



**RELEASE OF
CHEMICALS**
from
**INTERNATIONAL
BIOSYNTHETICS LTD**

A report of the investigation by the Health and Safety Executive
into the chemical emission from International Biosynthetics Ltd
on 7 December 1991



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Summary

1 At approximately 1130 am on 7 December 1991 some 3½ tonnes of chemicals were emitted from a reaction vessel at the factory of International Biosynthetics Ltd (IBIS), Lower Road, Halebank, Widnes, Cheshire. The cloud of vapour was blown by the wind 4 km, affecting about 60 people and staining some property blue. Some 35 individuals reported to local hospitals for treatment, but all were released after observation. The incident caused local concern about safety on the site and over apparent failings in the emergency response.

2 The process being carried out was a reaction between the very toxic substance phosgene and dimethyl aniline during the production of an industrial chemical. An unexpected chemical reaction led to over-pressurisation of the reactor and consequent failure of an inlet connection on a condenser. This resulted in the discharge of the reactor contents which were subsequently identified as N,N-dimethyl aniline, toluene, N,N-dimethyl amino benzoic acid and a small quantity of a blue by-product, gentian violet. The phosgene had fortunately been consumed in the reaction and was not detected in the release.

3 The incident is attributed to the unexpected presence of water in the reactor. This resulted in an exothermic (ie heat-producing) runaway reaction with the evolution of gas which could have been prevented if:

- (a) adequate thermochemical testing had been carried out;
- (b) the hazard assessment of the process had been sufficiently thorough;
- (c) the procedures for detection of water had not been flawed; and
- (d) sufficient account had been taken of problems which came to light during operations prior to the incident.

4 A prosecution under the Health and Safety at Work etc Act 1974 Sections 2 and 3 resulted in fines totalling £4000 being imposed by Huyton Magistrates' Court on 17 December 1992. A number of improvements to the company's arrangements were implemented before production recommenced in June 1992. The incident also identified failings in the emergency response which resulted in the setting up of a local incident forum under the chairmanship of Merseyside Police to review emergency response arrangements.

5 In view of the local public concern about the incident, and the belief that it has lessons for other chemical manufacturing companies and emergency planning authorities, the Health and Safety Executive (HSE) has decided to publish this report of its investigation. For the sake of brevity, it concentrates on the defects in the way in which the process was planned, the plant operated and the incident was handled and omits reference to many perfectly satisfactory arrangements identified during the investigation.

6 HSE is the enforcing authority for the health and safety legislation set out in paragraph 9. Its responsibilities extend to ensuring adequate planning for off-site emergency response requirements in the context of major hazard legislation. The incident forum convened by the local authority addressed wider public concerns about emergency response which go beyond HSE's responsibilities.

Background

Site

7 The factory is near the village of Halebank, 3 km north west of Widnes, in the Borough of Knowsley, Merseyside and close to the boundary between the counties of Merseyside and Cheshire (see map, Appendix 1). The factory site occupies an area of approximately 38½ acres, the northern part of the site being bounded by the Liverpool-Widnes dual carriageway (A562). The part of the site relevant to this incident is the phosgenation plant. The A562 road, at its nearest point, is 30 m from the site boundary and 100 m from the phosgenation plant. The land surrounding the site is flat and predominantly agricultural. The area is not densely populated, there being small scattered groups of houses around the site, with the closest housing estate nearly 1 km away.

The company

8 IBIS was a wholly owned subsidiary of Shell Holdings (UK) Ltd employing some 250 people in the manufacture of fine chemicals. (On 28 August 1992 the company changed its name to Namepack Ltd but remained a wholly owned Shell subsidiary. The site and operations were subsequently sold to another company.) Approximately 100 employees were present on the site during normal day-shift hours, while the remaining production and technical staff worked on a shift system in one of five shift teams. On the phosgenation plant, the normal complement of operators was five, led by a shift team leader.

Legislation

9 The Health and Safety at Work etc Act 1974 (HSWA) applied to the activities of IBIS at this site. The installation involved in the incident was subject to the Control of Industrial Major Accident Hazards Regulations 1984 (CIMAH) because of the use and associated storage of phosgene. Phosgene, used here in liquid form, readily vaporises to form a very toxic cloud of gas.

10 Section 2 of HSWA places a duty on all employers to ensure, so far as is reasonably practicable, the health, safety and welfare at work of all their employees. Section 3 requires them to conduct their undertaking in such a way as to ensure, so far as reasonably practicable, that people not in their employment are not exposed to risks.

11 The requirements of the CIMAH Regulations operate at two levels which can be summarised as follows. The general requirements (Regulations 4 and 5) apply widely and require the person in control of an

industrial activity (the 'manufacturer') to demonstrate at any time that he/she has identified the major accident hazards and that the activity is being operated safely (Regulation 4) and also to report to HSE all major accidents which occur on site (Regulation 5).

Regulation 5 also requires HSE to send certain information to the European Commission. In addition to the general requirements, the more stringent (top-tier) requirements (Regulations 7-12) apply where greater quantities of dangerous substances are involved, giving rise to potentially greater hazards. These additional duties require the manufacturer to submit a written safety report to HSE (Regulation 7), prepare an on-site emergency plan (Regulation 10) and provide certain information for the public (Regulation 12). The local authority must prepare and keep up to date an off-site emergency plan based on information provided by the manufacturer (Regulation 11). The safety report has to be regularly updated and resubmitted (Regulation 8). Detailed guidance on these requirements can be found in HSE booklet HS(R)21 (rev) *A guide to the Control of Industrial Major Accident Hazards Regulations 1984*.

12 The top-tier requirements applied to this installation because the process was one of those listed in Schedule 4 of the CIMAH Regulations and the quantity of phosgene liable to be involved was greater than the 750 kg threshold specified in Schedule 3.

Plant and process

Introduction

13 The part of the site used to carry out phosgenations, ie reactions involving phosgene, was known as Unit (U) 1000. The unit had two reaction vessels (known as reactors, and identified as V1301 and V1302) in which phosgenations were carried out, and further vessels for subsequent processes and solvent recovery/recirculation. The plant was computer-controlled from a control room situated at the edge of U1000. An outline of the plant is shown at Figure 1.

14 Most of the phosgenations used toluene as a solvent. During 1988/89 development work was carried out to allow the manufacture of a new product. The first stage of production involved the phosgenation of dimethyl aniline (DMA). The result of this reaction (an acid chloride) was transferred to other vessels for subsequent processing before the final product was obtained.

Process design

15 An early process design consideration was the exothermic reaction between phosgene and water. In an exothermic reaction, the consequent temperature increase (and, especially where gas is produced in a

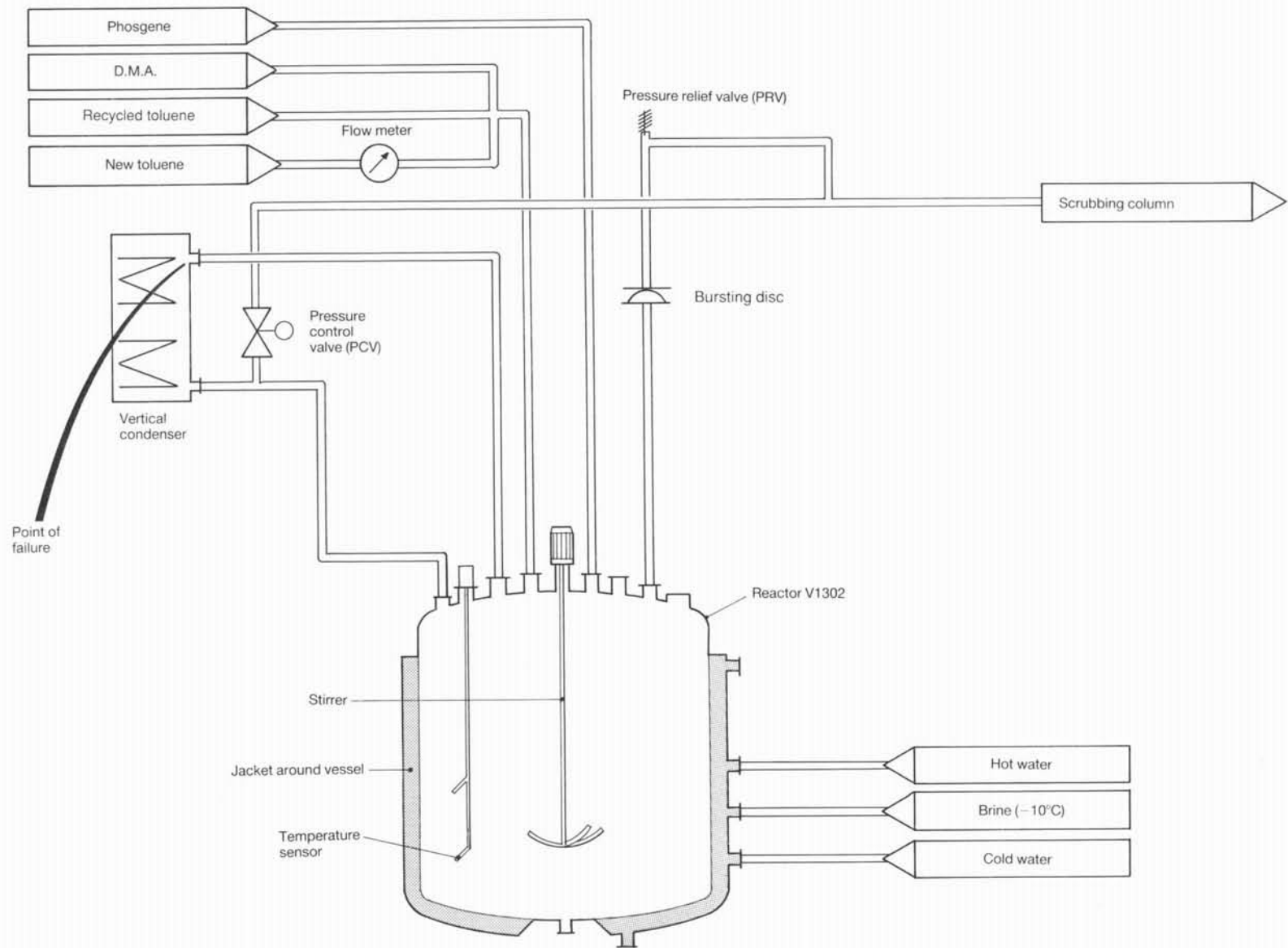


Figure 1 Phosgenation plant (simplified schematic diagram)

closed vessel, pressure increase) can have safety implications. It was proposed that, before fully charging the reactors with phosgene, a small quantity (10 kg) of phosgene should be added; a temperature rise (of more than 2.5°C) would indicate the presence of water. In 1986 IBIS commissioned a review of this proposed precaution. The report recommended, inter alia, that “the firm should consider whether the procedure of adding a small initial charge of phosgene would reliably indicate water contamination and, if the temperature change of 2.5°C was not sufficient indication, either increase the initial phosgene charge or modify instructions or procedures.”

16 The action taken on the review report included increasing the phosgene charge from 10 kg to 20 kg, and reducing the temperature rise detection level to 1°C. The report was then filed and because of staff changes was not known to key personnel at the time of the incident. It appears the company did not check whether the addition of 20 kg of phosgene to toluene/water would give a measurable temperature rise, under operating conditions.

17 The review identified additional complexity in the water/phosgene reaction when phosgene is dissolved in toluene. In a stirred reactor, the immiscibility of toluene and water creates droplets of water with which the phosgene reacts only slowly. It appears that water/toluene/phosgene do not react significantly even up to temperatures of 50°C. The addition of DMA at any temperature, however, produces an instant reaction between water and phosgene, whether the water is present in droplet form or as an unstirred layer at the bottom of the reactor. (After the incident, it was established that a small quantity of water may act as a catalyst for the DMA/phosgene reaction at a temperature of 65°C and result in rapid heat evolution.)

18 The process was designed to have brine (at -10°C) circulating in the jacket to cool the reactor contents during phosgene addition in order to reduce phosgene vaporisation. The firm did not consider the effectiveness of the water detection method if water in the reactor were frozen.

Process development

19 IBIS had a process laboratory with some facilities for identifying and carrying out thermochemical testing. There was also a pilot plant for detection of problems caused by scaling-up to full production quantities.

20 The development work for the new product was undertaken during 1988 and 1989 and involved a trial batch of 200 kg which was made on the pilot plant under atmospheric conditions. Further work was done both in the laboratory and on the pilot plant late in 1990 and early in 1991 to modify the new process to fit onto

U1000. Most of this work had operational objectives (eg ease of slurry transfer) and no specific attempt was made to identify any thermochemical safety-related problems.

21 Small pressure and temperature increases found during laboratory work led the company to assume that the process could easily be handled within the design criteria of the plant. The new process appeared less exothermic than the process already being carried out. The laboratory was not specifically directed to look for exothermic reaction problems.

22 Two of the four batches on the pilot plant showed some sign of exotherm and a pilot plant report issued in April 1990 stated that the reaction appeared to be slightly exothermic. During a pilot plant batch in April 1991 some effort was made, without success, to identify any exotherm. However, identification of exothermicity problems was not pursued in a rigorous manner and not under conditions designed to determine the rate of heat and pressure production that would occur on the full scale plant. In particular the pilot plant batches were heated slowly and were more dilute than the proposed production batches which made identification of any temperature rises very difficult.

23 The company had a procedure for testing products, residues etc which had to undergo heating (eg for drying) to determine if there were any exothermicity problems. This was carried out for the product and its residues. The acid chloride was not foreseen as being heated above 85°C and was not tested. After the incident, it was found that the acid chloride started to break down at about 120°C with evolution of gas.

Hazard assessment

24 A hazard and operability (HAZOP) study to examine in detail the hazards and the appropriateness of the precautions arising from manufacture of the new product was commenced early in 1991. The team was chaired by IBIS's safety manager, and consisted of competent and qualified representatives of a range of disciplines. The team had before it the limited indication from the laboratory and pilot plant of exothermicity. The effect of contamination by water was considered and the team was satisfied with the testing procedure which had been introduced as a result of the earlier review. Failure to control temperature to below 100°C was considered but, given maximum hot water temperature of 85°C in the reactor heating jacket, and “an apparently low (but unmeasured) exotherm of reaction”, it was concluded that a higher temperature was not realistically achievable. Emergency cooling was considered a sufficient control.

25 Calculations by a project engineer of the heat of reaction of the DMA phosgenation indicated that it was

mildly exothermic (-39 kJ/mole). This information was given to the HAZOP team. It was not accepted as being factually correct because of its theoretical derivation and because it was contradicted by evidence from the laboratory and pilot plant which indicated that exothermicity was not a problem. Other aspects of exothermicity such as rate of heat release and permanent gas generation were not considered. The HAZOP team concentrated on the next stage of the reaction which was significantly more exothermic (-140 kJ/mole) - for example arranging thermochemical testing.

26 The HAZOP team also considered the possibility of failing to add sufficient toluene to the reactor. Insufficient toluene would result in the toluene level in the reactor being below the level of the temperature detector. Any water in the reactor when phosgene was added would therefore not be detected through temperature rise. The addition of insufficient toluene would also result in a more concentrated mixture giving potential mixing and cooling problems. The team took the view that the provision of a flow meter in the toluene feed line was a sufficient precaution. They did not consider the consequences of this meter failing and giving a false, positive reading.

Plant design

27 Each reactor was constructed from glass-lined carbon steel and was of 6.3 cubic metres volume. Each was provided with a stirrer to ensure agitation of the contents and a surrounding jacket through which chilled brine, hot water, or mains cold water could be circulated as required by the process. After the incident, it was found that a build-up of sediment in the jacket reduced its effective volume and impaired heat transfer.

28 There were no hardwired trips on the plant. V1301/2 were protected against overpressure by a pressure control valve and a bursting disc/pressure relief valve. Both pressure relief systems were connected to a scrubbing system to remove phosgene from the emissions. Each reactor was connected by a 250 mm diameter line to the top of a vertical condenser. Toluene was pumped to the reactor from a bulk storage tank, the quantity being measured by a flow meter. Alternatively toluene could also be recycled from within Unit 1000. Five phosgene detectors were positioned around the plant to detect any leaks.

Computer control

29 The plant was controlled by a distributed computer control system which enabled the operators to view on visual display units in the control room a representation of the plant together with graphical and tabular representation of pressures, temperatures, levels and trend data.

30 Existing computer software had to be modified for the new product for the different temperatures,

quantities and times involved but jacket emergency cooling at 100°C had remained unchanged. Following the first batch, the software was amended to give hot and cold control of the jacket through an operator-selectable set point. Operation of the reactor was under computer control with operator prompts to initiate certain stages.

31 Emergency water cooling was programmed to come on when reactor temperature exceeded 100°C but due to a programme error this happened only if the jacket was under 'hot water circulation' conditions. Under other conditions, as in this incident, when 100°C was reached the computer isolated the coolant flow, which then had to be manually switched back on. Although not contributing to this incident, this defect had potentially dangerous consequences.

Safety report

32 IBIS was required by CIMAH Regulation 7 to submit a written safety report to HSE. This it did in 1990, the report describing a range of phosgenation reactions which could be carried out on the plant, and the associated safety procedures. HSE's assessment of the report and inspection of the plant predated the start of production of the new product. Such assessments ensure that the report contains the details stipulated in Schedule 6 of CIMAH. HSE was satisfied with the procedures described, its assessment including an on-site evaluation by a multi-disciplinary team of inspectors. The purpose of this was to test the implementation of the procedures, particularly in relation to the existing process. After assessment is complete, safety reports are used by HSE to direct planned inspection of installations. No further inspection of this installation had taken place before the incident.

Information to the public

33 Information had been given to people outside the site who were likely to be in an area which may be affected by a major accident, as required by CIMAH Regulation 12. This information had last been distributed by IBIS in August 1990 and dealt adequately with the risks and precautions arising from a release of phosgene. These are also the appropriate precautions to provide at least equivalent protection against other toxic substances. The off-site emergency plan contained arrangements for the information to be repeated, eg over local radio.

Transfer to production

34 The manufacturing instructions for the new product were prepared early in 1991. The steps for the DMA phosgenation were as follows.

- (1) Put brine cooling (-10°C) on jacket.
- (2) Add 1 tonne recycled toluene to reactor.

- (3) Add 2 tonnes new toluene.
- (4) Add 20 kilograms pre-charge of phosgene.
- (5) Add 0.8 tonne phosgene.
- (6) Feed 1.6 tonnes DMA maintaining temperature below 30°C.
- (7) Heat to 65°C.
- (8) Hold at 65°C for reaction time of 12 hours.
- (9) Transfer product for further processing.

35 The first phosgenation in July 1991 produced much more heat than expected. It had been envisaged that the reactor would hold at 65°C for the 12 hour heating period with some slight heat input, no cooling being provided at that time. The plant manager was informed in his office when the temperature reached 80°C and by the time he reached the plant, a few minutes walk, the temperature was approaching 100°C. At this temperature water cooling came on. The reactor temperature reached (and probably exceeded) the scale maximum of 130°C. The pressure control valve started to relieve, indicating a pressure in excess of the normal operating pressure inside the reactor.

36 The temperature excess was attributed to inadequate dissipation of the heat of reaction which had been evolved over a period of 1½ hours instead of 8-16 hours which was common. No attempt was made to calculate the heat input necessary to raise the temperature of the 5½ tonne reactor contents from 65°C-130°C, nor was the possible effect of the elevated temperature on thermal stability questioned.

37 A total of six batches recorded high temperatures before batch 78. Batch 23 led to an IBIS investigation because the temperature stayed relatively low while the pressure went relatively high. Both mechanical and procedural changes were introduced to correct the perceived problem. The other five exotherms were attributed to mechanical failures of valves or the cooling system. In each case the cooling brought on at 100°C had appeared to correct the problem.

38 On one occasion there had been a failure to transfer new toluene. The control screen was showing that toluene was being transferred but a supervisor found that a valve between the pump and V1302 had for some reason been closed, preventing flow. The immediate problem was resolved by the supervisor and the transfer successfully completed. The problems which could result from the incorrect screen display were not appreciated and the matter was not reported. After the incident on the 7 December 1991, it was found that the flow meter was defective and could send spurious signals to the computer, indicating flow when there was no flow. The incident investigation also

revealed that the valve had been closed by operators using the new toluene supply for another process. After use, they did not reinstate the valve to the open position.

39 These recurrent problems did not cause IBIS to carry out a fundamental review of the original hazard assessment.

The incident

On the plant

40 Batch 78 was started at 21 30 hours on Friday 6 December with the operator following steps 1 and 2 of the instructions, ie toluene was transferred into V1302 and brine cooling put on. It was left in this state for 9 hours while waiting for recycled DMA and toluene to become available. Any water present was likely to have frozen.

41 Early the following morning recovered material was still unavailable and so it was decided to proceed with new chemicals. The operator attempted (unknown to him, unsuccessfully) to carry out step 3, but no toluene was transferred because the valve between the pump and V1302 was closed. The control screen however displayed an increasing quantity being pumped to the reactor, the supply of toluene ceasing when the required quantity had apparently been delivered. Information about the level of toluene in the storage tank was available to the operator but, as there was no reason or instruction to consult this, the unchanged tank level was not detected. As a result of the failure to charge toluene, the liquid level in the reactor was below the temperature detector.

42 Steps 4 and 5 were completed shortly before the shift change at 07 00 hours on Saturday, 7 December, and steps 6 and 7 followed. When the operating temperature of 65°C was reached, the temperature continued to rise rapidly and within 15 minutes was well above 100°C. As the pressure rose with ever increasing rapidity the pressure control valve, pressure relief valve and bursting disc all operated as designed but were of insufficient capacity to deal with so violent a reaction. The condenser connection in the line from V1302 failed and the contents of the reactor were released to atmosphere at 11 27 am.

Emergency response

On-site plan

43 IBIS had prepared an on-site emergency plan for dealing with the consequences of possible accidents ranging in scale from the localised to major accidents affecting people outside the site. There were two alarms with different sounds denoting fire or a gas release and a further special alarm (known as the 'CIMAH alarm') to

inform the local population of a major release of phosgene. The plan placed on a nominated person (the emergency controller) the responsibility of deciding whether to:

- (a) call in the fire brigade;
- (b) declare a 'cloudburst' incident - the code name given to procedures adopted by Merseyside Emergency Services to deal with a large release of hazardous gas which threatens to affect areas off-site;
- (c) activate the off-site emergency plan by informing the fire brigade of a 'cloudburst' incident involving phosgene;
- (d) to sound the 'CIMAHA alarm';
- (e) notify other authorities eg water authority.

A 'cloudburst' incident could be declared without sounding the 'CIMAHA alarm'. The plan specifically required the 'CIMAHA alarm' to be sounded only for a major release of phosgene gas which may pass beyond the site boundary. The procedure required a 'cloudburst' incident to be notified to the emergency services if the 'CIMAHA alarm' was sounded.

Off-site plan

44 The off-site emergency plan had been prepared in June 1986 by the Chief Emergency Planning Officer (CEPO) of the Merseyside Fire and Civil Defence Authority (MFCDA). This was based on escape of phosgene gas.

Response to incident

45 When the incident occurred, the operators heard a rumble but there was no immediately obvious sign of damage to the plant. As a result of their training, operators were expecting to detect phosgene by smell or by the sounding of phosgene alarms around the plant, but there were no such signs. They also expected that, if the bursting disc had blown, the contents of the reactor would have gone to the scrubber, but there was no sign of steam or other emissions from the scrubber tower. A 'smoke cloud' and blue contamination on the plant were noticed. Operators then activated the on-site emergency plan (including the emergency team) by sounding the gas alarm. The U1000 shift chargehand immediately assumed the role of incident controller, taking responsibility for dealing with the incident on the plant. Simultaneously another, previously nominated, shift chargehand assumed the role of emergency controller (EC) and made his way to the emergency control centre in the factory gatehouse.

46 As the EC arrived at the gatehouse, a radio message was received from an operator on the plant that

contamination had been noticed on the road embankment and that it might be necessary to close the road. The gatehouse security man, acting on his own initiative, immediately called the local police station, alerting them to the possible need to close the road. This decision was not overruled by the EC. The call, made via the local exchange, was not one of the actions specified by the on-site plan which required a 999 call direct to Merseyside Fire Brigade by means of a special emergency telephone.

47 Following the incident it was found that the emergency telephone connection had been changed by British Telecommunications without the company's knowledge to the Cheshire exchange. This would have resulted in a delay in activating the off-site plan or other emergency action described in the on-site plan (paragraph 43).

48 The EC was receiving information over the emergency radio link that the incident appeared to be a burst joint or flange, with the implication that it was a small incident. At this stage there were no reports of damage on the plant and closed circuit television cameras scanning the north side of the plant were showing nothing unusual. Other employees, following the on-site emergency plan and moving up wind, had seen the dispersing cloud above the factory but there were no formal procedures for passing this information to the emergency control centre. The EC concluded that there was little off-site risk and there was no need to declare a 'cloudburst' incident, sound the 'CIMAHA alarm' or activate the off-site plan.

49 Shortly after the call to the police, the first patrol arrived. They had already been informed from Halewood Police Station of contamination off-site and discussed with the EC possible off-site effects. The available information indicated that whatever had happened was already over, that phosgene was not involved but that contamination had spread off-site. This was repeated to fire officers on arrival. Because of the apparent absence of phosgene the EC's decision not to activate the off-site emergency plan was reaffirmed at this stage.

50 Some 30 minutes after the incident, the emergency services were being co-ordinated in dealing with a significant incident, although not one involving the 'cloudburst' procedure or CIMAHA off-site plan. At about 12 30 pm, the company's safety officer and the police jointly surveyed the extent and nature of the contamination and found that one direction of the A562 had not been closed. This omission, caused by poor communication, was remedied immediately.

51 Measures were by this time in hand to identify the likely contents of the contamination and to inform the public concerning emergency decontamination. By

early afternoon the company, emergency services and relevant Government departments were discussing appropriate methods of cleaning and decontaminating affected property, roads and crops. Knowsley Environmental Health Department, National Rivers Authority, Ministry of Agriculture, Fisheries and Food and North West Water Ltd were involved.

Effects of the release

52 The path of the reactor contents was visible as a result of the blue dye produced as a by-product of the reaction. Some properties, crops and vehicles were marked over an area 4 km long by 500 m wide (Appendix 1). The cloud caused considerable alarm to people who were engulfed by it, some suffering streaming eyes and coughing. Some 35 people reported to hospital for treatment, of whom ten were detained overnight for observation and three were referred to Alder Hey Childrens' Hospital. Almost 60 people were thought to have been affected by the cloud but there were no serious injuries or long term environmental effects. The Department of Public Health Medicine of St Helens and Knowsley Health Authority has carried out a descriptive study of exposure to the chemical plume and its report has been presented to the Authority.

Investigation

53 An inspector from HSE's Field Operations Division was on site within a few hours of the incident and a team, led by a Principal Inspector of Factories, was set up to investigate the release. The team included HSE specialists in process safety, mechanical engineering, control and instrumentation, exothermic reactions and computer control. HSE also liaised with the IBIS and Shell teams who carried out their own wide-ranging and thorough investigation. HSE's Research and Laboratory Services Division (RLSD) was involved in evaluating the chemistry and the thermochemical data. The IBIS and Shell investigation included teams to identify the cause of the incident, to review the background to the plant and to investigate the handling of the emergency. They also put considerable efforts into the monitoring of short-term environmental consequences and the subsequent clean up.

54 A number of aspects of the process development were particularly reviewed. These included process design, product development, hazard assessment, plant design, computer control, transfer to production and the events immediately before the release. The company's on-site emergency plan was also assessed, particularly with regard to co-ordination with the off-site plan and arrangements for activation.

Report to Europe

55 Because of the quantities of toxic materials involved and the potential for serious danger to people,

HSE considered that the incident was a major accident as defined by Regulation 5 of CIMAH. A report of the incident detailing the circumstances, the substances involved, the preventative measures and other information as specified in Schedule 5 of the Regulations has therefore been sent to the Commission of the European Communities.

Emergency response review

56 The incident and the way in which it was handled by the emergency services raised questions about the workings of on-site emergency plans and their integration with the CEPO's off-site emergency plan. Questions were also raised about the purpose and functioning of the 'cloudburst' procedure and the use of the 'CIMAH alarm' for releases not involving CIMAH substances. It appeared that these same problems were relevant to other CIMAH sites and also to non-CIMAH sites where an incident could have significant off-site effects.

57 A meeting of interested parties was called by the CEPO on 19 December 1991 on behalf of the Merseyside Emergency Services Senior Co-ordinating Group. It was chaired by Merseyside Police, and it was agreed that action should be taken to identify, examine and resolve the issues brought to light by the incident: the IBIS incident forum was set up to achieve this. The organisations represented are shown at Appendix 2. Emergency planning arrangements were considered at a further meeting in March 1992. Ten significant items were identified for detailed consideration by smaller working groups. The CEPO co-ordinated the responses of the working groups and prepared a report for the MFCDA. HSE co-operated with this initiative to ensure that the forum considered the implications of the incident for CIMAH emergency planning arrangements. The recommendations of the working groups shown at Appendix 3 are included with the permission of the Committee. These recommendations extend well beyond the scope of HSE's responsibilities and would be for consideration by the Home Office and other parties.

Conclusions and recommendations

Cause of incident

58 The tests done by IBIS prior to the incident revealed a slight exothermic reaction between phosgene and DMA which had no significant pressure effects. They anticipated that, under normal operating conditions, the temperature would not exceed the hot water temperature of 85°C. The reactions occurring in batch 78 caused the temperature and pressure to rise significantly above the expected levels.

59 After this incident a number of chemical reactions were postulated to explain the observed effects of the incident, ie rate of rise of temperature and pressure, and

the absence of phosgene from the emission. These included:

- (a) catalysis of the DMA/phosgene reaction by water resulting in very rapid heat evolution creating vapour pressure effects;
- (b) reaction between water and phosgene which would have to come into play at about 60°C in order to have the required effect on temperature. Ice formation in the reactor chilled to -10°C could have inhibited the reaction until this temperature was reached; and
- (c) secondary exothermic reactions including the breakdown of the acid chloride occurring at about 120°C resulting in pressure effects from the production of gases.

60 It is likely that all three of these reactions played a part in the eventual overpressurisation of the plant. Explanations (a) and (b) require the presence of a small quantity of water in the reactor. There were several potential sources of water contamination, one of which was the recycled toluene. The water was not detected for three reasons:

- (a) on batch 78, the liquid level was below the temperature detector;
- (b) on batch 78, a phosgene/water reaction may not have occurred because of ice formation; and
- (c) for all batches, the temperature rise being sought was probably too small to be detected under operating conditions.

Conclusions about prevention arrangements

61 The company were unaware of the temperature/pressure profile of the reaction, having carried out inadequate thermal tests. In particular, they were unaware of the water catalysis problem. Additionally if they had recognised the problems caused by the breakdown of the acid chloride, they might have concluded that the exotherm was too close to the maximum temperature attainable in the jacket and its potential effects too severe for it to be disregarded.

62 Before carrying out production there should have been a broad and wide ranging hazard and risk assessment. This should have considered foreseeable eventualities such as equipment malfunction and the effects of likely contaminants. The consequences of a temperature above 100°C should have been considered once that temperature had been achieved on the first batch. Although the company **had** identified a mechanism for producing a temperature/pressure problem (ie the water/phosgene reaction) this was inadequately dealt with. No work had been done to

assess whether the temperature detection precaution was effective as the pre-charge technique was accepted custom and practice. The review commissioned by the company in 1986 indicated the possibility of overpressurisation of the reactor from a water/phosgene reaction and, although the precautionary measures were changed as a result of this, the warning about overpressurisation was not further pursued. The plant was protected against phosgene emission in the worst envisaged case (ie fire), but parts of it were not designed to cope with the evolution of large quantities of gas. The broad procedures described in the safety report were of a type, for example covering thermochemistry, which would have prevented this incident had they been implemented in sufficient detail.

63 HSE concluded that the company's arrangements prior to the incident were insufficient to fulfill their obligations under HSWA Sections 2 and 3. The reactions taking place were complicated and although the company had carried out thermochemical testing and hazard assessments, the procedures were not sufficiently rigorous. There were a number of defects in the plant hardware, computer software and staff training which contributed, even if in only a small way, to this incident. In particular, however, the exothermic runaway reaction could have been prevented if one or more of the following precautions had been taken:

- (a) adequate thermochemical testing;
- (b) a thorough hazard assessment of the process;
- (c) effective procedures for detection of water in the reactor; and
- (d) sufficient account had been taken of problems encountered during operations prior to the incident.

Recommendations

64 The investigations by HSE and the company identified a number of improvements needed in the company's arrangements:

- (a) rectification of the plant and software defects noted in this report;
- (b) improved communications, management and maintenance procedures;
- (c) revision of product development procedures to include thermo-chemical testing;
- (d) installation of hard-wire trips to supplement the software protection;
- (e) improved steps to prevent water ingress and detect its presence in raw materials;

- (f) addition of one reactant at a controlled rate to reduce the runaway problem; and
- (g) improvements in the on-site emergency plan particularly in relation to early activation of the off-site plan for a wider range of major incidents.

The company implemented these improvements before the plant was brought back into production in June 1992.

Other aspects of CIMAH

65 Because the off-site emergency plan was not activated, this incident cannot be used as a test of the arrangements in that plan. Despite the non-activation of the plan, some advice was given to the public by local radio.

Lessons for the chemical industry

66 This incident, as is the case with most accidents or dangerous occurrences, has highlighted a number of lessons which are of relevance to the chemical industry in general.

67 While many of these lessons may be familiar to the industry, chemical manufacturers should critically review their safety management systems to ensure that the issues are addressed in a sufficiently rigorous manner. In particular they should ensure that their procedures for monitoring and reviewing systems are adequate.

68 Particularly important lessons are:

- (a) the effect of water contamination should be considered for all reactions, particularly where small quantities may act as a catalyst (paragraph 59). If water can have an adverse effect the methods used to detect it should be validated (paragraph 60);

- (b) physical effects, such as immiscibility (paragraph 17) and the phase of the material (paragraph 18), may delay or otherwise affect chemical reactions;
- (c) laboratory and pilot plant procedures should simulate conditions to be expected on operational plant (paragraph 22);
- (d) assessments should consider not only the heats of reaction but also the rates at which heat or pressure may be produced (paragraph 22);
- (e) all procedures, including 'custom and practice' methods, should be subjected to rigorous assessment (paragraph 62);
- (f) hazard assessments, and the action taken as a result of them, should be documented and indexed to ensure easy retrieval (paragraphs 16, 24). They should be reviewed in the light of plant experience (paragraph 39);
- (g) maintenance procedures should ensure the effectiveness of cooling systems (paragraph 27);
- (h) The implications of instrument faults resulting in false, positive readings, and the need for double checking, should be considered (paragraph 38);
- (i) processes should where possible be made inherently safer, for example by controlled reactant feed (paragraph 64(f)), and by reducing inventories and operating pressure;
- (j) computer software will, almost inevitably, contain logic faults that, in certain circumstances, will result in operational 'errors'. Computer systems and software should receive a hazard assessment (sometimes known as a CHAZOP) similar to that applied to the physical plant and procedures (paragraph 31).

Appendix 1 Map of area

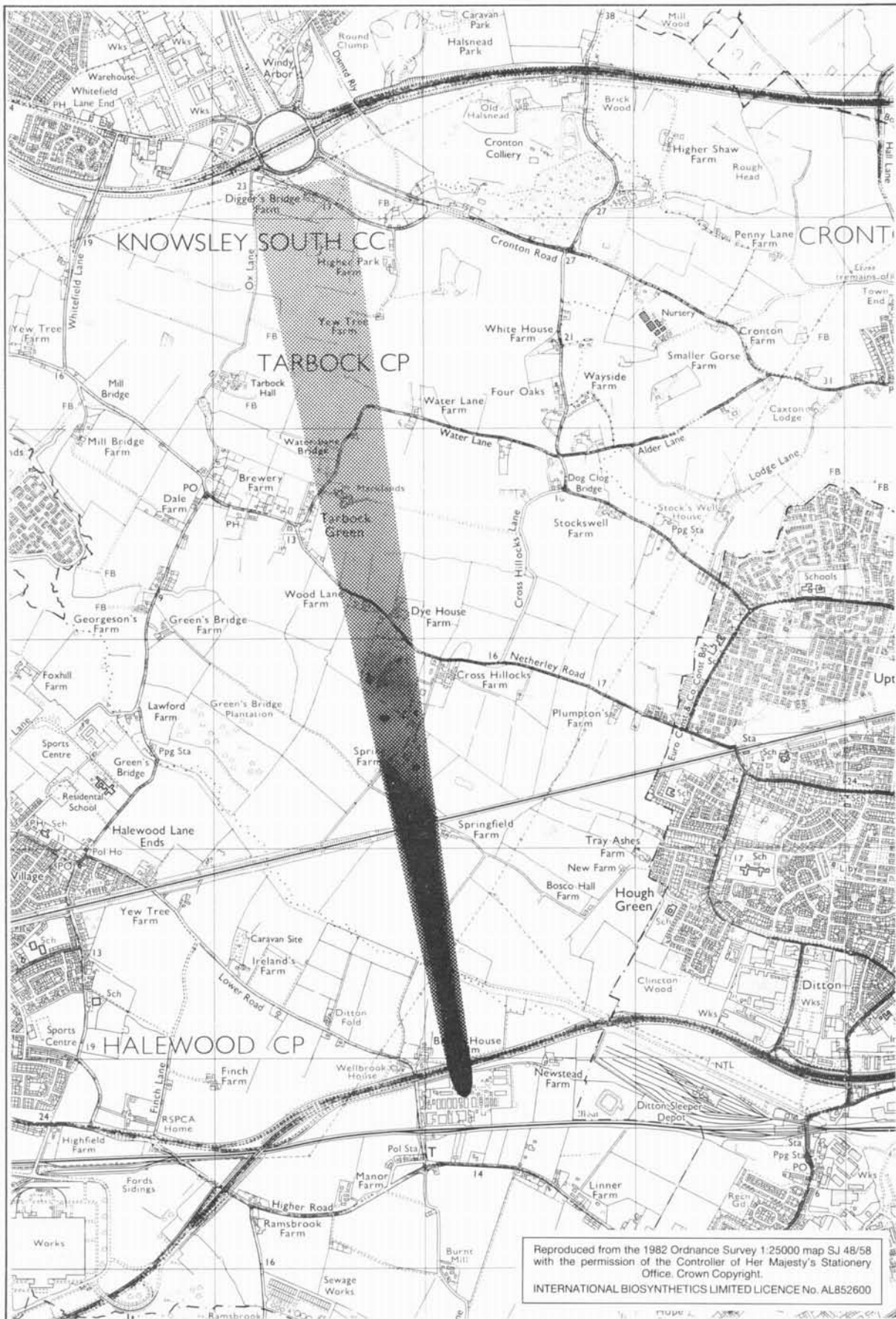


Figure 2 Path of cloud

Appendix 2 Organisations represented at IBIS incident forum

Merseyside Fire & Civil Defence Authority
- Merseyside Fire Brigade (MFB)
- Merseyside Emergency Planning Unit (MEPU)

Merseyside Police

Cheshire Emergency Planning Unit

Cheshire Constabulary

Cheshire Fire Brigade

Mersey Regional Ambulance Service

Mersey Regional Health Authority

St Helens and Knowsley Health Authority

Knowsley MBC

IBIS

North West Water

British Telecom

HSE

National Rivers Authority

MAFF

Appendix 3 IBIS incident forum

Summary of recommendations

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1 On-site planning arrangements

- (a) All 'notification' and other sites holding hazardous chemicals in significant quantities should have an on-site plan as part of a major accident prevention policy.
- (b) In respect of top-tier and 'cloudburst' sites:
 - (i) an initial meeting be convened with each operator, to examine characteristics of potential uncontrolled releases from each site (to be attended by MFB, MEPU, HSE and Environmental Health Department);
 - (ii) a senior fire officer from the operational side of the fire brigade should then be invited by each operator to make a formal visit at least once a year, to examine and discuss emergency arrangement contained in the on-site plan. The invitation should also be extended to the officer responsible for the off-site plan and the Borough Environmental Health Officer. Similar visits to 'notification' and other potentially hazardous sites should also be made wherever possible.
- (c) If the HSE inspectors are not involved in such meetings, they should routinely seek evidence of such meetings.
- (d) Site operators should review their on-site plans to:
 - (i) take into account the effects of all hazardous materials (including intermediate products) which may be significant in the event of an emergency, and
 - (ii) either include, or clarify, the circumstances and arrangements for initiating the off-site procedures.
- (e) All operators holding significant quantities of hazardous substances should be encouraged to review, and where necessary amend, their reporting arrangements.
- (f) Suitable training arrangements should then follow to take account of any new procedures.

2 Standing '999' arrangements

- (a) CIMAH and other installations with off-site risks should identify which lines could be used to contact emergency authorities and verify the '999' catchment of the exchange area on a routine basis. (BT Emergency Planning will facilitate.)
- (b) Any lines used to report or manage major incidents should be nominated for preferential working as part of the Government Telephone Preference Scheme.
- (c) BT will liaise with Merseyside and Cheshire Emergency Planning Units to try and identify any sites with potential anomalies.

3 Application of operational procedures

Consideration should be given to:

- (a) refining and implementing the 'intermediate hazard procedure' at the earliest opportunity;
- (b) The identification of further industrial sites in Merseyside, which present a potential off-site risk, with a view, if necessary, to extending the number of sites subject to the planned 'cloudburst' procedure;
- (c) extending the planned 'cloudburst' procedure in Merseyside to all industrial sites identified as top-tier sites under the CIMAH Regulations;
- (d) holding a suitable inter-county communications exercise at an early date, to establish the strengths and weaknesses of present arrangements;
- (e) establishing a joint Merseyside and Cheshire Emergency Services Working Group to examine the outcome of the exercise, and make recommendations for change, where necessary.

4 Application of 'cloudburst' procedure

- (a) Senior emergency services officers need to be reassured that their operational staff are familiar with information regarding the 'cloudburst' procedure.
- (b) Consideration should be given to establishing a small multi-disciplinary team of officers to make periodic visits to all top-tier and 'cloudburst' sites on Merseyside, to meet and discuss procedures with their senior managers (as currently operated by Cheshire).

- 5 (Amalgamated with other recommendations)

6 Off-site planned arrangements

- (a) Writers of both on-site and off-site plans should review their plans to include **all** substances associated with the respective processes, that could contribute to producing a major emergency.
- (b) It was also recommended to the Working Group discussing emergency services response procedures that all identified major accidents covered by company on-site plans at all top-tier and 'notification' sites be considered for inclusion in the operation 'cloudburst' procedure in respect of unplanned emissions. It was important, however, that the initiation of such procedures should be discussed in detail with the emergency services.
- (c) The Health and Safety Executive should be advised to re-emphasise this advice to off-site emergency planners in the forthcoming revision of guidance booklet HS(G)25, *Control of Industrial Major Accident Hazards Regulations 1984 (CIMAH): further guidance on emergency plans*.

7 Management of incidents involving chemicals

- (a) These arrangements should be covered at meetings with top-tier and 'cloudburst' site operators.

8 Intercounty activation arrangements

- (a) The Merseyside Force control room inspector will be responsible for monitoring all incidents that may have implications for neighbouring force areas. These will most likely be chemical related incidents at installations or involve transportation of hazardous substances by road, rail, air or water.
- (b) There will be a need to assess the incident in terms of its potential size, type, location and proximity to the force boundary, taking into account changes in wind direction and other environmental factors.
- (c) The Merseyside Force control room inspector will, at the earliest opportunity, inform the force control room of the neighbouring forces that an incident with potential police/local authority resource implications for that area is ongoing within the Merseyside area. Updates on the incident will be provided as required.

- (d) The inspector will inform the Merseyside Emergency Planning Unit and the five local authorities on Merseyside of the incident in the usual manner. It will be the responsibility of neighbouring forces to notify their own emergency planning unit and local authorities in accordance with normal procedure within their own area.
- (e) Neighbouring forces should be approached to adopt a similar procedure of cross-boundary notification in respect of incidents from outside Merseyside which may have implications on Merseyside resources. In Merseyside, when similar information is received from a neighbouring force, the inspector force control will immediately notify the Merseyside Emergency Planning Unit and the five local authorities on Merseyside.
- (f) An amendment to the Emergency Procedure and Major Incidents Manual will be published in due course.

9 Food and Environment Protection Act 1985

- (a) The Ministry of Agriculture, Fisheries and Food (MAFF) will continue to carry out regular review of its arrangements under the Act to take account of contaminated foodstuffs, in liaison with all interested agents, including the National Rivers Authority.

10 Press arrangements in the event of major incidents

- (a) The central co-ordinating role of the Police Press Office should be recognised as the basis for developing arrangements with companies and other organisations.
- (b) Each organisation involved should be requested to nominate media officers with 24 hour contact arrangements.
- (c) Each organisation should be requested to consider buildings in their ownership which could be readily converted to media briefing centres.
- (d) An annual exercise be held on an aspect of media liaison.

Appendix 4 References

HSE *A guide to the control of Industrial Major Accident Hazards Regulations 1984* HS(R)21 1990 HMSO
ISBN 0 11 885579 4

HSE *Control of Industrial Major Accident Hazards Regulations 1984 (CIMAH): further guidance on emergency plans* HS(G)25 1985 HMSO
ISBN 0 11 883831 8

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