Investigation into an explosion and fire in a mononitrotoluene manufacturing plant

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Abstract

In 1992 an explosion and fire occurred in the mononitrotoluene area of a chemical plant in England, resulting in five fatalities. The incident occurred during the cleaning of a vessel used for the separation of mononitrotoluene isomers. This paper describes work performed on samples removed from the plant to determine their reactivity and their sensitivity to initiation. The paper also collates some of the work performed by the other parts of HSE and identifies the possible causes of ignition. After interpretation of the test data, a likely incident scenario is identified, with self-heating of reactive residues in contact with a heated steam pipe being the most likely cause of the incident.

1. Introduction

In 1992 an incident occurred at a chemical plant in England resulting in five fatalities. The incident originated a horizontal cylindrical vessel about 8 m in length and 2.7 m in diameter. This vessel was used for part of the process of separating the isomers of mononitrotoluene. Prior to the incident it was thought that semi-solid residues had built up in the vessel and it was decided to remove these residues with a metal rake.

On the morning of the incident the steam heaters inside the vessel were switched on to soften the residues and a 50 cm diameter manway cover at the front of the vessel was removed. A vent of about 20 cm diameter at the rear of the top of the vessel was also opened. After some period of scraping the residues into a skip positioned at the front of the vessel under the manway, a blue flash was observed inside the vessel and a jet of flame was forced out of the manway. This rapidly intensified

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into a white-hot jet resembling a blow torch which cut through a pre-fabricated control room about 25 m in front of the vessel. The jet then travelled through a car parking area before striking an office block about 55 m away from the vessel. Four deaths occurred in the pre-fabricated area; the fifth was in the office block. Following the incident many samples were removed from the site for examination. These were taken from the feed stock tanks, the still base involved in the incident and from adjacent pipework. This paper describes tests to determine the thermal stability of the samples, their propensity to deflagrate and their sensitivity to initiation by various forms of stimulus.

2. Test methods used

2.1. Thermal stability

2.1.1. Differential scanning calorimetry (DSC)

A small sample (typically 1 mg) is heated at a predetermined rate inside a sealed pan. The energy absorbed or emitted by the sample is recorded against the programmed temperature by reference to a standard. The lowest temperature at which decomposition or self-heating is detected is known as the onset temperature.

2.1.2. Accelerating rate calorimetry, (ARC)™

This technique uses a sample of typically a few grams. The sample is held inside a bomb and its temperature and the pressure in the bomb are monitored. The temperature of the system is then raised to a predetermined level at which it is held adiabatically whilst the instrument assesses whether self-heating is occurring. If no event is detected the temperature is further ramped, in steps, until an event occurs. The instrument then follows the resulting exotherm in terms of temperature and pressure until the reaction is complete. An ARC plot will again give an onset temperature, and profiles of temperature and pressure against temperature. Because of the sample size and the sensitivity of the machine, the onset temperature measured by ARC is lower than that detected in DSC, and is more akin to the self-heating temperature of bulk materials.

2.1.3. Hot stage microscopy

A small sample is heated in an open crucible at a programmed rate. The sample's behaviour is observed through a microscope and phase changes, ignition or decomposition may be detected.

2.2. Mechanical sensitivity

It is well known that some materials are susceptible to decomposition or even explosion by mechanical means. The mechanical stimulus can come in the form of impact, friction or a combination of both. The UN manual for the classification of explosives for transport describes several impact and friction tests and the EC require-

ments for the notification of new substances duplicate one of the UN tests for both impact and friction sensitivity.

2.2.1. Impact sensitivity – BAM Fallhammer [1]

The sample is held in a retaining device on an anvil and an upper striker is placed in contact with the top of the sample. The striker is then impacted with a known weight falling vertically from a predetermined height. The reaction of the sample is noted and the result is expressed as the limiting impact energy (LIE) of the falling weight, expressed in Joules, which causes a positive result such as an explosion, flash or flame or complete decomposition.

2.2.2. Friction sensitivity – BAM friction machine [2]

A small amount of sample is spread onto a porcelain plate which is then dragged under a loaded porcelain peg, thereby subjecting the sample to friction. The reaction of the sample is noted and the result is expressed as the minimum loading of the peg, expressed in Newtons, which causes a positive result as described in Section 2.2.1.

2.2.3. Impacted friction [3]

A thin train of sample is spread onto an anvil of stone or steel and impacted friction is delivered by means of glancing blows with a wooden mallet or steel hammer. The strength of blows and the weight of the mallet or hammer may be varied.

2.3. Deflagration

Deflagration may be described as the subsonic propagation of a reaction front through a material without the necessary presence of ambient oxygen. Deflagration can be much faster than oxidative combustion but is not as rapid as detonation. If deflagration proceeds within a confined space it may undergo transition into detonation. The deflagration test used was the one used in the UN scheme for the transport classification of self-reactive substances.

2.3.1. Time/pressure test [4]

A 5 g sample is confined in a pressure vessel and subjected an incendive flame. A bursting disk, designed to fail at about 2200 kPa is fitted to the vessel and the resulting rise of pressure within the vessel against time is recorded. The time for the pressure to rise from 690 to 2070 kPa is used to assess the hazard that the sample presents of explosion by deflagration.

2.4. Flash point [5]

The flash point of a liquid may be defined as the lowest temperature at which the vapour pressure of the liquid is sufficiently high to produce the concentration of the lower flammability limit of the vapour in air under specified experimental conditions. The apparatus used for these studies was the Seta-flash closed cup method.

2.5. Autoignition temperature [6]

This is the lowest temperature at which a liquid or vapour will undergo autoignition under specified conditions without the use of a pilot flame. This work used the apparatus described in the British Standard BS 4056/66.

2.6. Ad hoc tests

2.6.1. Heated block tests

A few grams of sample were placed in a small glass tube which was then inserted into a pre-drilled hole in a metal block. The block was heated and the temperature of the block and sample recorded. By this method decomposition of the sample could be monitored.

2.6.2. Still base simulation

A non-scale model of the still base was made using a brass vessel of about 750 ml capacity. The vessel was laid on its side and orifice plates were fitted to the front and top to simulate the openings in the still base. Various masses of the sample 31146/92 were heated in the vessel by heater tapes around the circumference, and the temperatures of the sample and vessel were monitored.

3. Samples

Many of the samples were unhelpful to the investigation as they were inert, having been affected by the water used for fire-fighting or by the fire. The locations of the sampling points of the active samples are shown in Fig. 1, and the arrangement of the feed stock tanks and product stores with respect to the still base is shown schematically in Fig. 2.

4. Sample selection and preparation

The samples were screened in the "as-received" state using the DSC. Because only small amounts of the samples were available, the experimental work was limited to a selected range of samples. These were feedstock samples and materials removed from the pipework and pumps that removed the waste products from the still base into the residue store 193. These samples were subjected to rotary evaporation to remove volatiles. It was then considered that the resulting residues would be fairly representative of the materials present in the still base prior to the incident. Concentration of the samples was carried out by rotary evaporation at about 125 °C and about 0.1 mbar pressure. The non-volatile components remaining in the flask were typically either dark brown or black viscous liquids or amorphous soft granular solids.
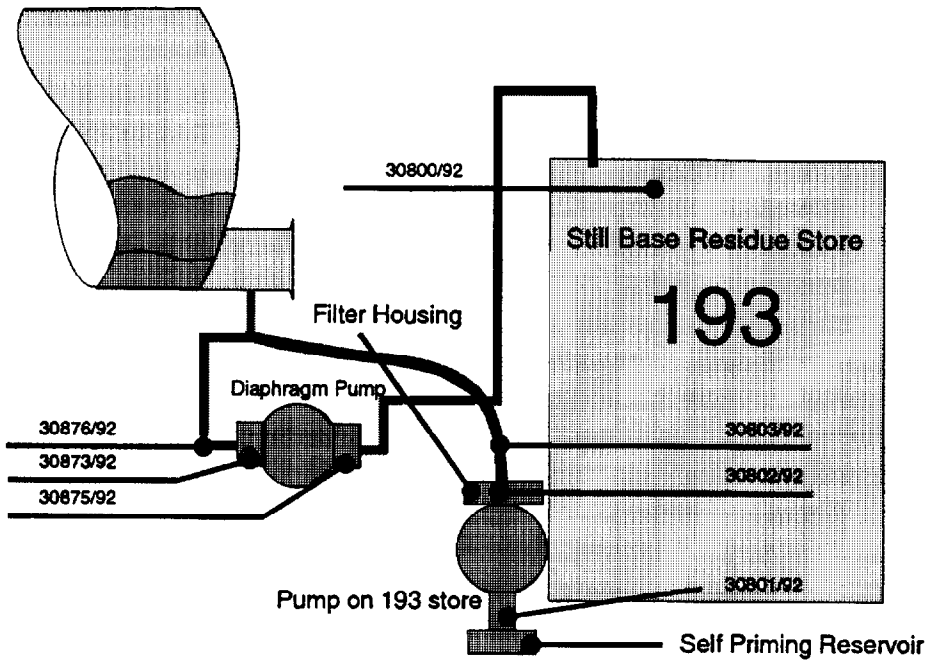
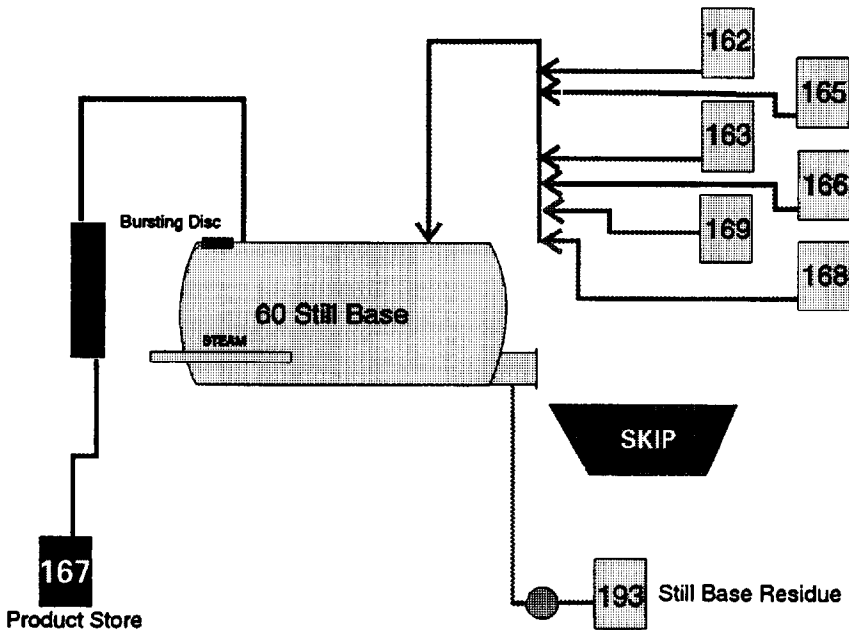Fig. 1. Samples from still base exhaust area.

Fig. 2. Arrangement of tanks and stores.

5. Results

5.1. DSC

All samples were analysed in stainless steel pans at a scanning rate of 5 K/min. Because some traces indicated reaction between the sample and the pan, and because some samples were still showing exothermic activity at 350 °C, a number of runs were done in gold pans which are inert and have a wider temperature operating range. The majority of the tests were carried out on the concentrated residues which remained after most of the more volatile components had been removed. However, since the chemical analysis of some of the samples from the site indicated the presence of the rust, some tests were performed on mixtures of the rust with the residues. The effect was variable, (Table 1), but on balance did not cause significant lowering of the onset temperature or increase in energy of decomposition. Where this energy was reduced it could be accounted for by dilution.

5.2. ARC™

Only the residues obtained from concentrating the as-received samples were analysed. The results for the onset temperatures showed the same trend as was apparent from the DSC (Table 2). The corrected onset temperature for material from 163

Table 1
Differential scanning calorimetry results

Sample	Description	Onset (°C)	ΔH (J/g)	Comments
30800/92	Liquid, top of 193	193	945	Residue
		250	934	Residue + rust
30801/92	Pump on 193	277	495	Residue
		243	1564	Residue; gold pan
		275	296	Residue + rust
30802/92	From filter housing above pump	281	372	As received
		298	749	Residue
		265	449	Residue + rust
30803/92	In line above pump	291	722	Residue
		229	2883	Residue; gold pan
		257	444	Residue + rust
30847/92	Sludge, 163 base	233	1333	Residue
		216	1980	Residue; gold pan
		214	906	Residue + rust
30873/92	From inlet to diaphragm pump	295	608	Residue
		234	1884	Residue; gold pan
		284	444	Residue + rust
30875/92	Sludge between pump and valve	293	2305	Residue
		314	1119	Residue + rust
30876/92	Sludge, pump inlet	284	1814	Residue
		270	2366	Residue; gold pan
31118/92	Ground and dried residue ex 163 store	197	1577	As-received

Table 2
Summary of ARC results

Sample	Description	Comments	Φ	Onset (°C)
30800/92	Liquid, top of 193	Residue	2.75	150[a]
30801/92	Pump on 193	Residue	2.36	166
30802/92	From filter housing above pump	Residue	3.98	148
30847/92	Sludge, base of 163	Residue	5.09	98
30873/92	From inlet to diaphragm pump	Residue	2.07	167[a]
30875/92	Sludge between pump and valve	Residue	4.18	157
31118/92	Ground and dried residue ex 163	As-received	2.49	117
31144/92	162 tank residues	Residue	2.27	186
31146/92	From base of 193	Residue	3.27	139[a]

[a] Indicates that the ARC bomb was burst.

tank, samples 30847/92 and 31118/92 were 98 °C and 117 °C, respectively. These corrected onset temperatures make allowance for the effects of thermal dilution arising from the partition of heat between the sample and the ARC bomb. These values are lower than those obtained for the residues from the samples collected from in and around the 193 store and the pipe work associated with 60 still base.

In Table 2 the column headed "Φ" refers to the "phi" factor, and is defined as the ratio of the thermal mass of the sample and bomb to the thermal mass of the sample alone.

5.3. Hot stage microscopy

A heating rate of 50 K/min was used. Most of the samples decomposed or "exploded" at temperatures in the range 250–300 °C. The most exceptional behaviour was shown by samples 30875/92 and 30876/92, both taken from the diaphragm pump on the exhaust line to tank 193. These both exploded at about 290 °C, with a bright flash, probably due to flame.

5.4. Impact sensitivity

Table 3 shows the limiting impact energy (LIE) of various samples.

Table 3
Results of impact tests

Sample	LIE (Joules)	Sample nature; comments
30800/92	4	Mobile liquid
30802/92	50	Damp sludge
30803/92	–	Solid; no ignitions in 6 tests @ 50 J
30847/92	20	Damp sludge
31118/92	–	Solid; no ignitions in 6 tests @ 50 J

5.5. Friction sensitivity

Friction tests are not normally applicable to liquids or damp samples, since a lubricating effect can be produced. Friction testing was therefore limited to those residues which were virtually dry after rotary evaporation. This reduced the number of samples to the residues from 30847/92 and 31118/92 (both from 163 store). No positive reaction was observed with either sample at a force of 363 N, the maximum loading obtainable with the apparatus.

5.6. Impacted friction

As with pure friction testing, the impacted friction testing is not suitable for liquid samples. Work was therefore limited to one sample of which we had sufficient supply, 31118/92. In tests using blows from a 680 g steel hammer on a steel anvil, no reactions were observed.

5.7. Time-pressure test

This test requires 15 g of sample, limiting the number of tests available. Several samples failed to ignite, possibly because their physical nature inhibited good contact with the igniter. Some samples which failed to ignite at ambient temperature were tested at about 100 °C to see whether an increase in temperature sensitised the samples. The results are shown in Table 4, where the fastest time for the pressure to rise from 690 to 2070 kPa is given in milliseconds.

5.8. Flash point

Tests were performed on the samples "as-received", before any rotary evaporation. Most samples had aqueous components and therefore gave unusual results

Table 4
Time–pressure test results

Sample	Approx. temp.	Fastest time
30800/92	Ambient	Failed to ignite
30800/92	100 °C	Failed to ignite
30801/92	Ambient	Failed to ignite
30801/92	100 °C	Failed to ignite
30802/92	Ambient	Failed to ignite
30802/92	100 °C	300 ms
30803/92	Ambient	123 ms
30845/92	Ambient	Failed to ignite
30847/92	Ambient	Failed to ignite
30847/92	100 °C	240 ms
30873/92	Ambient	Failed to ignite
31118/92	Ambient	489 ms

Table 5
Autoignition results on mononitrotoluenes (MNT)

Isomer	AIT (°C) (Approx)
2-MNT (Ortho)	400
3-MNT (Meta)	450
4-MNT (Para)	475

where either the test flame became elevated from the surface of the sample or was extinguished.

5.9. Autoignition

This test is time consuming and it was decided to test several "as-received" samples on a Go/No-Go basis at 300 °C. This is above the temperature of the steam pipes in the still base, and the testing was designed to establish whether the samples could autoignite when in contact with the pipes. No samples autoignited in any test over 10 mins. Testing was also done, to establish the approximate autoignition temperatures (AIT) of the isomers of mononitrotoluene. The results are shown in Table 5.

5.10. Block

These experiments used 10 g or 15 g samples in a glass vial of 25 mm diameter. In some tests the top of the vial was open and in others an orifice plate was fitted to restrict the flow of decomposition products. The heating rate of the block was about 7 K/min and the results in Table 6 show the temperature at which vigorous decomposition started as well as the maximum temperature attained by the residues in the vial after reaction (see Figs. 3 and 4).

Three further tests were then done with sample 31146/92. In all cases the samples showed self-heating with the sample temperature exceeding that of the block at about 260 °C. Spontaneous ignition then followed at temperatures in the range 298 °C to 307 °C, see Fig. 5.

Table 6
Heated block results

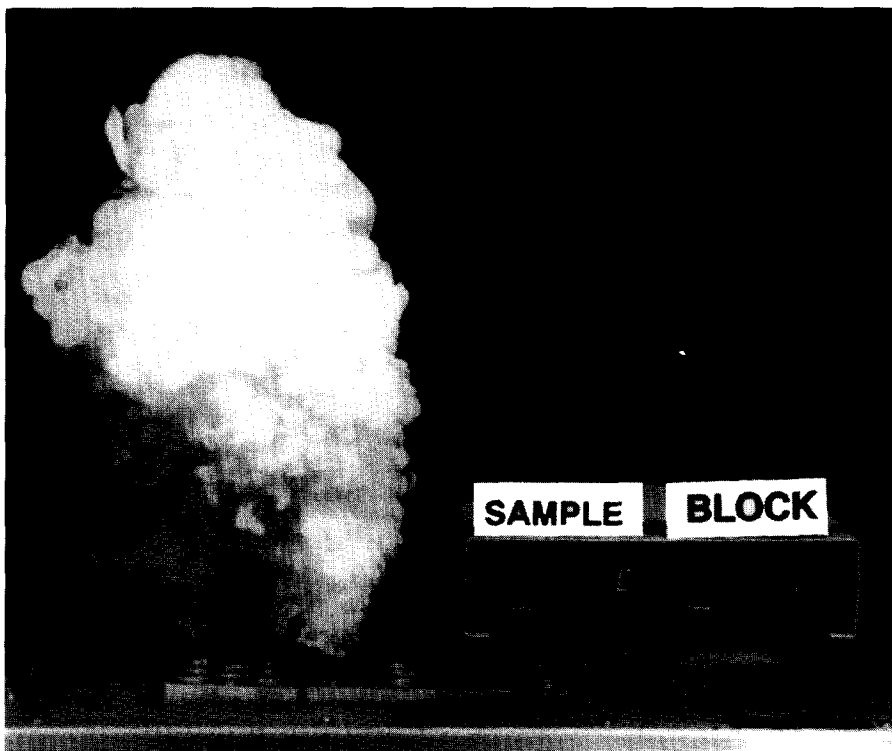| Sample	Mass (g)	Vent	T_{decom} (°C)	T_{max} (°C)
31145/92	15	Open	230	560
31145/92	10	3 mm	240	631
31145/92	10	1.5 mm	260	402
31145/92	10	3 mm	240	507
31145/92	10	Open	232	641

Fig. 3. Heated block experiment; sample 31145/92. Vigorous fuming at about 235 °C.

5.11. Still-base simulation

The results of the still-base simulation tests are shown in Table 7.

6. Discussion

Eye-witness accounts described the first ignition inside the still base as a blue flash. There are five possible causes for this as discussed below:

6.1. Autoignition

No ignitions were recorded with any of the 'as-received' samples at 300 °C. Although the thermocouple inside the vessel was recording the temperature of the vapour above the residues, work by HSE showed that the maximum temperature of the steam in the pipes in the vessel was about 180 °C. Hence it is clear that autoignition was not the original cause of the ignition.
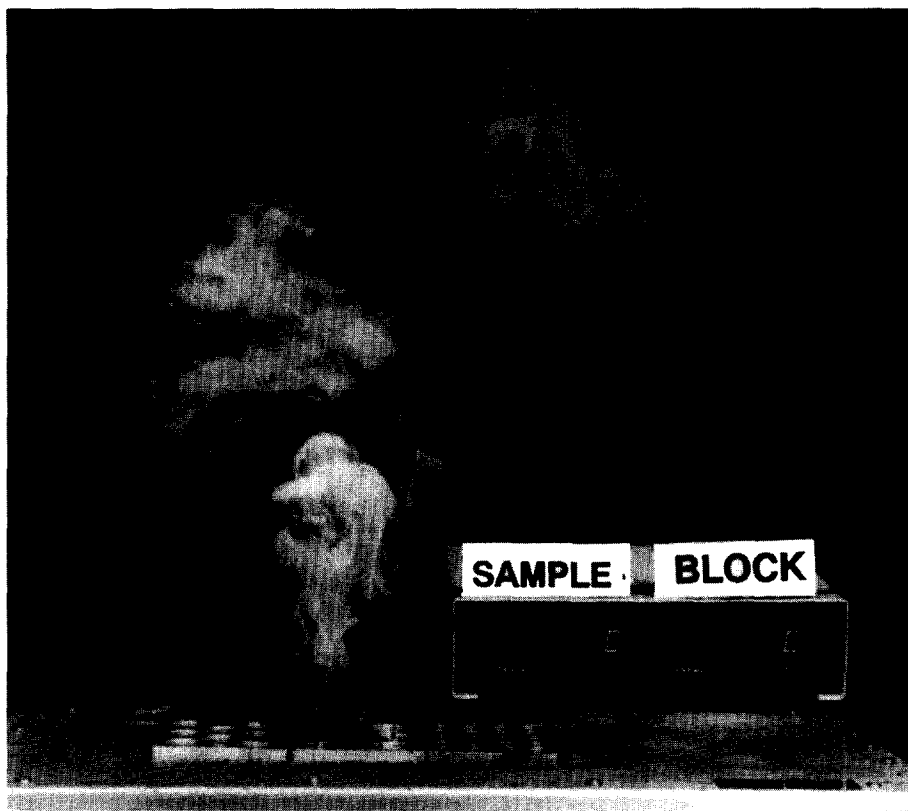
Fig. 4. Heated block experiment; sample 31145/92. Temperature of over 640 °C at end of experiment.

6.2. Ignition of residues by impact or friction

The results of impact sensitivity testing in Section 5.4 show that some of the reduced residues are sensitive to impact. Under UK law [7], any substance being placed on the market is regarded as having explosive properties if it has a limiting impact energy (LIE) of 40 J or less, but these results must be interpreted with care. The UN test prescription [1] specifies that there should be a 1 mm gap between the sample and the impacting collar. It also specifies the method of placement of the sample within the holder. The EC test prescription [8] is less well defined. Recent HSE work [9] has shown that the test result is dependent on the air gap and that the interpretation of impact test data on liquids is difficult; this applies to the result for 30800/92, a liquid. The other samples which gave a positive LIE were damp, and it is likely that compression of the air above the sample triggered the observed event. The dry samples were not sensitive in this test. An energy of 40 J is imparted by 5 kg falling from about 0.8 m. The mass of the rake used to clean out the still base was 5.12 kg, and the head weighed 890 g. This, and the
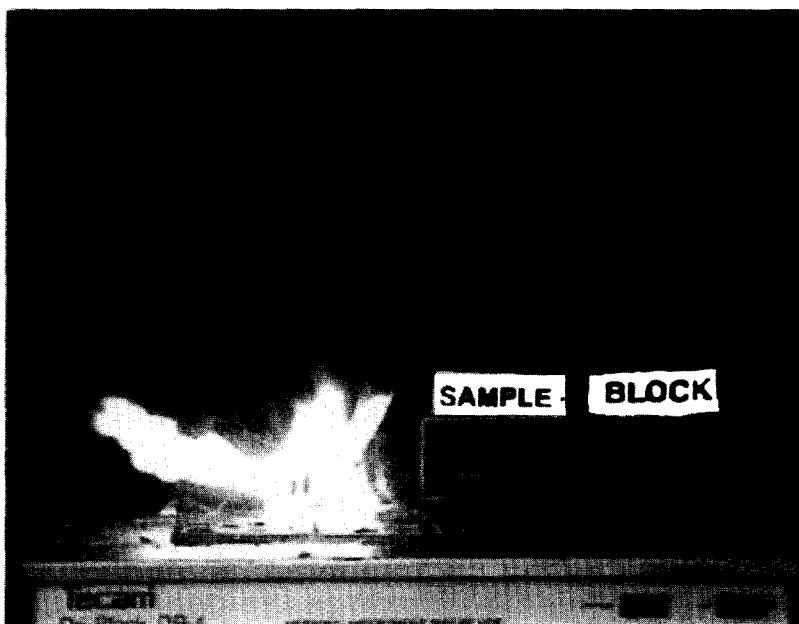
Fig. 5. Heated block experiment; sample 31146/92. Flaming combustion at end of experiment.

relative insensitivity of the samples to impact, suggests that impact was not the main cause of the initial ignition. Similarly, frictional ignition may be discounted since most of the residues were damp and the dry samples did not ignite under friction or impacted friction.

6.3. Ignition of vapours by impact or friction

An HSE expert was asked for his opinion on the possibility of this mechanism of ignition of vapours inside the still base. His conclusion was that "The use of a metal rake to scrape out material would not normally ignite common flammable solvents" [10].

6.4. Ignition of vapours by discharge of static electricity

An HSE expert commented on this mechanism of ignition as follows: "As is often the case it is difficult to totally rule out the possibility of an electrostatic ignition. However in view of the fact that the incident occurred outside, and the fact that the person involved was surrounded by earthed metal parts I think it highly unlikely that his activities led to an electrostatic ignition. Had he become charged by some means or other, I think it likely that he would have discharged himself to his surroundings rather than to the inside of the vessel" [11].

Table 7
Results of still-base simulation

Sample	Mass (g)	Top vent (mm)	Front vent (mm)	Result
31146/92	200	6.5	9.5	Ball of flame
31146/92	110	9.5	17	Fumes; no ignition
31146/92	110	9.5	17	Fumes; no ignition
31146/92	145	9.5	17	Jet of flame

Fig. 6. Still base simulation; sample 31146/92. Jet of flame from front of vessel.

6.5. Ignition caused by self-heating and thermal runaway

Most of the residues removed from the still base and the skip after the incident did not decompose exothermically. It is therefore not possible to make any statements about the nature of the materials inside the still base. However, from the residues removed from the feed stock tanks and from the pipework associated with the usual residue pumping system, a clear picture can be built up of the tank contents. Nearly all the residues showed self-heating in the ARC at temperatures well below the predicted temperature of the steam pipes. This means that it is reasonable to expect that these residues, in contact with the pipes, could self-heat and that

the heat of reaction which could not be adequately dissipated would further heat up the residues. In DSC many residues in the gold pans show heats of decomposition of about 2000 J/g or 500 cal/g. If a specific heat of about 2 cal/g/K is assumed for the residues, an adiabatic temperature rise of the order of 250 °C would be expected on decomposition.

The ad hoc tests with the heated block show that slow decomposition builds up to a rapid reaction with the temperature of the remaining materials often exceeding 500 °C sometimes with flame. The autoignition temperature determinations showed that all mononitrotoluene isomers will be ignited by a temperature over 475 °C in the standard apparatus and it can also be assumed that any flammable atmosphere in the still base would be ignited by a flame.

There is therefore experimental evidence to suggest that the events leading to the original ignition in the vessel are based upon self-heating of unstable residues in contact with the steam pipes followed increased exothermic reaction. This produced sufficient energy to ignite a mixture of mononitrotoluene vapours or decomposition products, either by autoignition or by a flame. The sequence of events following the first ignition is consistent with the fuel-rich flame in the vessel drawing air in through the manhole, this flame heating the residues in the vessel to deflagration. However, the energy from the exothermic decomposition could have been sufficient to heat the residues in the vessel to deflagration. Several samples showed the propensity to deflagrate, heightened by increased temperature. Once deflagration is established there is no further need for ambient air, or oxygen, this being consistent with the violent ejection of flame from the front, horizontal facing opening in the tank and also from the small vent on the top of the tank.

7. Conclusions

1. With the exception of one sample from the skip, no samples from the still base or the skip in front of the still base exhibited any energetic properties, due to fire or water damage. The work described in this paper was on samples taken from up-stream and down-stream of the still base, thought to best represent the contents of the still base itself.
2. The primary ignition inside the vessel was not due to autoignition of gases or vapours on the heated pipes of the steam battery.
3. Although some of the concentrated residues from the vessel were marginally impact sensitive in a certain specified test, it is unlikely that the first ignition was due to impact from the metal rake. However, the probability an ignition would have been reduced by the use of a wooden scraper or rake, or by using another cleaning method such as high-pressure water.
4. It is considered unlikely that the first ignition was caused by static electricity.
5. The most likely cause of the first ignition was self-heating of residues by contact with the steam pipes. There is experimental evidence to suggest that typical residues are unstable at the temperature of these pipes and are capable of then undergoing exothermic decomposition.

6. Such decompositions have been shown to be capable of producing temperatures above the autoignition temperature of mononitrotoluenes and can progress into flaming combustion.
7. Typical concentrated residues have shown the ability to deflagrate, whilst some that do not react at ambient temperature are sensitised by an increase in the temperature.
8. The jetting behaviour from the still base has been reasonably well reproduced by heating reduced residues from 193 store in a non-scale model.

References

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