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1 INTRODUCTION

This guidance provides Assessors with advice on hazards from chemical warehouses based on current knowledge. It has to be clearly understood at the outset that some of the technical issues involved in warehouse fires are complex and the aim of most assessments will be a reasonable, physically consistent but approximate treatment. Research continues in the areas of: fire behaviour of chemical commodities, production of toxic species, structural response and effects of emissions on human populations and the environment. Parts of this guidance may be superseded as new information becomes available.

2 WAREHOUSE SAFETY REPORTS

HSE has issued guidance on the topics that should be addressed by a COMAH safety report, but Occupiers are not obliged to follow the order suggested. In fact it makes more sense to describe a warehouse site first and then the stocks of chemicals held, therefore this is the order of the information presented in this document.

2.1 Site description

The safety report assessment manual lists all the aspects that should be addressed in the site description. This guidance make reference to the features that are important for a risk assessment:-

- Site location with maps.
- Plan of site.
- Brief site description.
- Nature of the warehousing operation.
- Indication of nature and location of materials stored. This should include details of area set aside for segregated storage of flammable liquids, highly toxics, self -reactives etc.
- Site drainage and sewage systems with plans.
- List of neighbours with hazard potential.
- Brief description of surrounding countryside (a much fuller description should be presented in a separate section dealing specifically with the site environs and the environmental survey).
- A description of nearby centres of population. This should include residential areas and places of work.
- The maximum number of persons on site and their likely locations.
- Wind rose data for the site.
- Description of the underlying and surrounding geology and hydrology if it is relevant.
- Description of nearby transport systems.
- Groups of nearby vulnerable people.
- High voltage overhead power lines.
- Nearby underground pipelines.

2.2 Hazardous substances on site

Agrochemical warehouses tend to contain substances with risk phrases that span the complete range given in the CHIP Regulations. A safety report must consider the hazards from **all** substances in a warehouse if the warehouse contains sufficient dangerous substances to bring it under the COMAH top tier regulations.

The aggregation rules, which allow occupiers to test which warehouses meet this criterion are as follows: -

- The threshold quantities listed in Schedule 2 Named Substances refer to pure substances. If any one of the listed chemicals is in the form of a solution, it is the mass of pure substance not the mass of the solution that should be compared to the quantities in columns 2&3.

Table 1: Substance categories and risk phrases

Class	Category	Risk Phrase	Risk
1	Very toxic	R26,R27,R28	T+
2	Toxic	R23, R24, R25	T
9	Dangerous for the environment	R50, R51	N
3	Oxidising	R8	O
4	explosive	R2, R3	E
6	flammable	R10, (liquid)	F
7	highly flammable	R17,R11 (liquid)	F
8	extremely flammable	R12 (liquid)	F+
0	Reacts violently with water	R14,	
10	Releases toxic gas on contact with water	R29	

- The quantities that should be aggregated and compared to the threshold quantities listed in Schedule 3 (Generic Categories) refer to the total quantity of preparations with a toxic, ecotoxic, oxidising or explosive label, irrespective of the concentration of active ingredient.
- Inventory threshold fractions for Classes 1,2 and 9 are aggregated with threshold fractions of named substances with the same risk phrases. Inventory threshold fractions of Classes 3,4,6,7,8 and threshold fractions of named substances with the same risk phrases are aggregated. Class 10 substances are only aggregated with names substances with the same class.

An agrochemical warehouse may store formulated products containing a toxic substance "X" at a concentration of 10%, which is insufficient to cause the them to be classified toxic. If there is another agrochemical in the same warehouse containing "X" at a sufficiently high concentration for it to be classified as toxic, the Operator is obliged to consider both products in his hazard assessment. However, the safety report only needs to provide the following information on the substances that meet the risk phrase criteria. These include:-

Chemical name (of active ingredient(s)).
 Structural formula.
 CHIP classification.
 Total quantity.
 Physical form (e.g. fusible solid, solution).
 Brand name.
 Flammability data.
 Solvent (where appropriate).
 Concentration.
 Packaging.
 Location.

If a site stores many tens of toxic substances it is unreasonable for Assessors to insist that the Occupier provides very detailed data on all of them. The most that can be expected is information on the 10 most hazardous inventories and standard data sheets for all other hazardous substance in an appendix.

Since the contents of many chemical warehouses change continually, Occupiers may be unsure how to calculate their total hazardous inventory although the regulations are quite clear on this issue. The quantities that should be aggregated are the greater of:-

- (a) The maximum quantity stored for a short period, even if that is less than one day, over a year taking account of seasonal demands and fluctuations in business activity.
- (b) The maximum quantity that is liable to be stored in the near future (1 year).

At first sight this information appears unambiguous, but in fact several issues are unresolved mainly because the variation in the stocks of particular chemicals in a warehouse usually has both a cyclic and random component. Some agrochemical stocks peak in the spring while others reach their maximum level in autumn. It would be overly conservative to assume that the inventory of each substance is at its maximum at the time of the accident because this does not happen in practice and the warehouse would not be big enough hold such large stocks. The correct approach should be based on the "worst" inventory for a short period at any time during the year, where worst is defined as the maximum of (peak quantity)/LD50 or any other similar measure of hazard.

The regulations require occupiers to provide data on the analytical methods available to determine the presence of all hazardous substances, or to refer to such methods in the scientific literature. They also demand that the degree of purity of each hazardous substance is given together with a list of the main impurities and their percentages. It is probable that these requirements were included in the regulations with bulk storage or process in mind. They cannot sensibly be applied to a mixed warehouse containing hundreds of different chemicals in small quantities and Assessors should only expect occupiers to know of methods in the literature for detecting broad classes of compound (e.g. organophosphate). They should not insist on lists of impurities and their percentage concentration in every substance.

The Regulations also require occupiers to briefly describe the hazards, which may be created by dangerous substances, but it is difficult to separate out hazards from individual substances in a warehouse. Occupiers are more likely to deal with this requirement by reference to: -

- Vaporisation of toxic substances in the event of a fire.
- Generation of toxic combustion products in a fire
- Thermal radiation from a warehouse fire.
- Environmental impact of fire fighting water run-off.
- Explosion hazards of explosive and oxidising substances.

2.3 Storage conditions

The safety report should describe the conditions, under which hazardous substances are stored paying attention to the following: -

- packaging types.
- Racking and height of storage.
- measures for dealing with damaged containers.
- pallets and their management.
- the warehouses: -
 - construction.
 - fire precautions.
 - security precautions.
 - bunding and drainage.
 - sprinkler systems.
 - venting systems.
 - electrical installations.
- fork-lift trucks used.
- segregation and separation procedures.
- the storage process.
- shipping-in and out procedures.
- record keeping - computer database.
- hazardous substance data sheets.

2.3.1 Packaging types

All of the types of packaging for hazardous substances should be described in a safety report even if these are only stored infrequently. Common packaging types include: -

Drums metal 200l 50kg 25l	Drums plastic 200l 25l 20 and 25kg	Bottles metal 500ml 1l and 5l 10l	Bottles plastic 1l 5 and 10l
Fibre Kegs 150kg	Plastic IBC 400l 1000l	Plastic sacks 10kg and 15kg 25kg and 50kg	

If safety arrangements are appropriate for a restricted range of packaging types then the safety report should contain unambiguous statements that other types of goods will not be accepted. An example of such statement would be "flammable or combustible liquids in plastic containers are never stored". Handling procedures for different containers should be outlined together with company rules on segregation, policies on loose packets and the breaking open of containers to fulfil special requirements. If shrink or stretch wrapping is employed, the equipment, procedures and safeguards should be described.

2.3.2 Racking

If the company's warehouses are racked, the safety report should demonstrate that the steel work complies with industry standards. Safety precautions and measures the company has introduced to protect the racking and prevent it being overloaded should be described. These could include: -

- Corner protectors.
- Tie bars or fixing points.
- Notices warning of maximum loading.
- Weight restrictions.
- Inspection procedures.
- Maintenance schedules.

In warehouses not fitted with racking, goods may be stored in "block stacks" up to 10 feet high. A safety report for these warehouses should describe the measures and procedures used to: -

- Control of the height of stack.
- The use of pallets within stack.
- Type of material/packaging that can be stacked.
- Segregation rules for substances and packaging types.

2.3.3 Measures for dealing with damaged containers

Companies should carry a supply of oversized metal and plastic drums for dealing with leaking containers. They should also have metal and plastic trays for leaking IBCs and written procedures for dealing with spills and damaged containers. Procedures for decanting and repackaging flammable liquids should give full details of arrangements to control static ignitions e.g. bonding of vessels, anti-static clothing, antistatic FLT tyres etc. Staff who deal with spills should have access to:

- Comprehensive data on the hazards.
- Compressed air breathing apparatus.
- A disposable chemical suits.
- A chemical splash suit.
- Several fume respirators with cartridges for organic and inorganic chemicals.
- A dust respirator.
- Protective footwear and gauntlets.
- Safety goggles.
- Face shield
- Medium density foam for control of vapours if appropriate .

Damaged or leaking containers should be stored in a designated area/building well away from the main warehouse that is well ventilated, equipped with appropriate security features and has segregated areas to ensure compliance with the segregation rules for hazardous substances.

2.3.4 Pallet management

Most of the goods arriving at a warehouse site for storage do so on wooden pallets, which remain the property of the customer and are returned at the end of the storage periods. Some companies use non-returnable pallets and these become the property of the warehouse keeper. Due to movements of part loads in and out of warehouses, most sites accumulate a large number of surplus pallets, which are used to replace substandard pallets and to facilitate transport and distribution of stored goods. A safety report should contain a short paragraph describing the storage, inspection, reuse and scrapping of pallets. Storage of large pallet stacks immediately adjacent to the warehouse is not usually acceptable because of the risk of fire spread through the wall - typically following arson.

2.3.5 Warehouses

A COMAH safety report should provide sufficient information on the warehouses used to store dangerous substances that Assessors are able to ascertain if they meet certain minimum standards. This includes: -

- A safe location.
- A secure perimeter fence.
- At least one emergency entrance point to the site.
- Safe secure construction.
- Impervious floor to each warehouse.
- Adequate fire fighting facilities.
- Smoke alarms.
- High quality electrical installation.
- Eye wash bottles.
- Stocks of absorbent materials for dealing with spills.
- Stocks of sandbags to form temporary containment barriers.
- Non sparking tools in warehouses storing highly flammable liquids.
- Adequate level of natural or artificial lighting.

Other highly desirable features of warehouses include: -

- Constructed of essentially non combustible materials (profiled metal/brick/block walls).
- Appropriately sized fire compartments formed by block walls.
- Bunding to a height of 1m.
- Fitted with in rack foam/water sprinkler system.
- Intruder alarms.
- Fire resistant doors.
- Site floodlighting.
- Perimeter lighting.
- A emergency generator.
- Night time patrols/guards.
- A gate office that is manned 24 hours/Day to day.
- Arrangements to accompany visitors all the time they are on site.
- Fusible plastic roof lights that reliably provide a defined level of venting in case of fire. These may be useful if the warehouse contains large stocks of volatile and toxic materials - this is discussed in more detail later in this document.

2.3.6 Fork-lift trucks

Three types of fork-lift truck are commonly used in warehouses, diesel, electric and LPG powered. Diesel trucks for use in highly flammable storage areas should be compliant with HSE Guidance Note PM 58S and electric trucks for these areas should comply with AS 3000 manufacturer's standard and shut down automatically if a flammable vapour is detected. Electric trucks should be charged away from warehouses in a purpose built, well ventilated building.

All fork-lift trucks should carry a fire extinguisher and be regularly maintained by a specialist contractor. Insurers usually require a biannual inspection of all trucks and associated attachments and lifting gear carried out by a competent expert. Servicing records should be held on a computer data base. Safe operating instructions should be available for each type of fork-lift truck used at a site and only qualified operators should be allowed to drive them. Staff who have undergone driver training and demonstrated adequate competence to an outside Inspector should periodically attend training and refresher courses.

The company should have a set of written safe operating procedures for fork-lift trucks, which include the following instructions: -

- Always travel with forks lowered.
- Do not carry passengers.
- Do not leave vehicle unattended with engine running.
- Do not leave keys in unattended vehicles.
- Trucks should not be parked randomly in warehouses.
- Trucks should be parked over night in designated areas and with the brakes on.
- Battery powered trucks should be put on charge at the end of each working day.
- Charging should be carried out in the approved area.
- Permission must be obtained from the warehouse manager before a truck can be taken on a public highway.
- Disciplinary action should be taken against anyone who disregards these instructions.

The following checks should be carried out on fork-lift trucks at the start of each working day: -

- Levels of oil, water and antifreeze are adequate.
- There are no leaks on radiator hoses.
- The fuel tank is full.
- The batteries are fully charged.
- All lights are operating correctly.
- There are no hydraulic oil leaks.
-

2.3.7 Segregation and separation procedures

In this section separation and segregation have the meanings specified in HSG 71. Separation means a distance of 3 metres or one gangway width (whichever is the larger) between two types of goods. Segregation means that two types of goods should not be kept in the same building compartment or storage compound.

The storage of dangerous chemicals should be in accordance with the following guidance notes: -

- HSE Guidance Note CS71 Chemical Warehousing - Storage of Packed dangerous substances.
- HSE Guidance Note CS3 - The storage and use of Sodium Chlorate and other Strong Oxidising agents.
- HSE Guidance Note CS21 - The storage and handling of organic peroxides.
- HSE Chemical Series advisory notes.

As a general rule, substances from different hazard groups should be segregated, although this is not always practicable. A key issue in many warehousing operations is the segregation of flammable materials (especially flammable or combustible liquids) from toxic materials. If this is not done the risk of toxic materials being transported by a fire may be significantly increased. This is discussed in more detail later in this guide.

Oxidising materials should be segregated from flammable solids or liquids. Strong acids should not be stored alongside strong alkalis and substances that react violently with water should not be stored with aqueous products. All substances arriving on site should be accompanied by a Chemical Data Sheet and any consignment that arrives without one should be put in a temporary store until its properties have been ascertained and the complete documentation is available on site.

2.3.8 Shipping-in and shipping-out procedures

Assessors should expect a safety report to contain information on delivery notes and unloading instructions. Vehicles should not be reversed inside the warehouse and unloading should take place outside using fork-lift trucks irrespective of weather conditions. The report should describe procedures for: -

- Dealing with damaged or deteriorated goods.
- Labelling of goods.
- Date stamping and batch numbering.
- Shrink/stretch wrapping.
- Assessing the maximum permitted stack height for block stacks.
- Stock rotation.
- Stock inspection.

Shipping-out procedures are usually similar to those for shipping-in stock, with additional checks being carried out on the trailer to ensure that it is:-

- The one specified on the paperwork.
- It is in good condition with no holes, protruding nails or splinters.

- It is clean and in good general condition.
- The loading and transport instructions are appropriate for that type of trailer.

Before leaving the site a driver of a loaded vehicle must obtain relevant the TREM cards from the warehouse office.

2.3.9 Record keeping

Most modern warehousing operations make use of computers for storing information on stock including: -

- Chemical names.
- Brand name.
- Hazard category.
- Location.
- Owner details.
- Storage details.

Under the COMAH regulations companies will have to keep information on the risk phrases of each substance so that their obligations under the regulations (lower tier or top tier), can be determined at any time. The computer used for this purpose should have its own uninterruptable supply of power and be capable of quickly providing hard copy details of all substances in a warehouse in an emergency situation. Stock data should be continually updated and should never be more than a few hours out-of-date. A copy of the stock data should be kept away from the warehouse, so that it can be retrieved quickly in the case of a fire. Hazard data sheets for every substance on site should be kept in a records office, manned by staff who understand the library arrangements and can locate data on any material at a moments notice.

Full details on each warehouse (in addition to chemical inventory) should be available in the event of an emergency. The information should include:-

- Construction details.
- Manning details.
- Fire fighting equipment.
- First aid equipment.
- Sprinkler data.
- List of other equipment in the warehouse.
- Details of electrical installation.
- Drainage details.
- Potential hazards to fire fighters.
- On site risks/hazards to buildings, plant, equipment etc. in the event of fire.
- Off-site risks/hazards to people and the built and natural environment.

The above information should be designed to assist fire fighting operations in the event of a major fire, enhance accident management and facilitate mitigation of its consequences, to staff, the public and the environment.

2.4 Management and control of the site

A warehouse site should have a well-defined management structure with responsibilities at each level clearly identified and understood by the relevant post holders. A COMAH safety report should include management organograms and detailed descriptions of the various management functions under normal operation and in the event of a major accident.

Key management personnel as far as general safety is concerned are: -

- The Site Manager/Director.
- Operations Manager.
- Quality Assurance Manager.

- Safety Manager.
- Site Service Manager.
- Administration Manager.
- Warehouse Managers.

The general Site Manager/Director should have considerable experience of all aspects of warehousing. In particular he should be very familiar with: -

- Chemical hazards.
- Chemical safety.
- Warehouse safety.
- Emergency procedures.
- Emergency/accident management.

The Operations Manager will be responsible for day to day warehouse and transport operations. He should have qualifications and experience similar to those of the General Manager, but in addition he should have experience of all transport activities.

The Quality Assurance and Health & Safety Manager are usually one and the same person who has considerable knowledge of chemical safety and general warehousing operations. His knowledge of chemical hazards is usually greater than anyone else on site and he should have at least a good understanding of the major accident hazards and their consequences. In general he is responsible for:-

- Occupational hygiene standards.
- Implementation of COSHH Regulations.
- General site safety.
- Site fire fighting services/equipment.
- Site first aiders and first aid equipment.
- Chemical Safety Sheets/documentation.
- Warehouse racking safety.
- Production of written safety and emergency procedures.

The Health and Safety Manager is a key member of the site safety committee and should attend meeting/ discussion that have an impact on site safety.

The Site Services Manager is responsible for buildings and equipment on site including fire fighting equipment, sprinkler system, heating and lighting, emergency generator, emergency communications system etc. His experience and qualifications should be commensurate with these responsibilities.

The Administration Manager usually acts as personnel manager and is responsible for accounts, stock administration, secretarial services and computer based records. He may be a designated emergency controller and may also be responsible for staff training including management training.

A Warehouse Manager is often a relatively junior position, but one calling for considerable experience of warehousing and chemical hazards.

Any or all of the above may have designated roles for emergency situations. There are two key positions, which should be identified in a safety report, these are: -

- Incident Controller.
- Executive Controller.

The Incident Controller is the person who assumes complete control of the site in an emergency and directs operations such as: -

- Staff evacuation.

- Fire fighting until Local Fire service assume control.
- Communication with Local Authority, police and emergency services.
- Warning local residents of any hazard.

The Executive Controller deals with communications with the media (press, radio and television), supervises public relations and liaises with relatives of any casualties. He also liaises with customers who may be worried about their goods. His primary function is to act as a shield for the Incident Controller so that he is not distracted from the task of emergency control/management.

At least two Senior Managers should be trained to assume the role of Incident Controller and two different manager should be trained to assume the role of Executive Controller. Alternatively three Managers should be able to take on either role.

2.4.1 Emergency management

Good emergency management is dependent on well thought out and practised emergency procedures for all eventualities. Warehouse sites should be fitted with break-glass fire alarms in strategic locations. All grades of staff should be instructed to not to hesitate to raise an alarm if a fire has broken out and looks as if it might get out of control. Immediately the alarm sounds the on-site fire fighting team should spring into action and attempt to bring the fire under control. If the fire is in a warehouse, the local fire service should be called immediately and the site fire alarm sounded. The senior member of the site fire fighting team makes decisions on these actions when the fire is not in a warehouse. The staff handbook for the site should discuss these matters at some length.

Once the site major emergency alarm is sounded, the emergency plan should swing into action and the following should be available:-

- An alarm system that can be heard by all employees.
- A tannoy system with its own emergency power supply.
- Several two-way radios for communication between Site Manager at different locations.
- A wind sock that all employees have little difficulty seeing.
- An anemometer and wind direction indicator.
- Two emergency evacuation assembly areas.
- Well rehearsed site evacuation procedures.
- A set of pathways that allow employees to avoid the smoke irrespective of the direction of the wind.
- A designated and well equipped emergency control room.
- A back-up emergency control room in case the main one is uninhabitable.
- A designated well equipped first aid room.
- Major emergency plans covering all eventualities including preventing fire fighting water run-off.

The site should have written instructions for dealing with potential run-off situations and for contacting and liaising with EA.

Staff movements and holiday rosters should be arranged so that the following members of staff are on site at all times:-

- An Incident Controller.
- An Executive Controller.
- At least two members of the site fire fighting team.
- At least one qualified first aider.

2.4.2 Site safety

A warehouse COMAH safety report should demonstrate that the site management has in place a comprehensive system of safety rules, equipment and procedures for all foreseeable eventualities. It should therefore contain descriptions of the safety procedures for buildings and equipment including: -

- access to roofs.
- scissors platforms.
- pallet inverters.
- conveyors.
- portable loading docks.
- trestles and jacks for trailers.
- fork-lift trucks.
- sprinkler system.
- emergency generator.
- container loading ramp.

The safety report should also describe the staff, systems and procedures for dealing with emergencies. These include: -

- The site fire fighting team.
- First aid team.
- Incident controllers.
- Instructions to contractors.
- Measures to deal with emergencies.
- Other safety measures.

The duties of the site Safety Officer should be described in respect of: -

- Safety audits and inspections.
- Safety/emergency equipment maintenance (e.g. eye wash bottles, breathing apparatus).
- Testing of smoke and intruder alarms.

A section should be devoted to describing the permit-to-work system that is in operation, paying particular attention to: -

- Hot work.
- Work on electrical installations.
- Entry into confined spaces.

The site should have a site safety committee that meets periodically to discuss safety issues, near misses and accidents. All accidents should be investigated and an accident report prepared.

The rules governing smoking, housekeeping, site security should also be described in this section.

2.4.3 Measures for dealing with emergencies

The safety report should describe in detail the measures and procedure that are in place to deal with spills of dangerous chemical, contamination of an employee, minor accidents, small fires and major emergencies. Inspectors should expect to see a short paragraph on the following: -

- The emergency siren.
- The emergency shower.
- Accident/Incident reporting and investigation.
- Emergency procedures: -
 - Fire drills.
 - Site evacuation.

- First aid.
- Action in the event of a spill.
- Action in the event of contact with a dangerous substance.
- Major incident control.

The major incident control section should include statements on liaison with the emergency services and the EA. The potential impact of a major accident on the environment should not be overlooked.

2.5 Staff training

The Operator of a COMAH site should provide comprehensive training programs for all levels of staff from the most junior warehouse operator to the site director. All new employees should undergo induction training, details, of which should be given in the safety report. The principal areas covered should include: -

- Site Safety and chemical safety.
- Accident Prevention.
- Fire precautions and alarm procedures.
- General background information.
- Works facilities and amenities.
- Company rules and procedures.

In addition to induction training, all staff should receive instruction on the COSHH Regulations, basic fire fighting and security. There should be at least one full-scale fire drill and one practise site evacuation annually.

Fork-lift Truck Drivers should pass a competence test set by an outside organisation before being allowed to drive fork lift trucks. Warehouse sites can train new drivers provided they have a qualified Instructor. All drivers should undergo periodic refresher courses and competence tests.

Certain supervisory staff should receive more extensive chemical safety training covering, chemical hazards, risks to individuals, the effects of chemicals on the human body, hazard sign recognition, dealing with leaks and spills and evacuation in the event of a major emergency.

Some warehouse personnel may receive training under the British Agrochemical Standards Inspection Scheme (BASIS). Ideally several warehouse keepers should hold a Nominated Storekeeper Certificate of Competence.

The Fire Team should train for 1-2 hours each week in order to ensure a permanent state of readiness and competency. Training courses should include: -

- simulated exercises.
- lecturers on fire and chemical hazards.
- videos.
- practical experience of wearing breathing apparatus.
- working with local fire brigade officers.

The first aiders on site should, from time to time, take part in simulated exercises with the site fire team, and practise recovery of "casualties" with specific injuries.

Managers should receive two types of training, the first to improve their proficiency and enhance their management skills and the second to practise their emergency management roles. This second type of training is particularly important and should include an annual full- scale practise major emergency lasting up to 3 hours. At these exercises, which ideally are organised by specialists, different managers should practise their roles.

2.6 Accident prevention, control and mitigation

The COMAH Regulations require occupiers to describe the measures taken to prevent, control and minimise the consequences of major accidents.

2.6.1 Prevention of accidents

Companies are obliged to take all necessary measures to reduce the probability of accidents particularly those, which have major consequences for people and/or the environment. This section of the safety report should summarise the measures that are in place to minimise the probability of an accident caused by an off-site event and then go on to discuss minimisation of on-site accident initiators.

The most common causes of fires in warehouses are arson, mal-operation of equipment, poorly controlled hot-work, static ignition of flammable liquids, poor electrical installation and smoking. A site should therefore be reasonably well protected against malicious fire raisers by: -

- A stout perimeter fence.
- Perimeter lighting.
- Locking unoccupied warehouses.
- Few windows or other opportunities for forced entry to warehouses.
- Security patrols at irregular intervals in the evening and at week ends.
- Intruder alarms connected to the local police station fitted in all warehouses.
- Smoke alarms fitted to all warehouses.
- A gate house manned 24 hours per day.
- Visitors accompanied at all times.

The safety measures and procedures designed to reduce the probability of on-site accidents that are described under potential sources of major accident should be summarised here. Below are some typical examples of the summaries Assessors should expect to see.

All fork-lift trucks used inside the warehouses are maintained and regularly serviced by specialist contractors working on-site. All new drivers undergo a period of training on joining the company and periodically attend refresher courses on stacking/loading techniques and safety. The vehicles are approved for the areas, in which they work in order to reduce the probability of one of them causing a fire due to poor driving or mal operation.

The probability of a heavy goods/delivery vehicle initiating a fire in one of the warehouse is kept very small by not allowing them to enter a warehouse. Each warehouse is equipped with an excellent array of fire fighting equipment, which can be used to quickly extinguish any vehicle fire. Smoking in warehouses is strictly forbidden.

Warehouses have few electrical fittings other than the lights. The wiring should be inspected regularly and all electrical equipment in warehouses storing flammable liquids should be flame proof. Fork lift trucks operating in the warehouses storing flammable liquids should be designed for use in Zone 2. In the event of a diesel fork lift truck stalling, tests and checks, detailed in written guidance notes, should be carried out before connecting the batteries and restarting the unit.

Processes involving a risk of ignition are not carried out in the warehouse or are subject to rigorous controls. These processes include shrink wrapping, transferring flammable solvents, hot work (i.e. grinding or welding).

2.6.2 Hazard control

The section dealing with the control of major accident hazards should summarise the precautions and measures that have been implemented to extinguish/control fires. These include: -

- Rehearsed site evacuation procedures.
- Two site evacuation assembly points.
- Two way radios for key management staff.
- A wind sock.
- Anemometer.
- Emergency tannoy system.
- Designated emergency controllers.

- Annual major emergency practices.
- An emergency control room plus backup.

2.6.3 Accident consequence mitigation

Top tier sites should have a battery of measures and systems to minimise the consequences of a major accident. These tend to be described in the early sections of the safety report, but are summarised here. They include:-

- A well trained first aid team.
- A designated and well equipped emergency first aid room.
- An emergency site entrance for fire fighting vehicles.
- Bunding arrangements to prevent contaminated fire fighting water run-off.
- Library of hazard data sheets.
- A computer that can provide information on stocks and warehouses.
- Plans drawn up in consultation with EA for mitigating environmental impact.

This section should paint a convincing picture that everything that is reasonably practicable has been done to prevent, control and mitigate the consequences of major accidents: -

- Segregation and separation of different types of hazard wherever possible e.g. flammables and toxics.
- Break glass fire alarms and smoke alarms. Staff procedures for fire alarms.
- Well trained and well equipped on-site fire service.
- Good fire fighting facilities in the warehouse.
- A sprinkler system.
- Fire hydrants and other sources of fire fighting water.
- Equipment and procedures for dealing with leaks and spills.
- Fire compartmentation.

3 BACKGROUND INFORMATION ON WAREHOUSE FIRES

Many warehouses contain large quantities of combustible material stacked to a height of many metres. A fire that is started in a pallet at a low level may grow rapidly upwards. Unless the fire is tackled in its earliest stages, it may be very difficult to control and will spread through the whole of the warehouse in less than one hour. The most important issues for a hazard assessment are: -

- Fire initiation.
- Building response.
- Toxic substances released into the smoke plume.
- Explosion potential.

- Dispersion of the smoke plume.
- Hazard range determination.
- Potential environmental impact.

The features of a warehouse that have a significant influence on the magnitude of the hazard are: -

- Its location.
- The inventory.
- Chemical and physical form of the hazardous substance.
- Packaging forms and stacking arrangements.
- Construction/design of the warehouse.
- Fire hazard mitigation systems.
- Fire-fighting water containment/hold-up systems.

These are discussed in the following sections.

3.1 Accident initiators

Studies in the UK and US (1,2) deduced frequencies of approximately 10^{-2} per annum for the frequency of fire starts in a given warehouse - averaged across all industry sectors.

Most surveys of the causes of fires in warehouses have concluded that malicious ignition is the dominant contributor followed by electrical faults, then friction heat and sparks and careless disposal of smoking materials (3). Fire statistics tend to highlight several minor initiators, but surveys often fail to provide a complete picture of the causes of major fires. Hot working, including shrink wrapping, grinding, cutting and welding, which are not explicitly mentioned in some accident study reports, have been responsible for many fires. Other important initiators that should not be overlooked are: -

- Malfunctioning fork-lift trucks.
- Lorry fires.
- Spillage of incompatible chemicals.
- Storage of unstable compounds near to steam pipes and other similar sources of heat.
- Ignition of spills of flammable liquids.
- Static ignition of flammable liquids during transfer operations

Nearly all fire initiators can be adequately controlled by relatively simple and inexpensive precautions, but it is difficult to protect premises against the determined arsonist, particularly if, as is often the case, he is an employee or ex-employee.

3.2 Fire spread in chemical warehouses

There are typically 100 major fires in warehouse premises in the UK each year. Usually the most significant factor in determining the rate of fire growth in a chemical warehouse is the flammability of the materials being stored. Some common categories in rough order of declining hazard are listed below

- Flammable liquids.
- Aerosols
- Low density flammable solids. In the context of chemical storage these may be packaging materials e.g. plastic foams, wood wool, bubble wrap.
- Flammable, free-flowing dusts
- Fusible combustible solids (e.g. thermoplastics, waxes and resins).
- High density combustible solids such as timber

- Aqueous solutions.
- Non combustible materials such as salt and cement.

The containers in which material are stored are also crucial in determining the rate at which fires spread. Those which assist the spread of fire include: -

- plastic IBCs or drums (especially for flammable or combustible liquids)
- plastic bottles in cardboard boxes (especially for flammable or combustible liquids)
- paper and plastic sacks (especially for free flowing flammable dusts)
- small plastic tubs
- cardboard boxes.

3.3 Case studies

Video recordings and detailed test reports are available from HSL Fire Safety Section (Health and Safety Laboratory) for many of the commodity types described below:

3.3.1 Flammable liquids in plastic IBCs

Flammable liquids in plastic IBCs represent a very high risk - internal storage of this type is prohibited under the American NFPA Flammable Liquids code NFPA 30. The risk arises for two reasons

i) Plastic IBCs are extremely vulnerable to fire exposure round the tap. A recent HSL test following a serious fire showed that the burning of a teaspoon full of solvent under the tap/cap of an IBC led to self-sustaining leakage of flammable liquid and loss of the entire contents.

ii) The failure of one IBC containing flammable or combustible liquid is almost inevitably enough to cause rapid and complete fire spread through any warehouse. It is currently not possible to design a sprinkler system to protect premises containing a significant number of plastic IBCs. The rate of burning of an ignited spill of flammable liquid in well ventilated conditions depends on the surface area of burning fuel. As a rule of thumb each square metre of exposed spill contributes around 3 MW to the total rate of heat release.

3.3.2 Flammable liquids in small plastic bottles

This is another high risk commodity. A typical example in the context of COMAH assessments are pesticides formulated in flammable solvents for final sale in 1 or 5kg lots. The bottles of liquid are packed in cardboard boxes and shrink wrapped on pallets. Again the risk arises for two reasons:

i) The commodity is easily ignited - for example a momentary application of a flame can ignite shrink wrapping. Flame moves rapidly along the plastic sheet producing a series of droplets of burning plastic. This material accumulates at the base of the pallet and will typically set fire to the cardboard and then to the bottles containing flammable liquid.

ii) Very high rates of fire spread and burning rate are observed as soon as the solvent/pesticide solution becomes involved. This commodity is also extremely difficult to protect using a sprinkler system. A sprinkler system delivering AFFF (foam) with in-rack heads above every pallet may give significant protection for racks up to three pallets high.

3.3.3 Flammable free-flowing dusts

The risks posed by this type of material were highlighted by a recent fatal fire involving finely ground rubber powder. Any combustible dusts or powders may burn very rapidly if bagged in paper or plastic and stored at elevation - for example in pallet stacks or on racks. As the powders run out of the burning bags they may become dispersed and burn violently as a dust cloud.

The extent to which this kind of risk can be successfully controlled with sprinklers is not yet clear. Water systems are likely to be appropriate.

Table 2: Burning rates and fire growth coefficients for commodities

No	COMMODITY	Heat release MW/m ²	COEFFICIENT NT (a) (KW/s ²)
1	Wood pallets, stack 0.46m high (5-12% moisture).	1.4	0.009-0.02
2	Wood pallets, stack 1.5m high (6-12% moisture).	5.2	0.025-0.123
3	Wood pallets, stack 3.1m high (5-12% moisture).	10.6	0.064-0.156
4	Wood pallets, stack 4.9m high.	17	0.064-0.178
5	Mail bags, filled, stored 1.9m high.	0.4	0.028
6	Cartons, compartmented, stacked 4.6m high.	1.7	0.28
7	Paper, vertical rolls stacked 6.1m high.		1.276-3.906
8	Cotton (also PE, PE/Cot. Acrylic/Nylon/PE) garments in 3.67m high rack.		0.567-2.268
9	"Ordinary combustibles" rack storage, 4.6-9.1m high.		0.013-0.625
10	Paper products, densely packed cartons, rack storage, 6.1m high.		0.004
11	Polyethylene letter trays, filled, stacked 1.5m high on cart.	8.5	0.031
12	Polyethylene trash barrels in cartons, stacked 4.6m high.	2	0.331
13	Polyethylene fiberglass shower stalls in cartons, stacked 4.6m high.	1.4	0.138
14	Polyethylene bottles packed in cartons, compartmented, stacked 4.6m high.	6.2	0.138
15	Polyethylene bottles packed.		0.178
16	Polyethylene pallets stacked 0.9m high.		0.044
17	Polyethylene pallets stacked 1.83-2.44m high.		0.278-1.111
18	Polyurethane mattress single, horizontal.		0.064
19	Polyurethane insulation board, rigid foam stacked 4.6m high.	2	15.625
20	Polystyrene jars packed in cartons, compartmented, stacked 1.5m high.	14	0.331
21	Polystyrene tubs nested in cartons, stacked 4.3m high.	5.4	0.069
22	Polystyrene toy parts in cartons, stacked 4.6m high.	2	0.064
23	Polystyrene insulation board, rigid foam, stacked 4.3m high.	3.3	27.78
24	Polyvinylchloride bottles packed in cartons, compartmented, stacked 4.6m high.	3.4	0.111

25	Polypropylene tubs packed in cartons, compartmented, stacked 4.6m high.	4.4	0.1
26	Polypropylene and polyethylene film rolls, stacked 4.3m high.	6.2	0.625
27	Distilled spirits in barrels, stacked 6.1m high.		0.625-1.6

3.3.4 Flammable liquids in steel drums

This type of storage is very common. A significant amount of fire exposure is required to trigger the failure of a steel drum even if it contains a volatile material such as acetone. As a rule of thumb for a full 210 litre drum full fire engulfment for around 5 minutes is necessary to cause drum failure. This clearly requires a relatively large and sustained fire. This risks associated with drum storage of flammable liquids therefore increase greatly if they are stored with other more readily ignited materials e.g. flammable liquids in any type of plastic container, timber pallets, packaging.

For less volatile liquids the burn through of pallets may cause falling and splitting of drums before they fail by internal pressurisation.

The failure of drums may cause a fireball (up to 30m diameter) a jet fire, a severe spreading pool fire or any combination of these. Once the first drum of flammable liquid spills its contents, fire spread through a drum stack or warehouse is highly likely.

This kind of storage should be protected with a foam sprinkler system. A properly specified system will significantly reduce the risk that an ignited leak will cause drum failure.

3.3.5 Empty plastic drums

This commodity is again fairly easily ignited. Fire spread is initially slow with the development of spreading pool fire of molten plastic. In the later stages this fire can grow more rapidly especially if there are a three or more levels of storage in a stack or on racks.

These fires respond well to ceiling level sprinklers.

3.3.6 Plastic and other goods in cardboard boxes

A large number of full scale tests have been carried out by Factory Mutual in the US (4). Many of the goods tested were packed in large cardboard boxes. Examples of results obtained are shown in Table 2. Fire growth results from these in these tests were fitted to quadratic curves i.e.

$$Q = \alpha \cdot t^2$$

The best fit coefficient α gives a measure of the rate of fire growth in the commodity.

3.3.7 Timber pallets

These are relatively hard to ignite but fire can spread quickly once it takes hold. The fully developed burning rates are very high - see Table 2.

3.3.8 Toxic aqueous solutions in plastic drums

HSL fire tests have shown that fire will spread through a large stack of HDPE barrels filled with water. The fire takes of order one hour to develop but if it is left all of the plastic barrels will be consumed and their contents spilled. This has obvious significance where toxic aqueous solutions are stored in this way. Fire detection in quiet hours is necessary.

3.4 Limits on fire growth

The fire stops growing when: -

- All surfaces of combustible/flammable material are on fire.
- The geometrical arrangements of combustible material prevent further growth.
- All combustible material is consumed.

- There is insufficient oxygen in the warehouse to support continued fire growth.
- There is effective fire brigade intervention or sprinkler operation

If a chemical warehouses contain significant quantities of flammable liquids it is likely that the fire will spread rapidly to the whole warehouse.

For relatively low risk warehouses there is some chance that the fire brigade may control the fire.

For most warehouses the amount of air required to burn the contents exceeds the initially enclosed air by several orders of magnitude. If the ventilation of the warehouse is limited and not increased through failure of elements of the cladding in the early stages of the fire, the concentration of oxygen will fall. Eventually the low oxygen levels will restrict the rate of heat release. The fire will typically continue to burn at a restricted rate that is determined by the available inflow of oxygen - this is known as ventilation controlled or ventilation limited burning. A rapidly growing fire in a relatively small store may reach the ventilation controlled regime in a few minutes. For fires that develop more slowly in large buildings the transition to ventilation controlled burning may take many tens of minutes. If the fully developed burning rate is low and the building is particularly leaky ventilation controlled burning may never occur.

Ventilation controlled fires are characterised by:

- Relatively low rates of consumption of fuel and toxic materials
- Low fume buoyancy and limited plume lift-off.
- Very high emission rates of volatile toxic materials
- Low emission rates for inert toxic powders e.g. heavy metals.

3.5 Building response

Eventually a major fire inside a warehouse will usually cause failure of a large area of the roof cladding and/or structural support. This cladding failure will generally end or significantly relax the ventilation control of burning rate. The size of the fire then increases dramatically typically producing a massive smoke plume with flames leaping to a height of many tens of metres. At this stage the off-site risks typically decline as plume lift-off becomes near complete. The most significant period for hazard assessment is usually during the earlier low buoyancy or ventilation controlled stage and a key issue in risk assessment is the time taken for significant failure of the building skin.

Simplified risk assessment of warehouse fires that consider a "worst case" scenario should normally focus on the early low buoyancy stage. It is not adequate to show that the plume lifts off completely once the building has completely collapsed. Even the simplest risk assessment must therefore include some consideration of the building ventilation and response to fire.

Most modern warehouses are constructed from plastic coated profiled steel sheets bolted onto a metal frame. Brick or concrete block walls separate fire compartments and often form the front wall of the warehouse. Roof lights are often double sheets of glass reinforced plastic (GRP) though glass or thermoplastics such as PVC and polycarbonate can be used.

Roofs of older buildings are commonly clad with asbestos cement. More modern buildings usually use profiled steel, sometimes as a double layer enclosing a thickness of insulating material such as polyurethane foam or rockwool.

Some appropriate approximate rules of thumb that may be used in predicting building response include:

- Profiled cement roofs fail immediately where they are exposed to flame.
- Steel or steel composite cladding is not significantly affected until the underlying structural steel work is displaced.
- Portal frame structures have an intrinsic fire resistance (due to their thermal inertia rather than any fire protection) of at least 20 minutes following the onset of flame impingement.

- Structures with trussed roofs have an intrinsic fire resistance of at least 10 minutes following the onset of fire impingement.
- The typical load ratio for structural steel in warehouses is relatively low and steel temperatures in excess of 900°C are required to cause collapse.
- GRP skylights cannot be relied upon to provide venting of a fire - the plastic component burns away leaving a mat of glass fibres. In some cases this is resilient enough to remain in place, blocking the vent.
- PVC or Polycarbonate skylights can be relied on to provide venting in the event of a major fire.

On many sites several large warehouses are joined together to form a single structure, raising the possibility of a fire in one spreading to the others. Primary considerations in this context are the ability of separating walls to withstand the fire, transmission of thermal radiation from the flame pillar through roof lights and possible effects on the dispersion of smoke.

Some sites operate high bay warehouses. These represent particularly high risks because of the high packing density, the vertical height of the combustible surfaces, the difficulty of carrying out effective fire-fighting and the “chimney effect” in which fire is drawn very rapidly upwards in the narrow gaps between stacks of goods.

3.6 Sprinklers

Some specific comments on the effectiveness of sprinkler systems in controlling risks for a range of commodities are included in the case studies - Section 3.3.

The existence of a sprinkler system should be taken into account when judging the fire frequency assumptions in some COMAH safety reports. This is one factor along with the quality of site security, site location, ignitability of contents, level of process activity in storage areas etc. that may contribute to the judgement that the fire frequency at a site will be significantly higher or lower than the historical average.

No allowance for the sprinklers should be made for warehouses storing flammable liquids in plastic containers.

3.7 Modelling of fires in warehouses

It is possible that COMAH safety cases may include mathematical models of fire in warehouses. These methods may be complex and liable to misuse or misinterpretation. If ALARP demonstrations rely critically on the results of models it may be appropriate to seek the advice of a topic specialist.

Risks vary considerably during the development of a fire. Some form of time dependent analysis may therefore be attempted in a safety case - in its simplest form this may be to set a time limit on the duration for which a worst case scenario is sustained.

The first stage of any form of time dependent assessment relies on an analysis of the rate at which fires grow. Models of fire spread should be empirically based. The assumed rate of fire development should be clearly identified and the early stages of (mainly vertical) fire growth should be broadly consistent with test results - e.g. Table 2. The later lateral stages of fire growth are very difficult to model or assess. Fires spread through radiative ignition of nearby commodities, roof level flame extension and flashover, collapse of burning stacks, flow of burning liquids and melts, burning brands and in many other ways. Some models may use the t^2 fires define in NFPA 72. In any case final rate of heat release should be consistent with the fire load and any limit on fire size imposed by restriction of ventilation. If the time for a fire to reach its fully developed state is less than 10 minutes or more than 30 minutes this should be justified carefully.

The next stage of an assessment is the calculation of the rate of emission of hot gas. Field modelling (CFD) provides a very precise method of analysing the movement of smoke inside a warehouse and through apertures in the roof. This may be appropriate if the location and development of potential fires as well as the venting of the building are clearly defined. Normally a wide range of fire scenarios are possible and the building response is less certain. A less sophisticated approach to calculating flows, such as zone modelling, is adequate.

As a rough rule of the thumb the flow velocity from small vents in warehouse during a serious fire is likely to be of order 10 m/s. Velocities up to 20 m/s are possible if the roof collapses. The temperature of the outflow is variable and obviously must be linked to the rate of burning. In the early stages of a fire a large proportion (>90%) of the heat released by the fire may be transferred into the fabric of the building. After roof collapse the proportion of heat lost from the plume is relatively small (<30%). In ventilation controlled fires heat transfer to (and eventually through) the building fabric may again be very efficient. The exact figure depends the type of fuel, extent of burning surfaces and ventilation area - 60-90% heat loss from the plume is typical.

Radiative heat transfer to the environment outside the warehouse is the main heat loss mechanism for large unconfined fires (5). The rate of heat loss from smoke depends on the size of the luminous flame pillar and the emissivity of the smoke. Most warehouse fires are characterised by an enormous plume of dense black smoke, which to a large extent, obscures the flame pillar. Close to the building the emissive power of the plume fluctuates widely as red/yellow flame blooms appear and disappear on a one or two second time scale, but further away the highly turbulent hot black smoke has an emissive power of less than 50 kW/m². A precise calculation of the fraction of heat lost from the smoke plume by radiation is difficult and a figure close to 0.30 is usually assumed.

The key to a reliable assessment is the calculation of ventilation rates in the fire state. This ventilation may occur through

- Leakage at the eaves, through ventilation grills etc.
- An array of fusible roofing panels.
- Vents, which open automatically if the temperature exceeds some set value.
- Manually operated louvres
- Smoke extraction fans

Vents are generally incorporated into warehouse roofs with the following objectives: -

- To facilitate the escape of warehouse personnel by minimising the spread of smoke to escape routes.
- To facilitate fire fighting by preventing smoke logging of the warehouse.
- To reduce the damage caused by smoke and hot gases.
- To prevent sustained ventilation controlled burning without after burning.

3.8 Fire fighting water

Sprinklers and fire-fighting activities of the local fire brigade tend to result in large quantities of water on the floor of a warehouse. Large quantities of fire fighting water can be held in on-site lagoons and in naturally bunded areas of the site, but these measures are only effective if there are no surface water drains close to the warehouse, which discharge into a local stream or river.

Many modern chemical warehouses are designed to retain spills and fire fighting/sprinkler water by use of a ramp at the entrance and bunding of between 0.5 and 1m. In the event of a fire which engulfs the whole warehouse, most aqueous products and a large proportion of the organic liquids end up on the floor together with metal drums, fusible solids and a variety of other debris. Overtopping of a 0.5m bund is a possibility in warehouses that store agrochemicals in liquid form that are stacked to a height of several metres over more than 50% of the floor area.

3.9 Combustion phenomena

COMAH sites by virtue of their classification store large quantities of very toxic, toxic, explosive and/or highly reactive substances. A fraction of these is released in the smoke plume during a fire, whilst the bulk of the contents of a warehouse is consumed by the flames and produce a variety of combustion products, some of which are toxic.

Many hundreds of different types of agrochemicals have been developed, but the combustion of only a few of them has been studied in the laboratory and then only under a restricted range of fire conditions. This lack of information presents problems for risk assessors and regulators wishing to predict the toxic effects of the smoke plume from a burning warehouse. Further complications arise from the wide variety of formulation methods and packing arrangements adopted by different manufacturers.

Experiments in which chemicals are burnt in flames or furnaces have been conducted in the UK and European laboratories with the aim of identifying the principal combustion products. There is reasonable agreement that chemicals with the appropriate heteroatoms can, under certain circumstances, release varying amounts of: -

- Carbon monoxide.
- Hydrogen chloride.
- Phosgene.
- Chlorine.
- Sulphur dioxide.
- Various oxides of nitrogen.
- Hydrogen cyanide.
- Ammonia.
- Oxides of phosphorus.
- Large fragments of parent molecules.
- Vaporised parent molecules - sometime recondensed on soot particles
- A wide variety of medium molecular weight organic compounds in small quantities.

The relative proportions of these compounds depends on the materials exposed and the conditions of the fire or test.

Despite the potential complexity suggested by the above list, almost all significant (acute) hazards arise from either:

- Survival of small amounts of unburned highly toxic materials
- Generation of large quantities of major toxic combustion products i.e. HCl, SO₂, NO₂ etc.

3.9.1 Survival of unburned toxics

Reference (6) reports measurements showing that the survival of medium molecular weight toxic organic compounds (e.g. pesticides) when burned in *well ventilated* pools is very low (<10⁻⁴). Unfortunately real warehouse fires are not usually simple pools. Both liquid and powdered materials are stored on racks well above the ground. If material is vaporised above the ground level in the intermittent section of a fire or carried up by the strong convection currents much larger survival fractions are observed (~30%). Overall survival fractions of around 10% are appropriate for high rack storage of materials where there is a large fire load *and the fire is well ventilated (6)*.

Much higher survival fractions are possible for ventilation controlled fires. This is particularly true of relatively volatile, stable species that are spilled in large quantities in the early stages of the fire before

the enclosed air is vitiated. The rate of consumption of the toxic material is greatly reduced by ventilation control of burning rate, so that the overall rate of toxic material emissions may be comparable in the ventilation controlled regime and following structural collapse. The former case is, of course, associated with far less heat and therefore constitutes a higher risk.

Elements that should appear in an analysis of a ventilation controlled fire, where this is a possibility, include:

- Estimation of ventilation rate (air supply)
- Estimation of rate of combustion inside the warehouse (this follows from the ventilation rate and the observation that residual oxygen levels are typically very low)
- Some reasonable allowance for **overburning**. This is the vaporisation of material over and above the amount that can burn internally. If large amounts of relatively volatile material are exposed this unburned material may exceed the amount that burns by a factor of up to three.
- Some discussion of the potential for **afterburning**. This is the burning of fuel rich emissions as they mix with fresh air. This is the norm in domestic fires where the size of doorways and windows in large compared with the room dimensions. Afterburning is much less likely where inlets and outlets are separated by distances much larger than their size - as is often the case in a warehouse fire. Unless the fact that fuel rich emissions will burn off is clearly demonstrated, a safety assessment should assume that all emissions survive into the far field.

3.9.2 Generation of toxic combustion products

One useful way of characterising combustion product formation is to determine the conversion efficiency with which the mass of elements such as chlorine, sulphur and nitrogen within agrochemicals is converted to HCl, SO₂, NO₂ and other toxic gases. These data enable the rate of production of low molecular weight toxic gases to be calculated if the rate of combustion of the parent agrochemical is known. A potential shortcoming of the approach is that some combustion products such as HCN and CO are themselves combustible and, when produced in a warehouse fire, might be consumed in the flames and fail to contribute to the off-site hazard. In spite of this problem, elemental conversion efficiencies are helpful indicators of the types and quantities of combustion products released by a fire and several laboratories world wide are engaged in their measurement.

Experiments carried out by HSL on the combustion of 10 nitrogen containing agrochemicals under well ventilated conditions found that the percentage of nitrogen converted to NO₂ varied from 0.7 to 5.5. Other experiments on bagged ammonium nitrate fires on wooden pallets found that the location of the fire and the type of pallet has a significant effect on the quantity of nitrogen dioxide produced. The maximum conversion efficiencies of nitrogen to NO and NO₂ were approximately 15% and 3.5% respectively.

Experimental work carried out at several laboratories has enabled agreement to be reached on the following:

- Combustion of chlorinated compounds generates near quantitative levels of HCl. Very little free chlorine or phosgene is produced unless the molecules are deficient in hydrogen. Trichloroethylene and perchloroethylene are important examples of this latter type of compound.
- Nearly all the sulphur in organic compounds is converted to SO₂.
- Concentration of NO₂ from nitrogen containing pesticides is fairly low. Most of the nitrogen forms N₂.
- Very small amounts of HCN are produced.

- The acute toxic effects of the host of minor products of combustion are always difficult to assess and usually are small. Some combustion products (e.g. polyaromatic hydrocarbons) may have important longer term effects but these are very difficult to assess.

Some laboratories quote the results of combustion experiments in terms of the fraction of elements converted to their oxide or chloride. A mass release rate of the combustion product in terms of the combustion rate of the parent compound is given by: -

$$\text{Conversion efficiency} = \frac{M_f \times N_p \times M_{wt_c}}{N_c \times M_{wt_p}}$$

where

M_f = mass conversion fraction.

M_{wt_p} = molecular weight of the agrochemical.

N_c = number of atoms of the element forming the combustion product.

N_p = number of atoms of the element in the agrochemical.

M_{wt_c} = molecular weight of the combustion product.

Conversion efficiency is defined as kgs of combustion product per kg of parent burnt.

For example if the conversion of nitrogen to NO_2 when dimethametryn burns is given as 0.25, the mass of NO_2 produced per kg of dimethametryn burnt is given by: -

Molecular weight of dimethametryn = 255.4

Molecular formula = $\text{C}_{11}\text{H}_{21}\text{N}_5\text{S}$

Molecular weight of NO_2 = 46

$$\begin{aligned} \text{Conversion efficiency} &= \frac{0.25 \times 5 \times 46}{1 \times 255.4} \\ &= 0.225 \text{ kg of } \text{NO}_2 / \text{kg of} \\ &\quad \text{dimethametryn burnt} \end{aligned}$$

Elemental conversion efficiencies that should be assumed in warehouse fire analysis are given below. Operators who use smaller figures should justify them: -

Table 3: Elemental conversion efficiencies

Element	Conversion fraction
Chlorine to HCl	0.95
Sulphur to SO_2	1
Nitrogen to HCN	0.05
Nitrogen to NO_2	0.05
Carbon to CO	0.05

Special consideration should be given to production of phosgene if rapid vapour leakage (into an external fire) from fire engulfed containers of chlorinated solvents is possible.

It would be sensible to include combustion products in a hazard assessment whenever they make a significant contribution to the hazard of the smoke plume, but this is not always easy to determine. There are situations where the hazard due to toxic smoke from the fire is completely dominated by vaporisation of highly toxic chemicals, (e.g. a warehouse filled with the pesticide phorate). But there are many other situations where the principal hazard is a result of the emission of toxic combustion

products from an essentially non-toxic compound (e.g. an ammonium nitrate warehouse fire). In general the hazards from chemical warehouses are likely to be due in part to toxic combustion products formed in a fire.

3.10 Toxicity of combustion products

Most of the components of the smoke plume from a warehouse fire are hazardous to health, but only some are regarded as acutely toxic. In the main these are the above low molecular weight gases and vaporised very toxic agrochemicals (such as phorate), which have escaped combustion in the flame pillar. Each substance has an associated toxicity value attached to it, which describes the concentration needed to inflict a *dangerous* dose upon a human. The dangerous dose or *Dangerous Toxic Load (DTL)* usually applies to an exposure time of typically 30 minutes for a specific concentration (30 minutes is assumed to be the average time required for countermeasures to be implemented). If a person receives the associated concentration for more than 30 minutes, then fatality is likely in some cases.

The relationship between concentration and dose can be linear or non-linear, depending on which substance is in question. Toxicity relationships can be represented in the form $C^n t = k$, where C is the concentration, t is the exposure time in minutes and k denotes the dose (units depend on power of n). Data is available for the light gases and it is possible to derive corresponding data for most agrochemicals using methods recommended by HSE. Human toxicity data for specific agrochemicals are sparse, but Dangerous Toxic Loads (dangerous dose) corresponding to the Land Use Planning SLOT criteria, can be derived using the following guidelines:-

Table 4 : Dangerous toxic load for some combustion products

Substance	Dangerous toxic load (ppm ⁿ .min)	'n' value
Hydrogen chloride	23,730	1
Phosgene	300	1
Chlorine	108,000	2
Sulphur dioxide	4,655,000	2
Hydrogen cyanide	300,000	2
Nitrogen dioxide	96,000	2
Carbon monoxide	3600	0.7

In general, if animal inhalation data are available then:-

- The predicted LC₅₀ for humans is given by the lowest reliable LC₅₀ concentration found in animal experiments.
- In the absence of animal data indicating the exposure conditions producing 1-5% lethality (LC₁₋₅), it is assumed that this would occur at ¼ of the LC₅₀ value.

If only oral data are available then:-

- The LD₅₀ for the most sensitive animal species is assumed to be applicable to humans.

The LD₁₋₅ for humans (i.e. the dose causing 1-5% mortality) is assumed to be ¼ of the LD₅₀ multiplied by 70 (the assumed weight in kg of an average individual). The air concentration required to produce a dangerous dose if inhaled for a period of 30 minutes is given by:-

$$C_{mg/m^3} = \frac{LD_{50} \times 70}{0.625 \times 4}$$

Note 0.625 m³ is the approximate volume of air inhaled in 30 minutes by an adult male weighing 70kg).

3.11 Mixtures of toxic substances

There is very little information available on the health effects resulting from exposure to mixtures of toxic substances, and there is a lack of a validated method for predicting whether such effects are additive, antagonistic, or synergistic in nature. For this reason, any approach developed to estimate the hazard range for a warehouse smoke plume containing a mixture of combustion products and their surviving parent compounds, such as agrochemicals, must be based on pragmatic default assumptions and will need to be refined as and when new data becomes available.

As far as COMAH safety reports are concerned Assessors should expect the consequence analysis to be based on the following pessimistic assumptions:-

1. The responses from the primary combustion products that attack the lungs on account of their corrosive nature (e.g. HCl, SO₂, etc), are additive. When the combustion products contain large quantities of nitrogen dioxide and hydrogen cyanide, it may be reasonable to add the doses fractions of these to the dose fractions of HCl and SO₂ received by members of the public in the absence of any other information.
2. Significant phosgene production may be possible because of co-storage of large quantities of chlorinated solvents and flammable liquids in a manner likely to lead to a high temperature vapour release into an engulfing fire. In this case the phosgene toxic dose fraction should be added to that from HCl and SO₂ etc. referred to above .
3. Doses from vaporised/particulate agrochemicals are additive.
4. The effective hazard range for the fire is calculated by adding the combined dose fraction from vaporised agrochemicals to the combined dose fraction derived for the combustion products.

The dose fraction referred to above is the fraction of a specified toxic load such as a dangerous dose. Thus when adding responses from different gases and vapours the following approach is recommended: -

$$Net\ DDose\ Fraction = \frac{(Dose)_A}{(DDose)_A} + \frac{(Dose)_B}{(DDose)_B} + \frac{(Dose)_C}{(DDose)_C} \dots$$

Although the above rules determine how the dose to individuals exposed to the smoke plume from a burning warehouse containing agrochemicals should be calculated, their application presents problems for practical situations. A typical warehouse is likely to contain hundreds of different products formulated and packaged in different ways. As the fire sweeps through the warehouse the toxic substances in the smoke plume are numerous and change continually.

A further problem is that many of the substances in a warehouse, which have toxic and consequently need only be considered if the accident involves "COMAH substances". Added to this is the possibility that a warehouse may contain a mix brand name agrochemicals all containing the same active ingredient but in different concentrations - see Table 5 for Lindane.

Table 5: Examples of formula products containing lindane

Brand Name	AI concentration	Formulation
------------	------------------	-------------

Atlas Steward	560g/l	suspension concentrate
Gamma-Col	800g/l	suspension concentrate
Fumite Lindane 10	20.8 g a.i	smoke generator
Fumite Lindane 40	84.4 g a.i	smoke generator
Gammasan	30% w/w	Flowable concentrate
Kotol FS	125 g/l	Flowable concentrate
Unicrop Leatherjacket pellets	1.8% w/w	ganular bait

It is possible that one formulation will carry a toxic label because of the high concentration of active ingredient while another with only marginally less active ingredient could have an irritating label. A warehouse could contain very much more of the second formulation than the first and if it is neglected in the hazard assessment, the predictions could be grossly optimistic.

The question arises, which substances should be included in the risk assessment? The answer is all formulations in the warehouse where dangerous substances are stored, but this makes derivation of the source term difficult. The problem is compounded by the fact that the location of the seat of the fire and the way the different compounds are distributed throughout the warehouse has a significant influence on the toxic load received by an individual down wind.

4 CONSEQUENCE ASSESSMENT FOR COMAH SAFETY REPORTS

A safety report should consider all off-site and on-site initiators of major accidents and discuss in qualitative terms their likelihood and consequences. It should quantify the consequences of the most probable accidents to people and the local environment. The accidents that can have a serious effect on nearby populations and the environment primarily involve fires. Spills into surface water drains generally have a small or insignificant effect on the local environment because eco-toxic substances are not stored in bulk and small spills should not leave the site.

The consequences of major fires, which need to be determined include: -

- (a) Emission of a toxic smoke plume.
- (b) Explosion.
- (c) Run-off of contaminated fire-fighting water.
- (d) Thermal radiation from the flame pillar.

At most warehouse sites a large number of hazardous substances are stored together for varying periods of time. Accident consequence analysis based on the inventory on a particular day is not necessarily appropriate for a COMAH safety report and for full compliance with the Regulations the hazards arising from annual worst case inventories, taking account of the maximum quantity of each substance that is likely to be stored should be analysed.

4.1 Accident initiators

When processing of chemicals is not carried out and there are no bulk liquid tanks on a site, the probability of a major fire is around 0.01/year. The events which can initiate a fire may be classified as external or on-site and include: -

External Events

- 1) An earthquake.
- 2) Subsidence.

- 3) Landslip.
- 4) Flooding.
- 5) Extreme environmental conditions.
- 6) Lightning.
- 7) An aircraft crash on the site.
- 8) Heavy vehicle impact/fire.
- 9) Impact by a train.
- 10) Nearby fire/explosion.
- 11) Collapse of a high voltage cable onto the warehouse.

The safety report should discuss all of these accident initiators and put forward reasoned arguments as why the risk is not significantly greater than for other similar sites in the UK. Some sites will in fact be subject to a higher risk than the average UK site from one or more of these initiators because they border a busy railway line, they are close to an airport, or the area is known to be prone to subsidence. In such cases the occupier should estimate the frequency of a major accident and attempt to show that it is tolerable.

There is little an occupier can do about the probability of accidents initiated by off-site events such as aircraft impact and earthquake. However, all reasonably practicable precautions should be taken to eliminate the possibility of adverse environmental events such as lightning strike, severe storms and high winds setting off a chain of events which could result in a fire. Assessors should expect to see some or all of the following measures mentioned: -

- Buildings fitted with lightning conductor.
- Buildings constructed to relevant standards.
- Buildings and plant designed to withstand the 1/100 year return frequency storm.

The probability of flooding leading to ground/river contamination should be low, and if the site is on the banks of a river, the safety report should describe the measures to prevent flooding. These should include:-

- 1) Historical evidence of flooding/high water marks.
- 2) Details of the freeboard height.
- 3) Measures to strengthen the river bank .
- 4) Sluices and/or bypass channels.
- 5) Bunding around plant/stores sensitive to flooding.

At sites located in an area liable to subsidence, bulk storage tanks should be supported on deep piles. Speed and other restrictions should be applied to on-site vehicles to ensure that the probability of one of them initiating a warehouse fire is extremely low. If a major highway bound the site, barriers should be in place to prevent an out-of-control vehicle crashing on to the site and causing a major accident. A chain link fence supported by steel posts may not be sufficient to halt high-speed vehicles and there should be at least a wall, a building or a large open area between warehouses and the perimeter fence. If a busy railway line passes through, or borders, the site, warehouses should be situated well away from the path of a crashing train.

The on-site accident initiators a safety report should address include: -

- A malfunctioning fork-lift truck.
- An overloaded electrical cable.
- Arson - children or a disgruntled employee.
- A lorry fire during unloading.
- Cutting, grinding or welding operations.
- Spillage of incompatible chemicals.
- Employees smoking.
- Ignition of a spill of a highly inflammable substance. (static, sparking electrical equipment, or a spark created by metal tools).

In principle, a spill of a highly volatile flammable liquid can result in a vapour cloud explosion but in order for this to be sufficiently severe to be counted as a major accident, a number of drums would have to spill their contents simultaneously. While this is conceivable in the event of an earthquake, the probability of such an event is generally considered to be low enough for it to be neglected. However, the safety report should address all of the other hazards mentioned above and describe the measures and procedures that are in force to reduce the risk to a tolerable level.

Spills of highly eco-toxic liquids during HGV loading or unloading of drums and IBCs can result in several tens of litres entering the site drainage system and escaping off-site before an isolation valve can be closed. Assessors should expect Operators to describe the measures they have taken to reduce the probability of this type of accident.

4.2 Major accidents hazard analysis

Assessors are likely to see a variety of different approaches used to predict the consequences of major fires at a mixed chemical warehouse and it is sometimes difficult to determine if the assessment satisfies the requirements of the COMAH Regulations. Many Operators do not have access to computer programs to calculate accident consequences and carry out very simple hand calculations, based on published information. They may employ a consultant in which case the hazard analysis is likely to be more detailed. Irrespective of the approach adopted, the CA should demand that a minimum standard is attained and as a general rule the simpler the approach, the more pessimistic the assumptions should be.

As far as the hazards from the smoke plume are concerned, Assessors are likely to see quite wide variations in the assumptions made about five main topic areas: -

- The worst fire scenario.
- The warehouse inventory involved.
- Toxic source term.
- Dispersion of the plume
- Hazard range criteria.

The following paragraphs discuss some of the more popular assumptions and comment on their level of conservatism.

4.2.1 Identification and analysis of important fire scenarios

One of the principal aims of a safety assessment for a chemical warehouse is to predict the extent of the consequences to people and the environment of the worst accident(s). Unfortunately it is not obvious what size of fire and building response will give rise to the greatest toxic hazard range and if a site has several warehouses, the fire which produces the greatest hazard to people is unlikely to be the same as that which maximises the environmental impact. A fire in the warehouse with the largest toxic inventory when the wind speed is high is likely to present the greatest hazard to people. However, a fire in the warehouse containing the largest quantity of ecotoxic substances and one that is brought under control by copious quantities of fire-fighting water, which then escape off-site will have the greatest impact on the environment.

If a mathematical model is used to predict the consequences of fires, it is reasonable to expect that sensitivity studies are carried out to determine the effect on nearby populations of varying the: -

- Wind speed.
- Direction of the wind.
- Warehouse location.
- Toxic inventory involved in the fire.
- Duration of the release of toxic substances.

4.2.2 Hazardous substances that should be considered

A variety of substances contribute to the toxicity of the smoke plume from a warehouse, but those which probably dominate the hazard are: -

- All toxic chemicals (Risk phrase R23/24/25).
- The combustion products of toxic substances.
- The combustion products of other substances in the warehouse that need to be considered.

4.2.3 Source term assumptions

FIREPEST 3 calculates the response of a warehouse to fire and determines a time dependent rate of release of toxic vapour and combustion products, but most computer programs used in the production of COMAH safety reports for warehouses do not have this level of sophistication. They usually assume that 5-10% of the toxic substances are released into the smoke plume over a period of 1-2 hours. These assumptions should be regarded as acceptable provided there is conservatism in other aspects of the modelling. If however, an Occupier takes a minimalist approach in all aspects of the consequence analysis (minimum toxic inventory, 5% release over 2 hours, a rising smoke plume etc.) then the results should be challenged.

It is probably overly pessimistic to assume that the whole of the warehouse is on fire, the roof has failed and the smoke plume is neutrally buoyant, because a fire in a large warehouse can generate several Gigawatts of heat. In practice once a fire has caused failure of the roof of a warehouse the smoke rises high into the atmosphere and disperses safely. The fire only poses a hazard in its early stages, therefore it is reasonable for a hazard analysis to assume that only a fraction of the inventory is released over a period of about 1 hour. One acceptable method of determining this fraction is to use the lift-off criterion: -

$$\frac{8.9 Q}{H U^3} = 0.18$$

where

- Q = heat content of the smoke plume (MW).
- H = height of the building (m).
- U = wind speed (m/s).

This allows Q to be determined and related to the area of warehouse on fire if a heat generation rate per square metre of fire can be determined. However, this calculation relies on knowledge of:

- The burning rate - which may include pool and stack burning.
- heat lost to the building and the environment.
- heat lost to fire-fighting/sprinkler water.
- incomplete burning of combustible substances.

Example: Well ventilated burning of formulated agrochemicals - three pallets high - building intact.

A pool fire and a stack fire for this several metres high generate of the order of 5MW/m². If together the loss processes are conservatively assumed to account for 90% of the heat generated, then the heat in the smoke plume (Q) is around 0.5MW/m². The maximum area of warehouse on fire that produces a smoke plume, which does not lift-off, is therefore given by: -

$$A = \frac{0.18 H U^3}{4.5}$$

This implies that if the height of the warehouse is 10m and the wind speed is assumed to be 10m/s, then the maximum area on fire that will produce a smoke plume which does not lift-off is approximately 400m². The toxic source term should therefore be calculated as either: -

$$m_{toxics} = M_{total} R \frac{400}{A}$$

or

$$m_{toxic} = M_p R$$

m_{toxic} = release of toxic substances (kg).

- M_{total} = total mass of toxics in warehouse (kg).
 A = palletted floor area of warehouse (m²).
 M_P = most toxic mass in a palletted area of 400m².
 R = release fraction (5%-10%).

The time of the release should generally be assumed to be in the range 1 -2 hours.

Clearly there is considerable scope for slightly different assumptions and Assessors should recognise that the uncertainty attached to the rate of release of any particular substance is at least a factor of 2.

4.2.4 Dispersion of the smoke plume

COMAH safety reports for warehouses may use a Gaussian dispersion model to predict down wind concentrations of hazardous substances. Such an approach should be considered acceptable if: -

- The plume is assumed to be neutrally buoyant.
- The virtual source is appropriately specified.
- The standard deviations of the plume are close to literature values.

The concentration that a person standing under the centre line of a neutrally buoyant plume is exposed to is approximately: -

$$C(x,0,1,0) = \frac{m}{2\pi\sigma_y\sigma_z U} \exp\left(-\frac{y^2}{2\sigma_y^2}\right) \left(\exp\left(-\frac{(H-1.6)^2}{2\sigma_z^2}\right) + \exp\left(-\frac{(H+1.6)^2}{2\sigma_z^2}\right) \right) \text{ where}$$

m = rate of release of combustion products (kg/s).

σ_y, σ_z = standard deviations in the Y and Z directions.

U = wind speed at a height of 10 m (m/s).

H = height of the plume centre line (m).

Numerous equations for the standard deviations of a Gaussian plume in different weather conditions and over different terrain have been proposed, but the spread they produce in concentration profile is generally less than the uncertainty resulting from other sources. For the purpose of warehouse hazard assessment it does not matter much, which equations are used.

Adaptations of Gaussian models to allow for buoyancy by simply elevating the source should be fully explained and justified.

The consequences of wind speeds up to 15 m/s should generally be examined.

4.2.5 Determination of hazard range

Most agrochemical warehouses contain formulations with a toxic label therefore in the event of a major fire, the smoke plume will contain some toxic substances and their combustion products. A hazard range should be calculated assuming that the dose fractions of all dangerous substances are additive. For example if a warehouse contains two toxic substances and a large quantity of non toxic substances as indicated in Table 7, the hazard range from the smoke plume is determined by calculating dangerous dose fractions for each toxic component as shown in Table 7. The result is 1.04 indicating that the hazard range is >100m.

Table 7: Typical analysis for an agricultural warehouse

Substance	Quantity in warehouse	Rate of release to smoke plume	DDose	DDose fraction at 100m during first 30minutes
X	M_x	m_x	DD_x	0.2
Y	M_y	m_y	DD_y	0.3
PVC (chlorine containing)	1,000	m_{HCl}	DD_{HCl}	0.17
Isoprothiolane (sulphur containing)	700	m_{SO2}	DD_{SO2}	0.22

Metamitron (nitrogen containing)	600	m _{NO₂}	DD _{NO₂}	0.15
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4.2.6 Other methods of predicting a toxic hazard range

Assessors are likely to see several other approaches used in COMAH safety reports including: -

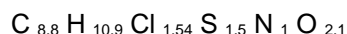
1. Toxic substances are converted to equivalent quantities of the most toxic by multiplying by the toxicity ratio.
2. The mass of the most toxic substance in the warehouse is assumed to be equal to the total mass of toxics.
3. More than 10% of the most dangerous inventory (product of mass and toxicity) over the past three years is assumed to be released over 30 minutes into a passive smoke plume.

All of these approaches introduce an acceptable amount of conservatism into the hazard range calculation, which Assessors need to balance against optimism incorporated in other parts of the consequence analysis.

4.2.6.1 Use of the Average Pesticide

There is a school of thought which believes that it will never be possible to build mathematical models to accurately predict the hazards from a burning pesticide warehouse that contains a large number of substances in different chemical and physical form and packaging arrangements. This school therefore recommends that the hazard analysis is based on a hypothetical "average" agrochemical which releases a variety of low molecular weight toxic gases when burnt. The composition of the average agrochemical is determined from the molecular composition and masses of different substances in the warehouses. The example shown in the table below illustrates how to calculate release rates of the different gases.

Table 8 shows how the composition of the average agrochemical can be determined from the inventory of three agrochemicals: -



The average molecular weight is 267 and if the burning rate of material in the warehouse was 20kg/s, then 74.8mols/s would be combusted. From this the rate of release of different products is:-

HCl	4.2kg/s.
SO ₂	7.2.
NO ₂	0.17.
HCN	0.1.
CO	19.7.

A hazard range based on the addition of fractional dangerous doses is then likely to be conservative unless the warehouse contains very large quantities of an extremely toxic substance such as phorate.

Table 8: Calculation of a representative substance for an agrochemical warehouse

Quantity	Mol. Weight	Composition	No. of kg atoms Carbon	No. of kg atoms hydrogen	No. of kg atoms chlorine	No. of kg atoms sulphur	No. of kg atoms nitrogen	No. of kg atoms oxygen
50,000	322.5	C7H7Cl3NO3P S	1,085	1,085	465	310	155	465
20,000	296.6	C9H4Cl3NO2S	606.9	2,698	202	134.8	67.5	138
40,000	380.5	C20H32N2O3S	2,102.5	3,364	0	210	210	315.5
			3,794.4	4,719	667	655	432.5	915
			8.8	10.9	1.54	1.51	1	2.1

5 EXPLOSIONS IN WAREHOUSES

Some substances are referred to as explosive because under certain conditions they are liable to undergo a rapid chemical reaction which produces large quantities of hot gas. There is not a precise

definition of the term explosive, but the three most important characteristics of explosives are the speed of the transformation to gas, the quantity of gas produced and the temperature of the gas. Unfortunately there are two distinct types of explosion which are referred to as deflagration and detonation and these tend to be confused in the literature on account of the fact that the effects of deflagration and detonations are not always a clear guide to the nature of the explosion. The destructive effects of a deflagration can occasionally be comparable to those of a detonation, but in general the characteristics of the two phenomena are rather different.

5.1 Deflagration and thermal properties

During a deflagration, the chemical reaction zone travels from one particle of the substance to another by thermal conduction and convection; therefore, the physical state of the substance has a marked effect on its explosive power. The velocity of the deflagration front in a solid in the open air is quite different from that in a solid contained in a closed vessel, because the velocity of reaction front increases with the pressure exerted on the solid by the combustion gases. Thus, in a closed container the deflagration front accelerates as pressure increases, but rarely exceeds 1m/s.

The strength of the container governs the maximum pressure rise, and hence the maximum speed and duration of the deflagration, which in turn governs the maximum air pressure generated by the explosion. Containment of explosives should therefore be avoided wherever possible. If this is not possible containers should be open or of low strength and should not be stacked high because this increases the confinement of the central and lower layers.

The characteristics of condensed explosive fall into two main groups the first of which contains chemical information such as composition and heat of formation at constant volume. The second group includes the physical properties of the substance and the conditions under which it is stored (exploded). The first group, together with the quantity, determines the consequences of an explosion should one occur, while the second relates to the probability of an explosion and hence the safety of the storage arrangements.

5.2 Explosive yield

Since an explosion is the rapid conversion of a solid into a gas at high temperature, the basic parameters governing explosive yield are the quantity of gas produced and the heat released by the reaction, which determines the maximum temperature reached.

The quantity of gas produced is usually expressed as a volume at 0°C and 1 atmosphere pressure per 1kg of the explosive. It is denoted by V^0 and is calculated from the chemical equation representing the explosive reaction, treating the gases as ideal gases.

The heat of the explosion is the quantity of heat released during the decomposition. It is determined by the chemical equation representing the explosion reaction in which the explosive products on the right hand side are in a physical state appropriate to the high pressure and temperature conditions of the explosion. Any water formed is in the vapour state. The heat of an explosion, measured per unit mass of explosive, is designated Q_v and is closely approximated by the heat of reaction; however, there is not a unique way of determining Q_v and different thermodynamic relations yield different results.

There is little point in striving for high accuracy in a calculation of explosive yield because not only is the final thermodynamic state of the products uncertain, but the physical state of the containment, storage conditions etc. can have a marked effect on the energy released.

Calculation and experiment have determined the energy of explosion of most common explosives, but in practice not all of the energy which could theoretically be released is actually converted into a blast wave. There are numerous reasons for this, but the main one is that only a fraction of the mass of the explosive actually explodes - the rest is dispersed. The ratio of actual energy released to that theoretically available is usually referred to as the explosion efficiency.

The energy released by an explosion is therefore the product of the mass of the explosive, the energy of explosion of 1kg of the substance and the explosion efficiency. The specific explosion energy is usually measured in terms of the energy of detonation of TNT and is referred to as explosive power: -

$$\text{Explosive power} = \frac{E_s}{E_{\text{int}}}$$

E_s = Energy of decomposition of 1kg of substances.

E_{int} = Energy of detonation of 1kg of TNT.

Since the consequences of explosions are documented in terms of the mass of TNT, the consequences of explosions of other substances are most conveniently determined by calculating an equivalent mass of TNT. This is defined as:-

TNT Equivalent = M x (explosive power) x (efficiency).

Once the TNT equivalent of a substance has been established, the effect of an explosion of M kg of that substance is easily determined by reference to documented effects of an explosion of an equivalent quantity of TNT.

5.3 Consequences of explosions

An explosion by its very nature releases a large quantity of hot gas in a very short period of time. This generates a pressure front which moves away from the source. As the explosion progresses on a microsecond time scale, the temperature and pressure disturbances move out with increasing speed and catch up earlier ones, resulting in the formation of a steeply rising pressure front or shock wave, which moves out with constant velocity.

Over the years data have been collected on the peak overpressure versus distance for various types of explosion. Although these exhibit considerable scatter they have been plotted in terms of equivalent mass of TNT. (R. Merrifield: *Simplified calculations of blast induced injuries and damage*, HSE Specialist Inspector's Report Number 37). Some typical results are shown below:

Scaled distance (m.kg ^{-1/3})	Peak overpressure (kPa)
5	32
10	11
20	4.2
30	3
40	1.9

5.3.1 Blast damage

The consequences of blast waves are often tabulated in terms of the effect of different levels of overpressure on people and buildings. Examples can be seen in the list below:

Serious level of death	500 mbar.
Dangerous level (1% lethality)	140 mbar
Windows usually shattered (all sizes)	35-70 mbar
Frame distortion of steel framed buildings	140-170 mbar
Rupture of oil storage tanks	210-280 mbar
Steel framed buildings pulled from foundations	210 mbar
Rail cars overturned	490 mbar
Complete destruction of all non-reinforced buildings	700 mbar

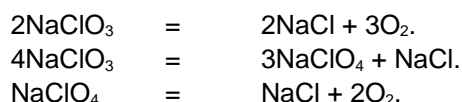
Damage to humans caused by explosions may be classified as primary or secondary. Primary damage includes being blown to pieces, being hurled through the air into a hard object or structure and suffering death via rupture of body organs. Inhalation of hot toxic and dusty gases, missile impact, collapse of buildings and fire may cause secondary damage. Experience has shown that roofing tiles, bricks and broken glass account for most missile injuries.

5.3.2 Sodium chlorate hazards

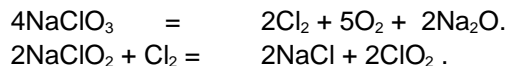
Sodium Chlorate is the most common explosive material found in mixed warehouses, it forms colourless hygroscopic crystals which are soluble in water (solubility is 790 g/l) and toxic. It melts at 248 °C and decomposes at 300 °C releasing oxygen. Sodium chlorate is strongly oxidising and mixtures containing combustible material are extremely sensitive to impact and flame. Fine powders and surfaces impregnated with sodium chlorate are likely to catch fire and/or explode spontaneously.

Sodium chlorate is normally transported in 25 or 50 kg steel drums but occasionally it is packed in paper bags lined with aluminium. It is classed as an oxidising agent and not an explosive, although its explosive and unpredictable behaviour is well known. There have been several incidents of sodium chlorate explosions and research, carried out by HSE has shown that, while drums of pure sodium chlorate engulfed in a small fire in the open are unlikely to explode, a small degree of confinement, such as that offered by a three sided roofed enclosure, is sufficient to cause a fire to produce an explosion.

The reaction mechanism of high temperature sodium chlorate is complex and not fully understood. The reactions which are generally thought to take part in the explosive decomposition are: -



Other possible reactions include: -



Many substances catalyse the thermal decomposition of sodium chlorate and some form explosive mixtures. Mixtures with organic materials such as sugar, sawdust, oil etc., and with inorganic substances, such as sulphur, finely divided metal acids etc., can be extremely sensitive to shock friction and/or heat and can burn or explode spontaneously. Spillage should be avoided at all cost and if they do occur should be removed with water by an operator wearing protective clothing.

5.3.3 TNT equivalent of sodium chlorate

The explosive power of sodium chlorate is usually assumed to be 0.14, indicating that the energy of decomposition is about 650 kJ/kg. The efficiency of sodium chlorate explosions is generally taken to be about 0.25, thus the TNT equivalent of a stack of sodium chlorate is: -

$$\begin{aligned}\text{TNT equivalent} &= M \times 0.14 \times 0.25 \text{ kg} \\ &= 0.035M\end{aligned}$$

5.4 Ammonium nitrate

Ammonium nitrate is a hygroscopic colourless crystalline solid, which is very soluble in water. In the dry state it is non-corrosive, but, when moist, it reacts with various metals forming a variety of compounds, some of which are highly unstable (e.g. copper nitrate tetramine). The main decomposition product when ammonium nitrate is heated above 200° C is N₂O, but above 250 °C other oxides of nitrogen can be formed.

The most common form of ammonium nitrate is fertiliser. This exists in a variety of forms but these are classified into two groups according to the nitrogen content. All fertilisers with a nitrogen content of more

than 28% are assumed to have the same hazard potential, although it is known that low density material and compounds containing potassium are more likely to detonate.

Pure ammonium nitrate is not shock or friction sensitive and cannot be induced to detonate under normal storage conditions; however, the following parameters increase its

sensitivity: -

- High temperature.
- Confinement.
- Contamination with organic substances.

Fertiliser is generally considered to be less hazardous than pure ammonium nitrate unless it is contaminated with substances that make it more sensitive.

There is some confusion and uncertainty in the literature and in safety reports about the explosive power of fertiliser. This can be traced back to the question - can a stack of fertiliser detonate or only deflagrate? Experiments have shown that, to all intents and purpose, it is incapable of doing either unless at least some of the stack is heated above its melting point. Detonation, which is characterised by a supersonic pressure wave moving through the material, can occur only if the dimensions of the explosive are greater than some particular value known as the critical charge diameter. For solid fertiliser this diameter is about 3m which implies that a stack of less than 300 tonnes is unlikely to detonate. The corresponding diameter for molten ammonium nitrate is only about 10 cm.

Deflagration is not constrained by dimensions and is said to occur when a subsonic combustion generated pressure wave moves through the material. Under certain conditions the energy released and the damage caused by the two process (detonation and deflagration) in a sample of ammonium nitrate can be different, but, in hazard analysis, it is not usual to distinguish between them and to refer only to an explosion.

The consensus of opinion on ammonium nitrate hazards is that, in the event of a large fire at an fertiliser store, a pool of liquid ammonium nitrate will be formed at the side of the stack that is nearest to the fire. If this pool is struck by a high speed missile (e.g. something falling or part of a drum that has exploded) then a local explosion will occur sending a shock wave into the main fertiliser stack that has not melted. If this stack contains just less than 300 tonnes it will not support a detonation but will deflagrate and, in doing so, will release an amount of energy equivalent to 41 tonnes of TNT. This figure is calculated on the basis of a TNT equivalence of AN of 55% and an efficiency of 25%. The 6.9×10^3 Pa (1 psi) overpressure hazard range from such an explosion is 600m.

Stacks of ammonium nitrate in the open are assumed to be incapable of exploding because the probability of an explosion trigger such as a girder falling into a molten pool is very low.

5.5 Organic peroxide hazards

Organic peroxides are highly reactive, combustible and thermally unstable due to the presence of the unstable -O-O- peroxy link in their molecular structure. Some are low flash point highly flammable liquids, while others are classified as explosive. Most are liquids, but some are produced in the form of a paste. In the pure state nearly all organic peroxides are detonable, but their reactivity is suppressed by dilution or phlegmatisation with liquids such as water or phthalates. Even so, essentially all of them are capable of self heating and runaway decomposition brought about either by temperature or contamination. The results of a runaway are a violent pressure burst of their container and a sudden release of hot flammable vapour which usually ignites spontaneously. If the container is particularly strong an explosion may occur.

All organic peroxides are characterised by a self- accelerating decomposition temperature (SADT) which tends to decrease with increasing packaging size. Clearly storage should be at a temperature well below the SADT. It is recommended that when the SADT is 20°C or less storage should be 20°C below the SADT. When the SADT is between 20 and 35°C storage should be at 15°C below the SADT, and when the SADT >35°C, the storage temperature can be 10°C below SADT or lower. If the

temperature in an organic peroxide store rises above the SADT, due to, for example, a fire in a neighbouring building, a rapid decomposition can take place and give rise to three types of major accident hazard, all of which should be addressed in a safety report. These are: -

- An explosion.
- A fireball.
- An intense fire.

The convenient way of determining the consequences of an explosion is to calculate the equivalent amount of TNT. Unfortunately TNT equivalence fractions are not readily found for all peroxides, but the values in the table below can be used in hazard analysis.

Table 9: TNT equivalent of some common organic peroxides

Substance	TNT Equivalent
pure dibenzoyl peroxide.	0.09
t-butyl-peroxyacetate (70%).	0.17
t-butyl-peroxypivalate.	0.14
t-butyl-peroxy maleate (pure).	0.14
methyl ethyl ketone peroxide 60%.	0.26
cyclohexanone peroxide 60%.	0.13
peroxyacetic acid.	0.05
tert-butyl peroxybenzoate.	0.4
dibenzoyl peroxy benzoate.	0.25
di-tert-butyl peroxide.	0.38

Use of a weighted average TNT equivalent for the contents of a mixed peroxide store will produce a conservative estimate of the blast potential.

5.5.1 Fireball hazard

Self-accelerating decomposition of a large quantity of organic peroxide produces a rapid rise in temperature and release of highly flammable vapours, which are likely to ignite. The result is a fireball with properties similar to fireballs from flammable hydrocarbon liquids:-

$$R = AM^{\frac{1}{3}}$$

$$t = \frac{4.5AM^{\frac{1}{3}}}{29}$$

$$Flux = E \times VF \times J$$

$$J = 1 - 0.009293 (\log k)^{1.389} H^{0.2868}$$

$$VF = \frac{xR^2}{(x^2 + R^2)^{\frac{1}{2}}}$$

where

R = fireball radius (m).

t = duration of the fireball (s).

A = substance specific constant (~29).

J = atmospheric transmissivity factor.

H = humidity.

VF= view factor between fireball and target.

x = distance between target and point on the ground under the centre of the fireball.

k = $(x^2 + R^2)^{1/2}$.

5.5.2 Intense fire

A fire in a peroxide store that does not result in an explosion or a fireball will burn very intensely and the thermal radiation from the flames may produce knock-on effects. Quantification of the hazard is difficult because the store may contain the flames, but this is unlikely. Complete failure of the roof is more probable and then the flames are likely to extend well above the walls of the building.

The extent of the hazard can be determined by assuming that the peroxide store forms a pool fire with a high burning rate. The difficulty with this approach is that burning rate data for most peroxides is sparse and at best uncertain. A figure that is probably conservative for most peroxide stores containing Type 1 compounds (see CS21) is 0.5 kg/s.m². This is about 10 times the burning rate of hydrocarbon liquids. If the stores contains mainly type 3 organic peroxides, this figure should be reduced to 0.2. The rate of heat release can be obtained from the mass burning rate by assuming an effective heat of combustion of around 30 MJ/kg.

The burning rate can be used to predict the flame height for a pool covering the whole of the floor of a peroxide store:-

$$L = 0.2[Q]^{0.4}$$

where

L = height of the flames (m).

Q = rate of heat release in kW.

There is little or no data in the literature on organic peroxide pool fires hence uncertainty surrounds the emissive power of the flame pillar. In the absence of more reliable data, a figure of 200 kW/m² over the whole length should be assumed. The duration of the pool fire should be accounted for in consequence calculations because at 0.5 kg/s.m², the contents of a small store may be consumed quickly.

6 THERMAL RADIATION FROM A BURNING WAREHOUSE

A warehouse fire, which is not burning fiercely and is covered by the roof does not radiate large quantities of heat to the surrounding area. The smoke it emits may be hazardous to members of the public at some considerable distance from the site, but the danger of escalation is limited if the local fire fighting services are able to confine the blaze to one building. A raging fire on the other hand has only a minor effect on members of the public, but may radiate sufficient heat to damage adjacent buildings. Of particular concern are nearby: -

- wooden buildings.
- diesel storage tanks.
- LPG storage tanks.
- flammable liquid storage tanks (adjacent site).
- flammable liquid/gas pipelines.
- residents houses.

Predictions of thermal radiation emitted by a warehouse fire are necessarily imprecise because the burning behaviour of the fire is uncertain and the rate of release of heat varies temporally and spatially. The controlling factors governing the size and intensity of the flames are:-

- The state of the roof (has it collapsed).

- The number of failed roof lights.
- Whether or not the doors are open.
- The effect of sprinklers.
- The strategy adopted by the fire service.

Wooden pallets on steel racking, which burn relatively slowly compared to cardboard packaging material and plastic, can provide a "structure" for the fire and enhance the burning rate by maximising oxygen availability. If the fire is not controlled by the sprinkler system, it quickly becomes very hot with flames leaping to a height of several tens of metres. After collapse of the pallets and failure of many plastic bottles containing flammable liquids, it resembles a pool fire with debris dispersed in it. Under these circumstances a rough estimate of the height of the flame pillar can be obtained using the Thomas correlation, assuming that the effective diameter is equal to the shortest side of the warehouse.

The flame length is weakly dependent on the burning rate of the pool, which cannot be accurately determined for mixtures. An approximate burning rate using data for the pure flammable liquids that make up the bulk of flammable pesticides stored in the warehouse can be derived as follows.

The burning rate for a pure substance is given by:-

$$\dot{m} = \frac{h_c}{1000(h_v + (T_b - T)C_p)}$$

where

- \dot{m} = burning rate (kg/s.m²).
- h_c = heat of combustion (MJ/kg).
- h_v = heat of vaporization (MJ/kg).
- C_p = specific heat (MJ/kg.K).
- T_b = boiling point (K).
- T_a = ambient temperature (K).

For a mixture of solvents the pool burning rate is: -

$$\dot{M}_T = \dot{m}_{s1} \frac{V_{s1}}{V_T} + \dot{m}_{s2} \frac{V_{s2}}{V_T} + \dot{m}_{s3} \frac{V_{s3}}{V_T} + \dots$$

where

- M_T = total average burning rate (kg/s.m²).
- V_{s1} = volume of flammable liquid 1 in the warehouse
- V_T = total volume of flammable liquid in the warehouse.
- m_{s1} = mass burning rate of flammable liquid (kg/s.m²).

If the warehouse does not contain appreciable quantities of flammable liquid, a stack mass burning rate for the Thomas correlation can be estimated as follows: -

$$skM_T = \frac{\sum_i \dot{Q}_i h_i}{\Delta \overline{H}_c}$$

$$\Delta \overline{H}_c = \frac{\sum \Delta H_i h_i}{\sum h_i}$$

where

- skM_T = effective stack mass burning rate (kg/s).
- DH_c = average heat of combustion of stack (MJ/kg)
- DH_i = heat of combustion of i'th substance in stack in (MJ/kg).
- h_i = height of i'th substance in stack.
- Q = heat generation of i'th substance in stack (MW/m.m²).

Where part of a stack contains two or more substances for which a net heat release rate is not available, a simple average value is used.

Configuration factors are notoriously difficult to calculate for most practical situations, but in the case of a tilted flame pillar a standard textbook expression may be appropriate. Alternatively the flame can be modelled as a point radiator that radiates of the order of 30% of the total heat released by combustion.

7 CONSEQUENCE ASSESSMENT - PRACTICAL CONSIDERATIONS

Although the rules for determining dose to individuals exposed to the smoke plume from a burning warehouse containing agrochemicals have been defined, their application presents problems for practical situations.

There are several ways in which doses from different pesticides can be added, but given the uncertainty attached to all of them, perhaps the best choice is the one involving the least amount of effort. The Agrochemicals Handbook lists 204 different types of pesticide, all of which presumably have a different effect on the body. However there are 86 listed organophosphorous compounds and these are known to be the most toxic of all pesticides. Other groups which have a large number of members and are relatively toxic include: -

Table 10: Number of pesticides in 4 typical groups

Type	No.	Example
Organophosphorus	70	chlorfenvinphos, chlorpyrifos, dichlorvos
Carbamates	45	aldicarb, pirimicarb, carbofuran
Organochlorides	45	lindane, heptachlor, endosulphan
Pyrethroids	29	cyhalothrin, esfenvalerate, cypermethrin

There are other agrochemicals that are particularly toxic but, which have few class members, these include bipyridyls such as paraquat and coumarins such as warfarin and difenacoum. These need to be considered separately.

It is recommended that when carrying out warehouse safety assessment, all members of each of the above 5 classes are added together according to the following prescription: -

- 1) The most toxic member of the group is identified.
- 2) An effective mass (EM) is calculated for all other members of the group: -

$$\text{Effective mass} = \frac{A_{\text{most toxic}} \times RF}{A \times RF_{\text{most toxic}}}$$

where

- A = toxic load to produce a dangerous dose in mg/m³.mins.

A_{most toxic} = toxic load to produce a dangerous dose.
 RF = release fraction.
 RF_{most toxic} = release fraction of the most toxic.

This approach is applied to the warehouse inventory shown in Table 11.

Table 11: Warehouse inventory - hazard data

Active Ingredient	Total mass kg	HSE-A Value ppm.min	Dang. Dose ppm.min	Mol Wt	LD50	Dang. Conc. mg/m ³	Release fraction	Mass released	Hazard Index
Chlorpyrifos	60,000	3,600	811	350.6	135	394.2	0.1	6,000	15.22
Bifenthrin	1,250		271	422.9	54.5	159.1	0.1	125	0.79
Cyanazine	2,137.5		1,234	240.7	141	411.7	0.1	213.75	0.52
Triclopyr	3,000		2,545	256.5	310	905.2	0.1	300	0.33
Imazalil	625		2,268	297.2	320	934.4	0.1	62.5	0.07
Cypermetherin	1,250		698	416.3	138	403	0.1	125	0.31
Lindane	25,000	2,650	427	290.9	59	172.3	0.1	2,500	14.51
Paraquat	50,000	11	360	186.3		93	0.1	187.5	53.76
Phorate	3,750	15	19	260.4		7	0.05		26.79
Chlorfenvinfos	15,000	201	141	359.6	24	70.1	0.1	1,500	21.4
Ioxynil	2,812.5	4,250	625	370.9	110	321.2	0.1	281	0.88
Fonofos	3,437.5		94	246.3	11	32.1	0.1	343.75	10.7
Diquat	1,000		1,429	184.2	125	365	0.04	40	0.11
Dichlorvos	625	85	534	221	56	163.5	0.1	62.5	0.38
Carbophenothion	2,500		61	343	10	29.2	0.1	250	8.56
Pirimicarb	1,875	8,830	972	238.3	110	321.2	0.05	93.75	0.29

Noting that phorate is the most toxic organophosphorus pesticide, paraquat is the most toxic bipyridyl and lindane the most toxic organochlorine. Table 12 illustrates how Effective Masses for each pesticide in the three dominant groups can be calculated.

The problem now reduces to assessing the hazard from releases of three pesticides: -

Substance	Mass	Release fraction
<i>phorate</i>	11,628	0.05
<i>lindane</i>	25,571	0.1
<i>paraquat</i>	50,102	0.1

Table 12: Hazard assessment sheet

Active Ingredient	Type	Total mass kg	Dang.	Release	Effective Mass
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			Conc. mg/m ³	Fraction	
Chlorpyrifos	Organophosphorus	60,000	394.2	0.1	2,130.9
Bifenthrin	Pyrethroid	1,250	159.1	0.1	
Cyanazine	triazine	2,137.5	411.7	0.1	
Triclopyr	Organochlorine	3,000	905.2	0.1	571.03
Imazalil	Imidazole	625	934.4	0.1	
Cypermethrin	Pyrethroid	1,250	403	0.1	
Lindane	Organochlorine	25,000	172.3	0.1	25,000
Paraquat	Bipyridyl	50,000	93	0.1	50,000
Phorate	Organophosphorus	3,750	7	0.05	3,750
Chlorfenvinfos	Organophosphorus	15,000	70.1	0.1	2,995.7
Ioxynil	Nitrile	2,812.5	321.2	0.1	
Fonofos	Organophosphorus	3,437.5	32.1	0.1	1,499.2
Diquat	Bipyridyl	1,000	365	0.04	101.92
Dichlorvos	Organophosphorus	625	163.5	0.1	53.52
Carbophenothion	Organophosphorus	2,500	29.2	0.1	1,198.6
Pirimicarb	carbamate	1,875	321.2	0.05	

Organochlorine (Lindane)	25571.034
Bipyridyl (Paraquat)	50101.918
Organophosphorus (Phorate)	11627.987

8 SUMMARY

This document is one of a series providing guidance on the assessment of COMAH safety reports. It is not intended to be prescriptive and Assessors are expected to use it intelligently and be flexible in the way they interpret its advice. Certain aspects of warehouse fire hazard modelling are still under review within HSE and Assessors should bear in mind that the guidance in this document is likely to be superseded at some time in the not too distant future.

Section 2 lists the main topics of a warehouse safety report and outlines the level of detail Assessors should expect. However, sites vary considerably and while every effort has been made to make the guidance generally applicable, occasions will arise when it is either inapplicable or lacking in detail. A safety report should contain maps, tables, plans, data sheets and environmental survey data, examples of which have been deliberately excluded from this document. Assessors are expected to use their own judgement to determine the acceptability of this type of information.

The background information on warehouse fires in Section 3 is designed to give an brief overview of the main topics of interest. An exhaustive review of the literature and a detailed description of the numerous problems faced by workers attempting to model the various phenomena is not attempted and if Assessors require more information they should consult the MSDU topic specialist.

Section 4 describes in detail the sort of consequence analysis that Assessors should expect to see in a COMAH safety report. There are numerous methods involving many assumptions that can be applied to warehouse fire hazards and some of the more popular that produce conservative results are

discussed. All of the more obscure approaches which Assessors may, from time to time, be required to comment on could not be addressed in this document and in these cases Assessors are advised to focus on the level of conservatism and to use FIREPEST 3 as a benchmark.

9 REFERENCES

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