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EUROPEAN COMMISSION.

IMPLEMENTATION OF THE DIRECTIVE ON  
MAJOR ACCIDENT HAZARDS OF CERTAIN  
INDUSTRIAL ACTIVITIES (82/501/EEC).

ARTICLE 19. REVIEW OF ANNEXES I, II AND III.

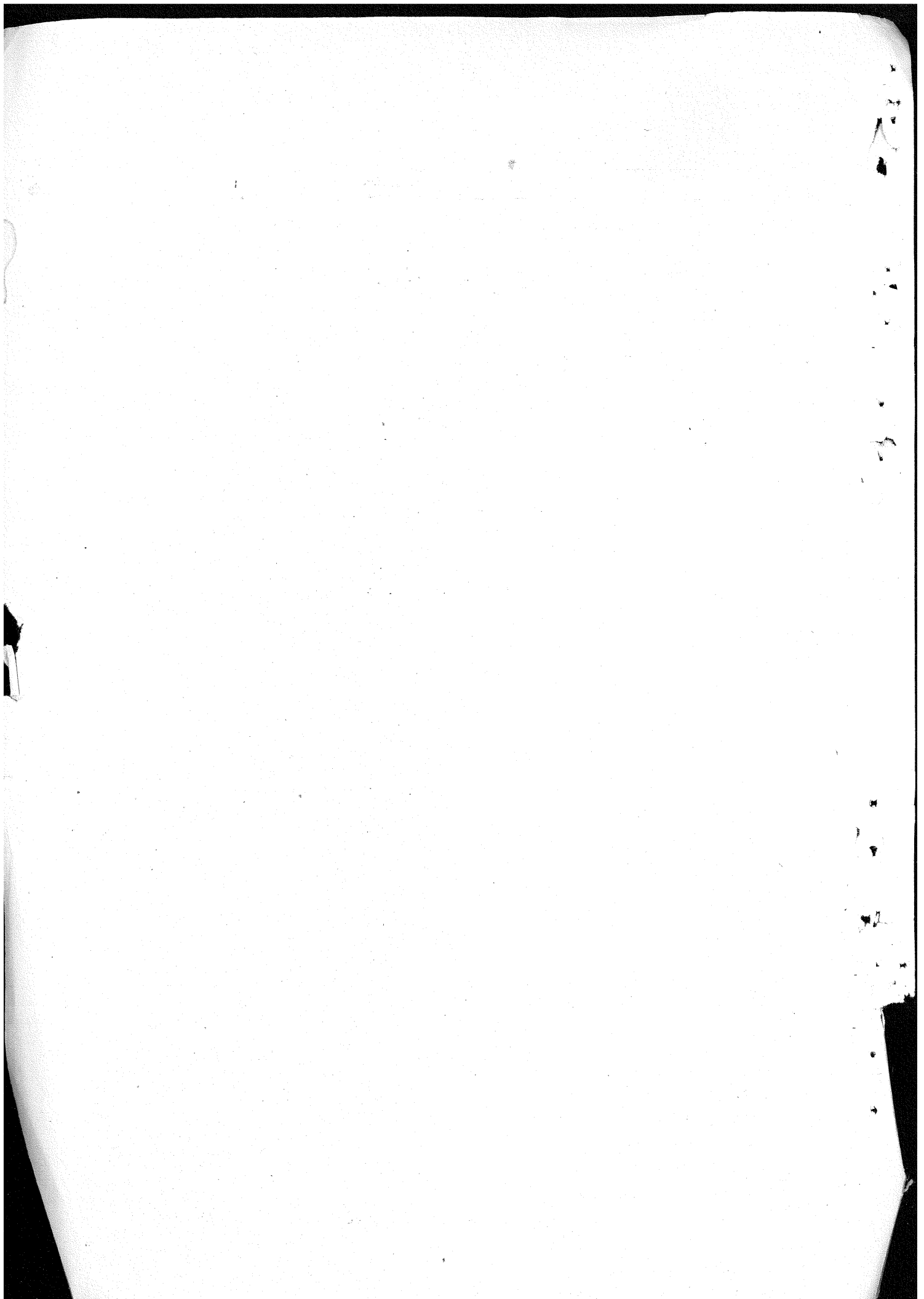
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Contract No. 84-B-6602-11-003-11-N.

For the attention of Dr. P. Testori Coggi.

FINAL REPORT.



## ABSTRACT.

The Report, after establishing its terminology, examines the basis for the Directive by reviewing the development of the major-accident hazards problem as it has evolved during this century. It examines the various forms of realisation of the hazards and draws attention to the significant part played by liquefied gases in giving rise to flammable, explosive or toxic clouds.

It proposes an "isotraumatic" principle for establishing threshold inventories in Annex III and Annex II, namely that these should be based, in most cases, on their potential to cause, in a typical realisation, ten fatalities. The quantity of the substance calculated to have this potential should then be approximated to a scale of 1, 2, 5, 10 . . . This quantification may be achieved, for some key substances, by a combination of the mortality index approach with the equal probability approach.

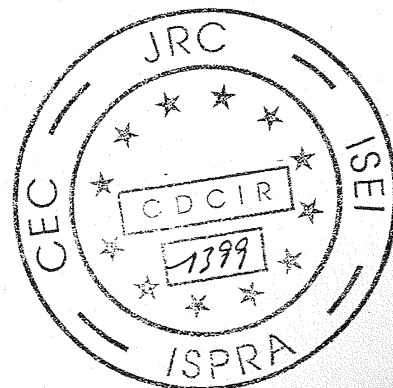
These validate the figure in Annex III for the standard explosive TNT but some explosives so listed have values inconsistent with their blast energies.

The Report concludes that the inventory level accorded to liquefied flammable gases stored at atmospheric temperature should be reduced to 50 tonnes.

Toxic substances, it is concluded, should not be included where they are solely chronic occupational hazards. The limitations of animal experiments as predictors of human fatalities are examined. Dispersive energy, persistence, tendency to cause multiple injuries etc are recommended as criteria to determine whether a substance should be listed and weightings are proposed for these factors.

The mortality index of chlorine is estimated as 0.5 fatalities per tonne. Mustard gas is examined as an example of a substance rated at 1 kg and shown to be less dangerous than chlorine. Methyl isocyanate is given a provisional mortality index of 12.5 and the Bhopal death toll is shown to be not inconsistent with this figure.

For practical considerations, the Report recommends listing two industries, those manufacturing pesticides and those processing polychlorinated aromatics, as falling under the provisions of Article 5, regardless of inventory levels of the dangerous substances involved.



## AUTHOR'S FOREWORD.

I have pleasure in submitting this Final Report which has been drawn up after consultation with those Member States which accepted my offer to consult them over their views on the amendment of the Annexes. These states, in chronological order of visiting, were the United Kingdom, Eire, the Federal Republic of Germany, Italy, France and the Netherlands.

Examination of the problem of the control of Major-Accident Hazards shows it to be complex as it has to deal with the potential for harm through a number of agencies, principally those of fire, explosion and toxic release, from a great variety of substances. These may be present under various conditions of temperature and pressure, and in differing states of matter and, if liquid or gaseous, in various states of subdivision. The potential for harm varies enormously from substance to substance. Toxic substances vary, for practical purposes, in their lethal properties, over many orders of magnitude. They differ also in their mode of attack upon humans and animals.

The Report argues that a satisfactory system of control of these hazards must be one which takes account of all these complexities. This is to avoid arbitrary assessments which may divert resources to the control of relatively minor hazards at the expense of neglect of real problems. Nevertheless, the Report also concludes that it is possible to devise a scientifically based system of classifying the hazards, and of quantifying the hazards which they pose to work people, to the general public, and to the environment.

The Report argues that, at the present, there do not exist satisfactory theoretical models for predicting the quantity of a dangerous substance which, in the event of a realisation, will give rise to an isotraumatic level of fatalities. This is not intended to discourage the search for such theoretical models, still less is it intended as a criticism of those models which some Member States are engaged in constructing to determine the radius of possible harm from given installations.

It has been found necessary to comment on Annex I because the nature of this Annex has implications for Annex II and for Annex III. The order of treatment which seems to be dictated by the need for a logical exposition of the subject is to comment first on the implications of the Directive, followed by detailed comment on Annexes III, II, I and IV in that order.

Notes by the author on proposed amendments to the threshold levels for chlorine, phosgene and methyl isocyanate in Annex III which were requested by the Commission during the performance of the Contract, and which were covered by its terms, do not form part of this Report.

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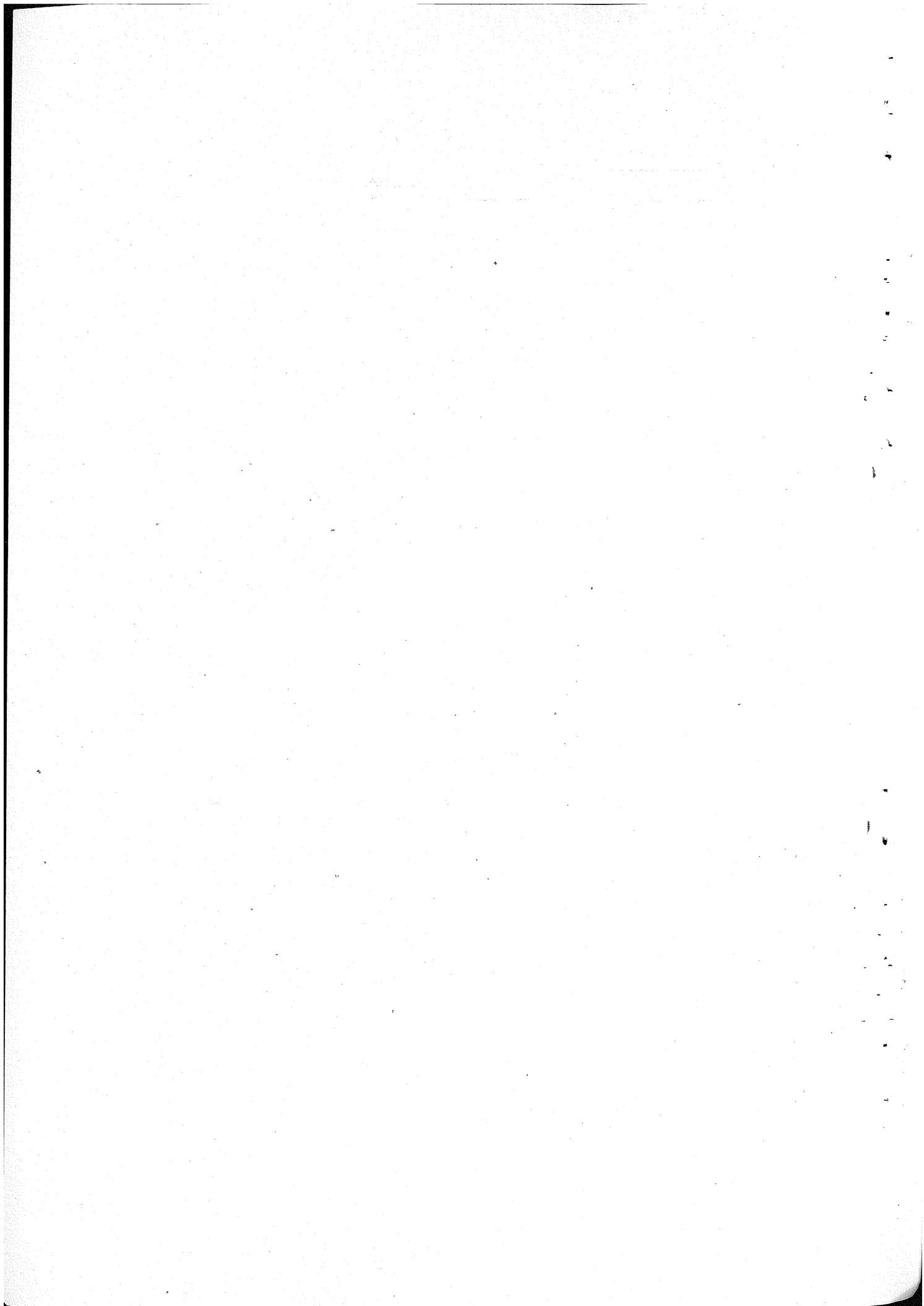
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## SECTION I.

### AIMS AND OBJECTS OF STUDY.

#### 1.1. TERMS OF CONTRACT.

These are set out in Annex I of the study contract as below.

##### *Introduction.*

Article 19 of the Council Directive on the major accident hazards of certain industrial activities (82/501/EEC) requires that the Council, on a proposal from the Commission, review Annexes I, II and III before 8.1.86.

The Commission will present in 1985 a limited and punctual revision with a view to correcting anomalies contained in Annexes II and III and will present later a more fundamental revision on the basis of systematic criteria.

##### *Contents of the Study.*

A. The study will examine the question of the fundamental revision of Annexes II and III. The methods and criteria through which a revision of the Annexes could be developed will be analysed and discussed. Account will be taken of the bases on which the present Annexes were prepared. The analysis will examine, in particular:-

- the validity of applying criteria which relate to the intrinsic properties of the substances such as explosivity, flammability, acute and chronic toxic effects, mutagenic and teratogenic effects, and effects which harm the ecosystem.
- the feasibility of using other criteria in combination with these, such as industrial significance, scale of usage, type of process and equipment in which used, and the likelihood of the substance escaping.
- the criteria to be used to determine the threshold quantities of the substances.
- any other matters relevant to the construction of a reasonable and justifiable list of substances and threshold values.

The study shall include the compilation of an indicative list of key substances, showing how the application of the conclusions reached under Study A would affect the inclusion of substances and the threshold levels of Annexes II and III of the Directive.

B. The study will examine also a limited number of questions relating to some entries and threshold quantities in the Annexes. The contractor will assist the Commission in analysing and resolving these questions

which have been raised in the Group of Competent Authorities, in order to accomplish in 1985 the punctual revision of certain entries in the Annexes in order that they correspond to a more realistic appraisal of the hazards of the substances and the characteristics of the processes in which they are used.

C. If required to do so by the Commission, the contractor will examine also possible revisions of Annex I.

#### *Planning and Organisation of the Work.*

Part A of the study, concerning the fundamental revision of Annexes II and III, will consist of a consolidated report. An interim report will be submitted before April 30th 1985 and a final report before 30th September 1985. Progress reports will be submitted to the Commission at regular intervals.

Part B of the study, concerning a limited number of questions relating to the punctual revision of Annexes II and III, will consist in preparing short documents to be used to support the work of the Commission within the Group of Competent Authorities. These documents will be prepared as and when requested by the Commission, in the first semester of 1985.

Part C of the study, should the contractor be required to carry it out, will be conducted concurrently with Part A.

The contractor shall consult the Competent Authorities in the Member States on the matters concerned in this study. This shall take place after the time of submitting the interim report and before the time of submitting the final report.

## SECTION 2.

### TERMINOLOGY.

#### 2.1. PROBLEMS OF TERMINOLOGY.

It seems to the author necessary, before discussing the substance of the report, to set out the terminology which will be used in it. The lack of an agreed terminology in the area under consideration has produced, in the past, in the English speaking world at any rate, a great deal of confusion. The words "hazard" and "risk" have been used interchangeably just as they are in everyday speech. As a result, the potential for harm of a given situation has been confused with the probability of its realisation. This has led to the same situation being described by one authority as constituting a "high risk" and by another

as constituting a "low risk".

It seems essential, therefore, in this study to use a set of terms which are self consistent and yet which do not conflict with everyday usage. The terms are defined below in a manner which accords with what is now a growing consensus in the United Kingdom as their usage. They also correspond with the way they are used in the Directive on Major-Accident Hazards of Certain Industrial Activities (hereafter referred to as "the Directive").

## 2.2. GLOSSARY OF TERMS.

A working Party of the British Institution of Chemical Engineers has produced a glossary of terms "Nomenclature for Hazard and Risk", [1] I.Chem.E. The definitions given below are taken from this glossary.

**HAZARD** a physical situation with a potential for human injury, damage to property, damage to the environment or some combination of these.

**RISK** the likelihood of a specified undesired event occurring within a specified period or in specified circumstances. It may be either a frequency (the number of specified events occurring in unit time) or a probability (the probability of a specified event following a prior event), depending on the circumstances.

**INDIVIDUAL RISK** the frequency at which an individual may be expected to sustain a given level of harm from the realisation of specified hazards.

**SOCIETAL RISK** the relationship between frequency and the number of people suffering a specified level of harm in a given population from the realisation of specified hazards.

**ACUTE** immediate, short-term. Relating to exposure: conditions which develop rapidly and may cause harm within a short time.

**CHRONIC** persistent, prolonged and repeated. Relating to exposure: frequent, or repeated, or continuous exposure to substances.

Added to these are further definitions not given in the above reference.

**AT RISK** having a significant probability of sustaining injury or damage in the event of the realisation of a hazard.

**REALISATION** to bring into being. Thus, of a hazard, to bring into being that which had been potential. Thus in the Study the phrase "realisation of a major-accident hazard" means the occurrence of such phenomena as fire, explosion or the dissemination of a toxic agent which represent the release of the potential of the hazard.

Definitions, for the purposes of this Report, of other technical terms will be given as they arise.

The author recommends that the Commission give consideration to the

possibility of compiling a multilingual dictionary of terms used in the field under discussion.

### **2.3. THE TERM "MAJOR ACCIDENT HAZARDS".**

The European Community's own term "Major-Accident Hazards of certain industrial activities" may be analysed in light of the above.

The term is concerned with Hazards and the qualifying clause "Major-Accident" delimits these hazards to those whose potential may be realised through a major accident.

The clause "of certain industrial activities" further delimits major-accident hazards, by the examples of such activities given in Annex I of the Directive, to what may be conveniently termed the hazards of the chemical and process industries. The hazards are thus "Chemical" Hazards.

The delimitation of hazards to those with the potential to give rise to accidents implies an acute event. It is self evident that fires and explosions are acute events but it is not self evident that toxic releases are an acute event. Such releases may be continuous giving rise to chronic effects in both the work place and in the surrounding area. They may give rise over a long term to environmental damage, sometimes, as with acid rain, up to considerable distances. Such hazards, it will be argued, are not appropriately dealt with by the Directive under discussion.

There are two forms of acute toxic releases. The first is an acute release which gives rise solely to acute consequences as, for example, a release of a non-persistent agent where such injuries as are sustained occur within, say, minutes or, at most, hours after release even if the onset of symptoms may be delayed. Examples are chlorine, where the effects are immediate, and phosgene, where the effects are delayed.

The second form is an acute event which gives rise to both acute and chronic consequences on account of its persistency. Examples are mustard gas and dioxin. In both of these cases the onset of symptoms is delayed. This seems to be general in such cases but this may not be universally true.

### **2.4. ABBREVIATION.**

The "Major-Accident Hazards" of the Directive will be abbreviated, where it is appropriate to do so in the report, to "MAH".

## SECTION 3.

### GENERAL METHODOLOGY OF THE STUDY.

#### 3.1. THE ADVISABILITY OF AVOIDING PIECEMEAL AMENDMENTS.

The author strongly advises that the making of piecemeal amendments to the Directive be avoided wherever possible. Amendment to the Directive should take place only against a background of an analysis of its purposes and against a rational framework of understanding of the inter-relationship and comparability of the hazards which the Directive aspires to control. To do otherwise may lead to the perception of anomaly where none exists, or to the increase in an anomaly when the intention is to reduce anomalies.

To this end the discussion commences by seeking to analyse the purposes of the Directive and by examining the events which led up to it.

#### 3.2. THE JUSTIFICATION FOR THE ADOPTION OF THE DIRECTIVE.

In common with much law of a national character the Directive itself deals only briefly with the justification for its adoption. In the preamble it states, *inter alia*,:-

"Whereas the protection of the public and the environment and safety and health protection at work call for particular attention to be given to certain industrial activities capable of causing major accidents; whereas such accidents have already occurred in the Community and have had serious consequences for workers and, more generally, for the public and the environment;"

It had earlier stated,

"and having regard to the principle that the best policy consists in obviating possible accidents at source by the integration of safety at the various stages of design construction and operation"

it states later,

"Whereas it is necessary to lay down that any person outside the establishment liable to be affected by a major accident should be appropriately informed of the safety measures to be taken and of the correct behaviour to be adopted in the event of an accident."

and, in Article 1;

"This Directive is concerned with the prevention of major accidents which might result from certain industrial activities and with the limitation of their consequences for man and the environment. It is directed in particular towards the approximation of the measures taken by the Member States in the field."

and, in Article 1, (c)

"Major accident means:

an occurrence such as a major emission, fire or explosion resulting from uncontrolled developments in the course of an industrial activity, leading to a serious danger to man, immediate or delayed, inside or outside of the establishment, and/or to the environment, and involving one or more dangerous substances."

Article 1 goes on to define "dangerous substances" by references to criteria in Annex IV of the Directive and/or by their being listed, together with a specified threshold quantity, in Annex III and Annex II.

### **3.3. SUMMARY OF THE PURPOSES OF THE DIRECTIVE.**

As a working definition, for the purposes of this Report, the purposes of the Directive may be summarised as below:-

"The Directive aims to avoid major accidents arising from certain industrial activities involving dangerous substances and which can give rise, inter alia, to major fires, explosions or toxic releases. Such accidents have been shown by the historical experience to have given rise to injury to workers and to the general public and to the environment. Such injuries to man or damage to the environment may be either immediate or delayed.

It aims also, in the event of such accidents, to mitigate their consequences.

To this end it lays down, in Annex IV, criteria which determine the intrinsic properties of toxicity, flammability and explosibility which render substances dangerous. In Annex III and Annex II it lays down an extrinsic criterion, that of mass, which constitutes the threshold above which an accident involving a dangerous substance is deemed to be a major accident."

It may be noted that neither the intrinsic criteria nor the extrinsic criterion are justified in the Directive. Nor does the Directive in listing particular chemical substances in Annex III or Annex II identify the particular intrinsic criterion which justifies the inclusion of the substance in either Annex.

### **3.4. THE PRINCIPAL TASKS OF THE STUDY.**

Based on the above, the principal tasks of the study are:-

- (1) To analyse, examine and justify
  - (a) The intrinsic criteria which determine the concept of a dangerous substance.
  - (b) The extrinsic criterion, i.e. mass, which determines whether a particular



substance, recognised as a dangerous substance by the application of intrinsic criteria, is present in sufficient quantity to justify its designation as a major accident hazard.

- (2) To examine the question as to whether there may be other criteria which, taken in conjunction with the above, may more effectively determine whether a substance is a dangerous substance or, if so, at what threshold level of quantity it may be deemed to constitute a major-accident hazard.

### **3.5. METHOD OF OPERATION.**

The study will

- (1) examine the circumstances which have given rise to the major-accident hazard problem.
- (2) it will consider the historical evidence both in the Community and outside it.
- (3) it will examine the difficulties inherent in determining the validity of this experience.
- (4) it will examine the intrinsic criteria of the Directive.
- (5) it will analyse the concept of a "major accident".
- (6) it will consider the extrinsic criteria to be used to determine whether a quantity of a dangerous substance constitutes a major accident hazard.
- (7) it will examine alternative criteria which may result in more effective control of some major accident hazards.

## **SECTION 4.**

### **SCOPE OF COVERAGE.**

#### **4.1. COVERAGE OVER TIME.**

Because the realisations of major chemical hazards are comparatively rare events, it is necessary to review such realisations over a considerable time span. This has drawbacks because circumstances are continually changing and the lessons of previous events are learned making them less likely to happen, or technology may change rendering dangerous processes obsolete. Thus a view taken over 60 to 70 years, on account of this factor, is likely to result in a pessimistic view of the frequency of realisation under present conditions. On the other hand the chemical and process industries have grown rapidly over recent decades and this tends to cancel out the reduction in frequency produced by better knowledge of how to control the hazards.

#### **4.2. GEOGRAPHICAL COVERAGE.**

Even worldwide, and especially for some hazards, the data on their realisation

are very sparse hazards to be present, let alone be too small to be studied. Therefore, the subject that the lessons

#### 4.3. FIXED INSTALLATIONS AND TRANSPORT.

The Directive except for the effects from transport effects, whether similar. It is not necessarily of the risks associated with fixed

existent. So, were consideration of major chemical hazards which have been realised in the European continent. In the European Community, the numbers of events would not permit conclusions from them. So far as possible, they should be studied on a worldwide basis with the assumption that in general, applicable to the EEC.

#### 5. FIXED INSTALLATIONS AND TRANSPORT.

fixed installations only; transport, including pipelines, on the site, is excluded. However lessons may be drawn from accidents which are applicable to fixed installations in that the risks of fires, explosions or toxic releases, are likely to be of a similar magnitude, however, that the risks of such realisations are of a similar magnitude. On general grounds it would be expected that the risks associated with transport would exceed those associated with fixed

### SECTION 5.

#### ORIGINS OF THE PROBLEM.

##### 5.1. THE FIRST ACCIDENTS.

The beginning of "modern process technology", late in the First World War. The process for ammonia

This process is a process technology for the conversion of atmospheric nitrogen into anhydrous liquid ammonia.

The existence of the technology for the manufacture of ammonium nitrate with TNT, to be used in conjunction with it was its use

However, in the several thousand and intended for severe and wide

##### THE TWENTIETH CENTURY.

It might conveniently be termed "modern process technology" immediately prior to the outbreak of the First World War with the commercial success of the Haber-Bosch process.

It brought together a number of salient features of today's process technology as a large scale continuous process, with catalytic action and pressure. It paved the way for the handling of ammonia via

the process, which provided also the raw material for nitric acid, made possible the large scale production of ammonium nitrate. In the succeeding war this was used, in admixture with TNT, as an explosive Amatol. It is used extensively today, as a commercial blasting explosive, ANFO. But it was the process which earned Fritz Haber a Nobel Prize.

The BASF works at Oppau, Ludwigshafen, a dump of ammonium nitrate mixed with ammonium sulphate was used as a fertiliser blew up, killing some 550 persons and producing a major accident. This marked the beginning of the major-accident

hazards problem producing a death toll for a MAH which was not exceeded until the Mexico City fire and explosion disaster of November 1985, and the Bhopal toxic release disaster of December 1985.

During the First World War there was a further development, this time in the use of poison gas. At Ypres, in April 1915, the discharge of 168 tonnes of chlorine killed, according to generally accepted figures, a total of ca 5,000 men. The chlorine was transported to the front line as a liquefied gas in cylinders and from that time onwards, the technology of handling chlorine as a liquefied gas progressed rapidly. There was an incident at Wyandotte, Michigan, USA in 1917 in which a release of 17 tonnes killed one person, and at St. Auban, France in December 1926, in which a release of 24 tonnes killed 19 persons.

Thus in the first half of this century there were major accidents involving unstable substances and liquefied toxic gases.

**5.2. MAJOR ACCIDENT HAZARDS SINCE THE SECOND WORLD WAR.**

The period from 1940 to the present day has seen a steady growth in the production of inorganic chemicals such as ammonia, chlorine and ammonium nitrate which continue to be Major-Accident Hazards. But there has also come into existence a whole range of new MAH principally through the growth of the technology of producing and handling hydrocarbons and their derivatives, especially those hydrocarbons containing up to four carbon atoms.

For example, today in Western Europe natural gas, which is mainly methane (CH<sub>4</sub>), accounts for 18% of total delivered energy [2] Anon. There has been also a steep growth in the market for Liquefied Petroleum Gas (LPG). This is a mixture principally of propane and butane and is used mainly as a fuel.

In the field of chemical manufacture, methane (CH<sub>4</sub>), ethylene (C<sub>2</sub>H<sub>4</sub>), propylene (C<sub>3</sub>H<sub>6</sub>) and butylene (C<sub>4</sub>H<sub>8</sub>) now play a very prominent part as feed stocks. With the exception of methane, which is mainly derived from natural gas, the other hydrocarbons are mainly derived from the cracking of petroleum fractions. Methane and ethylene may be stored and transported as refrigerated liquids, but propylene and butylene may be handled as liquefied gas. C<sub>3</sub> and C<sub>4</sub> hydrocarbons are not necessarily handled as liquefied gases. They may be handled at atmospheric pressure as refrigerated liquids. This is the case in the recently opened Mossmorran project in the U.K. In such a condition they present a lower hazard than when handled under pressure at atmospheric temperature.

An early major accident involving Liquefied Natural Gas (LNG) was that in 1944 at Cleveland, Ohio, where a storage tank burst and discharged over 1000 tonnes of LNG. This killed ca 130 people and caused severe damage to surrounding property.

Perhaps the earliest LPG disaster was at Meldrin, Georgia, USA in 1959, when a rail tank car discharged 36 tonnes and killed 18 people.

### 5.3. THE SPECIAL ROLE OF LIQUEFIED GASES.

What distinguishes hydrocarbons  $C_1$  to  $C_4$  is their flammability combined with volatility. They are either permanent gases (methane) and ethylene - (critical temp  $10^{\circ}C$ ), or may be handled as pressurised liquefied gases (propylene, butylene, butadiene, propane, butane). Paradoxically, though methane is much more volatile than propane, when handled in liquid form it has to be refrigerated and hence its rate of vaporisation in the event of spillage is governed by the rate of input of heat from its surroundings. Propane is usually handled as a liquefied gas and, on being spilled, it flashes, releasing vapour and spray.

As will be seen from the discussion above, there is difficulty over terminology. The general term "liquefied fuel gas" includes methane which must be refrigerated and also  $C_3$  and  $C_4$  hydrocarbons which may be handled either as refrigerated liquids or under pressure at ordinary temperatures. The term LPG will be used to refer to the latter circumstance and refrigerated LPG to refer to substances stored as liquids below atmospheric temperature and near to atmospheric pressure.

Some of the inorganics are handled as liquefied gases (examples being chlorine, ammonia and phosgene). These also flash when spilled giving rise to toxic clouds. In the case of ammonia, the cloud may also be flammable. Though the MAH problem is not exclusively caused by liquefied gases, they form the central core of the problem by their ability very quickly to form vapour clouds of a flammable or a toxic character.

### 5.4. THE INFLUENCE OF SCALE.

The intrinsic factors noted above would not, of themselves, create major-accident hazards. These factors also require the further extrinsic factor of mass to transform them from accident hazards into major-accident hazards.

It is very important to note that the growth of scale of the market has been matched by the growth of scale of process streams. It is a truism of chemical engineering that, especially for continuous processes, there are considerable economies to be derived from increasing the scale of process streams. In general the capital costs of an installation are approximately proportional to the stream capacity to the power two thirds. Supervision and process labour are virtually invariant with scale and so is, for example, computer control. As a consequence no producer will build two plants of capacity  $x$  in preference to one of capacity  $2x$ .

Allied with this has been the tendency for chemical manufacture and such allied processes as petroleum refining to be in the hands of powerful financial

groups. Today, for example, out of the top ten U.S. companies listed in Fortune magazine, five are petroleum refiners or chemical manufacturers. These factors taken together have led to the market demands for chemicals and petrochemicals to be met from a relatively few large scale manufacturing units.

Stream capacities for ammonia exceed 1,000 tonnes per day; similar figures exist for olefine manufacture.

The growth of stream capacities has led to a corresponding growth in storage capacities. Where the product is made for the market, storage capacity has to suit the pattern of transportation which involves such factors as plant break downs, rest days for drivers, adverse weather conditions, industrial disputes etc. Thus storage capacity at both despatching and receiving ends will certainly represent several days' production or consumption. Where the product is transported by sea, it will have to accommodate a ship load with some margin for the factors mentioned above. This may amount to a month's production or consumption and be measured in tens of thousands of tonnes.

#### **5.5. DOES BIGGER SCALE LEAD TO MORE ACCIDENTS ?**

This seems doubtful. The risk of loss of containment is probably invariant with scale, though this does not appear to be discussed in the literature. What is obvious is that the potential loss is closely related to stream capacity and that this applies both to the processing equipment and to storage tanks.

Thus large scale units mean fewer accidents but these fewer accidents have the potential for greater harm.

#### **5.6. SUMMARY.**

The last fifty years has seen a great increase in the number of harmful substances manufactured and also in the scale of their manufacture and storage. This has sharply increased the number of installations constituting major-accident hazards. But, of itself, this does not necessarily imply that the risk, i.e. the frequency of realisation of major-accident hazards, must increase. The risk is a measure of the degree of control.

It is also true that of late years the general recession in trade has produced a slowing down of growth of the industries, a notable exception being developments connected with North Sea Oil. Some of the older and smaller plants have been closed down.

## SECTION 6.

### THE HISTORICAL RECORD.

#### 6.1. THE VALUE OF THE HISTORICAL RECORD.

It may be said that legislation is seldom of a purely anticipatory character and that it generally arises from pre existing social ills. However, once the necessity for legislation is perceived, it is often true that the legislators try to look forward to anticipate social ills which are not yet manifest.

So it is with the Directive which arose because of the pressure of events, especially the disasters of Flixborough and Seveso. However, the Directive has not confined itself solely to regulating the agents responsible for these two disasters, or even to the regulation of those agents which have been implicated in other disasters which have occurred worldwide. Nevertheless there is a strong element of analogy in that many of the substances regulated have properties which are similar to those of substances which have been previously implicated in serious incidents.

Indeed, in one instance, what is regulated is a class of substances distinguished by their common property of flammability. Here the precise chemical composition or molecular structure is of little account. However with substances where the principal harmful property is toxicity, for reasons which will be discussed in greater detail below, it is much more difficult to treat them as a class.

The historical record has two valuable properties. The first is that it informs about the nature of the events which follow the realisation of hazards. The second is that it provides information on risk. This latter, for reasons outlined above in sub-section, has limitations because the level of risk changes with time as mankind learns from past experience.

#### 6.2. SOURCES OF HISTORICAL INFORMATION.

One general source of information is the book "Darkest Hours" [3] Nash, J.R. This is a compilation of information on disasters throughout history, both natural and man made. They are generally those in which twenty or more people lost their lives. This compilation is by a journalist and contains many errors. It is also far from comprehensive. Nash lists ca 100 examples of explosions of conventional explosives, ammunition or fire works, whereas [4] Biasutti, G.S. lists more than 600 similar explosions excluding those in ammunition dumps.

[5] Griffiths, R.F. and Fryer, L.S., who attempt to produce F/n curves\*

\* For discussion of F/n curves, see Section. 6.4.

for disastrous events worldwide, have acknowledged their debt to Nash.

Biasutti is the most useful source of data on the explosions of dense explosives but there are others, as for example, [6] Assheton, R., [7] Robinson, C.S. and [8] Healy, F. [9] NFPA covers dust explosions in North America up to 1957.

For vapour cloud explosions, there have been a number of published compilations, [10] Gagan, K., [11] ACMH, and [12] Davenport, J.A. are examples.

The most complete record of toxic releases appears to be [13] ACMH.

In the USA, the reports of the National Transportation Safety Board have produced much valuable information. However, these reports do not deal with events in fixed installations.

For a number of substances, as for example chlorine, phosgene and mustard gas, a great deal of information may be derived from the experiences of the Second World War in works such as [14] Prentiss, A.M.

Fig. 1 shows the chronological development of man-made disasters, not all of which fall within the area of the Directive.

### 6.3. LIMITATIONS OF THE HISTORICAL RECORD.

The limitations of the historical record fall into two main categories.

#### (1) Lack of comprehensiveness.

This has been noted above in the case of Nash with special reference to his record of explosions. However, even the far more comprehensive compilation of Biasutti, can be shown to be incomplete.

Considered on a worldwide basis, the number of incidents recorded from the USSR and the East European socialist countries is far lower than might be expected from the scale of their operations, and must be attributed to lack of candour on their part.

Fig 2. is a notional Venn diagram showing the relationship between the size of release and the number of fatalities on the one hand, and the extent to which it is reported on the other. In general it may be concluded that large releases with high casualty figures will attract worldwide attention. Smaller incidents will be less well reported, and trivial incidents not at all.

#### (2) Lack of accuracy.

It is common knowledge that reporting of major accidents by the mass media is likely to be inaccurate and that it should not be necessary to devote much space to this. However, the mass media shape public opinion and public shapes the form of legislation. Therefore media distortion may have adverse effects on legislation.

These adverse effects may take the form of the legislation placing undue

FIG 1 CHRONOLOGICAL DEVELOPMENT OF MAJOR HAZARDS.

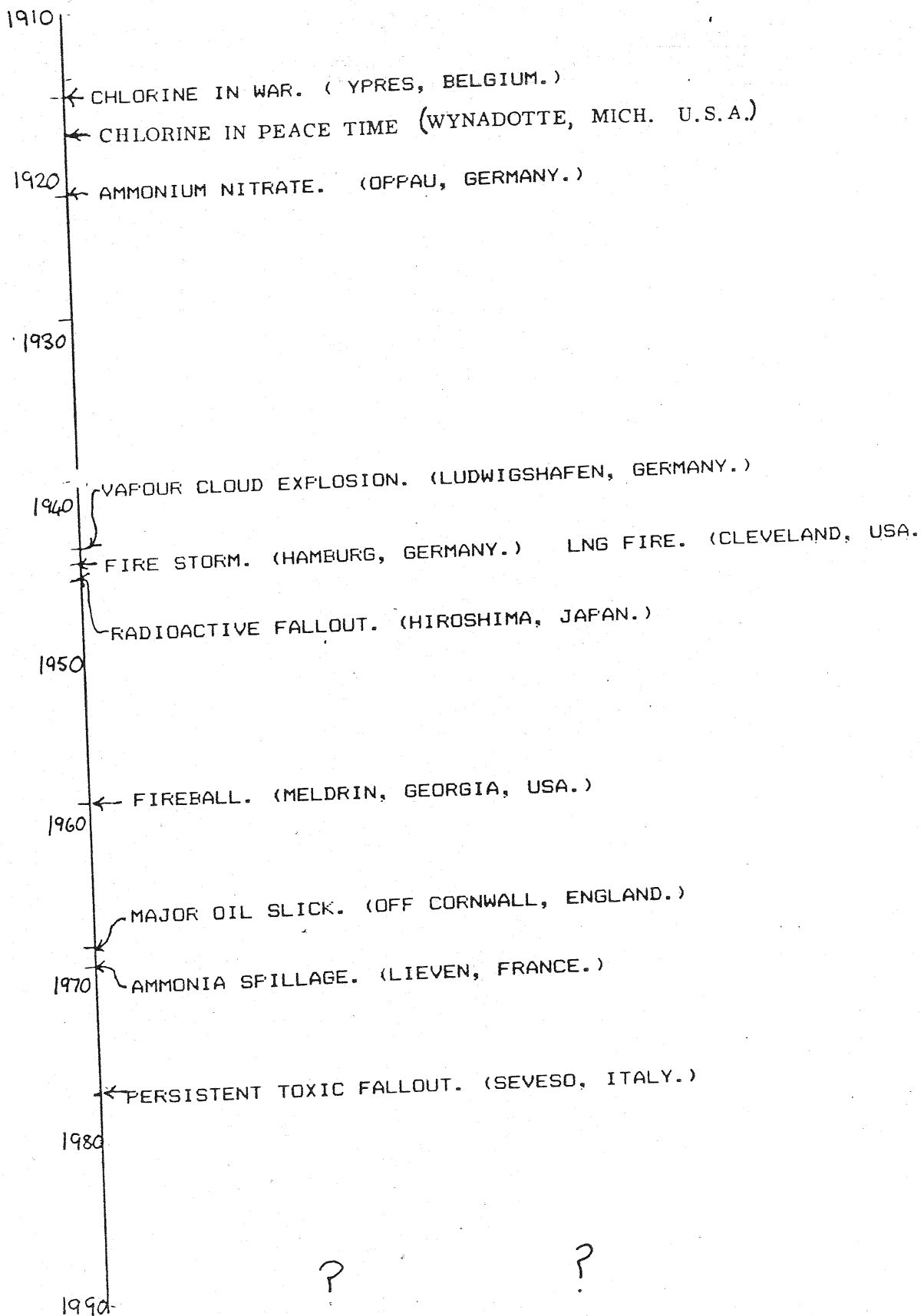
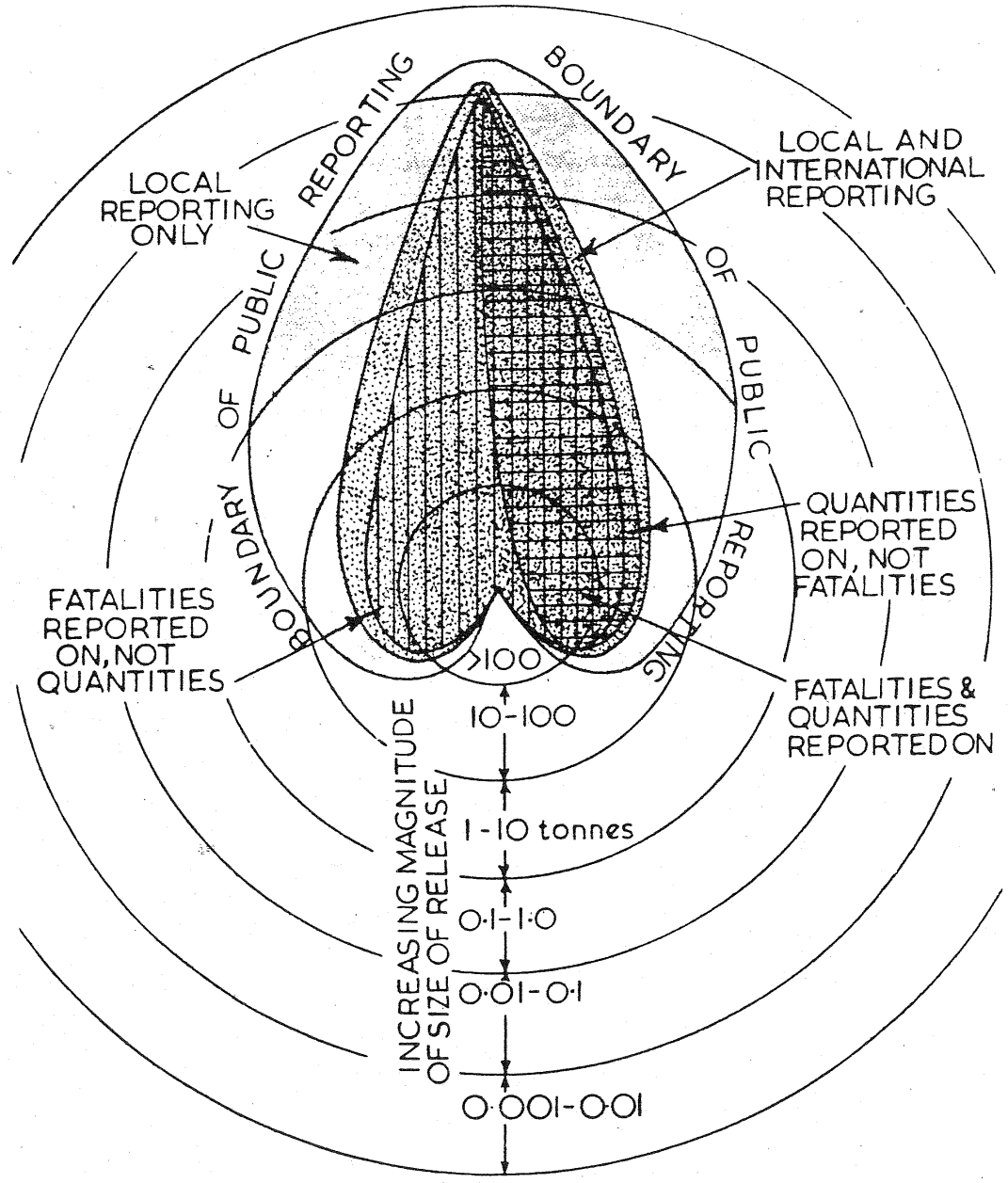




FIG 2 NOTIONAL VENN DIAGRAM OCCURRENCE & REPORTING OF MAJOR HAZARD EVENTS



emphasis upon certain aspects of a problem at the expense of others. The Report contends, at an appropriate place, that the Directive is unduly severe on the control of some, though not all, toxic substances.

Lack of accuracy in media reporting might not be so serious were it to be counter-balanced by objective reporting in the technical literature. Though this has had to some degree a corrective influence, it might be said that myths are more easily created than destroyed. An unfortunate tendency is that a particular piece of misinformation may become accepted by repetition by authors uncritically following upon each other. It may then be claimed that it must be true as ten or twenty authors all vouch for it. Even when, as at Flixborough, the Official Inquiry [15] Flixborough, decisively rejected a particular theory as to its cause, some authors have continued to seek to revive it.

There have been in the past many incidents on which information is far from complete. This has been due, in some measure, to lack of systematic expert examination. A useful paper in this area is [16] Roberts, A.F., from which Table I is derived.

#### **6.4. THE HISTORICAL RECORD AND THE ASSESSMENT OF RISK.**

It has been pointed out above in sub-section 4.1. that there are difficulties involved in estimating risk from the historical record. There is an uncertainty principle attached to the historical estimate of risk. This is that to focus on present day conditions produces too small a sample to give "statistical reliability". On the other hand, study of a long time span provides more "statistical reliability" at the expense of including conditions which may have passed away.

Two factors here act in opposite directions. The risk per individual installation was greater in the past because there was poorer control, but there were fewer and/or smaller installations.

The Report generally uses a time span of about seventy years for old established areas of production, and necessarily shorter time spans for such phenomena as vapour cloud explosions, which have all occurred in the past forty-two years.

The historical record may be used to draw F/N curves. These, strictly speaking, are  $F \propto N$  curves as they plot the frequency with which an event with consequences equal to, or greater than, n occurs; n may, for example, denote the number of fatalities per incident or the financial cost of the damage. For fatalities these are not curves but are step diagrams. Where n is small, this is clearly apparent, but for high values of n the steps may become small and closely approximate to a curve.

TABLE I. CHECKLIST OF INFORMATION REQUIRED FROM THE INVESTIGATION OF A MAJOR INCIDENT.

General	<p>Short narrative account of the incident.</p> <p>Description of site with plan of plant layout.</p> <p>Description of surrounding district with up-to-date map.</p> <p>Estimated timing of events.</p>
Release Conditions	<p>Size and position of breach.</p> <p>Normal operating conditions in vicinity of breach.</p> <p>Inventory of fluid available for release.</p> <p>Formation of liquid pools by bunds etc.</p>
Dispersion Effects	<p>Wind speed, atmospheric cloud cover, insolation.</p> <p>Size of released cloud as a function of time.</p> <p>Movement of released cloud across terrain.</p>
Fire and Explosion Effects	<p>Extent of flame spread</p> <p>Thermal radiation effects.</p> <p>Blast effects.</p> <p>Missile projection</p>
Toxic Effects	<p>Population exposure</p> <p>Vegetation damage.</p> <p>Absorbed chemicals.</p>

## SECTION 7.

### FORMS OF REALISATION OF MAJOR-ACCIDENT HAZARDS.

#### 7.1. FORMS SPECIFICALLY REFERRED TO IN THE DIRECTIVE.

Article 1 (c) refers to "an occurrence such as a major emission, fire or explosion . . . and involving one or more dangerous substances". Dangerous substances are classified in Annex IV as "very toxic", "other toxic substances", "flammable substances" or "explosive substances" for purposes of Articles 3 & 4 or, for purposes of Article 5, as those listed in Annex III and in Annex II in the quantities referred to in each Annex.

Explosive substances are defined as "substances which may explode under the effects of flame or which are more sensitive to shocks or friction than dinitrobenzene". This appears to refer to dense explosive rather than to admixtures of flammable substances with air such as have been implicated in vapour cloud explosions.

#### 7.2. OTHER POSSIBLE REALISATIONS.

Death or major injury may occur for the following departures from the normal conditions under which humans live:-

- (1) Abnormal heat.
- (2) Abnormal cold.
- (3) Abnormal pressure, including local overpressure due to crushing or impact.
- (4) Insufficiency of oxygen.
- (5) Inhalation of harmful substances.
- (6) Skin contact with harmful substances.
- (7) Ingestion of harmful substances.
- (8) Infection by pathogenic organisms.

Examples (1), (3), (5), (6), and (7) are covered by the categories of fire, explosion or toxic release. (2) is not. There can be little doubt, however, that any large spillage of a cryogenic fluid would be liable to kill people in the near vicinity by abnormal cold if they became engulfed in it. This is a reason additional to any other which may be adduced for controlling any particular cryogenic fluid.

Many people die in industry from cause (4), but they die in accidents that involve only small numbers of people. There is at least a theoretical possibility that a major accident could arise in which people are asphyxiated by a large release of liquid nitrogen. This case is not covered by the Directive.

The Directive does not include specifically the emission of pathogenic organisms discharged from an industrial process. These do not fall clearly into the

category of toxic substances. The author's terms of reference do not include consideration of biological releases of this character.

A further category not specified by definition is that of substances which, though not flammable themselves, may enhance combustion. The most obvious member of this category is oxygen which, in the form of liquid oxygen, appears in Annex II though not in Annex III.

## SECTION 8.

### VAPOUR CLOUDS.

#### 8.1. THE NATURE OF VAPOUR CLOUDS.

Examination of Annex II, III and IV shows that some of the dangerous substances stored in bulk and listed in these Annexes, are substances which have the capability of giving rise to vapour clouds. Examples are the toxic substances chlorine and ammonia and highly flammable substances such as propane.

These are particularly dangerous because they are liquefied gases which, if containment be lost, "flash" i.e. a portion of the substance almost instantaneously turns to vapour; simultaneously the temperature of the remaining liquid falls to its atmospheric pressure boiling point which is usually below 0°C. Propane, for example, cools to -40°C.

This flashing fraction varies from one substance to another and according to the temperature of storage. It is higher at higher temperatures of storage.

Flashing is so violent that liquid may be entrained as spray or froth and contribute to the size of the cloud as the fine droplets evaporate in contact with air.

Some authorities have claimed that the fraction of liquid so entrained may equal the fraction flashed off. Thus, on a warm day some liquefied gases, when spilled, are turned almost totally into vapour clouds.

This possession of internal dispersive energy makes liquefied gases the most hazardous class of compounds to be considered. Though, in theory, highly compressed toxic gases might be expected to be more dangerous, in practice their density is lower than for liquefied gases. There are few representatives of the class, carbon monoxide (not listed) and fluorine being examples.

There are significant differences between flammable vapour clouds and toxic vapour clouds. The former, once diluted with air below the lower flammable limit, become relatively harmless. This limit depends upon factors such as the molecular weight of the flammable substance but may be of the order of 2-3%, i.e. 20,000 to 30,000 p.p.m. by volume.

Toxic clouds may, on the other hand, be dangerous if the toxic substance be present at 50 p.p.m. by volume or less. Thus toxic clouds may have a far greater radius for harm than flammable clouds, as they may be still dangerous when diluted by a ratio of 100 to 500 to 1 below the level at which flammable clouds cease to be dangerous.

## 8.2. THE STATE OF KNOWLEDGE OF VAPOUR CLOUDS.

### 8.2.1. Physical factors.

The understanding of the mechanisms of formation and dispersion of vapour clouds only goes back to the early seventies when van Ulden made the first experiments, [17] van Ulden, A.P. Since that time, experimental work has been continued, and special reference should be made to the large scale trials at Porton Down and Thorney Island in the UK, [18] McQuaid, J., [19] McQuaid, J.

Laboratory experiments in wind tunnels have been conducted at Warren Spring, UK, [20] Hall, D.J. The understanding of the subject involves both fluid mechanics and meteorology.

Simultaneously with this work, there have been attempts to construct computer models, [21] Fryer, L.S. and Kaiser, G.D. It is hoped that, in the near future, when detailed results of the Thorney Island trials are available that a computer model, validated by field trials, may be constructed.

In the case of flammable clouds, there seem to be three possible scenarios.

- (1) Harmless dispersion.
- (2) Fire, perhaps resulting in a fire ball.
- (3) A vapour cloud explosion.

It seems likely, after the field trials, that a computer model which predicts how far a cloud will travel before dilution to a harmless condition may soon be available. This would be valid for various quantities released and for various atmospheric conditions.

The prediction of the physical behaviour of flammable clouds on ignition has advanced in recent years and has been reviewed, [22] Roberts, A.F. The most extreme form of behaviour is that of a fire ball which may last for up to 20 seconds and inflict death and serious injury.

The problem of predicting the circumstances which lead to a cloud, on ignition, giving rise to significant overpressure has not, as yet, been solved.

### 8.2.2. Human injury.

However, this is only half the story, the other half being the potential of such clouds to inflict injury to humans.

The understanding of the potential for human injury consequent upon the ignition of flammable clouds, has recently been advanced by Hymes, [23] Hymes, I. In broad terms, the probability of survival of anyone engulfed in a vapour cloud

at the time of ignition is very low and may be regarded as zero.

Controversy exists as to the distance at which persons outside of the cloud may die or suffer serious injury.

Though attempts have been made, with some degree of success, to predict the overpressure produced by vapour cloud explosions, [24] Wiekema, B.J., the author's own studies, which will be discussed later, suggest a higher death toll than would be predicted from, say, a TNT model.

However, the discrepancy between theory and practice is very marked in the case of theoretical models for toxic clouds which seem to yield figures for fatalities which may be two orders of magnitude higher than has occurred in practice. There has been a failure to bridge the gap between the physical sciences and the life sciences. As will be shown later, there are considerable difficulties in constructing a life science model which bridges the gap between animal experiments and the response of a human population subjected to a toxic release.

## SECTION 9.

### WHAT CONSTITUTES A MAJOR ACCIDENT ?

#### 9.1. THE RANGE OF THRESHOLD VALUES IN THE DIRECTIVE.

There is little ground for dispute that most of the substances designated by the indicative criteria of Annex IV and those listed in Annex III and Annex II are intrinsically dangerous to some degree. What is far more difficult to decide is the mass of the substance which must be present for it to acquire the potential of a major-accident hazard. The range of mass which constitutes this threshold value, as given in Annex III, is from 1 kg to  $5 \times 10^7$  kg. This seems extraordinarily wide and suggests that some substances listed, in themselves, are almost innocuous and only possess major-accident hazard potential when present in enormous quantities.

#### 9.2. THE RANGE OF POTENTIAL OF A HAZARD.

There is no single figure which can be used to express the potential of a hazard. Domestic fires can cause death and the frequency of fires involving fatality in the United Kingdom is about 700 per annum. This is a risk per dwelling house in the UK of the order of  $10^{-4}$  p.a. However, the frequency of fires causing two or more deaths is only about 10% of this figure, or  $10^{-5}$  and the frequency of causing ten or more deaths in all fires is about 0.15% of this figure, corresponding to a risk of about  $10^{-7}$  per annum. In 1981 there

was a fire in a dwelling house in Deptford, London, which killed 13 people. This is probably about the limiting number it would be possible to kill in a single house and corresponds to a risk of less than  $10^{-8}$ .

But if fire precautions in homes were to be based on the assumption that the potential of domestic fires is that they can kill 13 or more people, but without taking account of the low probability of an event of this character, then crippling burdens could be placed upon homeowners to meet the cost of fire precautions.

A similar situation exists with regard to chemical hazards. The upper limit of their potential, based either upon the historical record or upon theoretical calculation, may be very high, but the risk of realisation at this upper limit of their potential would be very low. To base the control of chemical hazards upon the maximum potential of dangerous substances would impose crippling burdens on the industry, because it would require even very minor amounts of the substances to be treated as major-accident hazards. A policy of this sort would discriminate against the chemical and process industries as, with the exception of the nuclear industry, other industries are not treated in this way.

### 9.3. THE QUEST FOR A CENTRAL TENDENCY.

It might be concluded, from the historical record of some dangerous substances, that sometimes substantial releases have led to no injuries at all whereas, in other cases, small releases have produced numerous injuries.

Greater knowledge of the actual circumstances may do much to explain these discrepancies. One obvious factor is the density of population in the vicinity, which in its turn may depend on the time of day.

But, from the point of view of prediction, the situation has to be viewed in the light of probabilities. Thus, on a given site, the population density during office hours may be four times the population density outside of office hours. But the time span of office hours is only about 25% of the total time the site is in operation. Thus a mean may have to be calculated which would be  $1.75x$  where  $x$  is the out of office hours population density. Thus the range of predicted fatalities is  $fx$  to  $Ax$ .

The use of the zero extreme as a measure of probable consequences is clearly unacceptable. The maximum value for predicted fatalities, as has been discussed above, is a very elastic figure whose value depends upon the scenario adopted, and is not suitable even for relative, let alone absolute, ranking of hazards.

There is a need, therefore, to establish a central tendency, a "most probable" realisation of a hazard. How this may be determined and how this may be



quantified & discussed below.

#### 9.4. THE QUANTIFICATION OF HAZARDS.

##### 9.4.1. The criteria for determining harm.

If, for the present, it may be assumed that a methodology exists for determining, either from the historical experience or from theoretical models, the various consequences of the realisation of a hazard, the question remains as to which of these consequences most satisfactorily characterises the harm which may ensue.

There seem to be five principal measures of harm which could be used:-

- (1) Fatality.
- (2) Non-fatal human injury.
- (3) Property damage.
- (4) Financial damage.
- (5) Environmental damage.

No one would contend that an accident which produces fatalities is not a serious accident. Nor would it be contended that an accident which killed, say, thirty people is not a major accident. Accidents which kill may also injure and thus large numbers of injuries almost always accompanies high fatalities. Major fires and explosions, clearly produce property and other forms of financial damage along with fatalities and injuries.

A major accident which leads to fatalities, injuries and damage to property may also inflict damage on the environment. An unresolved question is whether there may be major-accident hazards which in their most probably realisation could be anticipated to cause major effects in the categories (2), (3), (4) or (5) above, but not be expected to give rise to a significant level of fatality. Discussion of major accidents of this character will be deferred. They do not by any means constitute the central core of the problem, though the possibility of their existence cannot be ruled out. The question immediately to be considered will be those hazards which undoubtedly have the capability to bring about fatalities and injuries and which may have the capability also of causing property and financial damage and, in some cases, damage to the environment.

##### 9.4.2. The "Isotraumatic" approach.

If fatality is to be the principal, though not necessarily the sole, criterion for determining whether or not an accident hazard is to be treated as a major-accident hazard, it is necessary to decide on a level of fatality which represents the most probable level of realisation of a major-accident hazard.

Many people die in industry from accidents which involve one or two fatalities. No one regards these as major accidents. On the other hand, an accident which killed twenty people would not fail to be regarded by the public as a major

accident. The level of fatalities for a major accident could, therefore, be regarded as falling between 2 and 20. The Report suggests that the figure be taken as 10. 10 would be the central tendency, the most probable level of fatality resulting from the realisation of those hazards, which would just qualify as major-accident hazards.

To advance any figure between 2 and 20 is to invite controversy. However, unless there is some agreement on a figure, whether it be 10 or not, to apply across the board to all the dangerous substances under consideration, then the creation of a rational framework for control is impossible. To say this is not to ignore the difficulties of assessing the level of inventory which would correspond to such a central tendency, or to claim any high level of accuracy for the final result. But to base control upon a presumed central tendency of X fatalities for one substance and, say, 5X fatalities for another, makes consistent treatment impossible.

The author has coined the term "isotraumatic" (Greek "equal wounding") for the approach in which the threshold inventory of all hazards is based upon the same level of fatality, [25] Marshall, V.C. The Report argues that an isotraumatic approach is essential if public policy is to be directed to securing equitable treatment between one industry and another and between the different branches of the same industry.

It is also important from the point of view of resource allocation. It does not constitute the best use of resources to concentrate personnel on the surveillance of hazards which do not truly rank as major-accident hazards, to the neglect of those hazards which do.

#### 9.4.3. Early attempts to establish threshold levels.

This is not to say that, in the past, there has not been such an approach, at least at an intuitive level. If such an approach has been adopted, it has been based on an implicit, though not an explicit, acceptance of the isotraumatic approach.

Certainly there has been little public discussion on the philosophy of how to determine threshold levels. There have been a few papers only, of which [26] Marshall, V.C. and [27] Wilson, D. are examples.

Perhaps the earliest attempt was that of the United Kingdom Circular 1/72, [28] Department of the Environment. This was a circular concerned with the granting of planning permission in the vicinity of a hazardous plant. It set threshold values for substances on a site which if exceeded produced a situation in which planning authorities were advised to consult the Factory Inspectorate. It may be regarded as a direct ancestor of the annexes to the Directive

and is reproduced as Table II.

Of the categories listed in Circular 1/72, those concerned with dust explosions do not appear in the Annexes; (Dust explosions are excluded by the Directive if only because, in most cases, they do not involve "dangerous substances").

There was no public discussion in the UK as to how these threshold levels were arrived at, but it is safe to assume that they were based on the intuitive judgement of the Factory Inspectorate. Nevertheless in some categories there is a measure of agreement between Circular 1/72 and with the threshold values in Annex II and Annex III.

The United Kingdom Advisory Committee on Major Hazards (ACMH) made recommendations for threshold values, [29] ACMH. It used, as a supporting argument, the concept of the "Mortality Index" which the present author had developed, [30] Marshall, V.C., but it stopped short of explicit reference to an isotraumatic level to which these mortality indices would be related. The threshold levels recommended by ACMH were also similar in some cases to those in the Directive. Table III summarises the differing levels for some key substances, as proposed by Circular 1/72, in [31] ACMH and in the Directive.

9.4.4. Linking the central tendency to the isotraumatic level.

If the isotraumatic concept be accepted, and if the isotraumatic level were to be set at 10, and if the measure of hazard be the number of fatalities most probably realised by the hazard, the problem would then resolve itself into determining what quantity of a substance would give rise to ten fatalities as the most probable realisation.

This is not an easy task as will appear below, and it may be said at the outset that no precise figures may be expected to emerge.

TABLE II. MAJOR HAZARDS IN CIRCULAR 1/72.

Industry	Materials Involving Risk.	Total Storage Quantity requiring detailed investigation.
Petrochemical* and plastic polymer manufacture.	All	†
Other chemical works.	Acrylonitrile Ammonia Bromine Chlorine Ethylene Oxide Hydrogen Cyanide Phosgene Sulphur Dioxide	50 Tons 250 Tons 100 Tons 25 Tons 20 Tons 50 Tons 5 Tons 50 Tons
Fertiliser manufacture.	Ammonia	250 Tons
Aluminium and magnesium powder production.	All	†
Aluminium refining	Chlorine	25 Tons
Paper pulp manufacture.	Chlorine Sulphur Dioxide	25 Tons 50 Tons
Air liquification plants and steel works.	Liquid Oxygen	135 Tons
Flour and sugar silos.	Flour Refined white sugar	200 Tons 200 Tons
All	Liquefied Petroleum Gas	100 Tons.

† Economic size of plant would involve such quantities of materials that the risks would invariably be present.

\* Petrochemical manufacture is defined as the manufacture of chemicals from an oil refinery product or from natural gas.

## SECTION 10.

### THE SCALE FOR ANNEX II AND FOR ANNEX III.

#### 10.1. LINEAR AND LOGARITHMIC SCALES.

There are two possible scales to be considered for placing threshold inventories. The first is a linear scale. This suffers from the disadvantage that the higher the values become, the closer they are at each succeeding point. Whereas 2 succeeds 1 and is twice as large, 101 succeeds 100 and is only 1% larger. But probably the worst fault of a linear scale is that it would convey a spurious sense of the accuracy with which the values are determined. There are so many assumptions and so little reliable data that any figure calculated is not precise even though it will always, because of the nature of mathematical operations, appear to have a precise value.

The alternative, and it is that which has been adopted almost universally in the Directive, is to use a logarithmic scale. For reasons of practicality the scale, though it could in theory be to any base, as, for example 2, must be a decimal scale. It could therefore be the series 1, 10, 100 . . . However this is a very coarse scale and, for reasons of practicality, it needs to be subdivided. The multiplier, instead of being 10, could therefore be  $10^{0.5}$  or  $10^{0.333}$ . The former would yield a multiplier of 3.16 and one intermediate point, and the latter of 2.15 with two intermediate points. These are obviously inconvenient multipliers but they approximate to integer scales of 1, 3, 10, 30, 100 . . . and 1, 2, 5, 10, 20, 50, 100 . . . It is the latter to which, with two exceptions only, Annex III adheres. However one third of the inventories listed in Annex II do not adhere to this scale. It is to be noted also that below 1 tonne, with few exceptions, the very coarse scale of 1, 10, 100 is used. It seems difficult to see the justification for the exceptions referred to.

In view of the uncertainties there seems no justification for using any multiplier smaller than 2.15 as for example 1.8 which corresponds to  $10^{0.25}$ . This would, in any case, be difficult to reconcile with any integer scale.

#### 10.2. APPROXIMATING CALCULATED RESULTS TO THE SCALES.

The best practice here would seem to be to place the results for any actual calculation within the appropriate logarithmic interval and to assign to this interval the nearest integer. This would take this form:-

TABLE III. DIFFERING VALUES FOR THRESHOLD LEVELS.

	Circular 1/72.	(1) ACMH	Annex III	(2) Annex II.
Acrylonitrile	50	200	200	5000
Ammonia	250	1000	500	600
Bromine	100	400	500	-
Chlorine	25	100	50	200
Ethylene Oxide	20	50	50	-
Hydrogen cyanide	50	200	20	-
Liquefied Petroleum Gas.	100	300	200	300
Liquid Oxygen	135	10000	-	2000
Phosgene	5	20	20	-
Sulphur Dioxide	50	200	1000	500

All in tonnes, except for Circular 1/72 which is in Imperial tons.  
(1 ton = 1.016 tonnes)

- (1) Higher level equal to 10 times "notification" level, corresponding to major-accident hazards inventory.
- (2) For application of Article 5.

Calculated figure.	Assigned threshold level.
0.682 to 1.467	1
1.468 to 3.162	2
3.163 to 6.810	5
6.820 to 14.670	10 and so on.

## SECTION 11.

### METHODS OF QUANTIFYING HAZARDS.

#### 11.1. THE MORTALITY INDEX APPROACH.

This approach has been described in [32] Marshall, V.C. and it was to a degree adopted in [33] ACMH as a basis for determining inventories for the proposed UK Regulations on Major Hazards.

Essentially it seeks, by an analysis of the historical record, to determine an index which relates the number of fatalities arising from an incident to the quantity of the agent which gives rise to the incident. It may otherwise be described as "specific mortality". Essentially, whatever assumption is made as to the number of fatalities which constitute the realisation of a major accident hazard, for that agent its mortality index is the assumed number divided by the inventory (expressed in the common unit of mass). It has the form thus of fatalities per unit mass. In principle other levels of injury may be similarly expressed but relating it to injuries other than fatalities requires a definition of the level of injury.

There are difficulties in determining mortality indices. One is that they may be "scale dependent" i.e. the index may itself be a function of the mass. This seems to be true of explosives but may not be true of toxic releases. Another lies in the statistical difficulties associated with the handling of small numbers of data. Data on toxic releases which have caused fatalities are very few, perhaps 10 to 20 each for chlorine and ammonia but for other toxic substances, perhaps equally dangerous, there may be no reports at all. But in this latter case, it may be possible to proceed by analogy.

#### 11.2. THE F/N APPROACH.

This approach, which has been devised by the author for this study, consists in plotting  $F \propto N$  for incidents. In one plot  $N$  is a number denoting the mass of the agent, and in the second plot  $N$  is the number of fatalities which have been recorded in incidents involving the agent.

For agents where the effect is invariant with respect to scale, a mortality index of less than one where the mass is in tonnes will be indicated by the curve

for the plot,  $N$  = No. of fatalities, lying to the left of the plot  $N$  = No. of tonnes of agent. Where there is scale dependence the curves may intersect.

Though it may appear that the  $F/N$  plot approach is one which is based upon risk as well as hazard this is not so. The absolute value of risk is irrelevant as what is being compared is a ratio of risks. For an assumed isotraumatic value of  $\geq 10$  what is being determined is the quantity of agent for which the frequency of an incident involving  $\geq X$  tonnes is equal to the frequency of  $\geq 10$  fatalities occurring.

The use of such  $F/N$  plots will be demonstrated for explosives, flammable clouds and toxic releases in the appropriate sections.

### 11.3. THE AREA OF HARM APPROACH.

In essence this seeks, by theoretical modelling moderated by practical experience, to estimate the area within which human injury will occur as the result of the realisation of a hazard.

For the results to be meaningful the level of harm must be specified. This is because great inconsistency will arise if, for example, fatality were to be used as the criterion for explosives, but "severe burns or more serious injury" were to be used for vapour clouds.

Assuming this criterion to be agreed then it becomes necessary to relate an effect which can be expressed in terms of physical quantities such as overpressure, intensity of thermal radiation or concentration of a toxic agent into some biological effect such as fatality. And this has to be done against a background of human response which is very difficult to predict.

In the case of explosions though the level of overpressure which will kill in the open is reasonably well established, few people actually die of this as is discussed in the next section.

Matters are even worse with toxic agents where animal experiments are extremely unreliable for predicting human injury.

Because of the difficulty in relating the physical to the biological, recourse has to be made to the historical experience. The effect of this is to produce a situation in which the area of harm is deduced from the mortality index. Though knowledge of this area is an important factor in siting policy, there seems little merit in determining this area from the historically determined mortality index and then determining the inventory from this area when the inventory could be directly determined from the mortality index.



## SECTION 12.

### QUANTIFICATION OF EXPLOSIVES.

#### 12.1. SHOULD CONVENTIONAL EXPLOSIVES BE INCLUDED IN ANNEX III?

There seems to be an anomaly in that Annex III includes a number of conventional explosives of which Trinitrotoluene (TNT) may be quoted as an example. Yet Article 2 of the Directive states:- "This Directive does not apply to the following '.....(3) the manufacture and separate storage of explosives, gunpowder and munitions' ". It may be questioned, therefore, whether there is a need to include any conventional explosives in Annex III. This being said there remains the problem of regulating those substances which, though not used either as munitions of war or as commercial explosives, nevertheless have the potential, under certain circumstances, of creating significant blast effects. An example of a class of substances in this category is that of organic peroxides.

#### 12.2. THE EFFECTS OF THE EXPLOSION OF DENSE EXPLOSIVES.

Data for regulating what may be termed "adventitious" explosives, i.e. substances whose explosive properties are an undesired by product, are very few. A sounder approach is to study the behaviour of conventional explosives and then to apply a conversion factor which relates the blast energy of an adventitious explosive to that of a standard conventional explosive which, for convenience, may be that of TNT.

The study in this section is applicable only to "dense" explosives, i.e. to those which are solids or liquids at the time that they release blast energy, and not to the blast effects produced by the ignition of vapour clouds.

Extensive data exists on the effects of conventional explosives, but little of it up to now has been expressed in a form which is applicable to predicting the effects of industrial explosions.

As has been discussed briefly above, the laws of physics and chemistry, on their own, are not capable of predicting the level of harm which may be sustained by a human subject at a given radius from a given mass of an explosive. What they can predict, inter alia, and based upon experiment, is the level of overpressure which will be created at this point. Even so the variance in this overpressure is appreciable, as is demonstrated by the relationship between overpressure and radius as determined by different investigators, or, for that matter, looking at the scatter of the points obtained by a single investigator.

A very useful concept in studying the effects of explosives is Hopkinson's Scaling Law. This states, inter alia, that differing masses of explosives with the same specific blast energy will produce the same level of overpressure at

distances which are proportional to the cube root of their mass. Thus if 10 tonnes of an explosive produces a given level of overpressure at a radius X, then 1000 tonnes of this, or an equivalent explosive, will produce the same level at a radius of  $1000^{0.333}X$  or 10X. The quotient produced by dividing the radius associated with a given effect by the cube root of the mass of explosive creating it is known as the "scaled distance". This is a convenient index for relating levels of harm to the distance from an explosion.

Military research using animals, or observation based upon examples of human victims whose position was known at the time of the explosion, and where the scaled distance is known, have been able to determine the level of overpressure in the open at which, say, 50% of those exposed would suffer fatal or any other levels of injury. But the figures so obtained are not very helpful, as practice shows that explosives can produce death or other injuries at much greater radii than the observations referred to above would predict.

The reason for this is that in the open, and assuming "bare" charges, i.e. charges which are not encased in such a way as to give rise to lethal missiles, the cause of death should it occur will be by crushing of the thorax or rib cage. However, when an explosion occurs in a built environment, the explosive may be encased and give rise to deaths through missiles generated from this casing. (This is a feature which is deliberately exploited in military anti-personnel bombs). Additionally, whether the explosive is bare or not, secondary missiles may be generated by the disintegration by blast of objects in the environment. It requires very little energy to kill by missile impact against vital organs. Equally those exposed to blast may be hurled against buildings or other objects.

Post mortem examination of the victims of explosions may show that they died from a variety of causes as well as those discussed above, such as by crushing due to the collapse of structures or by asphyxiation from the same cause, or fire engendered by the explosion.

It is consideration of these factors which leads the author to conclude that models which fail to take account of these complexities are invalid as a basis for the calculation of threshold inventories.

In general the death toll, for a given population density and for a given mass of explosive, is likely to be higher in a built environment than in the open; [34] Marshall, V.C. suggests that it may be higher by a factor of 2 to 4. One major cause of this is that buildings and structures possess potential energy as work done against gravity in erecting them and this potential energy is capable of being released by explosions. Such a release of potential energy can give rise to effects ranging from total collapse of a building to minor events such as the dislodgement of roofing material. This latter however may nevertheless

prove lethal.

### 12.3. USING THE MORTALITY INDEX APPROACH.

#### 12.3.1. Scale dependency for explosives.

An approach discussed above which is advocated in [35] Marshall, V.C. and which was taken account of in [36] ACMH, is to study past events to see whether a central tendency may be discerned from data on the quantity of material involved and the fatalities produced in a given incident. The mean quotient of fatalities and quantity is the "mortality index". For explosives it appears from theoretical analysis, using Hopkinson's Scaling Law, that this index must be "scale dependent". This arises because, if it be assumed that, for example, a given probability of fatality exists at a given scaled distance, then the number of persons at this or lesser radius will be a function of the enclosed area, i.e. the distance squared.

Combining this with Hopkinson's Law gives:-

$$\text{Fatalities} = \text{constant} \times M^{0.666}$$

Where M = mass of explosive.

The mortality index, conversely, will be given by:-

$$M_1 = \text{constant} \times M^{-0.333}$$

Where  $M_1$  = mortality index.

#### 12.3.2. Analysis of the historical data.

Fig. 3 is a plot of mortality indices versus mass of explosive based on analysis of data provided in [37] Biasutti, G.S., (210 data points) and by combining data from [38] Assheton, R., [39] Robinson, C.S., and [40] Healy, F. to give a further 162 data points. In each case, data were grouped within classes of mass lying within a multiple of  $10^{0.5}$  to provide the data points plotted. Though examination of the two sets of raw data appeared to show that there was no overlap, the points from the two sources intermingle. It is not possible to claim any high level of statistical accuracy in spite of the relatively large sizes of the samples totalling 372 data points in all. Small explosions are liable to be under-reported, especially if they do not produce fatalities, and large explosions may in some cases be a succession of small ones which fail to produce the peak overpressure which would be associated with a single large explosion. Possibly also some large explosions may have been preceded by a small explosion which caused people to flee. These factors, either singly or in combination, would tend to make the slope of the line which correlates them more steep than theory would suggest. Fig. 4 shows data produced by combining the two sets and showing a best fit line with a slope of -0.56 as compared with a theoretical slope of -0.333.

The shelling and bombardment by rockets of unprotected civilian populations

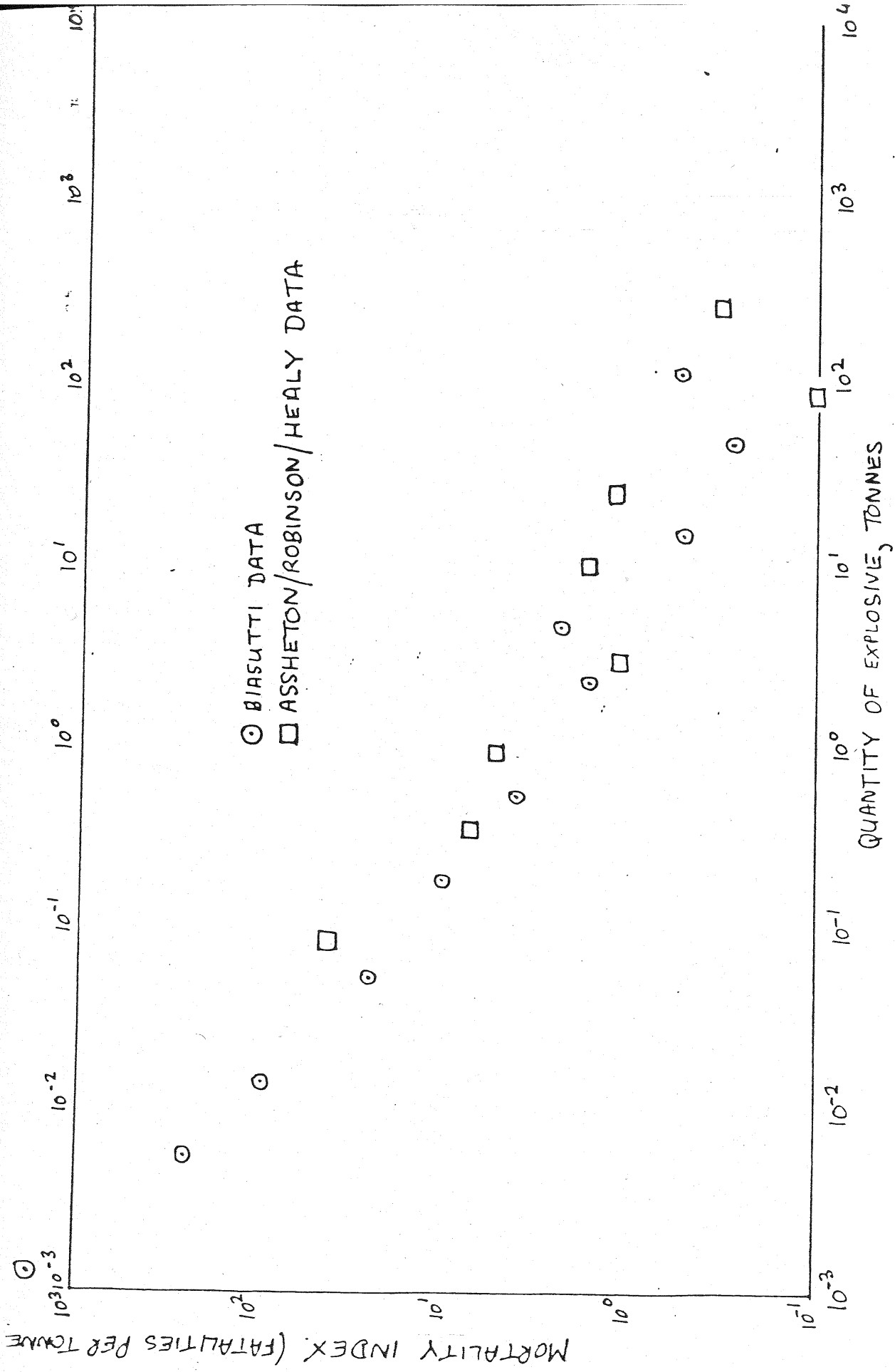


FIG 3 MORTALITY INDICES, TWO SETS OF DATA POINTS.

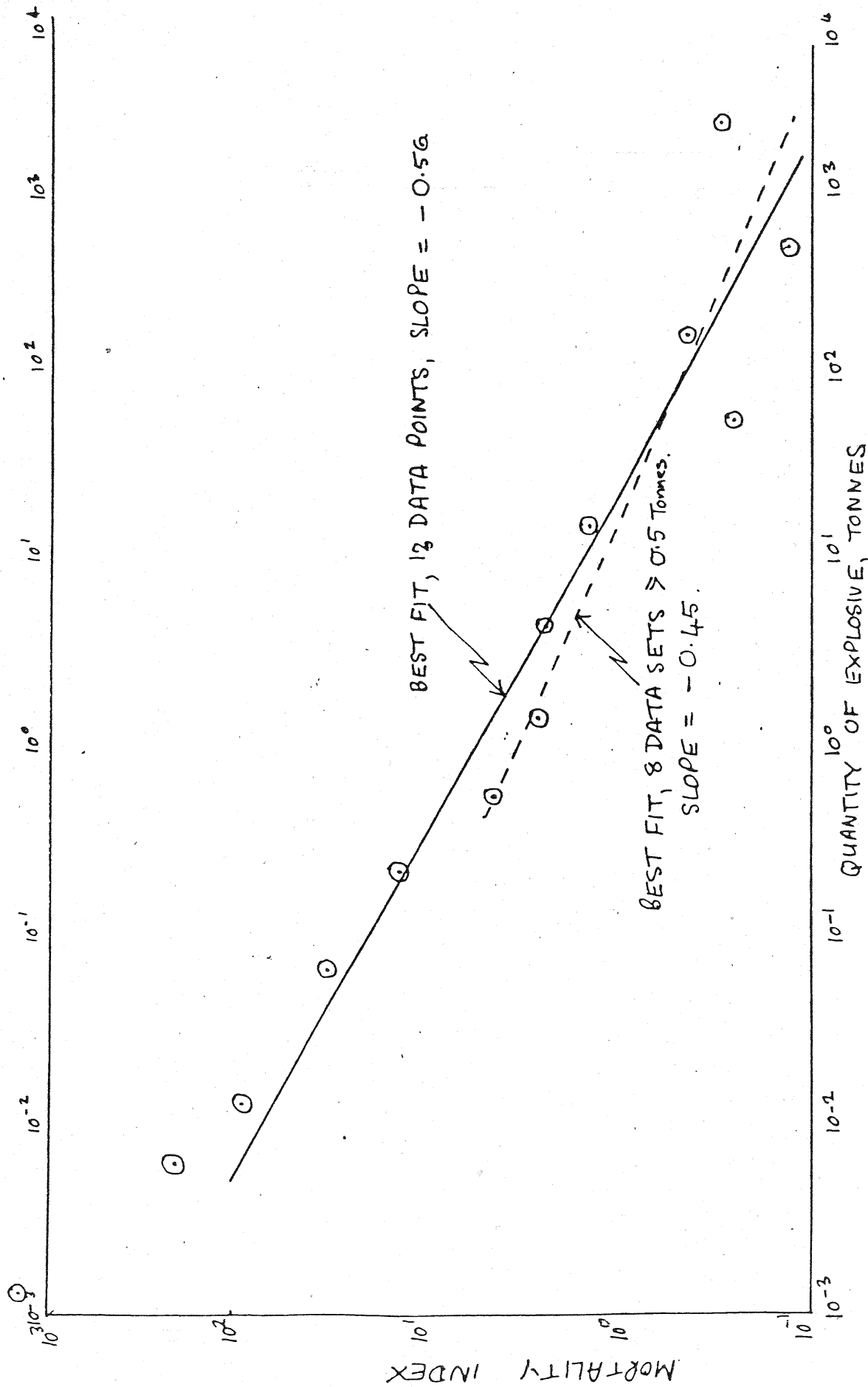


FIG 4 MORTALITY INDICES, DATA POINTS COMBINED.

in the two World Wars has been analysed in [41] Marshall, V.C. These data when normalised for a population density of 4000 per square kilometer and making an allowance for higher mortality from ground level explosions (rockets bury themselves before exploding) and which is the more likely circumstance in industrial practice, yield a mortality index of  $4 \times M^{-0.333}$  where M is the mass of explosive. Alternatively, and making allowance for population density:-

$$M_1 = \text{population density in thousands per sq kilometre} \times M^{-0.333}$$

12.3.3. Combining mortality index and Isotraumatic level.

Calculation of threshold values by combining the mortality index and the iso-traumatic level requires an assumption as to population density. The historical experience shows that the great majority of fatalities in a chemical works or process plant arising from explosions may be assumed to occur on site and that, therefore, the determining population density is the on-site population density.

This clearly varies with time of day and day of week and is a subject on which there is little published data. Figures obtained by the author from private sources for two major sites, one in the UK and the other in the FDR, suggest a 6 to 1 ratio between office hours and non-office hours population density, but taking office hours as one quarter of the working week and averaging the figures for the two sites, yields a mean figure of 850 persons per square kilometer. Thus in principle a range of fatalities of 6 to 1 seems possible. This may, however, be pessimistic in present day circumstances as there is now a considerable degree of segregation between many of the day-time population and the areas of greatest vulnerability.

Based on an assumption of an average of 850 persons per square kilometer on a typical chemical works and an iso-traumatic level of 10, what would be the threshold level for a typical explosive, say, TNT ?

$$\text{If } M_1 = 0.85 M^{-0.333} \text{ then } F (\text{No. of fatalities}) = 0.85 M^{0.666}$$

$$\text{If } F = 10 \text{ then } M = (10/0.85)^{1.5} = 40.35 \text{ tonnes.}$$

This compares with the figure of 50 tonnes given in Annex III for TNT (No.145). In line with the discussion in section 10 above, 40.35 tonnes would be approximated to 50 tonnes on the scale.

There is thus a good agreement on this key substance using the mortality index approach, between the threshold limit proposed in the Directive and its calculated potential to produce 10 fatalities from its most probable realisation. However, this should not lead to the considerable approximations involved in the calculation being ignored.

#### 12.4. USING THE EQUAL PROBABILITY APPROACH.

This approach, using F/N curves, has been applied to the combined data as is shown in Fig. 5. This figure is based upon a nominal time span of 100 years (the exact time span does not matter so long as the data for N as the number of fatalities or N as the quantity of explosive, are derived from the same set of incidents). The figure shows that the probability of 10 or more fatalities occurring is equal to the probability of 50 or more tonnes exploding. Thus the inventory for an isotraumatic value of 10, based on this approach, is 50 tonnes which corresponds to the value for TNT in Annex III.

However, too much should not be read into this apparent identity because of the inevitable approximation involved in such computations.

#### 12.5. CALCULATIONS FOR OTHER EXPLOSIVES.

##### 12.5.1. Application to other conventional explosives.

TNT has a blast energy which lies in the middle of those explosives in common use. Table IV below calculates the inventory level for a number of conventional explosives based upon their blast energy compared with that of TNT.

Annex III Number.	Substance	Blast energy ratio.	Inventory (Based on TNT=40 tonnes)	Rounded Off.	Annex III level.
132	Nitroglycerine	1.69	23.5	20	10
141	Picric Acid	1.06	40	50	50
Not listed.	Nitromethane	1.34	30	20	-
134	Cyclotrimethylene trinitramine(RDX)	1.31	30.5	20	50
166	Lead Azide	0.40	100	100	50
168	Mercury Fulminate	0.50	80	100	10

The table discloses a number of anomalies in Annex III.

There might possibly be a case for special treatment for mercury fulminate, as the detonation of this substance would no doubt lead to environmental damage from mercury compounds. Perhaps a combination of environmental damage with extreme sensitivity might provide a justification for moving it, and lead azide, down a scale point to an inventory of 50 tonnes.

##### 12.5.2. Application to adventitious explosives.

In principle it ought to be possible to apply the principles discussed above to other substances not manufactured as explosives but which possess explosive properties. For example Annex III lists a number of peroxides including a number

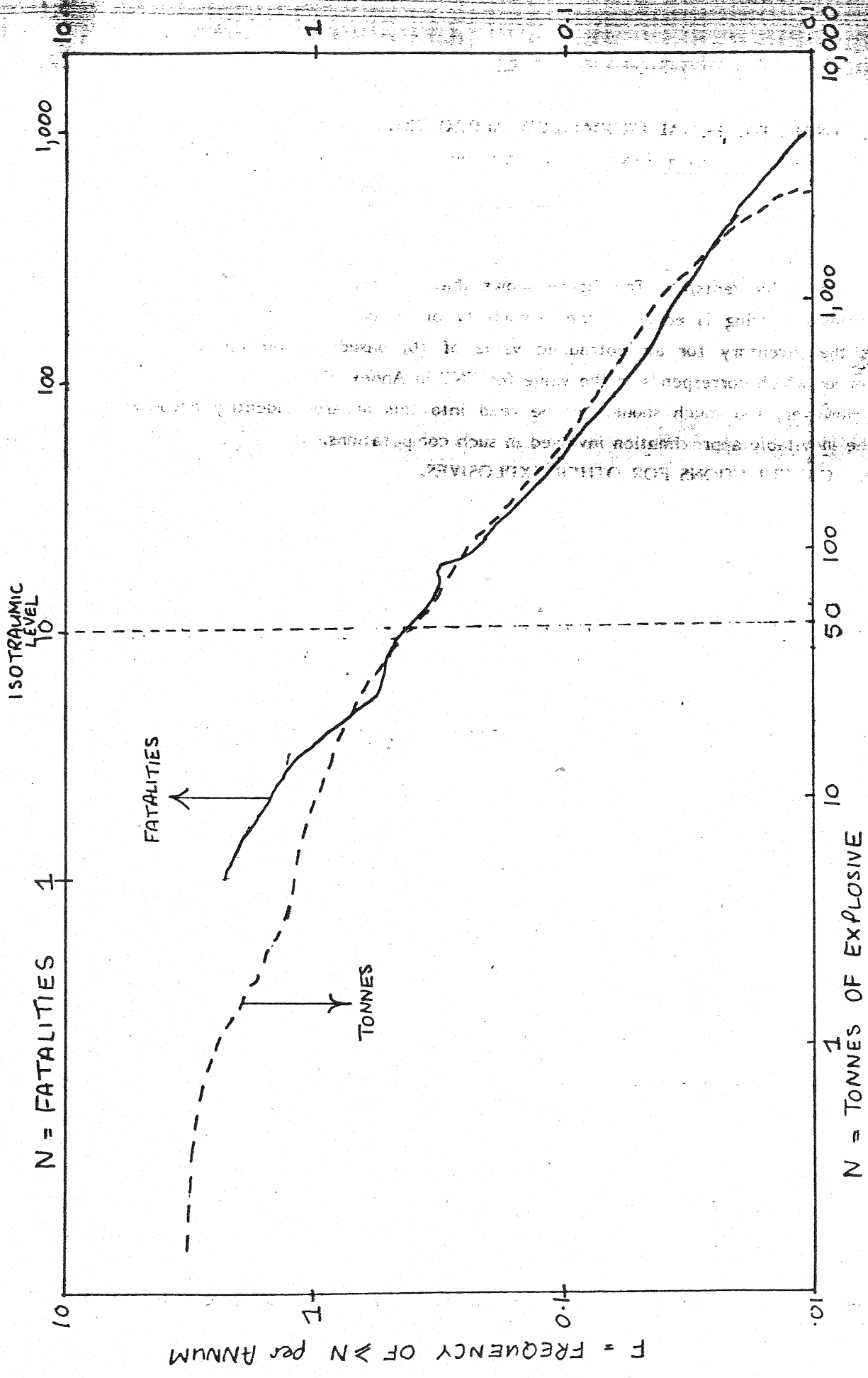


FIG 5 F/N CURVES FOR EXPLOSIVES.



of peroxides of the esters of tertiary butyl alcohol. It seems difficult to believe that the blast energy of substances of this character can be more than a small fraction of the blast energy of conventional explosives. The esters of butyl alcohol are quite stable substances and it is only the presence of a peroxide bond which renders the molecule unstable. The molecule, compared with TNT, is markedly oxygen deficient and TNT itself is oxygen deficient. The author lacks data on the blast energy of such compounds except for data on the blast energy of cyclohexanone peroxides which are rated at ca 0.20 of the blast energy of TNT. They would qualify them for a threshold inventory of 200 tonnes. Yet organic peroxides listed in Annex III are given an inventory of 50 tonnes which is the same as that of TNT.

In the author's view, the best way to deal with this problem would be to create a class of explosive substances and to give ranges of specific blast energy to which are assigned appropriate threshold inventories. How the question of promulgating threshold values for the numerous substances which fall into this category may best be accomplished will be discussed later as part of the general question of promulgating threshold values.

#### 12.6. THE INJURY TO FATALITY RATIO.

The question of how many people are non-fatally injured in an incident is not easy to resolve. One reason is that it is harder to define injury than it is to define death. The compilations available to the author do not distinguish between slight injuries requiring little more than first aid and injuries which may lead to permanent disablement. [42] Encyclopaedia Britannica gives figures for death, serious injury and slight injury from flying bomb and rocket attacks on London 1944/45. These yield the following ratios:-

Serious injury : death 2.75 : 1 All injuries to death 8.25 : 1

These data are likely to be as reliable as any as they relate to large numbers (tens of thousands) and were compiled using standardised criteria.

The figures may be rounded off for convenience to 3:1 and 8:1.

#### 12.7. SUMMARY.

The threshold inventory assigned in the Directive to TNT, which is a standard explosive, appears to accord with the historical experience and an isotraumatic level of 10 fatalities. This appears true both from the mortality index approach and from the equal probability approach.

However, the thresholds assigned in Annex III to some other conventional explosives are not consistent with the ratio of their specific blast energy to that of TNT.

This is also true of adventitious explosives whose thresholds, when judged by this criterion, seem to be unduly stringent.

## SECTION 13

### QUANTIFICATION OF VAPOUR CLOUD HAZARDS.

#### 13.1. THE COMPLEXITIES OF THE PROBLEM.

The analysis of vapour cloud hazards is more difficult than the analysis of the explosion of dense explosives. Dense explosives may be assumed to be quiescent until detonation, which involves the whole mass of the explosive, and which then gives rise instantaneously to a blast wave. It is this blast wave and its secondary effects which causes human injury. With vapour clouds there is a time lapse which is necessary to allow the cloud to form and this time lapse will generally be measured in minutes. This gives time for people to escape.

Dense explosives occupy a volume which is very small in relation to the volume of the space in which they may produce fatality. The author has calculated, based upon the effects of rockets and shells upon unsheltered civilian populations, that the nominal lethal radius, which is a scaled distance, within which the chance of escaping death is equal to the chance of being killed outside it, is  $18 \text{ metres/tonnes}^{1/3}$ , [43] Marshall, V.C. The scaled radius of the explosive itself, i.e. the radius of a spherical mass of 1 tonne of explosive, would be ca 0.5 metre. At Flixborough the corresponding radius was 125 metres and the vapour cloud contained ca 40 tonnes of vapour. This corresponds to a scaled distance of ca 48 metres based upon tonnes of vapour. The mean radius of the exploding cloud may have been about 100 metres corresponding to a scaled distance of about 40 metres, [44] ACMH. In other words the radius of the exploding cloud and its lethal radius were not greatly different at Flixborough and the author believes this to be generally true of other vapour incidents.

Whereas dense explosives are chemically self sufficient i.e. they do not require atmospheric oxygen, this is not the case with flammable vapours. Flammable vapours are only flammable if their composition lies within certain limits. Once diluted below the lower limit of flammability they cease to constitute a hazard. A cloud for which there is a long delay to ignition may have a considerable fraction of its vapour diluted below the flammable limit and thus not take part in the subsequent conflagration and/or explosion. In the extreme case dilution may be total and combustion does not occur at all.

The most dangerous situation is that which occurs when there is loss of containment of Liquefied Flammable Gases which are being stored at or near atmospheric temperature. Here "flashing" occurs and a substantial fraction

of the liquid turns more or less instantaneously into vapour. The fraction so released depends upon the substance and its temperature of storage. It may be 0.5 or more and, in addition, the violence of the process may give rise to frothing and to spray entrainment which, in extreme cases, may produce total vapourisation of the spillage. The atmospheric temperature has a considerable influence on the size of the fraction but it will be assumed in later discussion that the storage temperature is 20°C. Petrol on the other hand does not flash on being spilled though the gas phase above the surface is highly flammable. Nevertheless, in the opinion of the author, LPG, for example, is more hazardous than petrol by at least an order, and possibly two orders of magnitude.

Because of these difficulties flammable substances cannot, as with explosives, be classified solely by their energy release. Flammables may have similar values for their heat of combustion and yet present widely different hazards. Propane and fuel oil are examples of substances which have approximately the same heat of combustion but which differ widely in the level of hazard which they present.

With flammable gases and liquid the "source term" i.e. the circumstances of escape, is a very important factor. Where there is a failure of containment the size of the aperture, especially the ratio between the area of the aperture and the volume of hazardous material contained, is a crucial factor. Extreme cases where the area is large arise with catastrophic failure of storage tanks, the opposite extreme lies with fractures of pipelines. Where fracture occurs above the liquid level this may still constitute a very hazardous situation for LPG but a much less serious one for LNG.

An allied problem is that of estimating the fraction of the inventory of hazardous material in a ruptured container which participates in any eventual flash fire or explosion. This fraction does not appear to have a special name; the present author has coined the term "active fraction" and this is the term which will be used below. The active fraction will approach the value of 1.0 for the catastrophic failure of containment of a highly volatile substance such as propylene on a hot day and will approach zero for a loss of containment above the liquid level of a flammable substance of low volatility on a cold day. The author regards the basic problem with fire as that which arises immediately from the ignition of a vapour cloud i.e. as a flash fire or fire ball, and does not consider that a prolonged pool fire which can be brought under control by well tried methods of fire fighting, falls within the category of a major accident.

### 13.2. ANALYSING THE HISTORICAL RECORD.

The factors discussed above make the analysis of the historical record difficult. Most authors of compilations have been content to present lists of incidents

with the attendant circumstances but without seeking to analyse them. Such incidents have a great deal of commonality but there are anomalies in all of them. [45] Guban listed 100 incidents which, with one exception, occurred between 1932 and 1977. [46] Davenport, J. lists 152 incidents which occurred, with one exception, between 1939 and 1983. [47] Wiekema, B.J. analyses 165 events which, with one exception, occurred between 1932 and 1980. This analysis is a very valuable addition to knowledge and will be drawn upon below. However, unlike Guban and Davenport, Wiekema does not give all the details which are given by the others. Instead Wiekema distinguishes ten characteristic features such as the mass involved, the number of fatalities or whether it was an explosion or a fire and assigns, and provides the information by means of numbers in a grid formed from the incidents arranged in chronological order. Analysis shows that in 9% of the cases it was not known whether it was a fire or an explosion, in 39% of the cases the event was identified as a fire and in 52% of the cases the event was identified as an explosion. Wiekema provides no data on cases where a vapour cloud formed but did not ignite.

There are many interesting conclusions which may be drawn from the studies discussed above but the only ones which seem relevant to this study are those concerned with the relationship between the mass of agent and the number of fatalities caused.

### 13.3. USING THE MORTALITY INDEX APPROACH.

The author has examined Davenport's data where both fatalities and quantities of agent are quoted for some incidents. Using a technique similar to that used for dense explosives, namely by dividing up the data on quantity into classes each of which is greater than the other by  $10^{0.5}$  and then dividing the total fatalities in the class by the total mass of agent in the class, mortality indices are obtained for each class. The mortality indices so obtained are plotted in Fig. 6. The mortality index in the class 10 to 31 tonnes is especially high at 1.65 which arises from the very high death toll at Ludwigshafen in 1948. (The San Carlos incident of 1978 is not included in any of the compilations under discussion. Had this been included the mortality index would have been higher still). Whether or not Ludwigshafen is included, it is clear that the historical record suggests that the mortality for vapour cloud incidents is highly scale dependent. Caution has to be exercised in such an interpretation as it is probable that, as with dense explosives, small incidents are only reported if they lead to deaths. However the graph does not show meaningful results. Though the mortality index for the class 10 to 31 tonnes suggests that releases of this order are capable of yielding fatalities of 10 or more, a "best fit" line for the whole range suggests that there is no level of inventory which would

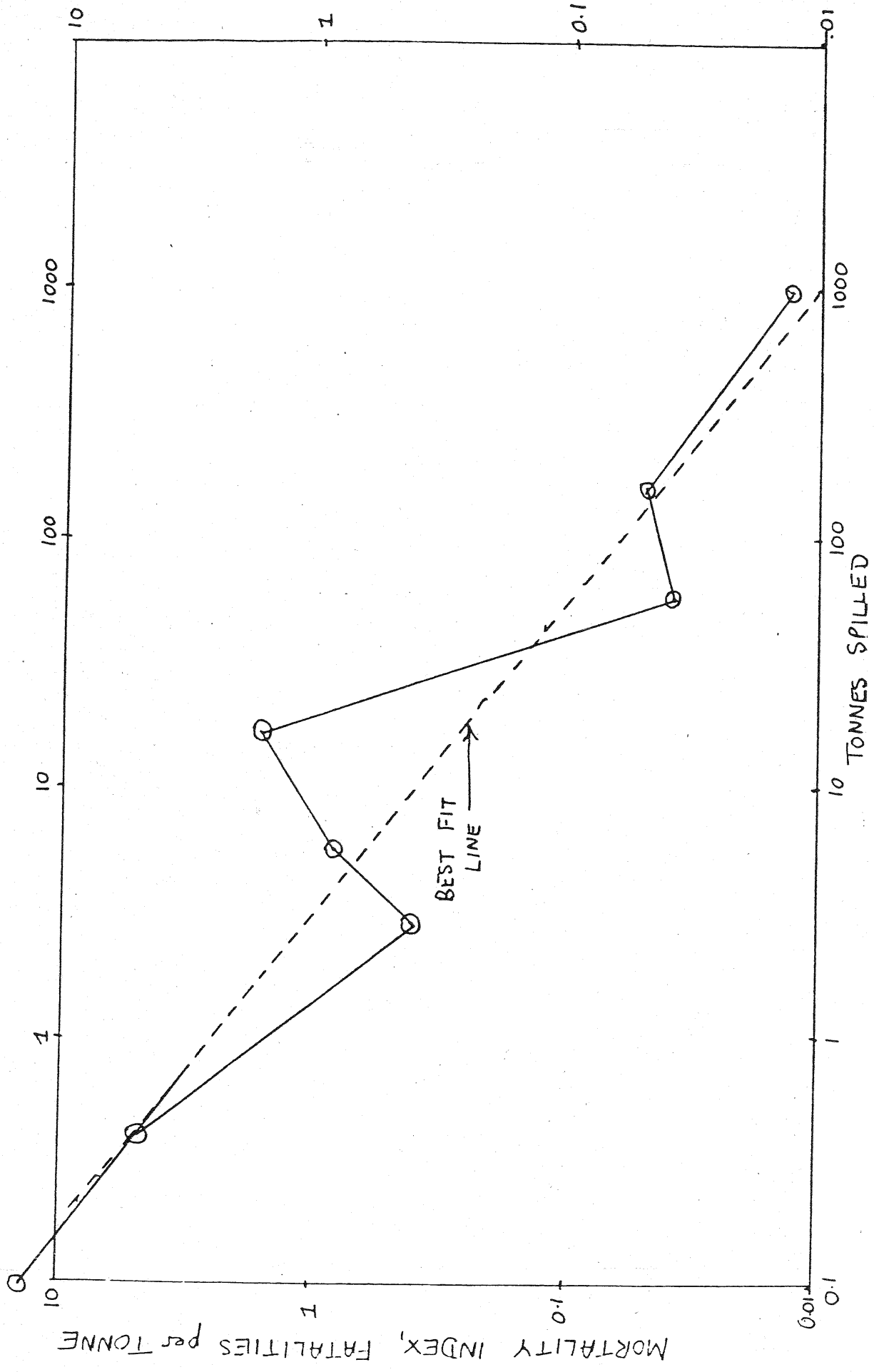


FIG 6 MORTALITY INDICES FOR FLAMMABLES BASED ON DAVENPORT.

yield 10 fatalities.

Examination of Wiekema's data yields other interesting results as Table V below demonstrates.

TABLE V. CORRELATION BETWEEN WIEKEMA'S FIGURES OF FATALITIES AND SIZE OF RELEASE FOR INCIDENTS INVOLVING FLAMMABLES.

Size of Release (Tonnes) \ Fatalities	Unknown	1-10	10-100	≥100
6 - 15	7	6	2	2
16 - 50	3	1	5	2
≥ 50	1	0	1	1
Totals	11	7	8	5

The table demonstrates that of the incidents in which 16 to 50 persons were killed and where the mass of material in the vapour cloud is known, 6 involved less than 100 tonnes in the vapour cloud and 2 involved more than 100 tonnes. Of the incidents involving more than 50 fatalities, 1 involved less than 100 tonnes and 1 involved more than 100 tonnes. Taking these together the most serious accidents involved less than 100 tonnes in 70% of the cases. Wiekema does not have a category of 10 to 15 fatalities but instead uses 6 to 15. For this category the figures are 8 involving less than 100 tonnes and

2 involving more.

A conclusion might be drawn from this that the isotraumatic level corresponds to a figure of less than 100 tonnes in the cloud. This is not the same as the original inventory which would in general be higher than the mass in the cloud. This will be further discussed later.

#### 13.4. USING THE EQUAL PROBABILITY APPROACH.

Davenport's data have been used in Fig.7 in the same way as the data on explosives have been used. The figure suggests that the probability of killing 10 or more persons is equal to the probability of generating a vapour cloud containing 60 or more tonnes. Wiekema's data, though more extensive than those of Davenport, do not disclose the same level of detail. They can however be plotted to show the probability of incidents involving  $\geq N$  where  $N = 1, 6, 16$  and  $50$  fatalities or the release of  $\geq N$  where  $N = 0.1, 1, 10, 100$  tonnes. These are plotted in Fig.8 and suggest that the equal probability figure for 10 or more fatalities is ca 50 tonnes. This agrees reasonably well with Davenport and with the discussion above.

#### 13.5. DETERMINING THE EQUIVALENT INVENTORY.

The question of what level of inventory corresponds to a given level of the mass in a cloud requires a knowledge of the active fraction. No information on this appears in any of the compilations. The only way to assess this lies in consideration of how, for example, liquefied gases behave. As has been discussed above there is a wide variation between the behaviour of the liquefied gases with the highest vapour pressures and, say, fuel oil. Perhaps a conservative view may be taken that, for the most active gases which would include propylene, propane and commercial LPG, this fraction is equal to 1.0. For butane it is clearly less but, for reasons of convenience and the impracticability of "fine tuning", it is recommended by the author that all liquefied gases stored at atmospheric temperature should be in the same category. In light of the evidence above, the author recommends this should be set at 50 tonnes. The category of liquefied gas would also cover all flammable substances which are gases at ordinary temperatures such as dimethyl ether and which are presently covered by Annex IV c i. The 50 tonne level of inventory should apply also to Annex IV c iii substances.

The figure of 50 tonnes would however be a somewhat conservative figure as there is also the factor of the probability of non-ignited escapes to be considered. No data is available on these, should there be a significant number this would shift the F/N curve for releases to the right and produce a higher value of  $\geq N$  for the size of release with a probability equal to that of inflicting  $\geq 10$  fatalities.

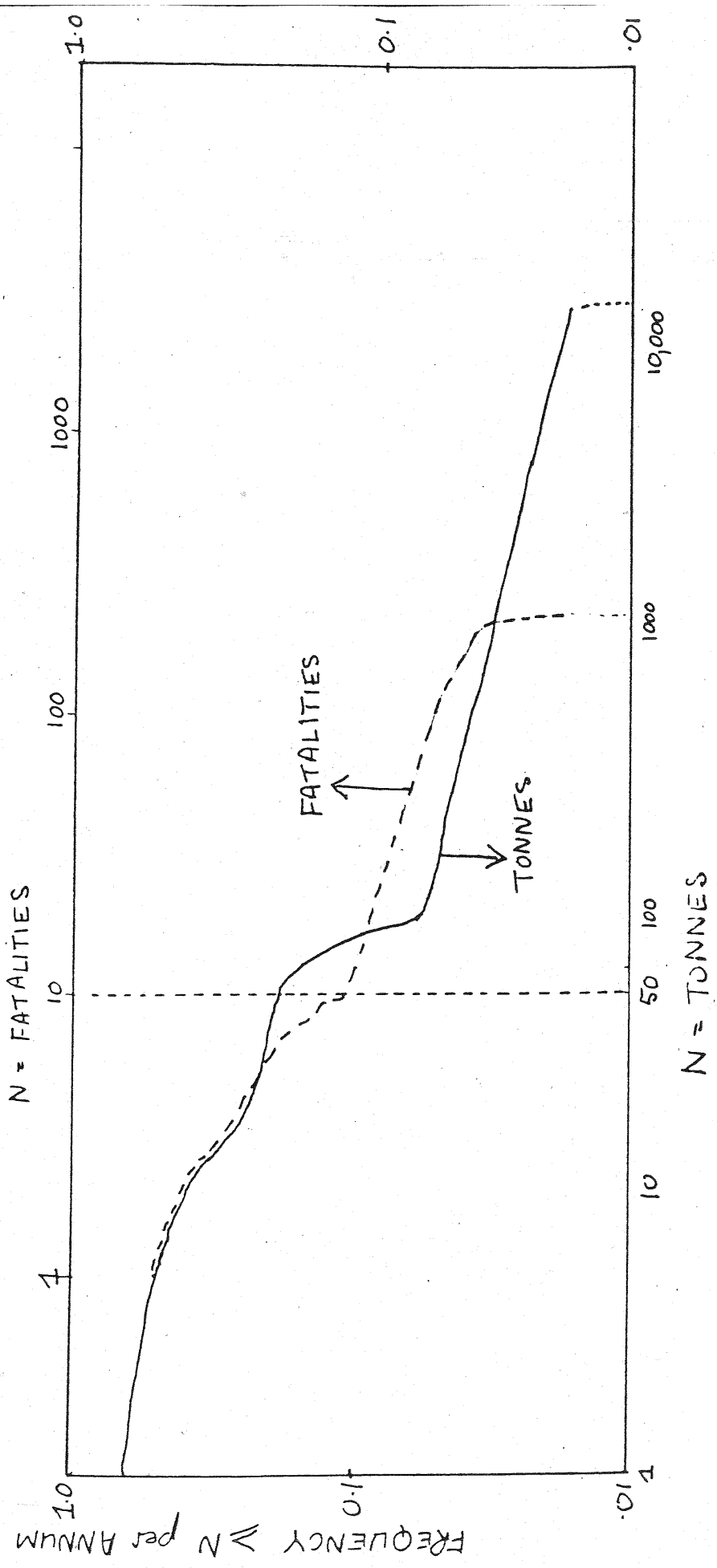


FIG 7 F/N CURVES FOR FLAMMABLES BASED ON DAVENPORT.



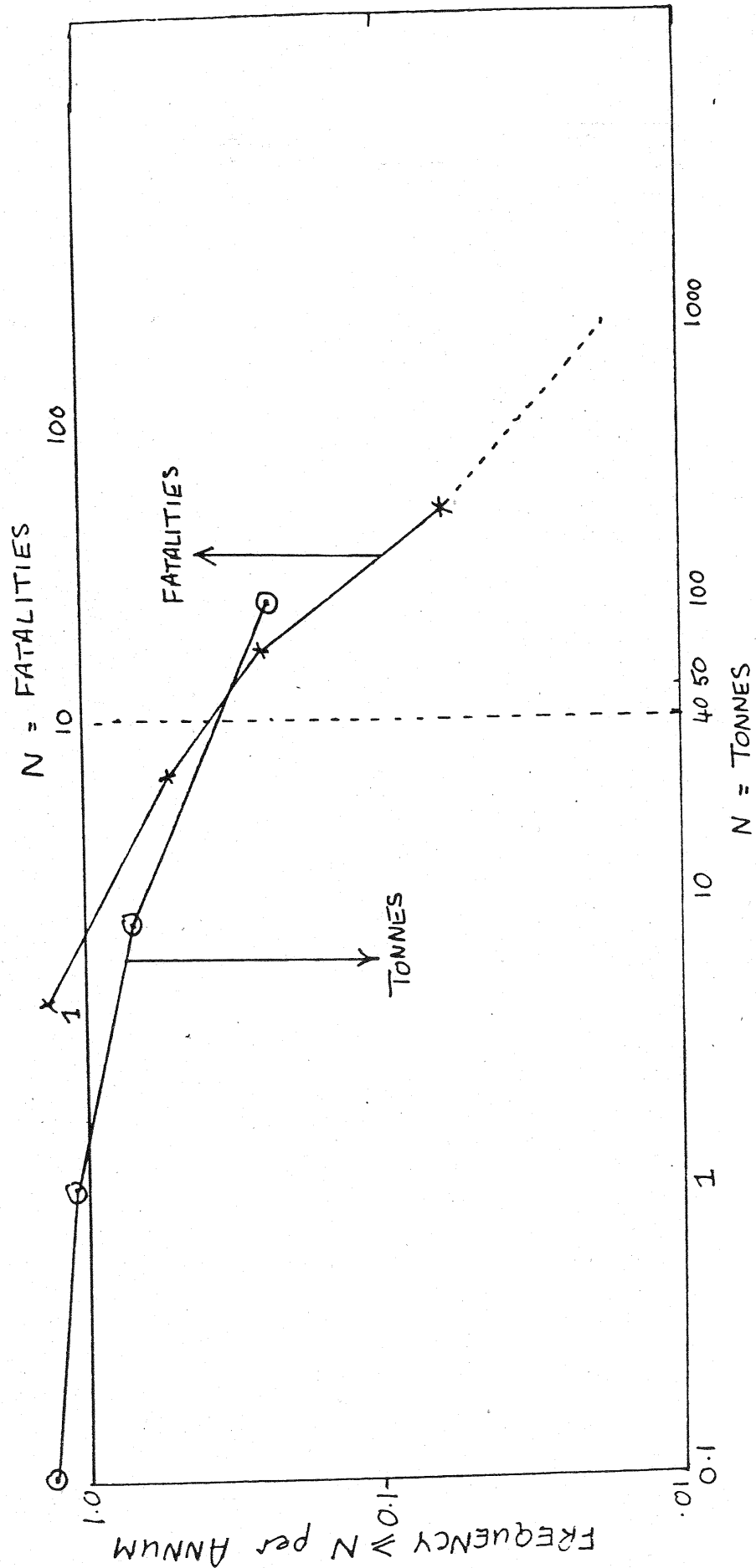


FIG. 8. F/N CURVES FOR FLAMMABLES BASED ON WIEKEMA.

The inventory for the refrigerated gases LNG, ethane and ethylene and for LPG, if handled in a refrigerated condition, the author recommends should be 200 tonnes and they should be given a separate category in Annex IV.

There may also be a case for assigning a 200<sup>tonne</sup> inventory to such volatile flammables as the pentanes and diethyl ether. This would also require a separate category in Annex IV.

It may perhaps be pointed out, as a postscript to the discussion, that the Flixborough disaster, which initiated United Kingdom activity in the field and which killed 28 people, involved an inventory of ca 120 tonnes of "flammable liquid" as defined in Annex IV c iii, that is well below the inventory in Annex III.

## SECTION 14.

### CRITERIA FOR THE INCLUSION OF TOXIC SUBSTANCES.

#### 14.1. ACUTE AND CHRONIC TOXIC HAZARDS.

Certain of the substances listed in Annex III (Nos. 1-5) have low levels of acute toxicity, though the threshold levels assigned to them are those associated with highly toxic substances. This is evidently because they are considered to be dangerous carcinogens.

The author understands that a decision has been made to ban them from industrial use throughout the Community as is the case in the United Kingdom. He does not disagree with this, but raises the question as to whether a Directive on Major-Accident Hazards is the appropriate legislative instrument for dealing with substances whose harmful properties are manifested almost entirely through chronic (long term) exposure in the work place. No one would question the need for strict controls over substances which manifest themselves as carcinogens, mutagens or teratogens, but it does not follow that a Directive on Major-Accident Hazards is the appropriate means of control.

The author accordingly recommends that, as a general principle, substances whose harmfulness is manifested solely through chronic effects be excluded from this Directive. An exception would be any substance, if such exist, which is likely to be emitted in an acute incident and which, by virtue of its persistence and resistance to decontamination and having the potential to produce the ill effects referred to above or to cause any other serious disease, could cause chronic environmental pollution. It might be more appropriate, were the Community to consider issuing a Directive on the control of carcinogenic substances, that it include an Article concerned with the prevention of the contamination

of the environment by carcinogenic substance even at a low level of risk.

In short, in the author's view, the Directive should not be used as a "catch all" for all the toxic problems of industry. Were it to assume this role then attention would focus, and wrongly in his view, on acute releases of carcinogenic substances at the expense of focussing on the real problem of carcinogens which is the chronic exposure to them of persons at work.

#### **14.2. THE CRITERIA OF TOXICITY.**

The most obvious criterion would seem to be "toxicity". However, this is not so straight-forward as it would seem. There are many difficulties in obtaining and expressing toxic data and these will be discussed.

Perhaps the most obvious problem to be resolved is the route of entry into the body. In practice this can take three forms. These are ingestion, skin contact including the eyes, and inhalation. There are other routes, such as injection, but they are not applicable to the problem under discussion.

It seems important, as has been pointed out by [48] Bridges, J.W., that the toxicity data used should be relevant to the anticipated mode of entry. The route of ingestion seems to have little validity for human victims of a toxic emission, though it may well apply to animals, especially grazing animals. As the basic criterion of this part of the Report is human fatality, it follows that ingestion may be dismissed as a significant route to human fatality in the event of the realisation of a toxic major-accident hazard. Unfortunately many of the data on toxicity are derived from ingestion.

The route via the skin is important in some cases, and data sometimes exists in this area. Entry via the skin seldom produces immediate effect and this means that few die before help can reach them. However, this help may come too late.

But for many important toxic chemicals, it is the inhalation route which is of prime importance. It is also important to use short exposure times as these are what is to be found in practice. Perhaps 30 minutes exposure would be appropriate.

#### **14.3. THEORETICAL MODELS AND ANIMAL EXPERIMENTS.**

There have been many attempts to model toxic clouds so as to be able to predict likely fatalities. Up to the present, none of these appear to have been successful. Though this is not the place for a lengthy dissertation on the subject, the author will attempt to summarise the factors involved.

It is necessary first to examine the question as to whether the models really have been unsuccessful. The only criterion for judging this is to take actual incidents and to compare the fatalities produced by actual incidents with what the models would have predicted. There have been enormous discrepancies

of the order of several magnitudes, and always in a pessimistic direction. Reference has been made in Section 8 to the validity of the models of gas dispersion which have only recently begun to inspire confidence. [49] Havens, J.A., writing in 1978, reported wide discrepancies in the prediction by various investigators of the behaviour of LNG vapour clouds.

One technique has been to model contours in the path of a toxic cloud which then constitute a "lethal dosage envelope". This envelope would enclose an area within which a person, in the open, and remaining in this area during the time the cloud would take to pass, would have a given probability, say 0.5, of receiving a fatal dose. Aside from the question of the validity of the dispersion model, which draws purely upon physical laws, the further stage is to link the concentrations predicted with physiological effects and with predictions of the behaviour of the victims.

Nevertheless it is necessary to ask why the results given by the models are invariably pessimistic? The explanation for this the author believes is disclosed in a point by point comparison of the factors in the animal experiments and with the situation of exposed humans. This comparison shows that, on every point, predictions from animal experiments are likely to be pessimistic. The discussion assumes that the entry mode of the toxic substance is by inhalation and that comparison is made with animals using this route. The factors are as follows:-

(1) Difficulty of transference.

There are considerable difficulties in transferring the results of animal experiments to humans. There is ample data to show that, even for closely similar classes of animals such as rodents, the value for  $LD_{50}$  can differ by orders of magnitude for a given agent. [50] Bridges, J.W. points out that ingested TCDD is about 100 times more acutely toxic to guinea pigs than it is to mice and 600 times more acutely toxic to guinea pigs than it is to golden hamsters. The figure for  $LD_{50}$  for guinea pigs has led to claims that dioxin is the most poisonous synthetic substance known to man but this would be by no means true were it to be based on the  $LD_{50}$  for hamsters.

(2) Uniformity of concentration.

It may be assumed for animal experiments that every attempt will have been made to produce an atmosphere of uniform concentration. In the industrial release situation the really dangerous vapour clouds are heavier than air (this includes the behaviour of ammonia clouds even though ammonia gas itself is lighter than air). This implies that the concentration will diminish with height and thus a person may survive because the concentration in the breathing zone is less than the mean concentration in the boundary layer.

(3) Confinement.

Animals are confined. In practice there is usually no barrier at the end of a toxic cloud and therefore humans may escape from it. This is recognised in the literature where there have been attempts made to quantify this factor. Escape may be purposeful, that is it is based upon observation of a toxic plume, and it may be assisted by mechanical transport. Advice on the best direction to escape may be given by the authorities.

(4) Individual protection.

Obviously this is inapplicable to animals. For members of the public, not provided with respirators, considerable protection from water soluble gases may be provided by breathing through a wet cloth. Such measures are recorded as having saved the lives of soldiers at Ypres in April 1915. This may be described as semi-instinctive.

(5) Shelter.

Is not provided for animals. Houses, however, provide a considerable measure of protection, [51] Purdy, G. & Davis, P.C. Retreat to a bathroom where wet cloths are readily available, together with blocking off ventilation, may be very effective. For buildings close to the point of release, it may be advantageous if the room be an upper storey room. Gas will leak in through walls, as was pointed out nearly 50 years ago, [52] Haldane, J.B.S., but nevertheless, over the time period likely in such cases, the cloud is likely to have passed before a dangerous concentration is achieved.

(6) Treatment.

In determining  $LD_{50}$  levels, animals are not given treatment but are left to die or not. There can be no doubt that prompt treatment can save lives in many cases, as for example, by administering oxygen or by giving injections of atropine to the victims of chlorine.

These pessimistic factors, taken in combination, may increase predicted fatalities by perhaps two orders of magnitude. The author's view is that no theoretical model is valid which does not take account of these factors.

Against this must be set the consideration that it is claimed that there is greater variation in the levels of physical fitness of a residential population than there is in a batch of experimental animals. However, too much should not be made of this. There is no real evidence that children are more susceptible than adults to toxic hazards and infants are more readily protected than adults against a short duration toxic cloud. The elderly may be at much greater risk but the probability of elderly people being caught in the open is less than for those in middle life.

## SECTION 15.

### CLASSIFICATION OF TOXIC SUBSTANCES.

#### 15.1. DIFFERENCES BETWEEN TOXIC SUBSTANCES AND EXPLOSIVES AND FLAMMABLES.

Dense explosives, so far as their effects are concerned, differ from each other primarily in their specific blast energy; their chemical composition is of little importance. Similarly flammable substances, so far as their effects are concerned, differ mainly in their flame speed and to a limited extent in their specific calorific value. This latter factor also influences their behaviour in the event of a vapour cloud explosion, though here their reactivity plays some role. Thus in these cases there are classes of substances with generally similar properties. This is not true of toxics which, though they have the common property of causing death, manifest their lethal properties in markedly different ways. Some of these different properties will be described below.

#### 15.2. CLASSIFICATION OF THE PROPERTIES OF TOXICS.

##### (1) Dispersive energy.

By "dispersive energy" is meant the energy which is available within the agent which enables it to be brought into contact with the victims. The quantity of energy will vary with the total pressure under which the agent is confined and with its vapour pressure under the conditions of confinement.

The agents which possess the highest level of dispersive energy are highly compressed gases above their critical temperature. However, for mechanical reasons, it is highly unlikely that the inventory in a single pressure vessel is high enough to justify treating any compressed gas as a major toxic hazard. Next, and much more important, are the liquefied gases such as chlorine and ammonia. Phosgene, which is also a liquefied gas, has a lower dispersive energy than chlorine at the same temperature because of its lower vapour pressure. Agents maintained as liquids above their atmospheric pressure boiling point in process units will have a dispersive energy which is related to their vapour pressures.

Next are the highly volatile liquids which, though inherently less dangerous than liquefied gases, are liable if spilled to have a high rate of evaporation especially in wind. They may be as dangerous as a liquefied gas, however, if capable of exothermal polymerisation, e.g. methyl isocyanate.

Liquids of low volatility and powdered solids may be assumed not to possess inherent dispersive energy. To disperse them requires a "vector". Some form of explosion, not necessarily a violent explosion, or admixture with an effluent stream such as flue gas, is needed. Solids in a massive form hardly seem to

qualify as major-accident hazards.

(2) Persistence.

Toxic gases used in war have been classified as "persistent" or "non-persistent". The former are liquids of moderate volatility of which the classic example is mustard gas. Others have been released as gases and their persistence, always relatively short, varies with atmospheric conditions and with terrain, chlorine being the classic example. Whereas the former class might have had a persistence measured in days in summer and weeks in winter, the latter had a persistence measured in minutes or, at the most, hours.

In industrial practice the differences may not be so clear cut. This is because tonnage spillages of liquefied gases such as chlorine or ammonia give rise to an immediate flash-off of, say, 15%. But the bulk of the spillage will evaporate only as fast as heat can transfer into the residual pool. Therefore a large spillage may take days to evaporate.

A factor which is important in the industrial context is how easily an area over which a toxic liquid or solid of low volatility has been deposited may be decontaminated. Some highly dangerous substances may be readily neutralised; an example of a substance of this kind is mustard gas. This could be neutralised by hypochlorites which are chemicals found in most kitchens in the form of household bleaches. An extreme case of the other sort is dioxin; no satisfactory decontaminant has been found for this in spite of extensive research.

However it may be said, in general terms, that the intrinsic persistence of toxics is least for the loss of containment of a toxic permanent gas, of which carbon monoxide is one of the few examples. This is followed by ammonia, which is a liquefied gas of relatively high buoyancy. Then follows chlorine, a liquefied gas much denser than air, then come highly volatile liquids such as methyl isocyanate, then liquids of low volatility such as mustard gas and finally solid toxics such as dioxin provided that they have been dispersed as aerosols or powders.

(3) Mode of attack.

As has been pointed out above, toxic agents vary greatly in their mode of attack on the human system. The author has not been able to find a classification of toxics, based on their mode of attack, which is appropriate to the chemical and process industries. There have been several classifications of war gases; one of these, the British between-the-wars classification, the author has modified to take account of present day circumstances. These are given with examples of each below. Where numbers are given they are the numbers assigned in Annex III.

- (a) Lung irritants.  
Chlorine, (16) Phosgene, (15) Chloropicrin, (Trichloronitro methane).
- (b) Vesicants.  
Mustard gas [Bis (2-chloroethyl sulphide)]. (39).
- (c) Sensory irritants.  
Diphenyl chloroarsine.
- (d) Lacrimators.  
Brombenzyl cyanide.
- (e) "Blood gases".  
Carbon monoxide.
- (f) Incapacitating agents.  
BZ Agent.
- (g) Nerve gases.  
Tabun, Sarin, Soman.

However, such lists do not include many of the toxic agents to be encountered in industry, such as ammonia and methyl isocyanate. On the other hand many of the substances in the war gas list have no industrial importance. Thus, though both sensory irritants and lacrimators may be chemical hazards, in the author's view they do not rank as major chemical hazards. Incapacitating agents are, by intention, non-lethal. The nerve gases listed appear to be manufactured solely for their end use which is to be stock-piled for military purposes and do not function as intermediates in organic synthesis. Thus they do not have industrial significance. They will, however, be briefly discussed below along with those pesticides to which they are chemically related.

(4) Inherent toxicity.

It would be useful to be able to rank toxics into broad categories of severity of the hazard presented. Fig. 9, part of which is derived from table 1 in [53] Bridges, J.W., shows however that there are no internationally agreed standards of classification. Moreover the categories are heavily biased towards ingestion; they are LD<sub>50</sub>s from oral administration to rats (Except for Col. 9). The most likely industrial hazards, those arising through respiration or through skin contact, are not covered.

The columns are as follows:-

- (1) As in the Directive Annex IV. Bridges claims that Col. 2 of Table 1 of that Reference is from this Annex, but the classifications in Bridges do not correspond with Annex IV.
- (2) Poisons and Deleterious Substances Control Law (Japan).
- (3) Federal Insecticide, Fungicide and Rodenticide Act (USA).
- (4) Transportation of Dangerous Goods (United Nations).



LD<sub>50</sub> mg/kg  
0.1

LD<sub>50</sub> mg/kg  
0.1

Col 1	Col 2	Col 3	Col 4	Col 5	Col 6	Col 7	Col 8	Col 9
Very Toxic Substances	Designated Poison	Category I	Group 1	Extremely Hazardous	Extremely Toxic	Highly Poisonous, Most Dangerous to Human Beings.	Dioxin (Mice)	Phosgene Hydrogen Cyanide
Very Toxic in some circumstances								
Other Toxic Substances	Poisonous Substance	Category II	Group 2	Highly Hazardous	Highly Toxic	Highly Toxic.	Dioxin (Hamster)	Chlorine
	Deleterious Substance							
		Category III	Group 3 Solids - liquids	Moderately Hazardous	Moderately Toxic	Moderately Toxic.	Potassium Cyanide Strychnine Arsenic Trioxide	Hydrogen Sulphide
		Category III		Slightly Hazardous	Slightly Toxic	Moderately Toxic	Ammonia.	
		Category III				Low Toxicity		

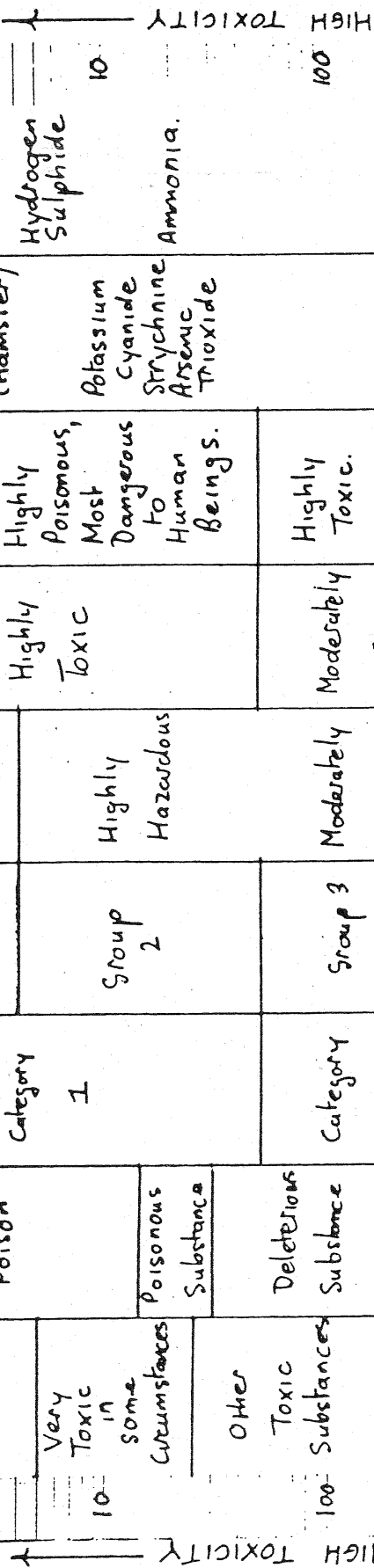


FIG 9 SOME CLASSIFICATIONS OF TOXIC SUBSTANCES.

- (5) Classification of Pesticides (World Health Organisation).
- (6) Hodge and Sterner Classification quoted in Bridges.
- (7) Classification adopted in USSR, derived from [54] International Labour Organisation.
- (8) Examples of acute toxicity by ingestion taken from [55] NIOSH.
- (9) Indicative levels of LD<sub>50</sub> derived from inhalation data in [56] NIOSH. These are nominal equivalents and are based upon the following assumptions:-
  - (a) All the toxic material inhaled enters the system.
  - (b) At high concentrations the product of time and lethal concentration is a constant.
  - (c) The index, respiration rate per Kg of body weight, is as in human subjects i.e.  $10^{-4}$  cu metres per minute per Kg of body weight based on a respiration rate of 7 litres per minute (resting) and an average weight of 70 Kg. Thus:-

$$\text{Dose (mg/Kg)} = \frac{\text{Toxic concentration (mg/cu metre) X time (mins)}}{10^4 \text{ (Kg mins/cu metres)}}$$

Where the lethal concentration is given in parts per million, this may be converted to mg/cu metre by multiplying by (Mol Wt of toxic X 0.0423).

- (5) Injury to fatality ratio.

Different toxic agents differ in their ability to injure as well as to kill. In the First World War, according to [57] Prentiss, A.M., Table X, for all belligerents, and for all causes of injury or death, there were approximately 3 non-fatally wounded per battle death. But for gas casualties the ratio was 13 to 1. Thus poison gas brings in its train more injuries per death than does high explosive. It does not follow that all toxic agents display the same injury to death ratio. There seems general agreement that mustard gas gave a particularly high injury to death ratio as compared, say, with chlorine. From the military point of view, especially when on the defensive, mustard gas was very effective. But the question as to whether chlorine or mustard gas is the more dangerous in an industrial situation is more difficult to answer. If, for a given mass of the agent, A produces W fatalities and X injuries and B produces Y fatalities and Z injuries and other things are equal provided  $W \geq Y$  and  $X \geq Z$ , it is clear that A is more dangerous than B. But if  $W \geq Y$  and  $X < Z$  a more difficult decision arises.

(6) Long term effects.

The extent to which the long term effects of exposure to toxic agents is known with certainty depends upon the availability of the subsequent medical records of those subjected to acute exposure. [58] Trevethick, R.A., of which the author was a medical practitioner in industry, states "It is very doubtful that chronic effects occur from inhaling chlorine. After each acute episode - recovery is complete . . . Chronic poisoning (by phosgene) is unknown in industrial practice but repeated acute exposure can lead to chronic chest disease . . . Where recovery takes place after a severe episode of cyanide poisoning there may be permanent effects due to malfunction of parts of the central nervous system".

There seems little doubt that a number of agents, of which mustard gas is a prime example, can cause permanent blindness, disfiguring scars and other disabilities. The author has not been able to find evidence of long term effects from acute sub-lethal exposure to nerve gases. [59] Heath, D.F. implies that there are none.

There has been considerable controversy over possible long term effects from dioxin. It is well known that exposure to dioxin can cause the disfiguring disease of chloracne in some exposed subjects. This does clear up eventually though in severe cases this may take about two years. It has also been alleged, based upon animal experiments, that teratogenic effects (damage to an unborn child) may occur. Medical examination of 34 fetuses, 30 from legal abortions, 3 from miscarriages, from women in the Seveso area, suggested that one may have been abnormal possibly exhibiting Down's syndrome. [60] Hay, A. quotes the medical team as saying "the results of the embryo-morphological studies do not have any hint of damage brought about by exogenous agents (dioxin) . . ." They added a rider that this did not necessarily indicate that dioxin does not bear a risk for mother and child. Analysis of birth defects subsequent to the disaster has given no clear picture. A certain number always occur in any population; [61] Hay, A. quotes a figure for Western Europe of 2.5 to 3 per hundred. The rate for the post disaster period at Seveso, according to Hay, was somewhat less than for Europe or for Italy as a whole. Other links have been alleged such as with cancer but there seems little evidence of an indisputable character for any of them. However, it may be as well, for the present, to leave a question mark over the long term effects, other than chloracne, which may be caused by dioxin.

(7) Industrial significance.

It would be very useful to be able to draw up a table showing the quantities of the various toxic substances by inventory and by the numbers of installations on which any given inventory is exceeded. Unfortunately this is impossible because the information is not published. At the present time in the UK, and probably in the other Member States of the EEC, there exists such lists which have been compiled in anticipation of the implementation of the Directive. Though it is against the law of the UK for the HSE to publish lists which refer to individual firms, there does not seem any legal barrier to publishing statistical analyses. The nearest approach is in [62] Ryder, E.A., where it was reported that it was anticipated that 200 to 250 large sites would be covered by the EEC Directive plus a further 1000 which have to be notified on account of holding stocks classified as highly toxic substances.

But it can be said that there are some things which are well known. One is that both chlorine and ammonia are stored in tanks with capacities of the order of hundreds of tonnes at both points of production and points of usage. On the other hand sulphur dioxide, which is produced on a considerably greater scale than chlorine, is hardly ever stored in quantity. This is because the greatest quantity produced is in the manufacture of sulphuric acid where it goes straight from a sulphur burner into a catalytic reactor, where it is converted immediately into sulphur trioxide. The greatest part of this latter substance is then immediately converted into sulphuric acid in an absorption tower. Neither sulphur dioxide nor sulphur trioxide are stored in quantities which reflect the scale on which they are produced.

In general, large scale storage is associated with centralised production and a large number of dispersed users.

On the other hand, it is clear that some toxic substances which attract considerable attention from the mass media, of which dioxin is an example, have very little industrial importance. Ranking in industrial importance, in the author's view, should determine the priority given to the establishment of definitive threshold values but should not influence the assigned value.

(8) Ranking of toxic agents.

Based on the classification given above it is possible, in principle, to give a ranking to toxic agents. This could be done by giving a weighting to each of the six factors discussed above which would influence ranking, and then grading each agent on a scale of, say, three or five points against each of the factors.

## SECTION 16.

### TWO DIFFICULT PROBLEM AREAS.

#### 16.1. THE PROBLEM OF POLYCHLORINATED AROMATICS.

The dioxin problem, which was one of the problems which gave rise to the Directive, is one of great complexity. Dioxin, the name by which it is commonly known, is a highly toxic substance even if the description that it is the most toxic synthetic compound known to man may not be true. It is also extremely persistent and resistant to decontamination. It is extraordinarily stable to high temperatures for an organic compound. Annex III gives it a threshold level of 1 Kg. It is of no industrial significance and only arises as an unwanted by-product in the processing of polychlorinated aromatic compounds. The dioxin of Annex III is 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD) and is listed as No.9.

[63] Hay, A. lists a whole family of dioxins, one of which, the 1,2,3,7,8 substituted dioxin, is barely distinguishable in toxicity from 2,3,7,8 dioxin. This particular chlorinated dioxin is not listed in Annex III. The only other dioxin out of the nine listed by Hay as having known toxic properties (there are 75 chlorinated dioxins theoretically possible of widely varying toxicities as well as chlorinated dioxins substituted by other elements the numbers of which are beyond calculation) is 1,2,3,7,8,9 dioxin listed as No. 96. This again is a substance of absolutely no industrial significance which is most unlikely to be present anywhere in a quantity equal to its inventory level of 100 kg.

Without reviewing in detail the Seveso incident which the author has studied in detail, it is his view that this constituted a freak occurrence with features that are most unlikely to be repeated and that it is unsound to use it as the basis for a rational framework for the control of toxic substances. This is especially true as it is unlikely in the extreme that anyone would deliberately synthesise and store it in future as part of an industrial process.

There are other related problems concerned with polychlorinated biphenyls (PCB) which are used, for example, as transformer oils. These are now recognised as being extremely dangerous especially if exposed to fire where they can be pyrolysed to dioxin. These are not listed in Annex III.

The author proposes that the dioxin and PCB problems be solved, not by specifically listing dioxins, or substances liable to be precursors of dioxin, in Annex III, but by designating all processes within the provisions of Annex I in which polychlorinated aromatic compounds are either raw materials or products, as falling within the provisions of Article 5 regardless of the level of inventory. Polychlorinated may be defined as having three or more chlorine atoms directly

attached to the aromatic ring.

## 16.2. THE PROBLEM OF PESTICIDES.

The greatest single class of toxic substances listed in Annex III are pesticides. The number of pesticides grows year by year and it would be impossible to list all those at present in existence. For example paraquat and diquat were involved in an incident at Morley, near Leeds in 1982, [64] ACMH. Here, as the consequence of a fire in a warehouse, several tonnes of these materials found their way into a watercourse causing considerable environmental damage. No one was injured and the incident was of the nature of a major-accident hazard which caused environmental damage only. But neither paraquat nor diquat are listed in Annex III.

There is a whole class of substances, the organophosphorus compounds, which are used as insecticides and which have the same general structural formula. An example of the class is parathion, listed as No. 63 in Annex III. Substances with similar structural formulae are the nerve gases tabun and sarin. Estimates of the number of theoretically feasible organophosphorus compounds of the same general formula give figures of the order of 75 million of which perhaps 100,000 have been synthesised.

It is the author's view that it is not practicable to try to list in Annex III all substances which are, or likely to be, used as insecticides and which are likely to be dangerous to man. The same applies to other pesticides whether used for killing mammals, weeds or fungi.

The author proposes that a similar procedure to that for controlling dioxins, namely that all installations within the provisions of Annex I and used for the purposes of manufacturing or processing pesticides, come under the provisions of Article 5.

## SECTION 17.

### THE QUANTIFICATION OF TOXIC HAZARDS.

#### 17.1. GENERAL.

The quantification of toxic hazards presents greater difficulties than the quantification of explosion and flammable hazards.

This arises because toxic effects, broadly speaking, are unique to the toxic agent, for reasons outlined above. Whereas for explosives it is reasonable to amalgamate the data for nitroglycerine with those of TNT and other explosives, with perhaps some allowance for differing specific blast energies, this is not permissible for toxics.

It is, the author believes, necessary, at least for the reasonably foreseeable future, to set aside theoretical models for quantifying toxic hazards. The reasons for this are set out above. It is necessary to fall back, for the present, on the historical experience, therefore, as the only source with any degree of reliability. This is not to say that theoretical modelling should not be encouraged. When it can be shown that a theoretical model is able to calculate fatalities for past incidents which accord with what actually happened, then this model should take over for quantifying toxic hazards.

Because of the uniqueness of toxic properties, each substance has to be studied on its own. There are only two substances of industrial significance on which there is any sort of data base and these are chlorine and ammonia. These data for chlorine are shown in Table VI. Phosgene is an important toxic chemical, for which there are data for a single large release in 1921 and where there is considerable information on its use in World War I.

The evidence for the calculation of a mortality index for chlorine and ammonia is examined below, together with the evidence for the calculation of a mortality index for mustard gas as an example of a very toxic substance.

**17.2. IS THE MORTALITY INDEX FOR TOXICS SCALE DEPENDENT ?**

With both explosives and flammables, there are theoretical reasons for assuming that fatalities will be proportional to  $M^{0.666}$  where M is the mass of the agent and where there is no time for evacuation. It is not obvious that the exponent of M should have the same value for toxics.

For a cloud where the height is invariant with the mass released, the area covered by a cloud before dispersion might be regarded as being directly proportional to the mass of the agent released, i.e. to  $M^{1.0}$ .

Where the clouds produced by two differing masses of agent are geometrically similar, the area covered by the cloud would be proportional to  $M^{0.666}$ . Hence, in practice, the exponent for M might be expected to be between 1.0 and 0.666. The author has seen evidence to suggest that some computer models predict areas with exponents for M lying between 0.90 and 0.80. However F/N curves suggest that fatalities are not scale dependent.

Unlike the situation with explosions, with toxics there may be time to take avoiding action and this means that fatalities may not be a linear function of the area covered by a toxic cloud. In view of the uncertainties, it is assumed below that fatalities for toxics are not scale dependent.

**17.3. THE EFFECT OF POPULATION DENSITY.**

Whereas for explosions and vapour cloud fires the worst effects may be assumed to lie within the site boundary, this is not necessarily true of toxic incidents where lethal effects may occur for a milometer or more. For this

TABLE VI. WORLDWIDE CHLORINE VAPOUR CLOUD INCIDENTS OVER 60 YEARS.

Location	Released from	Tonnes Released	Fatalities
Montana, Mexico	Railcars	300	17
Baton Rouge, La.	Storage Tank	90	Nil
Mississauga, Toronto	Railcar	60	Nil
Rauma, Finland	Storage Tank	30	19
Cornwall, Ontario	Railcar	28	0
Griffith, Indiana	Railcar	27	0
La Barre, Louisiana	Railcar	27	1
St. Auban	Store Tank	24	23
Syracuse, NY	Store Tank	24	1
Zarnesti, Rumania	Store Tank	24	60
Wynadotte, Mich.	Store Tank	17	1
Chicago, Ill.	Railcar	16	0
Niagara Falls, NY	Railcar	15	1
Walsum, West Germany	Store Tank	15	7
Brandtsville, Pa.	Railcar	8	0
Mjodolen, Norway	Railcar	7	3
Freeport, Texas	Pipeline	4	0
Lake Charles, La.	Pipework	3	0
Johnsonburg, Pa.	Railcar	2	0



reason it may be best to assume that the population density is likely to be of the order of 4,000 per sq. kilometer, though this figure does not enter into the calculations given below on the mortality index for toxic substances.

## SECTION 18.

### THE QUANTIFICATION OF CHLORINE HAZARDS.

#### 18.1. THE HISTORICAL RECORD.

The historical record for chlorine falls into two distinct categories, war experience and industrial experience. These will be treated separately and some comparisons will be made.

#### 18.2. WAR EXPERIENCE AND THE MORTALITY INDEX FOR CHLORINE.

The April 22nd, 1915, Ypres gas attack was the first substantial gas attack of the war. The chlorine was discharged from a line of cylinders and escape for the vast majority of those exposed was impossible. The quantity used, 168 tonnes, is well established, but the fatalities are not so clearly established; the incident in fact is not well documented. The present author discussed in [65] Marshall, V.C. the number claimed by the Germans as being 5,000 dead and has not since then found any evidence to the contrary. The number does fit reasonably well with the numbers likely to be present in the 7 kilometer section of front at the time.

Accepting that the dead numbered 5,000 gives a mortality index of ca 30 for unprotected persons under extremely adverse conditions. The  $LD_{50}$  for chlorine by inhalation is ca 3.6 mg/kg of body weight or about 1/5 gram per person. The chlorine actually consumed in killing soldiers was thus about 1 kg out of 168,000 kgs discharged. Put another way, the gas attack involved ca 200,000 lethal doses.

Evidence from later attacks show much lower mortality indices. Figures on quantities and fatalities are provided in [66] Prentiss, A.M. These have to be taken with caution as it was difficult to tell exactly how many were killed by gas as opposed to shells, bullets etc in any given attack; conditions of war precluded the possibility of post mortem examinations to determine whether death was due to gas or to other causes. For other cloud gas attacks, Prentiss attributes 2,312 deaths to 1041 tonnes of chlorine gas. This gives a mortality index of 2.23.

All in all, the figures suggest that with some degree of protection for the troops, but who were also at the time subject to the other harassments of war, the mortality index for chlorine was of the order of 2.25. One important factor

is that in water, unlike in industrial releases, the gas did not originate from a single point source. At Ypres it was a "line source" measuring some 7 kilometers. Few could escape by running out of it.

### 18.3. INDUSTRIAL EXPERIENCE AND THE MORTALITY INDEX FOR CHLORINE.

It is a matter of some importance to be able to derive a mortality index for chlorine because of its widespread use and its toxicity. Such an index could perhaps then be capable of yielding mortality indices for other bulk chemicals based on their toxicity relative to chlorine. Such a step has to be taken with caution but it could be at least indicative. [67] Marshall, V.C. concluded that the mortality index for chlorine in the industrial situation was ca 0.5. [68] ACMH reduced this to 0.3. However, the author notes that [69] CECAR, which makes use of his mortality index approach, suggests that for industrial releases it should be based upon data from the rupture of fixed store tanks rather than from transport vehicles. Table VIII lists incidents worldwide taken from [70] Marshall, V.C. and [71] ACMH with the addition of the incidents at Mississauga, Canada and Montana, Mexico. From this Fig. 10 displays the F/N curves for spill size and fatalities, the frequencies being related to the sixty year period covered by the table. It is possible here to move the scale for numbers of fatalities relative to the scale for size of spillage until the curves intermingle. The ratio between fatalities and spill size gives the mortality index. Clearly this is not an exact figure but a range over which it may be judged that the curves intermingle. Fig. 11 suggests a mortality index of 0.3 for all spillages; Fig. 12, for store tanks only, suggests an index of 0.5. What seems beyond doubt is that the index for chlorine, under industrial conditions, is less than 1.0.

A similar approach for ammonia, Fig. 13, yields values of ca 0.02 for the mortality index and thus an inventory for an isotraumatic value of 10 for ammonia of 500 tonnes. This is the threshold accorded in Annex III.

Some explanation is needed as to why the **inventory** is derived from these curves whereas with flammable gases the equal equivalence approach was used to calculate the mortality index of the **cloud** and the inventory was deduced from the "active fraction". It is assumed that the quantities used in the F/N curves for toxics are total inventories. With a flammable cloud there is a point of ignition and it is the quantity in the cloud at the time of ignition which determines the fatalities. Accordingly, investigations have generally endeavoured to deduce the quantity of vapour in the cloud at the time of ignition and it is this figure which is the N of the F/N diagram. Matters are different with toxic clouds where no such sharply defined intermediate event occurs and it is assumed that the fatalities are caused by exposure to the entire inventory

FIG. 10. F/N CURVES FOR CHLORINE SPILLAGES, ALL TYPES.  
FATALITIES AND SIZE OF SPILLAGE ON SAME AXIS.

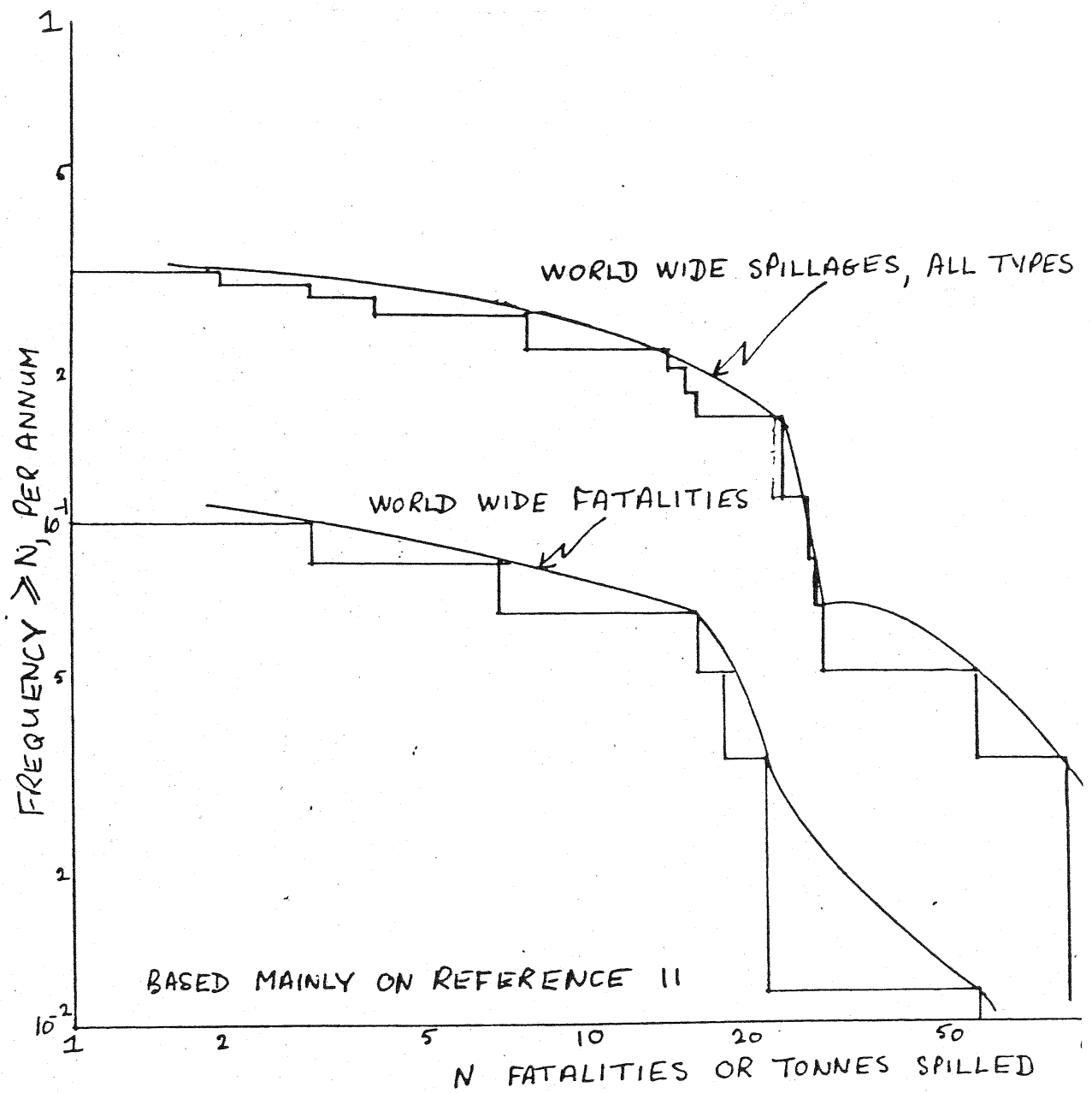


FIG. 11. F/N CURVES FOR CHLORINE SPILLAGES, ALL SPILLAGES,  
AXES DISPLACED.

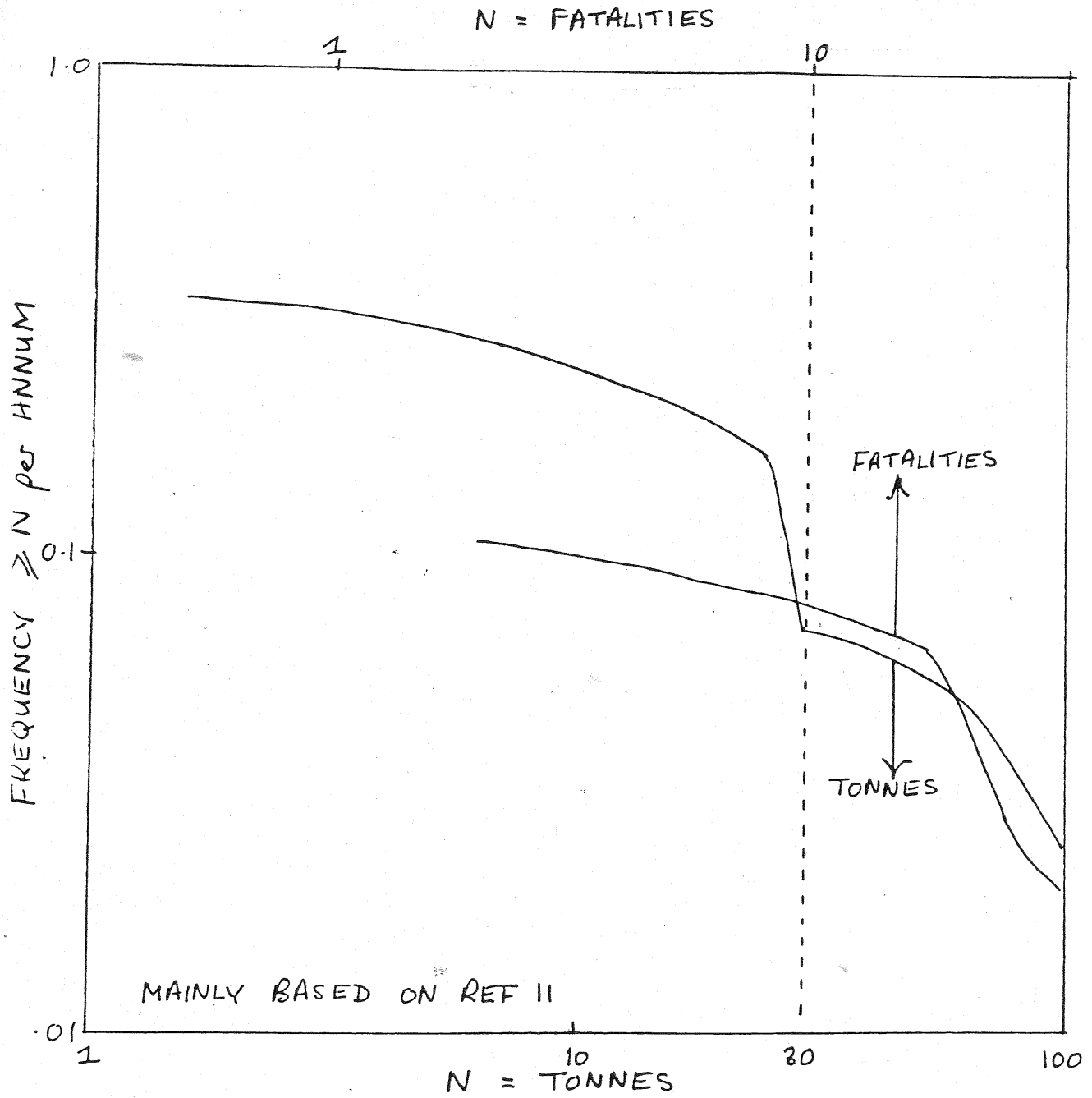


FIG. 12. F/N CURVES FOR CHLORINE SPILLAGES, STORE TANKS ONLY, AXES DISPLACED.

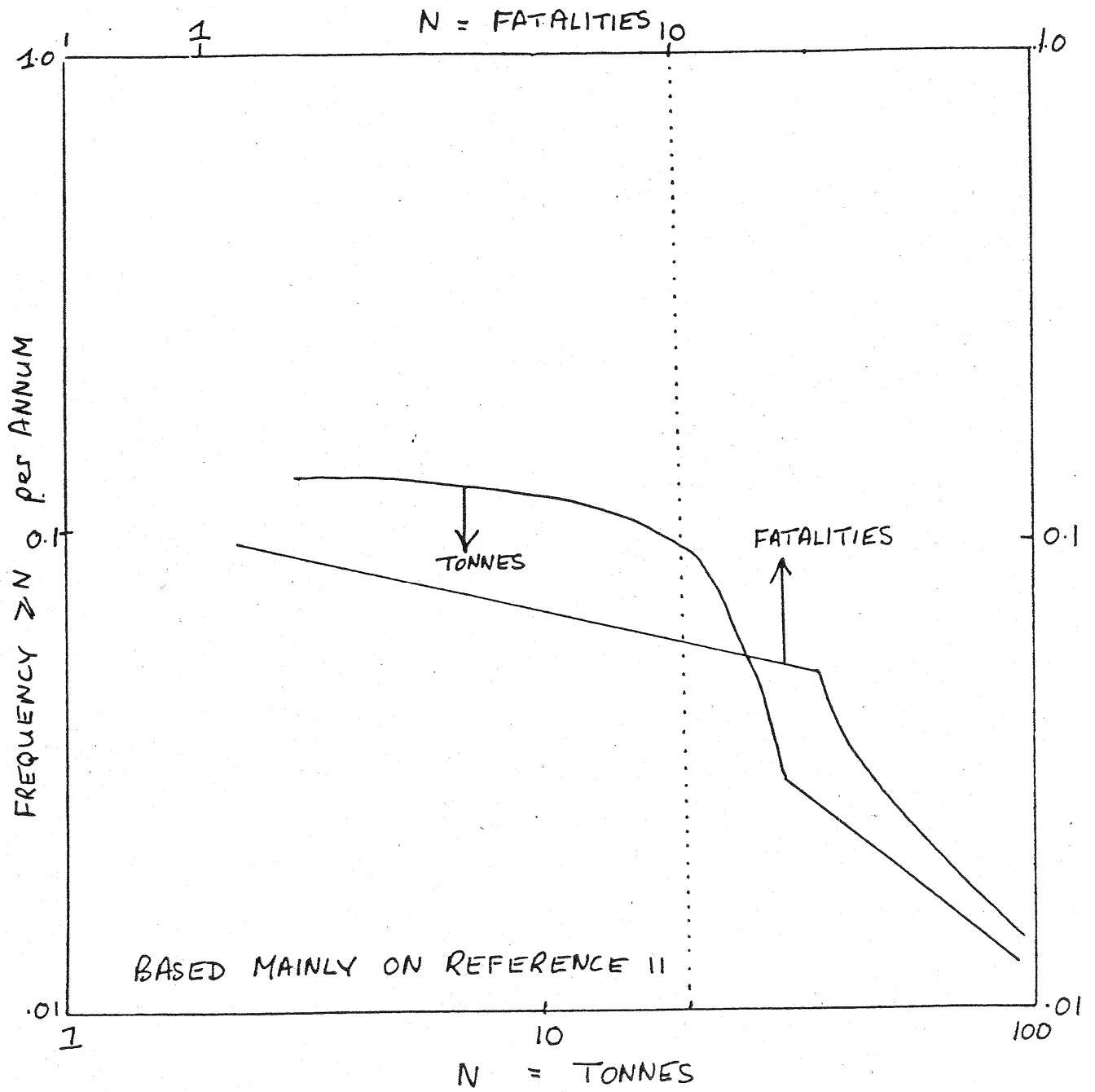
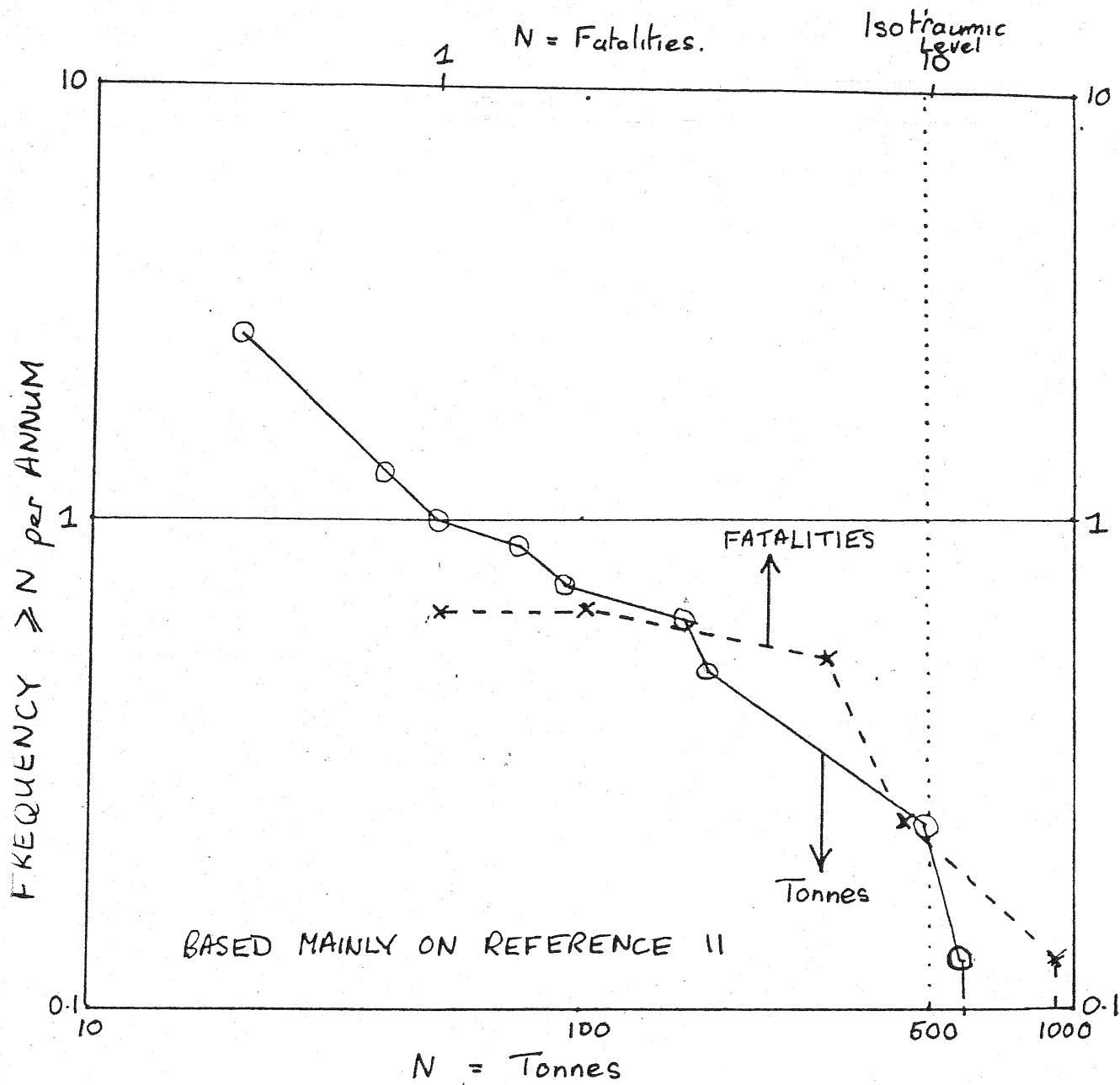


FIG. 13. F/N CURVES FOR AMMONIA.



even if the rate of release varies enormously between the flashing phase and the slow evaporation of the pool left at the end.

## SECTION 19.

### QUANTIFICATION OF MUSTARD GAS HAZARDS.

#### 19.1. THE PROPERTIES OF MUSTARD GAS.

Mustard gas [Bis (2 chloroethyl) sulphide] is listed as No. 39 in Annex III and given a threshold inventory of 1 kg.

According to a table given in [72] Clarke, R., mustard gas in the purified form known as "distilled mustard" is a colourless to amber coloured oily liquid with a faint garlic odour. It is a solid below 14 C and has a boiling point above 200 C. It has a volatility of 960 mg per cu metre at 25 C. It has a delayed action effect varying from 1 to 48 hours to the onset of symptoms, no pain is experienced at the time of first contact. Symptoms include severe blisters to the skin, injuries to the eyes, leading in some cases to temporary or permanent blindness, and injuries to the lungs as the concentrations in the vapour phase may be lethal. As used in the First World War it was at a lower level of purity than that available today. It is one of the types of gas known as a vesicant.

[73] NIOSH gives for a human subject a lowest recorded lethal dose through the skin of 64 mg/kg (the LD<sub>50</sub> for chlorine by inhalation is ca 3.6 mg/kg) and an LC<sub>50</sub> by inhalation of 1500 mg/cu metre for 1 min. The former transforms to a lethal dose of ca 4.5 gms and the latter to a lethal dose of 10.5 mg. There is thus a considerable discrepancy between the skin and inhalation doses. However, the NIOSH concentration is very much higher than anything likely to be encountered in the open air (cf the volatility of 960 mg/cu metre at 25C).

#### 19.2. WAR EXPERIENCE WITH MUSTARD GAS.

[74] Prentiss, A.M. argues very strongly that mustard gas was very effective at producing casualties in the First World War quoting a figure of 60 lbs (27 kg) per casualty (casualty was defined as causing the person to have to be removed from the firing line and thus included those injured as well as those killed). For war gases as a whole there were 20 casualties per fatality according to Prentiss. However, according to Table XVII in Prentiss which gives data on the principal gas attacks, for mustard used on its own, ca 12000 tonnes produced 61,500 casualties out of which 1,130 were fatalities. This corresponds to a mortality index of ca 0.1. Thus the mortality index for mustard was about 1/25 of that of chlorine as used in World War 1.

[75] Hersh, S.M. quotes an example from the Second World War, in which

there was no significant use of gas warfare. A ship, the S.S. John Harvey, which was carrying about 100 tonnes of mustard gas, was subject to a severe air attack in an Italian harbour. There were 600 casualties, 83 of them fatal, when the sailors from this and other ships attacked in the harbour at the same time, tried to swim through water covered with a layer of mustard gas. It was not realised till too late what had happened and this delay in applying suitable treatment may have caused a substantial number of fatalities which might otherwise have occurred. It perhaps would not be safe to attribute more than a very tentative figure of ca 0.83 as the mortality index to this particular incident in which the circumstances were peculiarly adverse for the victims.

Mustard, if promptly treated by commonly available bleaches containing hypochlorites, can be neutralised, though any which has already penetrated the skin will cause injury. These common reagents are effective at decontaminating clothing or buildings, [76] Home Office. According to [77] Hersh, S.M., mustard gas, otherwise known under the code name of HD, is classified by the US military as a "Non lethal blister agent, although at certain exposures it can be lethal".

The sum total of this evidence is that mustard gas, as used in warfare, is at least an order of magnitude less lethal than chlorine. This makes it all the more surprising that, according to the Directive, whereas the Annex III inventory for chlorine is 50 tonnes, the much less lethal mustard gas has an inventory of 1 kg. Chlorine, in addition, as a liquefied gas, possesses a far greater amount of inherent dispersive energy than does mustard.

## SECTION 20.

### THE QUANTIFICATION OF METHYL ISOCYANATE HAZARDS.

Only one incident is available for estimating the mortality index for this substance and that is the Bhopal disaster of 3/12/84. According to [78] NYT, there were some 45 tonnes of methyl isocyanate (MIC) in the store tank and afterwards 15 tonnes of what may have been a polymer remained behind. The release could, therefore, be assessed at 30 tonnes. The death toll is stated to have exceeded 2,000 with 200,000 injured. If the death toll be taken as the official figure of 2,500, then the mortality index would be ca 80. This compares with 30 for unprotected soldiers in the chlorine gas attack at Ypres.

In common with many of the substances listed in Annex III, data on the toxicity of MIC are rather few. The figures in [79] NIOSH suggest that the substance is most lethal when inhaled. NIOSH gives only one figure of significance and that is an  $LC_{50}$  for rats of 5 ppm for 4 hours. There is nothing in NIOSH



to compare it with but [80] I.Chem.E. refers to a paper, [81] Bell, D. & Elmes, P., which gives for chlorine a figure of ca 120 ppm for 3 hours using rats. This might be extrapolated to about 100 ppm for 4 hours. Allowing for the difference in molecular weights this would make MIC  $100/5 \times 71/57$  or 25 times more toxic than chlorine. Too much perhaps should not be read into this figure but it is all that the author has at his disposal.

If the Ypres model be set aside as having too many factors which set it apart from industrial circumstances and the mortality index of 0.5 which the author has recommended for chlorine be used, this would indicate a mortality index for MIC of 12.5. There is thus a ratio of 0.15:1 between the calculated and the actual mortality index. But, if population density be taken into account, the discrepancy may disappear. However, MIC appears to undergo exothermal polymerisation when suitably catalysed and thus a given quantity may give off more vapour in, say, an hour than chlorine which, after flash off about 15%, then evaporates relatively slowly. The great majority of store tank incidents involving chlorine have occurred in chemical works with population densities in the neighbourhood which must have been far less than in the shanty towns in the immediate vicinity of the Bhopal plant. Press photos make it obvious that the homes of the unfortunate victims could not have afforded shelter from the cloud in the way that European or American houses would have done.

## SECTION 21.

### THE QUESTION OF CRITICAL MASS.

There seem to be exceptions to the concept of the isotraumatic approach associated with certain substances. These are clearly capable of causing fatalities but which appear to have a critical level of mass. Below this mass, their hazard is very low but, above it, they have the potential to kill considerable numbers of people. An example is ammonium nitrate, which, in a grade in general use as a fertiliser, appears to have such a critical mass. This mass is of the order of thousands of tonnes. The author has not attempted to validate the threshold given to it in the Directive but accepts the principle that the number of fatalities at the threshold for this substance may be much in excess of 10 as the historical experience appears to demonstrate. It is recommended that further study be given to this problem.

A further substance also believed to possess a critical mass is sodium chlorate. This is given a threshold value in the Directive of 250 tonnes. Based on a specific blast energy of 0.15 relative to TNT this threshold corresponds almost

exactly with the isotraumatic index of 10 fatalities. The author recommends that all thresholds should be related to the 1,2,5 . . . scale and, if this basis be accepted, the threshold for sodium chlorate would be approximated to 200 tonnes.

## SECTION 22.

### THE REVISION OF ANNEX III.

#### 22.1. THE PROMULGATION OF THRESHOLD VALUES.

The examination of Annex III in the Report demonstrates, among other things, that it fails to be comprehensive and that were it to attempt to be comprehensive it would be vastly longer than it is at present.

The question may then be raised as to whether the Directive ought to try to establish a once and for all definitive list of threshold values. An alternative would be to delete Annex III and to promulgate threshold values, as and when they are validated, by means of Regulation with the force of EEC Law.

This latter proposal is favoured by the author as one which would provide for flexibility and ease of amendment of existing values. Amendments may arise from further studies or in application of the lessons drawn from incidents both inside and outside of the Community. Clearly too frequent amendment could have the effect of bringing the Directive into disrepute but the need could arise from new circumstances such as the discovery of a hitherto unsuspected hazard.

It is clear that, in the case of toxic substances, even where criteria are established on the lines of the present Annex IV, there would be considerable scope for differences of opinion between the Member States as to whether any particular substance satisfied the criteria. Thus, in order to preserve equality of competition, it would be necessary for the Commission to promulgate a common view as to the threshold value to apply.

No doubt some interim mechanism would be required, were this proposal to be accepted, to effect an orderly transition from Annex III to Regulation. For example the existing thresholds would hold good until superceded by Regulation. Reference below to Annex III would apply to such Regulations.

#### 22.2. THRESHOLDS FOR EXPLOSIVES.

These, it is recommended, should be based upon a logarithmic scale of blast energies determined by a set procedure and as set out in Section 25, which is intended to be indicative rather than definite. The central value would be the blast energy of TNT which would approximate to 50 tonnes.

### 22.3. THRESHOLDS FOR FLAMMABLE GASES AND LIQUIDS.

This section would be linked to a revised Annex IV which would establish the following categories:-

- (1) Liquefied flammable gases. Substances which are flammable and gaseous at or below 20°C and which are stored as liquids by pressure alone.
- (2) Substances which have a flash point below 2 and which are processed at a temperature above their atmospheric pressure boiling point and have a vapour pressure exceeding 1.5 bars absolute.
- (3) Refrigerated liquefied gases. Substances as defined in (1) above, but which are stored at or near atmospheric pressure by means of refrigeration.
- (4) Highly volatile flammable liquids. Liquids with a flash point below and a boiling point between 20°C and 50°C.
- (5) Liquids with a flash point below 20°C and a boiling point above 50°C.

The proposed inventories are:-

- (1) and (2) 50 tonnes.
- (3) and (4) 200 tonnes.
- (5) 50,000 tonnes.

The possibility remains for an intermediate category between (4) and (5) with an inventory of, say, 1000 tonnes.

### 22.4. THRESHOLDS FOR TOXIC SUBSTANCES.

It is recommended that this be related to the logarithmic scale elsewhere commented upon. In principle, substances would be allocated a point on this scale related to the logarithm of their LD<sub>50</sub> value assessed in relation to the likely circumstances, i.e. inhalation or skin contact.

The 1 kilogram inventory would be point zero on this scale, 10 kilograms would be point 3, 1 tonne point 9, 1000 tonnes point 18, etc. Should there be a need for an inventory lower than 1 kg, this would be given a negative number.

After the provisional allocation based on inherent toxicity, scale points would then be subtracted for circumstances which aggravate the hazard and added for circumstances which mitigate the hazard.

The scale would be "tuned" so that point 14 (50 tonnes) would correspond to a toxic substance with the following characteristics. A liquefied gas with inherent toxicity = 3.6 mg/kg (as chlorine), non persistent, attack by inhalation, moderate ratio of injury to fatality and no long term effects, i.e. Point=14+0-0=14.

The proposal is set out schematically in Table VII.

TABLE VII. INDICATIVE SCALE POINTS FOR VARIOUS FACTORS RELATING TO TOXIC SUBSTANCES.

Factor	Negative Score	Positive Score
<b>DISPERSIVE ENERGY.</b>		
Liquefied Gas at atmospheric pressure or under process conditions.	0	0
Liquefied Gas stored under refrigeration.	-	3
Volatile Liquid, B Pt below 50°C.	-	1
Liquid, Bt above 50°C.	-	2
Powdered solid	-	3
<b>PERSISTENCY.</b>		
Highly persistent	4	-
Moderately persistent	2	-
Slightly persistent.	1	-
Non persistent.	0	0
<b>MODE OF ATTACK.</b>		
Attack through inhalation.	0	0
Attack through the skin.	-	2
<b>INJURY FACTOR.</b>		
High injury to fatality ratio.	2	-
Long term injury	4	-
<b>INHERENT TOXICITY.</b>		
	$14 - 3 \times \text{Log} \left[ \frac{\text{LD}_{50} \text{ for substance}}{\text{LD}_{50} \text{ for chlorine}} \right]$	

Examples. Chlorine. Inherent toxicity = Scale point 14.  
 Persistency = -1  
 Other factors = 0  
 Threshold = 14 - 1 = 13 = 20 tonnes.

Methyl Inherent toxicity = 14 - 3 log 25 = 10.

Isocyanate. Dispersive energy = +1  
 Persistency = -2  
 Injury factor = -3  
 Threshold = 10 + 1 - 2 - 3 = 6 = 100 kg.

## **22.5. THRESHOLDS FOR OTHER SUBSTANCES.**

Annex IV would require a category of "Other substances", i.e. substances which though not dense explosives, flammable liquids or highly toxic substances, nevertheless are deemed to have properties which, in the view of the Commission, cause them to constitute major-accident hazards. This category would include hydrogen, liquid oxygen and ammonium nitrate.

## **SECTION 23.**

### **THE REVISION OF ANNEX II.**

#### **23.1. TERMS OF ANNEX II.**

Annex II (isolated storage) concerns storage at installations other than those covered by Annex I.

The preamble to Annex II states "The quantities set out below relate to each installation or group of installations belonging to the same manufacturer where the distance between the 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 approximately 500 m".

Examples of such installations may be the storage of energy gases at such installations as a brick works or a glass works or for space heating. It would include the storage of such gases for wholesale or retail distribution. Ammonium nitrate may be stored for wholesale or retail distribution for agricultural purposes. Liquid oxygen may be stored at a steel works which does not use electrical heating for maintaining the iron in molten condition.

It would appear, therefore, that the purpose of Annex II is to apply the Directive, for a limited range of substances or groups of substances, to a wider range of industrial activities than is covered by Annex I.

#### **23.2. COMPARISON OF INVENTORIES.**

When an entry appears in both Annex II and Annex III, Table VIII shows that the threshold for the application of Article 5 in Annex II bears no constant relationship to that in Annex III such as would arise from a general conclusion that isolated storage presents a lesser hazard than storage on an Annex I site or vice versa.

TABLE VIII. COMPARISON OF INVENTORIES.

Substances or groups of substances.	For application of Article 5.		Relationship of Annex II to Annex III.
	Annex II.	Annex III.	
1. Flammable gases as defined in Annex IV(c) (i).	300	200	Higher
2. Highly flammable liquids as defined in Annex IV(c) (ii).	100,000	50,000	Higher
3. Acrylonitrile	5,000	200	Much higher
4. Ammonia	600	500	Nearly equal
5. Chlorine	200	50	Higher
6. Sulphur dioxide	500	1,000	Lower
7. Ammonium nitrate	5,000	5,000	Equal
8. Sodium chlorate	250	250	Equal
9. Liquid oxygen	2,000	Not listed	-

### **23.3. ARE THE LEVELS OF HAZARD DIFFERENT ?**

If the principles set out in this Final Report are accepted as the sole guide, the hazard for a particular substance arises from a combination of intrinsic properties such as temperature, pressure, flammability, explosibility and toxicity with the extrinsic property of mass.

If the intrinsic properties of a substance in one location are the same as that in another, it would follow that the mass which corresponds to a given level of hazard will be the same regardless of the location.

On this basis, there is no justification for any differentiation between the isotraumatic threshold level in isolated storage from that in an Annex I installation. It remains to consider whether there are other factors which may influence the assigned threshold level.

### **23.4. THE QUESTION OF POPULATION DENSITY.**

If there were to be any difference of a general character between Annex I and Annex II conditions, as, for example, if "isolated" meant isolated from people, then a higher assigned threshold level for isolated storage might be justified.

No evidence for a difference of this character seems to exist. In any case, as has been demonstrated above, there is not a consistent relationship between Annex II and Annex III thresholds.

### **23.5. THE QUESTION OF RISK.**

Were there to be some palpable difference between risk, as probability of the realisation of the hazard, it might be conceivable as an act of policy, to assign a threshold higher than the isotraumatic threshold to take account of a diminished risk.

The lack of a consistent relationship between the Annex II and Annex III thresholds is not consistent with the view that risk is either higher or lower for Annex II than it is for Annex III.

Examination of the modes and causes of failure of pressure vessels suggests that none is more or less likely in either isolated or process storage. Indeed it might be argued that the conditions of operation of a pressure vessel are more or less the same in both cases.

An important element in risk is that of the quality of safety management. The quality of safety management is related to its organisation and to the qualifications and experience in managing major-accident hazards of those entrusted with the surveillance of installations.

Here a generalisation may be appropriate. It is that the safety management directed to the control of major-accident hazards in Annex I installations is likely to be of a higher standard than those installations covered only by Annex

II. This is because the basic technology of Annex I is that of the chemical and process industries. This is not necessarily true of Annex II installations.

Were this factor to apply, then there might be a case for setting Annex II thresholds lower than Annex III by, say, 1 scale point.

[82] Lees, F.P. has examined the relative risk, by which that author seems to mean the societal risk, of materials in storage or in process. This study is not making precisely the same comparison as the present paper, as it is concerned with comparing the risk arising from process units with that from their associated storages. Lees concludes "Thus the idea that material in storage presents a much lower risk than in process is a half truth and cannot be accepted without qualification. As far as concerns multiple fatality accidents, and in particular large multiple fatality accidents, the contribution of storage is appreciable".

This study thus gives no support to the idea that an isolated storage is less of a hazard than a combination of storage with process plant. It should be borne in mind also that an isolated storage strictly speaking cannot exist, as it must have facilities for charging and discharging and may possibly be associated with a process not covered by Annex I.

#### 23.6. RECOMMENDATION.

Taking account of the above, and concluding that the factor of management is not sufficiently strong as to justify a lower threshold in Annex II, it is recommended that the threshold levels assigned for the application of Article 5 be the same as those of Annex III. In the case of liquid oxygen, the threshold level should remain at 2,000 tonnes.

The threshold level for the application of Articles 3 and 4 should be set at one tenth of those for the application of Article 5.

### SECTION 24.

#### THE REVISION OF ANNEX I.

##### 24.1. THE GENERAL PROBLEM.

A problem may lie in the definition as to what constitutes an "Industrial Installation". In this European Legislation may not correspond to the definitions used by some Member States. The opening section, (1), seems ambiguous. Does it mean all production or processing of all organic or inorganic chemicals of which the thirteen processes listed are merely examples or is it restricted to these? The thirteen processes named are not an exhaustive list of chemical processes, for example "reduction" is not listed. Nor is it solely a list of "unit



processes" as it includes four entire manufacturing processes which may be multistage and involve several of the above unit processes.

This section could be rewritten so that it is clear that the unit processes are merely examples. The question may then be raised as to whether this adds anything to understanding.

#### **24.2. AN ALTERNATIVE FORM OF ANNEX I.**

A better way may be to write it as:-

- (1) Installations which are for the production or processing of chemicals and in which chemical reaction or changes of physical state occur, except for installations whose sole purpose is to burn fuel to raise steam or for other heating purposes.
- (2) Unchanged.
- (3) "
- (4) "
- (5) "
- (6) Installations for the production of metals or non metals by electrolysis.
- (7) Installations for the production of metals by any wet process.
- (8) Any installation in which water is treated by the addition of chemical substances except solely for purposes of water softening.
- (9) The liquefaction and separation of gases from air.
- (10) Installations for the formulation or packaging of chemicals or energy gases.

#### **24.3. ADDITIONS TO ANNEX I.**

It is proposed to add to Annex I the following special categories:-

- (11) Notwithstanding any of the above, all installations which manufacture or process, including formulation of any pesticides, shall be deemed to be major-accident hazard installation without regard to any inventory in Annexes II or III.
- (12) Notwithstanding any of the above, all installations which manufacture or process any polychlorinated aromatic organic chemical compound which shall be deemed to be a major-accident hazard installation without regard to any inventory in Annexes II or III.

### **SECTION 25.**

#### **REVISION OF ANNEX IV.**

##### **25.1. TOXICITY.**

The object of the criteria here should be to identify those substances which, on account of their toxic properties, constitute "dangerous substances". There

is no ground for distinguishing between "very toxic" and "other toxic substances" as the Directive and its Articles make no such distinction. It is well known that it can be argued that any substance is toxic at, or above, some level of concentration, and that there is an LD<sub>50</sub> value for every substance. However, common sense has to be applied and Annex IV accordingly has to provide a level of toxicity such that any substance less toxic than this will be exempted from the provisions of the Directive however large its inventory should its toxicity be its only dangerous property.

It is proposed, therefore, that a single set of criteria be adopted for toxicity, provisionally at the level in Annex IV b. As has been argued previously, there seems little justification for the lower value attributed to the ingestion route and it is proposed that this be deleted.

The two categories of LD<sub>50</sub> (cutaneous) and LD<sub>50</sub> (inhalation) should be approximated to give the same LD<sub>50</sub> for both routes based on the assumption that, in both cutaneous and inhalation experiments, there is total absorption by the skin or the lungs.

## 25.2. FLAMMABLE SUBSTANCES.

This, it is recommended, should have categories:-

- (i) Liquefied flammable gases. As presently defined in (c) (i).
- (ii) Refrigerated flammable gases. Substances which are in the gaseous state at 20°C and which when mixed with air become flammable, and which are stored as refrigerated liquids at, or near, atmospheric pressure.
- (iii) Highly flammable liquids. Substances which have a flash point lower than 21°C and the boiling point of which lies between 20°C and 50°C.
- (iv) Flammable liquids. Liquids which have a flash point below 20°C and a boiling point at normal pressure above 40°C.
- (v) Pressurised flammable liquids. As presently defined in IV c (iii).

## 25.3. EXPLOSIVE SUBSTANCES.

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

- (a) Substances with a specific blast energy  $\geq 1.5 \times 10^6$  joules per kg.
- (b) Substances with a specific blast energy  $\leq 1.5 \times 10^6$  to  $\geq 6.66 \times 10^5$  joules per kg.
- (c) Substances with a specific blast energy  $\leq 6.6 \times 10^5$  to  $\geq 3.0 \times 10^5$  joules per kg.
- (d) Substances with a specific blast energy  $\leq 3.0 \times 10^5$  to  $\geq 1.3 \times 10^5$  joules per kg.
- (e) Substances with a specific blast energy  $\leq 1.3 \times 10^5$  to  $\geq 6 \times 10^4$  joules per kg.

[These would be accorded scale points with examples as follows:-

- (1) = 13. PETN, Nitroglycerine, RDX.
- (2) = 14. TNT, Picric Acid, Trinitrobenzene, 2,4 dinitrotoluene.
- (3) = 15. Mercury Fulminate\*, lead azide\*.
- (4) = 16. Sodium chlorate, cyclohexanone, peroxides.
- (5) = 17.

\* Unless scaled down to take account of possible environmental pollution].

#### **25.4. OTHER SUBSTANCES.**

The criteria of toxicity, flammability and explosibility do not exhaust the possibility that other properties of substances may not render them dangerous. Substances may be prescribed by Regulations from time to time as dangerous substances when at or above a certain quantity either in process or in isolated storage.

### **SECTION 26.**

#### **SUMMARY AND CONCLUSIONS.**

##### **26.1. TERMINOLOGY.**

There should be an agreement first on the English terminology for future documents on Major-Accident Hazards. This should be followed by the preparation of a multilingual dictionary of terms used to describe major-accident hazards.

##### **26.2. AMENDMENTS TO ANNEXES III AND II.**

Piecemeal amendments to these Annexes should be avoided and they should accord with the structure and principles laid down in the Report.

##### **26.3. MODELLING OF MAJOR-ACCIDENT HAZARDS.**

The Community should encourage the development of modelling, with an eventual aim of adopting models which are capable of being validated against past incidents. Until then the best answers which can be obtained from the study of past incidents, or by analogy to past incidents, should be used to determine threshold levels.

##### **26.4. THE CRITERIA FOR EVALUATING WHAT IS A MAJOR-ACCIDENT HAZARD.**

The primary criterion should be the potential to cause human fatality. A major-accident hazard would have the potential, under the circumstances of the most probable realisation, of causing the isotraumatic level of fatalities. It is proposed that this level be ten.

Purely environmental hazards, i.e. those with the potential to cause severe

environmental damage without, in the typical case, having the potential to cause human injury, seem to be very unlikely. Certainly, at present, no convincing scenarios for such events do not exist, though such scenarios may emerge in the future. Even so, proposals in the Report that certain industries be designated as potential major-accident hazard industries should take care of the most likely source of any such releases.

#### **26.5. THE SCALE FOR ANNEXES III AND II.**

This should be the scale 1,2,5,10,50 . . . All threshold levels should be approximated to this scale.

#### **26.6. EXPLOSIVES.**

Annex II should list bands of blast energy related to inventory levels based on the ratio of the blast energy of the substance to that of TNT. TNT is calculated as having an inventory of 50 tonnes when related to the isotraumatic level of 10. These bands should be linked to the 1,2,5,10 . . . scale. A lower level than that indicated by blast energy alone may be allocated to lead azide and mercury fulminate if it be considered that they have potential to contaminate the environment in addition to their blast potential.

#### **26.7. FLAMMABLES.**

It is not possible to predict with certainty whether a given flammable cloud will give rise to a fire ball or to a vapour cloud explosion. But there is little to choose between fire balls and explosions in their potential for causing fatalities. Explosions do give rise to more widespread damage effects than fire balls. Based on the equal probability approach, the threshold quantity for materials such as LPG, when stored at atmospheric temperature, should be lowered to 50 tonnes. This inventory would also apply to Annex IV c (iii) liquids. The 200 tonne inventory should be retained for flammable substances of high vapour pressure or for flammable permanent gases when stored at or near atmospheric temperature using refrigeration and for flammable substances with boiling points lying between 20° and 50°C.

#### **26.8. CRITERIA FOR THE INCLUSION OF TOXIC SUBSTANCES IN THE PROVISIONS OF THE DIRECTIVE.**

Substances whose potential for harm is realised solely through chronic exposure should be deleted from the provisions of the Directive and controlled by other, and more appropriate, means. This would eliminate carcinogenic substances from Annex III unless they are capable of giving rise to acute effects. The exception to this would be carcinogenic substances capable of being deposited on the environment, with such persistence or difficulty of decontamination as to give them the potential to give rise to chronic exposure.

The criteria of toxicity of substance should be relevant to the mode of entry into the body. Ingestion is very unlikely to be the route and therefore those toxic indices for skin contact or inhalation, whichever is the more likely in any particular case, should be the indices to use.

The results of animal tests may lead to extremely pessimistic conclusions if uncritically applied to predict fatalities among a population at risk. It is necessary to take account of lack of homogeneity in the composition of clouds, the ability of human to use personal protection, to shelter, to escape, or to receive medical treatment. These factors, if ignored, may lead to predictions which are pessimistic by several orders of magnitude.

#### **26.9. CLASSIFICATION OF TOXIC SUBSTANCES.**

There is a need to classify toxic substances with acute effects and which is of relevance to the chemical and process industries. This needs to take account firstly of inherent toxicity relevant to the mode of attack and of such factors as dispersive energy, persistence, mode of attack, injury to fatality ratio and long term effects. Industrial significance should be the criterion which determines the priority with which such assessments are made. A provisional assessment in the Report, giving weight to these various factors, suggests that some substances, with inventories of 1 kg in the present Annex III, may rank as major-accident hazards no higher than chlorine which has an inventory in the Annex of, at the present time, 50 tonnes.

#### **26.10. THE PROBLEMS OF POLYCHLORINATED AROMATICS AND PESTICIDES.**

It is impractical to list exhaustively the enormous numbers of hazardous substances which could fall into these categories.

It is proposed, therefore, to create a category of "major-accident hazard industries" which would be subject to Article 5 regardless of their inventories of dangerous substances. These would initially be those industries processing polychlorinated aromatics and those manufacturing pesticides.

It would be anticipated that control of these would largely cover any problem of acute environmental contamination.

#### **26.11. SCALE DEPENDENCY OF TOXICS.**

For the present, and pending more accurate information, the mortality index of toxic substances should be treated as being invariant of mass. This assumption is likely to be, if anything, pessimistic so far as large scale releases are concerned.

#### **26.12. QUANTIFICATION OF CHLORINE HAZARDS.**

The use of both the mortality index approach and the equal probability approach suggests a mortality index from store tank failures of 0.5. This agrees

with earlier conclusions based upon mean value

#### 26.13. QUANTIFICATION OF MUSTARD GAS

Comparison of the mortality index for mustard gas in the First World War, suggests that mustard gas caused far fewer fatalities than chlorine per tonne. However, the cost of injury, for mustard gas was much higher. The categorisation of mustard gas as a "non lethal" substance, and the fact that mustard gas has 50,000 times the persistence in the environment than has chlorine, even though it is a liquid at room temperature, casts doubt upon other low inventories.

#### 26.14. QUANTIFICATION OF METHYL ISOCYANIDE

Data on the toxicity of methyl isocyanide, the substance, when inhaled, is about 25 times that of chlorine, would give it a mortality index of about 12.

The horrendous death toll at Bhopal can only be made for the very high population density and the flimsy nature of the housing.

#### 26.15. THE FUTURE OF ANNEX III.

It is proposed that, in future, inventories of toxic substances and that, accordingly, Annex III be phased out.

The bases for regulating explosives, should be as recommended in 26.6, 26.7 and in 26.8.

#### 26.16. REVISION OF ANNEX II.

It is proposed that this Annex be retained in its present form. It is proposed that Article 5 should be retained in Annex III or in any Regulations which may supersede it. Articles 3 and 4 should be, uniformly, retained in Annex II and it is proposed that this fraction be one-tenth.

#### 26.17. REVISION OF ANNEX I.

It is proposed that a more general definition of "chemical processes" be given in the detailed listing of chemical processes. Electrolysis should be substituted for "by means of electrical energy".

It is proposed that water treatment, air conditioning, and the formulation and packaging of explosives should be added to the list.

index.

with that for chlorine gas, which caused far fewer fatalities (i.e. including non-fatal injuries) than chlorine in the current American inventory. Yet Annex III rates mustard gas as a major-accident hazard and chlorine is not. This simple comparison casts doubt upon the current inventory.

#### ANNEX III.

but they suggest that the current inventory of chlorine. This would be a significant improvement.

is figure, if allowance is made for the flimsy nature of the housing.

ed by means of Regulation.

toxic releases would be reduced.

inventories for the application of those set out in Annex II. Inventories for application of those of Article 5 should be, uniformly, retained in Annex II and it is proposed that this fraction be one-tenth.

en for (1) in place of (2). It is proposed that the definition of "chemical processes" be given in the detailed listing of chemical processes. Electrolysis should be substituted for "by means of electrical energy".

ion and separation of chemicals and energy gases should be added to the list.

#### 26.18. REVISION OF ANNEX IV.

(a) The indicative criteria for toxic substances be reduced to one category an LD<sub>50</sub> of less than 400 mg/kg by the cutaneous route or by an equivalent value for inhalation.

Any substance less toxic would not constitute a "dangerous substance" within the provisions of the Directive.

(b) Flammable substances should be treated as falling within at least 5 categories.

(1) Flammable gases as liquefied gases stored at atmospheric temperature but above atmospheric pressure.

(2) Flammable gases as liquefied gases stored at or near atmospheric pressure but maintained at a temperature below atmospheric by refrigeration.

(3) Highly volatile flammable liquids stored at atmospheric temperature.

(4) Flammable liquids stored at atmospheric temperature.

(5) Flammable liquids maintained as liquids by pressure above their atmospheric pressure boiling point.

It may be desirable to add an intermediate category between (3) and (4).

(c) Explosive substances should be categorised by their blast energy relative to TNT.

(d) Annex IV should provide for the existence of other categories which may be deemed to be dangerous but which do not fall within the categories listed above.

## APPENDIX I.

### THE VALIDITY OF LD<sub>50</sub>.

In the field of risk analysis there has been criticism of the use of LD<sub>50</sub> (or LC<sub>50</sub> which can be converted to an LD<sub>50</sub> value). There have been arguments in favour of LD<sub>10</sub>, or even LD<sub>01</sub>, as a basis for estimating radii of harm.

The present author believes that these are not of value for estimating threshold values. Their application to the determining of threshold values appears to be unrealistic on three principal grounds:-

- (1) Such reliable theoretical models do not exist.
- (2) At such low LD values the disparity between the fatalities deduced from animal experiments and actual fatalities would be wider still.
- (3) To assess LD<sub>10</sub> and LD<sub>01</sub> values would call for an enormous research programme involving vast numbers of animals and it may well be that there would be serious public resistance to such widespread animal experimentation which, to obtain statistical reliability, would kill even more animals than would be killed in establishing LD<sub>50</sub> values.

It is recommended instead that, using the rank order of the industrial significance in the Community of the substances concerned to determine priority, there be an attempt to assess LD<sub>50</sub> values in the first instance from the literature. Where no satisfactory assessment can be so made, and only then, should fresh animal experiments, under closely standardised conditions, then be instituted.

It must be borne in mind that LD<sub>50</sub> for an animal is, at best, only a coarse indicator of lethality in man. Even so, the author would contend that a set of inventories related to chlorine by even coarse indicators would be more valuable than the present Annex III which is almost totally lacking in rationale.



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