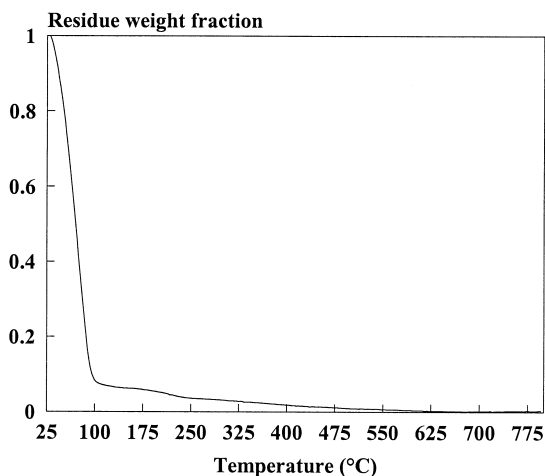


Fig. 3. TG curve obtained for a sample of the material that caused the accident (pure N₂, heating rate of 20°C/min).

Direct conventional DSC measurements of thermal effects during sample heating were not possible. Pressure build-up during DSC screening was too high to use sealed crucibles. Using pierced-lid (open) crucibles, the broad endothermic peak and the mass loss due to the evaporation of the organic solvents made unreliable the identification of thermal effects in the temperature range of interest (130–250°C).

The volatile fraction of the batch that caused the accident was separated by bulb-to-bulb distillation under vacuum (1 mmHg) at ambient temperature. GC and GC-MS were used to identify the components of the distilled fraction. The batch that caused the accident resulted mainly composed of nonchlorinated aliphatic solvents (alcohols, ethers, esters and ketones). Identified components were: ethylacetate, methyl ethyl ketone, isobutyl acetate, isobutanol, *n*-butanol, cyclohexanone, and ethylene glycol monobutyl ether.

The same analytic procedure was applied to the sample collected from tank D1 after the accident. The comparison of the GC analyses of the two samples did not show relevant differences, neither in the number of GC peaks present or in the relative area of peaks. Thus, no relevant changes were detected in the composition of the volatile fraction of the material after processing, at least within the limits of the experimental technique. This result seems to indicate that the volatile components of the batch that caused the accident were thermally stable, and thus, to exclude that the accident could have been caused by the decomposition of a volatile component. Therefore, the accident was probably caused by the distillation residue of the material.

TG runs were performed in order to study the thermal stability of the nonvolatile fraction of the material that caused the accident. A sample was heated in the TG furnace at 130°C in nitrogen, using a constant heating rate of 20°C/min, and was maintained at that temperature for 30 min. The weight loss of the sample is shown in Fig. 4. A solid

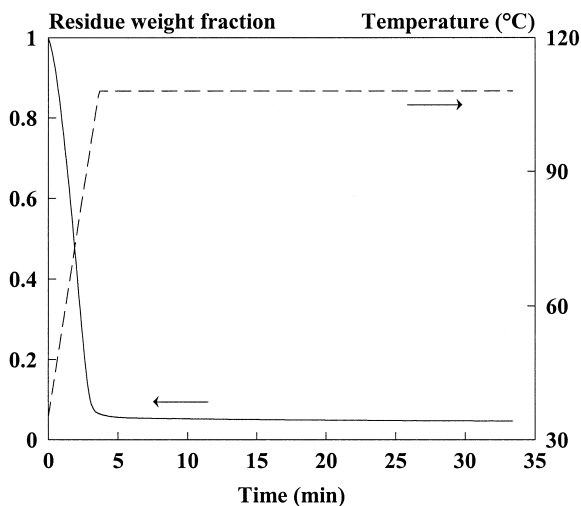


Fig. 4. Weight loss with respect to time and temperature during the heating at 130°C of a sample of the material that caused the accident.

residue (5.6% of initial sample weight) was obtained from this procedure. The results of the TG analysis of the residue, carried out using a constant heating rate of 10°C/min are shown in Fig. 5(a). The figure evidences a 35% weight loss between 130 and 250°C. Further weight loss (up to about 90% of initial weight of the residue) was experienced by the sample at higher temperatures. The weight loss phenomena, taking place in pure nitrogen, may be attributed to decomposition reactions yielding volatile products.

The thermal effects present during the heating of the nonvolatile fraction of the sample were investigated using the same technique applied for TG analysis. A sample was heated in the TG furnace in nitrogen using a constant heating rate of 20°C/min from 35 to 130°C, and was maintained at that temperature for 30 min. DSC analysis of the residue in inert atmosphere was carried out using an ‘open’ crucible, a constant heating rate of 10°C/min and a pure nitrogen flow of 50 ml/min. The results of DSC analysis are reported in Fig. 5(b). An exothermic decomposition reaction is present

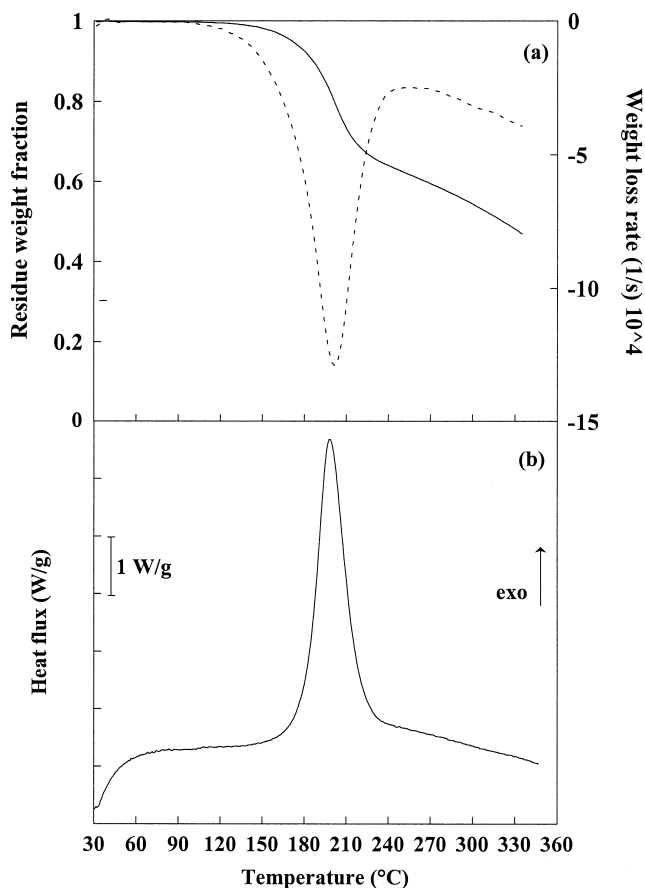


Fig. 5. TG (a) and DSC (b) curves obtained for the nonvolatile residue of the batch that caused the accident (pure N₂, heating rate of 10°C/min).

between 135 and 245°C in the conditions of DSC run. The total heat released by the sample was calculated integrating the heat flux curve using the DSC software. Integration of the exothermic peak between 135 and 245°C yields a value of 757 J/g (181 kcal/kg) for the heat of decomposition of the sample. It must be remarked that this value may be underestimated, due to the possible contemporary presence of endothermic evaporation phenomena allowed by the use of an ‘open’ crucible in DSC analysis.

The comparison of TG curve reported in Fig. 5(a) with DSC curve in Fig. 5(b) shows that in the temperature range of the exothermic peak (135–245°C), the sample experienced a 34.7% weight loss.

Fig. 6 reports the results of TG (a) and DSC (b) analysis of a sample collected from the material present in tank R1 after the accident. Fig. 6(b) shows that the exothermic peak observed in Fig. 5 is not present in the DSC curve of the material collected in tank R1 after the accident. The slight endothermic effects shown in Fig. 6(b) above 180°C are

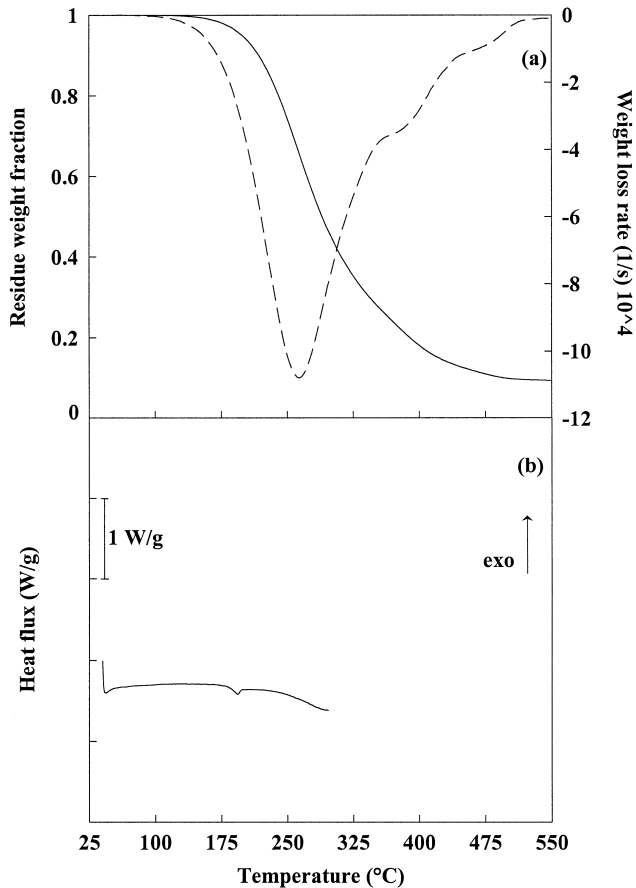


Fig. 6. TG (a) and DSC (b) curves obtained for the material collected in tank R1 after the accident (pure N₂, heating rate of 10°C/min).

probably associated to evaporation or decomposition reactions yielding volatile products. This is confirmed by the weight loss of the material above 150°C, evidenced in the TG curve of Fig. 6(a).

The ultimate analysis of the material that caused the accident was carried out in order to detect the presence of nitrogen-containing compounds. The results indicated that the 0.46% by weight of nitrogen was present in the sample. The ultimate analysis of the fraction obtained by bulb-to-bulb distillation was also performed. The nitrogen content of the distilled fraction resulted below detection limits. Thus, by a mass balance, it was possible to estimate that approximately an 8% by weight of nitrogen was present in the distillation residue.

The presence of a relevant quantity of nitrogen in the distillation residue may justify the hypothesis of the presence in the residue of nitrocompounds or of other high-energy nitrogen-containing compounds, that may have caused the accident. The value of 390 kJ/mol, reported in the literature for the decomposition of a nitro-group [1], may well-justify the order of magnitude of the decomposition energy of the sample, obtained from DSC experimental runs.

FTIR analysis of the residue obtained from bulb-to-bulb distillation of the sample that caused the accident was also carried out. The high chemical complexity of the distillation residue made difficult the interpretation of the FTIR spectra. Thus, it was not possible to identify the components of the residue, although the FTIR spectrum indicated the presence of carbonylic and esters functional groups. However, no evidence of nitrogen-containing high-energy groups (as nitro- or diazo-) was found by the analysis of FTIR data.

Nevertheless, the results of the chemical and calorimetric analyses of the available samples are consistent and seem to indicate that the accident was caused by the highly exothermic decomposition (757 J/g) of a component of the solid residue. The identification of the component was not possible, but the presence of about 8% of nitrogen by weight in the distillation residue strongly suggests the presence of nitro- groups, even if it was not possible to detect them by FTIR analysis.

The decomposition caused the sudden formation of volatile products (2% by weight of initial tank R1 charge, 35% by weight of the material present in the tank at the moment of the accident). The tank was heated from 147 to more than 200°C in less than 5 min during the accident. The formation of a relevant quantity of volatiles in a limited amount of time caused the pressurization of the tank and the subsequent explosion. From the level indicator of D1 tank, it could be assumed that about 300 kg of material was still present in tank R1 at the moment of the accident. The analysis of the TG curves shows that the formation of about 100 kg of volatiles that originated from the decomposition of the residue possibly took place. It may be concluded that the immediate cause of the accident was an unforeseen exothermic decomposition reaction.

However, this study shows that the accident could be avoided if a testing procedure to evaluate the thermal stability of the process feed was present. The thermal instability and the possible exothermic decomposition of the wastes that caused the accident comes out even from a rapid DSC screening. Moreover, no process hazard analysis was done and the supervisors of the plant were not aware of the possible problems that the thermal instability of the wastes could cause to the safety of the process and of the operators.

Thus, the main underlying cause of the accident was the absence of safety culture in the plant management.

4.2. Thermal stability of the nonvolatile fraction of waste solvents

At the moment of the accident, a relevant amount of waste solvents was present on the plant, waiting to be processed. A preliminary investigation on the thermal stability of the nonvolatile fraction of these materials was carried out. The characterization was mainly aimed to verify the importance of the problem, and, if possible, to identify the source of the more hazardous wastes. Calorimetric techniques were used in order to test the thermal stability of the nonvolatile fraction of the materials. The volatile fraction of the samples was evaporated maintaining the samples in the TG analyzer at 110°C for 1 h in pure nitrogen (50 ml/min). A DSC and a TG run were carried out on the solid residue. A constant heating rate of 10°C/min and a 50 ml/min nitrogen flow were used during DSC and TG experiments. ‘Open’ crucibles were used for DSC runs.

The experimental screening required the development of a sampling procedure, since the waste solvents were mainly stored in drums. During plant operation, before the processing of each batch, the content of the drums was transferred to tank R1 and mixed. This operation was simulated collecting significant samples from each drum of a single batch feed and blending the samples in a 5-l stirred laboratory glass vessel. Samples used for calorimetric characterization were collected from the vessel. Fifty-nine samples were examined following this procedure. The results of the screening are summarized in Fig. 7. The figure shows that the DSC analysis of almost all the samples evidenced the presence of exothermic peaks that may be attributed to decomposition reactions. However, the intensity of the peaks was usually quite lower than that of the material that caused the accident (757 J/g). The temperature range of the exothermic peaks varied with respect to the different samples examined. Fig. 8 shows the onset temperatures of the exothermic peaks evaluated using the DSC software for the 20

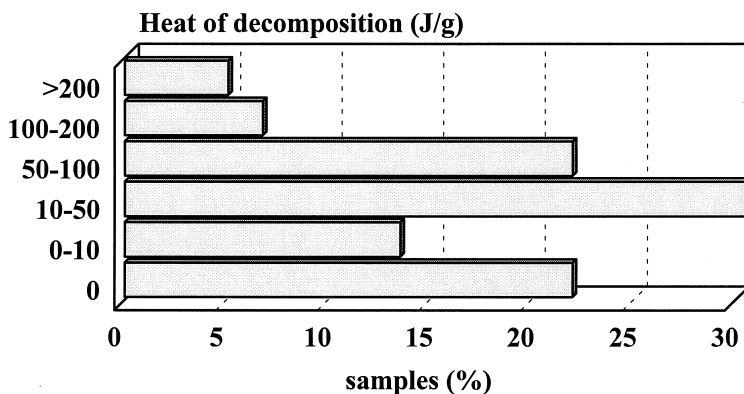


Fig. 7. Values of the heat of decomposition obtained for the 59 samples analyzed from DSC data.

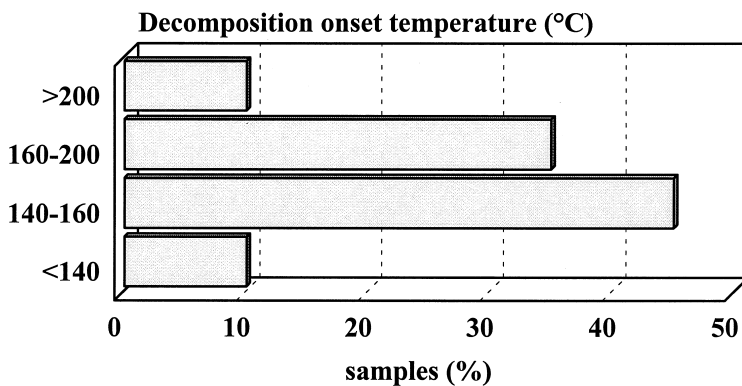


Fig. 8. Onset temperature of the exothermic decomposition phenomena obtained for the 20 samples with heat of decomposition higher than 50 J/g.

samples with decomposition energy higher than 50 J/g. As shown in the figure, the onset temperature of the 80% of the samples with higher thermal effects range between 140 and 200°C. The onset temperature of the sample that caused the accident was 161°C.

In order to identify the sources that originated the more hazardous wastes, six samples coming from well-known industrial activities were also characterized, using the same technique. The results are summarized in Table 1. Some of the samples analyzed exhibited an exothermic decomposition, although the heat of decomposition was significantly lower than that of the sample that caused the accident. From a qualitative point of view, the more hazardous materials were, as expected, those coming from factories producing paints for different applications.

The simplified analysis procedure developed allowed an effective identification of exothermic decomposition phenomena of the nonvolatile fraction of the materials tested. The presence of exothermic decomposition reactions was detected for a relevant number of samples analyzed (78%), as shown in Fig. 7. Thus, the thermal instability of the waste solvents and of the solvent-containing wastes resulted to one of the main problems in solvent recovery operations. These phenomena were detected for solvent wastes that originated from a number of different industrial activities. Therefore, the safe operation of solvent waste processing plants requires an accurate analysis of the hazards due to the thermal instability of process feed.

4.3. Process hazard analysis

Accidents caused by exothermic decomposition reactions in batch processes involving solvent recovery or distillation are well-known. Several of these accidents are reported in the literature and in industrial accidents databases. A search on FACTS database [2] resulted in six major accidents involving ‘run-away-reaction’ or ‘reaction chemical’ during solvent recovery operations. Two accidents were reported in MARS

database [3]. Other similar accidents are reported in the Loss Prevention Bulletin and by other sources [4–6].

These accidents are known to have two main causes: (i) solvent decomposition due to temperature and/or catalytic effects of the impurities concentrated in the process; or (ii) decomposition of the distillation residue. The latter was probably the cause of the accident discussed in the present study.

The more hazardous conditions for the process take place when the solvents are almost completely evaporated and the solid residue is present in the reactor or distillation vessel at high temperature. At this stage, all the unknown high-boiling point impurities originally present in the solvents are concentrated and process temperature is near to that of the heating oil.

The prevention of these accidents requires the application of well-established but time-consuming and costly experimental procedures aimed to the characterization of the thermal stability of process feed [7,8]. Experimental tests in adiabatic calorimeters as Phi-Tec, VSP or ARC are generally required [9]. However, the usual procedure used for plant and process design requires to carry out the experimental analysis only once, during the initial stage of process development. In the case of a waste processing plant, where a broad variability is present in the characteristics of process feed, this is not possible. A 'safe region' of process operating conditions cannot be assessed during the project phase of the plant, as usually done for normal process plants. Furthermore, safety devices can't be designed on the basis of well-defined conditions. An inverse procedure should be adopted: plant and process characteristics should be defined 'a priori' using maximum achievable safety criteria. The suitability of each batch for processing should then be assessed using experimental techniques based on adiabatic calorimetry. In particular, pressure–time data should be available to verify the venting capacity of the vessel.

A further problem is caused by the characteristics of process feed. Waste solvents are mainly stocked in drums before processing. The availability of representative samples of each batch charge would require the pre-mixing of drums content or the implementation of quite complex sampling procedures as those used for the present study.

Thus, the process hazard analysis suggested:

- to introduce a testing procedure for the thermal stability of the process batch.
- to introduce limited plant modifications to improve process safety and flexibility.

4.4. Testing procedures for process feed thermal stability

The acceptability of each batch for processing should be tested in order to verify that the venting capacity of the solvent evaporation vessel is not exceeded.

The screening procedure based on DSC data used in the present study gives immediate results on the stability of the thermal residue of the process, yielding data on the more hazardous phase of the process, when the solvents are almost completely evaporated. However, a very important limitation is that this technique does not give information on the pressure–time trend during the heat-up of the samples. Thus, DSC data are not sufficient to define a safety threshold for the exothermic effects, since no

information can be obtained on the possible pressure build-up in the solvent evaporation vessel.

Another important limitation of this procedure is that it does not give any information of the thermal stability of the volatile fraction of the sample, and in particular of components evaporating at temperatures lower than 110°C.

The procedure used above, based on the DSC screening of the thermal stability of the residue, may give only preliminary data on the presence of exothermic decomposition reactions of the residue. A full safety assessment of the process requires the use of adiabatic or low-phi factor calorimetry to investigate the thermal stability of the process feed and to enhance process safety.

Therefore, a suitable testing procedure should require to:

1. Obtain samples using the procedure described above or from a pre-processing blending vessel.
2. Test the thermal stability of the samples using adiabatic calorimetry. The temperature field of the tests should range at least from ambient to heating oil temperature.
3. Verify the venting capacity of the solvent evaporation vessel on the basis of the experimental data obtained, using the methods described in the literature [10,11].

4.5. Process and plant modifications

The modifications required for the improvement of process safety concerned:

- process operating conditions
- safety devices.

As stated above, these were based only on ‘maximum achievable’ safety criteria compatible with the specifications of the process. The main limitation to process changes was that the solvent content of the solid residue in tank R1 at the end of the process should not be above 50 g/kg, to minimize landfill costs.

With respect to process operating conditions, the modifications implemented were:

- the introduction of a vacuum pump connected to the vent lines of condenser E1 and tank D1
- the limitation of R1 evaporating vessel operating temperature to 80°C
- the limitation of oil temperature in R1 jacket to 140°C.

Reduced pressures obtained by the vacuum pump allowed the process to be carried out at lower temperatures. The selected maximum operating temperature is about 50°C lower than the observed onset temperatures of the samples analyzed. Oil temperature limitation was suggested to avoid local overheating of heat exchange surfaces in vessel R1. Obviously, the pressure in R1 vessel should not be below the values that allow the condensation of the solvents in condenser E1.

With respect to the safety devices, the modifications suggested were:

- the increase of vessel R1 emergency venting capacity
- the introduction of a high temperature alarm
- the introduction of an emergency cooling system.

R1 emergency venting capacity could be increased introducing a 400-mm bursting disk. Since no aprioristic criteria were available to select the bursting disk diameter, this was chosen on a ‘maximum achievable’ safety criterion.

The high temperature alarm seems the only device that can be used to alert operators of the possible system runaway. A high pressure alarm would give a more rapid response to system deviations, but can't be used, since R1 is operated under vacuum in batch.

The high viscosity of the material in vessel R1 at the end of the process, and the presence of vacuum don't allow the implementation of a dumping system. Alternatively, the introduction of an emergency cooling system is suggested by the narrow safety margins allowable for the process. An emergency cooling of R1 vessel obtained lowering the temperature of the fluid in the jacket seems insufficient, since the effect on vessel R1 internal temperature would be too slow. The selected operating temperature (80°C) makes possible the use of a direct contact water quenching system. Nevertheless, this could be used only since reactor temperature is below water boiling point, due to the risk of steam explosion.

5. Conclusions

An accident in a solvent waste recovery plant was examined using analytic, calorimetric and thermogravimetric techniques. The immediate cause of the accident was an unforeseen exothermic decomposition reaction. The main underlying cause of the accident was the absence of safety culture in the plant management, that was responsible of the lack of a testing procedure to evaluate the thermal stability of the process feed. Although the consequences of the accident were limited, it must be remarked that the effects would be more serious in larger plants. Thus, the lessons learnt from the analysis of the accident are of particular importance for large plants that process wastes coming from different industrial activities.

A simplified screening procedure based on differential scanning calorimetry was used in order to test the thermal stability of the nonvolatile fraction of the solvent-contaminated wastes. More than 75% of the samples examined showed exothermal decomposition phenomena starting at temperatures higher than 100°C. These phenomena were common to waste solvents originating from a relevant number of different industrial activities. Thus, the thermal instability of the waste solvents and solvent-containing wastes is one of the main problems in solvent recovery operations.

Waste solvent recovery plants may be an environmental-friendly alternative to incineration or landfilling. However, these processes are more likely to lead to an accident if proper controls and procedures are not in place. Our analysis of the accident suggested that the safe operation of waste solvent recovery processes needs an accurate characterization of the thermal stability of the process feed. This may require the use of rather complex sampling procedures and of experimental techniques based on adiabatic calorimetry. The relevant number of different solvent wastes that showed exothermal decomposition phenomena also suggested that the thermal stability characterization procedure should be repeated for each batch of wastes, particularly if wastes of different origin are fed to the plant.

Process safety is also increased by an adequate emergency vent and an accurate control of operating temperature, that may be reduced operating under vacuum. Safety devices may also include a water supply for emergency quench.

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