APPENDIX I

Definition of the Term "Installation"

1. Installations for the production or processing of organic or inorganic chemicals using for this purpose, in particular:

    - alkylation
    - amination by ammonolysis
    - carbonylation
    - condensation
    - dehydrogenation
    - esterification
    - halogenation and manufacture of halogens
    - hydrogenation
    - hydrolysis
    - oxidation
    - polymerization
    - sulphonation
    - desulphurization, manufacture and transformation of sulphur-containing compounds
    - nitration and manufacture of nitrogen-containing compounds
    - manufacture of phosphorus-containing compounds
    - formulation of pesticides and of pharmaceutical products

2. Installations for the processing or organic and inorganic chemical substances, using for this purpose, in particular:

    - distillation
    - extraction
    - solvation

- mixing
- drying

3. Installations for distillation, refining or other processing of petroleum or petroleum products.

4. Installations for the total or partial disposal of solid or liquid substances by incineration or chemical decomposition.

5. Installations for the production or processing of energy gases, for example, LPG, LNG, SNG.

6. Installations for the dry distillation of coal or lignite.

7. Installations for the production of metals or non-metals by the wet process or by means of electrical energy.

8. Storage of dangerous materials identified in Appendices II and III.

9. Transportation Distribution Systems:[1]

- Pipelines (quantities between block valves)
- Shipping and terminal facilities (including in-land waterways)
- Road
- Rail

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[1] There may be an overlap between these guidelines and many national and international regulations, and guidelines concerning transfer of hazardous substances. When a national or international regulation applies to a particular installation, the World Bank guidelines should be used only as a check to ensure that all safety aspects have been identified and controlled.

APPENDIX II

List of Hazardous Substances Requiring A Major Hazard Assessment

(A) "Very Acutely Toxic" Substances

The following indicative criteria are used to identify any "very toxic" substance requiring a major hazard assessment. These criteria are independent of the quantities of the substance stored, or processed, or that are formed by an unwanted by-product reaction.

Very toxic substances are defined as:

- substances which correspond to the first line of the table below;
- substances which correspond to the second line of the table below and which, owing to their physical and chemical properties, are capable of entailing major-accident hazards similar to those caused by the substance mentioned in the first line:

	LD 50 (oral) (1) mg/kg body weight	LD 50 (cutaneous) (2) mg/kg body weight	LC 50 (3) mg/l (inhalalation)
1	LD 50 <5	LD 50 <10	LC 50 <0.1
2	5<LD 50<25	10<LD 50<50	0.1<LC 50<0.5

Note: (1) LD 50 oral in rats.
Note: (2) LD 50 cutaneous in rats or rabbits.
Note: (3) LC 50 by inhalation (four hours) in rats.

If an LC 50 value is available for a shorter exposure time "t" the LC 50 (4 hr) may be estimated as follows:

$$\text{LC 50 (4 hr)} = \frac{\text{LC 50 (t hr)} \times t}{4}$$

(B) Other Acutely Toxic Substances

(1) The following quantities of toxic substances represent the threshold above which compliance with Section 4.1 is required.

Named Substances	Quantity Tonnes
Phosgene	2
Chlorine	10
Hydrogen fluoride	10
Sulphur trioxide	15

Acrylonitrile	20
Hydrogen cyanide	20
Carbon disulphide	20
Sulphur dioxide	20
Bromine	40
Ammonia (anhydrous or as solution containing more than 50% by weight of ammonia)	60

(2) In addition to the above named substances, the following indicative criteria are used to identify other toxic substances which, owing to their physical and chemical properties, may cause a major accident and are stored or processed in quantities of greater than 1 tonne:

LD 50 (oral) (1) mg/kg body weight	LD 50 (cutaneous) (2) mg/kg body weight	LC 50 (3) mg/l (inhalalation)
$25 < \text{LD } 50 < 200$	$50 < \text{LD } 50 < 400$	$0.5 < \text{LC } 50 < 2$

Note: (1) LD 50 oral in rats.
Note: (2) LD 50 cutaneous in rats or rabbits.
Note: (3) LC 50 by inhalation (four hours) in rats.

3) **Highly Reactive Substances**

1) The following quantities of "highly reactive" substances represent the threshold above which compliance with Section 4.1 is required.

Named Substances	Quantity Tonnes
Hydrogen	2
Ethylene oxide	5
Propylene oxide	5
tert-Butyl peroxyacetate	5
tert-Butyl peroxyisobutyrate	5
tert-Butyl peroxymaleate	5
tert-Butyl peroxy isopropyl carbonate	5
Dibenzyl peroxydicarbonate	5
2,2-Bis(tert-butylperoxy) butane	5
1,1-Bis(ter-butylperoxy) cyclohexane	5
Di-sec-butyl peroxydicarbonate	5
2,2-Dihydroperoxypropane	5
Di-n-propyl peroxydicarbonate	5
Methyl ethyl ketone peroxide	5
Sodium chlorate	25
Liquid oxygen	200

General Groups of Substances	Quantity Tonnes
Organic peroxides (not listed above)	5
Nitrocellulose compounds	50
Ammonium nitrates	500

(2) In addition to the above named substances, the following indicative criteria are used to identify potential explosive hazards, irrespective of materials stored or processed.

- Substances which may explode under the effect of flame or which are more sensitive to shocks or friction than dinitrobenzene.

(D) Flammable Substances

The following quantities of "flammable" substances represent the threshold, above which and compliance with Section 4.1 is required.

Class of Flammable Substances	Quantity Tonnes
1. Flammable Gases:	
Gas or any mixture of gases which is flammable in air and is held as a gas.	15
2. Liquefied Gases and Flammable Liquids in Process at Pressure and/Temperature Above Ambient Levels:	
A substance or any mixture of substances which is flammable in air and is normally held in the installation above its boiling point (measured at 1 bar absolute) as a liquid or as a mixture of liquid and gas at a pressure of more than 1.4 bar absolute. (e.g. LPG's).	25 being the total quantity of substances above the boiling points whether held singly or in mixtures.
3. Refrigerated Liquefied Gas	
A liquefied gas or any mixture of liquefied gases, which is flammable in air, has a boiling point of less than 0°C (measured at 1 bar absolute) and is normally held in the installation under refrigeration or cooling at a pressure of 1.4 bar absolute or less (e.g., LNG).	50 being the total quantity of substances having boiling points below 0°C whether held singly or in mixtures.

4. Highly Flammable Liquids

A liquid or any mixture of liquids not included in items 1 to 3 above, which has a flash point of less than 21°C.	10,000

5. Flammable Liquids at High Temperature and Pressure

Substances which have a flash point lower than 55°C and which remain liquid under pressure, where particular processing conditions, such as high pressure and temperature, may lead to a major accident hazard.

APPENDIX III

List of Acutely Toxic and Reactive Hazardous Substances

Group A:

Very Toxic Substances
(See definition Appendix II, Page 17)

Aldicarb

4-Aminodiphenyl

Amiton

Anabasine

Arsenic pentoxide, Arsenic (V) acid and salts

Arsenic trioxide, Arsenious (III) acid and salts

Arsine (Arsenic hybride)

Azinphos-ethyl

Azinphos-methyl

Benzidine

Benzidine salts

Beryllium (powders, compounds)

Bis (2-chloroethyl) sulphide

Bis (chloromethyl) ether

Carbofuran

Carbophenothion

Chlorfenvinphos

4-(Chloroformyl) morpholine

Chloromethyl methyl ether

Cobalt (powders, compounds)

Crimidine

Cyanthoate

Cycloheximide

Demeton

Dialifos

OO-Diethyl S-ethylsulphinylmethyl phosphorotioate

OO-Diethyl S-ethylthiomethyl phosphorothioate

OO-Diethyl S-isopropylthiomethyl phosphorodithioate

OO-Diethyl S-propylthiomethyl phosphorodithioate

Dimefox

Dimethylcarbamoyl chloride

Dimethylnitrosamine

Dimethyl phosphoramidocyanidic acid

Diphacinone

Disulfoton

EPN

Ethion

Fensulfothion
Fluenetil

Fluoroacetic acid

Fluoroacetic acid, salts

Fluoroacetic acid, esters

Fluoroacetic acid, amides

4-Fluorobutyric acid

4-Fluorobutyric acid, salts

4-Fluorobutyric acid, esters

4-Fluorobutyric acid, amides

4-Fluorocrotonic acid

4-Fluorocrotonic acid, salts

4-Fluorocrotonic acid, esters

4-Fluorocrotonic acid, amides

4-Fluoro-2-hydroxybutyric acid

4-Fluoro-2-hydroxybutyric acid, salts

4-Fluoro-2-hydroxybutyric acid, esters

4-Fluoro-2-hydroxybutyric acid, amids

Glycolonitrile (Hydroxyacetonitrile)

1, 2, 3, 7, 8, 9-Hexachlorodibenzo-p-dioxin

Hexamethylphosphoramide

Hydrogen selenide

Isobenzan

Isodrin

Juglone (5-Hydroxynaphthalene-1,4-dione)

4,4' - Methylenebis (2-chloroaniline)

Methyl isocyanate

Mevinphos

2-Naphthylamine

Nickel (powders, compounds)

Nickel tetracarbonyl

Oxydisulfoton

Oxygen difluoride

Paraoxon (Diethyl 4-nitrophenyl phosphate)

Parathion

Parathion-methyl

Pentaborane

Phorate

Phosacetim

Phosphamidon

Phosphine (Hydrogen phosphide)

Promurit (1-(3,4-Dichlorophenyl)-
3-triazenethiocarboxamide

1,3-Propanesultone

1-Propen-2-chloro-1,3-diol diacetate

Pyrazoxon

Selenium hexafluoride

Sodium selenite

Stibine (Antimony hydride)

Sulfotep

Sulphur dichloride

Tellurium hexafluoride

TEPP

2,3,7,8-Tetrachlorodibenzo-p-dioxin (TCDD)

Tetramethylenedisulphotetramine

Thionazin

Tirpate (2,4-Dimethyl-2,3-dithiolane-
2-carboxaldehyde O-methylcarbamoyloxime)

Trichloromethanesulphenyl chloride

1-Tri(cyclohexyl)stannyl-1H-1,2,4-triazole

Triethylenemelamine

Warfarin

Group B:

Other Toxic Substances (See definition Appendix II, Page 17)

Acetone cyanohydrin (2-Cyanopropan-2-ol)

Acrolein (2-Propenal)

Acrylonitrile

Allyl alcohol (2-Propen-1-ol)

Allylamine

Ammonia

Bromine

Carbon disulphide

Chlorine

Ethylene dibromide (1,2-Dibromoethane)

Ethyleneimine

Formaldehyde (concentration > 90%)

Hydrogen chloride (liquefied gas)

Hydrogen cyanide

Hydrogen fluoride

Hydrogen sulphide

Methyl bromide (Bromomethane)

Nitrogen oxides

Phosgene (Carbonyl chloride)

Propyleneimine

Sulphur dioxide

Tetraethyl lead

Tetramethyl lead

Group C.1:

Highly Reactive Substances and Explosives

Acetylene

Ammonium nitrate (where it is in a state which gives it properties capable of creating a major accident hazard)

2,2-Bis(tert-butylperoxy) butane concentration > 70%)

1,1-Bis (tert-butylperoxy) cyclohexane (concentration > 80%)

tert-Butyl peroxyacetate (concentration) > 70%)

tert-Butyl peroxyisobutyrate (concentration > 80%)

tert-Butyl peroxy isopropyl carbonate (concentration > 80%)

tert-Butyl peroxymaleate (concentration > 80%)

tert-Butyl peroxyphivalate (concentration > 77%)

Dibenzyl peroxydicarbonate (concentration > 90%)

Di-sec-butyl peroxydicarbonate concentration > 80%)

Diethyl peroxydicarbonate (concentration > 30%)

2,2-Dihydroperoxypropane (concentration ≫ 30%)

Di-isobutyryl peroxide (concentration ≫.50%)

Di-n-propyl peroxydicarbonate (concentration ≫ 80%)

Ethylene oxide

Ethyl nitrate

3,3,6,6,9,9-Hexamethyl-1,2,4,5-
tetroxacyclononane concentration ≫ 75%)

Hydrogen

Methyl ethyl ketone peroxide (concentration ≫ 60%)

Methyl isobutyl ketone peroxide (concentration ≫ 60%)

Peracetic acid (concentration ≫ 60%)

Propylene oxide

Sodium chlorate

Group C.2:

Explosive Substances

Barium azide

Bis (2,4,6-trinitrophenyl) amine

Chlorotrinitrobenzene

Cellulose nitrate (containing > 12.6% nitrogen)

Cyclotetramethylenetetranitramine

Cyclotrimethylenetrinitramine

Diazondinitrophenol

Diethylene glycol dinitrate

Dinitrophenol, salts

Ethylene glycol dinitrate

1-Guanyl-4-nitrosaminoguanyl-1-tetrazene

2,2',4,4',6,6'-Hexanitrostilbene

Hydrazine nitrate

Lead azide

Lead styphnate (Lead 2,4,6-trinitroresorcinoxide)

Mercury fulminate

N-Methyl-N,2,4,6-tetranitroaniline

Nitroglycerine

Pentaerythritol tetranitrate

Picric acid (2,4,6-Trinitrophenol)

Sodium picramate

Styphnic acid (2,46,6,-Trinitroresorcinol)

1,3,5-Triamino-2,4,6-Trinitrobenzene

Trinitroaniline

2,4,6-Trinitroanisole

Trinitrobenzene

Trinitrobenzoic acid

Trinitrocresol

2,4,6-Trinitrophenetole

2,4,6-Trinitrotoluene

APPENDIX IV

Background Information for a Major Hazard Assessment (Section 4.1)

Section 4.1.3 specifies the details required to be included in a major hazard assessment prepared in accordance with these guidelines.

The details required in Section 4.1.3 are discussed below as separate items but it is for the developer to determine the most appropriate or convenient method of presenting the required information. In particular, general issues (e.g., pressure vessel inspection arrangements) could be referenced and any variations or departures from the generally accepted practice will suffice.

The item-by-item guidance given below in relation to Section 4.1.3 is by example rather than by lists of topics to be covered. The latter approach suffers the twin disadvantages of not being truly comprehensive while at the same time giving the impression that each listed topic is of equal importance. In practice, the depth of information required on each topic will vary according to the circumstances of the individual installation.

Sections 4.1.3.1 and 4.1.3.2 require factual information about the dangerous substances and the installations handling them. Section 4.1.3.3 relates to the management control of the activity. Section 4.1.3.4 requires information about the sources and nature of potential major accidents and the measures taken to prevent and control them.

Section 4.1.3.1 (Substance Name)

The information required under this sub-heading is concerned with identifying the dangerous substance which qualifies the activity or storage for the requirement to make a major hazard assessment the wording should be self-explanatory.

Section 4.2.3.1 (Monitoring Methods)

Where standard analytical methods are used by the firm this item need only identify the method and any departures from it. Provision of gas detection equipment could be referred to here or left if appropriate to the discussion of preventive measures under Section 4.1.3.4.

Section 4.1.3.1 (Hazards of the Substances)

Information given under this sub-item should cover (a) the route of the harm to man (skin contact, inhalation or ingestion for toxic substances, and flame contact, thermal radiation or blast for flammable or explosive substances); (b) the dose-response relationship, where known, citing standard published references as appropriate (e.g., the Chemical Industries Association's table of the toxic effects of chlorine at various concentrations); and (c) the nature of the trauma, where this is not obvious (e.g., chloracne from exposure to dioxin).

In relation to the hazards from the substance to the environment, information is not required about the obvious effects of flame or blast from explosive or flammable substances. For toxic substances such information as is readily available should be given or be referred to, including the route of the harm (e.g., the pollution of water courses); the effect on flora and fauna which may be exposed; and an indication of the substance's persistence.

Section 4.1.3.1 (Composition of Process Streams)

This item requires information about the composition of the substance so that the effects of diluents or impurities which have a significant effect on the hazard can be assessed. For example, where an organic peroxide is present in an activity, the name and percentage of any stabilizer should be given.

The presence of significant quantities of impurities could also affect the behaviour of a substance and these impurities and their percentages should also be identified. An example would be the alteration of the toxic properties of chloromethyl methyl ether by the presence of bis (chloromethyl) ether. It is not necessary to list the minor components of mixtures being processed where these have an insignificant effect on the potential hazard (e.g., a hydrocarbon mixture might be described as 70% butane, 25% propane, 5% higher hydrocarbons).

Section 4.1.3.2(i) (Location)

This map is required to indicate where the installation is located, showing its position in relation to local geographic features, such as roads and towns. In general it will be sufficient to use the latest available map or maps on a scale which includes both the site and the surrounding features. Changes (such as a new motorway) which have occured since the printing of the map and which are known to the firm should be shown; it is not intended that this should involve any extended research effort. For many sites a scale of 1 to 10,000 will be appropriate.

Section 4.1.3.2(ii) (Plot Plan)

The intention of this item is to identify clearly, both in location and quantity, the main parts which contribute to the total inventory of the dangerous substance. In addition, the plan should be annotated to indicate the lesser quantities which make up the stated total. For example, an estimate of the quantity of the substance which is present in pipework around a particular plant should be made.

It may be convenient to combine the response to this item with that to Section 4.1.3.4, and in particular, Section 4.1.3.4 item (ii).

Section 4.1.3.2(iii) (Process/Flow Description)

The intention of this requirement is that a sufficient description of the process be given to enable discussion on later items to be understood and placed in context. The amount of description required will depend on the complexity of the process. For example, a water treatment plant using chlorine will require only a brief account of the water dosing process, whereas a chemical plant producing qualifying quantities of a very toxic substance as an intermediate will require sufficient information to enable the critical aspects of the process chemistry to be understood. In this latter example, the information will be supplemented by the information given under Section 4.1.3.4 and it will be for the developer to determine the most appropriate method of presentation.

The conditions under which the substance is normally held should be stated, including the physical state and pressure and/or temperature at the main stages of storage and process, e.g., butane is held in storage as a refrigerated liquid at 0°C; vaporized in a direct-fired evaporator and fed as a gas to a process vessel at 10 bar, 90°C.

Section 4.1.3.2(iv) (Personnel on site)

The number given should be accompanied by sufficient explanation to show how it was derived. Account should be taken of the number of people who may be present at shift changeover; people who may be employed from the site but who may be present only for short periods (e.g., sales staff or delivery drivers); regular visitors to the site (e.g., contractors); and casual visitors. Exact numbers are not required.

Section 4.1.3.2(v) (Local Land Use and Population Distribution)

The information required is about the use of land or water surrounding the activity and the location of people who may be affected in the event of a major accident. This can be provided by annotations on a suitable map, indicating broad categories of land use (e.g., dwellings, other factories, schools, sports facilities, agricultural land, etc.). It is not necessary to give numerical estimates of population in the areas covered by each category, though any unusually high densities such as shanty towns, blocks of flats should be marked as such.

The choice of the phrase 'in the vicinity of' rather than definite distances is intended to allow for flexible interpretation in relation to the potential hazard. For example, for a flammable liquid tank farm the 'vicinity' might be less extensive than for bulk chlorine storage. A degree of judgment is thus called for and a brief explanation should be given of the choice of vicinity illustrated on the map.

Section 4.1.3.3 (Management)

The aim of this item is to demonstrate that the developer has a proper management system and technical staff to control the major hazard aspects of his activities. The required information is general, insofar as it relates to the management control of the site as a whole, in contrast to the greater detail that may be needed under Section 4.1.3.4 to demonstrate that there are adequate arrangements to prevent and control particular hazardous events. The extent of the response to this item should be seen against its importance in providing a framework in which the rest of the safety case may be set and which will to some degree color the credibility of the whole submission.

Section 4.1.3.3(i) (Responsible Person and Staffing)

A description of the management structure should be given which covers reporting relationship and the experience and qualifications of staff at the different levels. It is important to show how accountability for decisions which affect the potentially hazardous activity is assigned to staff who have the appropriate level of expertise and the relevent professional discipline. Reference should also be made to the developer's policy towards the appointment of competent deputies to cover key positions.

This section should also cover the arrangements which management have set up for identifying and dealing with safety issues arising from the potentially hazardous activity, with references as appropriate to the group, division and site safety policies, and the role of safety representatives and safety committees. This section should include an account of how management decisions about the potentially hazardous activity are made with due regard for their safety implications, and how these decisions are monitored.

Section 4.1.3.3 (ii) (Quality Control for Safety)

The importance of the containment of dangerous substances is such as to require an adequate account of the management of the engineering system. This should include a discussion of the developer's approach to the design of important plant items and safety systems (e.g., use of standard or company codes); the arrangements for quality assurance; the inspection and testing procedures (who carries them out? how frequently? who decides on the necessary action in the event of deficiencies being discovered? who monitors these actions and how?); the provision of operating manuals and instructions and the procedures for revising them in the event of process changes; the procedures for ensuring that plant modifications are adequately designed, installed and tested; and the system for general maintenance.

The response to this item should not contain lengthy abstracts from written company procedures, but should aim to give a coherent justification for the system of engineering controls exercised over the potentially hazardous activity.

Section 4.1.3.3(iii) (Training)

Information should be given about the standards of relevant training, both on- and off-the-job, for people on site with a significant role in the control or operation of the major hazard activity, including the senior management and engineering staff involved. A brief account should also be given about how training needs are identified and met.

Section 4.1.3.4 (Potential Major Accidents)

The response to this item will provide the heart of the major hazard assessment. Though the information required is specified in some detail, it will be essential for developers to interpret this item with commonsense and flexibility. As noted in the general discussion of the term, "major hazard assessment", the developer must investigate those potential major accidents which may produce adverse consequences outside the plant boundary using hazard analysis techniques such as described in the World Bank manual (ref (9)). Sufficient evidence must be provided to support his conclusions.

Section 4.1.3.4(i) (Identification of Potential Major Hazard Events)

This item requires the manufacturer to identify the ways in which a major accident might occur. "Major accident" is defined in Section 2 and guidance on its interpretation is given in this section. Suitable techniques for identification are hazard analysis, hazard and operability studies, reactive chemicals studies, engineering flow chart review, and review of past accidents and near misses etc. The concept of the major hazard assessment allows the developer the opportunity to argue in the response to this item that his activities are not capable of giving rise to a major accident, provided that they are satisfied that such an argument can be fully and properly justified. In some cases, a submission of this sort may be relatively easy to support. For example, a toxic hazardous substance may be stored in separate cylinders, and the quantity in each one may not be sufficient to give rise to a major accident. If the cylinders were disposed around the site so that the possibility of an incident affecting them simultaneously could be ruled out, then the argument that a major accident cannot arise on the site may be reasonably straightforward. In other cases the evidence necessary to justify such an argument may prove to be as extensive as a response to this item which accepts that major accidents may occur, and then goes on to describe how they are prevented; it will be for the manufacturer to decide initially which option better fulfills the objectives of the major hazard assessment. If it can be shown that the activity is not capable of giving rise to a major accident, then the remaining parts of Section 4.1.3.4 need not be answered. It is in this section that the quantification of the magnitude of hazardous events by means of hazard analysis techniques are required.

In most cases it will be necessary to describe the potential sources of a major accident (the World Bank "Manual of Industrial Hazard analysis Techniques" provides guidance in this respect). Storage and process vessels which contain significant quantities of the dangerous substance should be examined for the most probable ways in which their inventories may be released, and these should include consideration of, spontaneous failure (due to original defects or those arising in the course of operation); failure due to excursions from normal operating conditions (including such matters as operator error, loss of services, and failure of control devices); failure due to events elsewhere on site (e.g., fire, explosion); and failure due to external events (e.g., flooding, seismic activity). For a complex chemical or petrochemical works or a refinery, where the number of vessels and pipes for individual plants may be very large (but built to common standards), it may be appropriate to be more selective in examining the potential sources of a major accident by considering only the largest vessels in detail and then referring to smaller vessels or groups of vessels in general terms.

Section 4.1.3.4(ii) (Process Flow Diagrams)

This item calls for judgment by the developer as to which sections of the plants containing the dangerous substance need to be illustrated in diagrammatic form. Such diagrams should show the process vessels, storage facilities and instrumentation on the plants concenred in sufficient detail to enable the discussion under Section 4.1.3.4 (i) and (iii) to be readily understood. For vessels in the plants which have been identified in Section 4.1.3.4(i) as significant as regards the potential for a major accident, details should be shown on the diagram of their designed maximum working capacities, their design temperatures and pressures, and their normal operating conditions. It may be convenient to combine this with the response to Section 4.1.3.2(ii). For example, a large vertical cylindrical storage vessel containing the dangerous substance would require a diagram showing the vessel, its connections, instrumentation and external safety features such as water sprays and bunds; for complex plants diagrams of only the largest or most significant vessels are required.

Section 4.1.3.4(iii) (Preventative and Control Systems)

The third part of Section 4.1.3.4 requires a response in two parts. First, relating to the preventive and control measures which check any sequence of events which could foreseeably result in a major accident, and secondly, relating to measures which may be taken after such a hazardous outcome to minimize its adverse consequences. It is important to realize that it is better to prevent a release occurring rather than trying to control the consequences, which may, in part, be impracticable.

The first part of the response should concentrate on those preventive or control measures which are critical in counter-acting significant hazards, though many of these measures will also be appropriate to preventing or controlling lesser events.

The interpretation of certain key words in this part of Section 4.1.3.4 may usefully be discussed in relation to examples; say, a large pressure storage sphere of LPG, representing the risk of fire and explosion, and for an example of toxic risk, a large pressure storage sphere of ammonia.

"Measures taken to prevent" relate to ensuring the safe operation of the plant under normal operating conditions or within specified process limits. They are those measures which are intended to prevent the initiation of a sequence of events which could lead to a significant hazardous outcome and would include consideration of design, engineering standards, constructional and quality assurance, inspection and maintenance, and control systems insofar as these were concerned with controlling the process during normal operation. These preventive measures derive their validity from the way in which the overall management of the plant and company exercises control over them and ensures their effectiveness. Thus, a sufficient account of the relevant parts of the management system, expanding on the general information given in Section 4.1.3.3 will be needed to support any arguments about the probability of initiating a sequence of events with a hazardous outcome. In relation to the ammonia sphere example, "measures taken to prevent", would include a discussion of the arrangements for checking ammonia purity and special vessel inspections in connection with the problem of stress corrosion cracking.

"Measures taken to control" relate to the interventions permitted by the design of the plant (e.g., valves) or safety hardware (e.g., dump tanks) which may counter an event so that the dangerous substance is retained within the plant. The operation of a "measure taken to control" assumes that a sequence of events has been initiated and the control is intended to prevent the sequence proceeding to a major accident. In relation to the LPG sphere example, a spillage of LPG near the tank which ignited, could be prevented from escalating to a BLEVE (boiling liquid expanding vapour explosion) of the whole sphere by the effective operation of a water spray system on the sphere. The discussion of this control measure should include reference to the the capacity of the water storage system, the water application rate; how the company ensures that the system will in fact operate effectively when required to do so; and the system reliability.

The second part of the response to this item covers "measures to minimize the consequence", which relate to those measures which can be taken after the major accident has actually occurred. Examples of minimization include: bunding, water curtains, foam blankets, and emergency procedures. In relation to the ammonia sphere, the effects of a release of ammonia from a pipe at a sufficient rate to lead to a lethal concentration of gas at (say) the nearest domestic dwellings might be minimized by the application of a water curtain around the sphere, and, through the emergency services, by evacuation of those people who are downwind of the escape.

Section 4.1.3.4 (iii) refers to the prevention or control of major accidents identified in Section 4.1.3.4(i). It is therefore not necessary to include information about measures directed solely at preventing small releases or those which have only minor consequences, unless these have the potential to escalate to a major accident.

Section 4.1.3.4(iii) by concentrating on preventive measures, is intended to draw out discussion on the positive aspects of the major hazard assessment. However, because the sequence of cause, effect and consequence are closely intertwined, it is not possible in practice to confine such a discussion to prevention without mentioning the potential consequences of the potential major accidents discussed in the major hazard assessment. Estimates of consequences will in any case be required in order to formulate adequate advice to the authority responsible for drawing up off-site emergency plans (see Section 5).

Section 4.1.3.4 (iv) (Emergency Procedures)

Section 5 requires the developer to produce a plan for dealing with emergencies on-site. The operator/developer should be able to present the whole document for examination if necessary, but that is not the intention of this part of the major hazard assessment. On the other hand, it will not be sufficient merely to state that the emergency plan exists. The response to this item should describe the procedures in outline; indicate the nature and extent of emergencies with which the plans are intended to cope, drawing as necessary on the information in other parts of the major hazard assessment; mention those arrangements which may be critical to the success of the plans such as access for emergency services, the provision of adequate supplies of fire-fighting water, the remote siting of emergency control points and the evacuation of non-essential site personnel; and confirm that the plans have been discussed with the relevant outside bodies and practiced with them.

Section 4.1.3.4 (v) (Meteorological Conditions)

Data should be obtained from the nearest Meteorological Office weather station as to the prevailing weather conditions in the vicinity of the site, and if necessary confirmed by actual measurements on the site.

Section 4.1.3.4 (vi) (Numbers at Risk)

This estimate should include those people normally working on the plant concerned and any major concentrations of people in the immediate vicinity of the plant, e.g., office buildings. As for Section 4.1.3.2 (iv), exact numbers are not necessary.

APPENDIX V

Summary of Reactive Hazards

Process Unit	Process Step	Nature of Hazard	Means of Control
1	Thin film evaporator.	Runaway polymerization of Chemical A at >170°C in the presence of traces of catalyst.	- Use of thin film evaporation. Steam at 150°C, water dousing system, relief to blowdown drum Temp. Alarms and interlocks. - Small quantities only in process.
2	Reaction step-nitration of Chemical B	Highly exothermic reaction with catalyst.	- Continuous reaction system with small quantities of reactions in large quantity of liquid catalyst recycle. Reactants metered by dosing pump system with special safeguards. Reaction takes place in pump after static mixer. Temp. alarms and interlocks to prevent runaway reactions. - Small quantities of reactants
3	Reaction step-nitration of Chemical C	Highly exothermic reaction with H_2SO_4 as catalyst.	
4	Reboilers of distillation columns in purification stages.	Runaway polymerization reaction.	- Small qunatity of material with temperature control. Safe discharge of reboiler contents to an enclosed area away from other process equipment and personnel via a rupture disc relief system and vent angled at 45° to horizontal <100kg products.
5	Reaction step - Hydrolysis of Chemical D at 160°C and 4 atmos. All reactants are added at start of batch and heated to operating temperature of 150°C.	Highly exothermic in 10 m^3 reactors. Scale up from 100 litre pilot plant and operating experience on 3 m^3 reactor with similar reactants.	- Over designed external coil cooling system for heat of reaction of 41 kcal/mol cf. actual value of 14 kcal/mol. - Manual blow-down system on reactor. - Semi-automatic blowdown system from control room. - Computer control to minimize human error. - Relief valve system to blowdown.

Process Unit	Process Step	Nature of Hazard	Means of Control
6	Two step reaction process. First step involving catalytic reduction of Chemical E to Chemical F is the hazardous step.	If insufficient active catalyst (i.e., due to poisoning or inadequate addition), and too low a reaction temperature, a build up of an intermediate product occurs. This intermediate can cause a runaway reaction if the temperature is raised too quickly. - Note this system has been scaled up from 100 litre pilot plant. Same size reactors in use on similar raw materials.	- Extended batch reaction cycle from 1/2 hour to 3 hours - keep reaction temperature > 80°C - control flow of H_2 - shut off flow of H_2 if temp. <80°C - use an excess of catalyst - remove 10% of catalyst at each batch and replace with fresh catalyst - 3-4 m^3 reactors.
7	Catalytic reduction of Chemical G in a continuous reactor at 60 atmosphere's pressure.	Similar reaction hazard as Unit 6, if the intermediate forms due to insufficient active catalyst and too low temperature. This is the first time this reactor system has been used to produce Chemical H. Has been used for similar reactions and an extensive computer control/safety system has been developed.	- Fully computer controlled. - Hydrogen addition regulated according to heat balance calculations. - Auto shut-off of H_2 if heat balance shows generation of intermediate. - Initially there will be no recycle of catalyst but may recycle as gain experience. - Reactor blow-down system installed. - Safety interlocks. - Significant volume of chemicals present.

APPENDIX 3

Summary of Potential Sources of Ignition

LIST OF IGNITION SOURCES

Industrial plants contain a great number of possible ignition sources. It is common practice to reduce as far as practical possible ignition sources in areas where there is a risk of flammable releases. This is achieved by enforcing regulations that;

- restrict activity in the area (using a "permit to work system")
- only allow suitable equipment in the area
- restrict access to the area (by fencing off the area)

Lees has listed likely ignition sources. The list is repeated here with suggestions on how they are controlled within the restricted area.

1. Burner flames.
   Layout of plant, trip systems.
2. Burning operations.
   Permit to work.
3. Hot soot.
4. Cigarettes.
   No-smoking in restricted area.
5. Smouldering material.
6. Hot process equipment.
   Design.
7. Distress machinery.
   Design and maintenance.
8. Small process fires.
9. Weldings and cutting.
   Permit to work.
10. Mechanical sparks.
    Special non-sparking tools are available.
11. Vehicles.
    Ordinary vehicles excluded from areas of flammable hazard.

12. Arson.
    Security procedures implemented in hazardous areas.

13. Self heating.
    This occurs through slow oxidation of a solid. A typical source is oily rags. "Good Housekeeping" should prevent this.

14. Static electricity
    This complex problem cannot be reasonably treated here. The reader is referred to specialist tests such as "Electrostatics in the Petroleum Industry" by Klinkenberg and van der Minne.

15. Electrical equipment.
    Electrical equipment to be positioned in these areas have to be built to special standards. In the UK and in many other countries the areas at risk are classified according to the severity of the risk with a different electrical equipment standard for each classification.

APPENDIX 4

Selected Data on the Properties of Some Hazardous Materials

ISOLATED STORAGE

The list of storage quantities given below has also been prepared by the EEC (1982), and applies only where the storage is effectively isolated from all other operations. It is reproduced here to provide an indication of the levels of concern.

The quantities set out below relate to each installation or group of installations belonging to the same manufacturer where the distance between installations is not sufficient to avoid, in foreseeable circumstances, any aggravation of major accident hazards. These quantities apply in any case to each group of installations belonging to the same manufacturer where the distance between the installations is less than 500 metres.

Substances of groups	Quantities (tonnes)	
Substances or groups of substances (Column 1)	For application of Regulation 4 (Column 2)	For application of Regulations 7 to 12 (Column 3)
Acrylonitrile	350	5,000
Ammonia	60	600
Ammonium nitrate	500*	5,000*
Chlorine	10	200
Flamamble gases	50	300
Highly flammable liquids	10,000	100,000
Liquid oxygen	200	2,000*
Sodium chlorate	25	250*
Sulphur dioxide	20	500

* Where this substance is in a state which gives it properties capable of creating a major accident hazard.

MANUFACTURING PROCESSES

The quantities which are liable to cause hazards if accidentally released from a processing plant, are usually significantly smaller than in the table above, and many more substances are involved.

Compound	Limits of flammability	
	Lower (%v/v)	Upper (%v/v)
Acetone	2.6	13.0
Acetylene	2.5	100.0
Ammonia	15.0	28.0
Amylene	1.8	8.7
Benzene	1.4	8.0
n-Butane	1.8	8.4
i-Butane	1.8	8.4
Butene-1	2.0	10.0
Butene-2	1.7	9.7
Carbon disulphide	1.3	50.0
Cyclohexane	1.3	7.8
Decane	0.8	5.4
Ethane	3.0	12.4
Ethylene	2.7	36.0
Ethylene dichloride	6.2	15.9
Ethylene oxide	3.0	100.0
Heptane	1.2	6.7
Hexane	1.4	7.4
Hydrogen	4.0	75.0
Methane	5.0	15.0
n-Pentane	1.8	7.8
Propane	2.1	9.5
Propylene	2.4	11.0
Styrenene	1.1	6.1
Toluene	1.3	7.0
Vinyl chloride	4.0	22.0
2,2-Dimethylpropane	1.3	7.5
2,3-Dimethylpentane	1.1	6.8

TABLE OF CONSTANTS FOR VARIOUS TOXIC GASES

Constants in equations $Pr = A_t + B_t \ln(C^n t_e)$, where c is in ppm and t is in minutes.

	A_t	B_t	n	Reference
Chlorine	-5.3	0.5	2.75	DCMR 1984
Ammonia	-9.82	0.71	2	DCMR 1984
Acrolein	-9.93	2.05	1	USCG 1977
Carbon Tetrachloride	0.54	1.01	0.5	USCG 1977
Hydrogen Chloride	-21.76	2.65	1	USCG 1977
Methyl Bromide	-19.92	5.16	1	USCG 1977
Phosgene	-19.27	3.69	1	USCG 1977
Hydrogen Fluoride (monomer)	-26.4	3.35	1	USCG 1978

FLAMMABLE PROPERTIES

The models presented in Section 4 require upper flammability limits (UFLs) and lower flammability limits (LFLs). Below are some data for common hazardous materials presented as volume per cent in air.

If data are not available for a particular material it is possible to estimate a flammability limit by taking data for a similar material and applying

$$(LFL)_A = \frac{M_B}{M_A} (LFL)_B$$

M_A and M_B are the relevant molecular weights.

TOXIC PROPERTIES

During the last 10 years, probit equations have been derived for estimating, from dose relationships, the probability of affecting a certain proportion of the exposed population. These have been based almost exclusively on animal test data, which are often very imprecise anyway, and can sequentially they are not very reliable. In particular they do not possess the accuracy which could be ascribed to the formula as used in calculations of consequential effect, and they only apply to acute effects of accidental exposures. In recent years, some of the original equations have been subject to much scrutiny and criticism, and this has resulted in alternative equations being proposed.

In the following table are listed the latest, or only, equations available for a variety of toxic gases, but it is important that the origin of each equation is correctly referenced so that the effect of using alternative equations can be quickly established. The difference in results can be exceedingly large in some instances.

Probit Equations take the form

$$Pr = A_t + B_t \ln (C^n t_e)$$

where Pr is the probability function (expressed in units of standard deviation, but with an offset of +5 to avoid the use of negative values)

A_t, B_t, and n are constants, and

C is concentration of pollutant to which exposure is made, and is ppm v/v

t_e is the duration of exposure to the pollutant, measured in minutes.

Note: if the unit of C and/or t_e are changed, e.g. to mgm/litre v/v, then the values of the constants will change. All units should therefore be quoted.

b) Other toxic substances

The substances showing the following values of acute toxicity have physical and chemical properties capable of producing major accident hazards.

LD50 (oral)(1) mg/kg body weight	LD50 (cutaneous)(2) mg/kg body weight	LC50(3) mg/l inhalation
25 < LD50 < 200	50 < LD50 < 400	0 < LC20 < 2

(1) LD50 oral in rats.
(2) LD50 cutaneous in rats or rabbits
(3) LC50 by inhalation (four hours) in rats.

c) Flammable substances:

i) flammable gases:
substances which in the gaseous state at normal pressure is mixed with air become flammable and the boiling point of which at normal pressure is 20°C or below;

ii) highly flammable liquids:
substances which have a flash point lower than 20°C, and the boiling point of which normal pressure is above 20°C;

iii) flammable liquids:
substances which have a flash point lower than 55°C and remain liquid under pressure, where particular processing conditions, such as high pressure and high temperature, may create major accident hazards.

d) Explosive substances

Substances which may explode under the effect of flame or which is more sensitive to shocks or friction than dinitrobenzene.

INDICATIVE CRITERIA

The European Economic Community (EEC 1982) have drawn up a list of criteria which indicate the potential for harm from a wide variety of hazardous material. These cover toxic and flammable substances, and according to defined criteria indicate the levels for very toxic substances, for toxic substances, and for flammable and explosive substances.

These criteria are a useful way of examining the potential of a particular substance to cause harm if released into the environment in an accident. LD50 represents the concentration required of a toxic material if infested to cause a 50% chance of fatality, and similarly LC50 represents the gaseous concentration inhaled (for four hours) of a substance which may cause a 50% chance of fatality. Of necessity the data used for these determinations is animal data, but they are assumed to be similar to the levels likely in man.

a) Very toxic substances

- substances which correspond to the first line of the table below.
- substances which correspond to the second line of the table below and which, owing to their physical and chemical properties, are capable of producing major accident hazards similar to those caused by the substance mentioned in the first line:

	LD50 (oral)(1) mg/kg body weight	LD50 (cutaneous)(2) mg/kg body weight	LC50(3) mg/l inhalation
1	LD50 < 5	LD50 < 10	LC50 < 0.1
2	3 < LD50 < 25	10 < LD50 < 50	0. < LC50 < 0.5

(1) LD50 oral in rats.
(2) LD50 cutaneous in rats or rabbits
(3) LC50 by inhalation (four hours) in rats.

APPENDIX 5

Bibliography

Abraham, G. (1963).
"Jet diffusion in stagnant ambient fluid". Delft Hydraulics Laboratory, No. 29 Hydraulics Laboratory, Delft, Holland.

Cox. R.A. (1980). "Methods for Predicting the Atmospheric Dispersion of Massive Releases of Flammable Vapour". Proc. Energy. Comb. Sci. Vol. 6, pp 141-149. Pergamon Press.

Cox, R.A. and Roe, D.E. (1977)
"A Model of the Dispersion of Dense Vapour Clouds".
2nd Intl. Loss Prevention Symposium, Heidelberg, 1977.

Cox, R.A. and Carpenter R.J. (1979).
"Further Development of a Dense Vapour Cloud Dispersion Model for Hazard Analysis". Paper presented at the Symposium 'Schwere Gase' at Battelle Institute, Frankfurt am Main, September 1979.

Cude, A.L. (1975).
"The Generation Spread and Decay of Flammable Vapour Clouds". IChemE Course "Process Safety - Theory and Practice", Teeside Polytechnic, Middlesborough, 7-10 July 1975.

Ellison, T.H. and Turner, J.S. (1960).
"Mixing of Dense Fluid in a Turbulent Pipe Flow".
JFM.8., 514-544.

Fauske, H.K. (1965).
"The Discharge of Saturated Water through Pipes". CEP Symp. Series 61, p.210.

Keffer, J.F. and Baines, W.D. (1963). "The round turbulent jet in a cross-wind". J. Fluid Mech. 15, 481-496.

Lapple, C.E. (1943).
"Isothermal and Adiabatic Flow of Compressible Fluids". Trans. Am. Inst. Chem. Engrs. 39, 385.

Moody, L.F. (1944).
Trans. Am. Inst. Soc. Mech. Engrs 66 671.

Morrow, T.B. et al. (1980). "The Dispersion of Chemical Vapours emitted from Marine Chemical Carriers". 3rd Int. Symp. on Loss Prevention and Safety Promotion in the Process Industries. Basle.

Ooms, G. (1972).
"A New Method for the Calculation of the Plume Path of Gases Emitted by a Stack". Atmospheric Environment, Pergamon Press, 1972.

Ooms, G., Mahieu, A.P. and Zelis, F. (1974).
"The Plume Path of Gases Heavier than Air". 1st Int. Loss Prevention Symposium, The Hague/Delft, 1974.

Pasquill, F (1974). "Atmospheric Diffusion". 2nd Edition, Ellis Horwood, Chichester.

Perry, J.H. (1963).
Perry, J.H. (Ed), "The Chemical Engineers Handbook". 4th Edition, McGraw-Hill.

Perry, R.H. and Chilton, C.H. (1973). Chemical Engineers Handbook. 5th Edition. McGraw-Hill. Kogakusha.

Peterson, R.L. and Cermak, J.E. (1979). "Plume-Rise for Varying Ambient Turbulence, Thermal Stratification and Stack Exit Conditions in Numerical and Laboratory Evaluation". 5th Int. Conf. on Wind Engineering. Fort Collins. Colorado.

Turner D.B. (1969). Workbook of Atmospheric Dispersion Estimates. U.S. Dept. Health, Education and Welfare. PHS Pub. No. 995-AP-26.

F. Briscoe and P. Shaw Evaporation from Spills of Hazardous Liquids on Land and Water. SRD R100 1978.

R.A. Cox and D.R. Roe, "A Model of the Dispersion of Dense Vapour Clouds". Loss Prevention and Safety Promotion p359, (1977).

R.A. Cox and R.J. Carpenter, "Further Development of a Dense Vapour Cloud Dispersion Model for Hazard Analysis". Heavy Gas and Risk Assessment, ed. S. Hartwig, (1980).

D.J. Hall, C.F. Barrett and M.O. Ralph, "Experiments on a Model of an Escape of Heavy Gas". Report LR 217, Warren Spring, Stevenage, Herts., (1975).

R.G. Picknett, "Field Experiments on the Behaviour of Dense Clouds", Report Ptn. 1154/78/1, Chemical Defence Establishment, Porton Down, Wilts.

A.P. van Ulden, "On the Spreading of a Heavy Gas Released near the Ground". 1st International Loss Prevention Symposium, The Hague/Delft (1974).

"Flare Radiation" API RP521.

J. Hajek and E. Ludwig, Petrochem. Eng. Part 1. (1960).

W. Jost "Explosion and Combustion Processes in Gases". McGraw-Hill, New York (1946).

M. Zabetakis and E. Burgess, Bureau of Mines Report. Invest 5707. (1961).

J. Moorhouse and M.J. Pritchard. "Thermal Radiation Hazards from Large Pool Fires and Fireballs". A literature Review. The Assessment of Major Hazards Symposium, Manchester (1982).

A.F. Roberts. "The Effect of Conditions Prior to Loss of Containment in Fireball Behaviour". The Assessment of Major Hazards Symposium, Manchester, (1982).

D.E. Jarrett, "Derivation of the British Explosives Safety Distances". Ann. N.Y. Acad. Sci. No 152, (1968).

Toegepast - Naturweteschappelijk Onderzoek (TNO): Methods for the calculation of the physical effects of the escape of dangerous material ("TNO Yellow Book) (1979).

Perry and Green: Perry's Chemical Engineers' Handbook, (Sixth Edition, 1984).