GUIDANCE NOTE No.47

FLAMMABLE SOLVENTS AND THE HAZARD OF STATIC ELECTRICITY

Introduction

Most organic solvents are generally combustible under the right conditions. Exceptions include those that are heavily halogenated. There are certain criteria that have to be met before ignition will occur.

1. For a vapour ignition, the air and vapour must be present within certain concentrations and an ignition source present.

2. For a liquid fire sufficient air and high enough temperature have to be present to ignite the liquid. The temperature may be from the ignition source such as a static spark or from the liquid itself being above its auto-ignition temperature.

Auto-ignition Temperatures and Explosive Limits.

Auto-ignition occurs when the solvent to air ratio is correct and the liquid is at an elevated temperature, usually well above the boiling point of the material. This type of incident can occur during manufacturing, e.g. the failure of a pump seal in the high temperature loop resulting in loss of containment and almost instantaneous fire.

Auto-ignition Temperatures vary considerably and Table 1 shows some typical examples.

Explosive limits

When the vapour to air ratio is within certain limits, an ignition source would create an explosion rather than just a fire and after the explosion there will be an associated liquid fire.

Lower Explosive Limit **(LEL)**

When the concentration of the vapour is below this figure there is insufficient vapour present to cause an explosion i.e. too lean in vapour, too much air.

Upper Explosive Limit **(UEL)**

When the concentration of the vapour is above this figure there is insufficient air present to cause an explosion i.e. too rich in vapour, insufficient air.

Table 1 shows examples for several types of solvents.

Table 1 [Ref 1]

Substance	Closed Flash Point °C	Lower Explosive Limit % v/v	Upper Explosive Limit % v/v	Auto-ignition Temperature °C
Pentane	-49	1.5	7.8	285
n-Hexane	-22	1.2	7.5	233
Acetone	-18	2.6	12.8	485
iso-Octane	-12	1.1	6	411
Benzene	-11	1.4	7.1	560
Methyl Ethyl Ketone	-7	1.8	11.5	505
Ethyl Acetate	-4	2.2	11.4	460
n-Heptane	-4	1.2	6.7	215
Toluene	4	1.3	7	535
Methanol	10	7.3	36	455
iso Propanol	12	2	12	425
Ethanol	13	3.3	19	365
n-Octane	13	1	3.2	210
n-Butyl Acetate	24	1.7	15	370
m-Xylene	25	1.1	7	525
n-Nonane	31	0.74	2.9	205
n-Butanol	35	1.4	11.2	340

Explosion

An explosion will occur if the vapour concentration above the liquid is between the lower (LEL) and upper explosive limits (UEL). n-Octane, n-Heptane, iso-Propanol and Toluene fall within this category at normal storage temperatures and if an ignition source is present an explosion will occur followed by a liquid fire.

Flash Point

The flash point of a liquid is a measure of the temperature at which the vapour air ratio attains the lower explosive limit. There are many different pieces of equipment (open cup and closed cup). There are also different methods to determine a flash point and invariably each method gives slightly different results. Determinations using open cups are affected considerably by external conditions, such as air movements. Closed cup determinations are more repeatable.

There are two distinct types of flash point method, dynamic or static.

Dynamic Method

The material under test is heated from a temperature below its expected flash point and testing occurs at a set temperature difference below its expected flash point. This method burns off the lighter ends of the material under test and some loss of vapour occurs, as the equipment is not gas tight. The initial testing is continued until the vapour/air ratio is at the lower explosion level when very minor explosion occurs. As the vapour that ignited was not the same as the original, the flash point obtained will be above the true flash point unless the material under test is a pure substance such as, ethanol, methanol or meta-xylene etc. Meta-xylene is used as a flash point standard for calibration.

Static Method

The material under test is held at static test temperature until the air and vapour are equilibrated and only one test is carried out giving a go/no-go flash point. This can be repeated with fresh samples at ascending/descending temperatures until the flash point is determined. This method is closer to the true flash point but, as the test equipment is again not gas tight, a very slightly high result is obtained unless the material under test is a pure compound.

Ignition Sources

There are many possible ignition sources where solvent vapours are present. The Explosive Atmospheres Regulations (ATEX 1 and 2) addresses many of the problems by ensuring areas are zoned and only equipment suitable for the zoned area is used. The zones[Ref2 and Ref 14] are :-

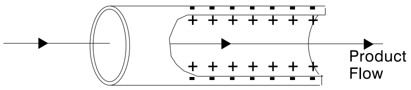
ZONE 0	In which an explosive gas/air mixture is continuously present, or present for long periods.
ZONE 1	In which an explosive gas/air mixture is likely to occur in normal operation.
ZONE 2	In which an explosive gas/air mixture is not likely to occur in normal operation, and if it occurs, it will exist only for a short time.

Other ignition sources such as mobile telephones, pagers, vehicles etc should not be present in a zoned area. Any work within these areas e.g. maintenance or repair must be subject to risk assessment and a "Permit to Work" system which is required under the Dangerous Substances and Explosive Atmospheres Regulations 2002.

Static Electricity

Static electricity is produced by pumping of materials or by any other means of motion, such as agitation when the movement separates electrical charges which accumulate in the liquid and the containment system (lines, tanks drums etc). The charge on the containment system is dissipated quickly by earthing, but the charge in the liquid remains and is slowly dissipated, depending on the conductivity of the liquid.

Diagram 1 shows what occurs during pumping a liquid through a line
Diagram 1



The more turbulent the flow the more static electricity is produced. The Reynolds Number $^{\text{Ref 2 Sec 5-4}}$ is a measure of turbulence within a pipe. The Critical Reynolds Number when flow changes from laminar to turbulent is about 2-3000 Reynolds Number $^{\text{Ref 2 Sec 5-4}}$. Table 2 shows the Reynolds Number for 4" (100 mm) pipe and a 2 centipoise viscosity liquid.

The Reynolds Number is calculated as (Calculation 1):-

$$\frac{\rho \times d \times v}{\mu}$$

ρ = Density
d = Pipe diameter
v = Velocity
μ = Viscosity

Table 2 (These figures demonstrate that turbulence occurs at very low flow rates)

Flow M/sec	Diameter M	Diameter Inches approx	Density Kg/M3	Viscosity centipoise	Viscosity Kg/M*sec	Reynolds Number	Pumped Volume L/hour
0.2	0.025	1	800	2	0.002	2000	353
0.3	0.025	1	800	2	0.002	3000	530
0.1	0.05	2	800	2	0.002	2000	707
0.15	0.05	2	800	2	0.002	3000	1060
0.05	0.1	4	800	2	0.002	2000	1414
0.08	0.1	4	800	2	0.002	3200	2262
0.04	0.15	6	800	2	0.002	2400	2545
0.05	0.15	6	800	2	0.002	3000	3181
0.025	0.2	8	800	2	0.002	2000	2827
0.035	0.2	8	800	2	0.002	2800	3958

Conductivities of Solvents

The static charge built up within a liquid will dissipate by migrating from the liquid to an earthing point. The rate of dissipation depends on how readily the liquid will conduct electricity. Hydrocarbons do not readily conduct electricity and oils boiling in the range of 350-500°C have extremely low conductivities and are used as insulators in large transformers. More polar materials such as alcohols, ketones and acetates readily conduct electricity as can be seen in the table below.

Conductive liquids are defined as having conductivities greater than 10^4 pS/m and do not pose a hazard due to static electric charge accumulation in typical hydrocarbon and chemical processing and handling operations, provided that equipment is conductive or static dissipative and is grounded. Liquids having conductivies of 50 pS/m to 10^4 pS/m are considered semiconductive [Ref 16].

The following table of conductivities (Table 3) is from empirical data[Ref 13] using readily available industrial solvents. The figures are for comparison only as the values will vary depending on trace impurities such as water, sulphur, traces of acids or even trace quantities of metals present.

Care must be taken when measuring conductivities that the result has not been distorted by polarisation and a high enough oscillating current has been used during the measurement.

Table 3

Substance	Conductivity pS/M
Methanol	7000000
Acetone	6000000
Methyl Ethyl Ketone	5000000
n Butanol	4000000
Ethanol	4000000
iso Propanol	2000000
Ethyl Acetate	2000000
n Butyl Acetate	2000000
n-Hexane	24
n-Pentane	24
m-Xylene	9
n-Octane	9
Toluene	5
n-Heptane	4
iso Octane	1

Operations which generate static Ref 4 Section 4.4.3.2

(a) High velocity and turbulent conditions for example in pipelines, or the discharge of jets from nozzles and tank mixing.
(b) Filtration, particularly through micropore elements with a large surface area exposed to the flow.
(c) Liquid droplets or foam falling through a vapour, for example a spray or mist formation in vapour spaces, splash filling of tanks, tankers, drums or intermediate bulk containers, especially if the tank is of plastic. An example is fire fighting foam projected onto a semi-confined oil surface i.e. a floating roof tank with hydrocarbon above the roof.

(d) Settling water droplets through liquid hydrocarbon i.e after a line has been pigged off into a tank with water.
(e) Bubbling of gas or air through liquids.
(f) Mechanical movements such as belts or pulleys used as air blast coolers.
(g) The movement of vehicles, fans or even people.
(h) Movement or transport of powders. There have been many incidents involving, so called, harmless materials such as flour, where static build-up has caused an explosion of flour dust.
(i) High velocity release of steam to atmosphere.

Mitigation Measures (Storage and Handling)

Tank and Vessel Earthing and Bonding.

Earthing establishes a continuous electrical path to earth.
Bonding ensures that all the plant is at the same equal potential.

The earthing/bonding of tanks and vessels is essential to reduce the likelihood of static discharge and potential plant damage from^{Ref 5 Sec 2.1} :-

(a) Faults between live conductors and non-current carrying metal work.
(b) Lightning strikes
(c) Induced currents and voltages from radio frequency radiation.
(d) Accumulation of static charges.

The I.P. Electrical Safety Code^{Ref 6 Table 4 Part 1BS5958 and Ref5 Sec 2.5.1} recommends the following

Table 4

Type of installation	Electrical Zones	Recommended Maximum resistance to earth Ω	Comments
Tanks	0,1,2	10	Normally 2 earthing connections are required but on larger tanks more are needed. See Notes 1 & 2 below.
Large fixed metal plant	0,1,2	10	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	0,1,2	10	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 not be satisfied.
Transportable metal containers (drums, ISO containers, IBC's road and rail tanks etc.)	0,1,2	10	Special earthing connection will normally be required.

More information on other structures can be obtained from the IP Electrical Safety Code and BS 5958.

Note 1

The IP Electrical Safety Code recommends that tanks over 30 metres diameter should have 3 earth connections. BS 6651[Ref 7 Sec 22.2.5.1] 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 lightning protection for a tank is far greater than that required for safe static dissipation.

Note 2 [Ref 6 Part 1 Sec 13.2.2]

Calculations have shown that a safe resistance to earth for static dissipation of $10^6\ \Omega$ and even $10^8\ \Omega$ is safe in many situations. The code points out that achieving an earth resistance of less than $10\ \Omega$ presents no practical difficulties and therefore recommends a $10\ \Omega$ maximum resistance to earth.

Tank/Tank transfers [Ref 6 Part 2 Sec 13.3.4]

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

When transferring liquids with conductivities below 50 pS/m (i.e. hydrocarbons) the linear velocity should be kept below 1m/sec until the inlet pipe is covered. After this the pumping rate could increase up to 7 m/sec but it advisable to keep as low as reasonably practicable, typically 2-3 m/sec. If a second phase is present i.e. water, the pumping rate should be kept to 1 m/sec.

Dipping and Sampling

Once a tank has been transferred or mixed it may be necessary to dip or sample. During the period of transfer or agitation, static charge will have built up within the tank, sufficient time must be allowed for this charge to dissipate (relaxation time). Most hydrocarbon tanks contain a small amount of second phase i.e. water and the recommended relaxation period before sampling or dipping is 30 minutes [Ref 6 Part 2 Sec 6.3.2]. If no free water or second phase is present the relaxation time can be shortened to 10 minutes [Ref 6 Part 2 Sec 6.3.3]

Dipping or sampling [Ref 6 Part2 Sec 6.2] must not be carried out whilst transferring or mixing. The equipment for dipping should be of metal or natural fibre and be earthed. Sampling cords should also be of natural fibres with resitivities, which are unlikely to give rise to the accumulation of static charge.

Dipping and sampling of flammable liquids should not be carried out in extreme adverse weather conditions [Ref 6 Part 2 Sec 6.4]i.e snow or hail storms or during a thunderstorm

Loading and filling operations (transportable metal items)

Road/Rail (Bulk)

When being filled, unless special earthing connections are made, the resistance to earth of a lorry with pneumatic tyres on dry concrete could well exceed $10^6\,\Omega$. Provision must be made to reduce this resistance to $10\,\Omega$ [Ref 6 Part 2 Sec 7.2.1]. Rail tanks are earthed through the rail, during loading there is no requirement to use a special earth. If any doubt exists on the electrical continuity between the running gear and the tank, then a special earth should be used with a maximum resistance of $10\,\Omega$ to earth [Ref 6 Part 2 Sec 9.4.1]

Splash filling a tank should be avoided and at the start of filling the pumping rate should be no greater than 1m/sec [Ref 6 Part 2 Sec 7.3.1]. Once the inlet pipe is covered the pumping rate can be increased and calculated in terms of linear velocity u (in m/sec) and the diameter of the pipe d (in meters).

The pumping rate should always be below 7 m/sec ($u \leq 7$)[Ref 6 Part 2 Sec 7.3.3]

$$\mathbf{ud \leq N}$$

Where N is between 0.38 and 0.5 m^2/sec. In the UK the value of N is nominally 0.5. but 0.38 is used by some companies.

Thus for a 100 mm pipe the maximum linear flow should 5 m/sec during loading. This figure should not be exceeded and in practice the pumping rate would normally be lower than this, typically nearer 1.5 m/sec which would be about 42,000 litres/hour.

If a fine filter is used the static charge must be allowed to dissipate before filling the lorry (relaxation). A relaxation chamber [Ref 6 Sec 2.21] is part of a liquid flow system which provides sufficient residence time for the charge to be reduced to a safe level. Typical residence time required for hydrocarbons with conductivities >= 2 pico Siemens/metre is given by (Calculation 2):-

$$\tau = \frac{\epsilon\epsilon_o}{\gamma} \times 10^{12}$$

Where :-

τ = Relaxation time in seconds
ϵ = Relative permittivity of the liquid.
ϵ_o = Permittivity of the free space. (8.85×10^{-12} F/m).
γ = Conductivity of the liquid (in pS/m).

For a liquid with a conductivity of 2 pS/m and relative permittivity of 2, τ the relaxation time is 8.85 seconds. The code recommends an additional factor of 3τ as a minimum relaxation time i.e. about 30 seconds. For liquids with conductivities less than 2 pS/m a minimum relaxation time of 100 seconds is required. This may involve introducing a large earthed pipe section (relaxation chamber) into a loading system before discharge into the road/rail tank. There have been several publications specifically on the safety of loading of road tankers with fuel and the associated risks of static ignition [Ref 8, 9 & 10]. Highly refined materials, especially hydro-treated gas oils with sulphur contents below 50 ppm, appear to have a higher risk of electrostatic ignition [Ref 10]

The formula above was developed for use with hydrocarbons and would indicate that there is little requirement to allow a dissipation time for polar solvents. However there is still a finite time required for the charge to dissipate and containers must still be earthed.

ISO containers must be earthed directly to the loading system and will tend to build up a greater charge as they are normally one compartment of about 30-35 M^3 capacity, rather than a multi-pot vehicle where the typical compartment is 7.5 M^3. The charge build up is reduced where there are baffles as they help to dissipate the static.

Switch Loading

Switch loading is where the compartments are not cleaned between deliveries and a product is loaded where there is vapour from the previous load. This is a hazardous procedure, especially where the previous load was highly flammable and the next load is high flash and viscous. This is typically done loading gas oil/derv after petrol. There have been several incidents of explosion/fire arising from this procedure.

Filling IBC Containers (Metal)

These should not be splash filled and must be earthed directly back to the loading system. The frame around the IBC 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. If there is earth bonding between the tank and frame only one earthing point is needed.

Filling should be to the bottom of the IBC and the linear fill velocity should not exceed 1 m/sec. There is no means of measuring the tank volume and IBC's must be loaded via a metering system to ensure overspill does not occur.

Filling IBC Containers (Plastic)

The cost of metal IBC's is high and there is a trend to the use of plastic IBC's with their much lower cost and availability. Plastic IBC's cannot be earthed unless there is special provision within the container. Low flash solvents should not be filled into plastic IBC's as static charge could build up during filling and take considerable time to dissipate (see SIA guidance on filling IBC’s). Filling materials with a flash point below ambient temperature will mean that the vapour concentration above materials will go from zero to between the lower and upper explosion limits, and either exceed the upper explosion limit or remain within the band.

Under these circumstances it is inadvisable to use plastic IBC's, as there is no guarantee that the static charge will dissipate safely.

Filling drums/cans

Drums/cans should not be splash filled and must be earthed directly back to the loading system. Filling should be to the bottom of the drum/can and the linear fill velocity should not exceed 1 m/sec. 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. Drums and cans must be earthed with a special earth clip that penetrates the paint coating and ensures that the earth resistance is not greater than 10.Ω

Static Dissipation

The dissipation of static electricity is dependent on good connections to earth i.e. resistance less than 10Ω and the conductivity of the material. The value of τ in Calculation 2 gives the time for 37% of the charge to be dissipated [Ref 6 Sec 1.8.2.2] after 3τ, only 5% of the charge should remain.

Antistatic Additives

Anti-static additives work by migration of the additive to the tank walls carrying the charge with them, thus reducing the relaxation time. However, the anti-static additives can continue to migrate to the tank walls even after the charge has dissipated. A material dosed with anti-static additive may return to the original state of low conductivity and care must be taken to ensure that the additive is still active if pumping at high linear velocities is to take place.

Antistatic additives can be a useful additional safety margin where flow speeds are compliant with the requirements for low conductivity liquids [Ref 15]. The Solvents Industry Association [Ref 11] does not recommend the addition of antistatic additives to solvents for the sole purpose of enabling higher flow speeds and it is incorrect to assume that the addition makes the solvent safe to use without taking additional precautions.

If those handling solvents wish to use antistatic additives, then they are not to be used in isolation and other safety measures must be in place to ensure the safe dissipation of static.

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