

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 promotes best practices 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. ESIG has developed this document to explain the main characteristics of solvent flammability and provide recommendations for safe handling and 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

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 “Key Applications” on the ESIG website (<https://www.esig.org/key-application>).

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 causes of many such incidents include insufficient understanding of the solvent properties that govern the hazards and insufficient knowledge of the measures available for controlling the risk. This Safety Guide aims to provide this understanding and knowledge.

A summary of the recommended measures is provided in the Top Ten Tips box.

For more detailed guidance, we have identified the root causes of incidents (Section 1.2) and provided general recommendations for prevention (Section 1.3). Implementation of these recommendations requires an understanding of the properties that make solvents hazardous and a knowledge of the measures for risk management. 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 application-specific guidelines (e.g. the safety measures for spray coating and painting in References 1 to 9), in the Safety Data Sheet (SDS) or in the information provided by your supplier for your identified use.

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: know where flammable atmospheres could occur and what ignition sources may ignite them. General information is provided in Part 2. Product-specific hazard information can be found in the Safety Data Sheet (SDS) for the product. It is the supplier's legal obligation to provide an SDS for each hazardous product that you use.
2. Eliminate ignition sources, e.g., no smoking, safe work systems, equipment selection, and control the build-up of electrostatic charge (see Part 3) with suitable equipment, flow rates and earthing arrangements.
3. Ensure good ventilation by working in open atmospheres (e.g., keeping doors and windows open) or using adequate ventilation systems.
4. Work at ambient temperatures or below: try to keep the working temperature below the Flash Point (FP) by a suitable margin wherever possible (see section 2.2.3).
5. Provide information, guidance, training and Personal Protective Equipment (gloves, flame retardant clothing, antistatic 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.

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1.2 ROOT CAUSES OF INCIDENTS

Common root causes of incidents are:

- Lack of training, leading to insufficient Manager/Supervisor/Operator awareness of risk or competence in risk management.
- Use of contractors who are not aware of the risks or how to manage them
- Poor communication both internally and with contractors. Communication is particularly important after process changes. The consequences of poor communication can be catastrophic ^{Ref10}.
- Low understanding of how and where flammable atmospheres could occur
- Low understanding of the importance of safeguarding against electrostatic discharges
- Poor control of solvent use, especially in hot areas
- Heating solvents without adequate controls
- Poor housekeeping
- Poor implementation of control measures such as restricting the release of flammable vapours or eliminating ignition sources
- Poorly designed equipment or installation, leading to unnecessary emissions or leaks
- Using equipment not suited to the job: use only ATEX approved equipment ^{Ref11} selected according to the zoning defined in the ATEX workplace directive ^{Ref12}
- Poorly designed tasks that either create hazards or leave excessive scope for human error (e.g. lack of controls to prevent overfilling)
- Inadequate or poorly managed maintenance activities
- Equipment failure
- Badly managed transfer operations such as the filling and emptying of equipment
- Loading and unloading solvents without adequate precautions

1.3 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 involves minimising/controlling the generation of flammable atmospheres, having a complete awareness of where flammable atmospheres may, nevertheless, occur and controlling the presence of ignition sources to ensure that a flammable atmosphere and an ignition source do not occur together. It thus requires that managers and supervisors have:

- a. Hazard awareness: the knowledge and training needed to recognise how and where flammable atmospheres could occur and what ignition sources might potentially be present and in need of control (see 1.3.1 and Part 2).
- b. Knowledge of the measures that can be used to control these hazard factors once they have been recognised (see 1.3.2 and Part 3).

It is then vital that the hazards and control measures are effectively communicated to all operators, both in-house and contractors ^{Ref10}.

1.3.1 Knowledge and training for hazard awareness

- 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 the air can be raised to before there is a risk of self-ignition (see 2.3.2.1). 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.). The risk of accumulating a hazardous level of charge in a solvent depends on its electrical conductivity. For a general assessment of this hazard, it is sufficient to know whether the minimum solvent conductivity – measured in picosiemens/metre (pS/m) – could be classified as Low (≤ 50 pS/m), Medium (50 pS/m to 10 000 pS/m) or High ($> 10\ 000$ pS/m)^{Ref 13}.
- Low conductivity solvents may generate hazardous voltages on liquid surfaces during simple liquid handling operations such as filling tanks, drums or other containers or when cleaning tanks with liquid sprays. Therefore, all low conductivity liquids are handled with an increased level of static-control precautions (filling rate restrictions, constraints on the 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. Nevertheless, they may 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 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.
- Be aware that in the presence of a solvent mist or spray, the atmosphere may be flammable even if the solvent is well below its FP. Avoid mists or sprays where practicable.
- Be aware of the wide range of ignition sources 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 with 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.

1.3.2 Good operating practice and control measures

Take an appropriate combination of the following measures to minimise the occurrence of flammable atmospheres:

- Maintain equipment in good condition to ensure that solvent leaks are avoided.

→ Regularly inspect equipment such as containers and hoses and retire any that are damaged.

→ Minimise the risk of damage, e.g., by good housekeeping and careful use of powered equipment such as forklift trucks.

- Where practicable, use a combination of the following measures to maintain the solvent vapour concentration well below the Flammable Range.

→ Keep 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).

→ Ensure adequate ventilation. This is particularly important when working above the FP cannot be avoided. 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 be acceptable to permit a higher fraction of the LEL, subject to a rigorous risk assessment.

→ Where possible, the easiest way to assure ventilation is by opening doors and windows, but this may not be adequate to keep the vapour concentration reliably below 25% of the LEL. Mechanical ventilation is often necessary: it 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 airflow detector should be used in the ducts and linked to an alarm in case of a possible extraction system failure.

→ Store solvents in correctly rated containers or tanks and ensure adequate secondary containment.

→ Apply basic housekeeping practices. Prevent unnecessary

vapours by using no more solvent than is required, keep lids on containers and use sealed containers for solvent contaminated waste. Do not leave solvent impregnated rags lying around.

→ Remember that solvent vapours are heavier than air and settle in low areas such as drains. Check these areas before working on them and ensure that transmission through drains will not take vapours into uncontrolled regions.

→ 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 (at a low level because flammable solvents accumulate in low areas).

→ Prevent or minimise solvent spray or mist formation.

- Eliminate all sources of ignition from hazardous areas within 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) 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 “dissipative” according to the criteria in IEC 60079-32-1^{Ref 13}. Hoses classified as “Conductive” or “Electrically bonded” according to EN12115^{Ref 14} meet these criteria

– 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 ≤ 5 litres) and suitably designed IBCs (see 3.3.6) unless the FP of all solvents is handled in the vicinity is $> 60^\circ\text{C}$

Note: The use of conductive or antistatic 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 other industrial ignition sources listed previously.

→ Use explosion-proof or intrinsically safe (Ex marked) electrical equipment.

→ Eliminate hot spots.

→ Ensure that vapour temperatures and equipment surface temperatures are below the AIT by solvent choice or control of process conditions.

→ As a precautionary measure, prevent the use of battery-operated equipment such as mobile phones or calculators in hazardous areas.

- If vapour concentrations in the Flammable Range cannot be avoided, and ignition sources or hot spots cannot be totally eliminated, use inert gas to reduce the oxygen concentration below the level that will support combustion (e.g., by nitrogen blanketing).

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 confined spaces should be strictly controlled, and warning notices should be provided.

- Implement the following general safety measures.

→ Follow work permit procedures scrupulously.

→ When working in confined spaces is unavoidable, a company-approved safe work system must be implemented (work permit procedure) with adequate emergency arrangements, including evacuation procedures.

→ Report faults, 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 firefighting 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.

PART 2 Flammability and ignition

2.1 INTRODUCTION

For a fire or explosion to occur, there must be a flammable atmosphere (flammable material in the right concentration range for combustion), sufficient oxidiser (usually oxygen from the air) and a source of ignition. The solvent properties and process characteristics that determine flammability are covered in section 2.2, and ignition sources and criteria for ignition are covered in section 2.3.

2.2 FLAMMABILITY

2.2.1 General

Combustion (a flash fire, flame or explosion) can only occur if the concentration of flammable material is in the Flammable Range (also referred to as the Explosive Range). Outside the Flammable Range, a propagating flame or explosion will not occur even if a highly energetic ignition source is present. For a solvent in air, the flammable material is usually present as a vapour. However, in some operations (e.g., spray painting and tank cleaning), it may also be present as a mist. The Flash Point (FP) of the solvent gives an approximate indication of the lowest temperature at which it can produce a vapour concentration within the Flammable Range in the air at atmospheric pressure. These properties, along with the role of mists in augmenting flammability, are now discussed in more detail.

2.2.2 Flammable Range

The borders of the Flammable Range are defined by:

- The lower explosive limit (LEL): the lowest concentration (in volume%) of the solvent that is flammable in air.
- The upper explosive limit (UEL): the highest concentration (in volume%) of the solvent that is flammable in air.

These limits vary from solvent to solvent and between vapour and mist. For the mist, they also vary with droplet size.

NOTE: For a vapour at equilibrium with its liquid, the vapour concentration, C_v , in volume%, is related to the vapour pressure of the liquid, P_v , and the local atmospheric pressure, P_a , by $C_v = 100P_v / P_a$. The standard atmospheric pressure is $P_a = 101.3 \text{ kPa}$. In this case, C_v is close to the vapour pressure in kPa.

If the concentration is below the LEL, the mixture is too lean for combustion, above the UEL, it is too rich. The LEL and UEL vary significantly with temperature, pressure and oxygen content. The values for a solvent vapour are given in section 9 of the supplier's SDS. They are based on combustion in air at 20 °C and atmospheric pressure (101.3 kPa) unless otherwise specified. Some examples are given in Table 1.

The general effect of increasing the temperature is to lower the LEL and raise the UEL. If you work at raised temperature, remember that the flammable range is broader than indicated in Table 1.

Table 1: Flammability properties of selected solvents in the air at atmospheric pressure

Substance (HSPA name)	Closed Cup Flash Point, °C	Lower Explosive Limit, % v/v	Upper Explosive Limit, % v/v	Autoignition Temperature, °C
Pentane	-49 ^{Ref 16}	1,5 ^{Ref 16}	7,8 ^{Ref 16}	260 ^{Ref 16}
n-Hexane	-22 ^{Ref 16}	1,1	7,5 ^{Ref 16}	225 ^{Ref 16}
n-Heptane	-4	0,8 ^{Ref 16}	6,7 ^{Ref 16}	204
iso-Octane	-12	1,1 ^{Ref 16}	6,0 ^{Ref 16}	418
n-Octane	13	1,0 ^{Ref 16}	6,5 ^{Ref 16}	206
n-Nonane	38	0,7 ^{Ref 16}	5,6 ^{Ref 16}	205
Hydrocarbons, C7-C9, n-alkanes, isoalkanes, cyclics	1	0,8	8,0	>200
Hydrocarbons, C9-C11, n-alkanes, isoalkanes, cyclics, < 2% aromatics	39	0,6	6,5	>200
Hydrocarbons, C9-C12, n-alkanes, isoalkanes, cyclics, aromatics (2-25%)	38	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
Hydrocarbons, C9, aromatics	47	1,0	7,5	>350
Acetone	-18	2,2 ^{Ref 16}	13 ^{Ref 16}	465
Methyl Ethyl Ketone	-9	1,8 ^{Ref 16}	11,5 ^{Ref 16}	505 ^{Ref 16}
Methanol	9,7	6 ^{Ref 16}	50 ^{Ref 16}	455
Ethanol	13	3,3	19	369
iso Propanol	12	2,0 ^{Ref 16}	12,0 ^{Ref 16}	399
n-Butanol	35	1,4 ^{Ref 16}	11,3 ^{Ref 16}	355
Ethyl Acetate	-4	2,0 ^{Ref 16}	12,8 ^{Ref 16}	426
n-Butyl Acetate	22 ^{Ref 16}	1,2 ^{Ref 16}	7,6 ^{Ref 16}	415

NOTES:

1. *There are multiple sources of flammability data that often give different values. Data for single species are taken from ^{Ref 15} unless indicated as ^{Ref 16}. Data for hydrocarbon mixtures are guide values taken from the previous edition of this document: actual values may differ slightly from one supplier to another.*
2. *There is no link between Lower Explosive Limit (LEL) and Occupational Exposure Limit (OEL)*

Many LELs and UELs are obtained by theoretical calculation and should be regarded as guide values only. Because of the uncertainties in LEL 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. The maximum concentration for safe operation is usually expressed as the maximum acceptable percentage of the LEL. A value of less than 25% is often specified. Where practicable, the aim should be to prevent any vapour formation (e.g., by good housekeeping and keeping vessels full of liquid).

2.2.3 Flash Point (FP)

The Flash Point (FP) is a property that is used by several hazard classification systems, including the Globally Harmonised System (GHS) and the European Regulation (EC) No. 1272/2008 (CLP), 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 in the associated vapour space 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 vapour flammability. However, 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 temperatures) tend to have lower FPs. For solvents such as white spirits (C9–C12 Hydrocarbons) 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.

The FP of a solvent is given in section 9 of the SDS provided by the supplier. Some typical examples are given in Table 1.

FP determination in the laboratory is influenced by many factors, including type of test equipment, sample size, ignition source,

temperature, ambient pressure, sample homogeneity, draughts and operator bias. During the test, one must 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. However, it is recommended that a wider margin is adopted wherever practicable.

The worst-case FP depends on the circumstances. Solvents with lower FP produce higher vapour concentrations at the liquid surface. If the FP is more than about 30 °C below the liquid surface temperature, the mixture strength at the liquid surface tends to be too rich for combustion (see Annex 1). However, in open spaces (e.g., above open trays or spills), mixing with the surrounding (vapour-free) air causes the vapour concentration to decrease with distance from the liquid. Hence, there is always a flammable zone at some distance from the surface, and somewhere in this zone, the mixture has the most readily ignitable vapour concentration. For solvents with lower FP, the increased surface vapour concentration allows the flammable zone to extend further from the liquid and increases the risk that an ignition source will be encountered. Thus, the ignition risk in open spaces tends to increase as the solvent FP reduces.

The situation is different in an enclosed vapour volume, such as a tank ullage space. The outer boundary of the volume is a solid surface rather than air, so there is not necessarily a flammable zone created by mixing at the edge and, at least in small spaces, the vapour concentration is likely to approach the solvent surface value over the entire space. In these circumstances, low FP solvents (FP more than about 30 °C below the liquid surface temperature) tend to produce vapour concentrations that are over-rich: the atmosphere inside the petrol tank of a car is a common example. In contrast, intermediate FP solvents (FP roughly between 30 °C below the surface temperature and the surface temperature – see Section 2.2.5.2 and Annex 1) tend to produce vapour concentrations that are flammable. Of these, the solvents with FP around 20 °C below the surface temperature generally produce

the most easily ignited vapour concentration and therefore have the highest ignition risk. For example, when the solvent surface temperature is 20 °C, solvents with FPs between -10°C and 20 °C are the most likely to produce flammable mixtures in enclosed spaces and, of these, the solvents with FP close to 0 °C will tend to be the most easily ignited. Toluene and n-heptane are prime examples.

NOTES:

1. *Switch loading (loading a higher FP solvent into a container that previously carried a low FP solvent without freeing the container of vapour and liquid between loads) can lead to a flammable atmosphere when loading high FP solvents.*
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 hazard statements and Classification, Labelling and Packaging (CLP) criteria commonly found in section 2 of SDS.

Table 2: CLP criteria for flammability assignment of hazard statements ^{Ref 17}

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.

Solvent mists 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, such as the degreasing of metal parts or paint spraying, that involve spraying techniques.

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

Mists can propagate a flame if the quantity of solvent present is high enough. Explosion could occur in confined conditions.

Mists are characterised by LEL and UEL in the same way as vapours. However, 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.

2.2.5 The Practical Occurrence of Flammable Atmospheres

Liquid flammability classifications, such as the CLP criteria in Table 2, assign solvents unambiguously to particular types. However, the flammability of vapour-air mixtures also depends on the operating conditions (particularly the temperature), and this must be considered to obtain a more application-oriented

indication of how and where flammable atmospheres occur. There are three main categories of operation.

2.2.5.1 Low vapour pressure operations

These are operations in which the equilibrium vapour concentration produced by the solvent is below the LEL by an acceptable margin (see Section 2.2.2), even at the highest temperature expected in the operation. This is often indicated by the FP being above the maximum solvent temperature by an appropriate margin (see Section 2.2.3)¹. Despite the low vapour pressure of the solvent, a flammable atmosphere may be produced under the following circumstances:

- Inside a vessel or container:
 - Switch loading: that is filling in the presence of residual vapour from a previous operation involving a medium or high volatility solvent
 - Filling in the presence of a solvent mist in the vapour space or foam on the liquid surface
 - Drawing in flammable vapour from outside (e.g. in a hazardous area or if there is an external spill) when emptying a vessel or container or cooling the contents
 - If the solvent temperature has risen above the expected range
 - Cleaning with a vigorous jet that produces a fine mist or spray
- Outside a vessel or container:
 - Filling with open venting when the solvent temperature has risen above the expected range.
 - Around open dishes or trays, leaks or spills if the solvent temperature is higher than expected.
 - In the presence of vapours from other operations (hazardous areas).

¹ Because the mean atmospheric pressure at sea level is ~100 kPa, the equilibrium volume percentage of vapour in air is approximately equal to the vapour pressure in kPa. Hence the classification definition implies that the maximum vapour pressure of the solvent (i.e., for mixtures, when very little has evaporated) in kPa at the highest operating temperature is below the LEL. At altitude, the maximum vapour pressure is lower in proportion to the atmospheric pressure.

Examples of low vapour pressure operations include handling solvents with $FP > 60\text{ °C}$ at normal ambient temperatures.

2.2.5.2 Intermediate vapour pressure operations

These are operations in which the equilibrium vapour concentration produced by the solvent could lie between the LEL and the UEL at a temperature within the expected operating range. In closed spaces, such as the ullage space of a tank, vapour concentrations are often close to the equilibrium value, so vapours in closed spaces are particularly vulnerable to ignition in intermediate vapour pressure operations.

In intermediate vapour pressure operations, a flammable atmosphere may be produced under the following circumstances.

- Inside a vessel or container:
 - There will normally be a flammable atmosphere except transiently at the start of filling a vapour-free vessel/container or far above the liquid surface in a large tank.
- Outside a vessel or container:
 - During filling with open venting, the displaced vapour may produce a flammable atmosphere around the vent. The extent of this external flammable zone is more limited than in high vapour pressure operations, but if the external vapour does ignite, the flame can propagate back into the vessel or container with potentially disastrous (explosive) consequences.

(Distressing examples of this type of ignition have occurred in countries with fuel specifications that allow diesel fuel with an intermediate vapour pressure at ambient temperatures. Several coach accidents have resulted in fires that flashed back into the diesel tank resulting in explosions and multiple fatalities).

- Around open dishes or trays, leaks or spills.
- If the solvent is sprayed.
- If a vessel or container is overfilled and a spill occurs, either directly or later, as a result of thermal expansion.

The equilibrium vapour pressure typically reaches the LEL when the temperature is a few degrees below the FP (a margin

of 5 °C to 15 °C is commonly allowed, see Section 2.2.3), and for many solvents, it reaches the UEL at 30 °C to 40 °C above the FP (see Annexe 1). These temperatures are useful for identifying the most at-risk operations in closed spaces. Working below the FP by an adequate margin prevents ignition but working above the UEL temperature does not provide a reliable (over-rich) safety measure because air ingress or incomplete mixing may give regions of reduced vapour concentration and, for mixtures with a wide boiling range, the vapour pressure falls as the fraction evaporated increases.

Examples of intermediate vapour pressure operations include loading toluene or ethanol into trucks or containers at common ambient temperatures.

The most readily ignitable mixture strength (slightly richer than stoichiometric) lies near the middle of the flammable range and, for an equilibrium vapour, it typically occurs at about 20 °C above the FP. Intermediate vapour pressure operations at these temperatures (e.g., toluene at $\sim 24\text{ °C}$, n-heptane at $\sim 16\text{ °C}$) are particularly sensitive to ignition.

2.2.5.3 High vapour pressure operations

These are operations in which the equilibrium vapour concentration of the solvent is above the UEL by a considerable margin even at the lowest operating temperature and, for wide boiling range solvents, the highest degree of evaporation associated with the operation. The high vapour pressure reduces the ignition risk in closed spaces because the atmosphere tends to be over-rich but increases it in open spaces, e.g., above open trays or around spills. The increased risk arises in open spaces because there is always a flammable zone between the region of high vapour concentration and the surrounding air. In a high vapour pressure operation, this zone is larger and extends further from the vapour source, which increases the risk of encountering an ignition source.

In high vapour pressure operations, a flammable atmosphere may occur under the following circumstances.

- Inside a vessel or container (closed spaces):
 - With ventilation of the vapour space
 - In the early stages of filling an initially vapour-free vessel or container

- When drawing air into the vapour space as solvent is pumped out or as warm solvent cools
- If the solvent temperature has fallen below the expected range
- If most of the solvent has evaporated so, there is little of the more volatile components left
- With stratification or limited mixing in the ullage space of a large tank.

It is often not possible to rule out ignition risks inside a vessel or container in these operations, but the probability of ignition is lower than in intermediate vapour pressure operations.

- Outside a vessel or container (open spaces):
 - At openings and vents, particularly when filling the vessel or container. The extent of the external flammable zone is greater than for intermediate vapour pressure operations, but fires that start in these external regions cannot propagate back into the tank when the internal mixture is too rich.

(A common example, closely related to solvent handling, arises at the filler opening of a car petrol (gasoline) tank. Gasoline tank filling is a high vapour pressure operation, and several ignitions occur every year at self-service stations when customers who have become electrostatically charged return to their vehicle to unlatch a hands-free nozzle. These ignitions produce a flash fire around the opening, but the vapours in the tank do not ignite. There are many online videos).
 - Indoors: with poor ventilation, vapours escaping from container vents could create an extensive flammable zone in the surrounding area. This may spread unexpectedly via drains.
 - Around open dishes or trays, leaks or spills. The risk is greater with high volatility solvents because of the larger flammable zone they produce.
 - If the solvent is sprayed.
 - If a vessel or container is overfilled and a spill occurs, either directly or later, as a result of thermal expansion.

2.2.6 Controlling Flammable Atmospheres

2.2.6.1 Inside vessels or containers

- Avoid switch loading as far as practicable
- Allow warm solvents to cool before loading
- Use inerting if flammable atmospheres could occur and ignition sources cannot be prevented

2.2.6.2 Outside vessels or containers

- Avoid the use of open trays as far as practicable
- Avoid free jets and spraying as far as practicable
- Consider using closed systems with vapour balancing rather than open venting
- Provide adequate ventilation in working areas
- Minimise the risk of leaks from pipes, hoses or containers by:
 - Ensuring, as far as practicable, that forklift trucks do not damage containers or hoses
 - Inspecting equipment regularly and removing damaged items from service
 - Checking couplings and flanges do not leak
- Prevent the overfilling of tanks, vessels and containers by using overfill protection where necessary, e.g., particularly with opaque walls and ensure that the maximum permitted fill level has an appropriate allowance for thermal expansion.

2.3 IGNITION

2.3.1 Sources of Ignition

Many industrial activities involve conditions, processes or activities that could readily ignite the vapours of common solvents. As noted in Section 1.3, these ignition sources require strict control wherever a flammable atmosphere may occur. They can be classified into four categories:

2.3.1.1 Flames and Smouldering

This category includes all naked flames such as welding torches, matches, gas burners (including pilot lights), and sporadic sources such as the exhaust of an engine.

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

2.3.1.2 Hot Surfaces

Hot surfaces may ignite flammable solvent/air mixtures either directly or indirectly. Direct ignition can occur if the surface is at a temperature above the auto-ignition temperature of the solvent/air mixture. Indirect ignition results from the burning or smouldering of material initiated by a hot surface.

Hot surfaces are common in industrial areas: examples are the walls of ovens and furnaces, electrical equipment, heating pipes, welding operations and surfaces heated by high intensity lights or lasers. They may also be produced by mechanical faults.

2.3.1.3 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 (e.g., on a hose end coupling) strikes rusty steel, can produce sufficient energy to ignite flammable vapours.

2.3.1.4 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 2) and to select appropriate electrical equipment for each zone. Electrical discharges are widespread and often

hidden. They can originate from the following primary 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, and 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). Electrical equipment may also have hot surfaces. To avoid these issues, all electrical equipment used in solvent service must be ATEX approved ^{Ref 11} (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 a heat build-up in materials.
 - The interruption of stray currents, such as those that can flow around low resistance earth loops formed by ship's mooring cables, pipelines, railway lines etc., can give rise to incendive "break flash" discharges. ^{Refs 13, 18}
- Electrostatic discharges
 - Static electricity is such an important source of incidents when handling solvents, particularly 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 19}.

2.3.2 Criteria for Ignition

2.3.2.1 Auto-Ignition Temperature (AIT)

This section is for solvent users working at elevated temperatures or where there is a risk that equipment may produce high temperatures, e.g., due to mechanical fault or chemical reaction.

A mixture of solvent vapours in air or oxygen will ignite spontaneously if the temperature is high enough. The Auto-Ignition Temperature (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 a particular test method. It is not an absolute value as it depends on the test parameters (e.g., volume of the test container and nature of the wall material). In the most common method (ASTM E659 ^{Ref 20}), small quantities of liquid are injected into a 500 ml borosilicate glass round bottom flask that has been heated to a known temperature. The AIT is determined by the chemical structure of the molecule and is not linked to either the boiling point or the FP of the solvent (it is usually well above the boiling point). The AIT of a solvent is given in section 9 of its SDS. Some examples are provided in Table 1.

AITs are significantly lowered when the pressure is increased above atmospheric or in the presence of catalysts, some of which, including metals, are commonly present in industrial equipment.

In view of the potential difference between the AIT and the real auto-ignition temperature of a process, it is important to note that the AIT should not be regarded as providing a clear cut-off between no-ignition and self-ignition conditions. Instead, it gives just a very rough indication of the maximum temperature to which flammable mixtures can be exposed without self-ignition. Therefore, a significant safety margin must be allowed between the measured AIT and the operating temperature.

The surface temperature of equipment in hazardous (zoned) areas must not exceed the AIT of the relevant solvent vapour. Therefore, the T class of equipment in the area must be correctly rated for all solvents that could be used.

2.3.2.2 Minimum Ignition Energy (MIE)

An electrical spark 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 the 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, if solvent vapours were present at a near-optimum concentration, the occasional, barely perceptible electrostatic shocks that can be experienced in buildings or when opening car doors² would probably initiate fires.

² Note: 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. Often, the first indication of static is a spark, which may 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.

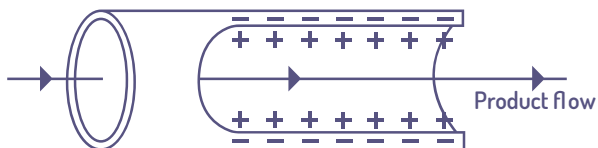


Figure 1: Charge separation in pipe flow (the opposite polarity also occurs)

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 (less than 50 picosiemens/metre (pS/m)), the solvent charge (positive in Figure 1) can only dissipate relatively slowly. In this case, when the solvent collects in a tank, the accumulation of charge in the liquid can create high surface voltages that lead to sparks with enough energy to ignite the 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. Sparks may 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 solvent handling are:

- Filtration (high/very 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 with a large surface area exposed to the flow.
- High velocity and turbulence, for example, in flow through pipelines or in the 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 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 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^{Ref 21}, 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 vehicles.
- 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 the 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 IEC 60079-32-1^{Ref 13} or CENELEC TR 50404^{Ref 18}.

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. Hazardous surface voltages can only occur if dissipation is slow. If dissipation is fast, hazardous voltages are prevented.

Dissipation usually obeys Ohm's Law, and the rate of dissipation is described by the relaxation time of the liquid, τ , 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 about 5% (0.37^3) of the initial charge remains, i.e. 95% has been dissipated.

The relaxation time is determined primarily by the electrical conductivity of the liquid. With a high conductivity, charges 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, dielectric constant and relaxation time for some typical solvents are given in Table 3.

Table 3: Conductivities and relaxation times

Substance	Conductivity pS/m	Dielectric constant	Relaxation times s
Acetone	6x10 ⁶	21	3.1x10 ⁻⁵
Methyl Ethyl Ketone	5x10 ⁶	19	3.3x10 ⁻⁵
n-Butanol	4x10 ⁶	18	4.1x10 ⁻⁵
Iso-Propanol	2x10 ⁶	18	8.1x10 ⁻⁵
Ethyl Acetate ³	2x10 ⁶	6.2	2.8x10 ⁻⁵
n-Butyl Acetate	2x10 ⁶	5.0	2.2x10 ⁻⁵
Ethanol	4x10 ⁶	25	5.6x10 ⁻⁵
Methanol	7x10 ⁶	33	4.2x10 ⁻⁵
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 in industrial grade solvents. Only the large difference between hydrocarbons and oxygenated solvents figures 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. In particular, the conductivities of higher-grade hydrocarbon solvents can be much lower than those shown in Table 3 (e.g. the conductivity of n-heptane or n-hexane is readily reduced to 10^{-2} 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. Because they provide slow dissipation, they are vulnerable to electrostatic ignition and need to be handled with increased levels of control against electrostatic ignition hazards ^{Refs 13, 18}.

The polar solvents listed in Table 3 include alcohols, ketones and acetates. These all have high conductivity (see section 1.3.1) and short relaxation times that allow rapid charge dissipation. They are consequently much less vulnerable to electrostatic ignition. Nevertheless, circumstances occasionally arise where electrostatic ignitions can occur with high conductivity solvents. For example, when they are splash-loaded into unbonded conductive containers, containers made of non-conductive material (e.g., plastic buckets) or containers with non-conductive coatings or linings, the unbonded container or non-conductive material can isolate the liquid electrically from the earthed parts of the containment system and allow charge accumulation despite the high liquid conductivity. Care must therefore be taken with all flammable solvents.

3.2.4 Quantifying Relaxation Time

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

$$\tau = \epsilon \epsilon_0 / \kappa$$

where:

τ = Relaxation time (s)

ϵ = Relative permittivity of the liquid

ϵ_0 = Permittivity of free space (8.85 pF/m)

κ = Liquid conductivity (pS/m)

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

$$\tau = 18/\kappa$$

Hydrocarbon solvents usually have conductivities less than 10 pS/m (e.g. 5 out of 7 samples in Table 3: the two higher values are associated with impurities). 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 such as the C9–C12 hydrocarbons product in Table 1 can have a conductivity of 0.5 pS/m which gives 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, the acquisition of charge can raise the conductivity significantly. The charge then dissipates faster than is indicated by the relaxation time. Generally, it may be assumed that the 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

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.

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.

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 the 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 Ω or less (or 100 M Ω 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 Ω (or 100 Ω for some hoses – see section 3.4) is often specified because a higher resistance may indicate an unreliable connection. It may be acceptable to exceed the 10 Ω limit (but not the 1 M Ω or 100 M Ω limit) if the reason is known and it is clear that the measured value is not vulnerable to further deterioration (see also Annex 2). For example, if the earthing or bonding is via an antistatic 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 Ω may be acceptable, provided it is stable and consistent with the geometry and material properties of the system.

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

The earthing/bonding requirement applies to all conductive items, including those introduced temporarily during maintenance. Unbonded conductive trash (e.g. empty cans, buckets) must not be left in tanks or vessels either in service or after maintenance.

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 the 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 Devices

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 or container (tank, truck compartment, IBC, drum etc.) where the charge could accumulate, and a flammable atmosphere could be encountered. A residence time of at least 3τ , up to a maximum of 100 s should be allowed for this purpose.

NOTE: The relaxation time, τ , should be calculated using the lowest conductivity that could occur. If this is unknown, the maximum residence time of 100 s should be adopted.

For high conductivity polar solvents (see Section 1.3.1 and Table 3), the required residence times 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

People carrying out activities in hazardous areas should wear antistatic footwear. Walkways and flooring should be antistatic so that the total resistance from operator to earth via footwear does not exceed 100 M Ω .

NOTE: The grounding of people for electrostatic hazard prevention does not require a short circuit. A resistance of 1 M Ω is sufficient. Often even 100 M Ω (as in the footwear requirement) is sufficient. For protection from electric shock, the grounding resistance should not be less than 10 k Ω .

Where gloves are worn, they should be antistatic wherever possible. If antistatic gloves cannot be used (e.g. because antistatic gloves that provide other necessary hand protection are not available), the operation should be carefully analysed either to eliminate the manual handling or to provide other means of earthing items carried by operators.

NOTE: The use of antistatic bracelets to earth an operator may not earth carried equipment if insulating gloves are being worn.

Overalls should be antistatic: natural fibres such as cotton are normally antistatic, 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^{Ref 22}. 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 might occur (e.g. metal can, steel-rimmed spectacles, steel comb or pen) could 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 man lids, use overalls with no top pockets or only zipped top pockets that must be fastened).

3.3.4 Electrostatic safety requirements for hoses

3.3.4.1 Suitable hose types

Hoses for use with flammable solvents or in hazardous areas

(Ex Zones) must meet the following continuity requirements to ensure electrostatic safety:

1. The couplings must be metallic, and the method of connection must provide a low resistance across the joint at each end.
2. The end-to-end bonding resistance between the hose couplings must not, under any circumstances, exceed 1 M Ω . If the bonding is provided by a steel mesh, one or more metal reinforcing helices or one or more bonding wires, it must not exceed 100 Ω ⁴. Some hose standards specify a lower maximum resistance (e.g. BS 5842 – see below). In this case, the limit specified in the standard must not be exceeded.
3. To avoid hazardous spillages, the use of dry disconnect couplings should be considered, especially in Ex Zones.

The solvent industry predominantly uses hoses that conform to EN 12115^{Ref 14}, BS 5842:1980^{Ref 23}, BS 3492:1987^{Ref 24} and BS EN 13765: 2018^{Ref 25}.

Hoses made to EN 12115:2021 meet one of the continuity requirements specified in item 2) above and have an electrical continuity rating of either “Conductive” (Type Ω or Ω /T – conductance provided by antistatic wall material, the resistance between couplings \leq 1 M Ω) or “Electrically Bonded” (Type M or M/T – conductance provided by two helical wires, the resistance between couplings \leq 100 Ω). They are branded with an electrical continuity rating. The difference between the basic Type Ω or Type M hoses and the /T alternatives is that the alternative has an additional requirement that the resistance through the hose wall from the inner to the outer surface must not exceed 1 G Ω (10⁹ Ω).

BS 13765: 2018 covers thermoplastic multi-layer (non-vulcanised) hoses and hose assemblies for hydrocarbons, solvents and chemicals. Internal and external helical wires provide continuity, and the continuity requirement is for resistance of \leq 100 Ω between the couplings. There may be inner liners of solvent resistant material, such as PTFE or UPE. With low conductivity solvents, PTFE linings can be vulnerable to internal discharges leading to pinhole formation and possible leaks.

BS 3492: 1987 covers rubber road and rail tanker hoses for petroleum products. It requires hoses to provide continuity via

⁴ A higher resistance would indicate a problem with the internal connections

wires and reinforcing helices. It refers to a withdrawn standard, BS 5173 Part 4: 1977 ^{Ref 26}, for the continuity test method, but neither standard specifies a resistance limit. To maximise consistency with other hose types, ESIG suggest that the end-to-end resistance between couplings should be $\leq 100 \Omega$.

BS 5842 covers thermoplastic hose assemblies for dock, road and tanker use. There are inner and outer helical wires, and the standard requires that continuity is provided by electrically bonding these to the end couplings unless otherwise specified by the user. For solvent handling, the wires must be bonded to the couplings, and in this case, BS 5842 requires that the end-to-end resistance between the couplings must be $\leq 10 \Omega$.

Metal hose assemblies are less common and are manufactured using a spiral or annular corrugated liner and stainless-steel outer braid. All metal components must be reliably bonded to each other by welding together.

PTFE hoses can be made from virgin or black anti-static PTFE. Hoses with virgin PTFE inner layers can be vulnerable to internal discharges leading to pinhole formation and possible leaks.

PVC hoses can incorporate anti-static wires and plastic or steel helices. They may be suitable for use with flammable solvents or in hazardous areas if they meet the $\leq 100 \Omega$ continuity requirement and are chemically resistant and mechanically robust enough for the duty.

3.3.4.2 Hose inspection and testing

Hoses need to be inspected and tested in service to ensure they remain safe.

The electrical resistance between the couplings should be tested periodically: the industry standard test interval is 12 months. The test must be carried out on a dry non-conductive surface, and the reading should be taken with a meter that applies an open-circuit voltage of 500 V because the application of lower voltages may fail to break down thin oxide layers that do not present a hazard. The measured resistance must be below the maximum for the hose type. If it exceeds the maximum, the hose must be retired or repaired. Even if the measured resistance is below the specified maximum, an unusual increase should be investigated as it could be a warning of imminent failure.

Bonding wires and meshes are vulnerable to damage, and contact with the couplings may be lost in service. Continui-

ty testing does not reveal all issues (e.g. bonding is often via several wires or reinforcing helices in parallel. A continuity test may not fail until the last one breaks). Therefore, care must be taken not to damage hoses in service and hose condition must be regularly inspected, particularly if there is repetitive flexing during operation or an identifiable risk of damage, e.g. forklift operations. A daily inspection prior to use is recommended. It should look for physical damage such as:

- Blisters, bulges or dents
- Looseness of the outer cover
- Excessive softening or hardening of the hose
(any of the above may indicate fatigue, fractured or displaced reinforcement or a leaking liner)
- Kinks, twists
- Abrasion, cuts, excessive elongation
- End coupling integrity
- Collapse, corrosion, scuffing or serious displacement of outer wires
- Collapse of the inner wire
- Serious scuffing of the outer cover (through to inner reinforcing fabrics)
- Severe impact damage to hose body
- Damage or deformity to the seal

A hose exhibiting a significant visible defect in any of these areas should be retired or repaired, then re-examined and resistance tested before being returned to use. Any hose with reinforcement exposed should be removed from service and replaced if the extent of the damage exceeds manufacturer recommended limits.

3.3.5 Loading Tanker Trucks, Rail Tankers and ISO Containers

3.3.5.1 Earthing

The resistance to earth of a tanker truck or ISO container vehicle with pneumatic tyres standing on a dry surface could exceed $1 M\Omega$. Therefore, the first step in loading these vehicles ^{Ref 13, Ref 27 Part 2 Sec 7.2.1} should be to attach a temporary earth connection with a maximum resistance of 10Ω to the earthing pin of the truck or container

(see Figure 2). This connection should not be detached until all other operations have been completed. Automatic earth checking systems are available, and their use is recommended.

Rail tankers are earthed through the rail, and there is no general requirement to use 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 Ω ^{Ref 27 Part 2 Sec 9.4.1}.



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

3.3.5.2 Splash filling

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

In the initial stages of bottom loading, upward spraying of the product can increase liquid surface potentials and should be prevented by reducing the initial filling velocity and using a spray deflector or other similar device.

3.3.5.3 Flow velocity

At the start of filling, the pumping velocity, v , should be no greater than 1 m/s ^{Ref 13 Ch 7, Ref 18 Ch 5, Ref 27 Part 2 Sec 7.3.3}. Once the inlet pipe is covered to twice its diameter, the velocity can be increased to its full-flow value. For low conductivity solvents, the maximum full-flow velocity, in m/s, is determined from:

$$v \leq N/d$$

subject to an overall maximum of $v = 7$ m/s ^{Ref 13 Ch 7, Ref 18 Ch 5}. Here, N is a loading parameter (the “ vd limit”) that has a value of 0.38 m²/s for road tankers and 0.75 m²/s for rail tank cars, and d is

the pipe diameter in metres. Thus, for example, when loading a road tanker ($N = 0.38$ m²/s) with a low conductivity solvent through a 3 inch (76 mm) pipe ($d = 0.076$ m), the maximum permissible loading velocity would be $0.38/0.076=4.7$ m/s. Filling velocities for solvents 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.

NOTE: The pipe diameter used to establish the maximum flow speed should be that of the narrowest pipe section within a residence time of 30 s or three relaxation times of the fill pipe exit, whichever is lowest (see ^{Ref 13} for more details). The relaxation time used in this calculation should be that of the lowest conductivity liquid that could be loaded. If the lowest conductivity is unknown, a default residence time of 30 s should be used.

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.

A vd limit has not been established for ISO containers but would be expected to be similar to the rail car value. The charge build-up in ISO containers is reduced where there are baffles as they help reduce the voltage on the liquid.

NOTES:

1. Higher velocities may be acceptable with suitable compartment design (e.g. compartments segmented with baffles) see ^{Ref 13 Ch 7} or ^{Ref 18} for details.
2. Not all recommendations for loading fuels into trucks are applicable to solvents. In particular, the additional restrictions on loading rate that have been found to be necessary for low sulphur diesel ^{Ref 21} are not thought to apply to solvents.

3.3.5.4 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 3τ 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. This practice is

unsafe and not permitted for solvents such as hydrocarbons with low conductivity (< 50 pS/m).

Filters and wire screens should be cleaned or replaced if the pressure drop becomes excessive because charge generation increases when they are partially obstructed.

3.3.5.5 High-risk solvents and switch loading

The highest risk of electrostatic ignition occurs when loading a low conductivity (typically hydrocarbon) solvent with an intermediate vapour pressure at the loading temperature (see Section 2.2.5.2). A common example is toluene, other examples and more details are given in Annex 1.

A risk of ignition may also be introduced by switch loading, which is the practice of loading a high FP product into a compartment after a low FP product without freeing the compartment of flammable liquid and residual vapour between loads. In these circumstances, vapour from the first load may be present during the second and could create a flammable atmosphere even if the second product, on its own, would not⁵. Several incidents of explosion/fire have occurred when switch loading diesel fuel and solvents could be similarly affected.

Loading procedures (flow rate limits etc.) are designed to prevent ignition even when there is a flammable atmosphere and should prevent incidents even with high-risk solvents or switch loading. However, incidents have occurred. It is usually found that some other aspect of the rules was violated (e.g. there was splash loading, a floating, unbonded conductor such as an empty can was left in the compartment, or a filter sock was put on the end of the line). Nevertheless, where practicable, it is recommended to organise loading schedules to minimise switch-loading. It is also possible to avoid switch loading by cleaning out all vapour and liquid from compartments that previously carried a low FP liquid before loading a high FP liquid, but this is rarely practicable.

With a low conductivity solvent and either an intermediate vapour pressure or switch loading, it is particularly important to ensure that all other precautions are followed.

3.3.5.6 Compressed air

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

3.3.5.7 Line clearance with water

The use of water for line clearance of low FP products should be avoided.

3.3.5.8 Use of un baffled, single-compartment tank trucks

Normal driving conditions do not create enough liquid motion to cause an electrostatic static hazard in compartmented or baffled tank trucks. However, in un baffled, single-compartment tank trucks that are only partly filled, substantial liquid surges can occur during acceleration or braking, and several explosions have been attributed to the electrostatic charge generated by this motion. Therefore solvents of low conductivity (<50 pS/m) that have an intermediate vapour pressure (as defined in Section 2.2.5.2) at the transported temperature must not be carried in these vehicles.

3.3.6 Intermediate Bulk Containers (IBCs)

3.3.6.1 Selecting IBCs: suitability for different solvents

3.3.6.1.1 Metal IBCs

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

3.3.6.1.2 Plastic Composite IBCs

Plastic composite IBCs generally consist of a plastic “bottle” surrounded by a 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. 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 the earth by the bottle. Consequently, hazardous levels of charge may occur both

⁵ The vapour concentration typically decays continuously during a switch loaded fill as the pre-existing vapour dissolves in the second solvent and is only at the optimum for ignition for a short time. When loading a product such as toluene at an intermediate vapour pressure, the vapour concentration may be close to optimal for ignition throughout the fill.



Figure 3. Typical metal IBCs

during and after a fill. Therefore, with these IBCs, the solvent temperature must be kept below the FP 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.

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 cm²), a prominent external earthing point and possibly, an antistatic 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 FP solvents when a flammable atmosphere could be present (e.g. even when the liquid temperature could be more than the FP), provided the solvent has high conductivity (>10 000 pS/m).

NOTE: In Europe, ambient temperatures rarely exceed 45 °C, so static-unprotected plastic composite IBCs may generally be used for liquids with FPs 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 raise the surface of the liquid within the IBC above ambient temperature.

The conditions under which these static-protected IBCs may be safely used are not yet universally agreed upon. Therefore,

before using them with low FP 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 antistatic than an electrostatic-protected composite IBC. Some additional guidance is given in section A1.2 of Annexe 1.

NOTE: Static-protected plastic composite IBCs are considered to be electrostatically safe with low conductivity and low FP solvents in IEC 60079-32-1^{Ref13} and CENELEC TR50404^{Ref16}; the present advice is more cautious.



Figure 4. Typical plastic IBC

3.3.6.2 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, both the tank and frame should be earthed to the loading system during filling. If there is bonding between the tank and frame, only one earthing point is needed.

IBCs should not be splash filled. The 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 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 are no visual means of assessing the volume filled.

Fill levels should allow for thermal expansion.

A ventilation or vapour-balancing system should be available to remove vapours generated during filling operations and hence 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.

3.3.7 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 $> 60^\circ\text{C}$ and the temperature of the fluid surface is less than the FP by a suitable margin.

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

In the presence of solvent with FP $\leq 60^\circ\text{C}$ and if the container size is > 5 litres, use only metal, antistatic 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 Ω for metal containers or 1 M Ω 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: the 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

3.3.8 Buckets

Charge can accumulate to hazardous levels even with conductive liquids when filling a plastic or a metal bucket that is electrically isolated from the 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. Antistatic gloves, footwear and flooring, may provide the required earth contact. It is best to use a bucket with an integral funnel, cap and a flame arrestor in the funnel section. As a minimum, the bail of the bucket and the handle on the bail must be conductive.

3.3.9 Filling Fixed Storage Tanks and Vessels

3.3.9.1 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^{Ref19}. However, the earthing requirements for lightning protection are different from those for static protection and are outside the scope of the present guidelines.

Fixed equipment should be permanently earthed with built-in systems and, where relevant, should include facilities for the temporary earthing of transportable containers 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. The final step should be the removal of the connection.

3.3.9.2 Filling into storage tanks and vessels

Splash filling into storage tanks and vessels should be avoided by using the main inlet line at a 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 (≤ 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 or vessels with a diameter of 10 m or more.
- 3.5 m/s for tanks or vessels with a diameter 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 or vessels with diameters between 1.3 and 10 m, IEC 60079-32-1^{Ref13 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 $D/d > 25$, this permitted velocity exceeds 3.5 m/s, so the simple limit given above is acceptable. Most practical combinations of the 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^{Ref13} expression should be used if it is necessary to fill tanks with $D/d < 25$.

More details are given in IEC 60079-32-1^{Ref13}, CENELEC TR 50404^{Ref18} and BS 5958^{Ref27 Part 2} Sec 3.3.

External spillage should be avoided by preventing overfilling either using a level gauge (e.g., radar) that can be monitored or with an additional high-level trip that can stop the filling.

High internal pressure could damage the tanks; therefore, they should be fitted with correctly specified pressure relief valves.

3.3.10 Emptying Tanks, Vessels or Containers

When a tank, vessel or container is emptied, the liquid may become charged as it passes through the handling equipment. The hazards arise principally when this charged liquid arrives at its destination (e.g., another tank, container, spray booth etc.) rather than at the source tank. Provided all precautions appropriate to the destination are applied, there are no specific additional risks associated with emptying the tank or container. The inclusion of the source vessel in the earthing or bonding scheme for the process is the only requirement specifically relating to this part of the equipment.

3.3.11 Mixing and Blending in Storage Tanks, Vessels or Containers

Mixing in storage tanks, vessels or containers may be done by circulating the liquid (jet mixing) or 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 (> 1000 pS/m has sometimes been needed). More details are given in IEC 60079-32-1^{Ref 13 Sec7.9}. Specialist advice should be sought for these operations.

Where people are involved in emptying bags or drums into flammable solvents, the operation should, if possible, be organised to load the solids first and then add the liquid. People 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^{Ref 13}.

3.3.12 Dipping and Sampling

After the liquid has been transferred or mixed, it may be necessary to dip or sample a tank. During the period of transfer or agitation, the 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 the second phase, e.g., water and, to allow for settling, the recommended waiting time before sampling or dipping is 30 minutes^{Ref 13, Ref 27Part 2 Sec 6.3.2} 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^{Ref 27Part 2 Sec 6.3.1} or in extreme adverse weather conditions such as thunderstorms, heavy snow or hail^{Refs 13, 18, Ref 27 Part 2 Sec 6.4}.

The equipment used for dipping should be conductive (e.g., metal) or antistatic (e.g., wood or carbon-loaded plastic) and should be earthed or bonded to the tank. Sampling tapes or cords should be made 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^{Refs 13, 18}. 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.

3.3.13 Anti-static (Static Dissipater) Additives

Anti-static (static dissipater) additives function 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 an 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 using 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 measures. However, where antistatic additives are added, even though this may be done for other application purposes, they can provide a valuable additional safety margin where flow speeds are compliant with the requirements for low conductivity liquids.

ANNEX 1

Solvents that produce flammable atmospheres at ambient temperatures

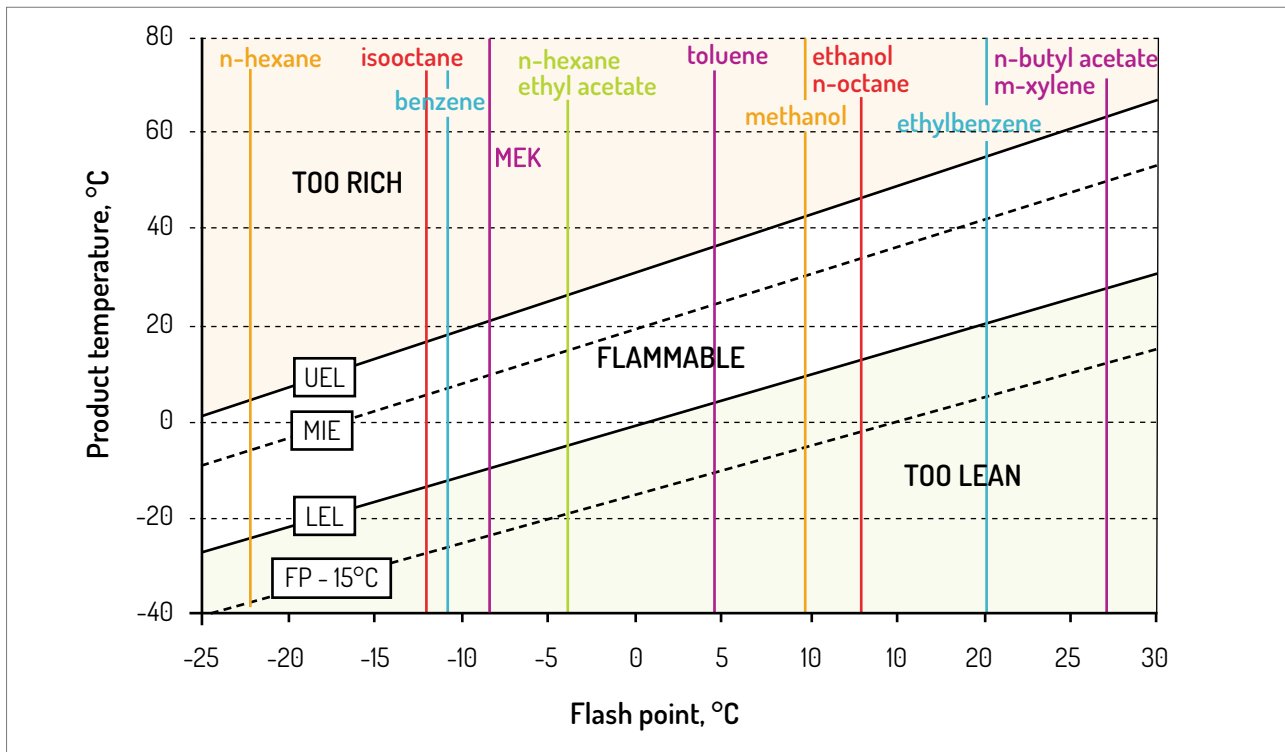


Figure 6: Flammability of equilibrium solvent vapours

A1.1 GENERAL

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 FPs. It can be regarded as the maximum recommended handling temperature to ensure that the vapours are Too Lean and include a margin for uncertainties in surface temperature, FP and product composition. However, it should 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) 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 a high energy ignition source is needed to initiate combustion towards the upper and lower boundaries (UEL and LEL). 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 enter the Flammable Range if it is temporarily reduced by the ingress of air into the vapour space (e.g., through temperature cycling or openings such as man lids) or if the concentration far above the liquid in a large ullage space with limited vertical mixing has not reached the equilibrium value. 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 FP scale (vertical lines with solvent names). The flammability range for other solvents may also be assessed approximately from Figure 6 if the FP is known.

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

1. To find the maximum recommended handling temperature for a solvent of known FP, read the corresponding temperature from the "FP-15C" line. The temperatures corresponding to the LEL, UEL and most easily ignitable mixture can be found similarly to the other lines on the diagram.
2. To check the flammability issues associated with a given operation, select the point defined by the FP of the product (x-axis) and the handling temperature (y-axis).
 - a. 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.
 - b. 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.
 - c. 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 because it is easily affected by the ingress against ignition.

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 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 LEL under relatively warm/hot summer conditions for a temperate climate. Common solvents of intermediate FP, 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 in 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 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 a charge if isolated by an insulating material such as a container lining (see 3.2.3).

A1.2 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 $-20\text{ }^{\circ}\text{C}$ and $45\text{ }^{\circ}\text{C}$ 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 FP of the solvent by a suitable margin, usually taken as $15\text{ }^{\circ}\text{C}$ (see 2.2.3). Using this rule suggests that a flammable vapour atmosphere will not be produced during the filling of IBCs at ambient temperature, provided the solvent has an FP of more than $60\text{ }^{\circ}\text{C}$.
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 FPs below $35\text{ }^{\circ}\text{C}$, although, with knowledge of specific process conditions, a narrower range of FP for enhanced concern can be identified in 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 reduces the risk of ignition from internal ignition sources when filling IBCs with very low FP solvents, particularly those with a FP more than $45\text{ }^{\circ}\text{C}$ below the loading temperature⁶.

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

ANNEX 2 Explosive atmosphere regulations (ATEX)

Existing European regulations (the ATEX workplace directive ^{Ref 12}) 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 ^{Ref 11}, 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 the 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 3 Information on earthing

The EI Electrical Safety Code ^{Ref 28} follows BS 5958 ^{Ref 27 Part 113.4.2 Table 4} in recommending that in Electrical Zones 0, 1, and 2, the earthing resistances for metal items, including tanks, fixed metal plants, 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 ^{Ref 28} and BS 5958 ^{Ref 27}.
2. The EI Electrical Safety Code recommends that tanks over 30 metres in diameter should have 3 earth connections. BS 6651 ^{Ref 29 Sec 22.2} 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 M Ω ^{Refs 13, 18, Ref 27 PART 1 Sec 13.2.2}. Even 100 M Ω 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.

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 the earth.

References

1. EN12921-3, *Machines for surface cleaning and pre-treatment of industrial items using liquids or vapour - Safety of machines using flammable cleaning liquids*
2. EN 12215, *Coating plants - Spray booth for application of organic liquid coating materials - Safety requirements*
3. EN 13355, *Coating plants - Combined booths - Safety requirements*
4. EN 12581, *Coating plants - Machinery for dip coating and electrodeposition of organic liquid coating materials - Safety requirements*
5. EN 1953, *Atomising and spraying equipment for coating materials - Safety requirements*
6. EN 1539, *Dryers and ovens, in which flammable substances are released - Safety requirements*
7. EN 12753, *Thermal cleaning plants (incinerators) for exhaust gas from surface treatment plants - Safety requirements*
8. EN 50176, *Stationary electrostatic application equipment for ignitable liquid coating material - Safety requirements*
9. prEN 50050, *Electrostatic hand-held spraying equipment - Safety requirements - Part 1: Hand-held spraying equipment for ignitable liquid coating materials*
10. *Amine regeneration unit explosion 2 June 2011, An overview of the incident and underlying causes, www.hse.gov.uk/comah/*
11. ATEX 1: ATEX 95 equipment directive 94/9/EC, *Equipment and protective systems intended for use in potentially explosive atmospheres.*
12. 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.*
13. IEC 60079-32-1, *EXPLOSIVE ATMOSPHERES - Part 32-1: Electrostatic hazards, Guidance*
14. EN 12115, *Rubber and thermoplastics hoses and hose assemblies for liquid or gaseous chemicals*

15. European Chemicals Agency database (<http://www.echa.europa.eu/>)
16. IPCS INCHEM database (<http://www.inchem.org/>)
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19. IEC 62305, 2006, *Protection against Lightning*
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24. BS 3492: 1987 *Road and rail tanker hoses and hose assemblies for petroleum products, including aviation fuels*
25. BS 13765: 2018 *Thermoplastic multi-layer (non-vulcanized) hoses and hose assemblies for the transfer of hydrocarbons, solvents and chemicals - Specification*
26. BS 5173: Part 4: 1977 *Methods of test for hoses Part 4. Electrical tests*
27. BS 5958 *Code of practice for control of undesirable static electricity: Part 1 General considerations and Part 2 Recommendations for particular industrial situations*, The British Standards Institute.
28. EI Model code of safe practice Part 1: *The selection, installation, inspection, and maintenance of electrical and non-electrical apparatus in hazardous areas, 8th edition, 2010*, Energy Institute.
29. BS 6651 *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


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For further information please visit
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