The UK Dangerous Substances & Explosive Atmospheres Regulations (DSEAR 2002) implement the EC Chemical Agents Directive 98/24/EC (CAD) and Explosives Atmospheres Directive 99/92/EC (ATEX 137). They replace and modernise much old legislation. In this context, a ‘Dangerous Substance’ is defined as one that has the potential to create risk to persons from energetic events and includes gases, vapours, mists and combustible dusts. The main requirements of DSEAR are to:

- Carry out risk assessment of work activities involving dangerous substances
- Eliminate or reduce risks as far as possible
- Provide equipment and procedures for accidents and emergencies
- Inform and train employees
- Classify places into zones and mark them

The first four requirements are already in place, but the final one is an addition. HSE claims that there will be minimal costs for companies to comply with DSEAR, beyond their obligations under previous legislation, but some companies anticipate significant costs for providing equipment which is certified under the Equipment and Protective Systems Intended for use in Potentially Explosive Atmospheres Regulations 1996 (EPS).

The regulations became effective on 30 June 2003 in their entirety for any new or modified processes. Existing processes must comply from that date for risk assessment, control and mitigation measures, but have until 30 June 2006 to fulfil the explosive atmosphere requirements (zone classification, EPS equipment and signage).

This paper describes a practical approach to complying with DSEAR 2002; it concludes with case studies of a low pressure hydrogen pipe in a well ventilated building and of a paint store.

KEYWORDS: DSEAR, dangerous substance, explosive atmosphere, risk assessment, hydrogen, paint

INTRODUCTION

The historical background to the Dangerous Substances and Explosive Atmospheres Regulations 2002 (DSEAR)\(^1\) has been comprehensively explained in several papers at a previous HAZARDS symposium\(^2\)–\(^4\). It is sufficient for the current paper to state that
DSEAR is the UK implementation of the European legislation Chemical Agents Directive 98/24/EC (CAD) and the Explosive Atmospheres Directive 99/92/EC (ATEX 137); it is based on risk assessment and replaces much old UK legislation on flammable substances and dusts.

In December 2002 the UK Health & Safety Executive (HSE) published a short guide to DSEAR, particularly for small and medium-sized businesses, and followed that in 2003 by a series of six Approved Codes of Practice and guidance (ACOPs) — one overall ACOP and five more detailed ACOPs dealing with the specific topics of design, storage, mitigation, and unloading of petrol from road tankers; the ACOPs are substantial documents, totalling almost 200 pages. HSE’s Safety Policy Directorate has posted a useful 21 page DSEAR overview and guidance on the HSE website. The UK Department of Trade & Industry has published a guide on the equipment and protective systems which may be used in potentially flammable atmospheres. We have distilled the main points of the various documents in order to describe a practical approach that will meet the requirements of many process industry designers and operators.

DEFINITION OF ‘A DANGEROUS SUBSTANCE’
The Regulations give a detailed definition of ‘dangerous substance’ but “it includes any substance or preparation, which because of its properties or the way it is used, could cause harm to people from fires and explosions. Dangerous substances include: petrol; liquefied petroleum gas (LPG); paints; varnishes; solvents; and dusts which when mixed with air could cause an explosive atmosphere, for example, dusts from milling and sanding operations.”

A substance is classified under DSEAR as a dangerous substance if any of the following apply:

1. The substance is classified under the Chemicals (Hazard Information and Packaging for Supply) Regulations 2002 (CHIP) in the supplier’s safety data sheet or in the HSC’s Approved List as explosive, oxidising, extremely flammable, highly flammable or flammable.
2. A risk assessment of the work activity on site means that a substance not subject to CHIP could nevertheless result in a fire, explosion or similar energetic event, for example:
   - a flammable solvent is produced and used only as an intermediate on the site;
   - diesel oil is used in a process at high temperature;
   - hot work (welding) raises the temperature of part of a vessel or pipe above its normal operating temperature;
   - chemical reactions have the potential for thermal runaway;
   - unstable peroxides are handled or stored.
3. The substance is a dust which, when dispersed in air to form a cloud, can explode if an ignition source is present. Further information on how to assess the risks of combustible and explosive dusts, and on the relevant safety precautions, can be found in the HSE publication, Safe handling of combustible dusts.
DSEAR covers only the harmful physical effects to people caused directly or indirectly by fires, explosions or energetic events, namely thermal radiation effects (burns), over-pressure effects (blast injuries) and oxygen depletion effects (asphyxiation). Any materials that are a potential hazard to health are subject to the COSHH Regulations instead of DSEAR (if non-flammable), or as well as DSEAR (if flammable).

SCOPE OF DSEAR
DSEAR applies in any workplace whenever the following conditions are satisfied:

- Work is being carried out by an employer or a self-employed person; and
- A dangerous substance is present or is liable to be present at the workplace; and
- The dangerous substance presents a risk to the safety of persons — whether employees, visitors or members of the public.

A ‘workplace’ means any premises or part of premises used for or in connection with work, including: all industrial and commercial premises; land-based and offshore installations; vehicles and vessels; common parts of shared buildings and industrial estates; domestic premises if work is being carried out by an employer or a self-employed person; and public roads if the road itself becomes the workplace e.g. during road repairing or work on utilities.

There are some exemptions, which briefly are:

- DSEAR does not apply to ‘normal ship-board activities of a ship’s crew’ on commercial vessels. However Royal Navy vessels and offshore installations are not excluded.
- The provisions in DSEAR for explosive atmosphere zoning does not apply to medical treatment areas; gas appliances used for cooking, heating etc.; manufacture of and work with explosives; mines, quarries and offshore installations; road vehicles and aircraft.

Regulation 3 in the DSEAR ACOP should be studied very carefully before concluding that a particular ‘workplace’ is not subject to some or all provisions of DSEAR. HSE has provided examples of the type of activities and substances commonly found at work that are likely to be covered by DSEAR:

- Storage of petrol used as a fuel for cars, motor boats, horticultural machinery, etc
- Use of flammable gases, such as acetylene, for welding
- Handling and storage of waste dusts in a range of manufacturing industries
- Handling and storage of flammable wastes including fuel oils
- Hot work on tanks or drums that have contained flammable material
- Work activities that could release naturally occurring methane
- Dusts produced in the mining of coal
- Use of flammable solvents in pathology and school laboratories
- Storage/display of flammable goods, such as paints, in the retail sector
- Filling, storage and handling of aerosols with flammable propellants, such as LPG
Transport of flammable liquids in containers around the workplace
Deliveries from road tankers, such as petrol or bulk powders
Chemical manufacture, processing and warehousing
Petrochemical industry — onshore and offshore

The last two examples above effectively cover all activities in the process industries!

MAIN REQUIREMENTS OF DSEAR
DSEAR requires employers (or self-employed persons) to carry out a risk assessment before commencing any new work activity involving dangerous substances. In the case of an employer with five or more employees, they must also record the findings of the assessment, including:

- The technical and organisational measures taken to eliminate and/or reduce risk;
- Sufficient information to show that the workplace and work equipment will be safe during operation and maintenance including:
  - Details of any hazardous zones
  - Any special measures to ensure co-ordination of safety measures and procedures, when employers share a workplace
- Arrangements for accidents, incidents and emergencies; and
- Measures taken to inform, instruct and train employees.

We will now briefly describe each of these requirements, which are described in considerable detail in the various ACOPs.

CARRY OUT A RISK ASSESSMENT BEFORE COMMENCING ANY NEW WORK ACTIVITY INVOLVING DANGEROUS SUBSTANCES
HSE emphasises that “The requirement to assess the risks from dangerous substances should not be considered in isolation. It should be carried out as part of the overall risk assessment required by ... the Management of Health & Safety at Work Regulations 1999, rather than as a separate exercise. The risk assessment will follow the normal sequence of activities, familiar to many in the process industry:

1. Identify all substances that may be present in the workplace during all relevant activities, including loading and unloading, storage, processing, sampling, cleaning, maintenance and dismantling. Then, as described above under “Definition of a dangerous substance”, check which substances if any are classified as dangerous substances.
2. For each dangerous substance, identify the scenarios that may cause it to be present in the workplace, including ‘normal’ activities such as filling, sampling and spraying; ‘atypical’ activities such as maintenance; and ‘failure’ cases such as leaks.
3. For each scenario, identify:
   - The potential for explosive atmospheres to form. This will depend on factors including the quantity released and whether or not there is ventilation. If a release is extremely unlikely to occur it may not be necessary to classify the area as hazardous; for example if the dangerous substance is being carried through a properly installed and maintained seamless pipe. Similarly, if the quantities potentially released are small and the area is not confined, it may not be necessary to classify the area as hazardous; for example spillage from a small bottle of solvent, or from small pre-packaged containers of dangerous substance displayed in retail premises. However, even for small releases, procedures would still be needed to clean up and dispose of any spillage/release and to control ignition sources such as smoking in the event of such a release.
   - The likelihood of unintentional ignition from equipment and employees (which may be caused by static discharges as well as more obvious ignition sources such as sparking electrical equipment or smoking);
   - The effectiveness of plant and equipment to mitigate the effects of an incident; and
   - The possible extent of harm to people (including those in connected spaces).

As always, the risk assessment should be reviewed: at regular intervals depending on the nature of the risks; if new information suggests that it is no longer valid; when any significant changes that might affect the risks occur in the workplace; and after an accident or dangerous occurrence.

**RECORD THE TECHNICAL AND ORGANISATIONAL MEASURES TAKEN TO ELIMINATE AND/OR REDUCE RISK**

*Every employer shall ensure that risk is either eliminated or reduced so far as is reasonably practicable — DSEAR Regulation 6 (1)*

This step follows the safety hierarchy which is well understood in the process industry namely Elimination/Control/Mitigation. Specifically for DSEAR:

- Eliminate dangerous substances — this is the best approach but HSE recognises that it is often difficult or impossible. However it may be possible to substitute a less dangerous substance (e.g. one with higher flashpoint) or design the process to be less dangerous (e.g. reduced inventory, or lower severity ie lower temperature or pressure).
- Control measures may include:
  - Minimising quantities of dangerous substances (e.g. by design as discussed above, or by operating procedures that maintain minimum working inventories)
  - Avoiding or minimising releases (e.g. by equipment design or operating procedures)
  - Controlling releases at source (e.g. by emergency shutdown valves)
  - Preventing formation of an explosive atmosphere (e.g. by ventilation)
  - Collect, contain and remove any releases to a safe place (typically by ventilation)
Avoid ignition sources — such as fixed plant (e.g. instrumentation, motors, grinders), portable equipment (e.g. phones, car key fobs, smoking materials), personnel (e.g. clothing, static from flooring) and hot work (welding)

Avoid dangerous process deviations

Keep incompatible materials apart

Mitigation measures may include:

- Reducing the number of employees exposed
- Providing plant that is explosion resistant
- Providing explosion suppression or explosion relief
- Taking measures to control or minimise the spread of fires or explosions
- Providing suitable personal protective equipment

DSEAR also specifies that the measures taken to minimise or reduce risk (some of which are already included above) should include:

- Design, construction and maintenance of the workplace (e.g. fire resistance, explosion relief)
- Design, assembly, construction, installation, provision, use and maintenance of suitable work processes, including all relevant plant, equipment, control and protection systems
- Appropriate systems of work including written instructions, permits to work and other procedural systems of organising work
- Identification of hazardous contents of containers and pipes, generally by marking, labelling or warning signs, or possibly by training, information or verbal instruction

RECORD SUFFICIENT INFORMATION TO SHOW THAT THE WORKPLACE AND WORK EQUIPMENT WILL BE SAFE DURING OPERATION AND MAINTENANCE

This step is to record items covered in more detail later, namely:

- Details of any hazardous zones
- Any special measures to ensure co-ordination of safety measures and procedures, when employers share a workplace

RECORD ARRANGEMENTS FOR ACCIDENTS, INCIDENTS AND EMERGENCIES

This topic represents normal practice in the process industries and the equipment and procedures provided may include:

- Alarm and communication systems
- Escape facilities
- Equipment and clothing for essential personnel dealing with incidents
- Practice drills
● Information to employees about emergency procedures
● Consulting with and briefing emergency services on the site’s emergency procedures
● Co-ordinating arrangements with any other employers who share the workplace

RECORD THE MEASURES TAKEN TO INFORM, INSTRUCT AND
TRAIN EMPLOYEES
Again, this topic represents normal practice in the process industries and should include:

● The names of dangerous substances and the risks they present (this would have been a major problem for the founders of our industry, who often gave substances artificial working names to preserve process confidentiality!)
● Providing access to:
  o Any relevant safety data sheet
  o Details of the legislation that applies to the dangerous substance
  o Significant findings of the risk assessment

REQUIREMENTS FOR PLACES WHERE EXPLOSIVE ATMOSPHERES
MAY OCCUR
The requirements are:

● Classify areas into hazard zones based on their likelihood and persistence: (zones 0–2 for gas, vapour and mist; and zones 20–22 for dust):
  o Zones 0 and 20: an explosive atmosphere is present continuously, for long periods, or frequently
  o Zones 1 and 21: an explosive atmosphere is likely to occur in normal operation occasionally
  o Zones 2 and 22: an explosive atmosphere is not likely to occur in normal operation — but if it does it will persist for short periods only
● Protect hazard zones from sources of ignition by selecting equipment and protective systems meeting the requirements of the EPS regulations\textsuperscript{13} although equipment already in use before 1 July 2003 can continue to be used indefinitely providing that the risk assessment shows it is safe to do so. The EPS equipment categories are:
  o Category 1 (required in DSEAR zone 0/20): either, in the event of failure of one means of protection, at least an independent second means provides the requisite level of protection; or the requisite level of protection is assured in the event of two faults occurring independently of each other.
  o Category 2 (required as a minimum in DSEAR zone 1/21): the requisite level of protection is provided even in the event of frequently occurring disturbances or equipment faults which normally have to be taken into account
  o Category 3 (required as a minimum in DSEAR zone 2/22): the requisite level of protection is provided during normal operation
Where necessary, mark entry points to a hazardous zone with an ‘EX’ sign, to warn of the precautions needed to avoid ignition sources.

Provide any employees who work in a hazardous zone with appropriate antistatic clothing (this should already be in place as part of the measures to control risk).

Have the overall explosion safety verified as safe by a competent person – who may be an installer, final user or independent.

DATES WHEN DSEAR COMES INTO FORCE
The ‘requirements for places where explosive atmospheres may occur’ come into force:

- From 30 June 2003, any new workplace or workplace that is modified must meet the requirements from the time it comes into use.
- From 30 June 2006, any workplace that is already in use before July 2003 must meet the requirements.

The other DSEAR requirements came into force on 30 June 2003.

REGULATORY IMPACT ASSESSMENT (WHAT WILL DSEAR COST?)
HSE conducted a Regulatory Impact Assessment (RIA). The RIA describes the issue that has given rise to the need for regulations; compares various options; and identifies costs and benefits to help inform public debate about regulations.

The findings of the RIA\textsuperscript{12} “showed that businesses complying with current legislation would expect little or no additional cost as a result of DSEAR. Those not fully compliant may need to review and enhance their current arrangements, although most of the costs incurred would relate to more rigorous compliance with current legislation, prompted by the introduction of DSEAR. For example, many businesses with work processes involving potentially explosive atmospheres stated that zoning was not currently formally recorded in risk assessments. They would also be affected by the requirement to mark zoned areas with a sign.”

The process industry certainly should be ‘complying with current legislation’ so it will be interesting to see if it does indeed experience ‘little or no additional cost as a result of DSEAR’.

CASE STUDY 1: LOW PRESSURE HYDROGEN PIPE IN A WELL VENTILATED BUILDING
DSEAR at first appears to be a regulation enforcing current good practice of identifying where flammable atmospheres could be present and then estimating their likelihood (Zones 0,1,2). The standard approach then ensures control of ignition sources, for example, no smoking, control of portable ignition sources and installation of intrinsically safe (IS) electrical equipment (e.g. motors and instruments). Once these two steps have been completed the hazard is generally regarded as being under control.
The following example shows that the application of the risk assessment process required by DSEAR can lead to significantly improved control of flammable hazards. Traditional precautions do not always add value whilst the Risk Assessment approach encourages the identification of more appropriate risk control measures to reduce the residual risks to tolerable levels.

The plant under consideration will use standard Chlor-Alkali technology for the electrolysis of brine (NaCl solution) to produce chlorine, caustic soda and hydrogen. This is carried out in large electrochemical plants, which are usually called Cellrooms. Sodium chloride is split up into chlorine gas and sodium. The chlorine is removed from the process as a product gas, and the sodium reacts with water to form caustic soda and hydrogen gas.

This basic process has been used since the mid 1890s as the main technology to produce chlorine and caustic soda. Invariably the electrochemical part of the process is housed in a building. The hydrogen hazard has therefore been present in hundreds of plants for over 100 years.

Historically most of these plants have not been zoned — most of the precautions against flammable atmospheres have been developed through experience. Small hydrogen fires do occur though recently the frequency has been much reduced, in particular by improved containment.

Hydrogen has some properties of interest with respect to flammable risk. It is of course very light so tends to rise away from any structures and in so doing becomes diluted with air (but can become trapped in unventilated roof spaces). It has wide flammability limits (4–75% in air) and an extremely low minimum ignition energy (0.0017 mJ – about 200 times more sensitive than methane). Hydrogen from electrolysis is saturated with water at 90°C and so is extremely visible on contact with air.

Chlor Alkali Plants have a very high energy use (typically over 1% of an industrial nation’s electricity consumption is for Chlor Alkali production). Although the new plant will be more efficient than existing plants, it is expected that heat losses will still be several MW. These heat losses will drive natural ventilation of the building.

The Risk Assessment Process flowchart (Figure 1) was developed specifically for this assessment. It has been generalized for use with other DSEAR Risk Assessments. The following headings summarise the findings of each stage.

IDENTIFY DANGEROUS SUBSTANCES
This first stage is easy — hydrogen is the only substance present in the cellroom that is capable of creating a flammable atmosphere.

RELEASE SCENARIOS
All identified scenarios were unintentional leaks. Most of these were from joints not sealing after maintenance. The potential of a drain/sample/vent valve being inadvertently...
Figure 1. DSEAR risk assessment process
left open was also considered, as was the possibility of a release following pipe damage e.g. through impact.

RELEASE RATES
Given the scenarios it is relatively straightforward to calculate release rates. The maximum pressure is 0.25 bar and therefore joint blow-out is not believed to be credible (the force on a section of joint between bolts was calculated as equivalent to 0.4 kg). The gas release includes over 70% by weight moisture so further simple calculations are required to determine the mass release of hydrogen following condensation of water vapour.

FREQUENCY OF RELEASE
The frequency for each scenario was calculated by estimating human failure rates e.g. for failing to tighten a joint. A cellroom consists of a number of interconnected production units known as electrolysers. These electrolysers are always given an independent leak test prior to operation and the frequencies of failure to detect leaks were included in the calculation. The frequency of damage to pipes that could cause leaks was also assessed.

LIKELIHOOD OF IGNITION
The likelihood of ignition was assumed to be 1. Many years of experience have shown that it is very difficult to prevent ignition — even release to the open atmosphere from vent stacks can be ignited by airborne static. The time delay before ignition of a hydrogen release will determine whether the consequence is a fire, a fireball or an explosion. Experience indicates rapid ignition (within a few seconds) is most likely, though a longer delay cannot be ruled out.

CONSEQUENCES
The consequence was modelled for each size of release as a torch fire (using the DNV PHAST methodology). The risk to personnel was calculated for each consequence taking into account the frequency of the release and the likelihood of a person being harmed. The largest release was also modelled as an explosion following delayed ignition (various methods were used to estimate the size of the flammable mixture within the building).

The consequences of fire/explosion on equipment were also examined and this actually identified the most significant flammable risk from the process. The off-take from each part of the electrolyser is through a 50 mm PTFE hose — extremely robust but of course not resistant to direct flame e.g. from a leak on an adjacent hose. As there can be several hundred hoses for each electrolyser with only a few mm gap between each, damage of a second hose resulting from flame impingement from a small leak on
the first, is a credible escalation scenario. This would turn a small 10 mm\(^2\) (equivalent area) leak into a 2000 mm\(^2\) hole.

Note that traditional (pre DSEAR) methodologies would not have identified this risk.

**MITIGATION**

We considered the hierarchy, discussed earlier, of measures to eliminate or minimise risk.

- **Reduce quantity** — hydrogen inventory is very low as the system only contains the quantity required for flow in pipes;
- **Avoid/minimize release** — use of good joints, made by dedicated technicians and independent leak testing;
- **Control at source** — hydrogen detectors, CCTV, and fire detectors all result in electrolyser shutdown with operation of an isolation valve and automatic nitrogen purging;
- **Prevent explosive atmosphere** — the large heat losses ensure very reliable natural ventilation, use of screens surrounding each electrolyser directs ventilation to the potential leak area and ensures any leaks are kept away from areas where people may be present;
- **Avoid ignition sources (including static)** — static is considered the cause of most hydrogen fires in cellrooms and, since static is always present, avoidance of other ignition sources is of limited benefit;
- **Avoid adverse conditions (e.g. process deviations) and incompatible substances** — we reviewed this topic but could not identify any additional risk control measures; and
- **Fire detection** — this was also identified as an essential control measure to avoid escalation (DSEAR correctly categorises fire detection as a mitigation measure).

**REVIEW**

All Risk Assessments need to be reviewed periodically. This DSEAR Risk Assessment will be reviewed once the design is finalised and again prior to commissioning. Assumptions made about the frequencies of leaks will be reviewed after about 6 months operation.

**CONCLUSION**

The assessment identifies hydrogen gas as the only substance requiring consideration under DSEAR within the new cellroom building. Due to the relatively low pressure (0.25 barg) large leaks are not anticipated. Where leaks occur, they will be immediately obvious due to the presence of water vapour.

It is assumed that due to the extremely low ignition energy for hydrogen, coupled with the large number of potential ignition sources, that all leaks will ignite. The consequences of ignition are dependent on whether it is immediate (i.e. a fire) or
delayed (i.e. a build up of an explosive atmosphere leading to an explosion). The conse-
quences of ignited releases (both immediate and delayed) have been examined against
company Tolerability of Risk criteria and found to be within the Tolerable region provid-
ing a number of control measures are applied.

The main control measures are to minimise inventory and possible leak sources. The
probability of joint leaks in particular will be minimised by best engineering practice and
leak-testing procedures. Comprehensive fire detection systems will minimise the conse-
quence of a fire.

It is concluded that although prevention of ignition sources being carried by people
contributes to personal risk reduction (e.g. by use of portable flammable gas detectors),
there is no benefit to be gained from insisting on the installation of electrical equipment
approved for explosive atmospheres. In terms of the regulations, the risk from the danger-
ous substance is not sufficient to require special protective measures (DSEAR Regulation 7
and Schedule 2).

CASE STUDY 2: PAINT STORE
This is a simple case study for a small modification that happened to be on a major hazard
chemical plant.

The on site painting contractor required a paint store for both new and partially used
tins of paint. The paint was marked as flammable (flash point 21–55°C) and further inves-
tigation identified a flash point of about 38°C. The store would be located outside of a
building in a dedicated metal container. The container would be fitted with vents and elec-
tric anti-frost heating. Lighting would also be required

The initial decision was that the area would be zoned (zone 2) simply because of the
presence of material with the ‘Flammable’ hazard warning label. This was reviewed and
we questioned why the local DIY store was not equally zoned. Examination of HSE docu-
mentation identified guidance within paragraph 182 of HSG 51\textsuperscript{17}. This discusses the
subset of flammable liquids with flash points between 32–55°C. In summary the guidance
says that IS equipment is not required. (Incidentally, HSG 51 includes guidance for the
larger DIY stores; the writer believes from his own observations that compliance is not
very high).

A DSEAR Risk Assessment was requested (to comply with the legislation and
record the reason for not zoning the building). The risk assessment identified a number
of additional control measures, in particular procedures to ensure lower flash point
materials were not introduced into the store and that mixing/dilution etc did not
produce a localised flammable atmosphere within the metal container.

The final result was a decision to zone the inside of the container for two reasons:

\begin{itemize}
  \item Initially from the practical viewpoint of being unable to ensure that the procedural
        controls were fully complied with.
  \item The decision was confirmed following consideration of the potential knock on conse-
        quences of a fire adjacent to Major Hazard Plants handling other flammable materials.
\end{itemize}
REFERENCES

6. Health & Safety Executive, 2003, Dangerous substances and explosive atmospheres, Approved Code of Practice and guidance. Dangerous Substances and Explosive Atmospheres Regulations 2002, HSE Books L138, ISBN 0717622037 (this is the overall ACOP; the following four references are more detailed ACOPs on specific topics).
