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Ignition Frequency in Process Risk Analysis at Solvay

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Roughly half of the scenarios identified in Process Risk Analysis are fires and explosions of gases, vapors or combustible dusts. These involve ignition sources including electrical equipment, hot surfaces, friction, incandescent substances, gas compression, ionizing radiation, static electricity etc. To judge whether the risk of a given scenario is acceptable or not, it is necessary to estimate the Severity of the consequences of an unwanted event for man and the environment, and the Probability of occurrence of the scenario.
This paper presents the semi-quantitative method used within Solvay to estimate the frequency of all types of ignition sources in such scenarios and to judge whether the risk level is acceptable or not.

1. Introduction

1.1 The Solvay method

Solvay has developed a method to identify risk scenarios and to evaluate the Severity, Probability and Risk associated with each one. If the risk level in any scenario applying to a project is unacceptable, then it has to be resolved before the project can be started up. In the case of an existing installation, the problem is flagged up at corporate level and has to be resolved within a one year period. During that time temporary measures are taken to reduce the risk level. The Solvay method is described elsewhere in this issue (Egan, 2016).

1.2 The problem

In order to judge the acceptability of risk in a scenario involving fires and gas or dust explosions, we need to take account of the frequency of ignition sources. The way we do that is described in this paper.

2. Describing the scenario

2.1 Method

1. We describe the scenario in chronological order, noting on separate lines, each of the Necessary and Sufficient causes to arrive at the unwanted event.
2. When the phenomenon occurs outside a vessel, we define the extent of the flammable cloud. In the case of a minor leak (rupture of gasket, pump seal, etc.) we refer to in house or external guidelines for sizing classified explosive zones. In the case of a major leak (rupture of pipework, etc.) we estimate the flow rate and the distance corresponding to the LEL using commercially available software.
3. We identify the cause (or causes) of the presence of oxidant and rate its frequency.
4. We identify the cause (or causes) of the presence of fuel within explosive limits and rate its frequency.
5. We identify ignition sources capable of igniting the mixture in question in the explosive zone defined above.
6. We check that the various causes are mutually independent.
7. We assess the effects of explosion (delayed ignition scenario) and fire (immediate ignition scenario). If the consequences are different then we study the scenarios separately.
8. We assess the consequences of the scenario (s) for humans and the environment.
9. We rate the Severity of the scenario (s).
10. We take account of the means of prevention already in place (or already foreseen in a project).
11. We estimate the residual risk level from the Solvay Severity-Probability-Risk matrix.

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2.2 Example

The following scenario was identified on a steel storage tank for toluene operating at atmospheric pressure under nitrogen:

- Cause 1: Plant nitrogen network failure or nitrogen reducing valve failure. During successive operations, the nitrogen atmosphere is replaced by air.
- Cause 2: Presence of toluene between LEL and UEL and thus formation of a toluene / air mixture within explosive limits.
- Cause 3: Ignition source due to electrical equipment fault or an grounding fault on a fixed part or an electrostatic brush discharge.
- Explosion of a gaseous mixture reaching 10 bar gauge whereas the design pressure is 1 bar gauge.
- Rupture of storage tank (5 m^3).
- Effects: blast wave and projection of fragments:
- 140 mbar (1% lethality) at 25 m,
- The number of people within a 25 m radius is less than 10.
- Human impacts: irreversible severe injury of one or more operators (**H**)
- Environmental impacts: internal damage (**L**)

3. Rating the frequency of ignition sources

3.1 General principle for rating ignition

There are extreme situations in the chemical industry. For example, in a mixing tank of electrically insulating viscous silicone, electrostatic discharges are continuously encountered. Silicone gets into the stirrer mechanism, such that the stirrer shaft and blades become insulated from the ground. The movement of the blades against the silicone causes them to become electrostatically charged. The electrical potential of the blades increases until it is sufficient to cause a so-called "spark" discharge between the stirrer and the walls. These discharges occur continuously and can be heard from outside the vessel. On the other hand, tens of thousands of drums of flammable solvents, such as toluene, can be found worldwide. The vapor space of a toluene drum is explosive, in that the oxygen concentration is 21% and the toluene concentration is between explosive limits, so long as the ambient temperature is between 4°C and 38°C. However, spontaneous explosion of drums of toluene, while they are sealed and in good condition, is not observed.

The frequency of ignition sources in the diverse and varied situations encountered in industry thus covers a very wide range. Between the two extremes, there is a ratio which must exceed 10^6. The rating of the frequency of ignition sources is a major difficulty, particularly as it is decisive for assessing the level of risk and thus for accident prevention. Rating the frequency of an ignition source should be based on objective criteria.

3.2 General principle for rating ignition sources

The frequency of ignition in each situation encountered is rated as follows.

Table 1: General principle for rating ignition sources

Description	Example	ATEX equivalent	Frequency class in Solvay method	Ignitions per incident
A situation which is clearly a continuous ignition source	Silicone mixing tank, Electric transformer		Continuous	10^0
A situation which is likely to give rise to an ignition source	Wearing insulating shoes		Very Frequent	$\approx 10^{-1}$
A somewhat substandard practice for handling flammable materials	Wearing dissipative shoes which are not checked regularly	Category 3 equipment (suitable for zone 2 or 22)	Frequent	$\approx 10^{-2}$
Good industrial practice for handling flammable materials	Wearing dissipative shoes which are checked regularly	Category 2 equipment (suitable for zone 1 or 21)	Possible	$\approx 10^{-3}$
Effective exclusion of ignition sources	Carburettor of petrol car engine	Category 1 equipment (suitable for zone 0 or 20)	Improbable	$\approx 10^{-5}$

3.3 Gases of groups IIA, IIB and dusts

For gases of groups IIA (e.g. methane) and IIB (e.g. ethylene) and for combustible dusts, we use the frequency ratings "**Continuous**", "**Very Frequent**", "**Frequent**" and "**Possible**" according to the judgment of the working group. We do not use the rating "**Improbable**" except in some exceptional cases where we can justify it.

3.4 Gases of group IIC

For gases of group IIC (hydrogen, acetylene etc.), as these are very easy to ignite, we only use the frequency ratings **Continuous**" and "**Very Frequent**". That is to say, in a risk scenario, even if everything has been done in terms of equipment and working practices to prevent ignition, we assume that ignition would still be "**Very Frequent**" on our scale.

3.5 Frequency of various ignition sources

In each scenario, examine the possible occurrence of ignition sources capable of causing the ignition of the mixture in question, using the tables given in the annex section to this paper. We select the highest frequency applicable to the scenario in question, according to the general approach described below:

1. Is there a continuous ignition source? If yes: frequency class: "**Continuous**".
2. Otherwise, is there a **Very Frequent** ignition source? If yes, class: **Very Frequent** "**VF**",
3. Otherwise, is there a **Frequent** ignition source? If yes, class: **Frequent** "**F**",
4. Otherwise, does the scenario correspond to good industrial practice? If yes, frequency **Possible** "**P**".
5. Otherwise, if the scenario is not in line with good industrial practice, there is necessarily an ignition source with a frequency greater than **Possible** "**P**".

4. Examples

4.1 Storage tank for a flammable liquid

Let us go back to our first example, a scenario of gas phase explosion inside a storage tank for a flammable solvent, such as toluene, which is normally under nitrogen and where good industrial practice has been followed to prevent ignition. The first cause, the presence of oxidant, is linked to the failure of the plant nitrogen network or failure of the control loop for the nitrogen inlet valve. We would rate this as "**Frequent**", meaning between once every ten years and once every year. We rate the second cause, the presence of fuel within explosive limits, as **Continuous** in this case. If we are applying good industrial practice to prevent ignition sources inside the tank, we can rate the frequency of ignition as "**Possible**". The explosion of the storage tank is estimated to lead to an overpressure level of 140 mbar, corresponding to 1 % lethal effects, at a distance of 25 m. The number of people inside this distance is less than 10, so the Severity is rated "High". The combination of one "**Frequent**" cause and one "**Possible**" cause leads to a probability level of 3 (once in ten thousand years). From the Solvay risk matrix this corresponds to a level 3 or "acceptable" risk. Indeed this type of situation is generally considered to be acceptable in the industry.

4.2 Storage tank for a heavy petroleum fraction

A heavy petroleum fraction is stored in a carbon steel tank under nitrogen. Now this type of material is often of a rather variable composition and usually contains small amounts of dissolved light hydrocarbons (butane, etc.) and also hydrogen sulfide. Over a period of years a reaction occurs between hydrogen sulfide in the gas phase and rust on the surface of the carbon steel, forming iron sulfide in a finely divided form. An obvious risk scenario is the loss of the nitrogen atmosphere, caused by the failure of the plant nitrogen network or failure of a control loop for the nitrogen inlet valve. When material is pumped out of the tank, air is drawn in. A flammable atmosphere is likely to be formed, because of the presence of light hydrocarbons. And when the finely divided iron sulfide is exposed to air it becomes incandescent and causes ignition of the gaseous mixture inside the tank. For the sake of simplicity we will assume that the tank is of the same size as in the first example and that the Severity of the explosion is "**High**". Only one cause is required: failure of the plant nitrogen network or failure of a control loop for the nitrogen inlet valve, which is rated as "Frequent". This corresponds to a Probability of 1-2 (about once every ten years). The Severity-Probability-Risk matrix indicates a Risk level of 1 i.e. Unacceptable. Indeed it is considered bad industrial practice to store heavy petroleum fractions under nitrogen in carbon steel tanks.

4.3 Storage tank for recovered sulfuric acid

Recovered sulfuric acid, derived from refinery operations, is stored in a tank at atmospheric pressure. It gives off light hydrocarbons, which are diluted with nitrogen and fed to a VOC treatment unit, containing a hot ceramic bed. The level of oxygen is monitored by an in-line analyzer. The nitrogen flow is controlled to give an oxygen level of 3 % (the Limiting Oxygen Concentration is estimated at 8 %). An obvious scenario is the failure of the analyzer, such that the nitrogen inlet valve closes. The gas mixture sent to the VOC treatment unit is within explosive limits and ignites on the hot ceramic bed in the VOC treatment unit. The flame blows back to the storage tank which then explodes. The tank is much larger than in the previous examples, so the distance to 140 mbar (1 % lethal effects) is further. However, as it is situated on a tank farm, the number of people in this zone is still below 10 and the Severity is still rated "High". We will first assume that there are no safeguards. Only one cause is required, the failure of a control loop, which is rated "Frequent", leading to Probability **1-2** and Risk **1** (**unacceptable**). Indeed this situation would not be accepted in the industry. The minimum requirement would be one safeguard consisting of a flame arrestor (this stops the flame going back, at least for a short period) plus an independent oxygen analyzer with a Safety Instrumented Function of SIL 1 which closes a block valve on the line (this acts more slowly, but once the block valve is closed it stops the scenario definitively). If this safeguard is installed, maintained and tested regularly it reduces the probability by a factor of 10 to level 2 (once every hundred years) and the Risk level to **2** (**intermediate**).

5. Conclusions

Solvay has developed a method for quoting the frequency of a wide range of ignition sources on a semi-quantitative scale. In this paper we have applied it to typical industrial situations and have demonstrated that the conclusions are in line with generally accepted ideas about good industrial practice for prevention of explosions and fires.

Reference

Egan S.M., 2016, Process Risk Analysis within Solvay, Chemical Engineering Transactions, Vol. 48.(on Press)

Annex: tables of ignition source frequency

The tables of ignition frequency are presented below in the following order:

- tables 2 and 3: **Continuous** ignition sources respectively inside and outside of vessels,
- tables 4 and 5: **Very Frequent** ignition sources respectively inside and outside of vessels,
- tables 6 and 7: **Frequent** ignition sources respectively inside and outside of vessels.

Table 2: Continuous ignition sources found inside vessels

Description	Example	Remarks
Naked flame	In line burner of off gases	If a flammable gas mixture is sent to an in-line burner then flash-back is expected
Hot surface T > AIT	VOC treatment bed	Hot ceramic bed of a Volatile Organic Compound (VOC) heat treatment unit
Incandescent solids	Activated Raney nickel Ferrous sulphide	Raney nickel or finely divided FeS becomes incandescent when placed in contact with air.
Brush discharge E ≤ 3 mJ - only incendive to gases	Filling of vessel with liquid	Spray filling Oil containing dispersed water Transfer rate > 10 m/s
Idem.	Electrostatic filter	The electric field in this type of filter is expected to cause electrostatic brush discharges
Idem.	Filling of vessel with powder	Powder having resistivity > 10^9 Ω.m. Transfer rate > 10 m/s.
Cone discharge E = 10 to 100 mJ	Filling of vessel with insulating powder	Powder having resistivity > 10^{12} Ω.m. Transfer rate > 10 m/s.

Table 3: Continuous ignition sources found outside vessels

Description	Example	Remarks
Friction spark	Vessel rupture	Group IIC gases (H_2, C_2H_2, CS_2, etc.)
Naked flame	Flare stack	
Hot surface T > AIT	Ordinary vehicle	If the explosive zone created in the event of leakage is capable of exceeding the plant limits, the ignition source should be considered to be continuous.
Electric arc	Non-classified electrical equipment	Group IIC gases (H_2, C_2H_2, CS_2, etc.)

Table 4: Very frequent ignition sources found inside vessels

Description	Example	Remarks
Friction spark	Ordinary shovel to unload solid from a filter	Incident of ignition of cyclohexane vapours when discharging a filter by hand.
Hot surface: AIT > T > 0.9 AIT	Heating surface above the liquid level	Hot oil jacket or high pressure steam coil
Activated charcoal bed (absorber, VOC treatment, etc.).	Activated charcoal beds are very frequently the site of exothermal decomposition or oxidation reactions.	Activated charcoal bed (absorber, VOC treatment, etc.).
Spark discharges $E = 0.5 CV^2$	Conductive item, with no reliable grounding or bonding, used with insulating or dissipative solid or liquid	A loose metal grid in the charging chute above a hopper for an insulating or dissipative powder Loose float on a level gauge in a stock tank for an insulating or dissipative liquid
Corona discharge E = 0.03 mJ	Sharp conductive item in contact with insulating or dissipating solid or liquid	Corona discharges can never be ruled out in an industrial facility.
Brush discharge E ≤ 3 mJ - only incendive to gases	Filling of a vessel with a liquid	Spray filling Liquid having resistivity > 10^8 Ω.m Transfer rate > limit IEC 60079-32-1.
Idem.	Filling of a vessel with a powder	Powder having resistivity > 10^9 Ω.m. Transfer rate 1 to 9 m/s.
Propagating brush discharge E ≤ 1000 mJ	Emptying of insulating powder from type A super sack	Powder having resistivity > 10^9 Ω.m
Idem.	Crystallisation in enamelled steel vessel.	Crystallisation of a solid from an insulating solvent (hexane) in a glass lined steel vessel.
Cone discharge E = 10 to 100 mJ	Filling of a vessel with a powder	Powder having resistivity > 10^{12} Ω.m. Transfer rate > 1 m/s.

Table 5: Very frequent ignition sources found outside vessels

Description	Example	Remarks
Friction spark	Sudden vessel rupture	Group IIA or IIB gases Vessel designed for pressure
Hot surface: AIT > T > 0.9 AIT	Ordinary vehicle on unrestricted roads inside plant.	In some cases it could be appropriate to classify the frequency as “Continuous”.
Electric arc Group IIA & IIB gases, dusts	Non-classified electric equipment	Whenever an ordinary switch is operated, an electric arc is produced inside it.
Electric arc Group IIC gases	ATEX category 1, 2 or 3 electric equipment	Group IIC gases are very easy to ignite
Spark discharge E ≤ 1000 mJ	Conductive item, with no reliable grounding or bonding	Metal valve on rubber transfer line.
Spark discharge E = 10 mJ	Non-grounded operator	Operator wearing insulating shoes or walking on a floor with an insulating surface (for example acid-proof) or with overshoes in a “white room”.
Brush discharge E ≤ 3 mJ - only incendive to gases	Emptying of insulating powder from type A or B super sack	The discharge occurs between the outer surface of the super sack and a nearby metal object.
Propagating brush discharge E ≤ 1000 mJ	Emptying of insulating powder from type A super sack	Powder of resistivity > 10^9 Ω.m

Table 6: Frequent ignition sources found inside vessels

Description	Example	Remarks
Friction spark	Stirrer with circumferential rate of > 10 m/s	Explosion of dust encountered on powder mixing tank.
Hot surface: 0.9 AIT > T > 0.8 AIT	Heating surface above the liquid level	Hot oil jacket or high pressure steam coil
Electromagnetic radiation	Category 3 (zone 2) invasive probe	Category 3 according to ATEX standards
Spark discharges $E = 0.5\ CV^2$	Conductive item, with no reliable grounding or bonding, used with a conductive solid or liquid	A loose metal grid in the charging chute above a hopper for a conductive powder Loose float on a level gauge in a stock tank for an conductive liquid
Idem.	Earthing fault on moving part	Dust filter with automatic filter cake removal, using compressed air. The filter cloth is supported by metal frames which are mobile and have to be electrically bonded to the filter casing.
Brush discharge E ≤ 3 mJ - only incendive to gases	Filling of a vessel with a liquid	Dip pipe Liquid having resistivity > 10^8 Ω.m Transfer rate > limit IEC 60079-32-1
Idem.	Filling of a vessel with a powder	Powder having resistivity > 10^9 Ω.m. Transfer rate ≤ 1 m/s.
Idem.	Idem.	Powder having resistivity between 10^8 and 10^9 Ω.m and transfer rate of 1 to 9 m/s.
Idem.	Idem.	Powder having resistivity < 10^8 Ω.m Transfer rate > 10 m/s
Propagating brush discharge E ≤ 1000 mJ	Filling of type A super sack	Powder having resistivity > 10^9 Ω.m
Cone discharge E = 10 to 100 mJ	Filling of a vessel with a powder	Powder having resistivity > 10^{12} Ω.m. Transfer rate ≤ 1 m/s.
Idem.	Idem.	Powder having resistivity between 10^9 and 10^{12} Ω.m and transfer rate > 1 m/s.

Table 7: Frequent ignition sources found outside vessels

Description	Example	Remarks
Friction spark Group IIA or IIB gases	Ductile vessel rupture	Atmospheric storage tank
Hot surface: 0.9 AIT > T > 0.8 AIT	Steam line or hot wall of furnace	
Electric arc	Category 3 ATEX electric equipment	Group IIA or IIB gases; dusts Category 3 corresponds to zone 2.
Spark discharge E ≤ 1000 mJ	Filling or emptying of a metal drum, grounded by a mobile line attached by the operator	The frequency of forgetting to attach a grounding line to the drum may be taken to be between 1/100 and 1/1000 times the frequency of the operation, which corresponds to **Frequent** on the Solvay scale in most cases.
Brush discharge E ≤ 3 mJ - only incendive to gases	Operator	Operator wearing clothing with < 65 % cotton or removing clothing in explosive zone.
Propagating brush discharge E ≤ 1000 mJ	Filling of type A super sack	Powder having resistivity > 10^9 Ω.m