ECONOMIC COMMISSION FOR EUROPE **INF.4E**

INLAND TRANSPORT COMMITTEE

Working Party on the Transport of Dangerous Goods

Joint Meeting of the RID Safety Committee and the
Working Party on the Transport of Dangerous Goods
(Bern, 20-24 March 2006)

Study on the relevance of the system of exemption for the transport of hazardous goods packed in limited quantities

Transmitted by the Expert from France

INERIS
INSTITUT NATIONAL DE L'ENVIRONNEMENT INDUSTRIEL ET DES RISQUES

Study on the relevance of the system of exemption for the transport of hazardous goods packed in limited quantities.

FINAL REPORT

Ministry of Equipment, Transport and Housing.

DTT / MD

Certification Division

FEBRUARY 2002

INERIS DCE 01 28739
Mko-R1-337

Study on the relevance of the system of exemption for the transport of hazardous goods packed in limited quantities.

Final report

Ministry of Equipment, Transport and Housing.

DTT / MD

FEBRUARY 2002

M-A KORDEK

	Drawn up by	Checked by	Approved by
NAME	M-A KORDEK	G MARLAIR	C MICHOT
Position	Assessment of Dangerous Goods Head of Unit	Accidental Risks Divisiont	Certification Division Manager
Initials			

CONTENTS

∗ INTRODUCTION

The regulations on the transport of hazardous goods, by whatever means, provide for the exemption from the majority of their provisions, in cases where the hazardous goods being transported are packed in limited quantities in combined packaging : indeed, the regulations on the transport of hazardous substances take the view that there is little or no risk for certain hazardous substances once they have been packed in limited quantities.

During the discussions which took place during the last biennial meeting of the UN Committee of Experts on the Transport of Hazardous Goods, several representatives of the authorities concerned expressed doubts about the safety of goods tranported under this system of exemption.

In France, summary analyses carried out on the occasion of recent events (accidents in tunnels) came to the conclusion that goods transported under this sytem of exemption could present not-inconsiderable risks in the event of an accident.

A study has therefore been carried out at the request of the Ministry of Equipment, Transport and Housing – in a letter dated the 15th of June 2001 – which consisted of assessing the consequences of accidents involving loads containing hazardous goods packed in limited quantities in comparison with loads of the same overall size containing goods in cases that do not enjoy the system of exemption for limited quantities.

This study sets out to confirm whether or not the assumption that there is no risk in the case of a substance that has been classified as hazardous when it is packed in limited quantities is borne out by the evidence.

This bibliographical study is not exhaustive. It describes examples in order to compare the risk and consequences between the following types of case :

- goods packed in limited quantities that enjoy exemption
- goods packed in large quantities that are subject to all the provisions of the regulations on hazardous substances.

∗ EXEMPTIONS RELATING TO THE TRANSPORT OF HAZARDOUS GOODS PACKED IN LIMITED QUANTITIES

This section sets out the exemptions relating to the transport of hazardous goods packed in limited quantities as given in the UN recommendations and in the ADR regulations on road transport.

In this study, the provisions for limited quantities laid down in the regulations on other means of transport have not been taken into account.

2.1 UN RECOMMENDATIONS :

A hazardous substance may be transported and exempted from the provisions relating to the transport of the specified substance simply by complying with the following provisions :

- Limited quantities :
  - the limited quantity applicable to each substance is specified in column 7 of the list of hazardous substances in section 3 of the UN recommendations,
  - for substances in classes 1, 6.2 and 7, no limited quantity is authorised. Some substances from other classes may also be banned for transport in limited quantities : the word "NONE" is then entered in column 7 of the list of hazardous substances.
- Packaging conditions :
  - Inner packages are placed inside appropriate outer packages. These packages must comply with other provisions relating to their construction. The gross weight of the case must not exceed 30kg.
  - The outer packages may consist of retractable or extensible covers if the inner package is not likely to break or be easily perforated. The gross weight of the case must then not exceed 20kg.
  - In class 8, packaging group II, there is a specific provision : if the inner package is fragile (glass, stoneware, porcelain), it must be placed inside a rigid compatible intermediate package.
- Provisions to be complied with :
  - The same case may contain different hazardous substances packed in limited quantities provided that these substances cannot react with one another in the event of a leak.
  - These cases do not have to show any special labelling. It is not necessary to impose, inside a vehicle or a container, provisions for the separation of these hazardous substances.
  - The words « in limited quantities » must be added to the description of the consignment.

A new provision on labelling appeared in the revised twelfth edition of the UN recommendations (ST/SG/AC.10/1/Rev.12) :

- A lozenge-shaped label must be attached to the case showing the UN number of the hazardous substance that is being transported in limited quantities. If the case contains several hazardous substances, all the UN numbers must be shown.

Moreover:

- **Hazardous goods packed in limited quantities and intended for personal use (packaging and distribution by retail sale) are exempted from displaying the official transport description and UN number on the packaging and they are likewise exempted from the requirements concerning the transport document.**

2.2 ADR

The European agreement on the international transport of hazardous goods by road (ADR) has transposed the exemptions for the transport of hazardous substances packed in limited quantities in the following way :

A hazardous substance may only be transported and exempted from the provisions relating to that substance in accordance with the following provisions :

- the limited quantity applicable is specified for each substance in Table A "List of Hazardous Goods ". All hazardous substances have been gathered together into limited quantity categories called "LQX": the table below "Table 1"(section 2.4) shows the classes and packaging groups corresponding to each LQ category.
  Each LQ category specifies :
- ➢ the authorised weight for the inner package
- ➢ the weight for the outer package

- ➢ for substances in classes 1, 6.2 and 7, no limited quantity is authorised.
- ➢ Some substances from other classes may also be banned for transport in limited quantities. All these substances are shown by the code "LQ0" in column 7 of Table A "List of Hazardous Goods" : it should be noted that substances in class 4.2 are not exempted from the provisions of the ADR regulations whatever the quantity per inner package.

- So the provisions to be complied with are :

  - ➢ For each LQ category, the nature of the outer package should also be shown.
  - ➢ The marking of the case should be as follows :
    - if a single type of hazardous goods is being transported, the UN number is to be affixed, preceded by the letters UN

    - if the case contains several different types of hazardous goods, the following information is to be affixed :
      - the UN numbers of all the different types of hazardous goods, preceded by the letters UN, or
      - the LQ letters, where LQ is an abbreviation of "Limited Quantities".
    - These various items of information are to be entered on a lozenge-shaped label.

2.3 Differences between UN and ADR

In the ADR, an assessment of the risks has been made by specifying LQ categories, which take into account the hazards presented by the various classes and, within these classes by making a gradation according to the packaging group : in this way a limited quantity is laid down for the inner package and the outer package.
In the UN recommandations, a limited quantity has been specified for the inner package according to the class and packaging group, if there is one. As regards the outer package, the provisions apply whatever the class or packaging group.
For each of these two sets of regulations, splitting the hazardous substance into smaller amounts enables it to be exempted from the provisions on the transport of hazardous goods.
However, no information is required on the total load of hazardous substances per unit of transport, so it is possible to have large capacity loads of hazardous substances in packages enjoying exemption under the limited quantities system. Such a load could be the same size as a load containing packages of hazardous substances not enjoying exemption under the limited quantities system.
We have therefore devoted our attention to the effect of the total quantity of hazardous goods packed in limited quantities on fire and on the environment.

2.4 Comparison between the 'UN and ADR :

In the following table, the limited quantities laid down in the UN recommendations and in the ADR are compared :

- (1) : column 1 is the LQ category in the ADR,
- column (2) gives details of the class and packaging group relating to this particular LQ category,
- column (3) gives details about the physical state of the substance,
- column (4) sets out the limited quantities per inner package according to the ADR and the UN recommendations. The information in brackets, indicates the quantity per outer package according to the ADR.

- column (5), shows the splitting up into smaller quantities as determined from the values given in the ADR. This splitting up corresponds to the ratio of the limited quantity per outer package to the limited quantity per inner package.

TABLE 1 :

LQ category in ADR (1)	Class, packaging group (2)	Physical state, comments (3)	Quantity : per inner package (per outer package) (4)		Splitting up into smaller quantities (5)
			ADR	UN	ADR
LQ0	1, 7, 6.2	No exemption	0	0	0
LQ1	2	Gases *	120 ml (30kg)	120 ml	250
LQ2	2	Gases**	1 l (30 kg)	1l	30
LQ3	3, I		500 ml (1 l)	0	2
LQ20	8, I	Liquid product n.s.a	100 ml (400 ml)	0	4
LQ21	8, I	Solid product n.s.a	500 g (2kg)	0	4
LQ29	9, II	3 polyhalogenated products	500 ml (2 l)	1 l	4
LQ4	3, II		3l (12 l)	1 l	4
LQ5	3, II	Alcoholic drinks 70% by volume	5 l (X)	1 l	X
LQ6	3, II	Vapour pressure at 50°C : 110 / 175 kPa	5 l (20 l)	5l	4
LQ7	3, III		5l (45 l)	5 l	9
LQ8	4.1, II		3 kg (12 kg)	0,5 kg	4
LQ9	4.1, III 6.1, III	Solid product	6 kg (24 kg)	3 kg	4
LQ10	4.3, II 5.1, II	Liquid product	500 ml (30 kg)	500 g	60

Gases* : this category comprises non-flammable and non-toxic gases that only show a single hazardous property and toxic gases with other hazardous properties.

Gases** : this category comprises aerosols and low capacity receptacles containing gases which only possess a single hazardous property.

TABLE 1 (continued)

LQ category in ADR (1)	Class, packaging group (2)	Physical state, comments (3)	Quantity : per inner package (per outer package) (4)		Splitting up into smaller quantities (5)
			ADR	UN	ADR
LQ11	4.3, II 5.1, II 5.2	Solid product 5.2 : solid OP of type D, E, F	500 g (30 kg)	500 g	60
LQ12	4.3, III 5.1, III	Except UN 1396 : 4.3, II	1 kg (30 kg)	4.3, III : 1 kg 5.1, III : 1 kg UN 1396 : 500g	30
LQ13	4.3, III 5.1, III	Liquid product	1 l (30 kg)	4.3, III : 1kg 5.1, III : 1 kg	30
LQ14	5.2	Liquid OP of type B, C.	25 ml (30 kg)	25 ml	1200
LQ15	5.2	Solid OP of type B, C.	100 g (30 kg)	100g	300
LQ16	5.2	Liquid OP of type D, E, F.	125 ml (30 kg)	125 ml	240
LQ17	6.1, II	Liquid product	500 ml (2 l)	100 ml	4
LQ18	6.1, II	Solid product	1 kg (4 kg)	500 g	4
LQ19	6.1, III 8, III	Liquid product	3 l (12 l)	1 l	4
LQ22	8, II	Liquid product	1 l (4 l)	1 l	4
LQ23	8, II	Solid product	3 kg (12 kg)	1 kg	4
LQ24	8, III	Solid product	6 kg (24 kg)	2 kg	4

LQ category in ADR (1)	Class, packaging group (2)	Physical state, comments (3)	Quantity : per inner package (per outer package) (4)		Splitting up into smaller quantities (5)
			ADR	UN	ADR
LQ25	9, II	Asbestos, Castor-oil plant	1 kg (4 kg)	none	4
LQ26			500 ml (2l)		4
LQ27	9, III	Solid product	6 kg (24 kg)	None except UN 3077 : 5 kg	4
LQ28	9, III	Liquid product	3 l (12 l)	5 l	4

OP : Organic Peroxides.

A code LQ26 was specified in the ADR, but this code is not assigned to any substance listed in the ADR's Table A "List of Hazardous Goods".

It should be noted that :

➢ alcoholic drinks (70% by volume) (class 3, Packaging group II) are exempted below an inner package quantity of 5l, but there is no limitation on the outer package ; the UN lays down a lower limited quantity of 1l.

- substances in class 4.2 are not exempted from the provisions of the ADR no matter what their quantities,
- substances in classes 4.1, 4.3, 5.1, 6.1 and 9 whose packaging group is I are not exempted from the provisions of the ADR.
- depending on the physical state of the substance, whether solid or liquid, for a substance in the same class and the same packaging group, the maximum authorised quantity under the limited quantity system is always lower in the liquid state than in the solid state.
- In the ADR some substances will have a limited quantity for the inner package greater than that in the UN recommendations, but the package overall will contain a lesser quantity of hazardous substances than under the UN recommendations.

∗ RISK ANALYSIS BY CLASSES OF GOODS

∗ THE RISK TO THE ENVIRONMENT

There can be a number of different types of risk to the environment, namely :
- air pollution,
- water pollution,
- toxicity for people intervening at the scene of the accident.

As regards air pollution, this risk may arise when toxic fumes are given off from a fire : we have not studied this point, as in a ventilated fire the phenomenon of dispersion will limit this risk by comparison with the effects of the fire, which will be studied later in the report.

The system of exemption for hazardous substances in limited quantities is not applicable to the goods which come under class 6.1, Packaging Group I, « highly toxic substances".
Consequently, the risk of a direct toxic effect for people intervening at the scene of an accident is substantially reduced.

We have concentrated more especially on the case of toxic substances which in the event of an accident may harm the environment and in particular the aquatic environment.
Some substances are liable to accidental spillage and so the consequences of any such pollution need to be known.
Splitting them up into smaller amounts should limit this risk. So we have studied a few examples of the effects of an accidental spillage of these products when packed in limited quantities.

The class mainly concerned by this risk is class 6.1, packaging group II (PG II = moderately toxic substances) and packaging group III (PG III = slightly toxic substances).
In the remainder of the study, we will analyse the risk according to the degree of toxicity of the substance :
- Moderately toxic substances, PG II,
- Slightly toxic substances, PG III.

∗ Class 6.1, packaging group II : moderately toxic substances

Goods that come under class 6.1 with a packaging group II are "moderately toxic substances".
The maximum inner and outer packaging quantities are respectively : 500 ml for the inner packaging, and 2 litres per case, making a total of four bottles per case, when a liquid is involved.

In the following examples, we will study the effects on the environment of the spillage of a 500 ml bottle containing a 100% concentrated substance. From the authorised legal contents, we will calculate the amount of water which may be polluted by the accidental spillage of such a toxic product.

∗ Aniline

This substance bears the official description UN 1547, Aniline.

According to the European Directive on Classification, Packaging and Labelling, its EC classification (EEC Directive 67/548) is :

- N (hazardous to the environment)
- R50 (highly toxic to aquatic organisms).

A concentration that is without toxic effects on the aquatic environment (= PNEC) was put forward in the risk assessment carried out under (EEC) Regulations n° 793/93. It is set at 1.5 µg/l. Above this PNEC, it is assumed that adverse effects on the ecosystem appear.

∗ Volume of water contaminated :

Assuming an accidental spillage into surface water (for example a lake), involving a single bottle containing 500 ml of the substance (i.e. about 500 g with a density of 1.022 at 20 °C), up to 333 350 m^3 of water can be contaminated simply by the effect of dilution. Assuming that all 4 containers (that is to say a complete case) break open, up to
1 333 350 m^3 of water can be contaminated.

A concentration without toxic effects on the working of effluent treatment plants was proposed in the risk assessment. It is set at 100 µg/l for municipal effluent treatment plants not adapted for aniline.

Assuming an accidental spillage into the sewers, substantial concentrations can build up at the entrance to the rainwater treatment plant. However, a certain amount of mixing with other liquid waste can be assumed in the settling and aeration tanks. In order to calculate the concentration in the aeration tank, the default values of 2000 m3/d (volume of effluent) and 7.8 hours (hydraulic retention time) proposed in the Technical Guidance Document on risk assessment for chemical substances (EC, 1996) for characterising a municipal effluent treatment plant can be used. [4]

Elimination by biodegradation in the aeration tank is not a valid hypothesis since the microorganisms will not have had time to adapt to the substance. The phenomena of adsorption on the activated sludge and volatilization could be taken into account, but can be regarded as negligible in the case of aniline.

With 500 ml of the substance (i.e. about 500 g with a density of 1.022 at 20 °C), a concentration of 770 µg/l may be reached in the aeration tank. Assuming that all 4 inner containers break open, a concentration of 3080 µg/l would be reached. In both cases, an adverse effect on the working of the effluent treatment plant may therefore occur.

* Chloroacetic acid

This substance bears the official description, chloroacetic acid in solution, UN 1750 : this substance presents a subsidiary risk : the risk of corrosion.
We were principally concerned with the risk of toxicity to aquatic environments.
According to the European Directive on Classification, Packaging and Labelling, its EC classification is :

- N (hazardous to the environment)
- R50 (highly toxic to aquatic organisms)

A concentration that is without toxic effects on the aquatic environment (= PNEC) was put forward in the risk assessment carried out under (EEC) Regulations n° 793/93. It is set at 0.58 µg/l. Above this PNEC, it is assumed that adverse effects on the ecosystem appear.

Assuming an accidental spillage into surface water (for example a lake), involving 500 ml of the substance (i.e. about 790 g with a density of 1.580 at 20 °C), up to 1 362 000 m^3 of water can be contaminated. Assuming that all 4 containers break open, up to 5 448 000 m^3 of water can be contaminated.

A concentration without toxic effects on the working of effluent treatment plants was proposed in the risk assessment. It is set at 1600 µg/l for municipal effluent treatment plants.

Elimination by biodegradation in the aeration tank is not plausible since the microorganisms will not have had time to adapt to the substance. The phenomena of adsorption on the activated sludge and volatilization could be taken into account, but can be regarded as negligible for chloroacetic acid.

With 500 ml of the substance (i.e. about 790 g with a density of 1.580 at 20 °C), a concentration of 1215 µg/l may be reached in the aeration tank. Assuming that all 4 containers break open, a concentration of 3645 µg/l would be reached. In this second case, an adverse effect on the working of the effluent treatment plant is possible.

∗ **Class 6.1, packaging group III : slightly toxic substances**

Goods that come into class 6.1 with a packaging group III are "slightly toxic substances".

The maximum inner and outer packaging quantities are respectively :3 litres and 12 litres

∗ Trichloroethylene

This substance bears the official description, trichloroethylene, UN 1710.

According to the European Directive on Classification, Packaging and Labelling of hazardous substances, its EC classification is :

- R52/53 (noxious to aquatic organisms, may lead to harmful long-term effects)

A concentration that is without toxic effects on the aquatic environment (= PNEC) was put forward in the risk assessment carried out under (EEC) Regulations n° 793/93. It is set at 115 µg/l.

Assuming an accidental spillage into surface water (for example a lake), involving 3 litres of the substance (i.e. about 4395 g with a density of 1.465 at 20 °C), up to 38 200 m^3 of water can be contaminated. Assuming that all 4 containers break open, up to 152 800 m^3 of water can be contaminated.

A concentration without toxic effects on the working of effluent treatment plants was proposed in the risk assessment. It is set at 1300 µg/l for municipal effluent treatment plants.

Elimination by biodegradation in the aeration tank is not plausible since the microorganisms will not have had time to adapt to the substance. The phenomena of adsorption on the activated sludge and volatilization could be taken into account. For trichloroethylene, an elimination by adsorption and by volatilization of 92% is estimated by the SIMPLETREAT model as proposed by EC (1996) [4].

With 3 litres of the substance (i.e. about 4395 g with a density of 1.465 at 20 °C), a concentration of 540 µg/l may be reached in the aeration tank. Assuming that all 4 containers break open, a concentration of 2160 µg/l would be reached. An adverse effect on the working of the effluent treatment plant is therefore possible in the second case.

* Tetrachloroethylene

This substance bears the official description, tetrachloroethylene, UN 1897.

According to the European Directive on Classification, Packaging and Labelling of hazardous substances, its EC classification is :

- R51/53 (toxic to aquatic organisms, may lead to harmful long-term effects)

A concentration that is without toxic effects on the aquatic environment (PNEC) was put forward in the risk assessment carried out under (EEC) Regulations n° 793/93. It is set at 51 µg/l.

Assuming an accidental spillage into surface water (for example a lake), involving 3 litres of the substance (i.e. about 4870 g with a density of 1.623 at 20 °C), up to about 95 500 m^3 of water can be contaminated. Assuming that all 4 containers break open, up to 382 000 m^3 of water can be contaminated.

A concentration without toxic effects on the working of effluent treatment plants was proposed in the risk assessment. It is set at 11 200 µg/l for municipal effluent treatment plants.

Elimination by biodegradation in the aeration tank is not assumed since the microorganisms will not have had time to adapt to the substance. The phenomena of adsorption on the activated sludge and volatilization could be taken into account. For tetrachloroethylene, an elimination by adsorption and by volatilization of 93.4% is estimated by the SIMPLETREAT model as proposed by EC (1996).

With 3 litres of the substance (i.e. about 4870 g with a density of 1.623 at 20 °C), a concentration of 494 µg/l may be reached in the aeration tank. Assuming that all 4 containers break open, a concentration of 1978 µg/l would be reached. An adverse effect on the working of the effluent treatment plant is unlikely in either case.

* **Conclusions on the risk to the environment**

In the case of the two moderately toxic substances from packaging group II chosen above, risks to effluent treatment plants have been demonstrated for both of them. Probable contamination effects on large quantities of surface water have also been quantified (> 1 000 000 m^3).

In the case of the two slightly toxic substances from packaging group III chosen above, risks to effluent treatment plants have been identified for only one of the substances. Probable contamination effects on smaller quantities of surface water have also been identified (< 1 000 000 m^3).

The above exercise needs to be repeated on a higher number of substances, but it is clear here and now that the spillage of even the small quantities connected with the limited quantities system is liable to have serious consequences on the aquatic environment, especially the moderately toxic substances from packaging group II.

These consequences are comparable to the effects of quantities close to 1000 litres of ecotoxic substances that are destined to be regulated in the context of the transport of hazardous goods. (LC50 <1mg/litre).

∗ THE "CORROSION" RISK

No information about this risk was found in the literature.

In the UN recommendations, substances in class 8 with a packaging group II and III are the ones which can be exempted from the provisions of the regulations on transport when they are packaged in limited quantities.

On the other hand, the regulations on transport by land (ADR) authorise substances in class 8 with a packaging group I to be transported in limited quantities.

Even in limited quantities of 100 ml, which is the value for class 8 packaging group I, this quantity is sufficient to cause skin damage to any person touching a case containing a bottle of this substance which might leak or be broken : indeed, these substances act rapidly, destroying whole thicknesses of tissue within 60 minutes.

No precautions are likely to be taken when loading or unloading this case, since no warning will appear on it. In fact, it is not compulsory to affix information on the cases about the classification and labelling of their contents.

For the substances in class 8 that belong to packaging groups II and III, this risk is smaller : these substances destroy skin tissues over a period of several days. Except in the event of a problem during transport, principally during loading and unloading, any intervention will only be of short duration. However it is important to note that once it has begun, the destructive action on the tissues may continue even after the period of direct exposure ceases.

It is also important to remember that certain substances in this class 8 may present other subsidiary risks such as toxicity.

The analysis of this risk would then proceed as studied previously (see section 3.1).

∗ THE "FIRE" RISK :

Even though the scope of this study is limited to hazardous substances in the conventional sense of the term, an examination of the fire risk must go beyond the notion of substances that are generally considered flammable, as listed in class 2, 3 or 4.

In fact, the potential scale of a fire initially involving flammable hazardous substances in limited quantities will be conditioned by the combustibility of many other components as the scenario unfolds : packaging, outer packaging, materials from which the trailers are made, as well as the presence of fuel used by the tractor units (the tank may contain up to 1,500 litres).

However, we have concentrated more especially on studying the "fire" risk with regard to two classes for which the consequences of this risk are considerable :

- class 2 : and within class 2 we have devoted our attention more especially to a particular object, namely : aerosols. In fact, when these aerosols are designed as consumer goods, the quantity per aerosol is often the value corresponding to the limited quantity value : the last provision of the section on exemptions relating to the transport of hazardous goods applies for this type of substance.
- class 3 : flammable liquids are also often packaged in limited quantities when they are then used as consumer goods.

∗ Class 2 : the example of aerosol dispensers [1]

∗ Description of aerosol dispensers :

Aerosol dispensers bear the official description "AEROSOL" and the UN number, 1950.

There are several types and they are distinguished by their classification code : this code represents the group of hazardous properties associated with the object.

These types of object are not subject to the provisions of the ADR if conditions LQ1 and LQ2 are satisfied :

-LQ1 : the maximum quantity in the inner package is 120 ml : the property that these aerosol dispensers have in common is their toxicity which is indicated in their classification code by their T letter and they have a classification code that contains several letters in addition to the T for toxicity.

-LQ2 : the maximum quantity in the inner package is 1 litre : these aerosol dispensers have a classification code containing a single letter which defines the hazard group to which they belong : asphyxiants A, oxidants O or flammable substances F but they are not toxic T.

∗ Description of the aerosols tested :

In order to estimate the effects and consequences of a fire involving aerosol dispensers stored in a storage area, fire tests were recently carried out by INERIS.
For our study, we repeated these tests and used them in the case of the transport of aerosol dispensers.
Indeed this type of object is often transported on pallets in lorries. Therefore the behaviour of such objects in a fire in transit will be identical to that observed in the case of a fire affecting a storage area : indeed, the packaging is identical and is retained for storage after the transport stage.

Among the aerosol dispensers commonly to be found on the market, and therefore transported, are the following :

- Hair spray : capacity 360ml
- Deodorant : 200ml
- Insecticide : 500 ml

These aerosols come into the category of non-toxic aerosols. They belong to the LQ2 group : their overall capacity is well below that set out in the table.

The componants of these aerosol dispensers are often flammable products such as LPG, ethanol, butane, …..(since CFCs were banned).

These aerosol dispensers are contained in cardboard boxes, which may be stacked on a pallet. The number of such dispensers in the boxes varies from 1 to a few multiples of ten.

One transport unit may comprise several pallets and therefore a considerable number of aerosol dispensers : the pallets may be arranged on two levels.

In these tests, the fire was started by setting fire to alcohol in tanks beneath each pallet at ground level : this type of scenario is similar to what could happen with a sheet of fuel leaking from the vehicle's tractor unit in the event of an accident followed by a fire.

During the transport stage, fire represents the main risk with this type of cargo.

∗ Their behaviour in the event of a fire :

During tests simulating a fire in a storage facility containing this type of object packed in cases, the following sequence of events took place :

- all the dispensers exploded, one after another over a period of several minutes,
- debris from the dispensers was hurled about,
- the flammable substances contained in the formulation burst into flames, in the form of a fireball which, at the height of the fire, was almost continuous above the seat of the fire.

The test configurations and the results obtained are shown in the following table :

N°	Type of dispensers	combustion heat (MJ/kg)	Number of pallets	combustion energy 200kg/pallet	Mean flow value * KW/m2	Total duration of the fire In seconds	Mean dimensions of the flames L = length, H = height, L = width
1	DME-based hair spray (360 ml)	2.85	3	17100	10	200	L = 9 m ; l = 3 m ; H = 7 m
2	DME-based hair spray (360 ml	28,5	6	34200	18	250	L = 11 m ; l = 4 m ; H = 12 m
3	DME-based hair spray (360 ml	28,5	9	51300	40	240	L = 13 m ; l = 5 m ; H = 15 m
4	LPG-based deodorant (200 ml)	34	6	40800	30	270	L = 11 m ; l = 4 m ; H = 12 m
5	Insecticide (500 ml) with 57% water and 36% LPG	18	3	10800	4	240	L = 9 m ; l = 3 m ; H = 7 m
6	Cleaning foam (500 ml) with 61% water and 7% butane	7,5	6	9000	1,5	-	The fire did not take hold

* : maximum value of the mean thermal flow measured at a distance of 10m.

When a fire breaks out in a system containing several boxes and therefore several dispensers, it is characterised by a very rapid development and by an intense radiation of the flames : there is a succession of BLEVEs (= Boiling Liquid Expanding Vapour Explosions). Each BLEVE corresponds to a single dispenser and gives rise to the appearance of a fireball measuring between 1 and 2 m in diameter, depending on the unit volumes involved. A BLEVE lasts less than 1 second.

At the height of the fire, BLEVE's are occurring at such a rate that several take place at the same time : the resulting fireball takes the form of a wall of flame the dimensions of which are proportional to how many BLEVEs occur at the same time.

The dimensions of this flame are found to be linked to the number of aerosol dispensers involved, and to the available combustion energy.

However, the scale of the thermal effects of this flame remains well below that of the fireball which would result from the instantaneous BLEVE produced by all the products contained in the dispensers : splitting up into smaller amounts and therefore the notion of limited quantities are justified as they make it possible to reduce the consequences of a fire.

∗ The thermal flow during a fire

From the time of the first explosion which occurs within slightly less than 1 minute after the start of the test, the mean thermal flow increases with instantaneous peaks of thermal flows of varying intensity.

The mean thermal flow reaches a maximum value at the height of the fire then this mean flow decreases as the fire diminishes in intensity. This thermal flow dies out as the explosions become more widely spaced out.

One of the parameters affecting this thermal flow value is the combustion heat of the product : the higher the combustion heat, the higher the thermal flow measured. (Table 2, section 3.3.1.3)

Moreover, the combustion heat is closely linked to the formulation contained in the aerosol dispensers : an aerosol dispenser which has a significant water content will have a lower combustion heat than an aerosol dispenser which only contains flammable constituents.

During tests in an unconfined environment, no excessive air pressure waves were produced.

∗ Conclusions about the fire risk posed by aerosol dispensers:

The effects produced by a fire involving aerosols in « limited quantities » (within the meaning of the standard regulations) are by no means negligible, although less substantial than those generated by the total mass of the contents if they had been placed in a single container.

Indeed, the power of the fire, the radius of action of the flames and the debris hurled about would be likely to considerably impede the actions of the emergency services in the event of an accident..

The presence of outer packaging in cases where there is combined packaging has virtually no effect on the consequences of a fire.

Finally, in the case of aerosols whose contents have a low combustion heat, the consequences are attenuated.

∗ **Class 3 : flammable liquids [2, 3]**

Class 3 : flammable liquids as defined by UN recommendations are liquids, mixtures of liquids or liquids containing solids in solution or in suspension (for example : lacquers, paints, varnishes, etc,… excluding however substances that are classified elsewhere because of their other hazardous properties) which give off flammable vapours at a temperature not exceeding 60.5°C in a closed test (or 65.6°C in an open test).

They can be transported in limited quantities without applying the provisions of the ADR if the inner package has the following maximum quantity:

- for liquids assigned to class 3 and whose packaging group is I : 0.5 l for the ADR and "none" for the UN recommendations.
- for liquids assigned to class 3 and whose packaging group is II : 5 l or 1 l for the ADR and 1 l for the UN recommendations.
- for liquids assigned to class 3 and whose packaging group is III : 5 l for the ADR and 5 l for the UN recommendations : with the maximum quantity per case being 45 l for the ADR.

There are no tests mentioned in the literature that are specific to this class of substance in terms of packaging for transport.
So, in order to assess these exemptions, we studied the results of fire tests on this class : these tests were carried out in order to assess fires affecting storage facilities containing pallets of these kinds of substances packed in various containers, whether stored in cardboard boxes or not and on the basis of the overall quantity.

These tests were carried out by several companies or bodies such as :

- Factory Mutual Research ,
- "National Fire Protection Research Foundation",
- "American Iron and Steel Institute",
- "Distilled Spirits Institute",

in order to be able to issue recommendations for the storage of flammable and combustible products. We used the tables of results published by these companies in order to analyse them in relation to the fire risk as applied to transport.
The tests selected to be used in our study are those in which the fire – in the majority of cases – was uncontrolled even in the presence of sprinkler systems : indeed, in a transport unit, there is no prevention system (set of sprinklers) to limit any outbreak of fire.
So, the conditions and consequences which most closely resemble a fire in a transport unit are those applicable to the tests where no sprinkler system was used or where the fire took hold even with the use of a set of sprinklers.

∗ The test conditions

For our study, we only took into consideration the following parameters :
- the nature of the product,
- the type of container and its capacity,
- the outer packaging.

During these tests, the layout of the pallets and the siting of sprinkler systems installed for safety purposes (type of sprinklers and configuration,…) were also studied : this type of test serves to determine the optimum position and operating conditions of sprinkler systems in storage facilities.

The substances tested were :
- heptane,"HEPTANES", UN 1206, class 3, PG II,
- 99% isopropyl alcohol, "ISOPROPANOL", UN 1219, class 3, PG III
- Ethyl alcohol,"ETHANOL or ETHANOL IN SOLUTION", UN 1170, class 3, PGE II or III,
- paint thinner, "PAINT or SUBSTANCES SIMILAR TO PAINT", UN 1263, class 3, PG I, II and III.
- kerosene, "KEROSENE", UN 1223, class 3, PG III,
- a 50/50 water-alcohol mixture,"ETHANOL or ETHANOL IN SOLUTION", UN 1170, class 3, PG II or III,

The letters "PG" correspond to the Packaging Group.
The following capacities were tested :
- 1 gallon : 3.79 litres
- 5 gallons : 18.92 litres
- 1 quart : 0.95 litres
- 1 pint : 0.47 litres.
- 16 oz : 480 ml
- 8 oz : 237 ml

The containers were of the following kinds :
- metal receptacles (for large capacity cans (5 gals), the metal receptacles are fitted with a polyethylene cap)
- plastic cans,
- glass bottles.

Depending on the nature of the containers, the test fires were started up in different ways. This will be indicated for each substance tested.

∗ Tests on heptane :

The tables below show the tests carried out on this product in two different kinds of containers with different capacities.

Heptane is a substance that comes into class 3, PG II :
- the limited quantity per inner package is 1 litre both for the ADR and for the UN recommendations.

The fires for all these tests were started in the same way : about 40 litres of heptane were poured out and then set alight.
Whatever the capacities used, all the containers tested were metallic.

* Tests on containers governed by the regulations on the Transport of Hazardous Substances

The first series of tests corresponded to an inner package size in excess of the limit which defines the limited quantity. This type of packaging must comply with the provisions of the regulations on transport.
According to these tests, it was found that :

- for tests S7 to S12 with the exception of S11, thanks to the sprinkler system, the fire was brought under control and there was no damage. These sprinkler systems came into operation between 35 and 40 seconds after the fire started.
- for test S11, when the same sprinkler system was installed, but for a larger overall quantity, as a result of the overall height of the pallets being higher, the fire was not brought under control.

Fires involving heptane, in containers of about 4 litres and making up overall quantities of about 600 to 6000 litres, were brought under control in storage facilities by means of sprinkler systems (which came into operation 40 seconds after the fire started) : in a transport unit however this type of safety device does not exist : it would not be possible to bring the fire under control since, as in test S11, the containers would burst open and allow the liquid to burn.
Moreover, the coming into operation of the sprinkler systems is closely linked to the start of the fire : this indicates the speed of a fire involving this type of substance.
These tests clearly show the speed of a fire involving this type of substance and underlines the importance of regulations for these large capacities.

* Comparison of the behaviour according to the packaging

For tests S40 and S41, it was found that the bigger volume containers were less fire-resistant than those with a smaller capacity : in fact, the 0.95 l cans were less damaged than the 3.79 litre ones. Therefore splitting up this hazardous substance into smaller amounts helps to limit the effects : a value of 1 l for heptane represents the correct value.
In test 48, the sprinkler system came into operation after 2 minutes 47s : the 0.95 l containers at the top of the pyramid exploded even when the sprinkler system had started up.
Even if the risk is reduced, it is still there, and so are the consequences.

* Effect of the outer packaging

When one looks at the results of tests S13 and 15, the 20 litre cans were more heavily damaged as a result of a fire than the smaller capacity (5 litre) cans: the smaller capacity (5 litre) cans were packed in boxes, whereas the 20 litre cans did not have any outer packaging.
These tests show the importance of the outer packaging in a fire (an extra barrier to the spread of the fire)

* Effect of the material from which the container is made

If we compare the behaviour of heptane in a fire when packed in plastic containers, we find that there was a tendency for the fire to spread, which was not the case when it was packed in metal containers : a sheet of liquid formed and then caught fire.
In test P6-2, 50% of the goods burned after the HDPE cans melted and allowed the heptane to escape. This phenomenon moreover was accentuated by the fact that this test was carried out on cans that had not been placed in any kind of outer packaging.

REF.	NATURE OF THE CONTAINER	OUTER PACKAGING	TOTAL QUANTITY In litres	SUCCESS IN CONTROLLING THE FIRE	COMMENTS
P6-2	HDPE jerrycan 5 gal (18.2 l)	None	606	FNC	The containers burned, melted and allowed the heptane to escape. Even with sprinkler : 50% loss :
S7-3	Metal container 1 gal : 3.79 l	Ordinary cardboard box	606	FC	Only the cardboard boxes burned. The heptane was not involved.
S8-5	Metal container 1 gal : 3.79 l	Ordinary cardboard box	1817	FC	Only the cardboard boxes burned. The heptane was not involved.
S9-9	Metal container 1 gal : 3.79 l	Ordinary cardboard box	3634	FC	Only the cardboard boxes burned. The heptane was not involved
S10-11	Metal container 1 gal : 3.79 l	Ordinary cardboard box	5450	FC	Only the cardboard boxes burned. The heptane was not involved
S11-12	Metal container 1 gal : 3.79 l	Ordinary cardboard box	7267	FNC	The cardboard boxes burned. 15 empty containers: burst open violently

FC : Fire brought under control ; FNC : Fire not brought under control.

S12-13	Metal container, 1 gal : 3.79 l	Ordinary cardboard box	6056	FC	Only the cardboard boxes burned. The heptane was not involved
S13	Metal container, 1 gal : 3.79 l in cardboard box 5 gal : 18.92 l	Cardboard box No packaging	3331	FNC	5 gal container: bulging and emptying through melted PE cap 1 gal container: bulging and one container split open violently
S15	Metal container, 1 gal : 3.79 l in cardboard box 5 gal : 18.92 l	Cardboard box No packaging	5299	FC	24 of the de 5 gal containers came open as a result of the PE cap melting
S40-11	Metal container, 1 gal : 3.79 l in cardboard box 1qt : 0.95 l	Containers in secondary packaging: cardboard boxes	4156	Fire suppressed	None of the containers burst open.

FC : Fire brought under control ; FNC : Fire not brought under control.

S41-12	Metal container, 1 gal : 3.79 l in cardboard box 1qt : 0.95 l	Containers in secondary packaging: cardboard boxes	4550	FNC	3 of the (1 gal) containers broke open and 40 to 50 containers were damaged. Three containers came open and 15 to 20 were leaking.
S48	Metal container, 5 gal : 18.92 l 1 gal : 3.79 l 1qt : 0.95 l	No outer packaging	757	FNC	The 1 litre cans were placed at the top of the pyramid of cans: consequently, several cans would have broken open due to falling. Several 0.95 l cans exploded even after the sprinkler system had come on (that is to say after 2 minutes 47s).

FC : Fire brought under control ; FNC : Fire not brought under control.

∗ The case of isopropyl alcohol :

The tables below show the tests carried out on this product in two different kinds of containers with different capacities.

Isopropyl alcohol or isopropanol is a substance that comes into class 3, PG II or III :

- the limited quantity per inner package is 1l both for the ADR and for the UN recommendations : it is only classifed in packaging group II.

The fire was started using rolls of cellulose soaked in a flammable liquid (a few hundred ml) or with isopropyl alcohol (10 l) in tanks.

∗ Tests on containers which are subject to the regulations on the Transport of Hazardous substances

The first three tests (P4, P5, P16) were carried out for containers whose capacity was greater than that below which exemptions for limited quantities are applicable. For these three tests, the overall quantity was similar. The parameter which varied was the outer packaging : only one type of packaging which was specifically fire-resistant made it possible to limit the damage : these tests were characterised by the formation of a sheet of liquid. It was also found in the case of the non-fire-resistant types of outer packaging that the fire very quickly became out of control in spite of the fact that the sprinkler systems had come into operation above the pallets.
These tests showed the importance of special measures with regard to the packaging of these kinds of substances when they are transported in quantities in excess of the limited quantities.

∗ Tests on containers which are not subject to the regulations on the Transport of Hazardous Substances

Tests P32, P34 and P35 were carried out on low-capacity cans : 1 quart : 0.95 l.
It was found that whatever the overall capacity, by bringing the sprinklers into operation very soon after the fire had started, it did not spread.
It is therefore easier to bring a fire under control when small containers are involved as the sprinkler system helps to bring the fire under control.
This leads us to conclude that in the case of storage facilities, these sprinkler systems are necessary in order to prevent a fire spreading due to sheets of burning liquid.
However, transport units are not and cannot be fitted with sprinkler systems, so the spread of a fire will be difficult to prevent.

Compared with larger capacity containers, flammable liquids packed in small containers help to slow down the effects of a fire, as there is less flammable substance involved. However this comment is true in the case of storage facilities fitted with sprinkler systems.
In a transport unit, this effect will be reduced, principally because of the absence of sprinkler systems : the spread of a fire involving class 3 goods will be reduced if they have been packed in limited quantities, but the task of bringing the fire under control will be just as difficult as in the case of a transport unit carrying unlimited quantities.

Moreover, for tests P36, P37 and P38, it was found that for the same overall capacity of flammable liquid, reducing the capacity of the containers helped to reduce the losses in a fire affecting a storage facility : this was achieved by bringing a sprinkler system into operation very quickly (1 minute 30 seconds) over the area that was on fire.
In this case where a fire involves such substances, the sprinkler system is of great importance : any delay in switching on the sprinkler system results in increased losses and there is time for a sheet of flammable liquid to form.

In the case of a fire in a transport unit, under such conditions, it is inevitable that a sheet of burning liquid will form.
The advantage of packing such flammable substances in limited quantities is to reduce the size of the blazing sheet and therefore help to prevent the fire spreading.
Another factor which limits the spread of a fire is the overall quantity involved.

REF.	NATURE OF THE CONTAINER	OUTER PACKAGING	TOTAL QUANTITY In litres	SUCCESS IN CONTROLLING THE FIRE	COMMENTS
P4-8	Plastic can - HDPE,1gal	Cardboard box: 4 pallets stacked to a height of 4 cardboard boxes.	1635	FNC	55% of the fuel burned. In less than 2 minutes 30 seconds, the burning liquid began to affect the environment.
P5-1	Plastic can – HDPE,1gal	Cardboard box coated with paraffin.	1438	FNC	Less than one pallet burned.
P16	Plastic can – HPDE 1gal	Fire-retardant cardboard box	1453	FC	No significant sheet of liquid even though 114 cans were damaged (sprinkler system first came on after 17 minutes)
P32	Plastic can – HDPE 1 pint	cardboard box	2907	FC	14 boxes damaged by the fire: that is to say 76 litres of alcohol consumed.. Sprinklers came on after : 56 s.
P34	Plastic can – HDPE 1 pint	cardboard box	2736	FC	1 box damaged by a burning can. Sprinklers came on after 25 s
P35	Plastic can – HDPE 1 pint	cardboard box	684	FC	20 boxes damaged : 95 litres consumed Sprinklers came on after 54 s
P36	Plastic can – HDPE 1 pint and 1 gal.	cardboard box	5928	FNC	32 boxes damaged Sprinklers came on after 1 minute 09s

FC : Fire brought under control ; FNC : Fire not brought under control.

P37	Plastic can HDPE 1 gal	cardboard box	4195	FNC	17 boxes damaged that is to say 238 cans burned..
P38	Plastic cans HDPE 0.47 and 0.95l+	cardboard box	4013	FNC	20 of the 1 gal and 15 of the 1 pint boxes burned : 190 burned. The fire began to spread in less than 1

					minute 30s.
P39	Plastic can HDPE 1 gal and 1 quart	cardboard boxes	5518	FNC	359 boxes damaged : 2691 l burned producing a sheet with a diameter of 10.7 m. The sprinklers came on after 2 minutes 10 s.

FC : Fire brought under control ; FNC : Fire not brought under control.

* Other class 3 substances

* Paint thinner :

This substance bears the description: "PAINTS or SUBSTANCES SIMILAR TO PAINTS", UN 1263, class 3 with three possible packaging groups.

In these tests P1, P2 and P3, we do not know to which packaging group these substances are assigned.

These tests were carried out with 3.79 litre capacity cans. The overall quantity was found to be either high (1,600 litres) or lower (600 litres). Even with the use of sprinklers, the fire was intense and a sheet of liquid formed. The fire burned intensely over this sheet of liquid with flames reaching a height of between 3 and 4.5 m for an overall quantity of 600 l.

The HDPE cans were unable to withstand the heat of the fire and melted allowing the paint thinner to escape and catch fire, thus spreading the flames.

* Kerosene

This substance bears the official description "KEROSENE", UN 1223, class 3, PG III.

The exemption for limited quantities applies to containers not exceeding 5 l.

Test P15 was carried out using 0.47 litre capacity bottles. Tests involving the use of fire-retardant material were carried out. The bottles were surrounded by a nylon cylinder and the resulting units were placed in fire-retardant cardboard boxes. The fire was not spread by the liquid sheet formed by the 322 damaged bottles : this sheet did not spread beyond the test zone.

* Ethyl alcohol

This substance bears the official description, "ETHANOL or ETHANOL IN SOLUTION", UN 1170, class 3, PG II or III.

A test P10 on ethyl alcohol was carried out using 237 ml capacity plastic bottles. It was found that the fire engulfed the entire pile of pallets and the fire gradually intensified, but no sheet of liquid was formed.

When this substance is in solution with water, it bears the official description,
" ETHANOL or ETHANOL IN SOLUTION", UN 1170, class 3, PG II or III.

Tests were carried out on this product when packaged in glass bottles : for tests G2 and G4, it was found that the bottles were unable to withstand the fire and started to explode as soon as the fire began : a sheet of burning liquid was formed. Moreover, it was found that the damage with this type of glass container was also more substantial : a large part of the cargo was destroyed.

RÉF.	PRODUCT	NATURE OF THE CONTAINER	OUTER PACKAGING	TOTAL QUANTITY In litres	SUCCESS IN CONTROLLING THE FIRE	COMMENTS
P1-2	Paint thinner	Plastic can HDPE, 1gal	cardboard box	681	FC after 6 minutes with sprinkler.	Containers distorted, melted, empty, as a result of intense sheet of flames. Flames reached a height of 3 to 4.5 m and the diameter of the sheet was 3.66 m.
P2-	Paint thinner	Plastic can HDPE, 1gal	cardboard box	681	FNC	intense sheet of flames (measuring 9.1 m in diameter) + sound of containers breaking open
P3-	Paint thinner	Plastic can HDPE, 1gal	cardboard box	1635	FNC	intense sheet of flames
P10	Ethyl alcohol (>50%)	Plastic-8oz (237 ml) aerosol	cardboard box	545	FC	The fire slowly got bigger with a single sprinkler: the pallets were engulfed in flames produced by the burning product, but there was no sheet of liquid.
P15	Kerosene	Plastic can HDPE, 1 pint + nylon cylinder	Fire-retardant cardboard box	1 022	FC	51 boxes and 322 containers were damaged: as a result there was a sheet of burning liquid in the test zone. No spread beyond this zone..
G2	Ethyl alcohol +water(1/1)	Glass bottle : 0.76 l	cardboard box	3997	FC	85% damaged 1 min 40 : the bottles began to break open..
G4	Ethyl alcohol +water (1/1)	Glass bottle : 0.76 l	cardboard boxes	34474	FC	sheet of liquid measuring 6.1 m in diameter + bottles broken open : 54% damage..

FC : Fire brought under control ; FNC : Fire not brought under control.

∗ Conclusions about class 3 substances :

These tests were carried out to determine the behaviour of flammable liquids in storage facilities. However the test samples were also representative of the sort of amounts that are transported, and the packaging materials concerned are also used for transporting such substances. The tests involved both containers covered by the « limited quantities » exemptions and also ones not covered by this scheme.

Important lessons can therefore be learned from these tests for the transport of flammable liquids.

It emerged that the flammable nature of these substances brings a real danger of a self-perpetuating fire, no matter what the type of container or quantity per container.

The spread of a fire can be slowed down by splitting up the flammable liquids into smaller volumes, but the choice of what kind of container to use is very important.

However, a fire involving these kinds of substances usually develops so rapidly that it is difficult to contain it : indeed, in all the storage facility tests, the sprinkler system was triggered right from the moment the fire first started.

It was found that this class of substances burns quickly and intensely.

The problem which has to be overcome with these substances is the formation of a sheet of liquid, as the containers are perforated or burst open one after another, since there is a danger that this will spread the fire.

Moreover, although it does have an effect, splitting up these flammable liquids into small-capacity containers does not always limit the consequences of a fire in a satisfactory manner. In certain cases (for example p5-1 and p38 with isopropyl alcohol) it proved easier to bring the fire under control in the case of containers which did not come within the « limited quantity » scheme.

Lastly, in several cases, the fire could not be brought under control even after the automatic sprinkler systems came into operation.

Of course the seriousness of the consequences and the scale of a fire involving the formation of a sheet of flammable liquid are linked to the total quantities involved.

* ANALYSIS BY TYPE OF CONTAINER

* THE CONTAINERS FOR AEROSOL DISPENSERS

* Description

The aerosol cans mentioned in section 3 were of the following types :

- tin plate cans with 3 components : 1 cylindrical body + 1 bottom + 1 dome-shaped top to which the valve is attached,
- aluminium cans cast in one piece, to which the valve is attached.

* Their fire resistance

As a fire begins to take hold, each dispenser is affected by a BLEVE which initially involves the receptacle (or can) bursting open. However, depending on the kind of dispenser involved, there are differences in the way it bursts open and in the amount of debris.

* Tin plate cans

These cans consist of a cylindrical body, a bottom and a dome-shaped top to which the valve is attached.

When they are involved in a fire, these cans break open in the area where the body is attached to either the bottom or the dome-shaped top.

As a result of breaking open in this way, the liquefied and overheated gases contained in the can are suddenly vaporised. It is the pressure associated with this vaporisation which causes debris to be hurled about :

- The dome-shaped top or the bottom only weigh a few grammes, and so these kinds of debris cannot be hurled very far.
- Debris consisting of the cylindrical body of the containers, because of its shape, seems to be helped on its way by a thrust similar to that required for propelling a rocket.
- The distances which may be travelled by this second type of debris vary since they depend on the angle of the axis of the dispenser to the horizontal at the moment when it bursts open : however, during the tests, instances of this type of debris being hurled up to a distance of about 100 metres were observed.

* Aluminium cans :

These cans consist of two components only : the aluminium body which is cast in one piece and the valve which is attached to the circular opening.

This kind of can may burst open in the area where the valve is attached, but usually in a fire it simply explodes, with the wall of the can being torn to pieces and the possible formation of small items of debris.

During fire tests on this type of can, the geometry of the debris was such that there was no rocket effect and the maximum distances over which the debris was hurled were well below 100 m.

During tests, it was found that the heat of the fire was sufficient to cause the aluminium to melt.

* Choice of an aluminium or tin plate can

In both these cases, very few dispensers escape undergoing a BLEVE during a fire : those that do are dispensers which receive a mechanical blow from a neighbouring dispenser which has exploded. This impact has the effect of hurling them sufficiently far away (10 to 20 m) to remove them from the intense radiation of the flames, but the impact may also be sufficiently violent to rupture their walls so that they lose their contents more or less rapidly, in the form of a jet of liquid and/or gaseous product which may or may not be on fire.

These dispensers, which correspond to the latter case and which lose their burning contents could be of an incendiary nature. This property will be confined to a short distance (no more than 20 m).

* **CONTAINERS FOR CLASS 3 SUBSTANCES**

During the tests shown in the tables in section 3, the following containers were tested :

- metal tins with a capacity of 1 quart (0.95 litres), 1 gallon (3.79 litres), and 5 gallons (18.92 litres). In the case of the large capacity (5 gal) tins, they were fitted with a polyethylene cap.
- high density polyethylene plastic cans with a capacity of 1 gallon (3.79 litres), 1 pint (0.47 litres) and 1 quart (0.95 litres).
- 0.76 litre glass bottles.

* **metal containers :**

This type of container often has a polyethylene cap on the 3.79 litre capacity containers : this orifice will serve as a safety valve for the product which is heating up inside the tin : the heat will cause it to melt and thus prevent pressure building up inside the container.

Out of all the tests reported here, in only one or two was there a violent rupturing of the metal container.

No test reported the formation of a blazing sheet of liquid which caused the fire to spread.

* **plastic containers :**

In all cases, the cans – regardless of their capacity – burned and melted, allowing the liquid inside to escape and form a sheet of liquid which caught fire and could cause the fire to spread. In the majority of cases, nearly 50% or more of the storage capacity was burned.

It was also found that limiting the overall quantity of product did not help to reduce the risk : indeed, in the case of plastic cans, the result was always the same, regardless of the overall quantity involved.

In the case of plastic cans, the capacity of which varied, the test results always showed that a sheet of liquid formed which then caught fire and therefore heightened the risk of the fire spreading.
Moreover, according to some tests [3], under certain conditions, plastic containers were heard to explode, even though plastic normally tends to melt : this indicates that there was a build-up of pressure in the container before the fire burnt the plastic.

* **Glass containers :**

The majority of the goods packed in glass containers were broken : over 50% in fact.
Moreover, glass containers were heard to explode due to the rise in pressure inside them.
In certain cases this then led to the formation of a sheet of burning liquid.

* **The behaviour of plastic bottles containing flammable liquids in a fire**

Class 3 products are packed in very thick polyethylene (PE) plastic bottles or polyethylene terephthalate (PET) plastic bottles.

The behaviour of these two types of bottles in a fire is very different when subjected to the same levels of heat :

- PET bottles : the heat increases the pressure within the bottle which then splits open : the product inside can then escape. The liquid will then catch fire and form a sheet of flames which spreads the fire up to a distance of 4 m from the position of the bottle.
- PE bottles : the heat causes these bottles to melt and form a bubble above the surface of the liquid. On the surface of this bubble, a hole is formed through which the liquid can escape : the fact of the product boiling does not bring about a rise in pressure inside the container. However, the vapours from the liquid above the hole may catch fire.

The nature of the plastic used to make the container for a flammable liquid is very important : it can help to spread the fire by allowing the burning liquid to escape.

∗ Conclusions about the choice of container for class 3 substances

These substances must be transported in limited quantities within the authorised values. The following recommendations could be made :

- The optimum level of safety is achieved when a metal container fitted with a plastic cap is used : in the event of a fire, this cap will melt thereby allowing the flammable liquid to be evacuated without forming a sheet which would spread the fire to neighbouring areas. Moreover, this would help to prevent a rise in pressure by allowing the product to evaporate through the orifice.
- The consequences are more severe when a plastic container is used : in the event of a fire, a sheet will form which will spread the fire
- The most unfavourable case is that of glass containers : because of the rise in pressure inside the container, the latter explodes, with the danger of solid debris and burning liquid being hurled about.

* PROPOSED IMPROVEMENTS TO THE SYSTEM OF EXEMPTING HAZARDOUS SUBSTANCES FROM THE NORMAL REGULATIONS WHEN TRANSPORTED IN LIMITED QUANTITIES

Whatever the risks studied, whether to the environment, from corrosion or from fire, packing hazardous substances in limited quantities does not do away with the risk, although splitting them up into smaller amounts can limit the consequences of an accident.

However, there is no simple relationship (for example of proportionality) between the extent to which a load of hazardous substances is split up and the seriousness of the consequences of an accident which may happen to this load.

The consequences – as measured from the tests studied – are substantial : hazardous goods transported under the « limited quantities » system cannot be regarded as harmless in safety terms.

So the posting of warning signs indicating that the transport unit is carrying hazardous substances is the least that should be required in order to make anyone who may come into contact with these substances whilst they are being transported from their source to their destination, as well as the emergency services in the event of an accident, aware of the dangers they present.

This could be adjusted to the total quantity carried in the load

Studies should be carried out on the minimum regulations required for inner packaging materials :

-plastic caps for metal containers filled with flammable liquids

-more severe limitations on, or (in certain cases), a complete ban on glass containers

Substances in packaging group I should not be allowed exemption under the limited quantities system (this comment is only applicable to the RID/ADR).

∗ REFERENCES

1 - "Caractérisation du phénomène d'incendie dans un stockage de générateurs d'aérosols", J.Chaineaux, December 2000.

2 - Directory of fire tests involving [the] storage [of] flammable and combustible liquids in containers, Schirmer Engineering Corporation, 2nd edition, October 2000.

3 - "Flammable liquids in drums and smaller containers", Factory Mutual Engineering Corporation, Loss Prevention Data, 7.29, September 1989.

4 - CE (1996) Technical Guidance Document in support of commission directive 93/67/EEC on risk assessment for new notified substances and commission regulation (EC) No 1488/94 on risk assessment for existing substances. European Commission. Office for Official Publications of the European Communities, Luxembourg, 1996