

# BEST PRACTICE GUIDELINES

Flammability

A safety guide for users

Safe working with industrial solvents

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## Foreword

The European Solvents Industry Group (ESIG) provides a single point of contact for information on oxygenated and hydrocarbon solvents in Europe. Through its work with industry and with industry partners, the group cultivates best practice in solvent usage, health, safety and environmental protection. Its main aims are to support responsible care in the use of solvents and to provide advocacy on issues affecting the producers of solvents.

Flammability is one of the main hazards associated with industrial solvents. This document has been developed by ESIG to explain the main characteristics of solvent flammability and to provide recommendations for safe use. It includes the following:

- a summary of the key recommendations that should be borne in mind when handling flammable solvents,
- information on solvent flammability characteristics for readers who need a more detailed understanding of the background to the recommended handling procedures,
- information on the ignition hazards presented by static electricity and details of the associated risk management measures.

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Each company based on its own decision making process may decide to use the Guidance in full, partially or not, as it suits its needs.

European Solvent Industry Group (ESIG)  
[www.esig.org](http://www.esig.org)

## PART 1 General advice for handling flammable solvents

### 1.1 INTRODUCTION

Solvents are crucial in many industrial processes and provide key properties for products such as paints, adhesives, inks, plastics and surface coatings. For further information see the ESIG website at [www.esig.org](http://www.esig.org).

Many hydrocarbon and oxygenated solvents are flammable. Those with a low boiling point produce flammable vapour/air mixtures at ambient temperatures and others can produce flammable vapour/air mixtures when heated. In many applications it is necessary to use either low boiling point solvents or elevated temperatures because, for example, the solvent must evaporate in order to leave behind the required paint or adhesive. Each year there are workplace incidents involving fires or explosions. The root cause of many such incidents is a lack of understanding of the solvent properties that govern the hazards and of the associated process requirements. This safety guide aims to provide the required understanding. A summary of the recommended measures is provided in the Top Ten Tips box.

To develop this theme, we identify the main causes of incidents (see 1.2) and provide key recommendations for prevention (see 1.3). The implementation of the key recommendations requires an understanding of the properties that make solvents hazardous and of the control measures. We provide this information in Part 2 and cover static electricity hazards and controls in more detail in Part 3.

This safety guide provides general advice common to most solvent handling operations but the provision of detailed advice for specific solvents or end uses is beyond its scope. That information can be found in your supplier's Safety Data Sheet (SDS) or, for many end uses, in application specific documentation. For example, safety measures for spray coating and painting are given in References 1 to 9.

# TOP 10 TIPS

## THE WORKPLACE CAN BE MADE SAFER BY FOLLOWING THESE TOP TEN TIPS FOR HANDLING SOLVENTS

1. Understand the solvents you are using and their properties. General information is provided in section 1.3, whilst product-specific hazard information can be found in the supplier's Safety Data Sheet (SDS), which must be provided for each hazardous product that you use.
2. Eliminate ignition sources e.g. No smoking, Safe Systems of Work, equipment selection, minimise static build up by using suitable equipment, flow rates and earthing arrangements.
3. Ensure good ventilation by working in open atmospheres (e.g. keep doors and windows open) or by using forced ventilation.
4. Work at ambient temperatures or below: try to keep the working temperature below the Flash Point by a suitable margin (see section 2.2.3) wherever possible.
5. Provide information, instruction, training and Personal Protective Equipment (gloves, flame retardant clothing, dissipative footwear, etc) to all persons handling solvents.
6. Report all incidents and near misses e.g. leaks. Evaluate and take actions to prevent recurrence.
7. Provide secondary containment solutions such as bunding or oversize drums and provide clean-up and disposal facilities for spills and leaks.
8. Take special precautions when loading or unloading vehicles and containers.
9. Develop a short, succinct Emergency Plan.
10. Consider inert storage solutions such as nitrogen blankets.

## 1.2 COMMON CAUSES OF INCIDENTS

Common causes of incidents include:

- Lack of training, leading to insufficient Manager/Supervisor/Operator understanding, awareness and competence
- Poor control of solvent use in hot areas
- Heating solvents without adequate controls
- Badly designed equipment or installation, leading to unnecessary emissions or even leaks
- Equipment not suited to the job: use only ATEX approved equipment<sup>Ref 10</sup> selected according to the zoning defined in the ATEX workplace directive<sup>Ref 11</sup>
- Equipment failure
- Poorly managed maintenance activities (especially in dismantling or disposal)
- Low understanding of the importance of safeguarding against electrostatic discharges
- Poor implementation of control procedures such as elimination of ignition sources
- Badly managed transfer operations such as the filling and emptying of equipment
- Loading and unloading solvents without taking adequate precautions.

## 1.3 KEY RECOMMENDATIONS FOR PREVENTION

Solvent storage, handling and processing conditions must be carefully controlled to prevent incidents. The control process is known as managing risk. Successful risk management systems minimise the unnecessary release of vapour to the atmosphere and control the presence of ignition sources. Key recommendations for achieving this are:

- Train operators to understand the hazard characteristics and safe handling methods for the specific solvents in their workplace.
- Read the SDS for solvent-specific hazard data. An SDS must be provided by the suppliers of all hazardous products and is often supplied voluntarily for non-hazardous products.
- Read any process-specific safety documentation that is available.
- Understand the significance of the following solvent properties for the assessment of ignition hazards:

**The Flammable (or Explosive) Range.** This denotes the range of solvent vapour concentrations in air for which combustion is possible (see 2.2.2). If measured concentrations are kept sufficiently far below the flammable range (e.g. by ventilation), combustion cannot occur.

**The Flash Point (FP).** This corresponds, very approximately, to the lowest temperature at which the solvent vapours can enter the flammable range. It can be used, with a safety margin of 5 °C or 15 °C as appropriate (see 2.2.3), either to indicate the highest solvent temperature that can be used without producing a flammable atmosphere or, in conjunction with a specified solvent temperature, to assess whether a flammable atmosphere is likely to occur.

**The Auto Ignition temperature (AIT).** This provides a rough guide to the maximum temperature that a mixture of solvent vapour in air can be raised to before self-ignition occurs (see 2.3).



A significant safety margin must be kept between the measured AIT and the operating temperature.

**The electrical conductivity.** If electrostatic charge can accumulate in a solvent, it may generate high enough voltages on the liquid surface to draw discharges capable of igniting a flammable atmosphere (see 3.2.3). The risk of accumulating hazardous charge in a solvent depends on its electrical conductivity. An exact conductivity value is not generally needed for assessing this vulnerability: it is generally sufficient to know whether the minimum solvent conductivity measured in picosiemens/metre or pS/m - could be classified as Low ( $\leq 50$  pS/m), Medium (50 pS/m to 10 000 pS/m) or High ( $> 10\ 000$  pS/m).

Low conductivity solvents can generate hazardous voltages on liquid surfaces during simple liquid handling operations such as filling tanks, drums or other containers. All low conductivity liquids are therefore handled with an increased level of static-control precautions (filling rate restrictions, constraints on location of fine filters etc).

Medium conductivity solvents do not usually accumulate hazardous levels of charge during simple operations such as tank filling and may not require the same level of enhanced precautions as Low conductivity liquids in these operations. They may, nevertheless attain hazardous levels of surface voltage in some specialised operations such as crystallisation or the stirring of two-phase mixtures to dissolve suspended solids. These more specialised end use operations are generally beyond the scope of the present document.

High conductivity solvents rarely accumulate hazardous levels of charge on liquid surfaces but have been known to under particular adverse circumstances (see 3.2.3).

Hydrocarbon solvents usually have low conductivity whilst most polar solvents (e.g. many oxygenated solvents such as alcohols) have high conductivity<sup>1</sup>.

- Be aware of the wide range of ignition sources that is capable of igniting flammable mixtures of solvent vapours and air.
  - The most common ignition source is static electricity (see Part 3).
  - Other ignition sources regularly encountered in industrial processes include: autoignition, hot surfaces, welding, naked flames (including pilot flames), smoking, grinding wheels, sparks from electrical switches, electric motor brushes, vehicle ignition systems, high energy light sources, lasers and certain types of metal tools falling on the floor or hitting other objects.
  - Be aware that solvents in rags/filters or other high surface area/volume materials can self heat from curing or other reactions.
  - The batteries in devices such as mobile phones and calculators can generally store enough energy for ignition and the short circuit currents can be high enough to ignite many common solvent vapours. Therefore it is possible that an accident to such a device could short-circuit the battery and cause ignition. Although the likelihood of such an accident may be very low, it cannot be ruled out.
- Understand the role of the following measures for preventing ignitions and apply appropriate combinations of these measures to ensure safety:
  - Where practicable, maintain solvent vapour concentrations well below the Flammable Range by:
    - Keeping solvent temperatures below the FP by a safety margin of 5 °C or 15 °C depending on the solvent and the operational circumstances (see 2.2.3).
    - Ensuring adequate ventilation. Solvent vapours should be diluted to a concentration of  $< 25\%$  of the Lower Explosive Limit (LEL - see 2.2.2) to ensure safe operation.

*NOTE: In some specialised operations with advanced LEL monitoring it may, subject to a rigorous risk assessment, be acceptable to permit a higher fraction of the LEL.*

The easiest way to assure ventilation, where it is possible, is by opening doors and windows. This may not be adequate to keep the vapour concentration reliably below 25% LEL. In many cases, mechanical ventilation is necessary. Ventilation is particularly important when working above the FP cannot be avoided. Ventilation should provide at least six air changes per hour in zoned hazardous areas and the ventilation exhaust should be located at least 3 m above the ground level and 3 m from building openings. An air flow detector should be used in the ducts and linked to an alarm in case of a possible extraction system failure.

- Applying basic housekeeping practices. Prevent unnecessary vapours by using no more than the right amount of solvent required, by keeping lids on containers and by using sealed containers for solvent contaminated waste. Do not leave solvent impregnated rags lying around.

- Remembering that solvent vapours are heavier than air and settle in low areas such as drains.

- Measurements with a combustible gas detector (explosimeter) may be useful to verify that vapour concentrations are below the Flammable Range (e.g. for work involving possible ignition sources done under a hot work permit). The explosimeter must be correctly placed (low because flammable solvents accumulate in low areas).
- Prevent or minimise solvent spray or mist formation
- Use inert gas to reduce the oxygen concentration below the level that will support combustion (e.g. by nitrogen blanketing). This approach is particularly useful if vapour concentrations in the Flammable Range cannot be avoided

and ignition sources or hot spots cannot be totally eliminated.

*NOTE: More people are killed by nitrogen asphyxiation than by the ignition of flammable vapours. It is invisible and has no odour or other warning properties. Access to inerted spaces should be strictly controlled and warning notices should be provided.*

- Eliminate all sources of ignition from hazardous areas in which flammable vapour/air mixtures might occur (treat areas with vapour concentration  $> 25\%$  LEL as potentially flammable). In all such areas:
  - Minimise the risk of static electricity build-up by the following measures (see Part 3 for details):
    - Earth (ground) and/or bond conductive equipment
    - Periodically verify that the earthing or bonding resistances meet the criteria set out in 3.3.1.
    - Do not splash fill flammable, low-conductivity solvents: use either dip pipes or bottom filling - Limit pipe flow velocity
    - Wait to allow the cessation of charging processes and the dissipation of charge before dipping, gauging or sampling
    - Use hoses that are conductive or static dissipative according to the definitions in CENELEC CLC TR 50404 Ref 12.
    - If a filter is used during filling operations, allow adequate residence time between the filter and the tank/container that is receiving the solvent.
    - Do not fill solvents into any insulating plastic containers or tanks other than small containers (capacity  $\leq 5$  litres) and suitably-designed IBCs (see 3.3.5) unless the FP of all solvents handled in the vicinity is  $> 60$  °C.

1. Ethyl acetate has been associated with a number of electrostatic ignition incidents and even though it has a high conductivity, it should be treated as a low conductivity material. It would be prudent to treat other light esters similarly

*NOTE: The use of conductive or dissipative plastic containers is acceptable provided the endorsement of the supplier is obtained.*

- Do not use compressed air for the line clearance of flammable products
- Wear antistatic and fire-resistant protective clothing and footwear
- Do not smoke, weld, use naked flames or permit any of the other industrial ignition sources listed previously.
- Use explosion-proof or intrinsically safe (Ex marked) electrical equipment.
- Eliminate hot spots.
- Ensure, by solvent choice or control of process conditions, that vapour temperatures and equipment surface temperatures are below the AIT.
- As a precautionary measure, prevent the use of battery operated equipment such as mobile phones or calculators in hazardous areas.
- Implement the following general safety measures
  - Follow work permit procedures scrupulously.
  - When working in confined spaces is unavoidable, a company-approved safe system of work must be implemented (work permit procedure) with adequate emergency arrangements, including evacuation procedures.
  - Report fault near misses and incidents, including minor spills or leaks. Company management should evaluate reports and take actions to prevent recurrence.
  - Have emergency procedures in place for dealing with

fires, spills or leaks that cover the following:

- Raising the alarm
- Calling the Fire Brigade
- Tackling the fire or leak using suitable fire fighting equipment for controlling a spill if it is safe to do so in line with defined procedures
- Shutting down the plant in a safe way
- Evacuating the plant safely
- Consult a specialist in case of doubt.

The successful implementation of many of these key recommendations requires an understanding of the relevant solvent properties and equipment/process characteristics. The most important properties and characteristics to be aware of are identified in Part 2.

## PART 2 Technical aspects of flammability and ignition

### 2.1 INTRODUCTION

This section of the Safety Guide considers the properties that make solvents vulnerable to ignition and identifies the ignition sources that could arise in solvent handling equipment. It covers:

- Flammability
  - Flammable range
  - Flash Point
  - Solvent Mists
- Auto Ignition Temperature (AIT)
- Minimum Ignition Energy
- Sources of Ignition

## 2.2 FLAMMABILITY

### 2.2.1 General

Three components must be present for a fire or explosion to occur:

- Flammable vapour (in the present context, solvent vapour), solvent mist or vapour plus mist, in the right concentration range for combustion,
- Sufficient oxidiser (usually oxygen from the air) and
- A source of ignition.

The “right concentration range for combustion” in air is known as the Flammable Range (also referred to as the Explosive Range) whilst the Flash Point (FP) is approximately the lowest measured temperature at which the solvent can produce vapour concentrations within the Flammable Range at atmospheric pressure. These properties, along with the role of mists in augmenting flammability, are now discussed in a little more detail.

### 2.2.2 Flammable Range

The Flammable Range of a solvent is the range of vapour concentrations in air that can undergo combustion. If the vapour concentration lies within the Flammable Range, a flash fire, flame or explosion will occur if the mixture is ignited. Outside the Flammable Range a propagating flame or explosion will not occur even if a highly energetic ignition source is present.

The borders of the Flammable Range are called the Lower Explosive Limit (LEL) and the Upper Explosive Limit (UEL) and are usually expressed in terms of percentage by volume of vapour in air.

- The lower explosive limit (LEL) is the lowest concentration of vapour in air at which the vapour/air mixture is flammable.
- The upper explosive limit (UEL) is the highest concentration of vapour in air at which the vapour/ air mixture is flammable.

If the vapour concentration lies below the LEL, the mixture is too lean for combustion whilst above the UEL, it is over-rich.

*NOTE: Under certain conditions, cool flames may occur in the over-rich region (above the UEL). Such flames are mildly exothermic; as a general rule a controlled temperature, of about 300–400 °C is to be applied for their initiation. Though this should not lead to an explosive combustion, it should be taken into account when examining potential sources of ignition in a system.*

The LEL and UEL vary significantly with temperature, pressure and oxygen content. Values are indicated in the suppliers Safety Data Sheets (section 9) and are based on combustion in air at normal atmospheric temperature (20 °C) and pressure unless otherwise specified. Some examples are given in Table 1. The general effect of increasing the temperature is to lower the LEL and to raise the UEL. If you work at raised temperature, remember that the flammable range is broader than at 20 °C.

*NOTE: There is no link between LEL (Lower Explosive Limit) and OEL (Occupational Exposure Limit).*

It should be noted that many LELs and UELs are obtained by theoretical calculation and as such should be regarded as guide values only. Because of uncertainties in LEL values and variations in process vapour concentrations with both location and time, vapours need to be diluted to well below the LEL to ensure safe operation. A level of < 25% is often specified. Where possible the aim should be to prevent vapour formation (e.g. good housekeeping, keep vessels full of liquid)

**Table 1: Flammability properties of selected solvents in air at atmospheric pressure (Ref 13 unless indicated otherwise)**

Substance (HSPA name in italics)	Closed Cup Flash Point, °C	Lower Explosive Limit, % v/v	Upper Explosive Limit, % v/v	Autoignition Temperature, °C
Pentane	-40	1,4	8,0	260
n-Hexane	-22	1,1	7,5	225
n-Heptane	-4	1,1 <sup>ref 14</sup>	6,7 <sup>ref 14</sup>	204
Iso-Octane	-12	1,1 <sup>ref 14</sup>	6,0 <sup>ref 14</sup>	418
n-Octane	13	1,0 <sup>ref 14</sup>	6,5 <sup>ref 14</sup>	206
n-Nonane	38	0,7 <sup>ref 14</sup>	5,6 <sup>ref 14</sup>	205
Light dearomatised hydrocarbon fraction (100–140 °C boiling range)* (Hydrocarbons, C7–C9, n-alkanes, isoalkanes, cyclics)	1	0,8	8,0	>200
Dearomatised white spirit (150–200 °C boiling range)* (Hydrocarbons, C9–C11, n-alkanes, isoalkanes, cyclics, < 2% aromatics)	39 to 41	0,6	6,5	>200
White spirit (150–200 °C boiling range)* (Hydrocarbons, C9–C12, n-alkanes, isoalkanes, cyclics, aromatics (2–25%))	38 to 40	0,8	6,5	>200
Benzene	-11	1,2	7,8	498
Toluene	4,4	1,1	7,1	480
m-Xylene	27	1,1	7,0	527
Aromatic solvent (160–185 °C boiling range)* (Hydrocarbons, C9, aromatics)	47 to 50	1,0	7,5	>350
Acetone	-18	2,2 <sup>ref 14</sup>	13 <sup>ref 14</sup>	465
Methyl Ethyl Ketone	-9	1,8 <sup>ref 14</sup>	11,5 <sup>ref 14</sup>	404
Methanol	9,7	5,5 <sup>ref 14</sup>	44 <sup>ref 14</sup>	455
Ethanol	13	2,5	13,5	363–425
iso Propanol	12	2,0 <sup>ref 14</sup>	12,0 <sup>ref 14</sup>	399
n-Butanol	35	1,4 <sup>ref 14</sup>	11,3 <sup>ref 14</sup>	355
Ethyl Acetate	-4	2,2 <sup>ref 14</sup>	11,5 <sup>ref 14</sup>	426
n-Butyl Acetate	27	1,2 <sup>ref 14</sup>	7,6 <sup>ref 14</sup>	415

*NOTE: There are multiple sources of flammability data that often give different values. In Table 1 the data for single species solvents are taken from Ref 13 if possible, otherwise from Ref 14. The data for hydrocarbon mixtures(\*) are representative guide values taken from the previous edition of this document: actual values may differ slightly from one supplier to another.*

### 2.2.3 Flash Point (FP)

The Flash Point (FP) is a property that is used by a number of classification systems including the Globally Harmonised System (GHS) as the main indicator of the flammability of a liquid product. It is defined as the temperature to which a liquid must be heated in a specified apparatus before a flame will propagate when an ignition source is applied. There are two main types of FP apparatus: open cup and closed cup. Closed cup FP data are preferred and generally produce lower results.

For practical purposes, the FP can be regarded as an approximate indicator of the lower temperature limit of flammability although it is generally several degrees above the temperature at which the equilibrium solvent vapour concentration reaches the LEL.

More volatile solvents (those with lower boiling temperature) tend to have lower FPs. For solvents such as white spirits that are characterised by a boiling range instead of a single boiling temperature, the FP may also depend on the breadth of the boiling range.

Your solvent supplier will have informed you of the FP of the materials they supply. FPs must be indicated in section 9 of the Safety Data Sheets provided by your supplier. Some typical examples are given in Table 1.

FP determination in the laboratory can be influenced by many factors including type of test equipment, size of sample, ignition source, temperature, ambient pressure, sample homogeneity,

draughts and operator bias. During the test, one must take care to ensure that the volatiles are not driven off before the flame is applied.

Because of the uncertainties associated with solvent composition, handling temperature and FP measurement, a safety margin of at least 15 °C should normally be applied when using FP data to assess flammability (i.e. the atmosphere should be treated as flammable when the liquid temperature exceeds FP-15 °C). It is acceptable to reduce the safety margin to only 5 °C when using a single species solvent with a well-established FP in well-controlled process conditions, although it is recommended that the wider margin is adopted wherever practicable.

Generally, the lower the FP the more hazardous the material is likely to be although in enclosed volumes such as tank vapour spaces, solvents with FPs between -15 °C and 10 °C are associated with the highest ignition risk (with unheated liquids), because they produce the most readily ignitable vapour concentrations at common ambient temperatures (see Annex 3).

#### NOTES:

1. *Switch loading, can lead to a flammable atmosphere even when loading high FP solvents unless compartments are cleaned and verified free of both residual vapour and liquid between loads.*
2. *Common vapour recovery lines can reintroduce vapours even where a high FP solvent is being loaded and compartments have been gas freed.*

All chemical products, including solvents, are classified in accordance with legislative requirements for both Supply (Use) and Carriage (Transport) and assigned Hazard Statements. Table 2 details the CLP criteria <sup>Ref 15</sup> and hazard statements commonly found in section 2 of Safety Data Sheets.

**Table 2: CLP criteria for flammability assignment of hazard statements** <sup>Ref15</sup>

Hazard statement		Classification criteria
H224	Extremely flammable liquid and vapour	Flash point < 23 °C and initial boiling point ≤ 35 °C
H225	Highly flammable liquid and vapour	Flash point < 23 °C and initial boiling point > 35 °C
H226	Flammable liquid and vapour	23 °C ≤ Flash point ≤ 60 °C

### 2.2.4 Mists of Flammable Liquids

Unlike vapours, fine solvent mists may be flammable at temperatures well below the FP.

Mists of solvents can be generated in two ways:

- uncontrolled condensation of saturated vapours resulting in droplets (mists) whose diameter is below 0.02 mm.
- atomised sprays with a range of diameters from 0.02 mm up to 1 or 2 mm.

Mists are common in processes that involve spraying techniques such as the degreasing of metal parts or paint spraying.

Solvent droplets whose diameter is less than 0.2 mm behave similarly to vapours and are likely to assist flame propagation.

Mists are capable of propagating a flame if the quantity of solvent present is high enough. Explosion could occur in confined conditions.

Mists are characterised by lower (LEL) and upper explosive limits (UEL) in the same way as vapours although it is difficult to obtain reliable values due to the lack of uniformity of the droplets. LELs are strongly affected by droplet size. Generally, larger droplets give higher LELs.

The overall %LEL of a mixture of droplets and vapour is obtained by adding the separate %LELs of the droplets and the vapour. Thus if the vapour concentration is 25% of the vapour LEL and the droplet concentration is 30% of the droplet LEL, the overall %LEL is 30% + 25% = 55%.

In situations where mists or sprays cannot be avoided, specific safety measures must be taken. Consult a specialist.



## 2.3 AUTO-IGNITION TEMPERATURE (AIT)

This section is for solvent users working at elevated temperatures.

A mixture of solvent vapours in air or oxygen will ignite spontaneously if the temperature is high enough.

AIT is the minimum temperature at which a mixture of combustible vapour and air can ignite without the presence of an ignition source, under the specified conditions of the test.

Usually the AIT is well above the boiling point of the material. There is no link with the flash point. The AIT is mainly linked to the chemical structure of the molecule and not with its boiling point.

AITs are not absolute values but depend greatly on the method by which they are obtained (volume of the test container and nature of the wall material). In the most common method (ASTM E659 <sup>Ref 16</sup>), small quantities of liquid are injected into a 500 ml borosilicate glass round bottom flask that has been heated to a known temperature.

AITs are significantly lowered when pressure is increased above atmospheric and the measurement can be affected by the cool flame phenomena mentioned in 2.2.2. AITs are significantly lowered in the presence of catalysts, some of which, including metals, are commonly present in industrial equipment.

The AIT of the solvent you use must be indicated in section 9 of your supplier's SDS. Some examples are given in Table 1.

In view of the important potential variations between AIT values and the real auto-ignition conditions of a process, it is important to note that AIT should not be regarded as a clear cut-off point between no-ignition / self-ignition conditions. Instead, AITs are just very rough indications of the

maximum temperature to which flammable mixtures can be exposed without self-ignition. A significant safety margin must therefore be allowed between the measured AIT and the operating temperature.

## 2.4 MINIMUM IGNITION ENERGY (MIE)

An ignition source must deliver at least a certain minimum level of energy, called the Minimum Ignition Energy (MIE), to the solvent vapour, in order to trigger combustion. The MIE of hydrocarbon or oxygenated solvents in air is typically between 0.1 and 1 millijoule. This is a small amount of energy: as an indication, it is close to the threshold of human perception for electrical sparks. Thus, the occasional, barely-perceptible electrostatic shocks that can be experienced in buildings or when opening car doors<sup>2</sup> would probably initiate fires if solvent vapours were present at a near-optimum concentration.

Many of the ignition sources encountered in industrial activities (see 2.5) can readily exceed the MIE of common solvents. These ignition sources require strict control wherever flammable atmospheres may occur.

## 2.5 SOURCES OF IGNITION

Sources of energy can be classified into 4 categories:

### 2.5.1 Flames and Smouldering

Under this heading come all naked flames such as welding torches, matches, and gas burners (including pilot lights), as well as sporadic sources such as the exhaust of an engine.

Smouldering covers all forms of incandescent material such as cigarettes, braziers and, less obviously, catalysts.

### 2.5.2 Hot Surfaces

Hot surfaces are common in industrial areas: examples are walls of ovens and furnaces, electrical equipment, heating pipes, welding operations and surfaces heated by high intensity lights or lasers.

Hot surfaces may cause ignition of flammable solvent/air mixtures either directly or indirectly.

Direct ignition will occur if the surface is at a temperature above the auto-ignition temperature of the solvent/air mixture in the particular conditions considered.

Indirect ignition results from the burning or smouldering of material initiated by a hot surface.

### 2.5.3 Friction and Impact

Hot surfaces and incandescent sparks can arise from friction or impact and depend largely on the materials: for example, sparks produced during impacts involving some metals (e.g. magnesium and its alloys, iron) with grit or rock generate high heat. Some operations readily produce hot spots by friction: examples include grinding and cutting. The thermite reaction, which occurs when a metal such as aluminium on a hose end strikes rusty steel, can produce a sufficient energy to ignite flammable vapours.

### 2.5.4 Electrical Discharges

There is specific legislation aimed at ensuring that operators have adequately considered the risks posed by electricity. The regulations require operators to classify their sites in terms of zones (Annex I) and to select appropriate electrical equipment for each zone. Electrical discharges are widespread and often hidden. They can originate from the following basic sources:

- Electrical power
  - Electrical equipment operating from mains electricity and/or batteries can be a source of sparks with sufficient energy to ignite solvent vapour/air mixtures. The normal operations of transformers, motors, circuit breakers, switches, fuses as well as electrical failures such as damaged cables are common electrical ignition sources. Sparks from calculators or mobile phones may also be capable of causing ignition if the battery is short-circuited (e.g. by accidental damage to the device). All electrical equipment used in solvent service must be ATEX approved <sup>Ref 10</sup> (explosion proof, intrinsically safe etc.). Ordinary flashlights and extension cords must not be used.
  - Electromagnetic waves emitted by radio antennae may give rise to sparks in their vicinity or to a heat build-up in materials.
  - The interruption of stray currents, such as those that can flow round low resistance earth loops formed by ship's mooring cables, pipelines, railway lines etc. can give rise to incendive "breakflash" discharges <sup>Refs 12, 17</sup>.
- Electrostatic discharges
  - Static electricity is such an important source of incidents when handling solvents, and in particular hydrocarbon solvents, that Part 3 of this guide is fully dedicated to this topic.
- Lightning strikes and associated current flows.
  - These may affect solvent handling equipment, particularly in outdoor operations. It may be necessary to suspend outdoor liquid transfer operations while a thunderstorm is in the vicinity. Procedures for lightning protection are given in Ref 18.

2. These occur as a result of people becoming charged by walking over carpets or sliding off car seats.

## PART 3 Static electricity

### 3.1 INTRODUCTION

Static electricity is one of the most difficult ignition sources to understand and control. Similar operations can produce different levels of static on different days and often the first indication of static is a spark, which may of course be catastrophic in the presence of solvent vapours. This section of the guide gives a detailed account of how best to manage the threat of static electricity, along with some practical applications and mitigation techniques.

## 3.2 ELECTROSTATIC HAZARD MECHANISMS IN SOLVENT HANDLING

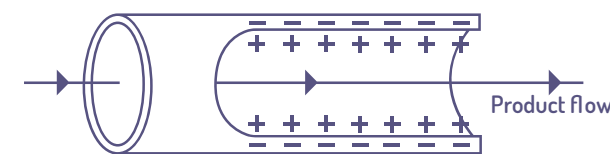
### 3.2.1 General Outline

#### 3.2.1.1 Charge generation

Static electricity is produced by relative motion between materials or by the separation of materials. In solvent handling this can arise from activities such as liquid flow, stirring, agitation or mixing, rubbing solid surfaces, removing packaging such as cling film wraps or walking on an unsuitable floor. The motion separates positive and negative charges, which may then build up (“accumulate”) either in the solvent, on the containment system (pipelines, tanks, drums etc) or on the associated equipment and people.

The main cause of concern in solvent handling is charging by liquid flow. Figure 1 shows how charge separation occurs during the flow of solvent through a pipe. Charging is particularly high during the passage of solvents through fine filters (<30 µm) and, to a lesser extent, pumps.

**Figure 1: Charge separation in pipe flow (the opposite polarity also occurs)**



#### 3.2.1.2 Charge dissipation and accumulation

Unless electrically insulating components (e.g. plastics) are used, the charge on the containment system (negative in Figure 1) is rapidly dissipated by earthing or bonding. However, if the solvent has a low conductivity ( $\leq 50$  pS/m), the solvent charge (positive in Figure 1) only dissipates relatively slowly. In this case, when the solvent collects in a tank, the accumulation of charge in the liquid can create high surface voltages and lead to powerful sparks that can ignite solvent vapours. If the containment system contains electrically insulating

components (e.g. plastics), dissipation may also be slow from the surface of the insulating material or from unbonded conductors (plant items, drums) that are electrically insulated by the plastic and sparks may also occur from these items.

In principle, charge may also accumulate on mists. However, sparks from mists require either very large mist volumes (e.g. during tank washing) or very highly charged mists such as are produced by very high speed flows or deliberate droplet charging (e.g. for electrostatic spraying). These conditions are rarely encountered in general solvent handling. More commonly the collection of charged mist droplets on unbonded conductors or insulating plastic surfaces (e.g. during paint spraying) may cause charge to accumulate.

### 3.2.2 Operations that Generate Static Charges

The most important static charging processes in general solvent handling are:

- Filtration (high charging)
- Pumping (high charging)
- Pipe flow
- The actions of people (e.g., pulling plastic wrapping off drums or boxes, removing clothing, dropping or leaving conductive items such as cans or sample containers into tanks, wearing insulating footwear and/or gloves and emptying drums or containers into reaction vessels).

Factors that enhance the charging in these processes include:

- Fine filters with micropore elements that have a large surface area exposed to the flow.
- High velocity and turbulence, for example in flow through pipelines or in the discharge of jets from nozzles during tank mixing. The faster and more turbulent the flow, the more static electricity is produced.
- High shear pumps.

- The presence of a second immiscible phase such as suspended particulates or entrained free water. Suspended solids or liquids can both substantially increase the generation of electrostatic charge by a hydrocarbon solvent when it is handled. It is not unusual to have water in solvents resulting from operations such as water washing or line flushing. This should be separated out as far as practicable. Care should be taken to avoid unnecessary mixing.
- Product type and processing. Some refined materials, especially hydro-treated gas oils with sulphur contents below 50 ppm, appear to have a higher risk of electrostatic ignition<sup>Ref 18</sup> which is thought to be associated with increased charge generation. Ethyl acetate is also thought to be associated with high charging.

Other processes that may produce charging in solvent handling or usage include:

- Crystallisation.
- Dissolving powders in low conductivity solvents.
- Spraying solvent-based paints or coatings.
- Movement of vehicle.
- Settling of water droplets or particles through liquid hydrocarbon e.g. after a line has been pigged off into a tank with water (only in large storage tanks) or if water bottoms or sediments have been disturbed.
- Bubbling of gas or air through liquids.
- Mechanical movements such as belts or pulleys.
- Movement of fan blades.
- Movement or transport of solvent-wet powders.

- High velocity release of steam to atmosphere or steam cleaning.
- Rubbing, cleaning or grinding plastic surfaces, especially where mechanical systems are involved (e.g. grinding or cutting holes in plastic sheets in a solvent handling area).
- Separating layers of insulating material (e.g. taking off clothing or removing plastic wrappings)

Precautions for these activities are given in CENELEC TR 50404<sup>Ref 12</sup> or IEC 60079-32-1<sup>Ref 17</sup>.

### 3.2.3 Charge Dissipation, Relaxation Time and Solvent Conductivity

The build up of static within a liquid as a result of electrostatic charging processes is opposed by the continuous leakage (dissipation) of charge from the liquid to the wall of the containment system. If dissipation is slow, hazardous voltage differences can occur between the liquid and the wall: if dissipation is fast, hazardous voltage differences are prevented.

Dissipation usually obeys Ohm's Law. In this case the rate of dissipation is described by the relaxation time of the liquid,  $\tau$ , which is the time taken for the charge to fall to 37% of its initial value when no charging process is active. After three relaxation times only 0.373 - 5% of the initial charge remains, i.e. 95% has been dissipated.

The relaxation time is primarily determined by the electrical conductivity of the liquid. With a high conductivity, charges can flow away readily and the relaxation time is short. With a low conductivity, charges flow away slowly and the relaxation time is long. Values of conductivity<sup>Ref 20</sup>, dielectric constant and relaxation time for some typical solvents are given in Table 3.

**Table 3: Conductivity & relaxation time**

Substance	Conductivity pS/m	Dielectric constant	Relaxation times s
Acetone	6x10 <sup>6</sup>	21	3.1x10 <sup>-5</sup>
Methyl Ethyl Ketone	5x10 <sup>6</sup>	19	3.3x10 <sup>-5</sup>
n-Butanol	4x10 <sup>6</sup>	18	4.1x10 <sup>-5</sup>
Iso-Propanol	2x10 <sup>6</sup>	18	8.1x10 <sup>-5</sup>
Ethyl Acetate <sup>3</sup>	2x10 <sup>6</sup>	6.2	2.8x10 <sup>-5</sup>
n-Butyl Acetate	2x10 <sup>6</sup>	5.0	2.2x10 <sup>-5</sup>
Ethanol	4x10 <sup>6</sup>	25	5.6x10 <sup>-5</sup>
Methanol	7x10 <sup>6</sup>	33	4.2x10 <sup>-5</sup>
n-Heptane	4	1.9	4.3
n-Hexan	24	1.9	0.71
Iso Octane	1	1.9	17
n-Octane	9	1.9	1.9
Toluene	5	2.4	4.3
n-Pentane	24	1.8	0.68
m-Xylene	9	2.4	2.4

3. Although ethyl acetate has a high conductivity it has been involved in a number of electrostatic ignitions. The detailed causes of these are unclear and until they are established it is recommended to treat ethyl acetate as a low conductivity material. It may be prudent to adopt the same approach with other light esters.



**NOTES:**

1. The conductivities in Table 3 were measured <sup>Ref 20</sup> in industrial grade solvents. Only the large difference between the figures for hydrocarbons and oxygenated solvents is significant. The differences between hydrocarbons arise from fluctuations in trace impurities such as water, sulphur, acids or soluble metal salt. Differences between samples of the same solvent are of the same magnitude as the differences shown between solvents. The conductivities of highergrade solvents can be much lower than those shown in Table 3 (e.g. the conductivity of n-heptane is readily reduced to ~10<sup>-2</sup> pS/m by removing polar impurities).
2. When measuring conductivity, care must be taken to ensure that the result is not distorted by polarisation or contamination. The latter is particularly important as it can give a false high value.

The data in Table 3 show that hydrocarbon solvents have low conductivities (50 pS/m or less) and correspondingly long relaxation times. They provide slow dissipation and are therefore vulnerable to electrostatic ignition. Consequently they are handled with increased levels of control against electrostatic ignition hazards <sup>Ref 12, Ref 16</sup>.

The listed polar solvents, which include alcohols, ketones and acetates all have high conductivities and short relaxation times that allow rapid charge dissipation. They are consequently much less vulnerable to electrostatic ignition. Nevertheless, circumstances can occasionally arise in which electrostatic ignitions can occur even with high conductivity solvents. For example, when high conductivity products are splash-loaded into containers with internal insulating coatings or linings, the coating or lining can isolate the liquid electrically from the earthed parts of the containment system and allow charge accumulation despite the high liquid conductivity. Clearly, care must be taken with all flammable industrial solvents, particularly when insulating materials are present in the handling system. Despite its high conductivity, ethyl acetate has been involved in a number of electrostatic ignition incidents and should be treated as a low conductivity solvent.

### 3.2.4 Quantifying Relaxation Time

The relaxation time depends on the conductivity and relative permittivity (dielectric constant) of the material via the relationship:

$$\tau = \epsilon \epsilon_0 / \gamma$$

where:

$\tau$  = Relaxation time (s)

$\epsilon$  = Relative permittivity of the liquid

$\epsilon_0$  = Permittivity of free space (8.85 pF/m)

$\gamma$  = Liquid conductivity (pS/m)

This expression was used to determine the relaxation times in Table 3. For most hydrocarbon solvents,  $\epsilon$  ~2 and the relaxation time can be approximated as:

$$\tau = 18/\gamma$$

Hydrocarbon solvents usually have conductivities of less than 10 pS/m (e.g. 5 out of 7 samples in Table 3). In such products the relaxation time is more than 1.8 s. Some hydrocarbons have conductivities very much lower than 10 pS/m (e.g. oils boiling in the range 350–500 °C have extremely low conductivities and are used as insulators in large transformers) and a hydrocarbon solvent with conductivity of 0.5 pS/m (e.g. classical mineral spirits) would have a relaxation time of about 36 seconds. These relaxation times are all long enough to allow hazardous voltages to develop on the liquid surface in tanks or containers during and after both product transfer and mixing processes.

At very low conductivity, charge dissipates faster than indicated by the Ohm's Law behaviour described above and generally it may be assumed that charge will be dissipated from a liquid in less than 100 s. For moderate levels of charging 30 s is sometimes considered sufficient.

## 3.3 STATIC CONTROL MEASURES FOR SOLVENT STORAGE AND HANDLING

### 3.3.1 General Earthing and Bonding Requirements for Static Dissipation

- Bonding establishes a continuous electrical path between different parts of the process equipment and thus ensures that all the bonded items are at the same potential.
- Earthing establishes, in addition, a continuous electrical path to earth.

The dissipation of static electricity from the liquid to the containment system depends on the liquid conductivity/relaxation time (see 3.2.3 and 3.2.4). Dissipation from the containment system requires the earthing or bonding of all conductive system components. Without earthing or bonding, high voltage differences and electrostatic sparks could occur either between components (e.g. between tanks or from tank to operator) or between components and earth.

It is usual to employ earthing rather than just bonding because without earthing, an external charging mechanism could act on the entire bonded system and raise it to a hazardous voltage.

*NOTE: If no external charging mechanism exists and the provision of an earth is difficult (e.g. because it might introduce a risk of electrical fault currents), bonding may provide an acceptable alternative.*

An earthing/bonding resistance of 1 M $\Omega$  or less (or 100 M $\Omega$  or less if no high charging process is involved) is low enough to prevent hazardous voltages from electrostatic charging but where the earth path is entirely metallic, a resistance of less than 10  $\Omega$  is usually specified because a higher resistance may indicate an unreliable connection. It may be acceptable to exceed the 10  $\Omega$  limit (but not the 1 M $\Omega$  or 100 M $\Omega$  limit) if the reason is known and it is clear that the measured value is not vulnerable to further deterioration (see also Annex 2).

If the earthing or bonding is via a dissipative or not entirely metallic path (e.g. the path along a loading arm with a swivel joint interrupted by an oil film) a resistance up to 1 M $\Omega$  may be acceptable provided it is stable and consistent with the geometry and material properties of the system.

All hoses should be electrically conductive <sup>Ref 12, 17, 21</sup> or dissipative according to the requirements in <sup>Ref 12</sup> to facilitate bonding.

Procedures should be in place for regularly checking that equipment complies with earth resistance requirements and that conductive or dissipative hoses meet end-to-end resistance requirements.

All equipment must be earthed even when handling high conductivity solvents because, although a high conductivity solvent provides rapid charge dissipation from the interior of the solvent to wall, the liquid conductivity is not necessarily high enough to provide adequate earthing of containers etc and gaps may occur in a liquid column.

### 3.3.2 Residence Time Requirements Downstream of High Charging Device

Devices such as pumps and, particularly, fine filters were identified in 3.2.2 as causing high charging. Downstream of such a device it is necessary to allow an adequate residence time for the excess charge to dissipate before the liquid enters a vessel (tank, truck compartment, IBC, drum etc) where charge could accumulate and a flammable atmosphere could be encountered. A residence time of at least 3 $\tau$ , up to a maximum of 100 s should be allowed for this purpose.

*NOTE: The relaxation time,  $\tau$ , should be calculated using the lowest conductivity that could occur. If this is not known the maximum residence time of 100 s should be adopted.*

For high conductivity polar solvents, the required residence times (see Table 3) are so short that they are provided by less than 1 mm of pipe. Hence no special residence time provision is needed for these products.



Even for low conductivity solvents, the required residence time is often provided by the normal piping but in some cases a special relaxation chamber or modified (widened) pipe section may be needed. The requirements will vary according to the operation and individual companies should seek advice from suppliers and safety practitioners.

### 3.3.3 People

Personnel carrying out activities in hazardous areas should wear electrostatic dissipative footwear and walkways and flooring should be dissipative so that the total resistance from operator to earth via footwear does not exceed 100 M $\Omega$ .

Where gloves are worn they should be dissipative wherever possible. If dissipative gloves are not available (e.g. because no dissipative gloves offer the other sorts of hand protection required for the operation) then the operation should be carefully analysed and either the manual handling eliminated or other means of ensuring the earthing of items carried by the operators provided.

*NOTE: Dissipative bracelets may be used to earth the operator but still may not earth carried equipment if insulating gloves are being worn.*

Overalls should be dissipative: natural fibres such as cotton are normally dissipative but those made from synthetic fabrics may not be. In order to ensure that overalls made from synthetic fabrics are suitable they should meet the requirements set out in EN-1149-5<sup>Ref 22</sup>. Overalls should be well fitting and fastened and clothing should not be removed in hazardous areas.

Operators should be careful that no insulated conductor from which an incendive discharge could occur (e.g. metal can, steel-rimmed spectacles, steel comb or pen) should be inadvertently dropped or introduced into tanks during filling, sampling or discharging operations. Operating procedures and clothing should be designed to minimise this risk (e.g. minimise top access where there are open manlids, use overalls with no top pockets or only zipped top pockets that must be fastened).

## 3.3.4 Loading Tanker Trucks, Rail Tankers and ISO Containers

### 3.3.4.1 Earthing

The resistance to earth of a tanker truck or ISO container vehicle with pneumatic tyres standing on dry concrete could exceed 1 M $\Omega$ . Therefore the first step in loading these vehicles<sup>Ref 17, Ref 23 Part 2 Sec 7.2.1</sup> should be to attach a temporary earth connection with a maximum resistance of 10  $\Omega$  to the earthing pin of the truck or container (see Figure 2). The final step should be the removal of this connection. Automatic earth checking systems are available.

Rail tankers are earthed through the rail and there is no general requirement to use a special earth. However, if any doubt exists about the electrical continuity between the running gear and the tank, then a special earth should be used with a maximum resistance of 10  $\Omega$ <sup>Ref 23 Part 2 Sec 9.4.1</sup>.



Figure 2. Typical bottom loading stand with provision for making earth connection to a tanker truck

### 3.3.4.2 Splash filling

Splash filling must be avoided by employing bottom entry or by using a fill pipe terminating close to the bottom of the tank.

### 3.3.4.3 Flow velocity

At the start of filling, the pumping velocity,  $v$ , should be no greater than 1 m/s<sup>Ref 17 Ch 7, Ref 12 ch 5, Ref 23 Part 2 Sec 7.3.3</sup>. Once the inlet pipe is covered to twice its diameter, the velocity can be increased. For low conductivity solvents, the full-flow velocity, in m/s, is determined from:

$$v \leq N/d$$

subject to an overall maximum of  $v = 7$  m/s<sup>Ref 17 Ch 7, Ref 12 Ch 5</sup>. Here,  $N$  is a loading parameter (the "vd limit") that has a value of 0.38 m<sup>2</sup>/s for road tankers and 0.75 m<sup>2</sup>/s for rail tank cars and  $d$  is the pipe diameter in metres. The diameter should be taken as that of the narrowest pipe section within a flow time of 30 s or three relaxation times of the fill pipe exit whichever is lowest (see Ref 17 for more details). For medium or high conductivity solvents a vd limit is not required but the overall maximum velocity of 7 m/s is retained as a precautionary measure.

If the solvent consists of two or more immiscible phases or if it is contaminated with suspended free water or dirt, the flow velocity must be restricted to 1 m/s throughout the filling process.

*NOTE: The relaxation time used to determine residence time should be that of the lowest conductivity liquid that could be loaded. If the lowest conductivity is not known a default residence time of 30 s should be used.*

A vd limit has not been established for ISO containers but would be expected to be similar to the rail car value.

*NOTE: Higher velocities may be acceptable with suitable compartment design (e.g. compartments or ISO containers segmented with baffles) – see<sup>Ref 12 Ch 5</sup> or<sup>Ref 17 Ch 7</sup> for details.*

Thus, for example, when loading a road tanker ( $N = 0.38$  m<sup>2</sup>/s) with a low conductivity solvent through a 3 inch (~80 mm) pipe ( $d = 0.08$  m) the maximum permissible loading velocity would be 4.7 m/s. Solvent filling velocities are normally lower than this: a velocity of 1.5 m/s is typical and corresponds to a flow rate of about 27,000 litres/hour in an 80 mm diameter line.

### 3.3.4.4 Filtration and residence time

If a fine filter is present in the loading line, the residence time between the filter and vehicle should meet the requirement specified in 3.3.2 (at least  $3\tau$  up to a maximum of 100 s) to ensure that the additional static charge can dissipate to a safe level before the liquid reaches the tank.

Fine bag filters are sometimes used over the end of loading lines for high conductivity solvents such as ethanol. For low conductivity solvents such as hydrocarbons with a conductivity of less than 50 pS/m this practice is unsafe and is not permitted.

### 3.3.4.5 Switch loading

Switch loading occurs when a high Flash Point product is loaded into a compartment after a low Flash Point product and the compartment is not made free of flammable liquid and gas residuals between the loads. In these circumstances, vapour remaining from the first load is likely to be present during the second and may often create a flammable mixture even when the second product, on its own, would not. There have been several incidents of explosion/fire arising from this practice even though the filling rules are designed to cover this eventuality. It is thought that some aspect of the rules (e.g. the no splash loading provision) was probably violated in these events. Despite this, the flammability risk associated with switch-loading is less than that experienced during the loading of solvents such as toluene that naturally produce flammable atmospheres through most of the loading period at typical loading temperatures<sup>4</sup>. Annex 3 lists some common solvents that produce flammable atmospheres over a standard ambient temperature<sup>4</sup> range (0 °C to 35 °C).

Switch loading risks could be minimised by cleaning out all vapour and liquid from compartments that previously carried low Flash Point liquids before loading a high Flash Point liquid but this is rarely practical. It is recommended to organise loading schedules to minimise switch loading.

4. The vapour concentration drops continuously during a switch loaded fill and is only at the optimum for ignition for a short time. When loading a product such as toluene, the vapour concentration may be close to optimal for most of the fill.

### 3.3.4.6 Compressed air

The use of compressed air for discharging low FP products or for clearing low FP products from transfer lines should be avoided.

### 3.3.4.7 Line clearance with water

The use of water for line clearance of products with low flash points should be avoided.

### 3.3.4.8 Related documentation

There have been several publications specifically on the safe loading of road tankers with hydrocarbon fuels and the associated risks of static ignition<sup>Refs 19, 24 & 25</sup>. These provide more detailed recommendations on loading procedures. Note that not all of these recommendations are applicable to solvents (e.g. the additional restrictions on loading rate that have been found to be necessary for low sulphur diesel do not apply to solvents).

## 3.3.5 IBCs

### 3.3.5.1 Selecting IBCs: suitability for different solvents

#### 3.3.5.1.1 Metal IBCs

Figure 3 shows typical metal IBCs. These may be used for solvents of any Flash Point or conductivity



Figure 3. Typical metal IBCs

#### 3.3.5.1.2 Plastic Composite IBCs

Plastic composite IBCs generally consist of a plastic “bottle” surrounded by metal sheet, mesh, or frame: a typical metal mesh example is shown in Figure 4. For IBC selection, a distinction should be made between Standard (static-unprotected) IBCs and Static-protected IBCs.



Figure 4. Typical plastic IBC

Standard (static-unprotected) plastic composite IBCs have no special measures for static charge dissipation. The metal frame or surround can/should be earthed to prevent sparks but the plastic bottle is usually made of an insulating material, such as high-density polyethylene (HDPE), that cannot be earthed and the liquid contents may be isolated from earth by the bottle. Consequently, hazardous levels of charge may occur both during and after a fill. With these IBCs, therefore, the solvent temperature must be kept below the Flash Point by a safety margin sufficient to ensure that flammable mixtures do not occur. A useful safety margin is 15 °C (see 2.2.3) but local codes of practice should be followed because the ambient temperature and required safety margin can vary from country to country.

*NOTE: In Europe, ambient temperatures rarely exceed 45 °C so static-unprotected plastic composite IBCs may generally be used for liquids with Flash Points of more than 60 °C (i.e. combustible liquids). Care is, however, needed in hot conditions or if loading takes place in direct sunlight, which may heat the surface of the liquid within the IBC above ambient temperature.*

Static-protected plastic composite IBCs have an internal earth contact for the liquid, specified levels of close contact between the bottle and the surrounding earth metal frame or grid (maximum gap, mesh size not bigger than 100 cm<sup>2</sup>), a prominent external earthing point and, possibly, a dissipative or conductive outer layer on the bottle. Static-protected IBCs reduce the risk of hazardous voltages and are generally considered suitable for use with low Flash Point solvents when a flammable atmosphere could be present (e.g. even when the liquid temperature could be more than the Flash Point), provided the solvent has a high conductivity<sup>5</sup> (>10 000 pS/m).

The conditions under which these static-protected IBCs may be safely used are, however, not yet universally agreed. Therefore, before using them with low Flash Point products, the user should conduct a risk assessment taking into

account the IBC manufacturer's recommendations, local codes of practice and the effectiveness of the static removal and earth proving systems across the whole supply chain. If there is any doubt it should be noted that a metal IBC is inherently more reliably dissipative than an electrostatic-protected composite IBC. Some additional guidance is given in section A3.2 of Annex 3.

*NOTE: Static-protected plastic composite IBCs are considered to be electrostatically safe with low conductivity, low flash solvents in CENELEC TR50404<sup>Ref 12</sup> and IEC 60079-32-1<sup>Ref 17</sup>: the present advice is more cautious.*

#### 3.3.5.2 Filling IBCs

The first step in loading all IBCs should be to attach a temporary earth connection with a maximum resistance of 10 Ω to the frame or earth point. The final step should be the removal of this earth connection.

*NOTE: For a metal IBC, the frame may or may not be bonded to the tank. The tank usually rests in brackets and contains cushioning materials to absorb shock during transit and, unless there is an earthing strap between the frame and the tank, when earthing the IBC to the loading system during filling, both the tank and frame should be earthed. If there is bonding between the tank and frame only one earthing point is needed.*

IBC should not be splash filled. Filling should be to the bottom of the IBC either directly or via the top opening with a dip pipe reaching to the bottom.

The linear fill velocity should not exceed 1 m/s. The uncontrolled gravity filling of solvents into IBCs should be avoided because it leads to unknown filling velocities and is not a safe practice.

If a fine filter is present in the loading line, the residence time requirements specified in 3.3.2 should be followed to ensure

5. Although ethyl acetate has a high conductivity it should be treated as a low conductivity solvent for the purposes of IBC selection (see 3.2.3 footnote 3).



that the additional static charge is dissipated to a safe level before the liquid reaches the IBC.

Measures such as metering, weigh scales or high level detection and cut-out should be taken to prevent overfilling. This is particularly important for metal IBCs as there is no visual means of assessing the volume filled.

A ventilation system should be available to remove vapours generated during filling operations and hence to reduce the risks of ignition and operator exposure.

The uncontrolled filling of IBCs at a customer's premises must not occur. The risk of over-fill, rupture or static discharge is high. IBCs should be returned to the supplier for filling. The only exception is a fixed filling installation with a supplier's safety audit confirming appropriate safeguards are in place.

### 3.3.6 Filling Drums and Cans

Do not fill solvents into any insulating plastic drums or cans other than small containers (capacity  $\leq 5$  litres) unless the FP of all solvents handled in the vicinity is  $> 60$  °C and the temperature of the fluid surface is less than the FP by a suitable margin.

*NOTE: Filling plastic containers larger than 5 l capacity in the presence of lower FP solvents may be permissible with suitable operating constraints (e.g. flow speed limits) after a strict and detailed risk assessment.*

In the presence of solvent with FP  $\leq 60$  °C and if the container size is  $> 5$  litres use only metal, dissipative plastic or conductive plastic drums and cans. Earth the container to the loading system with a special earth clip that penetrates any paint coatings and ensures that the earth resistance is not greater than  $10 \Omega$  for metal containers or  $1 M\Omega$  for plastic containers. The performance of the earthing system should be checked periodically. A typical earthing system for metal drums is shown in figure 5.

Drums should not be splash filled: filling should be via a lance extending to the bottom.

The fill velocity should not exceed 1 m/s.

If a fine filter is present in the loading line, the residence time requirements specified in 3.3.2 should be followed to ensure that the additional static charge is dissipated to a safe level before the liquid reaches the drum.

There is no means of measuring the volume filled into a drum or can and filling should be via a metering system to ensure overspill does not occur.



Figure 5. Typical mobile earthing for drums

### 3.3.7 Buckets

Charge can accumulate to hazardous levels even with conductive liquids when filling a plastic bucket or a metal bucket that is electrically isolated from ground. The use of plastic buckets should be avoided without a detailed evaluation of the risk and metal buckets should be earthed whilst being filled or emptied. Dissipative gloves, footwear and flooring may provide the required earth contact. The bail of the bucket and the handle on the bail must be conductive.

### 3.3.8 Filling Fixed Storage Tanks and Vessels

#### 3.3.8.1 Earthing

The earthing of fixed tanks and vessels is essential both to control the risks associated with static discharge (see 3.3.1) and to deal with lightning strikes. The earthing requirements for lightning protection are, however, different from those for static protection and are outside the scope of this document. Refs 18, 27 Sec 2.1.

Fixed equipment should be permanently earthed with built-in systems and, where relevant, should include facilities for the temporary earthing of transportable vessels during transfer operations (e.g. as in Figures 2, 4 and 5).

The first step in a transfer operation from a tank car, rail truck or other portable container should be to attach a temporary earth connection to the car or truck etc. The final step should be the removal of the earth connection.

#### 3.3.8.2 Filling into storage tanks

Splash filling into storage tanks should be avoided by the use of a main inlet line at low level, or a fill pipe to the tank bottom.

For multi-phase product mixtures in which the bulk phase

has a conductivity below 50 pS/m, (e.g. water in hydrocarbon or solvents with suspended solids), the flow velocity should not exceed 1 m/s at any stage during the fill.

When transferring low conductivity ( $\leq 50$  pS/m) single-phase liquids such as hydrocarbon mixtures, the flow velocity should be kept below 1 m/s until the end of the inlet pipe is covered to twice its diameter. After this initial period, the flow velocity can be increased to a full flow value that should not exceed:

- 7 m/s for tanks with a diameter of 10 m or more.
- 3.5 m/s for tank diameters of less than 10 m.

It is advisable to keep the flow velocity as low as reasonably practicable and filling velocities are usually below the above limits (typical full flow velocities for solvent handling are 2-3 m/s).

*NOTE: For tanks with diameters between 1.3 and 10 m, IEC 60079-32-1<sup>Ref 17</sup> Ch7 permits velocities up to a limiting value of  $v_{max} = 0.7(D/d)^{1/2}$  m/s subject to an overall limit of 7 m/s (D is the tank diameter and d is the pipe diameter). When  $D/d > 25$  the velocity limit of 3.5 m/s falls below the IEC limit and provides for acceptable loading conditions. Most practical combinations of tank and fill pipe diameter meet this condition. Thus for example, for a 1.3 m diameter tank the 3.5 m/s limit is suitable for pipe sizes up to 2 inch NPS (50 mm DN). The IEC 60079-32-1<sup>Ref 17</sup> expression should be used if it is necessary to fill tanks with  $D/d < 25$ .*

More details are given in IEC 60079-32-1<sup>Ref 17</sup>, CENELEC TR 50404<sup>Ref 12</sup> and BS 5958<sup>Ref 23 Part 2 Sec 3.3</sup>.

### 3.3.9 Emptying Tanks and Containers

When a tank or container is emptied the liquid may become charged as it passes through the handling equipment but the hazards arise principally when this charged liquid arrives at its destination (e.g. another container, spray booth etc.) rather than at the source container. Provided all precautions appropriate to the destination are applied there

are no specific additional risks associated with the vessel being emptied and the inclusion of this vessel in the earthing or bonding scheme for the process is the only requirement specifically relating to this part of the equipment.

### 3.3.10 Mixing and Blending in Storage Tanks and Vessels

Mixing in storage vessels may be done by circulating the liquid (jet mixing) or by mechanical agitation (stirring).

Mixing readily miscible liquids (e.g. different hydrocarbons) is comparable to a filling process and similar precautions and flow speed limits should be applied.

Mixing to dissolve suspended solids in a low conductivity solvent can generate very high levels of charge and may require limitations to the speed and size (or power) of the stirrer and/or the addition of static dissipater additive to provide a higher conductivity (> 1 000 pS/m has sometimes been needed). More details are given in IEC 60079-32-1 <sup>Ref 17 Sec7.9</sup>. Specialist advice should be sought for these operations.

Where personnel are involved in emptying bags or drums into flammable solvents the operation should, if possible, be organised to load the solids first then add the liquid. Personnel carrying out such operations should wear conductive or anti-static footwear and gloves. The total resistance from drum etc., to earth via gloves, operator, footwear and floor should not exceed 100 MΩ. In some cases the floor may need to be treated, modified or kept clear of insulating deposits to achieve this. Clothing should not be removed in areas where a flammable atmosphere may be present.

Care is needed to avoid hazardous charging of drum coatings and removable liners. Details are given in IEC 60079-32-1 <sup>Ref 17</sup>.

### 3.3.11 Dipping and Sampling

After liquid has been transferred or mixed it may be necessary to dip or sample a tank. During the period of transfer or agitation, static charge will have built up within the tank and sufficient time must be allowed both for this charge to dissipate (relaxation time) and for all charge generating processes (e.g. the settling of a suspended phase) to cease. Most hydrocarbon tanks contain a small amount of second phase e.g. water and, to allow for settling, the recommended waiting time before sampling or dipping is 30 minutes <sup>Ref 17, Ref 23 Part 2 Sec 6.3.2</sup>, unless a fixed sampling or sounding tube is fitted.

The dipping or sampling of flammable liquids must not be carried out whilst product transfer or mixing is in progress <sup>Ref 23 Part 2 Sec 6.3.1</sup> or in extreme adverse weather conditions such as thunderstorms, heavy snow or hail <sup>Ref 12, Ref 17, Ref 23 Part 2 Sec 6.4</sup>.

The equipment used for dipping should be conductive (e.g. metal) or dissipative (e.g. wood or carbon-loaded plastic) and should be earthed or bonded to the tank. Sampling tapes or cords should be of materials such as metal or natural fibres (e.g. hemp, sisal or manila), which have resistivities that are unlikely to permit the accumulation of static charge <sup>Refs 12, 17, 23</sup>. Note that chains should not be used because continuity may be lost between links.

Small sample containers may be conductive and earthed or made of higher resistivity materials such as glass or plastics.

### 3.3.12 Anti-static (Static Dissipater) Additives

Anti-static (static dissipater) additives work by increasing the conductivity of the liquid and thus reducing the relaxation time. However, additive concentration can be depleted by loss to a contacting aqueous phase or, particularly in newly additised systems, by migration to pipe or tank walls. Depletion may cause a liquid to return to a low conductivity state after being dosed with anti-static additive. Reliable

procedures must therefore be in place to ensure that the additive is still present and active if pumping at high velocities is to take place. This requires a carefully planned programme of conductivity measurement along with provision for possible re-additisation.

As an example, anti-static additives are used in aviation fuels and fuel conductivities have to be regularly checked throughout the distribution network to ensure compliance with specifications.

ESIG does not recommend the use of anti-static additives in solvents for the sole purpose of enabling higher flow speeds and it would be wrong for solvent users to assume that the addition of an anti-static agent necessarily makes the solvent safe to use without any other precautions. However where antistatic additives are added, even though this may be done for other application purposes, they can provide a useful additional safety margin where flow speeds are compliant with the requirements for low conductivity liquids.



## ANNEX 1 Explosive atmosphere regulations (ATEX)

Existing European regulations (the ATEX workplace directive <sup>Ref 11</sup>) address the problems of working with explosive atmospheres by requiring that hazardous areas are zoned. Ignition sources should not be present in a zoned area and any work, maintenance or repair within these areas must be subject to risk assessment or a permit to work system. Suitable equipment, defined and certified as described in the ATEX equipment directive <sup>Ref 10</sup> should be used within each zone.

**ZONE 0:** An explosive gas/air mixture is continuously present for long periods: for example inside processing vessels and tanks.

**ZONE 1:** An explosive gas/air mixture is likely to occur in normal operation. The extent of Zone 1 is defined as follows for particular situations:

- Open vessels: vertically from ground level to 1 m above the vessel and horizontally 2 m from vessel.
- Pumping inside a building: within any enclosure around the pump.
- Metered discharge point: within 2 m horizontally of the discharge point and from floor level to 1 m above the source.

**ZONE 2:** An explosive gas/air mixture is not likely to occur in normal operation and if it does occur will only exist for a short time. The extent of Zone 2 is defined as follows for particular situations:

- Closed process vessels: vertically from ground level to 2 m above the vessel and horizontally 2 m from the vessel.
- Open vessels: horizontally 2 m beyond the zone 1 boundary and vertically to a height of 3 m if the zone 1 area is <3 m in height.
- Pumping inside a building: within a horizontal radius of 4 m and vertically from the ground level 2 m above the unit.
- Metered discharge point: horizontally 2 m beyond the zone 1 boundary and vertically to a height of 3 m if the zone 1 area is <3 m in height.

## ANNEX 2 Information on earthing

The EI Electrical Safety Code <sup>Ref 26</sup>, follows BS 5958 <sup>Ref 23 Part 13.4.2</sup> Table 4 in recommending that in Electrical Zones 0, 1, and 2 the earthing resistances for metal items including tanks, fixed metal plant, pipelines and transportable metal

containers (drums, ISO containers, IBC's road and rail tanks etc.) should not exceed 10 Ω. Further comments on earthing requirements are listed in Table 4.

**Table 4: Earthing recommendations**

Type of installation	Comments
Tanks	Normally 2 earthing connections are required but on larger tanks more are needed. See Notes 1 & 2 below
Large fixed metal plant	Earthing is normally inherent in the structure. Occasionally items may be mounted on non-conducting supports and special earthing connections may be required
Metal pipelines	Earthing is normally inherent in the structure. Special earthing connections may be required across joints if there is doubt that the 10 Ω criterion will be satisfied.
Transportable metal containers	Special earthing connection will normally be required

**NOTES:**

1. More information on other structures can be obtained from the EI Electrical Safety Code <sup>Ref 26</sup> and BS 5958 <sup>Ref 23</sup>.
2. The EI Electrical Safety Code recommends that tanks over 30 metres in diameter should have 3 earth connections. BS 6651 <sup>Ref 27 Sec 22.2.5.1</sup> on lightning protection, recommends that metal structures should be protected by earthing and that the earthing points should not be more than 10 metres apart, equally spaced. A 30-metre diameter tank would therefore require 9 earthing points. The tank earthing requirements for lightning protection are far stricter than those required for the safe dissipation of static electricity.
3. Calculations have shown that an overall safe resistance to earth for static dissipation is 1 MΩ <sup>Ref 17, Ref 23 PART 1 Sec 13.2.2</sup>. Even 100 MΩ is safe in many situations. The code points out that achieving an earth resistance of less than 10 Ω presents no practical difficulties and therefore recommends a 10 Ω maximum resistance to earth.

## ANNEX 3

## Solvents that produce flammable atmospheres at ambient temperatures

## A 3.1 GENERAL

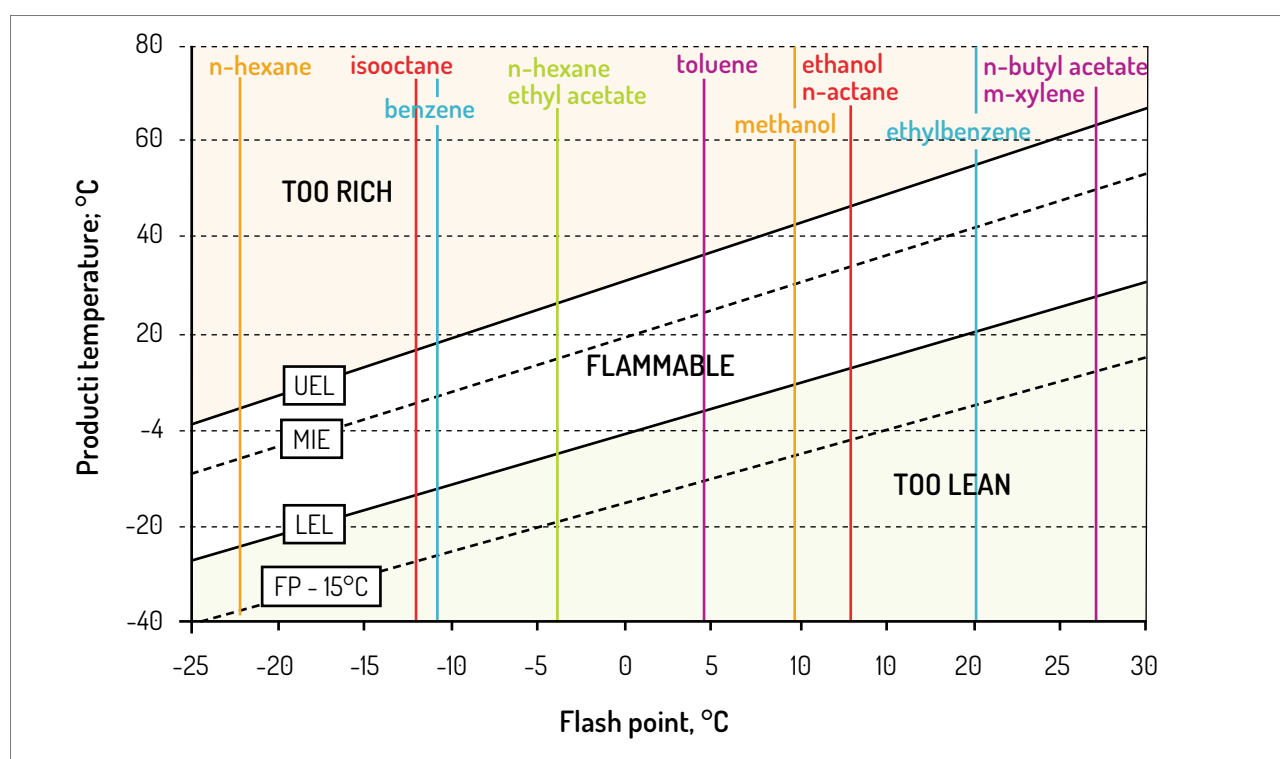


Figure 6: Flammability of equilibrium solvent vapours

Flammability data for the equilibrium vapours of some common solvents are shown in Figure 6, which includes the following:

- The approximate temperature range over which the equilibrium vapours of solvents with different flashpoints are too lean for combustion (green area). Temperatures in the Too Lean region are unlikely to produce explosive mixtures

and ignition cannot generally happen in this temperature range. The “FP -15C” line shows the temperatures 15 °C below the Flash Points. It can be regarded as the maximum recommended handling temperature to be sure that the vapours are Too Lean and includes a margin for uncertainties in surface temperature, Flash Point and product composition. It should, however, be noted that even when operating in the Too Lean region a flammable atmosphere may occur

if vapours from a more volatile liquid could be present, for example from previous operations with the equipment (e.g. switch loading) or as a result of nearby activities.

- The approximate temperature range over which the equilibrium vapours produce explosive mixtures (clear area). Ignition is possible throughout this region although towards the upper and lower boundaries (UEL and LEL) a high energy ignition source is needed to initiate combustion. The most easily ignitable mixtures occur around the MIE line, which lies on the rich side of the centre of the region. At temperatures close to the MIE line the equilibrium solvent vapours are at their most readily ignitable and particular care is needed to ensure that all precautions are scrupulously followed.
- The approximate temperature range over which the equilibrium vapours are Too Rich for combustion (orange area). Ignition is less likely to occur in this temperature range than in the Flammable range because the equilibrium vapour mixture is over rich. However, ignition or explosion cannot be ruled out because the vapour concentration may be temporarily reduced below the equilibrium value by the ingress of air into the vapour space (e.g. through openings such as manlids) and hence may enter the Flammable range. Consequently operation in the Too Rich region cannot generally be relied upon as the only measure for preventing ignition.
- The location of a selection of common solvents on the Flash Point scale (vertical lines with vent names). The flammability range for other solvents may also be assessed in an approximate fashion from Figure 6 if the Flash Point is known.

Figure 6 may be used in one of the following ways:

- To find the maximum recommended handling temperature for a solvent of known Flash Point read the corresponding temperature from the “FP-15C” line. The temperatures corresponding to the LEL, UEL and most easily ignitable mixture can be found in a similar way from the other lines on the diagram.
- To check the flammability issues associated with a given

operation select the point defined by the Flash Point of the product (x axis) and the handling temperature (y axis).

- If the point lies well within the too lean (green) zone (e.g. below the “FP-15C” line) there should not be ignition issues unless the product is handled in hazardous areas created by other materials or could be contaminated with other materials.
- If the point lies in the flammable zone there are likely to be ignition hazards. Ignition occurs most readily when the point lies close to the MIE line.
- If the point lies in the too rich zone the equilibrium vapour concentration is non-flammable and ignition hazards are reduced. However, ignition could still occur if the vapour concentration was reduced below the equilibrium value e.g. by mixing with fresh air. Therefore, the maintenance of such a condition should not be relied upon as the main or only safeguard against ignition because it is easily affected by the ingress of air.

To use n-heptane as a detailed example: the flashpoint is -4 °C. If the product temperature is 40 °C the equilibrium vapours will be too rich for combustion and ignition will only occur if there is a departure from equilibrium (e.g. around an opening). If the product temperature is 22 °C the equilibrium mixture strength lies just within the flammable range and ignition can occur. However, an ignition source would need to deliver considerably more energy than the MIE before ignition was possible. If the temperature is -14 °C the mixture strength is close to the MIE value and the vapour is at its most readily ignitable. Ignition hazards are at the most likely here.

At -8 °C the mixture strength is close to the LEL. Ignition may just be possible but a small departure from equilibrium would prevent it and the ignition energy is higher than the MIE. If the temperature is below -20 °C the mixture strength is well into the too lean zone and the vapour concentration will not be high enough to support ignition. Similar analyses show that for n-hexane the equilibrium vapours are Too Rich at tropical temperatures and temperate summer temperatures

whereas, in contrast, xylenes only just exceed the UEL under relatively warm/hot summer conditions for a temperate climate. Common solvents of intermediate Flash Point including n-heptane, ethyl acetate, toluene, methanol and ethanol produce vapours of near optimum concentration for ignition at commonly occurring temperatures in temperate climates and consequently are particularly vulnerable to ignition.

**NOTES:**

1. The LEL, MIE and UEL lines given on Figure 6 are regression lines obtained from data for the solvents shown. For all solvents shown on the graph the true values are close to the regression lines. For other solvents, the lines give reasonable approximate guidance but departures from the regression-line values may be greater.
2. Figure 6 does not provide a comprehensive coverage of common solvents. For example solvent mixtures such as white spirits or naphthas of the relevant boiling range are not shown but also commonly give rise to flammable atmospheres in the ambient temperature range.
3. Although the high conductivity solvents shown in Figure 6 are not generally susceptible to static charge accumulation, they may accumulate charge if isolated by an insulating material such as a container lining (see 3.2.3).

## A3.2 APPLICATION TO SELECTION OF IBCS

Figure 6 shows data that may be used, if required, in risk assessments relating to the selection of IBCs. Some key factors based on the assumption that the range of solvent loading temperatures encountered in Europe is between -20 °C and 45 °C are now picked out.

1. The essential condition for avoiding the production of a flammable vapour atmosphere is that the handling temperature should be less than the Flash Point of the solvent by a suitable margin, usually taken as 15 °C (see 2.2.3). This rule may be used where there is a good knowledge of loading conditions and solvent properties. If a simpler, more generic approach is required, the loading temperature range given above suggests that a flammable vapour atmosphere will not be produced during the filling of IBCs at ambient temperature provided the solvent has a Flash Point of more than 60 °C.
2. The greatest caution in recommending the use of static-protected IBCs should be exercised for those solvents that produce their most readily ignitable mixture strengths at common ambient handling temperatures. Generally these can be taken as all the solvents that have Flash Points below 35 °C although, with knowledge of specific process conditions, a narrower range of Flash Points for enhanced concern can be identified from Figure 6.
3. Users cannot rely on the presence of an over-rich atmosphere as a primary safeguard for filling operations. Nevertheless the generation of over-rich atmospheres does reduce the risk of ignition from internal ignition sources when filling IBCs with very low Flash Point solvents, in particular those that have a Flash Point more than 45 °C below the loading temperature<sup>6</sup>.

6. However these solvents produce copious amounts of vapour and are more vulnerable to ignition by vapour leaks encountering external ignition sources.

## Glossary

**Bonding:** A connection between conductors that provides electrical continuity.

**Combustible:** Capable of burning in air when ignited and, for liquids, having a Flash Point of more than 60 °C.

**Earthing:** A connection between a conductor or a bonded assembly of conductors and electrical earth.

**Flammable:** Capable of being ignited and, for liquids, having a Flash Point of 60 °C or less. See Table 2 for European criteria for flammability assignment of risk phrases. Incendive: Having sufficient energy to ignite an optimum flammable mixture.

**IBC:** Intermediate Bulk Container.

**Inert:** Incapable of supporting combustion.

**Inerting:** To render incapable of supporting combustion.

**Static Accumulator:** A liquid that, by virtue of its very low conductivity, is capable of retaining a significant electrostatic charge when in contact with earth.

## References

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2. EN12215, *Coating plants - Spray booth for application of organic liquid coating materials - Safety requirements*
3. EN13355, *Coating plants - Combined booths - Safety requirements*
4. EN12581, *Coating plants - Machinery for dip coating and electrodeposition of organic liquid coating materials - Safety requirements*
5. EN1953, *Atomising and spraying equipment for coating materials - Safety requirements*
6. EN1539, *Dryers and ovens, in which flammable substances are released - Safety requirements*
7. EN12753, *Thermal cleaning plants (incinerators) for exhaust gas from surface treatment plants - Safety requirements*
8. EN50176, *Stationary electrostatic application equipment for ignitable liquid coating material - Safety requirements*
9. prEN50050, *Electrostatic hand-held spraying equipment - Safety requirements - Part 1: Handheld spraying equipment for ignitable liquid coating materials*
10. 10) ATEX 1: ATEX 95 *equipment directive 94/9/EC, Equipment and protective systems intended for use in potentially explosive atmospheres.*
11. ATEX 2: ATEX 137 *workplace directive 99/92/EC, Minimum requirements for improving the safety and health protection of workers potentially at risk from explosive atmospheres.*
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27. BS6651 *Code for protection of structures against lightning*, British Standards Institute.



## Further reading

### *1. General hazard information*

*EI Model Code of Safe Practice Part 19: Fire precautions at petroleum refineries and bulk storage installations, 2007, Energy Institute.*

### *2. Aviation fuel requirements*

Specification DERD 2494 Issued by the British Ministry of Defence.

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EUROPEAN SOLVENTS INDUSTRY GROUP

Tel: +32 2 436 94 88 [www.esig.org](http://www.esig.org)  
[esig@cefic.be](mailto:esig@cefic.be)

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