

The explosion at the Dow chemical factory, King's Lynn 27 June 1976



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A report by HM Factory Inspectorate

The explosion at the
Dow chemical factory
King's Lynn
27 June 1976

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BEFORE An aerial view of the site taken some time before the date of the explosion.



AFTER This photograph is reproduced by courtesy of the Chief Constable of the Norfolk Constabulary. It shows the Clopidol plant at the centre of the explosion (mid-foreground), and damage to the roofs of nearby warehouses. The site plan on the centre pages shows the detail of the plant and the spread of the debris flung out by the force of the explosion.

This is the first of a series of OCCASIONAL REPORTS of incidents involving loss of life, injury and/or damage to plant, where it is thought that the publication of a report of an investigation undertaken by the Health and Safety Executive is in the interest of the public and will be of value to those concerned with occupational health and safety.

Acknowledgement is due to the Dow Chemical Company Ltd for their assistance and for permission to reproduce the photographs and site plans in the report.

Summary

1 On Sunday 27 June at approximately 17.10 hours, an explosion occurred at the Dow Company's chemical factory in King's Lynn, Norfolk, killing one man and causing extensive damage to plant and buildings on the site. Debris was scattered over a wide area and some substantial metal fragments were found outside the factory, but only minor damage was caused to property and no one outside the factory was injured.

2 The explosion involved a detonation of Zoalene, a poultry feed additive, which had been left inside a closed dryer vessel for a period of twenty-seven hours after the drying process had been completed. The insulation of the dryer maintained the Zoalene at a temperature between 120° and 130°C, and under these conditions the Zoalene began to decompose, with the evolution of heat causing self-accelerating decomposition which led to detonation.

The site

3 The factory forms part of an industrial area about a mile from King's Lynn. Two petrol storage and distribution depots and a large timber yard are also situated in the area, which is about three-quarters of a mile from the new North Lynn industrial estate.

4 The factory site is in the form of an equilateral triangle (see pages 10 and 11), bounded by the Great River Ouse, a timber yard and a factory. Private housing in the vicinity consists of a row of cottages, ten bungalows and a single cottage opposite the main factory entrance. Two schools accommodating about 570 children are within three-quarters of a mile of the site.

5 Seven continuous-operation chemical process plants are located on the factory site, each plant operationally independent and highly automated. The operating personnel rarely exceed three or four people per shift in each plant.

6 A total of 300 people are employed in the factory, which manufactures a range of chemical products, plastics and agricultural and veterinary products, but at the time of the explosion only nineteen people were on the site.

Development of the Zoalene process

7 Zoalene (3,5 di-nitro ortho-toluamide) was initially developed and manufactured by Dow at their headquarters in Midland, Michigan, USA, in 1959, and it had also been made at the King's Lynn factory up to five or six years ago.

8 The patent rights have now expired and the material is made by a number of firms in various countries throughout the world, including France and Spain. There are currently no known producers of Zoalene in the United Kingdom.

9 Early in 1975 it was discovered that the stocks of Zoalene at King's Lynn were low in infra-red assay, being of only 96-98 per cent purity instead of the minimum 98 per cent demanded by the specification of the Medicine Inspectorate of the Department of Health. The low assay was caused by the presence of impurities, principally water.

10 In the spring of 1975 it was decided to re-dry between 75 and 92 tonnes of the below-specification Zoalene using the dryer in the 'Clolidol' plant. Before implementing the decision the then-known hazards of Zoalene were re-checked. Several batches were re-dried in June and July 1975 and the plant was shut down again.

The Clolidol plant

11 The process building was approximately 40 metres long by 10 metres wide and sited about 150 metres from the western boundary of the works, 350 metres from the eastern apex and mid-way between the northern and southern apexes. The building was of two storeys, the north wall being of substantial brick construction, the south wall of light construction with steel cladding and the eastern wall was of brick, approximately 50 per cent of which was relieved by double-swing doors. The western walls were of brick. The floor between the two storeys was of steel plate and the internal walls were of twelve inch brickwork. Plans of the ground and first-floor levels of the building are on page 6. Adjacent buildings are the latex plant to the north, the Dowicil plant to the south-west and No. 2 warehouse to the east.

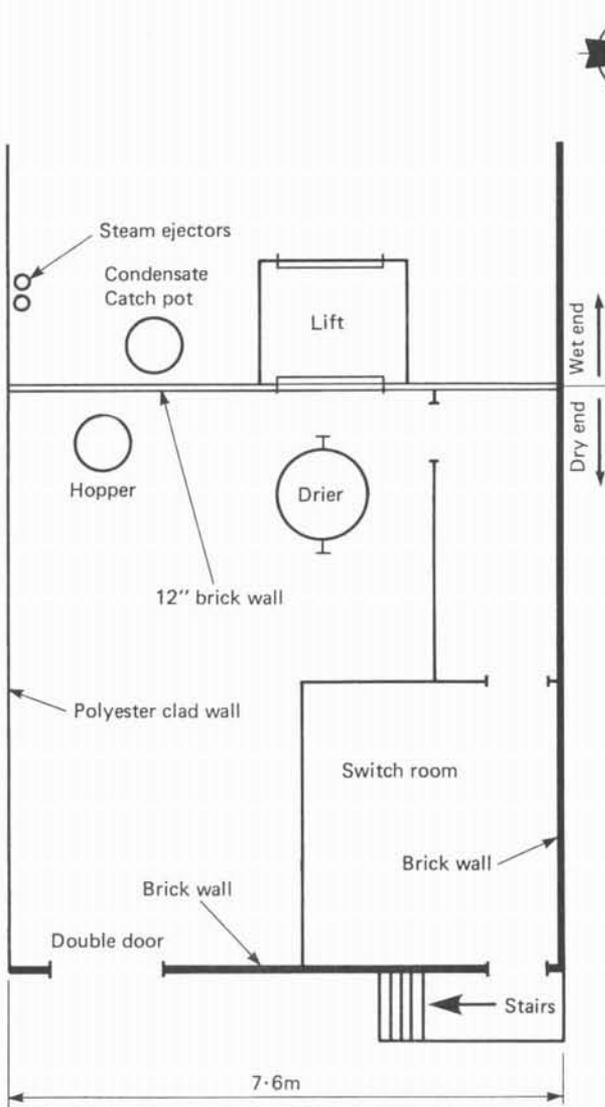
12 The plant was designed to manufacture and dry

Clopidol which is also a poultry feed additive. The primary risk associated with processing this material was believed to arise from the possibility of a dust explosion if finely divided material became dispersed in air. The plant and building were designed with this risk in mind and explosion relief, nitrogen inerting and Graviner dust explosion suppression devices were fitted to the plant handling the dried material.

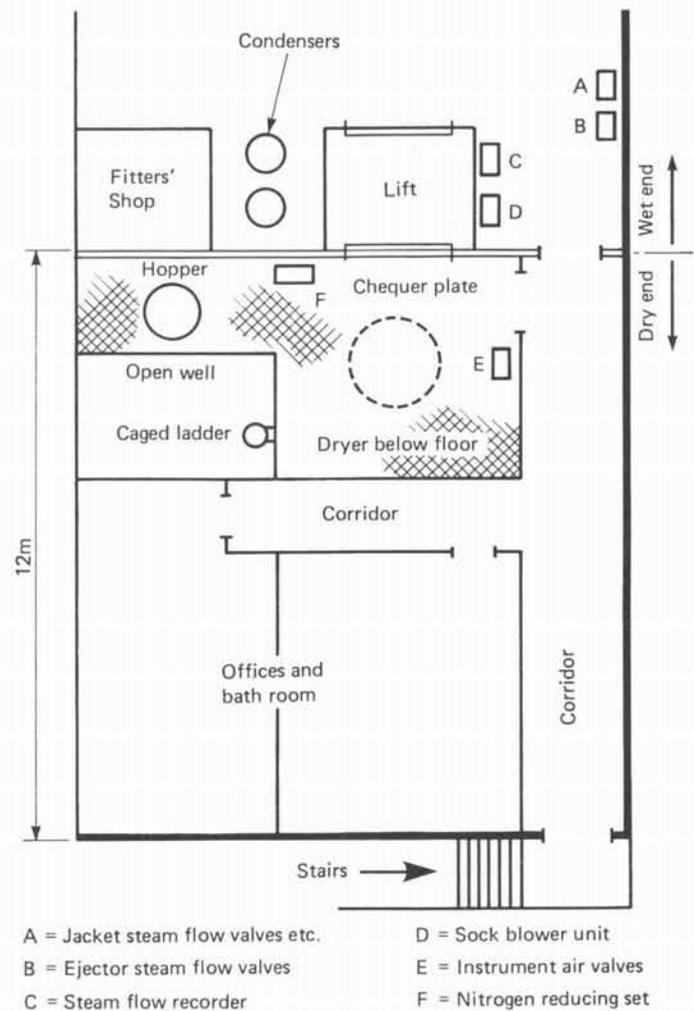
13 At the time of the explosion Clopidol was not being manufactured and the dryer, conveyor, holding hopper and grinding and bagging plant were being used for the Zoalene drying operation. A chemical description of the nature and process of manufacture of Zoalene is contained in the Appendix on page 17, and a diagram of the Clopidol dryer and associated plant is on page 7.

14 The dryer was a double-coned glass-lined steel vessel of $\frac{5}{8}$ inch mild steel with a lagged steam jacket of $\frac{3}{8}$ inch mild steel, with openings at the top and bottom for charging and discharging. Access to the charging opening was by means of a trap door in the steel plate of the first floor. The overall height of the drier was 2.34 m, with diameter 1.8 m, and it was mounted so as to rotate about its horizontal axis. This rotation was achieved by means of an electric motor operating through a gearbox to give speeds between one and eleven rpm. The dryer could be operated under vacuum, the air being withdrawn by steam ejectors.

15 After drying, the contents were discharged through a removable flexible sleeve to a Redler conveyor which transferred the material to a hopper from which it was discharged through a screw conveyor and grinder into



Ground floor plan – Clopidol plant



- | | |
|-----------------------------------|---------------------------|
| A = Jacket steam flow valves etc. | D = Sock blower unit |
| B = Ejector steam flow valves | E = Instrument air valves |
| C = Steam flow recorder | F = Nitrogen reducing set |

First floor plan – Clopidol plant

plastic kegs. The dryer and grinder were located in a separate room on the ground floor at the eastern end of the Clopidol building. The holding hopper spanned the space between the ground and first floors, and the conveyor passed from the ground floor to the top of the holding hopper.

The process

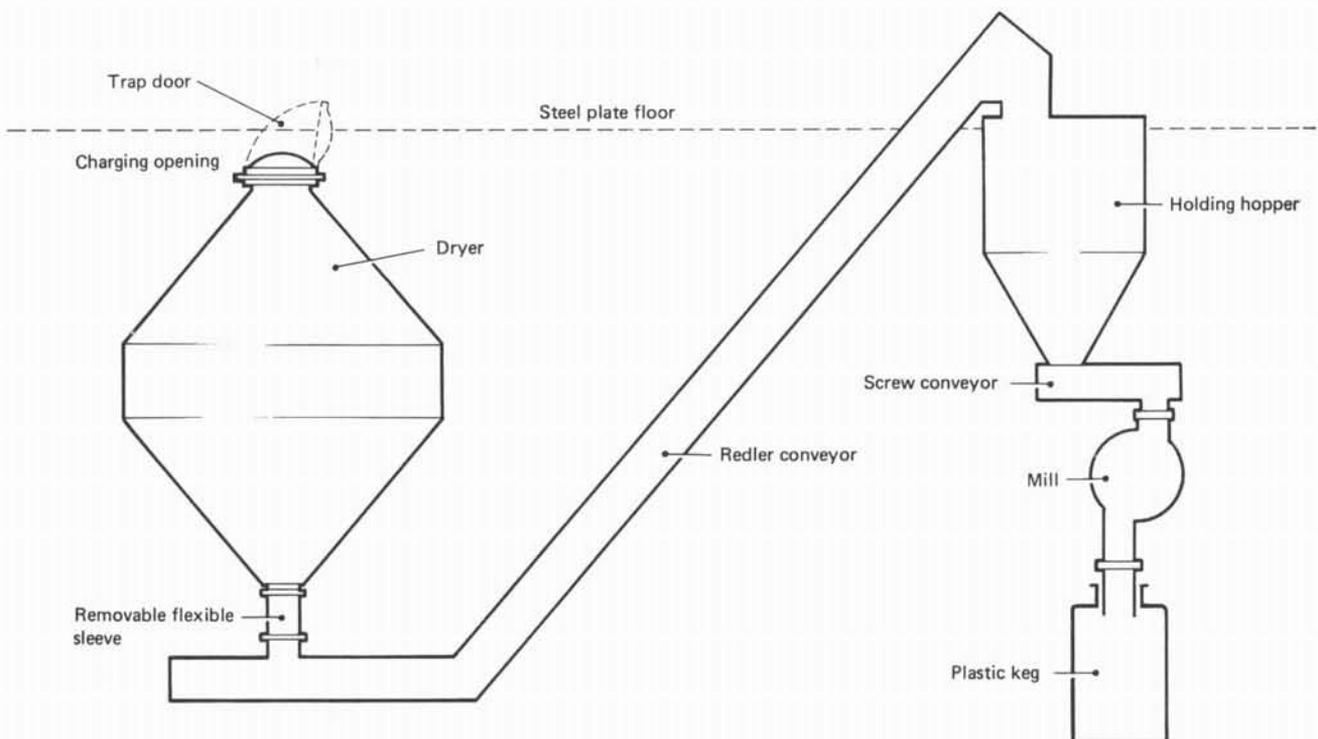
16 Zoalene was loaded into the dryer by hand from sacks, using a removable charging hopper. The total weight charged into the dryer varied, but the weight on 2 June at the start of the drying run was 1450 kilograms. During and after charging, the Zoalene in the dryer was wetted with water. After wetting, the lid was clamped and sealed over the charging opening and the dryer set in motion at $1\frac{1}{2}$ rpm. Steam was then admitted to the jacket at about 40 psi, producing a jacket temperature of approximately 130° to 140°C , and a vacuum of about 25 inches of mercury applied to the drier vessel. Water and other volatile substances driven off from the Zoalene were condensed in a catchpot.

17 The batch was left rotating under these conditions of temperature and vacuum. Occasional checks were made on the pressure and on the water level in the catchpot until it was seen that no more water was being condensed into the catchpot, a process which normally took twenty-four hours. The final temperature reached by the Zoalene would have been between 120° and

130°C . The steam supply to the jacket and the ejectors was then turned off, the vacuum broken with air through the valve at the catchpot and the dryer stopped with the charging opening at the top. The material was then discharged, ground and collected. Because the Clopidol process was not in operation, the charging of the Zoalene into the dryer and the discharging, grinding and packing were carried out by the day-shift crew of two men under a day-shift superintendent. This crew worked normal day-shift hours only, that is, from 0800 hours to 1600 hours on Mondays to Fridays inclusive.

18 When the Zoalene drying continued outside normal day-shift hours, the shift process foreman from the adjoining Dowicil plant, which was operating continuously twenty-four hours a day on seven days a week, would make occasional checks on the drier in the Clopidol building and would decide when drying was complete. He would then shut off the vacuum and the steam supply to the jacket and stop the dryer. He would then usually lift the lid of the charging opening and inspect the contents of the dryer. The charge would be left in the dryer until the day-shift crew was available; discharge would not be carried out by the shift process personnel.

19 The method used to dry the Zoalene in 1975 differed from the process at the time of the explosion in that in 1975 the Zoalene was slurried in a separate vessel and pumped through a filter into the dryer. The method of drying and subsequent handling in use in June 1976



Clopidol drying and packing plant

were, however, as described, and it appears that materials could have been left in the dryer for periods of twenty-four hours or more before transfer to the holding hopper. Although the Clopidol plant had originally been fitted with dust explosion suppression equipment, the adoption of the plant for Zoalene processing had shown an appreciable leakage of dust which necessitated fitting exhaust ventilation to the elevator and hopper.

20 A processing problem had arisen during the drying of Zoalene from the tendency of the dried material to build up as a hard cake on the sides of the drier. At approximately every third batch this cake had to be removed by half filling the dryer with water, after first discharging as much as possible of the previous batch. The dryer was then rotated and heated until the sides were clean. More Zoalene was then added from bags to make up a charge of approximately 1200 to 1400 kilogrammes, and the batch was then processed.

21 In the spring of 1976 a further demand for Zoalene was anticipated and on 2 June 1976 a consignment from Spain was processed. Of the ten batches processed three, including the batch which exploded, were batches resulting from washing the dryer. Only two

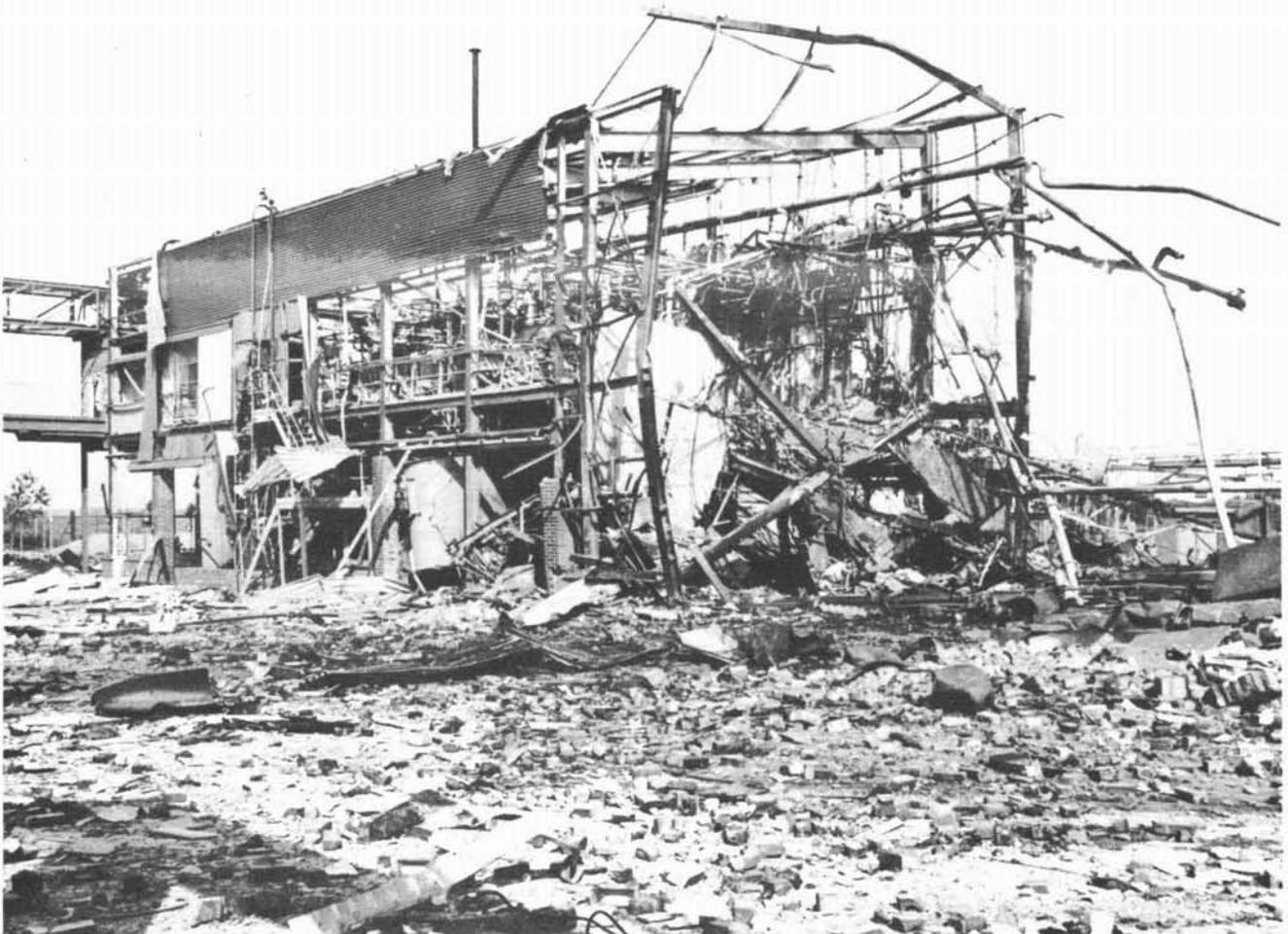
batches were left in the dryer for longer than twenty-four hours, though two others appear to have been left in for twenty-two hours.

The explosion

22 On Friday 25 June the day-shift crew had charged 350 kilogrammes of Zoalene from kegs into the dryer which already contained a slurry arising from residues of the previous batches. The quantity of Zoalene in the dryer is uncertain but it was probably about 1300 kilogrammes. Drying of this batch (No. 1066), the tenth of the run, commenced at 1500 hours on the same day.

23 The drying operation was checked by the Dowicil process foremen operating the evening and night shifts, and the catchpot was drained at 0900 hours on Saturday 26 June. At 1400 hours on that day the dryer was shut down, the steam supply to the jacket was turned off and the vacuum broken with air. The lid of the charging opening was lifted and the charge inspected. The dryer was left with the charging opening lid clamped loosely in place.

24 The foremen on the Saturday evening and Sunday morning shifts on the Dowicil plant continued their



The Clopidol building after the explosion.

routine checks of the Clopidol building and dryer and nothing abnormal was noticed. These were again checked at about 1540 hours on the afternoon of Sunday 27 June, and again nothing untoward was noticed.

25 At 1707 hours on the same afternoon the Dowicil shift foreman became aware of a hissing noise and saw white smoke pouring from louvres along the south side of the Clopidol dryer room. He sounded the fire alarm in accordance with the emergency procedure laid down and had just commenced telephoning the gatehouse through the 999 emergency system when an explosion occurred at 1710 hours. Emergency shutdown of all operating plants was carried out in accordance with the emergency procedures.

The fatality

26 The workman who was killed, Mr David Charles Walker, was an operator on the latex plant. He was a member of the works fire-fighting team and it appears that he was on his way to the team's assembly point when he was caught by the blast on the road at the north-east corner of the Clopidol plant.

Damage to buildings and plant

27 There does not appear to have been any external fire associated with the explosion apart from a minor one involving one of two Telone storage tanks, and this appears to have been extinguished almost immediately by the deluge system fitted to those tanks.

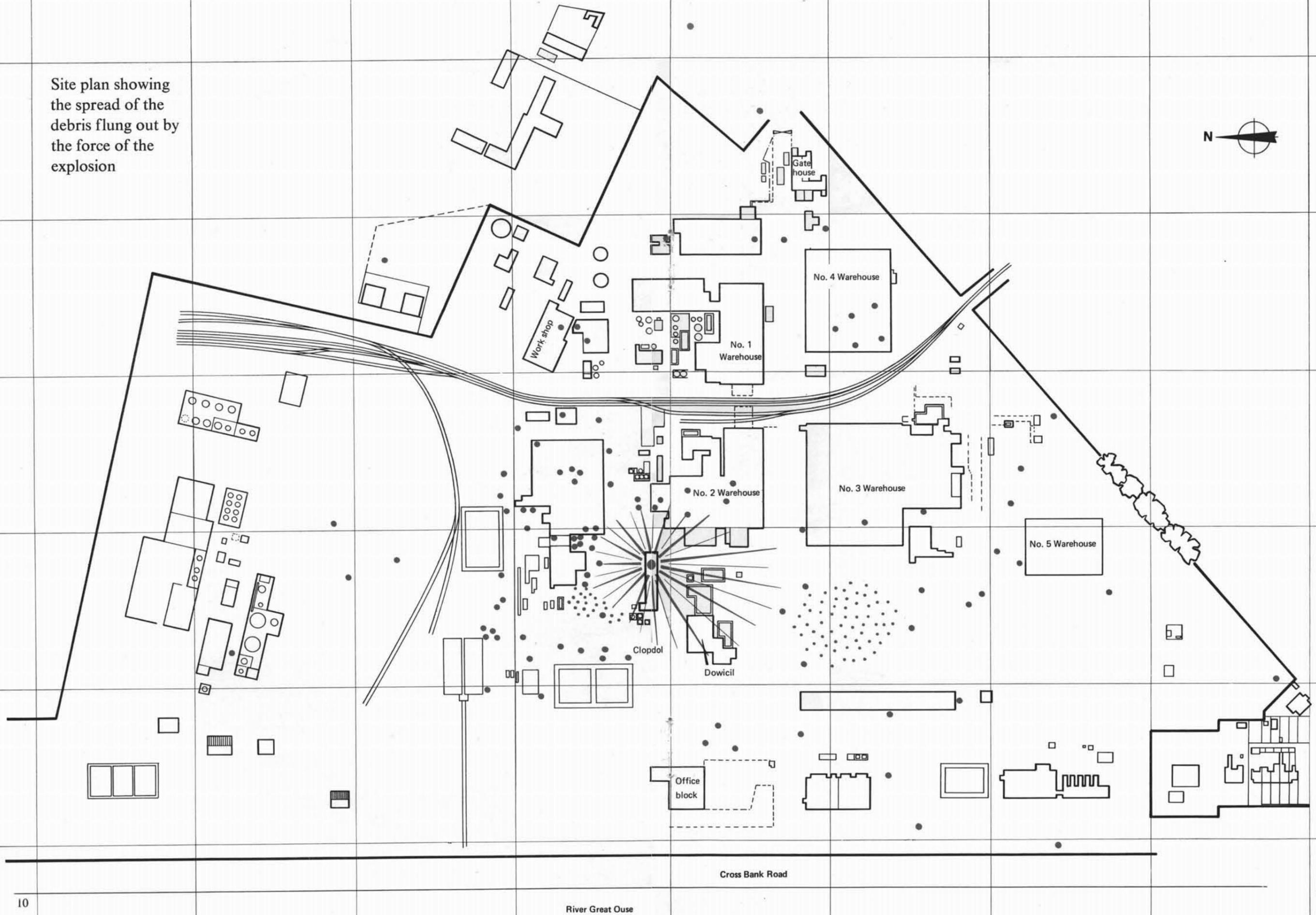
28 The Clopidol building had been designed with the possibility of a dust explosion in mind. Consequently it had been built with a lightly structured south wall which would relieve in the event of a dust explosion, leaving the rest of the structure largely intact. The explosion which occurred released considerably more energy than that available from a dust explosion, but the design minimised the damage to other areas of the factory.

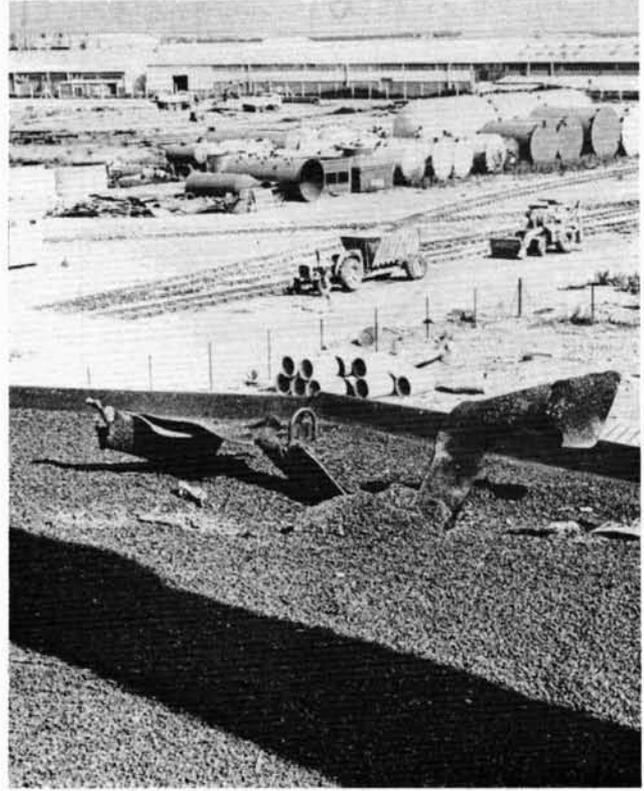
29 The entire eastern half of the Clopidol building was demolished, the dryer being fragmented. The conveyor and hopper were found some thirty metres to the south of their original position. Pieces of the dryer and its jacket were found a considerable distance from the site of the Clopidol building, as were pieces of the steel plate flooring and structural steelwork of the building. At least two substantial pieces of steel plate



Another view of the Clopidol building showing the collapsed pipe bridge.

Site plan showing
the spread of the
debris flung out by
the force of the
explosion





Top left A piece of steel flooring weighing 143 kg which was found over 200 metres from the centre of the explosion.

Top right Steel flooring embedded in the roof of the boiler house, 99 metres from the area of the explosion.

Lower A contractor's van parked about 90 metres away from the site of the explosion virtually sliced in two by a 10 metre length of RSJ.



Interior of a room off the No 2 warehouse showing roof damage and a collapsed cable tray.

were found outside the factory site, one in Cross Bank Road near St Edmunds Terrace and another near the wall of the cottage opposite the main gate. No major damage or injuries were reported from outside the site. However, a substantial number of windows were broken, and the ceilings of two cottages were brought down.

30 Inside the site there was considerable damage to the Dowicil building and No. 2 warehouse, where brick walls were demolished. Light cladding materials were stripped off building frames and asbestos cement roofs shattered. The south wall of the latex plant was cracked and some cement sheet shattered. Throughout the site windows were broken and asbestos cement roofs shattered by projectiles. A careful search was made for debris and nearly 100 identifiable fragments of varying sizes and weight were retrieved from many parts of the factory. The heaviest piece of debris found weighed 300 kilogrammes. Much of the debris was composed of twisted metal floor sections and RSJ's. One such RSJ

fragment weighing about 12 kilogrammes was found outside the factory about 700 metres from the centre of the explosion, while a 13.6 kilogramme piece of $\frac{1}{4}$ inch plate was retrieved from the river bank. Other smaller fragments of metal were found outside the factory. Total plant damage is estimated to be in the region of £1.25 millions.

Technical considerations

31 In view of the now known explosive potential of Zoalene and additional evidence later supplied by the Royal Armaments Research and Developments Establishment (RARDE) Woolwich, sabotage has been discounted. Likewise, other agencies which might have initiated an explosion such as friction and electrostatic charge are unlikely. Following a search of the debris, one of the steam isolating valves and one of the steam stop valves on the steam line to the dryer jacket were retrieved and found to be in satisfactory working order. The nature and circumstances of the incident suggest strongly that the explosion was caused by thermal decomposition of Zoalene. Accordingly an extensive investigation of the thermal behaviour of Zoalene was instituted by Dow and by RARDE.

32 Dow relied basically upon accelerating rate calorimetry (ARC) for their technical investigation. ARC is a new thermochemical technique which they themselves have developed. Their investigations showed that a typical batch of Zoalene could self-heat to destruction if held under adiabatic conditions at 120°–125°C for twenty-four hours. These conditions are very close to the actual conditions in the Clopidol dryer prior to the explosion, where it is estimated that the material would attain a temperature of about 130°C on completion of drying, falling to about 118°C after 27 hours. These conditions are essentially adiabatic, i.e. conditions in which heat neither enters nor leaves the system. Previous tests conducted by Dow in 1962 using differential thermal analysis (DTA) had shown that Zoalene exhibited exotherms (heat outputs) at 274°C and 284°C, i.e. at temperatures more than 130°C above those attained during drying. The ARC tests also showed that the presence of impurities in Zoalene may lead to a small but significant increase in the thermal instability of that compound. Identification of these impurities by high performance liquid chromatography (HPLC) is in progress and it is hoped to quantify the effect of impurities on the thermal behaviour of Zoalene.

- 33 The tests carried out at RARDE were of two kinds:
- (i) an examination of the explosive properties of Zoalene, and
 - (ii) an investigation of its thermal stability.

The explosive performance showed that Zoalene could liberate about 60 per cent of the energy available from the equivalent weight of picric acid but that it was not sensitive to shock or friction. Conventional vacuum stability of the material was good, and samples heated

at 140°C for 28 hours and at 150°C for 26 hours showed only darkening of the material. Differential scanning calorimetry (DSC) was applied to samples which had been preheated under similar conditions to those obtaining in the Clopidol dryer at Dow, and had shown exotherms at a lower temperature (248°–259°C) than samples which had not been so treated (273°C). These results provide evidence of the thermal instability of Zoalene in a qualitative sense, but do not provide the quantitative assessment available from ARC. Had DSC been applied by Dow before the reprocessing of Zoalene began, the results would not have alerted them to the unstable properties of the substance at temperatures as low as 130°C.

34 Decomposition of energy-rich (thermally unstable) compounds is accompanied by a release of heat with concomitant rise in temperature. The rise in temperature continues until a condition of thermal balance is reached, i.e. the heat evolved by the material is equal to the loss to the surroundings; otherwise the material heats itself to destruction. An everyday example of decomposition generating heat is the garden compost heap where the decomposition and heat evolution is slow and leads, without incident or hazard, to usable compost. If the conditions imposed on a thermally unstable material are adiabatic, or nearly so because of low heat losses due to bulk etc the process will always lead to self-destruction. An important factor to be considered is that of critical mass, which is the largest mass which can be in a state of thermal balance for a stated set of conditions, i.e. heat evolved equals heat lost, and is dependent on factors such as cooling area, specific heat etc. The simplest illustration is offered by comparing the behaviour of a compost heap with that of a decomposing haystack. The same process of decomposition is involved in each case, but the end result is markedly different; compost in the former instance and frequently a destructive fire in the latter.

35 The latter situation is similar to that which almost certainly occurred in the Clopidol dryer. The temperature in the dryer would have increased over the weekend at an ever-increasing rate until the Zoalene ignited and burnt to detonation. This would have manifested itself in an extremely rapid pressure rise to, probably, well over 10,000 psi, which forced the cover off the dryer and led to its rupture. This pressure rise would have occurred in a very short time span. The energy released in this event was approximately equivalent to 200–300 lb of TNT. Pieces of the dryer and metalwork from the structure of the plant were flung considerable distances. Pieces of the drier were also found with fused glass, originating from the liner, adhering to them, indicating that a temperature in excess of 800°C had been reached before detonation.

36 Calculations have shown that the failure of the drier would have taken place in two stages. The lid, which was held only by a hinge and one clamp, would fail at about 100 psig, whilst the drier itself would have

failed between 600 and 750 psig static loading. Pressures of up to 12,000 psig in the shock wave would have generated inside the drier at detonation.

Observations

37 Investigation of the circumstances under which this explosion occurred have required detailed examination of the current state of knowledge of the known properties of Zoalene. It has also entailed a review of the Dow management structure and its effectiveness.

38 It is considered that the management of the King's Lynn factory could not reasonably have been expected to know of the exothermic properties of Zoalene and its detonation characteristics at the temperatures at which the dryer vessel was operating. Zoalene is only one of many thousands of reactive chemicals being handled by Dow internationally, and although the company's own newly developing research technique of accelerating rate calorimetry (ARC) could have revealed those characteristics, in the judgment of those responsible in the USA for the application of the technique there was no reason to give priority to Zoalene for ARC treatment. An investigation by means of differential scanning calorimetry of the explosibility of Zoalene undertaken at RARDE after the explosion gave results near enough to those obtained by Dow using DTA in 1962 to suggest that the decision not to submit Zoalene to early ARC investigation was not unreasonable.

39 It is clear, with hindsight, that the hazard evaluation of Zoalene by Dow's reactive chemicals committee on the basis of the application of differential thermal analysis (DTA) was inadequate and indeed misleading to a plant superintendent who relied upon that evaluation for his guidance.

40 The Clopidol plant superintendent was not aware that ARC techniques were available, neither was he aware of the inadequacies of DTA as a hazard evaluation technique.

41 Dow have no ARC facilities in Great Britain. Basic ARC development has been carried out in Midland, Michigan, USA, the company's international research and development headquarters, with a second less developed unit at the firm's laboratories in Terneuzen, Holland.

42 The company, as part of their safety and loss prevention programme, have a reactive chemicals advisory board in Midland, Michigan, with the function of approving equipment and procedures for basic hazard evaluation tests, and of co-ordinating and directing the manufacturing divisions of the company in establishing their own reactive chemical committees in Europe and the UK.

43 It was at the instigation of the reactive chemicals committee that screening tests had originally been carried out upon Zoalene. These tests included differential thermal analysis (DTA), shock sensitivity, flammability

tests and thermodynamic computations. It was clearly recognised that the different environments existing in the laboratory, in manufacturing and in storage would have significant effects on the reactive properties of any materials. It was also recognised that a large number of other tests and hazard evaluation techniques were being developed. One such technique being developed, accelerating rate calorimetry, is described in Appendix 3. This technique was new at the time of the incident. Out of thousands of chemicals handled by Dow internationally, relatively few runs had been made by the ARC equipment on a number of products none of which appear to have been handled at the King's Lynn factory. It has been estimated that 5 per cent of all Dow chemicals had been tested by ARC at the time of the incident. The ARC techniques are not mentioned in the reactive chemicals hazard evaluation programme safety and loss prevention book, dated August 1969. The King's Lynn factory had no control in deciding on the priorities or criteria for chemicals to be tested by ARC. It is understood that these priorities were based on the following considerations by Dow in Midland, USA:

- (1) a history of past incidents
- (2) whether the product was in widespread use
- (3) where a large amount of chemical knowledge existed about a specific chemical with a view to confirming that knowledge.

Zoalene failed to qualify as an early candidate for testing under any of the above headings.

44 No separate process procedures had been prepared for the original manufacture of Zoalene or the redrying of the out-of-specification material. It appeared to Dow that the Clopidol plant drying procedures were completely suitable and that no separate Zoalene procedure was necessary. Nevertheless it appears that the Clopidol plant specification was amended insofar as it related to drying rate and the use of inert nitrogen for breaking the dryer vacuum, which were the subject of separate instructions to the operating staff. No instructions had been prepared concerning the handling of dried Zoalene or for its discharge from the vessel on the completion of drying. The exothermic properties of Zoalene at the low temperatures prevailing were not then appreciated, so the need for special instructions was not recognised. On the other hand, Zoalene was known to be a reactive chemical and on general grounds the material should not have been left for this period of time in a process vessel at an elevated temperature.

45 The decision to reprocess the out-of-specification Zoalene was not taken lightly. It was taken deliberately, after a meeting of senior personnel and in the light of the information then available about the properties of Zoalene. In the view of the Dow management when the decision was taken, the redrying process consisted merely of the reintroduction of the tail-end of a process that had been successfully carried out over a number of years.

46 Since Zoalene had been manufactured by the company in USA for some fifteen years, apparently without incident, and since the redrying operations at King's Lynn during 1975 and earlier in 1976 under conditions of temperature and vacuum substantially similar to those pertaining at the time of the explosion also were carried out without untoward incident, the question arises why there had not been an earlier explosion when Zoalene was being dried, especially as some previous batches had apparently been left in the dryer vessel for a period of about twenty-four hours. No clear answer has been found to this question.

47 It would appear that the following factors may have been relevant in the circumstances which led up to the explosion.

(1) This batch probably contained a higher proportion of impurities than most batches because of the presence of rewashed material, a proportion of which may have undergone a number of heating cycles.

(2) The long period, exceeding twenty-four hours, during which a material known to have a history of thermal instability was retained in the dryer vessel at an elevated temperature.

(3) The fact that the dryer vessel was not cooled by passing cold water through the jacket, as had apparently been done when Zoalene was dried during the former manufacturing process at King's Lynn. This cooling had been undertaken for ease of handling the material rather than from considerations of safety; nevertheless, if the dryer had been kept cool in this way, it is likely that this unforeseen and possibly unforeseeable explosion would not have occurred.

(4) The possibility that the batch which exploded in the dryer therefore had not only been dried but had been cooked. It was dry by 1200 hours on Saturday 26 June and further drying up to 1400 hours on Saturday may have had the effect of cooking and heating it.

(5) The absence of an accurate temperature and moisture indication system on the dryer and its jacket. Accuracy of moisture indication relied entirely on the operator's observation of water draining into the catchpot. There were no temperature sensing or recording devices or temperature override and cut-off devices fitted. Although the knowledge Dow possessed at that time about the chemical properties of Zoalene may not have positively indicated the need to fit such devices on the dryer, sufficient was known about the general characteristics of the substance to suggest that their use would have been advisable.

Safety organisation

48 Dow has a written safety policy for the King's Lynn factory. The safety organisation aims at a consistent approach to identify hazard potential, and the company has issued a series of training manuals and

safety and loss prevention guides, including one concerned with reactive chemicals hazard evaluation. There is an emergency procedures plan for the factory, last revised in August 1975, and it appears that those procedures were followed when the explosion occurred. The formal organisation for safety at the factory consists of ten joint accident prevention committees, each covering a separate plan or operating area. There is a monthly site safety council chaired by the works manager which is attended by plant superintendents and foremen and by shop floor personnel in rotation. Site safety audits are understood to be carried out annually by the appropriate American Corporate headquarters; three or more times a year by the European Safety and Loss Prevention Group; and four times a year by the works management. There is an experienced and qualified safety officer who is responsible for non-process safety including the evaluation and monitoring of safety systems and procedures and operator training. He reports to a European Safety Manager based in Switzerland. The factory management is responsible for process safety, and plant superintendents and process engineers are qualified in a relevant discipline. There is a procedure for training plant operators in the safe operation of process plant.

Management structure.

49 The headquarters of the Dow Chemical Company is in Midland, Michigan, USA, and its operations are international. The organisation is such that while every plant has access to the full scientific and technical resources of the company, there is sufficient autonomy at plant level to ensure that there can be a prompt response to local needs, and local management is held accountable for the effective operation of each plant, in respect of safety no less than in other respects. The Dow management failed to prevent this explosion at their King's Lynn plant. It does not appear, however, that this failure is properly attributable to any defect in the management structure or organisation; it is attributable rather to the lack of a full knowledge (at all levels of the organisation) of the chemical properties of Zoalene. A failure of this kind, in the circumstances in which it occurred at King's Lynn, is not explicable in terms of any specific defect of management structure or organisation.

Inspectorate involvement

50 Since the factory contains substantial quantities of both toxic and flammable materials, it has been the subject of inspection over the past two years. Because of the complexity and divergency of the industrial processes carried on in the factory it was divided into four inspection units, one of which was the Clopidol plant. This was inspected in February 1975 and a detailed assessment made of the process risks then seen. The last visit by the Inspectorate to the factory prior to the incident was on 6 April 1976. The earlier pro-

cessing of Zoalene and the later redrying of this material in the Clopidol dryer were not known to the Inspectorate and there had been no discussion between the Inspectorate and Dow as to the safety of the drying operations or the handling of the Zoalene product.

Action following the incident

51 The following is a summary of the action that has been taken arising from the explosion on 27 June 1976.

(1) An immediate decision was taken by the United Kingdom Managing Director of Dow to suspend any further Zoalene processing or handling in the United Kingdom.

(2) Dow employed an international team of experts and the company's own considerable research facilities to investigate the problem posed by this explosion. After ARC had revealed the instability of Zoalene, Dow realised that the information they obtained was of the greatest significance to the chemical industry at large and it was disseminated widely throughout the industry.

(3) At King's Lynn the company immediately commenced a further re-examination of existing reactive chemicals, using, where appropriate, the new ARC technique.

(4) Dow has also commenced a review of its organisation and training for safety. As part of this they propose to have a safety superintendent continuously monitoring changes in plant processes, and he will communicate and co-operate with other parts of the company as necessary. The King's Lynn factory has also equipped those concerned with pocket beepers to improve communications, and radio telephones will be used rather than relying on the public telephone system when it is necessary to communicate with a person who is not on the site.

(5) Dow have reviewed their arrangements for handling and storing hazardous substances upon the site and made a number of detailed improvements aimed at increasing their security in the event of an explosion, even though no material other than Zoalene was involved in or affected by the explosion on 27 June.

(6) Large quantities of hazardous materials are stored and used on the King's Lynn site. This severe explosion caused extensive damage on the site, but it did not cause any of the hazardous substances to be liberated; this is attributable in a large measure to the care that Dow took in locating their storage facilities upon the site and emphasises the importance of such planning in chemical works; nevertheless the Health and Safety Executive is undertaking a comprehensive appraisal of the nature and degree of the hazard that arises from Dow's King's Lynn operation. This report will be drawn to the attention of the Advisory Committee on Major Hazards of the Health and Safety Commission.

Conclusions

52 There is no doubt that the explosion was caused by an exothermic decomposition of Zoalene held under adiabatic conditions in the Clopidol plant dryer vessel for twenty-seven hours at a temperature between 118°C and 130°C.

53 There appears to be no substantial grounds for criticising the Dow management or operating personnel for undertaking and conducting the operation that led to the explosion in the way they did. None of the hazard evaluation techniques available to the King's Lynn factory would have predicted the danger of the drying operation. There was a general lack of knowledge of the destructive potential of Zoalene at such temperatures in adiabatic conditions. This lack of knowledge was the fundamental reason for the explosion that occurred.

54 Nevertheless, with hindsight it is apparent that in view of Zoalene's general characteristics the following matters should have received closer attention:

- (1) The incorporation, in the case of certain batches,

of re-washed material likely to contain a higher proportion of impurities.

- (2) The length of time during which batches were retained in the vessel after processing.
- (3) The procedure for cooling the material.
- (4) The instrumentation in respect of temperature and moisture content.

Recommendations

55 It is recommended that manufacturers and users of substances that are liable to exothermic reaction (and in particular nitro-aromatic compounds) in any condition of process or of use should re-appraise the explosive potential of those substances in near adiabatic conditions. Attention is drawn to the value of ARC for the purpose of such investigations. It is also important that those who are concerned with the processing of such materials should ensure that the known and likely effects of their decomposition are taken into account at the design stage, and further that the implications of variations from normal practices are fully understood by all concerned before such variation is made.

Appendix 1 Zoalene: technical information

1 Zoalene is the Dow registered trade name for 3, 5 di-nitro ortho-toluamide. The chemical synonym is 2. methyl 3, 5 di-nitro benzamide. It is also referred to as DOT or DNOT.

2 The material is a coccidiostat for the poultry industry and has a crystalline powder form. It is blended with wheat middlings to form a poultry feed additive sold as Zoamix. Zoalene has been manufactured by Dow Chemical Company at Midland, Michigan, USA, since 1959, and from 1961–71 it was manufactured at King's Lynn intermittently.

3 The summary of the processes used in Zoalene manufacture is as follows:

- (i) 3, 5 di-nitro-ortho-toluic acid, DNCTA, was dried azeotropically by distilling off the water with perchlorethylene.
- (ii) The resulting perchlorethylene DNOTA slurry was pumped to the reactor vessel and treated with phosphorus pentachloride at a temperature of between 50°–60°C, producing 3, 5 di-nitro-ortho-toluy chloride.
- (iii) The 3, 5 di-nitro-toluy chloride was then pumped at a controlled rate into the amidation vessel which contained aqueous ammonia. The temperature was kept below 50°C by the circulation of refrigerated brine through the vessel's jacket. 3, 5 di-nitro-ortho-

toluamide (Zoalene) was precipitated as a finely divided solid.

4 The resulting slurry was filtered and washed, dug off into drums and trays for drying.

5 Up to about 1970 the product was dried in trays in ovens, but after that time a Pfaudler type CD 48 vessel was used.

6 The CD 48 dryer vessel operated under the following conditions:

- (a) The vacuum was as high as possible, i.e. about 27 inches of mercury.
- (b) Steam at 45 psig was admitted to the dryer jacket, to produce a temperature of about 140°C in the jacket.
- (c) The dryer was rotated slowly at first, that is, two turns every thirty minutes for the first two hours, followed by steady rotation at 2 rpm for the next two hours. The dryer was then rotated at 10 rpm until the batch was dry.
- (d) When the batch was dry, the steam to the jacket was turned off and the vacuum released. In order to permit immediate handling, the batch was cooled by passing cold water through the jacket for about forty minutes. The batch was then collected in drums and if necessary ground.

Appendix 2 Commentary by HM Inspector of Explosives

Decomposition of energy-rich compounds is accompanied by a release in heat with consequent rise in temperature. The temperature will increase until a condition of thermal balance occurs, i.e. the heat evolved by the material is equal to the loss of heat to the surroundings, or the material is completely decomposed. If the conditions imposed on the material are adiabatic, or nearly so, the process will always lead to complete decomposition. This statement is based on a concept of Frank-Kamenetskii, i.e. that of critical mass. The critical mass is the largest mass which is in thermal equilibrium for a stated set of conditions, i.e. heat evolved is balanced by heat lost. The critical mass is obviously a function of the environment and the physical properties of the material; factors such as cooling area and specific heat are important.

The temperature rise due to self-heating follows an accelerating course, since the rate of decomposition is essentially exponential. This type of decomposition can result in anything from gassing of the material to an explosion. It is fairly difficult to predict what will happen at this point without an exhaustive and detailed series of tests to determine the chemical, physical and explosive properties of the sample. Factors such as particle size, packing density and critical diameter (see glossary) determine whether the sample proceeds to explosion or detonation or just burns.

After completion of drying, the charge of Zoalene in the dryer at King's Lynn has been estimated to have cooled from 130°C to 118°C over a period of twenty-seven hours. Under these virtually adiabatic conditions the stage was set for a self-accelerating decomposition as described above. The evidence suggests that on this occasion the temperature of the Zoalene had been rising at an ever-increasing rate until it finally ignited and then burned to detonation. This manifested itself in an extremely rapid pressure rise to, probably, 12,000 psi in the shock wave, forcing the cover off the dryer and leading to its rupture. It is estimated that the cover would have been forced off at a pressure of 100 psi and that rupture of the dryer would have occurred at 750 psi. This pressure rise would have occurred in a very short time span. The energy released in this event was approximately equivalent to 200–300 lb of TNT. Pieces of dryer and general debris and metalwork from the structure were flung considerable distances. Pieces of dryer were also found with fused glass, originating from the liner, adhering to them, indicating that temperatures in excess of 800°C had been reached before detonation.

The investigation from this point resolved itself largely into a question of how to substantiate the above hypothesis, and a thorough investigation of the thermal properties and explosive performance of Zoalene was instituted by Dow and RARDE.

Dow based their approach largely on the use of

accelerating rate calorimetry, a new thermochemical technique which they themselves have developed. They found that typical production samples of Zoalene would self-heat to decomposition if held under adiabatic conditions at 120°C to 125°C for twenty-four hours. (Although this is a bald statement of fact, Dow scientists did a great deal of work to achieve the result.) This result is direct evidence of the phenomena postulated as having occurred in the Zoalene dryer. Dow have also shown that the presence of impurities in Zoalene may lead to a small but significant increase in the thermal instability of that compound. Identification of the impurities by high-performance liquid chromatography (HPLC) is in progress and it is hoped to quantify the effect of specified impurities on the thermal behaviour of Zoalene. Although Dow will not now process Zoalene in the UK, this information will be of value for operations elsewhere.

The work at RARDE falls into two categories; examination of the explosive properties of Zoalene and an investigation of its thermal stability. Under the first heading it was found that using a ballistic mortar with a No. 8 detonator, Zoalene gave an energy output of 50–60 per cent of that of an equivalent weight of picric acid. Time versus pressure studies show that Zoalene exhibits a pressure rise from 100 psi to 300 psi in approximately 900 milliseconds (compared with values of 100 milliseconds and 1700 milliseconds for trinitrobenzene and p-dinitrobenzene respectively). The Koenen test gave a minimum venting aperture of 1 mm diameter. These results illustrate the explosive potential and hazard associated with Zoalene.

Conventional vacuum stability showed good thermal stability for Zoalene; when heated at 120°C for forty-eight hours only 0.38 ml of gas was evolved. Similarly samples heated at 140°C for twenty-eight hours and 150°C for twenty-four hours showed only slight darkening of the samples which may have indicated the onset of decomposition. Auto-ignition tests on the sample gave results ranging between 216°C and 303°C. When Zoalene was tested by a differential scanning calorimetry technique, scanning from room temperature at a rate of 10°C/min showed an endotherm (heat input) at 178°C (melting point) and an exotherm (heat output) at 273°C. A parallel run starting at 50°C gave an endotherm at 178.5°C and an exotherm at 274°C. Samples were then preheated for various periods and then tested by DSC. A sample heated to 130°C for 16 hours and then cooled to 50°C and scanned at 10°C/minute showed an endotherm at 179.5°C and an exotherm at 259°C. Another sample heated at 127°C for twenty hours and then scanned at 10°C/minute showed an endotherm at 176.5°C and an exotherm at 248°C. Although these results provide definite evidence of the thermal instability of Zoalene, in a qualitative sense they do not match the more precise assessment available from ARC. The main reason for this disparity is that

ARC offers the opportunity to study thermal processes under adiabatic conditions. It is believed that the Dutch testing authority TNO are developing a seemingly similar technique.

Glossary

Zoalene: 3, 5 di-nitro-ortho-toluamide.

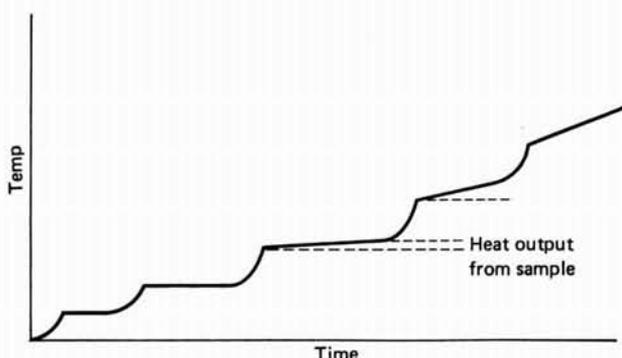
Detonation: a process whereby a chemical reaction proceeds through a reactive material at velocities greater

than sonic for that material. The effect of detonation is severe and is typified by severe ripping of metal structures and shrapnel formation.

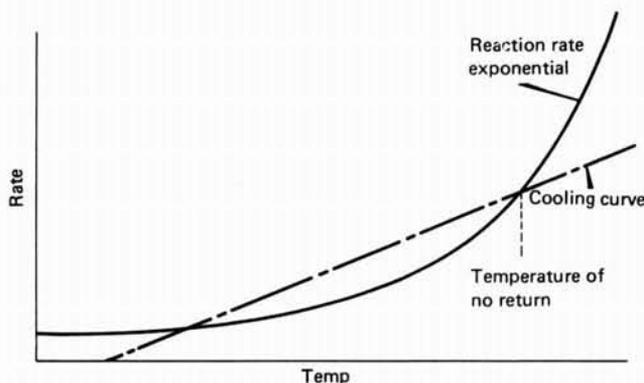
Diameter effects used as a criterion of explosibility. The shock front in a detonation is initially convex and at small charge diameters energy losses are such that propagation becomes impossible.

Appendix 3 Accelerating rate calorimetry

This new thermochemical technique has been developed by Dow to study chemical processes in terms of both rates of reaction and thermodynamic parameters. Basically the technique consists of heating a sample (typically 10 g) in a bomb, with a bursting disc of 1000 psi or greater, under adiabatic conditions and studying the temperature–time profile. A typical chart would be as shown.



The temperature is increased incrementally (typically by 10°C steps) until there is a measurable rate of increase associated with the test compound undergoing a chemical reaction. The rate of temperature rise is then recorded for various temperatures and the activation energy of the process can be calculated using the Arrhenius equation extrapolated back to any desired temperature. The information obtained can be plotted in a variety of ways, for example:



This form of presentation would be used typically to assist in plant design for a chemical reactor. The straight line represents the heat transfer characteristics of the chemical process and the equipment used and indicates that once the temperature of no return is reached the heat generated by the process is greater than the cooling properties of the system, and the temperature rises at an accelerating rate. Obviously, by improving the heat transfer properties the line has an increased slope and the critical temperature is increased. This technique can therefore be used to predict the temperatures and times within which a catastrophic event (such as a runaway reaction) will occur but it will not predict what the catastrophe will be (e.g. pressure burst, deflagration explosion or detonation) and to a large extent this is unpredictable.

The technique offers considerable advantages over other thermochemical methods such as differential thermal analysis (DTA) and differential scanning calorimetry (DSC). The major advantage is that the sample can be examined under adiabatic conditions. Furthermore, it may be considered that the test is a true scaled-down simulation of a reaction runaway.