Conference: Day One
The Pharmaceutical Supply Chain Initiative – An Overview

Presented by

Julie Brautigam
Head of Procurement, Risk, Sustainability & Performance
Takeda Pharmaceuticals

Vice-Chair, PSCI
Sustainability is expected of us

Our stakeholders’ expectations are changing:

• The global marketplace has created more complex supply chains, with increased social, economic and environmental risks

• The extent to which we manage our supply chains responsibly is becoming a key measure of our Corporate Social Responsibility competence

• Global companies are subject to increased scrutiny by NGOs, and the media in relation to their supply footprint

• Consumers increasingly expect to buy from companies who "purchase responsibly", respecting the rights of citizens in local communities
Meeting the sustainability challenge

To increase the sustainability of our supply chains, we must understand:

• What impact our supply chain has in the communities where we buy

• The social, health, safety and environmental risks associated with our products and companies

• What we can do, either independently or in conjunction with our supply chain partners, to reduce or manage these risks cost effectively

• How we can use our collective influence to improve labor, health & safety, and other rights of workers across the pharmaceutical supply chain
Using our collective influence to drive change

Our ethos?

One company can't change the supply chain on its own. The member companies of the PSCI joined forces to address the issue of responsible supply chain management across the pharmaceutical industry. We believe that by sharing knowledge and expertise, the industry-wide PSCI can drive complex, global change more effectively than one organization alone.
What is the PSCI?

The Pharmaceutical Supply Chain Initiative

An industry body formed by the pharmaceutical sector whose members share a vision for responsible supply chain management, to deliver better social, health, safety and environmental outcomes in the communities where they buy...
Our Board

**Steven Meszaros, Chair**
Corporate Senior Director Business Resiliency & Business Development
Pfizer

**Julie Brautigam, Vice Chair**
Head of Procurement, Risk, Sustainability & Performance
Takeda Pharmaceuticals

**Marcell Reid, Secretary**
Senior Manager, Supplier Sustainability
AbbVie

**Gary Wilson, Treasurer**
VP CSR & Sustainability
West

**Andy Rayment**
Risk and Assurance Lead, Global Procurement
AstraZeneca
As a first step, the PSCI created the Pharmaceutical Industry Principles for Responsible Supply Chain Management ("the Principles")

These Principles address five areas of responsible business practices and the relevant standards any business operating within the pharmaceutical supply chain is expected to uphold:

- ETHICS
- LABOR
- HEALTH & SAFETY
- ENVIRONMENT
- MANAGEMENT SYSTEMS
Our vision is that, through the application of the PSCI Principles for ethics, labor, health & safety, environment and management systems, better environmental, social and governance outcomes will result for all those involved in the pharmaceutical supply chain.
We've made great progress...

**PSCI Principles**
Developed the Pharmaceutical Industry Principles for Responsible Supply Chain Management, which outline our expectations for sustainable supply chains in our industry.

**Assessment & Audits**
Developed and deployed tools to assess supply chain against our principles. These tools including the PSCI Self-Assessment Questionnaire and Audit Protocol.

**Capability Building**
We conduct supplier capability building events, including webinars, conferences and share best practice documents through a resource library on the PSCI website.
Benefits of following the PSCI Principles

1. Utilizing a common standard across the supply chain

2. Benchmarking and sharing of best practices with other pharma companies, and other sectors

3. Being recognized as a supporter and advocate of Responsible Supply Chain Management

4. Suppliers gain a more in-depth understanding of customers' expectations for responsible business practices and raise their profile as a high-performing and sustainable supplier for current customers and future prospects

5. Suppliers have the opportunity to collaborate with customers to build the sustainability capabilities of their facilities

6. Both the Self-Assessment Questionnaire and Audit allow suppliers to cut down on duplication of effort in supporting multiple assessment requests from customers
Benefits for suppliers

Resource library
Our supplier resource library is available at
www.pscinitiative.org/resources

Training / capacity building events
We will be posting information about training/capacity building events on key issues for suppliers

Webinar
• On current topics impacting our industry

Supplier Conference
• To support technical capacity building

Watch our website for details
How can you get involved?

• Join PSCI and collaborate with us to further improve the pharmaceutical supply chain (for more information contact info@pscinitiative.org)

• Go to the PSCI website and use the tools in the Resource Library to make improvements

• Participate in upcoming supplier capability building events
The Pharmaceutical Supply Chain Initiative

Need more information?

Visit: www.pscinitiative.org
Email: the PSCI Secretariat at info@pscinitiative.org
Key Note Speech

Presented by

Dr. Vahid Ebadat, Ph.D.
Chief Technical Officer – Process Safety
DEKRA
Preventing Catastrophic Events through Effective Process Safety Competency and Culture

Chilworth Technology (A DEKRA Insight Company)
Chief Technical Officer
Director - Process Safety N. America, Asia Pacific & India
Preventing Catastrophic Events
through
Effective Process Safety Competency and Culture

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Pharmaceutical Supply Chain Initiative
Supplier Conference
Enhancing Supplier Capabilities:
A Deeper Dive into Responsible Business Practices
Renaissance Shanghai Putuo Hotel | Shanghai, China | September 19-22, 2016
What do these brands have in common?
What do these brands have in common?

• All were part of Union Carbide (UCC) in 1984
• UCC had 100K employees and 500 plants
• Was a component of the Dow Jones Industrial average
• After Bhopal disaster in December 1984:
  o Share price dropped 50% -- Takeover attempts
  o Divested films packaging, major portions of metals business, specialty polymers & composites, home, battery, automotive, and agricultural products businesses
  o Dropped to 14,000 employees, and eventually acquired by and absorbed into Dow Chemicals
Bhopal Disaster

- A gas emission incident on December 2\textsuperscript{nd}, 1984 at Union Carbide India pesticide plant in Bhopal
- Considered world's worst industrial disaster
- Methyl isocyanate (MIC) gas and other toxic substances made their way into shanty towns located near the plant
- Some 3,800 deaths, >560,000 injuries, including approximately 3,900 severely and permanently disabling injuries
- Cause remains under debate!
  - Indian government and local activists argue that slack management and deferred maintenance created a situation where a backflow of water into a MIC tank triggered the disaster
  - Union Carbide Corporation (UCC) contends water entered the tank through an act of sabotage
Major Process Safety Incidents

Fire, flash fire, explosion, and/or runaway chemical reaction hazards can occur where flammable gases, vapors, dusts, as well as toxic and reactive chemicals are generated, processed, handled, or stored;

- These hazards can lead to catastrophic events involving fatalities/injuries, production losses, facility damage, and environmental impact
- In US alone, each major industrial incident costs an average of $80 million
- Workplace injuries & illnesses cost U.S. businesses some $170 billion/year in often preventable expenses
Process Safety Management Models

There are many models for process safety management, including:

- Company-specific approaches (e.g. DuPont 1968)
- Responsible Care code (late 1980s)
- Early CCPS process safety management model (1989)
- OSHA PSM rule (1990)
- EU’s Seveso I, II, and III directives
- CCPS 2007 risk-based PSM model
Process Safety Management Models

• Each model identifies a number of PSM elements that comprise essentially a checklist of activities suggested for organizations wishing to manage process hazards.

• Most companies involved in manufacture, storage, use, and transportation of highly hazardous chemicals have adopted one or more versions of these models.

• Yet, we continue to see many serious and catastrophic incidents each year.
Continuing Major Incidents

- **BP Texas City** - March 2005
  - 15 Killed, >170 Injured

- **Imperial Sugar Refinery** - February 2008
  - 14 Killed, 42 Injured

- **BP Deepwater Horizon** - April 2010
  - 11 Killed, others Injured, $50B cost

- **Chevron Richmond** - August 2012
  - 15,000 residents were sent to hospital

- **West Texas Fertilizer** - April 2013
  - 15 Killed, 160 Injured, 150 Buildings Damaged

- **Tianjin warehouse fire & explosion** - August 2015
  - Blast severity equal to 21 tons of TNT
  - 173 killed and 797 injured (as of September 12th, 2015)
  - Serious property loss in 1.6 km radius
Continuing Major Incidents

Often a company may predict “deviations” in a process while performing Process Hazard Analysis (PHA’s), but could underestimate the consequences, for example:

- Event not seen as credible (BP Texas City)
- Prevention systems not available (UCC, Bhopal)
- Mechanical Integrity requirements ignored / postponed (Chevron, Richmond, CA )
- Weak preparedness for tsunamis. Identified, but underestimated (Fukushima)
Effective Risk-Based Compliance

• Continuing major incidents are reminders to companies to more effectively understand and manage process safety hazards and risks

• Leaders must create a culture that focuses on:
  o Identifying exposures to hazards,
  o Ensuring that hazards are identified & fully understood,
  o Prioritizing hazard-reduction efforts,
  o Acting on controlling hazards before events occur, and
  o Making consistent execution the rule.
## Effective Risk-Based Compliance

<table>
<thead>
<tr>
<th>Work Stream</th>
<th>CCPS Element</th>
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</table>
| **1** Culture & Organization | 1. Process safety culture  
2. Workforce involvement  
3. Conduct of operations – operational discipline |
| **2** Capability/Competency | 1. Compliance with standards  
2. Process knowledge management  
3. Process safety competency  
4. Training & performance assurance |
| **3** Incident response | 1. Stakeholder outreach  
2. Emergency management  
3. Incident investigation |
| **4** Risk Management | 1. Hazard identification and risk analysis |
| **5** Operations    | 1. Operating procedures  
2. Safe work practices  
3. Operational readiness  
4. Contractor management |
| **6** Asset integrity | 1. Asset integrity & reliability  
2. Management of change |
| **7** Accountability | 1. Measurement & metrics  
2. Auditing  
3. Management review & continuous improvement |
Effective Risk-Based Compliance

Gluing the PSM elements together
Effective Risk-Based Compliance

- People with the right knowledge and experience in the right roles / activities
- Supported by information derived from accurate, relevant, up-to-date data
- Analyzed with models and tools that are properly fit for purpose
- Drawing upon robust institutional knowledge

A three pronged approach to effective Risk-Based Compliance:

1. Sound process safety management systems
2. Competency based on education, training, experience, and data/information in the related process safety areas
3. Safety culture that starts at the top and flows down to the shop floor level,
Organizational Capability/Competence

Having appropriate and relevant expertise in **Process Safety Management**; for example:

- Management of change programs
- Pre-start up safety reviews
- Safety auditing methods
- Contractor management
- Management of hazardous activities such as hot work permits
- Mechanical integrity programs throughout the project lifecycle
- Competency assessment and development programs
- Carrying out PHA’s and updating / following-up on previous PHA recommendations?
Organizational Capability/Competence

Having appropriate and relevant Process Safety Engineering expertise; for example:

- Hazardous area management (NEC/NFPA in US, ATEX in EU)
- Fire and explosion hazards
- Electrostatic hazards
- Chemical reaction hazards
- Pressure systems and over-pressure protection
- Process safety data requirements and their use
- Incident investigation
- Consequence modelling / toxic hazards
- Facility siting
- PHA techniques e.g. HAZOP / QRA / What if
Organizational Capability/Competence

Laboratory Testing/Process Safety Data

- Process Safety data is the starting point for assuring process safety. **NO DATA, NO SAFETY**

- Hazardous properties/data of materials and processes, including:
  - Flash Fires and Explosions,
  - Flammability
  - Self Heating & Spontaneous Combustion
  - Shipping/Transportation of Hazardous Chemicals & Regulatory Requirements
  - Runaway Reactions
  - Static Electricity
Organizational Culture

Leaders create and sustain a strong process safety culture

• To create a strong process safety culture critical leadership behaviors need to be addressed
• This begins with leaders demonstrating that they have safety as a strong personal value through what they do and say
• It continues with leaders:
  • Discussing exposure and risk, and using metrics to provide feedback
  • Employing the safety leadership practices that build culture
What Level is Most Influential

- Senior Leadership
- Middle Management
- Front-Line Supervision
- Employees
What Should you Do?

- Benchmarking - Against other companies in your industrial sector (gap analysis - to industry average or “best-in-class”)
- An analysis of your current safety enabling programs (e.g. Process safety Management Systems) and suggestions for improvements
- An analysis of your current Sustaining Systems as they apply to safety, such as definition of roles, responsibilities, and required competencies for both safety and operations personnel and safety goal settings
- An assessment of Organizational competencies to include audits of plant highlighting current Process Safety Engineering deficiencies together with recommendations for immediate and for enduring change
- Assessment of safety culture with benchmarking against leading organizations
- Discussions with management regarding safety goals
- Discussions with senior management leading to a strategy for change and intervention/transformation plan (road map) addressing systems, organizational competence, organizational culture, and/or metrics as appropriate
Concluding Remarks

• Process Safety Competence & Culture
  o A “root cause” for many PS Events
  o Critical to “glue” PSM programs
  o Correlates with PS performance
  o All global companies face these challenges
  o How to develop, embed, and sustain?
  o Active corporate sponsor to make it happen
  o Engagements at different levels/profiles
About Chilworth Technology

A DEKRA Insight Company

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USA

Phone  609 799 4449
Web    www.Chilworth.Com
Legacy Chilworth Technology - An Overview

- Leading provider of **specialist process safety services** in the world - since 1986
- Over 150 staff including engineering professionals, scientists and laboratory technicians with specialist process safety expertise
- Objective, practical advice
- Chilworth Technology was acquired by **DEKRA SE** in July 2011
### DEKRA Insight - Process Safety Centers of Excellence

<table>
<thead>
<tr>
<th>Region</th>
<th>Locations</th>
</tr>
</thead>
</table>
| North America | • Princeton, New Jersey  
  • Chicago, Illinois  
  • Forreston, Illinois |
| Europe     | • United Kingdom  
  • Spain  
  • France  
  • Italy  
  • Netherlands |
| India      | • New Delhi  
  • Mumbai  
  • Hyderabad |
| China      | • Shanghai |
Process Safety - Definition

- **Process Safety** - The prevention and control of fires, explosions, and accidental chemical releases in chemical & process industries
- Such incidents may result in serious injury, property damage, lost production, and environmental impact

2015 - Warehouse Fire & Explosion, Tianjin, China
173 killed and 797 injured *(as of September 12th, 2015)*

2008 - Imperial Sugar, Georgia
14 Killed, > 40 injured
DEKRA Insight - Process Safety Business

- We help process industries avoid fire, explosion, and loss of containment events and improve performance.

- Combining specialist process safety management (PSM) and process safety engineering expertise, with generation and use of process safety data allows us to help our clients achieve the most effective and practical approaches to safe and efficient operations and processes, globally.
# DEKRA Insight - Process Safety Portfolio

<table>
<thead>
<tr>
<th>Consulting</th>
<th>Laboratory Testing</th>
<th>Competence Development</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Process Safety Management</strong>&lt;br&gt;- Program Implementation &amp; Improvement&lt;br&gt;- Gap Analysis&lt;br&gt;- Process Hazard Analysis&lt;br&gt;- Quantitative Risk Assessments&lt;br&gt;- Consequence Modeling&lt;br&gt;- Incident Investigations</td>
<td><strong>- Combustible Dust Fire &amp; Explosion&lt;br&gt;- Gas &amp; Vapor Flammability&lt;br&gt;- Thermal Instability&lt;br&gt;- Chemical Reactivity&lt;br&gt;- Static Electricity&lt;br&gt;- DOT &amp; UN Transportation of Hazardous Materials&lt;br&gt;- Explosivity / Energetic Materials&lt;br&gt;- Customized &amp; Large-Scale Testing</strong></td>
<td><strong>- Courses Covering all Key Aspects of Process Safety&lt;br&gt;- Continuing Education Units (CEU’s)&lt;br&gt;- Multiple Languages&lt;br&gt;- Multimedia&lt;br&gt;- Instructor-Led Content&lt;br&gt;- Computer-Based Training</strong></td>
</tr>
<tr>
<td><strong>Process Safety Engineering</strong>&lt;br&gt;- Dust Flash Fire &amp; Explosion Hazards&lt;br&gt;- Gas &amp; Vapor Flammability Hazards&lt;br&gt;- Electrostatic Hazards&lt;br&gt;- Chemical Reaction Hazards</td>
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</tbody>
</table>
DEKRA Insight - Process Safety Client Industries

- Bulk & Fine Chemicals
- Agro-Chemical
- Energy / Power
- Food & Drink
- Flavor & Fragrance
- Machine/Equipment Mfg
- Government Agencies
- Engineering / Consultants
- Legal/Insurance/Risk

- Primary Metals & Machining
- Automotive & Aviation
- Personal & Household Products
- Oil & Petrochemical
- Pharmaceuticals
- Plastics & Rubber
- Pulp & Paper
- Wood / Forestry
- Consumer Electronics
Fire and Explosion Hazards in the Pharmaceutical Industry
Cain Wang
王侃云

CIH, CSP
Process Safety Consultant
Cain.Wang@dekra.com.cn

- Over 10 years experience of process safety and EHS in North America and Asia pacific
- Expertise include DHA, Electrostatics, chemical reaction and PSM
- Excellent understanding in NFPA, ASTM, IEC standards
Summary

• Process characteristics of pharmaceutical industries
• Operation characteristics of pharmaceutical industries
• Potential hazards in pharmaceutical industries
Process characteristics of pharmaceutical industries

• Continuous innovation
• Thousands of ingredients
• Small quantities with high risks
Operation characteristics of pharmaceutical industries

- Batch operation with small units
- A lot of combustible dust & flammable liquid/vapor/gas
- A lot of manual operations
Potential hazardous materials in pharmaceutical industries

- Combustible dust
  - Flammable liquid/gas/vapor
  - Reaction hazard
Fuel + Oxygen = Light + Heat + Gaseous Combustion Products
Dust Explosion

- Fuel
- Oxidant
- Suspension
- Confinement
- Ignition Source

Diagram illustrating the components of a dust explosion:
- Solid combustible material
- Effective ignition source
- Dust explosion

Text:

Dust
Explosion

Suspension

Ignition Source

Confine-
ment

Fuel

Oxidant
Dust Explosion

Illustration of how the combustion rate of a given mass of combustible solid increases with increasing sub-division

(a) slow combustion
(fixed flame-front)

(b) fast combustion
(fixed flame-front)

(c) Flash-Fire or Explosion
(Moving Flame-Front)
DEFLAGRATION IN A CLOSED VESSEL

Pressure/Time Relationship

In a closed vessel
Is Your Powder Explosible?

30% non-combustible

70% combustible

Usually, if the solid material is combustible, its fine dust will be explosible.

If in doubt, tests should be conducted to determine if a dust is explosible.

The A/B test determines explosibility of a dust cloud.
When concentration of dispersed dust cloud in air is below a certain value, **Minimum Explosible Concentration**, an explosion can not propagate. The atmosphere is fuel-lean.

**Maximum Explosible Concentration** - the concentration above which an explosion can not propagate. The atmosphere is fuel-rich. The Maximum Explosible Concentration is not always easily defined, it is difficult to establish in the laboratory.
Is Dust Cloud Concentration within the Explosible Range?

- Explosion violence of the cloud increases as the dust concentration increases until an optimum concentration is reached giving the highest explosion violence.
- At higher concentrations explosion violence decreases or stays roughly constant.

*Ref: (Geoff Lunn, 1984)*

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**Explosible Dust Cloud Concentration**

<table>
<thead>
<tr>
<th>Dust Concentration (g/m³)</th>
<th>Explosion Violence</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>10</td>
</tr>
<tr>
<td>250</td>
<td>5</td>
</tr>
<tr>
<td>500</td>
<td>0</td>
</tr>
<tr>
<td>750</td>
<td>0</td>
</tr>
<tr>
<td>1000</td>
<td>0</td>
</tr>
</tbody>
</table>

爆炸威力

粉尘浓度 (g/m³)

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**Explosion Violence**

爆炸威力

**Dust Concentration (g/m³) 粉尘浓度 (g/m³)**
Range of explosible dust concentrations in air at normal temperature and atmospheric pressure for a typical natural organic dust (maize starch), compared with typical range of maximum permissible dust concentrations in the context of industrial hygiene, and a typical density of deposits of natural organic dusts (Eckhoff)

**Industrial Hygiene**

**Explosible Range**

**Dust Deposits**

**Mass of Powder/Dust per Unit Volume**

(g/m³)
A cloud of 40g/m³ of coal dust in air is so dense that a glowing 25W light bulb can hardly be seen through a dust cloud of 2m (~ 6.6 ft) thickness (Eckhoff).
Illustration of how the blast wave from a primary explosion entrains and disperses a dust layer, which is subsequently ignited by the primary dust flame (Eckhoff).
Is the Particle Size Distribution Capable of Propagating Flame?

- Powders include pellets, granules, and dust particles
- Pellets have diameters greater than 2mm, granules have diameters between 0.42mm and 2mm, and dusts have diameters of 0.42mm (420µm) or less
- The finer the particles the greater the surface area and thus the more explosible a given dust is likely to be
- When the dust is made up of a series of particle sizes ranging from fine to coarse, the fines may play a more prominent part in the ignition and the explosion propagation
- *If the material is friable the presence of dusts should be anticipated in the process stream, regardless of the starting particle size of the material*
Dust Particle Sizes

Four Sheets Copy Paper ~ 400 microns

- 75 micron particle
- 420 micron particle
When combustible dusts and flammable vapors or gases co-exist

A Hybrid Mixture is hazardous for the following reasons:

• When combustible dusts and flammable gas/vapor mixtures are present below their respective flammable limits, they may form an explosible (hybrid) atmosphere when mixed together.

• Dust mixtures in the presence of flammable vapors/gases may be more easily ignitable in air, even if the concentration of the vapor/gas is below its LFL.

• Powders that are too coarse to be explosible may become explosible when in the presence of a flammable vapor/gas even if the vapor/gas is below its LFL.
Atmosphere Must Support Combustion

- To produce combustion, a sufficient amount of oxidant must be available.

- Oxidants are materials that are capable of “burning” metals, and organic compounds, by reacting with them to form more stable compounds.

- Typical oxidants include oxygen, fluorine, chlorine, bromine.

- The concentration of oxidant below which a deflagration cannot occur in a specified mixture is referred to as the **Limiting Oxidant Concentration (LOC)**.
Flammable liquid/gas/vapor
DEFINITIONS

TEMPERATURES
- Flash Point
- Lower Temperature Limit of Flammability (LTL)
- Fire Point
- Auto-ignition Temperature
- Boiling Point

CONCENTRATIONS
- Lower Flammable Limit (LFL)
- Upper Flammable Limit (UFL)
- Flammability Range
- Limiting Oxidant Concentration (LOC)
TEMPERATURE DEFINITIONS

- **FLASH POINT**
  The lowest liquid temperature at which sufficient vapor is given off to form an ignitable mixture with air when a source of ignition is present.

- **LOWER TEMPERATURE LIMIT OF FLAMMABILITY**
  The lowest liquid temperature at which sufficient vapor is given off in equilibrium with the liquid to form an ignitable mixture with air when a source of ignition is present.
TEMPERATURE DEFINITIONS

- **FIRE POINT**
  The lowest liquid temperature at which sufficient vapor is given off to form a continuous ignitable mixture with air when a source of ignition is present.

- **AUTO-IGNITION TEMPERATURE**
  The lowest temperature at which the vapor/gas will spontaneously ignite with air without any external ignition source.
TEMPERATURE DEFINITIONS

• BOILING POINT
  The liquid temperature at which sufficient vapor is given off to create a vapor pressure equal to the surrounding pressure.
TEMPERATURE DEFINITIONS

● RELATIONSHIP BETWEEN TEMPERATURES

● LTL, Flash Point, and Fire Point have values that are relatively close
  — LTL is lower than Flash Point
  — Flash Point is lower than Fire Point

● Boiling Point and Auto-ignition Temperature do not have values that are close to each other or to the other temperatures.
  — Boiling Point is lower than Auto-ignition temperature.
CONCENTRATION DEFINITIONS

- **LOWER FLAMMABLE LIMIT (LFL)**
  - Lowest volume concentration of a vapor or gas that will create an ignitable mixture with air when a source of ignition is present.
    
    \textit{Below this concentration, the vapor will not ignite.}

    \textit{Note: Previously called Lower Explosive Limit (LEL)}

- **UPPER FLAMMABLE LIMIT (UFL)**
  - Highest volume concentration of a vapor or gas that will create an ignitable mixture with air when a source of ignition is present.

    \textit{Above this concentration, the vapor will not ignite.}

    \textit{Note: Previously called Upper Explosive Limit (UEL)}
FLAMMABILITY RANGE

Range of vapor volume concentration that will create an ignitable mixture with air when a source of ignition is present.

Flammability range is between LFL and UFL

Methane

5% V/V

15% V/V
CONCENTRATION DEFINITIONS

- **LIMITING OXIDANT CONCENTRATION (LOC)**
  - Minimum volume concentration of oxidant required to support combustion
  - Typically, LOC is the minimum oxygen required for fuel to burn. Below this, fuel will not burn even if its concentration is within its Flammability Range.

Technically, “O” in LOC stands for oxidant.
- Recognizes that chemicals other than oxygen can react with fuel to cause a fire or explosion.
- For most cases, the oxidant is oxygen, typically oxygen in air (air is 21% oxygen).
LIQUID/GAS DEFINITIONS

- FLAMMABLE LIQUID (NFPA 30)

  - A liquid with a Flash Point below 100 °F (37.8 °C).
  - Flammable Liquids are classified as:
    - Class IA - Flash Point below 73 F
      Boiling Point below 100 F
    - Class IB - Flash Point below 73 F
      Boiling Point above 100 F
    - Class IC - Flash Point above 73 F (& below 100 F)
      Boiling Point above 100 F
LIQUID/GAS DEFINITIONS

– COMBUSTIBLE LIQUID (NFPA 30)

• A liquid with a Flash Point above 100°F (37.8 °C).
– Combustible Liquids are classified as:
  — Class II- Flash Point between 100 & 140 F
  — Class IIIA- Flash Point between 140 & 200 F
  — Class IIIB- Flash Point above 200 F
LIQUID/GAS DEFINITIONS

- IGNITIBLE MIXTURE

- A mixture of vapor or gas with an oxidant that will ignite in the presence of an ignition source.

- Examples:
  - The vapors of liquids at temperatures above their Flash Points.
  - Flammable gases between LFL and UFL concentrations.
– **MINIMUM IGNITION ENERGY (MIE)**

Lowest amount of energy required to ignite a concentration of fuel and oxidant (i.e., an Ignitible Mixture).

The MIE occurs when the fuel concentration is between the LFL and the UFL, and typically close to the stoichiometric concentration.
LIQUID/GAS DEFINITIONS

- HYBRID MIXTURE
  - Material that includes both:
    - Flammable Gas or Vapor
    AND
    - Combustible Dust

DANGER: A Hybrid Mixture causes:
- Flammable gas/vapor to ignite below LFL
- Combustible Dust to ignite below MEC
- MIE to decrease (compared to dust)
- $K_{st}$ to increase
LIQUID/GAS DEFINITIONS

- MISTS
  - Small liquid droplets entrained in a gas
  - Created by:
    - Atomizing liquid using gas
    - Quenching hot vapors with cold gas
    - High pressure jet discharge

Note: Mists can be flammable even if the Liquid is below its Flash Point.

This means liquid Flash Point cannot be used to assess the flammability hazard of mists.
LIQUID/GAS DEFINITIONS

- **PURGING**
  - Displacing the gas inside a container with another gas.
  - Container could be a pipe, vessel/tank, room, etc.

- **INERTING**
  - Purging with a non-reactive “inert” gas.
  - Example Gases: Nitrogen, CO$_2$, natural gas, flue gas

- **VENTILATION (Local and General)**
  - Purging with air
Reaction hazards
Definitions Relating to Thermal Hazards

- Causes of overpressurisation
- Heat of reaction
- Adiabatic temperature rise
- Arrhenius relationship
- Thermal runaway
- Phi factor
- Heat loss (changes with scale)
- Reagent accumulation
Hazards Arise from Pressure

• There are three potential sources of overpressure:-
  – Gas Generation from the normal process
  – Vapour pressure effects (as a consequence of heat from the normal process)
  – Heat from the normal process leading to secondary reactions at elevated temperature (causing gas and/or vapour pressure effects)
HEAT OF REACTION

- \( \Delta H_r \) (measured in kJ.mol\(^{-1}\))
- For the reaction:
  \[ \text{A} + \text{B} \rightarrow \text{Products} \]
- The HEAT OF REACTION is the quantity of heat released or absorbed as products are formed
  - \(-\) Exothermic, Heat released
  - \(+\) Endothermic, Heat absorbed
ADIAVATIC TEMPERATURE RISE

• The total temperature rise in a reacting system due to exothermic activity were there no heat loss to the surroundings. \( \Delta T_{ad} \) (measured in K)

\[
\Delta T_{ad} = \Delta H_r N / (m.C_p)
\]

Where :-
- \( N \) No Moles of reactant (mol)
- \( C_p \) Heat capacity (J.kg\(^{-1}\).K\(^{-1}\))
- \( \Delta H_r \) Heat of reaction (J.mol\(^{-1}\))
- \( m \) Mass in reactor (kg)
REACTION RATE

- **ARRHENIUS RELATIONSHIP**
  
  \[ k = A \cdot \exp\left(-\frac{E}{RT}\right) \]

  Where:
  
  - \( k \) Rate constant
  - \( A \) Frequency factor
  - \( E \) Activation energy
  - \( R \) Gas constant

- Rate of heat production is dependent on reaction rate (for pseudo 1st order reaction) by

  \[ \frac{dQ}{dt} = k \cdot \Delta H_r \cdot N_B \]

  Where:
  
  - \( \frac{dQ}{dt} \) Rate of heat production
  - \( k \) Rate Constant (1st Order)
  - \( N_B \) Quantity of reagent B available at time \( t \)
THERMAL RUNAWAY

REACTION RATE INCREASES EXPONENTIALLY WITH TEMPERATURE

\[ \frac{dQ}{dt} \]

Temperature
PLANT COOLING CAPACITY

• Reactor cooling capacity is dependent on the heat transfer characteristics of the reactor.

\[ \frac{dQ}{dt} = U \cdot A \cdot \Delta T \]

Where  
- \( U \) = Heat transfer coefficient (W.m\(^{-2}\).K\(^{-1}\))
- \( A \) = Heat transfer area (m\(^2\))
- \( \Delta T \) = Temperature difference between contents and jacket (K)

COOLING CAPACITY INCREASES LINEARLY WITH TEMPERATURE
Thermal Runaway

Heat generation due to exothermic process

Heat removal due to cooling

\[ \frac{dQ}{dt} > U.A. \Delta T \]

Temperature (K)

Critical Temperature

Reaction out of control

Thermal Runaway
THERMAL RUNAWAY

Desired reaction

- Heat generation not problem if vessel correctly designed and vented.
- Safety systems will contain or allow controlled release of pressure.

Secondary Decompositions

- May be initiated at high temperatures
- If not considered during vessel design may cause over pressurisation

Rapid, simple screening method required to alert against problem
The heat generated in an exothermic reaction is consumed in three ways:

- To raise the temperature of **REACTION MASS**
- To raise the temperature of the **REACTOR**
- Heat loss to the **ENVIRONMENT**
PHI FACTOR

\[ \phi = \text{Heat Capacity Sample} + \text{Heat Capacity Container} \]

Heat Capacity Sample

NB : Heat Losses not considered

- 1 m³ Glass lined reactor (Jacket empty) \( \phi 1.41 \)
- 10 m³ Glass lined reactor (Jacket empty) \( \phi 1.13 \)
- 10g Carius tube screening test (best) \( \phi 2.5 \)
- Accelerating Rate Calorimeter (best) \( \phi 1.5 \)
- Adiabatic Pressure Dewar Calorimeter (best) \( \phi 1.05 \)
- 250 ml Round bottomed flask (best) \( \phi 1.1 \)
# Heat Loss Considerations

<table>
<thead>
<tr>
<th>Vessel</th>
<th>Time taken for 1° C drop at 80° C</th>
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<tbody>
<tr>
<td>25 m³ reactor</td>
<td>233 minutes</td>
</tr>
<tr>
<td>12.7 m³ reactor</td>
<td>59 minutes</td>
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<tr>
<td>2.5 m³ reactor</td>
<td>21 minutes</td>
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<tr>
<td>10 cm³ test tube</td>
<td>11 seconds</td>
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<tr>
<td>100 cm³ beaker</td>
<td>17 seconds</td>
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<tr>
<td>1 l glass Dewar</td>
<td>62 minutes</td>
</tr>
<tr>
<td>1 l Dewar with -1 K oven</td>
<td>247 minutes</td>
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</tbody>
</table>
PHI FACTOR

Temperature

Time

Low $\phi$ → Explosion → High $\phi$

Probability of SECONDARY DECOMPOSITION Overpressurisation Loss of Containment
TESTING

Testing should:

• Consider the consequences of all conceivable process deviations.

• Be conducted under plant scale heat loss conditions (or have an appropriate safety factor applied).

• Replicate plant conditions in all ways possible (including use of plant materials, consideration of materials of plant construction)
REACTANT ACCUMULATION

A condition where:

Rate of Reactant addition > Rate of reaction

Rapid Kinetics

Slow kinetics

Work off period
REACTANT ACCUMULATION

Determined by process analysis

Causes (Not exhaustive) :

• Wrong kinetic assumptions
• Inefficient agitation
• Poor temperature control
• Impurities
• Incorrect initiation
When reviewing any data it is critical to identify:

- the test method (and standard, if applicable)
- the test conditions
  - (ramp rate, scale, thermal inertia, adiabaticity, etc)
- limitations of the test
  - is it appropriate to your particular situation
- errors / reproducibility
  - hence safety factors / margins required
- reliability of the source of the data
- competence of source to provide interpretation
BREAK
制药企业工艺安全管理与可持续发展

Presented by
高波
高级工艺安全顾问
Dekra 德凯达管理咨询（上海）有限公司
Agenda

1. 什么是工艺安全

2. 工艺安全 - 从事故开始

3. 工艺安全，是制药行业可持续发展的要求

4. 工艺安全与EHS管理有关吗？

5. 工艺安全管理 - 了解更多

6. 工艺设计与工艺安全

7. 工艺危害分析

8. 回顾：我们学到了什么？
第1节
什么是工艺安全？
工艺安全的基本概念

- 精细化工企业发生的过程安全事故通常表现为着火、爆炸或者有毒物暴露等不同的形式，但都可以归咎于物料的泄漏或能量的释放。因此，精细化工企业“过程安全”的一个基本出发点是：预防工艺物料（或能量）泄漏。

“工艺安全”所倡导的事故预防：强调采用系统的方法对工艺危害进行分析。
- 根据工厂不同生命周期或阶段的特点，采取不同的方式辨别存在的危害、评估危害可能导致的事故频率及后果，以此为基础，设法消除危害以避免事故，或减轻危害可能导致的后果。工艺安全的侧重点是工艺系统或设施本身。
第2节

工艺安全管理-从事故开始
典型事故与工艺安全相关的立法

<table>
<thead>
<tr>
<th>年份</th>
<th>事故及地点</th>
<th>工艺安全相关立法</th>
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<tbody>
<tr>
<td>1974</td>
<td>Flixborough英国，化学品泄漏，蒸气云爆炸(环己烷氧化装置泄露后爆炸，28人死亡)</td>
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<td>1975</td>
<td>Beek荷兰，蒸气泄漏，蒸气云爆炸</td>
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<td>1977</td>
<td>Seveso意大利，阀门破裂，有毒物泄漏(环己烷泄露，30人死亡，22万人疏散)</td>
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<td>1982</td>
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<td>SevesoI指令，欧洲</td>
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<tr>
<td>1984</td>
<td>Bhopal印度，有毒物泄漏</td>
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<td>1988</td>
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<td>Responsible Care责任关怀，美国</td>
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<td>1989</td>
<td>Texas美国，反应器物料泄漏，蒸气云爆炸</td>
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<td>1990</td>
<td>Texas美国，污水罐投入运行时发生爆炸</td>
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<tr>
<td>1992</td>
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<td>OSHA PSM，美国</td>
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<td>1996</td>
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<td>SevesoII指令，欧洲；KOSHAPSM，韩国</td>
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<td>1997</td>
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<td>石油天然气加工工艺危害管理，中国</td>
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<tr>
<td>1999</td>
<td></td>
<td>EPA净化空气法案CleanAirAct：风险管理规定Risk Management Program，美国</td>
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</table>
### 精细化工企业爆炸事故频发

<table>
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<th>市</th>
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<td>1979年8月</td>
<td>吉林省</td>
<td>洮安</td>
<td>洮安制药厂</td>
<td>吉林省洮安县洮安制药厂浸煮罐爆炸</td>
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<td>1982年3月</td>
<td>福建省</td>
<td>福鼎</td>
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<td>福建省福鼎县制药厂汽油爆炸</td>
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<td>2003年2月</td>
<td>江苏省</td>
<td>盐城</td>
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<td>盐城制药厂发生爆炸</td>
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<td>2004年9月</td>
<td>福建省</td>
<td>厦门</td>
<td>迈克制药厂</td>
<td>海沧一制药厂生产车间发生爆炸事故</td>
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<td>2004年11月</td>
<td>辽宁省</td>
<td>沈阳</td>
<td>福宁制药厂</td>
<td>药厂爆炸临时工身亡</td>
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<td>2005年2月</td>
<td>陕西省</td>
<td>西安</td>
<td>力邦制药厂</td>
<td>西安北郊一制药厂厂房发生爆炸</td>
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<td>2005年4月</td>
<td>重庆</td>
<td>重庆</td>
<td>重庆制药厂</td>
<td>重庆制药厂静电引起粉尘爆炸</td>
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<td>2005年5月</td>
<td>江苏省</td>
<td>苏州</td>
<td>苏州医药集团有限公司</td>
<td>苏州医药集团有限公司第一制药厂爆炸</td>
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<td>2005年10月</td>
<td>辽宁省</td>
<td>沈阳</td>
<td></td>
<td>沈阳一制药厂乙醇罐发生爆炸四层楼被大火笼罩</td>
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<td>2005年12月</td>
<td>辽宁省</td>
<td>沈阳</td>
<td>东北制药厂</td>
<td>沈阳市“东北制药厂”再传爆炸声</td>
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<td>2006年3月</td>
<td>黑龙江省</td>
<td>哈尔滨</td>
<td>医药供销公司</td>
<td>哈尔滨一药厂爆炸一名工入身亡三名工人重伤</td>
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<tr>
<td>2006年11月</td>
<td>湖北省</td>
<td>武汉</td>
<td>远大制药集团制药厂</td>
<td>武汉远大制药集团制药厂夜发爆炸无人员伤亡</td>
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<tr>
<td>2007年1月</td>
<td>福建省</td>
<td>福州</td>
<td>屏山制药厂</td>
<td>福州屏山制药厂发生爆炸5人不同程度烧伤</td>
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<td>2007年6月</td>
<td>河南省</td>
<td>荥阳市</td>
<td>康泰制药厂</td>
<td>荥阳一制药厂爆炸千余人疏散</td>
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<td>2007年9月</td>
<td>重庆</td>
<td>重庆</td>
<td>新原兴制药厂</td>
<td>重庆渝北区一制药厂发生爆炸100多人溴气中毒</td>
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</tbody>
</table>

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### 精细化工企业爆炸事故频发

<table>
<thead>
<tr>
<th>日期</th>
<th>省</th>
<th>市</th>
<th>公司名称</th>
<th>事故案例</th>
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<td>云南省</td>
<td>澜沧药业有限公司</td>
<td>药厂乙醚爆炸起火 1人死亡3人获救</td>
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<tr>
<td>2007年12月</td>
<td>广西省</td>
<td>北海市</td>
<td>兴安达化学有限公司</td>
<td>广西北海一化学药厂发生爆炸事故一人死亡</td>
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<td>2008年1月</td>
<td>四川省</td>
<td>华阳市</td>
<td>四川华阳一药厂化学合成车间爆炸</td>
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<td>浙江省</td>
<td>龙泉市</td>
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<td>龙泉一制药厂发生爆炸1人死亡数人受伤</td>
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<td>天津开发区某药厂甲醇罐起火爆炸</td>
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<td>安徽太和县药厂发生爆炸事故1死4伤</td>
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<td>朝阳制药厂</td>
<td>制药厂爆炸 气浪推倒围墙</td>
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<td>华洲药业有限公司</td>
<td>制药厂亚硝酸钠爆炸消防员穿防化服排险</td>
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<td>山西威奇达药业有限公司</td>
<td>药厂仓库大火伴随爆炸</td>
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<td>西高新一制药厂5层厂房着火者呼吸系统受损</td>
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<td>西安市</td>
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<td>创新生化制品有限公司</td>
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<td>河北省</td>
<td>石家庄市</td>
<td>华曙制药厂</td>
<td>石家庄一制药厂发生火灾 现场有爆炸</td>
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<td>安徽省</td>
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<td>江阴市</td>
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</table>
预防工艺物料（或能量）的泄漏

（1）工艺安全的一个基本出发点是预防工艺物料（或能量）泄漏。虽然化工和石化行业发生的各类事故通常表现为着火、爆炸或有毒物暴露等不同的形式，但都可以归咎于物料的泄漏或能量的释放（也可以视为一种泄漏形式）。

工艺系统一旦出现泄漏，就有可能导致灾难性的工艺安全事故。化学品泄漏或能量释放可能发生于正在运行的工艺装置、储存原料或产品的区域、长途输送管道、铁路和公路装运化学品的槽车以及化学品水运船舶等等。

以涉及易燃物料的工艺系统为例，如果仅仅是泄漏且物料在泄漏出来后很快形成蒸气并扩散开去，危害相对较小；较多的情形是，泄漏出来的物料蒸发，并且形成蒸气云，蒸气云体积增大并蔓延，接触到着火源后发生着火或爆炸。可燃物着火燃烧时，烘烤临近的设备或管道，导致它们破裂；爆炸也可以造成周围设备或管道破裂；这样以来，就出现了更多的泄漏，形成更大范围的着火或数量更多的爆炸。

泄漏→蒸气云→(着火源)→着火或爆炸→更多泄漏→更多着火或爆炸

反之，如果工艺物料按照原本的设计意图，以预想的状态（温度、压力和相态等等）停留在设备或管道内，整个工艺系统就处于安全的状态；
灾难：因忽视工艺安全导致

1、事故简介
硝酸胍车间发生爆炸；截至2012年2月29日14点，已经造成17人死亡，伤者40余人。

2、河北省重点建设项目
据《石家庄日报》2010年5月报道，该企业专业生产农药、医药中间体以及其他化工产品。

3、利税过亿
当时该制药厂的订单已经排到了3年以后，其中不乏德国拜耳一类的国际大型医药企业，系列项目完全建成后，企业可实现年销售收入7亿元，利税过亿元。
灾难：因忽视工艺安全导致（续1）

2012年2月28日9时30分，河北省石家庄市赵县克尔化工厂硝酸胍车间发生爆炸。截至3月4日，已造成25人死亡、46人受伤。
灾难：因忽视工艺安全导致（续2）

爆炸震碎方圆2000米内房屋玻璃

邻近车间毁坏
灾难：因忽视工艺安全导致（续3）

现场炸出直径十几米大坑

发生事故的1号车间已经基本上被炸平，爆炸地点出现了一个直径十几米的大坑，空气中弥漫着刺鼻的气味。
爆炸三要素

爆炸必须具备的三个条件

1. 爆炸性物质
2. 氧气
3. 点燃源
硝酸胍

克尔化工现有产品：硫酸铵、硝酸胍、硝基胍、咪唑烷、N-甲基硝基胍、双氯西林酰氯、邻氯西林酰氯、氟氯西林酰氯、苯唑西林酰氯、邻氯西林钠、双氯西林钠、氟氯西林钠、苯唑西林钠

此次爆炸事故是由于一车间硝酸胍反应釜（用来完成硫化、硝化、氢化、聚合、缩合等工艺过程的压力容器）引起的爆炸
事故统计模型：海因里希金字塔模型

海因里希模型
Heinrich Pyramid

1. 死亡
2. 损失工时的受伤
3. 轻微受伤（无损工时）
4. 未遂事件
5. 不安全行为

灾难
工艺事故
损失统计模型：事故冰山模型

事故导致的真实损失

不仅是保险赔偿的部分

- 公司声誉
- 业务/生产中断
- 危机
- 债务
- 破产

事故冰山模型

You NEED a Program!
The real costs of accidents can be measured and controlled.

保险赔偿的部分

- Direct, visible, $1
  - Medical payments
  - Compensation
  - Disability

不能入保的部分

- Time lost by other employees who stop work
- Time spent in first aid attention
- Costs due to damage to machines, tools, and/or spoiled material
- Costs that occur in consequence of the excitement
- Costs due to interruption of production failure to fill orders
- Cost to the company under the employee welfare and benefit system
- Cost to keep the employee working, but not at his regular job
- Costs of overhead expenses which continue, although the employee cannot work.
- Time lost by the supervisor and others assisting the victim, investigation, reporting, training, etc.
- Suffering and worrying to the victim and his/her family (this generally cannot be measured in money, but the impact is usually many times more important than all of the other costs combined.)
中国PSM法律法规标准

- 《首批重点监管的危险化工工艺目录的通知》
- AQT 3033-2010_化工建设项目安全设计管理导则
- AQT 3034-2010_化工企业工艺安全管理实施导则
- GB50058_爆炸和火灾危险环境电力装置设计规范
- SH3018-2003T_石油化工安全仪表系统设计规范
- GB50351-2005_储罐区防火堤设计规范
- SH3097-2000_石油化工静电接地设计规范
第3节
工艺安全，是制药行业可持续发展的要求
跨国制药公司如何选择供应商

要求：
供应商能在规定时间，
提供优质的产品！

价格

供应链的稳定性

产品质量

1. 管理系统
2. 法律符合性（License to Operate）
3. 工艺安全
4. 员工健康
5. 环境保护
6. 劳动力保护
7. 伦理道德
EHS/PSM在原料药行业的发展趋势

1. 管理系统
2. 法律符合性（License to Operate）
3. 工艺安全
4. 员工健康
5. 环境保护
6. 劳动力保护
7. 伦理道德

*上述7项均为PSCI（制药工业供应链协会）推荐的供应商审核内容
为何如此关注供应商的EHS管理

企业社会责任

供应链稳定性

管理更优的供应商

跨国制药公司最担心：供应商意外停止供应他们需要的产品！！！

一原料药厂：一反应釜底部放料阀（用导热油伴热）处导热油泄漏着火，遇易燃易爆原料之后，一车间发生爆炸事故。生产中断，无法给制药企业提供中间体。
第4节
工艺安全与EHS管理有关吗？
什么是工艺安全

PSM（工艺安全管理）

- Process Safety Management-工艺安全管理

EHS （职业健康安全与环保）

- Environmental Protection-环境保护
- Occupational Hygiene-职业健康
- Occupational Safety-职业安全
工艺安全是EHS管理的延伸
风险管理实施方案

PSM与EHS综合管理实施方案
第5节
工艺安全管理-了解更多
API/中间体企业EHS/PSM现状

API/中间体生产厂特点：
- 涉及危险工艺
- 现场使用易燃/有毒化学品
- 自动化程度低（非本质安全）
- 没有完整的EHS/PSM风险控制方案
- 产品研发没有系统化风险管理方案
- 事故频发

侧重点不同的风险管理：
- 合规性管理（适用于所有企业）
- 职业健康安全与环境管理-EHS（适用于制剂厂）
- 工艺安全管理-PSM（适用于API/中间体厂）
| 1 | 光气及光气化工艺  
Phosgenation process | 9 | 重氮化工艺  
Diazotization process |
|---|---|---|---|
| 2 | 电解工艺（氯碱）  
chlor-alkali production | 10 | 氧化工艺  
Oxidation process |
| 3 | 氯化工艺  
Chlorination process | 11 | 过氧化工艺  
Peroxidation process |
| 4 | 硝化工艺  
Nitrification process | 12 | 胺基化工艺  
Amination process |
| 5 | 合成氨工艺  
Ammoniacal synthesis process | 13 | 磺化工艺  
Sulfonation process |
| 6 | 裂解（裂化）工艺  
Cracking process | 14 | 聚合工艺  
Polymerization Process |
| 7 | 氟化工艺  
Fluorination process | 15 | 烷基化工艺  
Alkylation Process |
| 8 | 加氢工艺  
Hydrogenation process |   |   |

中国法定高风险化学工艺
工艺安全管理：难题？

质量要求太高了
预算控制，安全经费不够
承包商人员素质太差
工期太紧
新手太多

所以我们常听到：
……项目哪有不出事的！
……别出大事就行，出点小事难免！
……这么高要求，还能干活吗？
确实是这样吗？
工艺安全管理：难题？

我的HSE部门人数不少

我已经为安全花了很多钱

我已经尽力了

我们有HSE体系

我还有什么需要做的吗？

然后呢？

……如果？
工艺安全管理：机会！

► 事故经济损失占企业成本的比例，各工业国最低的为3%，最高的达到8%以上，甚至超过很多行业的平均利润率。

► 英国安全卫生执行委员会（HSE）的研究报告显示：工厂伤害、职业病和非伤害性意外事故所造成的损失，约占英国企业获利的5%~10%。

► 我国企业界一年发生70多万起事故，直接经济损失达到2500多亿元。

► 全美安全理事会（NSC）的一项调查表明：企业在安全管理上每1美元的投资，平均可减少8.5美元的事故成本。
工艺安全管理（PSM）要素

**OSHA 29CFR1910.119**
- 工艺安全信息
- 工艺危害分析
- 变更管理
- 开工前安全检查
- 操作规程
- 培训
- 机械完整性
- 动火作业许可证
- 承包商
- 应急准备和响应
- 事件调查
- 商业机密
- 符合性审核
- 员工参与

工艺安全管理模型图
工艺安全管理（PSM）体系各要素（活动）是相互依存，并且必然由两个先决条件所联系在一起：
- 组织的能力
- 组织的有效性/文化

组织的工艺安全

Organizational EFFECTIVENESS

风险管理
操作
事件响应
责任

设施完整性

Organizational CAPABILITY
工艺安全管理

A. 工艺安全管理

- 符合性审计 → 商业机密
- 操作程序（SOP） → 培训 → 开车前安全审查（PSSR）
- 变更管理（MOC） → 工艺安全信息（PSI）
- 工艺危害分析（PHA） → 变更管理（MOC）
- 员工参与 → 事件调查 → 应急准备与响应
- 机械完整性 & 预防性维修
- 动火许可
- 承包商管理
工艺安全管理的职责分配

工艺安全 (PSM) 管理

执行秘书

工艺与技术
  - 工艺危害分析
  - 工艺安全信息
  - 操作步骤
  - 安全程序
  - 变更管理

设备设施
  - 质量保证
  - 机械完整性
  - 投运前安全检查
  - 变更管理

人员
  - 应急
  - 承包商管理
  - 审核
  - 培训
  - 事件调查
  - 变更管理
工艺安全管理的职责分配

工艺安全管理（PSM）十四个要素：

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工艺设计与工艺安全
API生产企业量产化流程

在生产前应检查：
01、试验设计与基础数据
02、试验操作流程
03、试验项目风险评估
04、改进措施实施状况
05、试验人员资质
06、个人防护
07、实验室安全准备
08、培训完成状况

在生产设计前，应具备：
01、PRA结果
02、中试故障与问题记录
03、工艺设计信息
04、相关法律法规
05、设计人员资质
06、概念设计框架

1. 审批流程1
   - 小试
2. 审批流程2
   - 中试
3. 审批流程3
   - 量产设计
4. 量产开车

中试开始前，应检查：
01、小试故障与问题记录
02、化学品兼容性分析
03、反应设备与化学品兼容性分析
04、危险Scenario描述分析
05、P&ID图
06、对P&ID的PHA
07、改进措施实施状况
08、SOP/BPR
09、培训
10、使用PSSR实施全面核查

量产开车前，应检查：
使用PSSR实施全面核查
01、PHA是否完成
02、分析结果是否核实
03、P&ID图是否与现场完全一致
04、各种设备是否齐备
05、自控系统是否调试完毕
07、SOP/BPR是否完成
10、培训是否完成
工艺设计与工艺安全

小试装置

中试装置
Assessment of Thermal Safety Risks

Cooling failure runaway scenario

RC1

MTSR

Tprocess

Normal process

Cooling failure

Decomposition reaction

$\Delta T_{ad, \text{decomp}}$

$\Delta T_{ad}$

DSC, ARC, Phi-Tec

Time

TMRad-24 h

Enhancing Supplier Capabilities: A Deeper Dive | 19-22 September 2016 | Shanghai |
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工艺设计：热力学平衡计算与安全评估

**Temperature**

- **MTT:** Maximum Temperature for Technical reasons
- **MTSR:** Maximum Temperature of Synthesis Reaction

**T@TMRad24**

**Tp Process temp**

**Index**

1. 2. 3. 4. 5.

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工艺设计：热力学平衡计算与安全评估

Build runaway scenario: Assessment of severity

Criticality?

1-2
Process is not critical
No measures are required

3-4
Process is critical
Design technical measures

5
Process is critical
Redesign process
商业化生产

商业化生产装置
火三角的概念与惰性气体保护
保护层洋葱模型
保护层的成功与失败
第7节
工艺危害分析
工艺危害分析（Process Hazard Analysis）

工艺危害分析

工艺危害分析

在工艺装置设备整个生命周期开展工艺危害分析

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PHA的时机

PHA的时机：

早期开发阶段中的筛选 → 详细工艺安全分析 → 基准和周期性工艺安全分析

项目建议书 → 可行性研究 → 初步设计 → 施工图设计 → 施工建设

工艺安全预审

试生产 → 开车 → 运行

最终项目安全报告

封存、拆除 → 封存、拆除工艺危害分析
危险和可操作性研究（HAZOP）分析

优点

- 系统地分析所有和最初设计意图相背离的偏差
- 非常适合新技术和工艺
- 容易归档
- 适用于化学工艺过程也可适用于其它制造过程
危险和可操作性（HAZOP）分析

局限性

- 假设设计在正常工况下是正确的
- 需要准确的模型或图纸
- 容易“跑题”
HAZOP分析步骤

- 从这里开始对每个节点进行分析

选择节点
解释节点的设计意图
选择参数和引导词
建立相关的偏差
列出原因、后果和保护措施
评估是否需要加强风险控制

对所有引导词重复这个过程
确定节点

- 选择节点
- 确认设计意图
引导词与工艺参数

<table>
<thead>
<tr>
<th>运用引导词</th>
<th>工艺参数</th>
</tr>
</thead>
<tbody>
<tr>
<td>无(None)</td>
<td>流量</td>
</tr>
<tr>
<td>多(More)</td>
<td>温度</td>
</tr>
<tr>
<td>少(Less)</td>
<td>压力</td>
</tr>
<tr>
<td>反向(Reverse)</td>
<td>时间</td>
</tr>
<tr>
<td>部分(Part of)</td>
<td>液位</td>
</tr>
<tr>
<td>以及(As Well As)</td>
<td>混合/搅拌</td>
</tr>
<tr>
<td>异常(Other Than)</td>
<td></td>
</tr>
</tbody>
</table>
偏差矩阵

<table>
<thead>
<tr>
<th>引导词</th>
<th>设计参数</th>
<th>多于</th>
<th>少于</th>
<th>无</th>
<th>反向</th>
<th>部分</th>
<th>以及</th>
<th>此外</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure</td>
<td>High Pressure</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>时间</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
放热反应的反应釜
甲苯分装到200Kg桶
保护层分析LOPA

- 保护层是一类安全保护措施，它是能有效阻止始发事件演变为事故的设备、系统或者动作。兼具独立性、有效性和可审计性的保护层称为独立保护层（Independent Protection Layer, IPL），它既独立于始发事件，也独立于其他独立保护层。正确识别和选取独立保护层是完成LOPA分析的重点内容之一。典型化工装置的独立保护层呈“洋葱”形分布，从内到外一般设计为：过程设计、基本过程控制系统、警报与人员干预、安全仪表系统、物理防护、释放后物理防护、工厂紧急响应以及社区应急响应等。

在工业实践中一般在定性的危害分析如HAZOP，检查表等完成之后，对得到的结果中过于复杂的、过于危险的以及提出了SIS要求的部分进行LOPA，如果结果仍不足以支持最终的决策，则会进一步考虑如QRA等定量分析方法。
典型的化工装置的独立保护层呈“洋葱”形分布，从内到外一般设计为：

1. 过程设计
2. 基本过程控制系统
3. 警报与人员干预
4. 安全仪表系统
5. 物理防护
6. 释放后物理防护
7. 工厂紧急响应
8. 社区应急响应等
第8节
回顾：我们学到了什么？
EHS与全面损失控制

损失控制-风险管理

- 产品监管
- 社区意识
- EHSR 法律法规符合性
- 危害识别与风险评估
- 工艺安全
- 员工职业健康与安全
- 环境管理
- 企业社会责任
- 安防
- 产品运输安全
- 社区意识

Enhancing Supplier Capabilities: A Deeper Dive | 19-22 September 2016 | Shanghai |
All Conference Materials Intended for Attendees Only | Not For Broader Distribution
EHS管理金字塔模式

风险管理的实施要素

风险
管理方案

危害识别
与风险评估

识别EHSR法律法规
符合EHSR法律法规要求

EHSR
法律法规符合性

危害识别
与风险评估

PDCA循环：又称“戴明环”

工艺安全

员工职业
健康与安全

环境管理

企业社会责任
CSR

安防

产品监管

产品储运安全

社区意识
工艺安全管理（PSM）

——Process Safety Management

►工艺安全管理（PSM）的主要目的：是预防化学品（或能量）的意外泄漏，特别是防止它们泄漏到员工或其他人员活动的区域，使相关人员遭受伤害。

►工艺安全管理（PSM）的主要对象：是处理、使用、加工或储存危险化学品的工厂和设施。

►工艺安全管理（PSM）关心工艺系统的“偏差”，例如液位偏高、流量过大、压力过大等。
A. 工艺安全（Process Safety Management）

制药企业EHS管理的核心是工艺安全。完善的工艺安全管理系统不但能帮助减少人员伤害，也能避免重大的财产损失，消除和减少工艺系统中存在的操作隐患，提高工艺设备的可靠性，减少不必要的停车，提高生产效率。

PSM的特点：
● 工艺安全的一个基本出发点是预防工艺安全物料（或能量）泄漏；
● 是在设计、建造、操作和维修工厂工艺设备和设施过程中，运用工程知识、原理与经验，消除或减少与工艺相关的危害；
● 工艺安全有别于传统的“安全”概念；
● 工艺安全的侧重点是工艺系统和设施本身；
● 工艺安全已是一门独立的学科。

管理要素：
01、工艺安全信息（PSI）
02、工艺危害分析（PHA）
03、操作程序（SOP）
04、员工参与（管理系统共用）
05、培训（管理系统共用）
06、承包商管理
07、开车前安全审查（PSSR）
08、机械完整性与预防性维修（MI&PM）
09、动火许可系统（管理系统共用）
10、变更管理（MOC）
11、事件调查（管理系统共用）
12、应急准备与响应（EPR）（管理系统共用）
13、符合性审计（管理系统共用）
14、商业机密
谢谢！
LUNCH
Typical ignition Source Analysis in Pharmaceutical companies
Summary

• Burning & explosion
• Accident introduction
• 10 myths for ignition sources
• Introduction of ignition sources
Burning & explosion
Burning & explosion

“Ignition sources are the only thing we get for free in the chemical industry” – T. Kletz
Burning & explosion

1. the temperature
2. the total energy supplied
3. the rate at which it is supplied, or the time period over which it is delivered
4. the area over which it is delivered
Accident introduction
Accident introduction
Accident introduction
Accident introduction
Accident introduction
10 myth for ignition sources

<table>
<thead>
<tr>
<th>NO</th>
<th>Myth</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>I’ve been loading powder to that reactor via an open manway for 30 years and have never had an explosion so I can’t have an ignition problem. 我在这个反应器处投料已经做了30年，但是从来没有发生过爆炸，所以我这个岗位没有点燃问题</td>
</tr>
<tr>
<td>2</td>
<td>I operate the process below the liquid flashpoint so I’m safe. 我操作的工艺温度是低于液体闪点的，所以我是安全的</td>
</tr>
<tr>
<td>3</td>
<td>We can use literature data for our dust ignition properties, materials don’t vary. 对于粉尘我们采用的是文献数据，我们认为这个数据很靠谱，不会发生变化</td>
</tr>
<tr>
<td>4</td>
<td>We don’t have an ignition problem because we use a hot work permit. 我们不会有点燃风险，因为我们已经使用了动火许可证</td>
</tr>
<tr>
<td>NO</td>
<td>Myth 误区</td>
</tr>
<tr>
<td>----</td>
<td>-----------</td>
</tr>
<tr>
<td>5</td>
<td>My operators can’t become electrostatically charged; they don’t rub against anything. 我的操作人员作业不会产生静电，因为他们并没有摩擦作业</td>
</tr>
<tr>
<td>6</td>
<td>Everything is earthed so I have no problem with static. 所有的东西都接地了，所以我没有静电的问题</td>
</tr>
<tr>
<td>7</td>
<td>We must bond across all pipework joints. 我们必须跨接所有的管件</td>
</tr>
<tr>
<td>8</td>
<td>We use an earth clip for drums, so we are safe. 我们使用接地夹夹住金属桶，所以我们很安全</td>
</tr>
<tr>
<td>9</td>
<td>I don’t have any isolated conductors on my plant and it’s metal to metal contact so it should be earthed - right? 在我的工厂没有任何孤立的导体，而且都是金属和金属的连接，所以可以认为是接地的，不是吗？</td>
</tr>
<tr>
<td>NO</td>
<td>Myth</td>
</tr>
<tr>
<td>----</td>
<td>-------</td>
</tr>
<tr>
<td>10</td>
<td>We issue static dissipative footwear so we don’t have a problem with sparks from people or hand-held tools and I didn’t think people could ignite flammable vapours anyway.</td>
</tr>
</tbody>
</table>

我们的员工使用的都是静电消散鞋，所以我们不会有人员发生火花放电的风险，也不会有手持工具的火花放电风险，我们不认为我们的员工会点燃易燃蒸汽。
10 myth for ignition sources

**Typical ignition sources**

- Smoking
- Open flames
- Welding
- Cutting
- Grinding
- Hot surfaces
- Frictional heating
- Mechanical impacts
- Electric sparks
- Electrostatic discharges
- Lightning strikes
- Exothermic runaway chemical reactions
- Self-heating / spontaneous combustion / decomposition
Ignition Sources

- Hot surfaces
- Flames and hot gases (including hot particles)
- Mechanically generated sparks
- Electrical apparatus
- Stray electrical currents, cathodic corrosion protection
- Static electricity – five different types of electrostatic discharges
- Lightning – atmospheric static
- Radio Frequency (RF) electromagnetic waves from \(10^4\) Hz to \(3 \times 10^{12}\) Hz
- Electromagnetic waves from \(3 \times 10^{11}\) Hz to \(3 \times 10^{15}\) Hz
- Ionising radiation
- Ultrasonics
- Adiabatic compression and shock waves
- Chemical reactions / thermal decomposition leading to self-ignition

EN1127-1: FULL IGNITION SOURCE LIST (NOT ALL WILL BE “EFFECTIVE”)
Introduction of ignition sources

Legend:
A = mechanical friction/heating
B = smoldering
C = static discharges
D = fire, flames
E = self heating
F = hot surfaces
G = hot work
H = electrical equipment
I = unknown, not determined
J = other

Ref: BIA Report 11/97: 600 incidents
Introduction of ignition sources
Introduction of ignition sources

- Machinery generated sparks
- Open fire (example: welding)
- Electrical equipment
- Hot surfaces
- Electrostatics
- Self heating
- Adiabatic compression
Introduction of ignition sources

4 main characteristics

1) Temperature

2) Total energy supplied

3) The rate at which it is supplied, or the time period over which it is delivered

4) The area over which it is delivered
Machinery generated sparks
Machinery generated sparks
Machinery generated sparks

\[ 2\text{Al} + \text{Fe}_2\text{O}_3 \rightarrow \text{Al}_2\text{O}_3 + 2\text{Fe} + \text{heat} \]
Machinery generated sparks

Can Dropped Objects ignite flammable vapor?
Machinery generated sparks

Low energy: 10 J

Medium energy: 1 kJ

High energy: over 1 MJ

<table>
<thead>
<tr>
<th>Object moved</th>
<th>Object struck</th>
<th>Substance ignited</th>
</tr>
</thead>
<tbody>
<tr>
<td>aluminum hand tool</td>
<td>brickwork</td>
<td>ammonium</td>
</tr>
<tr>
<td>boot or shoe nails</td>
<td>caked material</td>
<td>perchlorate</td>
</tr>
<tr>
<td>brass rod</td>
<td>concrete</td>
<td>carbon disulfide</td>
</tr>
<tr>
<td>metal pipe</td>
<td>steel</td>
<td>cellulose lacquer</td>
</tr>
<tr>
<td>connector</td>
<td></td>
<td>denatured alcohol</td>
</tr>
<tr>
<td>steel hand tool</td>
<td></td>
<td>diazonium salt</td>
</tr>
<tr>
<td>various heavy metal objects moved</td>
<td></td>
<td>ethylene</td>
</tr>
<tr>
<td></td>
<td></td>
<td>gasoline</td>
</tr>
<tr>
<td></td>
<td></td>
<td>grain dust</td>
</tr>
<tr>
<td></td>
<td></td>
<td>hydrogen</td>
</tr>
<tr>
<td></td>
<td></td>
<td>LPG</td>
</tr>
<tr>
<td></td>
<td></td>
<td>paint thinner</td>
</tr>
<tr>
<td></td>
<td></td>
<td>propane</td>
</tr>
<tr>
<td></td>
<td></td>
<td>thermite</td>
</tr>
<tr>
<td></td>
<td></td>
<td>town gas</td>
</tr>
</tbody>
</table>
Machinery generated sparks

<table>
<thead>
<tr>
<th>Fuel gas</th>
<th>Min. load for ignition (N)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>At 5 m s(^{-1})</td>
</tr>
<tr>
<td>hydrogen</td>
<td>120</td>
</tr>
<tr>
<td>propylene oxide</td>
<td>250</td>
</tr>
<tr>
<td>ethylene</td>
<td>250</td>
</tr>
<tr>
<td>methanol</td>
<td>850</td>
</tr>
<tr>
<td>diethyl ether</td>
<td>900</td>
</tr>
<tr>
<td>propane</td>
<td>1100</td>
</tr>
<tr>
<td>acetone</td>
<td>1200</td>
</tr>
</tbody>
</table>
Machinery generated sparks

Iron in the fire
Open fire

Welding spatter
Open fire

Welding spatter

<table>
<thead>
<tr>
<th>Target fuel</th>
<th>Particle dia. (mm)</th>
<th>Ignition time (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>acrylic batting</td>
<td>1.1</td>
<td>&lt; 1</td>
</tr>
<tr>
<td>cardboard, corrugated</td>
<td>2.5</td>
<td>7 – 8</td>
</tr>
<tr>
<td>cotton cloth</td>
<td>3.1</td>
<td>5 – 6</td>
</tr>
<tr>
<td>cotton wool</td>
<td>0.9</td>
<td>&lt; 1</td>
</tr>
<tr>
<td>ethanol</td>
<td>1.1</td>
<td>&lt; 1</td>
</tr>
<tr>
<td>gasoline</td>
<td>1.4</td>
<td>&lt; 1</td>
</tr>
<tr>
<td>kerosene</td>
<td>1.5</td>
<td>NI</td>
</tr>
<tr>
<td>kerosene-soaked cloth</td>
<td>1.3</td>
<td>&lt; 1</td>
</tr>
<tr>
<td>newspaper</td>
<td>2.5</td>
<td>4 – 5</td>
</tr>
<tr>
<td>oil, light</td>
<td>2.0</td>
<td>NI</td>
</tr>
<tr>
<td>oil, light, soaked in cloth</td>
<td>1.9</td>
<td>&lt; 1</td>
</tr>
<tr>
<td>polyurethane foam</td>
<td>0.9</td>
<td>&lt; 1</td>
</tr>
<tr>
<td>polystyrene foam</td>
<td>1.3</td>
<td>3 – 4</td>
</tr>
<tr>
<td>sawdust</td>
<td>1.5</td>
<td>&lt; 1*</td>
</tr>
<tr>
<td>wood shavings</td>
<td>1.9</td>
<td>4 – 5</td>
</tr>
</tbody>
</table>

* smoldered after 4 – 5 s
NI – no ignition
Open fire

2_3_Dangers_of_Hot_Work
Electrical equipment
Electrical equipment

• Electrical arc
• Overheating wires
• Overheating electrical connections
• Ejection of hot particles
Electrical Equipment Marking

Model PT 4-20

Worldwide Ex Inc.
Industrial Park Road 1, 6812 AR Safety, Netherlands

Ex d [ib] IIC T4 Gb
Ex ta IIIC T500 120 °C Da

Ex d [ib] IIC T4 Gb
Ex ta IIIC T500 120 °C Da

Class I, Div 1, Groups ABCD T4A;
Associated Apparatus [Ex ia] Provides IS
outputs for Class I, Div 1, Groups ABCD
Class II, Div 1, Group EFG-T(12OC)

Specific ATEX
markings

Specific IECEx
markings

Marking required by the
standards used under
ATEX, IECEx, INMETRO
and Canada (Zones)

Specific
INMETRO
markings

Specific
US specific
markings

Canada and
US specific
markings
Hot surfaces
Static Discharges

- Six types of industrial electrostatic discharges, as follows:
  - Spark
  - Brush
  - Enhanced (or transitional brush discharges)
    Propagating brush
  - Cone
  - Corona
- Also outside type
  - Lightning type
- Effective / available energy depends on source of discharge
Static Discharges
Static Discharges
Static Discharges
## Static Discharges

<table>
<thead>
<tr>
<th>Charged object</th>
<th>Capacitance (pF)*</th>
<th>Stored energy (mJ)**</th>
</tr>
</thead>
<tbody>
<tr>
<td>Small metal items</td>
<td>10 to 20</td>
<td>1 to 2</td>
</tr>
<tr>
<td>(scoop, funnel, nozzle, …)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Small containers</td>
<td>10 to 100</td>
<td>1 to 10</td>
</tr>
<tr>
<td>(bucket, 50l drum)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Medium containers</td>
<td>50 to 300</td>
<td>5 to 30</td>
</tr>
<tr>
<td>(200l drum, …)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Plant items</td>
<td>100 to 1000</td>
<td>10 to 100</td>
</tr>
<tr>
<td>(reactors, …)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Person</td>
<td>100 to 300</td>
<td>10 to 30</td>
</tr>
<tr>
<td>Road tanker</td>
<td>Up to 1000</td>
<td>Up to 100</td>
</tr>
</tbody>
</table>

* 1 pF = 1x10^{-12} F
** Based on a potential of 10 kV – Can be +/- higher
Static Discharges
Case Study – Barton Solvent Fire & Explosion

Key Lessons for Safe Handling and Storage of Flammable

- Ensure that equipment, such as fill nozzles and hoses, is bonded and grounded and designed for flammable service
- Use dip pipes when top-filling portable tanks
- Install fire suppression systems in flammable packaging areas
- Separate flammable packaging areas from bulk storage areas
Case Study – Barton Solvent Fire & Explosion
Case Study – Barton Solvent Fire & Explosion

Class IB flammable liquid.

Table 2. Electrical conductivities of selected liquids.

<table>
<thead>
<tr>
<th>Liquid</th>
<th>Electrical Conductivity, ( \gamma ), pS/m</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Conductive liquids</strong> (( \gamma &gt; 10^4 ) pS/m)</td>
<td></td>
</tr>
<tr>
<td>Ethyl acetate (25°C)</td>
<td>( 4.6 \times 10^4 )</td>
</tr>
</tbody>
</table>
Case Study – Barton Solvent Fire & Explosion

Top-Filling & bottom fill
Case Study 2 – Barton Solvent Fire & Explosion

ISSUES

- Nonconductive flammable liquids can accumulate static electricity during transfer and storage.
- Static sparks can readily ignite flammable vapor-air mixtures inside storage tanks.
- Material Safety Data Sheets (MSDSs) often do not adequately communicate hazard data and precautions.
Case Study 2 – Barton Solvent Fire & Explosion

VM&P naphtha tank and photo of an example float

Emergency Pressure Relief Device

Pressure/Vacuum Valve

Liquid Level Tape Gauging System

Gauging View Glass

Float

Transfer Pump

Tanker-Trailer

Storage Tank

Bonding & Grounding
Case Study 2 – Barton Solvent Fire & Explosion
Case Study 2 – Barton Solvent Fire & Explosion
Case Study 2 – Barton Solvent Fire & Explosion

Barton solvent
Self heating
Pressure

\[
\frac{T_f}{T_o} = \left( \frac{P_f}{P_o} \right)^{(\gamma-1)/\gamma} = \left( \frac{v_o}{v_f} \right)^{\gamma-1}
\]

For air \( r = \frac{C_p}{C_V} = 1.4 \)
Process Safety Accidents in Pharmaceutical Industry
Cain Wang
王侃云

CIH, CSP
Process Safety Consultant
Cain.Wang@dekra.com.cn

- Over 10 years experience of process safety and EHS in North America and Asia pacific
- Expertise include DHA, Electrostatics, chemical reaction and PSM
- Excellent understanding in NFPA, ASTM, IEC
Summary

- Seveso accident
- Spray dry fire
- ABC company hybrid deflagration
SEVESO
Stage 1
1. 2. 4. 5-Tetrachlorobenzene

\[
\begin{align*}
\text{Cl} & \quad \text{Cl} \\
\text{Cl} & \quad \text{Cl} \\
\quad + 2 \text{NaOH} \\
\end{align*}
\]

\[
\begin{align*}
\text{Cl} & \quad \text{Cl} \\
\text{Cl} & \quad \text{Cl} \\
\quad \quad + \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad + \text{NaCl} \\
\text{ONa} & \quad \text{Cl} \\
\text{Cl} & \quad \text{Cl} \\
\end{align*}
\]

2. 4. 5-Sodium Trichlorophenate

Stage 2

\[
\begin{align*}
\text{Cl} & \quad \text{Cl} \\
\text{Cl} & \quad \text{Cl} \\
\quad \quad + \quad \quad \text{HCl} \\
\end{align*}
\]

\[
\begin{align*}
\text{Cl} & \quad \text{Cl} \\
\text{Cl} & \quad \text{Cl} \\
\quad \quad + \quad \quad \text{NaCl} \\
\end{align*}
\]

2. 4. 5-Trichlorophenol
SEVESO

Stage 2

\[
\begin{align*}
\text{Cl} & \quad \text{ONa} \\
\text{Cl} & \quad \text{Cl}
\end{align*}
\]

+ HCl

\[
\begin{align*}
\text{Cl} & \quad \text{OH} \\
\text{Cl} & \quad \text{Cl}
\end{align*}
\]

+ NaCl

2. 4. 5-Trichlorophenol

\[
\begin{align*}
\text{Cl} & \quad \text{Cl} \\
\text{Cl} & \quad \text{Cl} \\
\text{Cl} & \quad \text{Cl}
\end{align*}
\]

\[
\begin{align*}
\text{Cl} & \quad \text{Cl} \\
\text{Cl} & \quad \text{Cl}
\end{align*}
\]

\[
\begin{align*}
\text{Cl} & \quad \text{Cl} \\
\text{Cl} & \quad \text{Cl}
\end{align*}
\]

\[
\begin{align*}
\text{Cl} & \quad \text{Cl} \\
\text{Cl} & \quad \text{Cl}
\end{align*}
\]
### A LD$_{50}$ to various animal species

<table>
<thead>
<tr>
<th>Species</th>
<th>LD$_{50}$ (µg/kg)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Guinea pig</td>
<td>0.6</td>
<td>Schwetz et al. (1973)</td>
</tr>
<tr>
<td>Rat</td>
<td>22</td>
<td>Schwetz et al. (1973)</td>
</tr>
<tr>
<td>Rat (female)</td>
<td>45</td>
<td>Schwetz et al. (1973)</td>
</tr>
<tr>
<td>Rabbit</td>
<td>115</td>
<td>Schwetz et al. (1973)</td>
</tr>
<tr>
<td>Rabbit (female)</td>
<td>115</td>
<td>Schwetz et al. (1973)</td>
</tr>
<tr>
<td>Mouse</td>
<td>114</td>
<td>Vos et al. (1973)</td>
</tr>
</tbody>
</table>

### B Relative toxicity of some highly toxic materials

<table>
<thead>
<tr>
<th>Substance</th>
<th>Minimum lethal dose (moles/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Botulinus toxin</td>
<td>$3.3 \times 10^{-17}$</td>
</tr>
<tr>
<td>TCDD</td>
<td>$3.1 \times 10^{-9}$</td>
</tr>
<tr>
<td>Strychnine</td>
<td>$1.5 \times 10^{-6}$</td>
</tr>
<tr>
<td>Sodium cyanide</td>
<td>$2.0 \times 10^{-4}$</td>
</tr>
</tbody>
</table>
SEVESO

V: 13875 L  
Psteam: 12 bar  
Tsteam: 188 degree C  
No automatic control of heating
SEVESO

2000kg TCB
1050kg NaOH
3300kg Ethylene glycol
600kg Xylene

Friday: 16:00 final reactor batch started
Saturday: 5:00 Final reactor batch interrupted
6:00 shift ended
12:37 Bursting disc on reactor ruptures
SEVESO

Outcome of the accident

729 people evacuated
14 yrs after the accident
- 193 cases Chloracne
- Peripheral neuropathy
- Cancer (lymphatic and hematopoietic tissue neoplasms, gastrointestinal cancer, breast cancer)
SEVESO

Accident direct Cause

(1) Interruption of the production cycle.
(2) Method of distillation.
(3) Set pressure of bursting disc.
(4) Failure to install collection/destruction system for material vented.
Root Cause

- Lack of knowledge for chemical reactions
- Inadequacy of the measuring equipment for a number of fundamental parameters
- Absence of any automatic control system
- Measurement of acidity was carried out manually by immersion of a rod with an indicator chart (sic) through a secondary inspection window
- The reactor vessel was not given a hydraulic test as the reactor was considered to operate at atmospheric pressure.
- The fitting of the bursting disc was not reported to the state pressure vessel inspectors.
SEVESO

Root Cause Decomposition

• 1\textsuperscript{st} peak at 185 degree C (induction time 2.1 hours)

• 2\textsuperscript{nd} peak at 255 degree C (0.5 hours)

Side reaction:

\[
\text{HOCH}_2\text{CH}_2\text{OH} + 2\text{NaOH} \rightarrow \text{NaOCH}_2\text{CH}_2\text{ONa} + \text{H}_2\text{O} - Q
\]

(230 degree C, rising rapidly to about 400 degree C)
SEVESO

Lessons from SEVESO
• Public control of major hazard installations
• Facility siting
• Acquisition of companies operating hazardous process
• Hazardous of ultratoxic substances
• Hazards of undetected exotherms
• Hazard of prolonged holding of reaction mass
• Inherently safer design of chemical processes
• Control and protection of chemical reactors
• Adherence to operating procedures
• Planning for emergencies
• Difficulties of decontamination
Important follow ups from this cases

• improved regulatory arrangements for the control of hazardous plants

• Generate Seveso Directive
Safe Drying of Powders on an Industrial Scale

Incidents and Case Study: Spray Dryer Incident
“Hot” off the Press

- Fire-fighters called to factory producing milk products, at 1am (AEDT) Tuesday 21 Feb. They managed to contain the blaze to one room.

- "The fire is the result of a large dust explosion within the milk drying chamber that has extended into the collection and transfer ducting and surrounding equipment," CFA operations officer Ian Pattie told AAP. "The quick action of fire-fighters prevented the spread of the fire in to the packaging and storage area adjacent to the drying plant."

- Estimated $3 million damage caused to the milk drying chamber and surrounding equipment, little structural damage done to the building.

- The factory is expected to be able to continue its wet milk operations, but the dried milk operations could be shut down for weeks.
Dryer Incidents
Spray Dryer Milk - Incident - Scenario

• Incident occurred 2004 in plant operating for many hours
• Spray dryer 10 m diameter - fixed nozzles / milk powders
• Incident resulted in plant overpressure
• Explosion propagation to sieve room
• Proprietary vents on dust filter did not open
• Fire damage
• Internal plant walls blackened
• Atomiser air inlet filter melted
Incident photographs

View of top of spray dryer
Incident photographs
Incident photographs
Incident photographs
Incident photographs
Analysis – flammable atmosphere?

- Flammable atmosphere 1. Milk powder
- Flammable atmosphere 2. Carbon monoxide (CO)
# Milk powder data

<table>
<thead>
<tr>
<th>Classification of data</th>
<th>Ignition sensitivity</th>
<th>Explosion severity</th>
<th>Static properties</th>
<th>Burning behaviour</th>
<th>Thermal decomposition</th>
<th>Limits</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Test parameters</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LIT</td>
<td>MIE</td>
<td>MIT</td>
<td>20 litre P\text{\textsubscript{max}} K\text{\textsubscript{St}}</td>
<td>Resistivity</td>
<td>Burning rate (BZ)</td>
<td>Bulk Cell °C</td>
</tr>
<tr>
<td>°C</td>
<td>mJ</td>
<td>°C</td>
<td>bar g bar ms\textsuperscript{-1}</td>
<td>Ωm</td>
<td>°C</td>
<td>°C</td>
</tr>
<tr>
<td>Dust layer</td>
<td>Dust cloud</td>
<td>Bulk powder</td>
<td>Dust cloud</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Milk powder</td>
<td>360</td>
<td>10 – 30</td>
<td>360</td>
<td>8.7</td>
<td>149 \textsuperscript{(St 1)}</td>
<td>6\textsuperscript{*}10\textsuperscript{12}</td>
</tr>
</tbody>
</table>
Bulk Powder Diffusion Cell Screening

![Diagram showing temperature change over time for different series]

- Series 2
- Series 3
- Series 4
- Series 5
- Series 6
- Series 7

Temperature °C vs Time in minutes (> 40 hours)
Bulk Powder Isothermal Test

![Graph showing Bulk Powder (Diffusion Cell) Isothermal Test @ 200°C]

- Temperature (°C) vs. Time (mirs) for different samples and oven temp.

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Thermal Decomposition Test Data

Thermal Stability Characterisation

Bulk powder (diffusion cell) test ($T_o$ - onset temperature, °C)
- Isothermal @ 200°C
- Isothermal @ 180°C
- Isothermal @ 160°C

Aerated cell test ($T_o$ - onset temperature, °C)
- Isothermal @ 200°C

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Activity</th>
</tr>
</thead>
<tbody>
<tr>
<td>283°C</td>
<td>Limited exothermic activity</td>
</tr>
<tr>
<td>227°C</td>
<td>Limited exothermic activity</td>
</tr>
</tbody>
</table>
Thermal Stability Tests
Plant Operating Temperatures

• Operational parameters in the spray dryer were

- Inlet drying air temperature : 152 °C
- Base of dryer temperature : 68 °C
- Cross-over pipe to filter : 100 °C (fines drawn to filter)

- NOTES:
  » MIE = 10 – 30 mJ
  » MIT = 360 °C
  » LIT 5 mm = 360 °C
Ignition Sources

- Hot surfaces
- Flames and hot gases (including hot particles)
- Mechanically generated sparks
- Electrical apparatus
- Stray electrical currents, cathodic corrosion protection
- Static electricity – five different types of electrostatic discharges
- Lightning – atmospheric static
- Radio Frequency (RF) electromagnetic waves from $10^4$ Hz to $3 \times 10^{12}$ Hz
- Electromagnetic waves from $3 \times 10^{11}$ Hz to $3 \times 10^{15}$ Hz
- Ionising radiation
- Ultrasonics
- Adiabatic compression and shock waves
- Chemical reactions / thermal decomposition leading to self-ignition

EN1127-1: FULL IGNITION SOURCE LIST (NOT ALL WILL BE “EFFECTIVE”)

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Potential “Effective” Ignition Sources

- Smouldering nest / particles
- Main factors affecting thermal decomposition
- Electrostatic discharges
- Overheating bearing
Recommendations

1. Fit CO detection system to respond
2. Fit effective measures to prevent explosion propagation
3. Determine specific thermal decomposition data for onset temperature / duration – select operational parameters
4. Avoid deposits & build-up in ducts (engineering solutions)
5. Earth all fixed and mobile items
6. Operator Training - more aware (and beware) of hazards
ABC company fire accident

Powder handling unit - Blender

DCS control by sequence
   a. inerting
   b. feed IPA automatically
   c. open valve
   c. feed powder automatically

Powder: MIE <20mj
   Volume resistivity >10 Ohms.m
ABC company fire accident

Powder handling unit - Blender

Accident description

a. Valve cannot be closed
b. Maintenance has a discussion with manufacturing team
c. Use constant nitrogen gas to inert system
c. Manual feed by 2 operators
d. A deflagration happen
e. Two operators are seriously burned
ABC company fire accident

Accident direct cause

1) Electrostatics ignition source
2) Hybrid deflagration
3) Ineffective blanketing

Accident root cause

1) Lack of MOC
2) Ineffective PHA lead to ineffective control
3) Safety culture
4) Poor arrangement of working place
5) Lack of PPE
THE END
CLASSIFICATION OF HAZARDOUS AREAS

Presented by

Tomsen Sheng
Senior Process Safety Consultant
DEKRA (Shanghai) Co., Ltd.
Agenda

1. Available Guides for Gas / Vapour HAC
2. Philosophy of Hazardous Area Classification
3. 5 Steps to Performing a Hazardous Area
4. EQUIPMENT SELECTION
Philosophy of Hazardous Area Classification
危险场所分类原理

• Area classification assesses the probability of flammable atmospheres occurring inside of plant, the workplace, and elsewhere

• 危险场所分类评估工厂，车间及其他区域内产生爆炸性气体环境的可能性

• Once the probability is established, ignition sources can be prevented to match this

• 评估区域爆炸可能性后，可作为依据来进行点火源的控制
Available Guides for Gas / Vapour HAC 相关标准

- IEC 60079-10-1 (2008), EN 60079-10-1 (2009)
  - International methodology standard 国际标准
  - essential but limited guidance on zone extent
  - GB3836-14(2000) = IEC 60079-10-1
  - National methodology standard 中国标准
  - NFPA497
  - USA methodology standard 美国标准
- IP15 3rd Edition, 2005
  - Code of Practice, Institute of Petroleum (Energy Institute) 石油协会
    but contains many useful examples for all industries with installations handling flammable liquids
5 Steps to Performing a Hazardous Area Classification (HAC)

- Step 1 - Obtain data
- Step 2 – Identifying sources of release
- Step 3 – Assigning a grade of release
- Step 4 – Assign Zone number and extent of zone
- Step 5 – Record and document
Step 1 – Material Data Requirements

- HAC for gases and vapours requires the following data:
  - flash point
  - explosion limits
  - auto-ignition temperature
  - gas group
  - vapour density*
  - liquid density*
  - molecular weight*

*not flammability data

*not flammability data
Step 2 – Identify Sources of Release 识别释放源
- Think First? 先思考？

- Are there any sources of release?
- 哪些地方是释放源？
- Can sources of release be eliminated?
- 释放源是否可以消除
- Is there enough flammable material to produce a dangerous volume of explosive gas atmosphere?
- 是否有足够的易燃物质产生可导致危险量的爆炸性气体环境？
- Can continuous sources be changed to primary ones and primary sources to secondary?
- 持续释放源是否能降低到一级或者二级释放源？
- Can poor ventilation be improved?
- 差的通风能否改良？
- Can availability of ventilation be improved?
- 通风的可靠性能否提高？
Steps 2 – 3: Identify Release Points / Grades
识别释放源/等级

- Full (up to date) plant drawings
  最新的厂区图纸
- Written operating instructions
  书面的操作说明
- List of changes to plant or process
  工艺过程的变更清单
- Observation of operations
  现场操作观察
Grade of Release

Continuous grade
- continuously, or for long periods, or frequently
- 持续，长期，经常的

Primary grade
- periodically or occasionally during normal operation
- 正常操作中周期性或者偶尔存在的

Secondary grade
- not in normal operation
- only infrequently and for short periods
- 非正常操作中的
- 只是偶尔并短期释放的
EXAMPLES OF SOURCES OF RELEASE

• **Continuous**
  - Surface of flammable liquid (e.g. in vessel)
    易燃液体表面（如容器内部）

• **Primary**
  - Pump or valve seals where release normally expected
    预期正常情况下会泄露的泵或者阀门密封
  - Water drainage points for flammable liquid vessels
    易燃液体容器的排水系统
  - Sample points used as part of normal operation
    正常操作中的取样点
  - Relief valves, vents, etc. active during normal operation
    正常操作中会开启的泄放阀，排气阀等
EXAMPLES OF SOURCES OF RELEASE

• **Secondary 二级**
  – Pump or valve seals, release not normally expected
  – 预期正常操作时不会泄露的泵或者阀门密封
  – Sample points not used in normal operation
  – 非常规操作的取样点
  – Relief valves, vents not normally active
  – 正常操作中不会开启的泄放阀，排气阀
  – Flanges, connections, pipe fittings
  – 法兰，连接件，管道配件处
Hazardous Explosive Atmosphere
“small quantities量很少”?

- 1 litre of liquefied propane in aerosol can
  1升的液化丙烷罐可以

- When released forms 260 l of gas如果释放可以释放260L的气体

- Diluted in air to the LEL (propane = 2 % v/v) produces 13,000 litres (13 m³) volume of explosive atmosphere在空气中稀释到爆炸下限的浓度（丙烷爆炸下限2%）可形成13,000升（13立方）的爆炸性气体环境
Not Sources of Release for HAC 非释放源

The following situations would **not** usually warrant a release 以下情形通常不作为释放源:

• Covered holes and openings in side of well sealed vessels

• Overfill vents of tanks with high integrity level protection

• 有高液位连锁保护的罐体的溢流口

• Releases from all-welded pipework (of good weld quality)

• 全焊接管道（质量良好）的泄露

• Releases of low pressure natural gas in well ventilated areas (recent HSE work)

• 通风良好场所低压天然气的释放

• Releases of liquids at a temperature less than 5 °C below their flashpoint (provided they cannot be heated after release)

• 释放的液体温度低于闪点5度以下（确保液体释放后不会被加热）
Eliminating Sources of Release

• Measures to minimise likelihood and extent of vapour / gas atmospheres:
  – Keep lids on open vessels with solvents
  – Minimise use of ‘open’ filling and decanting of solvent
  – Good maintenance of pumps, relief valves and pipework
  – Frequent inspection and leak testing of all flexible hoses
  – Use of all welded pipework
  – Back balancing of road tankers
  – Use of closed sample systems
  – Use of ‘sealess’ pumps (e.g. magnetic drive)
  – Use of local extraction ventilation (LEV)
  – Avoid venting tanks to atmosphere
  – Washing filters with water before replacing
  – Closed addition systems for powder additions to flammable liquids
Internal Zoning 内部分区

- Plant internal zoning is also important - affected by:
- 装置内部分区也很重要 - 受以下影响:
  - Inerting 惰化
  - Vacuum operation 真空操作
  - Variability of contents (filling / emptying frequently?) 物料变化（加料/卸料频繁？）
  - Access ports 进入口
Effect of Inerting on Grade of Release
惰化对释放等级的影响

- Use of inert gas e.g. nitrogen allows a less severe grade of release 使用惰化气体如氮气可以降低释放源等级
- Example: In an inerted reactor: 例如在一个惰化反应釜
  - Primary grade if it can be proven that inert atmosphere is reliable and the oxygen concentration adequately low
  - 一级释放：如果可以保证惰化环境可靠，氧气含量足够低
  - Secondary (or non-hazardous) if above conditions met and inerting system is high integrity (would require a quantified assessment to justify and possibly IEC 61508 review)
  - 二级释放或非危险场所：如果符合上述情况并且惰化系统具有很高的完整性（需要进行认证分析来证明）
Effect of Vacuum on Grade of Release

真空对释放等级的影响

- Use of vacuum can allow a relaxation of the grade of release
- 使用真空操作可以降低释放源等级
- Example: vacuum pumps can justify:
  - Primary grade when equipment is running, often little oxygen or fuel rich (or both) – start up/shut down?
  - 真空操作时降低为一级释放源，通常氧气不够或者燃料过多（或都有）- 开启前或者关闭时？
- Continuous grade should be assumed when pulling vacuum e.g. from pan filters where air can be pulled through in normal operation.
- 真空操作时如果有气体带入，如正常操作时空气通过过滤系统进入要认作持续释放源
Zone definition: An area in which an explosive atmosphere consisting of a mixture with air of flammable substances in the form of gas, vapour or mist is….

Zone 0
• …. present continuously or for long periods or frequently
• 持续存在或者长期或者经常存在

Zone 1
• …. likely to occur in normal operation occasionally
• 正常操作过程中间可能间断发生

Zone 2
• …. not likely to occur in normal operation but, if it does, will persist for a short period only
• 正常操作过程中不会发生，如果发生，也只是短期存在

Note: Normal operation includes expected abnormal, but not catastrophic events
注意：正常操作包括预期的正常情况，但是不包括灾难性事件
Step 4 - Grades of Release and Zones

<table>
<thead>
<tr>
<th>Grade</th>
<th>Duration of release</th>
<th>Zone</th>
</tr>
</thead>
<tbody>
<tr>
<td>Continuous</td>
<td>&gt; 1000 hours per year</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>&gt; 1 hour per shift</td>
<td></td>
</tr>
<tr>
<td>Primary</td>
<td>&lt; 1000 hours per year</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>&gt; 10 hours per year</td>
<td></td>
</tr>
<tr>
<td>Secondary</td>
<td>&lt; 10 hours per year</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>&lt; 1 minute per shift</td>
<td></td>
</tr>
</tbody>
</table>
Step 4 – Extent of Zones

- **Method 1: The direct example method** 引用标准例图

- **Method 2: The point source (source of release) method** 释放源模型

- **Method 3: Calculation** 计算
Step 4 - Direct Example

Taking into account relevant parameters, the following are typical values which will be obtained for this example:

- $a = 3 \text{ m from vent openings}$;
- $b = 3 \text{ m above the roof}$;
- $c = 3 \text{ m horizontally from the tank}$.

Example from IEC-60079-10-1: Outdoor tank for flammable liquid
Step 4 - Direct Example

- Outdoor, ground level pump with mechanical seal

- Other examples include:
  - indoor pump
  - breathing valve from vessel
  - valve in pipework
  - indoor process mixing vessel
  - outdoor oil / water separator
  - enclosed hydrogen compressor
  - outdoor storage tank
  - outdoor tanker filling station
  - mixing room in paint factory
  - tank farm

Dimensions:
- \( a = 3 \) m horizontally from source of release (radius)
- \( b = 1 \) m from ground level to 1 m above source of release
Step 4 - IP15 Direct Example案例图
Road Tanker Unloading槽车卸料

Note: Ullage space in the road tanker should be classified as Zone 0.
Step 4 - IP15 Point Source Example

Liquid Pool Due to Spillage

- In open areas the zone should be Zone 2 (secondary release)
- If the length of the spill (L) is:
  - < 5 m then $R_1 = 3\ m^*$
  - 5 – 10 m then $R_1 = 7.5\ m^*$
  - 10 or more then $R_1 = 15\ m^*$
- The height is usually 1 $m^*$

Note:
Example for Category C liquid up to 50 °C but for volatile liquids or elevated temperature, ‘h’ may be up to 3 m or more
Cat C: Liquids above their flash points
Step 4 - IGE/SR/25 Point Source Example

<table>
<thead>
<tr>
<th>Operating pressure (bar g)</th>
<th>Zoning distance (x) under normal conditions (m)</th>
<th>Zoning distance (x) under adverse conditions (m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>2.5</td>
<td>9.5</td>
</tr>
<tr>
<td>19</td>
<td>1</td>
<td>3</td>
</tr>
<tr>
<td>2</td>
<td>0.5</td>
<td>1.5</td>
</tr>
<tr>
<td>0.1</td>
<td>0.5</td>
<td>1</td>
</tr>
</tbody>
</table>
Ventilation

- Poor ventilation can lead to larger or more severe zone designation (e.g. Zone 2 to Zone 1)
- 很差的通风可以导致升高区域的级别和范围（如2区变为1区）
- Also, high ventilation rates can be used to relax the classification, sometimes even as far as “non-hazardous” because zone is of “negligible extent”
- 当然，高的通风率可以减低分区等级，有时甚至成为非危险区，因为分区的范围小到忽略不计
- Such high degree of ventilation is virtually only applicable to local artificial ventilation
- 这样的高等级通风通常只适用于局部通风
- Availability of ventilation is crucial
- 通风的可靠性是另外一个重要因素
Ventilation: Indoor Areas

- **Air speeds are low** 风速很低
  - Outdoors usually 室外 > 2 m s\(^{-1}\) (rarely 很少 < 0.5 m s\(^{-1}\))
  - Indoors 室内 0.3 m s\(^{-1}\) maximum tolerable 可忽略不计
- **ACH (air changes per hour) in buildings** 室内换气次数
  - Typically 通常为 0.5 – 2
- **Air conditioning may recirculate all or part of the air**
- **Results in** 空气可能是全循环分或者部分循环
  - build-up from small amounts 易燃蒸汽的积累
  - poor dispersion, dead spots and/or layering 分散不均，死角及或者分层
- **Generally, classify the whole room** 通常对整个房间进行分区
- **EN 60079-10-1 (App B) calculation for ventilation efficiency** 通风等级计算
VENTILATION CALCULATIONS 通风等级计算
(IEC 60079-10-1, appendix B)

- Minimum fresh air flow rate \((dV/dt)_{\text{min}}\) to dilute given release to required concentration below the LEL
  - based on release rate, LEL and safety factor \(k\) (= 0.25 or 0.5 based on grade of release)

\[
(dV/dt)_{\text{min}} = \frac{(dG/dt)_{\text{max}}}{k \times \text{LEL}_m} \times \frac{T}{293}
\]

-(dG/dt)_{\text{max}}\ is maximum rate of release (typically might use 0.001 kg.s\(^{-1}\) as small source, 0.01 kg.s\(^{-1}\) as large source) 最大释放率

- LEL\(_m\) is the mass LEL 单位体积质量爆炸下限(kg.m\(^{-3}\))
- \(T\) is ambient temperature 环境温度(K)
VENTILATION CALCULATIONS通风等级计算
(IEC 60079-10-1, appendix B)

- Since for a room with volume of $V_0$, air change rate, $C$, is given by:
- 

$$C = \frac{(dV_0/dt)}{V_0}$$

a notional volume, $V_k$, at the desired concentration can be calculated:

$$V_k = \frac{(dV/dt)_{\text{min}}}{C}$$
Hypothetical volume 假设体积($V_z$) can be calculated:

$$V_z = f \times V_k$$

where $f = 1$ to $5$: depends on “efficiency” (to allow for impeded flow, where $1$ is ideal)

- $V_z < 0.1 \text{ m}^3$ - “High” ventilation
- $V_z > V_0$ - “Low” ventilation
- $0.1 \text{ m}^3 < V_z < V_0$ - “Medium” ventilation
- $0.1 \text{ m}^3 < V_z << V_0$ - Hazardous areas based on $V_z$
VENTILATION CALCULATIONS通风等级计算
(IEC 60079-10-1, Appendix B)

Persistence time \( (t) \) estimation持续时间估算:

\[
t = \frac{-f}{C} \ln \left( \frac{\text{LEL} \times k}{X_0} \right)
\]

where \( X_0 \) is the initial concentration in the vicinity of the release
释放源的初始浓度 (in the same units as LEL单位和LEL一致).

Can be used in conjunction with timescale of operation and
acceptable flammable atmosphere durations for different zones
可用于操作时间周期及爆炸性气体环境持续时间的比较来划分分区
Effect of Ventilation

• Example:
• Room 25 m x 15 m x 14 m - secondary toluene release \((2 \times 10^{-5} \text{ kg s}^{-1})\) from a 1 mm diameter hole in flange.
• Where \(k = 0.5\): \(f = 5\) (for \(C = 2 - 6\)) or \(f = 1\) (for \(C = 12 - 20\))

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Number of ACH (C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>((\frac{dV}{dt})_{\text{min}}) in m³ h⁻¹</td>
<td>3.4</td>
</tr>
<tr>
<td>(V_z) in m³</td>
<td>8.6</td>
</tr>
<tr>
<td>(t) in h</td>
<td>9.8</td>
</tr>
<tr>
<td>2</td>
<td>3.4</td>
</tr>
<tr>
<td>6</td>
<td>3.4</td>
</tr>
<tr>
<td>12</td>
<td>3.4</td>
</tr>
<tr>
<td>20</td>
<td>3.4</td>
</tr>
<tr>
<td>12</td>
<td>0.3</td>
</tr>
<tr>
<td>20</td>
<td>0.17</td>
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<tr>
<td>20</td>
<td>0.3</td>
</tr>
<tr>
<td>20</td>
<td>0.2</td>
</tr>
</tbody>
</table>
Ventilation Calculations

Scenario:
Release of ethanol vapours from a pool of liquid (summer)

Release characteristics:
- Flammable material
- Source of release
  - LEL in (kg/m³) - given: 0.067
  - LEL in (kg/m³) - estimated: 0.00
- LEL in (vol.%): 3.5 (used in LEL estimation and for persistence time calculation)
- Molecular weight M in (kg/kmol) (used in LEL estimation)
- LEL in (kg/m³) used in calcs: 0.067 (choose either given or estimated value)
- Grade of release: C, P or S
- Safety factor k: 0.50
- Release rate (dG/dt)max in (kg/s): 3.00E-03
- Initial concentration at release point Xo in (vol.%): 100

Ventilation characteristics:
- Indoor/outdoor situation: indoors
- Room dimensions L, B, H in (m):
  - L = 10.00
  - B = 10.00
  - H = 3.50
- Room volume Vo in (m³): 350
- Ventilation fresh air flow dVtot/dt in (m³/h): 350
- Number of air changes C in (1/h) - calculated: 0.0
- Number of air changes C in (1/h) - given: 12.0
  - C in (1/s) = 0.00E+00
  - C in (1/s) = 3.33E-03
  (choose from the calculation results above)
- Number of air changes C in (1/s) used in calcs: 3.33E-03
- Quality factor f: 5
  (ranges from f=1 for ideal situation, to f=5 for impeded air flow)
- Ambient temperature T in (degrees C): 35
- Temperature coefficient (T/293 K): 1.05

Calculation results:
- Minimum volumetric flow rate of fresh air (dV/dt)min: 0.09 m³/s, 9.41E-02 m³/s, 3.39E+02 m³/hour
- Estimation of hypothetical volume Vz: 141.35 m³, 1.41E+02 m³
- Time of persistence t: 6074 s, 101.2 min, 1.7 hour
Ventilation: calculations通风等级计算
(IEC 60079-10-1, Appendix B)

Availability of ventilation defined as通风可靠性分为:

- **Good** 良好: Virtually continuous通风连续存在

- **Fair** 一般: Expected during normal operation. But occasionally lost, infrequent, or short periods在正常运行时预计通风存在，允许短时，或者不连续通风

- **Poor** 差: Ventilation present, but not ”Good” or “Fair” or expected to be lost for long periods通风存在，但是满足良好或一般通风的要求，可能会长时间不连续通风
Guide to Ventilation 通风实施指南 (IEC 60079-10-1)

<table>
<thead>
<tr>
<th>Grade of release</th>
<th>Degree</th>
<th>Availability</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>High</td>
<td>Medium</td>
</tr>
<tr>
<td></td>
<td>Good</td>
<td>Fair</td>
</tr>
<tr>
<td>Continuous</td>
<td>(Zone 0 NE) Non Hazardous&lt;sup&gt;a&lt;/sup&gt;</td>
<td>(Zone 0 NE) Zone 2&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td>Zone 0</td>
<td>Zone 0 + Zone 1&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>Primary</td>
<td>(Zone 1 NE) Non Hazardous&lt;sup&gt;a&lt;/sup&gt;</td>
<td>(Zone 1 NE) Zone 2&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td>Zone 1</td>
<td>Zone 1 + Zone 2&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>Secondary</td>
<td>(Zone 2 NE) Non Hazardous&lt;sup&gt;a&lt;/sup&gt;</td>
<td>(Zone 2 NE) Zone 2&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td>Zone 2</td>
<td>Zone 2</td>
</tr>
</tbody>
</table>

Good, Fair or Poor

---

Notes:
- "+" signifies "surrounded by".
- a – Zone 0 NE, 1 NE, or 2 NE indicate theoretical zones of negligible extent under normal conditions.
- b – Zone 2 area created by secondary grade of release may exceed primary or continuous; in this case the greater distance should be taken.
- c – Zone 0 if ventilation is weak and release such that explosive atmosphere exists virtually continuously (i.e. approaching "no ventilation" condition).
Density Effects

- Heavier-than-air gases tend to sink to lower levels.
  - extend zone to ground level
  - extend zone over the ground
  - even neutral gases can be heavy due conditions (cold)
  -即使是天然气也有可能比较“重”
- Reverse for very light gases (H₂)
  -比重轻的气体上浮（氢气）
Step 5 - Drawings and Report

- Show Zones on site plan
- 图纸上标注分区
- Side / plan views
- 立面/平面图
- Include temperature class / gas group where possible
- 如果可能的话包括温度/气体组别
- All data, assumptions, example, calculations used in report not on drawings
- 所有图纸上没有的数据，假设，例图和计算
- Severity, heights, and shapes of zones to be mentioned in report
- 报告中描述分区的大小，高度和形状
- Other relevant information
- 其他相关信息
Summary - Area Classification Procedure

Find potential sources of release
识别潜在的释放源

Identify the duration (grade of release)
识别持续性（释放等级）

Consider ventilation
通风效果

Assign zone numbers
定义几区

Estimate zone size
评估区域大小

Report, Drawings
报告，绘图

Mark zones - EX signs
标志

Train staff of HAC locations and hazards
对员工进行HAC位置及危害培训
EQUIPMENT SELECTION 电气设备选型
for hazardous areas 危险场所
ATEX – Electrical Equipment Marking

**Model PT 4-20**

Ex d [ib] IIC T4 Gb
Ex ta IIC T500 120 °C Da

Class I, Div 1, Groups ABCD T4A;
Associated Apparatus [Ex ia] Provides IS
outputs for Class I, Div 1, Groups ABCD
Class II, Div 1, Group EFG T(120°C)

Ex d [ib] IIC T4 Gb
Ex ta IIC T500 120 °C Da
Class I, Zone 1, AE Ex d [ib] IIC T4
Class II, Zone 20, AE Ex ta IIC T500 120 °C
ATEX – Electrical Equipment Marking

<table>
<thead>
<tr>
<th>Category 1</th>
<th>Category 2</th>
<th>Category 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>G: Gases, D: Dusts</td>
<td>G: Gases, D: Dusts</td>
<td>G: Gases, D: Dusts</td>
</tr>
<tr>
<td>Use in Zone 0</td>
<td>Zone 20</td>
<td>Zone 1</td>
</tr>
<tr>
<td>Environment Protection</td>
<td>Very high level of protection</td>
<td>High level of protection</td>
</tr>
<tr>
<td>Equipment group</td>
<td>I: Mining</td>
<td>II: All applications except mining</td>
</tr>
<tr>
<td>Directive</td>
<td>Corresponds to 94/9/EC</td>
<td></td>
</tr>
<tr>
<td>Material group</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Equipment Type

- Category 1: Very high level of protection
- Category 2: High level of protection
- Category 3: Normal level of protection

Applications

- G: Gases
- D: Dusts

Zones

- Zone 0
- Zone 20
- Zone 1
- Zone 21
- Zone 2
- Zone 22
### Ex d [ib] IIC T4 Gb

<table>
<thead>
<tr>
<th>Ex</th>
<th>d [ib]</th>
<th>IIC</th>
<th>T4</th>
<th>Gb</th>
</tr>
</thead>
<tbody>
<tr>
<td>IEC Ex Marking</td>
<td>Protection Type</td>
<td>Group</td>
<td>Temperature Class</td>
<td>Protection level</td>
</tr>
</tbody>
</table>

**Bootplate：**

- 常见防爆方式：
  - 本质安全型：ia/ib/ic
  - 隔爆型：d
  - 浇封型：ma/mb/mc
  - 正压型：p:pxa/pyb/pzc
  - 充沙型：q
  - 充油型：o
  - 增安型：e
- 无火花型：nA 无火花
- nL 低能量限制
- nR 限制呼吸
- nC 阻断
(Enclosed Break)

- 矿用：I
- 非矿用气体：II
- Sub-Group：Group IIA/IIB/IIC
- 如下防爆方式需要标识Sub-Group：l,d,e,m,n

**爆炸性气体环境中的最高表面温度分为六个等级：**
- T1: 450摄氏度
- T2: 300摄氏度
- T3: 200摄氏度
- T4: 135摄氏度
- T5: 100摄氏度
- T6: 85摄氏度

**Group**
- Ⅲ气体防护等级分为：
  - Da
  - Db
  - Dc
Selection of Electrical Apparatus 电气设备选型

• Zone 0
  – Ex ia 本安
  – Ex s (specially certified) 特殊认证

• Zone 1
  – any suitable for Zone 0
  – Ex d 隔爆 - Ex p 正压
  – Ex q 充砂 - Ex o 油浸
  – Ex e 增安 - Ex ib
  – Ex m 浇注

According to EN 60079-14

• Zone 2
  – any suitable for Zone 0 or 1
  – Ex n (Ex N) 无火花型

• In addition, the maximum surface temperature must be considered 另外，必须考虑最高表面温度:
  – determined by AIT 由自燃温度决定
  – usually as temperature classes 通常是温度组别

According to EN 60079-14
Gas Groups

- Indicates sensitivity to ignition (based on MIC) and ability for propagation through gaps (based on MESG)
- Relates properties to typical gases for each group

- I Methane (mining) 甲烷（煤矿）
- IIA Propane 丙烷
- IIB Ethylene 乙烯
- IIC Hydrogen 氢气
ATEX – Electrical Equipment Marking - group
防爆电气标签-组别

<table>
<thead>
<tr>
<th>Mining</th>
<th>Surface Industry</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Group I</strong></td>
<td><strong>Group II</strong></td>
</tr>
<tr>
<td>Electrical equipment for mines</td>
<td>Electrical equipment for places with</td>
</tr>
<tr>
<td>susceptible to firedamp</td>
<td>an explosive gas atmosphere</td>
</tr>
<tr>
<td>Sub-Division</td>
<td>Ignition Energy</td>
</tr>
<tr>
<td>IIA</td>
<td>260 Microjoules</td>
</tr>
<tr>
<td>IIB</td>
<td>95 Microjoules</td>
</tr>
<tr>
<td>IIC</td>
<td>18 Microjoules</td>
</tr>
</tbody>
</table>

- Group III C: Conductive $ R \leq 10^3 \, \Omega \, m$
- Group IIIB: Non-conductive $ R > 10^5 \, \Omega \, m$
- Group IIIA: Partical size $ > 0.5 \, \text{mm} $
# Temperature Class of Electrical Equipment

<table>
<thead>
<tr>
<th>Max. surface temperature (°C)</th>
<th>T-class US</th>
<th>T-Class CENELEC &amp; IEC</th>
</tr>
</thead>
<tbody>
<tr>
<td>450</td>
<td>T1</td>
<td>T1</td>
</tr>
<tr>
<td>300</td>
<td>T2</td>
<td>T2</td>
</tr>
<tr>
<td>280</td>
<td>T2 A</td>
<td></td>
</tr>
<tr>
<td>260</td>
<td>T2 B</td>
<td></td>
</tr>
<tr>
<td>230</td>
<td>T2 C</td>
<td></td>
</tr>
<tr>
<td>215</td>
<td>T2 D</td>
<td></td>
</tr>
<tr>
<td>200</td>
<td>T3</td>
<td>T3</td>
</tr>
<tr>
<td>180</td>
<td>T3 A</td>
<td></td>
</tr>
<tr>
<td>165</td>
<td>T3 B</td>
<td></td>
</tr>
<tr>
<td>160</td>
<td>T3 C</td>
<td></td>
</tr>
<tr>
<td>135</td>
<td>T4</td>
<td>T4</td>
</tr>
<tr>
<td>120</td>
<td>T4 A</td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>T5</td>
<td>T5</td>
</tr>
<tr>
<td>80</td>
<td>T6</td>
<td>T6</td>
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</tbody>
</table>
## ATEX 100a Equipment Categories

<table>
<thead>
<tr>
<th>Gas Group</th>
<th>Temperature Class</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>T1: Methane</td>
</tr>
<tr>
<td>IIA</td>
<td>T2: Acetone</td>
</tr>
<tr>
<td></td>
<td>T3: Ethanol</td>
</tr>
<tr>
<td></td>
<td>T4: Diesel fuel</td>
</tr>
<tr>
<td></td>
<td>T5: Acetaldehyde</td>
</tr>
<tr>
<td></td>
<td>T6:</td>
</tr>
<tr>
<td></td>
<td>T1: Methane</td>
</tr>
<tr>
<td>IIA</td>
<td>T2: Cyclohexane</td>
</tr>
<tr>
<td></td>
<td>T3: Aircraft fuel</td>
</tr>
<tr>
<td></td>
<td>T4:</td>
</tr>
<tr>
<td></td>
<td>T5:</td>
</tr>
<tr>
<td></td>
<td>T6:</td>
</tr>
<tr>
<td></td>
<td>T1: Ethane</td>
</tr>
<tr>
<td></td>
<td>T2: Propanol 2</td>
</tr>
<tr>
<td></td>
<td>T3: N-Butyl alcohol</td>
</tr>
<tr>
<td></td>
<td>T4: N-Hexane</td>
</tr>
<tr>
<td></td>
<td>T5: Heptane</td>
</tr>
<tr>
<td></td>
<td>T6: Kerosene</td>
</tr>
<tr>
<td></td>
<td>T1: Methanol</td>
</tr>
<tr>
<td></td>
<td>T2: Propanol 2</td>
</tr>
<tr>
<td></td>
<td>T3: N-butane</td>
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<tr>
<td></td>
<td>T4:</td>
</tr>
<tr>
<td></td>
<td>T5:</td>
</tr>
<tr>
<td></td>
<td>T6:</td>
</tr>
<tr>
<td></td>
<td>T1: Toluene</td>
</tr>
<tr>
<td></td>
<td>T2: Propane</td>
</tr>
<tr>
<td></td>
<td>T3: Acetic Acid</td>
</tr>
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<td></td>
<td>T4: Ammonia</td>
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<tr>
<td>IIIB</td>
<td>T5: Coal Gas</td>
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<td></td>
<td>T6: Ethylene</td>
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<tr>
<td></td>
<td>T1: Ethylene oxide</td>
</tr>
<tr>
<td></td>
<td>T2: Ethylene glycol</td>
</tr>
<tr>
<td></td>
<td>T3: Hydrogen Sulphide</td>
</tr>
<tr>
<td></td>
<td>T4: Ethyl Methyl Ether</td>
</tr>
<tr>
<td></td>
<td>T5: Propanol 1</td>
</tr>
<tr>
<td></td>
<td>T6: Tetrahydrofuran</td>
</tr>
<tr>
<td></td>
<td>T1: Propanol 1</td>
</tr>
<tr>
<td></td>
<td>T2: Methyl Ethyl Ketone</td>
</tr>
<tr>
<td></td>
<td>T3:</td>
</tr>
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<td></td>
<td>T4:</td>
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<tr>
<td></td>
<td>T5:</td>
</tr>
<tr>
<td></td>
<td>T6:</td>
</tr>
<tr>
<td>IIIC</td>
<td>T1: Hydrogen</td>
</tr>
<tr>
<td></td>
<td>T2: Acetylene</td>
</tr>
<tr>
<td></td>
<td>T3:</td>
</tr>
<tr>
<td></td>
<td>T4:</td>
</tr>
<tr>
<td></td>
<td>T5:</td>
</tr>
<tr>
<td></td>
<td>T6:</td>
</tr>
</tbody>
</table>

AQ3009—2007
### Ex ta IIIC T500 120 °C Da

<table>
<thead>
<tr>
<th>Ex</th>
<th>ta</th>
<th>IIIC</th>
<th>120 °C</th>
<th>Da</th>
</tr>
</thead>
<tbody>
<tr>
<td>IEC Ex Marking</td>
<td>Protection Type</td>
<td>Group</td>
<td>Temperature Class</td>
<td>Protection level</td>
</tr>
</tbody>
</table>

#### Protection Type
- **Ⅲ**
- Dust protection等级分为:
  - Da
  - Db
  - Dc

#### Group IIIC
- **120 °C**
- Da

#### Da
- 粉尘防护等级分为:
  - Da
  - Db
  - Dc

#### Protection level
- 粉尘下的最大表面温度为:
  - T = T_a + T_b
  - T_a: 最大表面温度
  - T_b: 最高环境温度
  - T_c: 设备的最高温升

#### Group III
- 粉尘防护等级分为:
  - Da
  - Db
  - Dc
Dust Protection 粉尘防爆 - Temperature

In zones 20, 21 & 22, surface temperature not to exceed the lower of:

- 2/3 of M.I.T. of a dust cloud 粉尘云
- M.I.T. of dust layer (5 mm) minus 75°C 粉尘层
## Dust Protection 粉尘防爆 – GB12476-1

<table>
<thead>
<tr>
<th>粉尘类型</th>
<th>20 区</th>
<th>21 区</th>
<th>22 区</th>
</tr>
</thead>
<tbody>
<tr>
<td>非导电性粉尘</td>
<td>tD A20; tD A21</td>
<td>tD A20; tD A21; tD A22</td>
<td>tD A20; tD A21; tD A22</td>
</tr>
<tr>
<td></td>
<td>tD B20; tD B21</td>
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Dust Protection Ex tD – 粉尘防爆-外壳保护型

- Most common protection type used
  - 最常用的防爆类型
- Dust tightness is main requirement
  - 通常要求尘密型
    - IP6X for Zone 20 / 21
    - IP6X for Zone 22 with conductive dust 导电粉尘（ρ > 10^3 ohm.m）
    - IP5X for Zone 22 with non-conductive dust 非导电粉尘

- Note if dust layers > 5 mm, need to allow a lower maximum surface temperature
  - 注意如果粉尘层>5mm。需要定义最高允许表面温度
Thank you!
END OF DAY 1