Flashpoint, Flammability or Frustration?

Decoding Section 9 Testing Requirements

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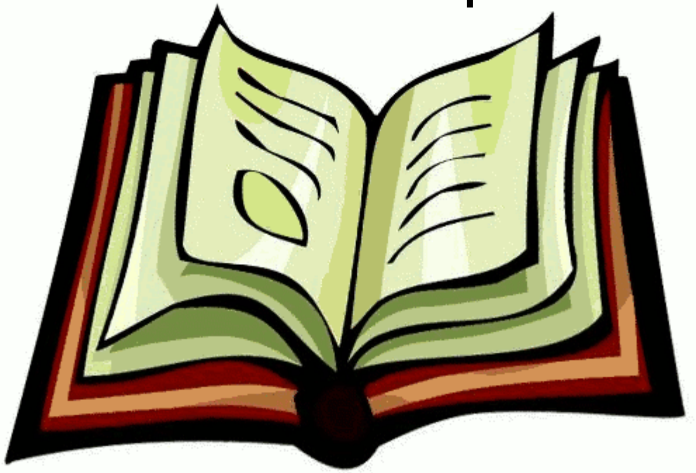
Agenda

- Goal
- Basics of Safety Data Sheets
- Flammability Testing
- Plant/Transportation (UN/DOT) Testing
- Characterize the Explosion Potential of a "Powder Material"
- To Conclude

Goal

- Provide guidance for Section 9 testing and a reference for decision-making
  - Intent is that the physical property data be used for safety assessment purposes.
- What if the information is wrong?
- Likely to occur with flammability measurements – difficult/complicated tests



Basics of Safety Data Sheets

- There are 16 headings in an SDS
  - 1. Identification
  - 2. Hazard(s) identification
  - 3. Composition/information on ingredients
  - 4. First-aid measures
  - 5. Fire-fighting measures
  - 6. Accidental release measures
  - 7. Handling and Storage
  - 8. Exposure controls/personal protection
  - 9. ***Physical and chemical properties***
  - 10. Stability and reactivity
  - 11. Toxicological information
  - 12. Ecological information
  - 13. Disposal considerations
  - 14. Transport information
  - 15. Regulatory information
  - 16. Other information

Section 9 – Physical and Chemical Properties

a) Appearance (physical state, color etc.);
b) Odor;
c) Odor threshold;
d) pH;
e) Melting point/freezing point;
f) Initial boiling point and boiling range;
g) Flash point;
h) Evaporation rate;
i) Flammability (solid, gas);
j) Upper/lower flammability or explosive limits;
k) Vapor pressure;
l) Vapor density;
m) Relative density;
n) Solubility(ies);
o) Partition coefficient: n-octanol/water;
p) Auto-ignition temperature;
q) Decomposition temperature;
r) Viscosity.

- Required content to be included
  - If available!
  - Often not available
  - Often data inputted from other sources without fact checking
  - Often data inputted without units or with assumed units
- Very rarely is the method that was used to determine the physical property mentioned

Very rarely is the method that was used to determine the physical property mentioned

- There are different standards bodies
  - ASTM
  - ISO
  - IEC
  - CEN/CENELEC
  - UL
- Methods maybe slightly different between bodies
  - Apparatus used
  - Test parameters
  - Measurement criteria, etc.
- Methods change over time as experiments are reviewer and “improved”

EU Registration, Evaluation, & Authorization of Chemical Substances (REACH) Testing Services

- Determination of Physico-Chemical Properties
  - Test A.9: Flashpoint
  - Test A.10: Flammability (Solids)
  - Test A.11: Flammability (Gases)
  - Test A.12: Flammability (Contact with Water)
  - Test A.13: Pyrophoric Properties of Solids and Liquids
  - Test A.14: Explosive Properties
  - Test A.15: Auto-Ignition Temperature
    - (Liquids & Gases)
  - Test A.16: Relative Self-Ignition Temperature for Solids
  - Test A.17: Oxidizing Properties (Solids)

REACH
COMPLIANCE

Flammability Testing

- Assess flammability hazards:
  - Hazards related to handling, shipping, and storing chemicals
  - Spontaneous ignition of chemicals

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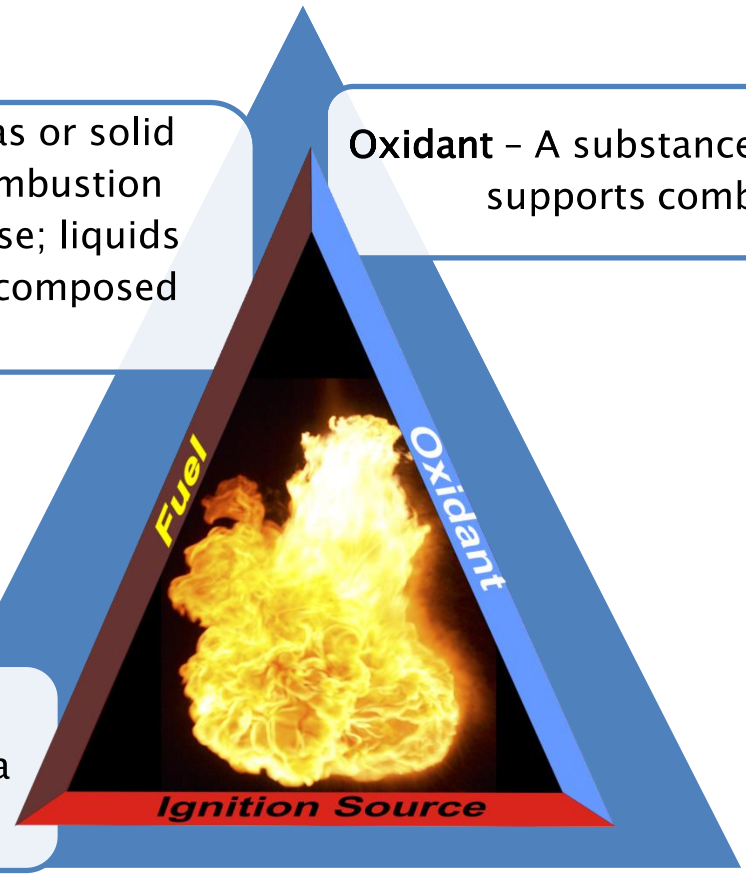
Flammability Testing

- Flash Point
- Sustained Burning/Combustibility (Fire Point)
- Temperature Limits of Flammability (LTFL)
- Autoignition Temperature (AIT)
- Flammability Limits (LFL, UFL)
- Limiting Oxygen Concentration (LOC)
- Minimum Ignition Energy (MIE)
- Explosion Severity (P_{max}, K_G)
- Flash and Spontaneous Ignition Temperature of Plastics
- Heat of Combustion (HOC)

Fire Triangle

Fuel – Liquid (vapor or mist), gas or solid capable of being oxidized. Combustion always occurs in the vapor phase; liquids are volatized and solids are decomposed into vapor prior to combustion

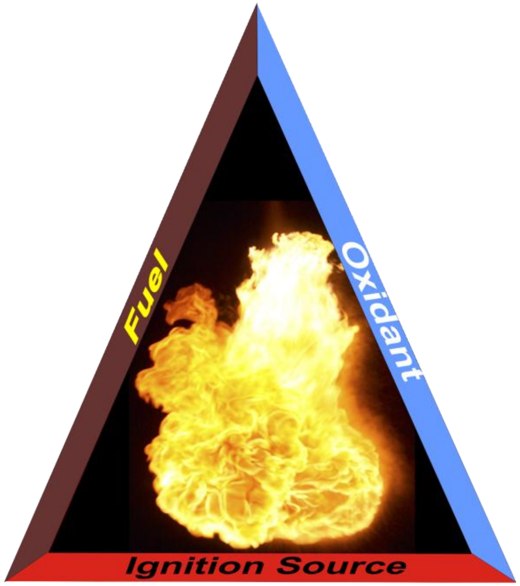
Oxidant – A substance which supports combustion



Ignition Source – An energy source capable of initiating a combustion reaction

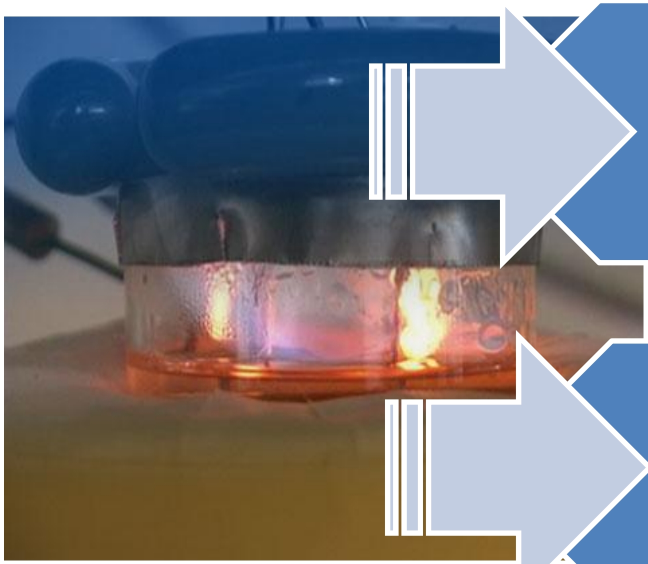
Conditions for a Vapor Explosion

- Liquid must be above its flash point temperature
- Concentration must be within flammable range
- Atmosphere must support combustion
- Ignition source must be of sufficient energy



Flash Point Temperature (FP)

Minimum temperature at which the liquid gives off sufficient vapor to form an ignitable mixture with air near the surface of the liquid:



Flash point temperature can be determined in open or closed test vessels, depending on what the data is to be used for (i.e., an open spillage or a sealed reactor vessel)

Open cup flash point is generally higher than the closed cup flash point

Standard Methods for Determination of Flash Points

Method	Use	Test Method
Tag Closed Cup	Liquids with a kinematic viscosity below 5.5×10^{-6} m^2/s at 40℃ or below 9.5×10^{-6} m^2/s at 25℃, and a FP below 93℃ – except cutback asphalts, liquids which are a FP below 2000°F	ASTM D56
Tag Open Cup	Liquids having flash points between -17.8°C and 168°C	
Pensky-Martens Closed Cup	Fuel oils, lube oils, suspensions of solids, liquids that tend to form a surface film under the test condition, and other liquids	ASTM D93
Setaflash Closed Cup	Enamels, lacquers, varnishes, and related products and their components having flash point between 0℃ and 110℃, and a viscosity lower than 150 stokes at 25℃	ASTM D3278
Cleveland Open Cup	All petroleum products, except fuel oils and those having an open cup flash point below 79℃	ASTM D92

Flash Points – which to choose?

- Small-scale vs Large-scale
  - Due to heat loses to the environment size of test apparatus can affect results
  - Larger apparatus give better results that can compare to real world accident scenarios
  - Smaller apparatus require less material and are easier to use
- Open vs Closed
  - Loss of vapors from open system
  - Loss of heat from open system
  - Closed produce lower flashpoints
- Liquid viscosity and suspension of other liquids or solids
  - Need to stir the liquid

Typical Flash Point Values

Ref: Industrial Ventilation, 12th edition, American Conference of Industrial Hygienists

	Closed Cup (ºC)	Open Cup (ºC)
Acetone	-18	-9
Toluene	4	7
Methanol	12	16
Xylene	17	24
n-Butanol	29	43

Addition of small amount of volatile can have a significant effect on flash point.

For example:

- Flash point temperature of Ethylene Glycol = 111 °C; and flash point temperature of Ethylene Glycol + 2% Acetaldehyde = 29 °C
- Mist /sprays can be flammable well below their flash point temperature

Sustained Burning and Fire Point

- Large-scale
  - ASTM D92 Standard Test Method for Flash and Fire Points by Cleveland Open Cup Tester
  - Require lots of liquid
- Small-scale
  - ASTM D4206 Standard Test Method for Sustained Burning of Liquid Mixtures Using the Small Scale Open-Cup Apparatus
  - Does not require much liquid
  - Did we take a representative sample
  - Temperature gradients affect results

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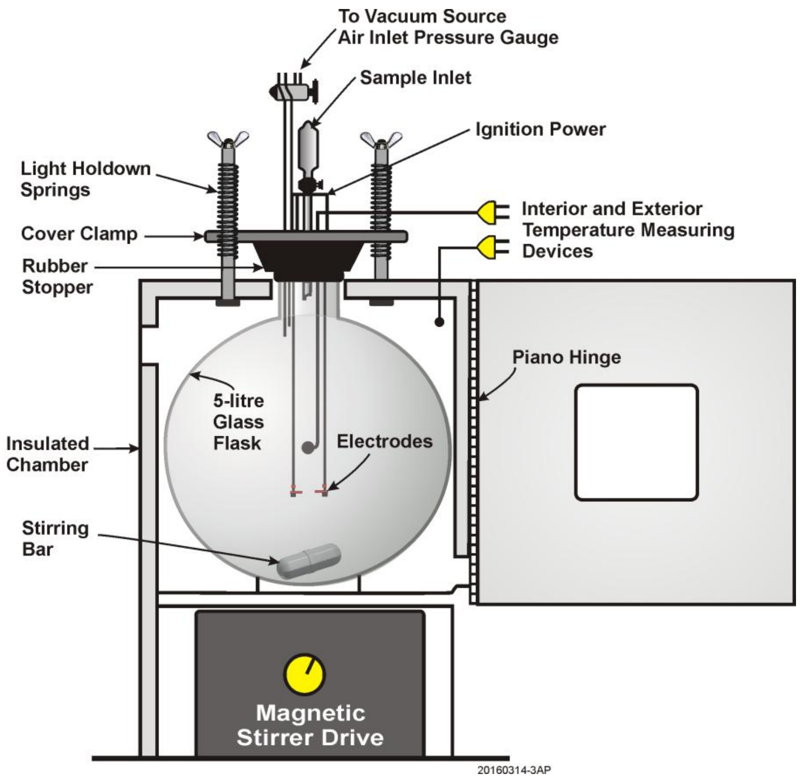
Temperature Limit of Flammability (TLF)

- ASTM E1232
- Determination of the minimum temperature at which vapors concentrations are sufficient to form flammable mixtures
  - In air
  - At atmospheric pressure
  - In equilibrium with a liquid (or solid) chemical
- TLF temperature values lower than Flash Point temperatures.



What is the better value?

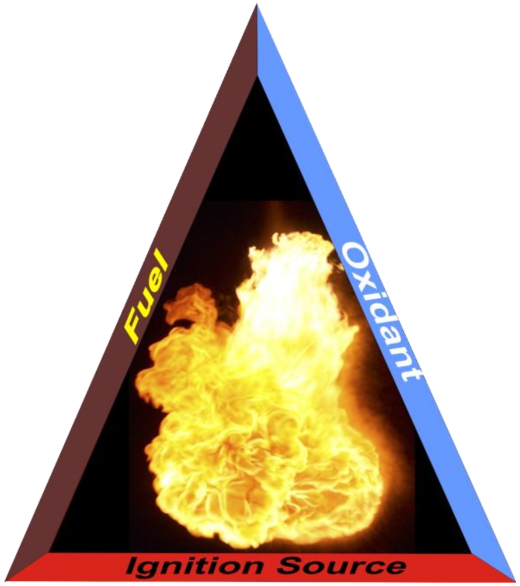
- Flashpoints provided for Hazard Risk avoidance
  - Safety Assumption - the material will not ignite below this temperature
  - In actuality, flashpoint is an artifact of the test method used
- Which value to use?
  - Which has the lower temperature?

    TLF < $FP_{closed\ cup}$ < $FP_{open\ cup}$
  - Which better reflects your usage case?
  - Can you provide all this detail in a SDS?

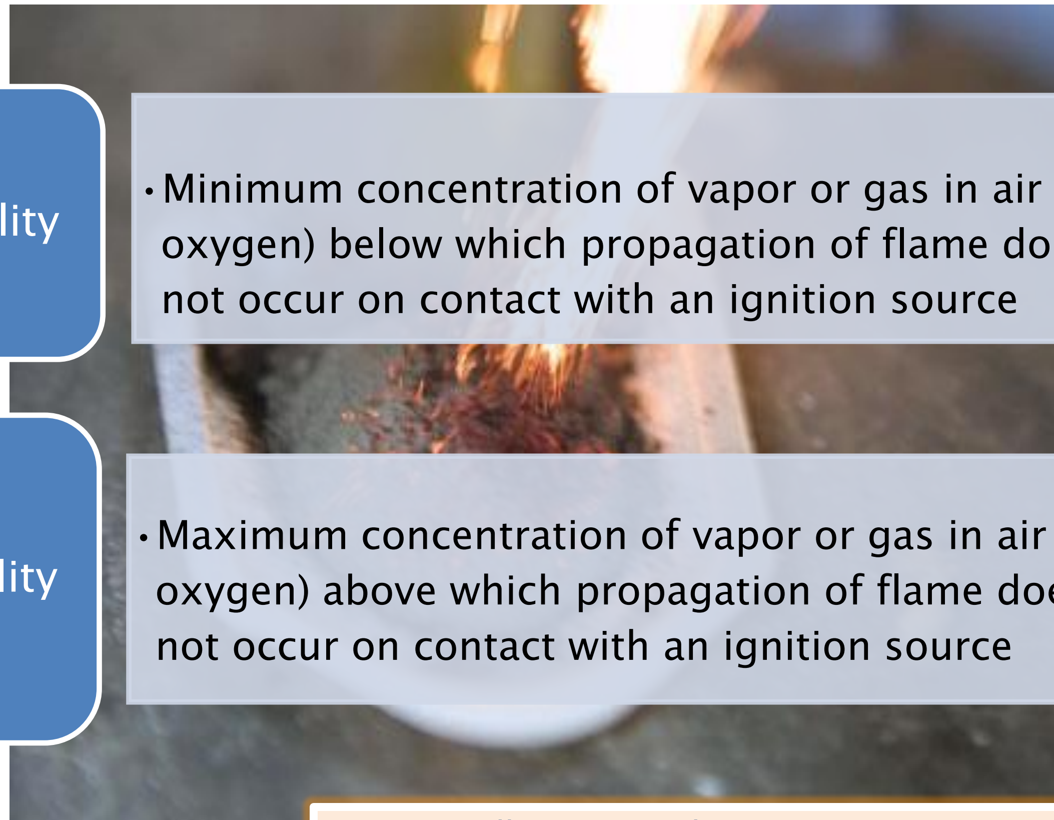
Include method information when reporting!

Conditions for a Vapor Explosion

- Liquid must be above its flash point temperature
- Concentration must be within flammable range
- Atmosphere must support combustion
- Ignition source must be of sufficient energy



Limits of Flammability



Lower Flammability Limit

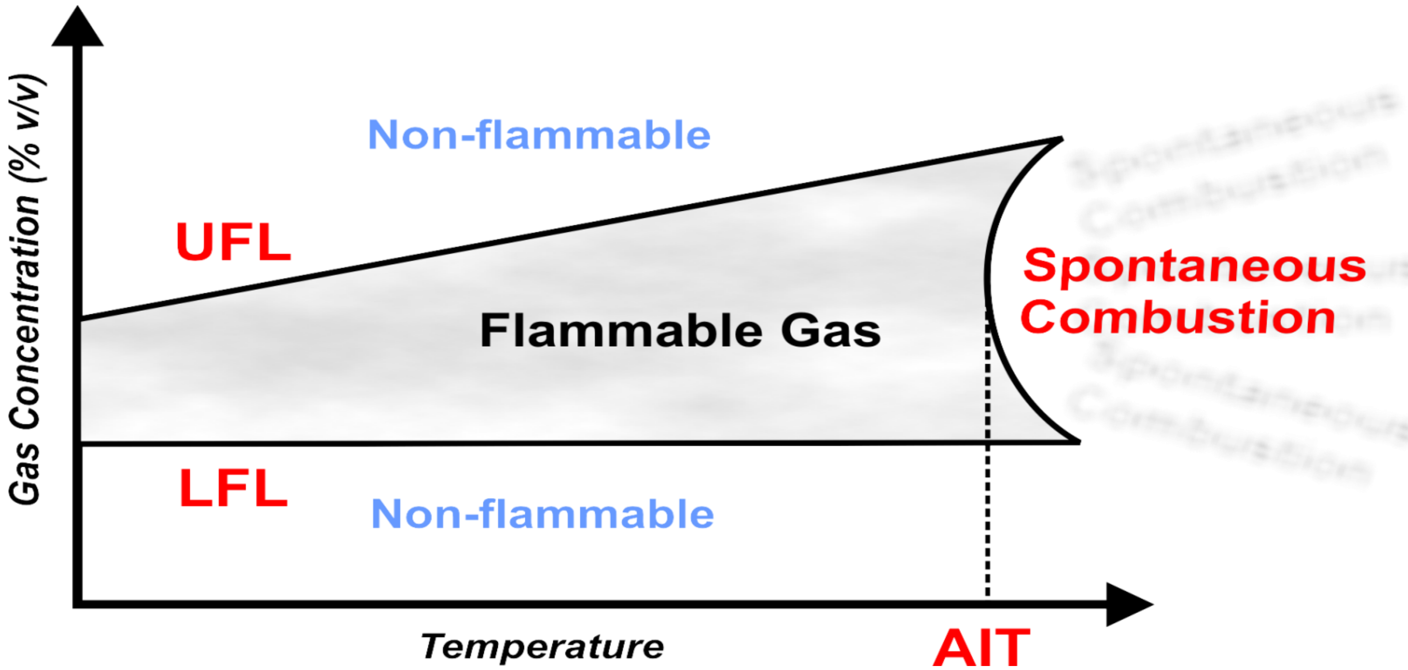
- Minimum concentration of vapor or gas in air (or oxygen) below which propagation of flame does not occur on contact with an ignition source

Upper Flammability Limit

- Maximum concentration of vapor or gas in air (or oxygen) above which propagation of flame does not occur on contact with an ignition source

Normally expressed as %v/v in air at atmospheric pressure.

Relationship Between Temperature & Gas Concentration



Terms: Lower Flammability Limit (LFL)
Upper Flammability Limit (UFL)
Autoignition Temperature (AIT)

Typical Flammability Limits

Ref: Fire Protection Guide to Hazardous Materials, NFPA, 11th Edition

		LFL (%v/v)	UFL (%v/v)
LIQUIDS	Acetone	2.5	12.8
	1-Butanol	1.4	11.2
	Toluene	1.1	7.1
	Carbon-disulfide	1.3	50
	Methyl Alcohol	6	36
GASES	Hydrogen	4	75
	Butane	1.9	8.5
	Methane	5	15
	Ethylene	2.7	36

Can I use LFL & UFL data?

- Some limitations!
- Slight differences between European and ASTM methods
  - ASTM has glass vessel with visual criterion; other standards use a closed chamber with a pressure criterion
- Some historic data generated before International Standards adopted
  - Still in use
- Tests performed at room temperature but LFL and UFL can change with temperature
  - Include temperature and method information when reporting

Estimating Temperature Effects

- The flammable range widens as the temperature increases. The following equations derived by Zabetakis can be used to estimate the temperature effects on flammable limits:

$$LFL_{t2} = LFL_{t1} - \left[1 - \left(\frac{0.75}{H_c}\right)(t_2 - t_1)\right]$$

$$UFL_{t2} = UFL_{t1} + \left[1 + \left(\frac{0.75}{H_c}\right)(t_2 - t_1)\right]$$

- Where:

H_c = Heat of Combustion (Kcal/mole)

T = test temperature (°C)

For many flammable gases and vapors, LFL decreases by approximately 8% and UFL increases by approximately 8% as the temperature increases by 100°C.

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Effect of Temperature on Flammability Limits

	Temperature (°C)	Measured LFL (%v/v)	Calculated LFL (% v/v)	Measured UFL (%v/v)	Calculated UFL (%v/v)
Toluene	25	1.1	0.92	7.1	5.39
	50	0.90	---	5.5	---
	100	0.80	0.86	5.8	5.72
	250	0.60	0.75	6.6	6.37
Benzene	25	1.2	1.13	7.8	5.47
	50	1.10	---	5.6	---
	100	0.95	1.05	6.1	5.86
	250	0.70	0.88	7.4	6.64

Mists and Sprays

- Liquid droplets in air **obtained** by atomizing the liquid

OR

- Flashing hot liquid and subsequently quenching the vapor with cold gas

Mists can be flammable even if the liquid is at a temperature below its flash point.

a. What does this mean for safety?
b. Can I have a fire below the flashpoint and below the LFL?
c. Include caution about flammable mists in SDS Section 9

Conditions for a Vapor Explosion

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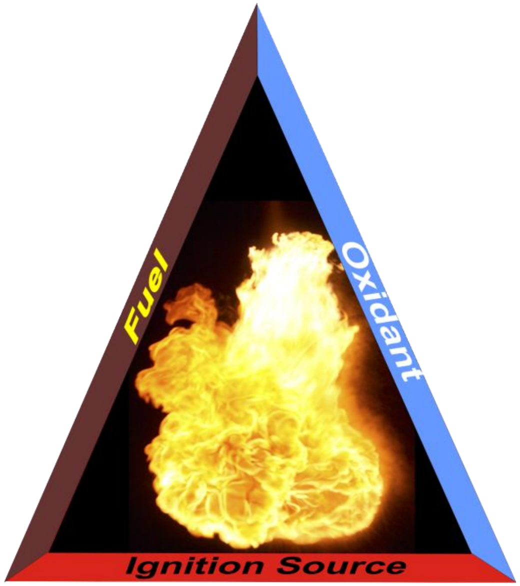
- Concentration must be within flammable range
- Atmosphere must support combustion
- Ignition source must be of sufficient energy



Atmosphere Must Support Combustion

- To produce combustion, sufficient amount of oxidant must be available
- Oxygen in air is the most common oxidant
- Explosion prevention can be accomplished by depletion of oxidant
  - ~8% v/v for organic material
- The concentration of oxidant below which a deflagration cannot occur in a specified mixture is referred to as the Limiting Oxidant Concentration (LOC)
- Optional to include in SDS – not a requirement
- If you choose to report; include the method used

Estimating Limiting Oxidant Concentration for Combustion

Ref. NFPA 69

- Limiting Oxygen Concentration (LOC) required for combustion with nitrogen can be estimated from oxygen required for complete combustion at the Lower Flammable Limit (LFL):

$$LOC = LFL \times \left(\frac{\text{moles } O_2}{\text{moles fuel}} \right)$$

- Example: Methyl Alcohol (Methanol), CH_3OH LFL of Methyl alcohol in air is 6.7% v/v [$CH_3OH + 1.5\ O_2 = CO_2 + 2\ H_20$]

$$LOC = 6.7 \times 1.5 = 10.0\% \frac{v}{v}$$

Experimental LOC value = 10.0% (v/v)

As Limiting Oxygen Concentration is easily measured, testing is recommended.

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Typical Values of LOC
(at Atmospheric Temperature & Pressure)

Value differs for nitrogen vs carbon dioxide

	N_2 (% v/v)	CO_2 (% v/v)
Toluene	9.5	–
1-Butanol	–	16.5 (150°C)
Acetone	11.5	14.0
Benzene	11.4	14.0
Carbon Disulfide	5.0	7.5
Hydrogen	5.0	5.2
Hydrogen Sulfide	7.5	11.5
Methyl Alcohol	10.0	12.0
Propylene	11.5	14.0

Ref: NFPA 69

Conditions for a Vapor Explosion

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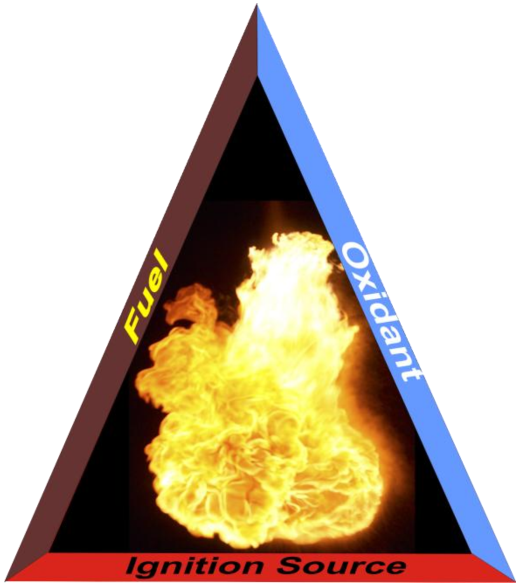
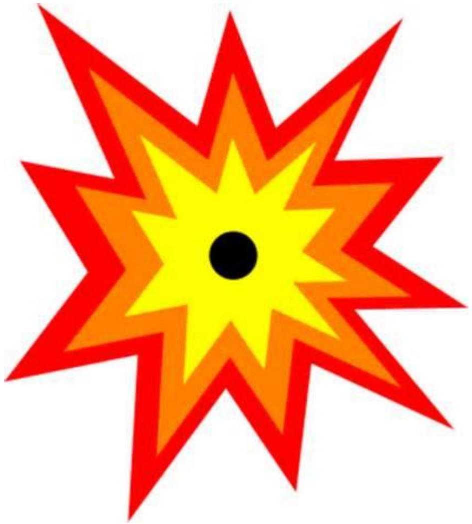


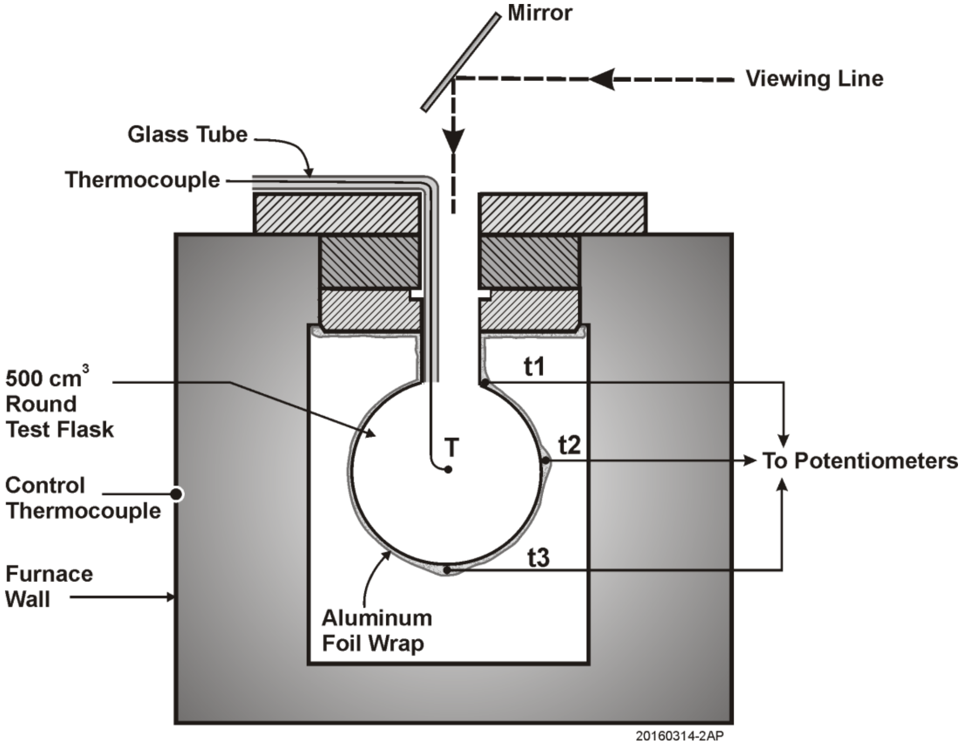
Autoignition Temperature

- If the temperature of a flammable atmosphere (fuel/oxidant mixture) is sufficiently increased, the heat from the environment will cause the flammable atmosphere to self-ignite
- The Autoignition Temperature (AIT) is defined as the lowest temperature at which vapors ignite spontaneously from the heat of the environment



Autoignition Temperature of Chemicals

- ASTM E659
- Determination of hot- and cool-flame autoignition temperatures in a uniformly heated vessel
  - liquid chemical or gas/vapor
  - in air
  - at atmospheric pressure(ish)
- Really only look at hot-flame
- Affected by vessel volume
- Catalytic affects possible



Autoignition Temperature

- The AIT is dependent upon:
  - Ignition delay period (can be >5 min.)
  - Vapor concentration (rich or lean mixtures have higher AIT)
  - Vessel volume (larger volumes decrease the AIT)
  - Initial pressure (increase in pressure decreases the AIT)
  - Oxygen content (increase on O_2 decreases the AIT)
  - Catalytic material (surface coatings)
  - Turbulence

- European method slightly different that the ASTM method
  - They copied from us originally but when we updated our standard based on new scientific data they did not follow

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Typical Autoignition Temperature Values

Ref: Fire Protection Guide to Hazardous Materials, NFPA, 11th Edition

LIQUIDS	AIT °F (°C)
Acetone	869 (465)
1-Butanol	650 (343)
Toluene	896 (480)
Carbon-disulfide	194 (90)
Methanol	867 (464)

GASES	AIT °F (°C)
Hydrogen	932 (500)
Butane	550 (287)
Methane	999 (537)
Ethylene	842 (450)

Effect of Pressure on Autoignition Temperature

When interpreting the AIT data, note that the value may be different if your operating pressure is not near atmospheric

Ref: Frank T. Bodurtha, McGraw-Hill

	AIT (°C) MINERAL OIL	AIT (°C) KEROSENE
25 kPa		593
50 kPa		464
100 kPa	350	229
1 MPa	250	
10 MPa	200	

Minimum Ignition Energy (MIE)

- ASTM E582 - 07(2013) - Standard Test Method for Minimum Ignition Energy and Quenching Distance in Gaseous Mixtures
- This test method covers the determination of minimum energy for ignition and initiation of explosion
- European method very similar but not the same
- The lower the MIE the greater the risk of an explosion

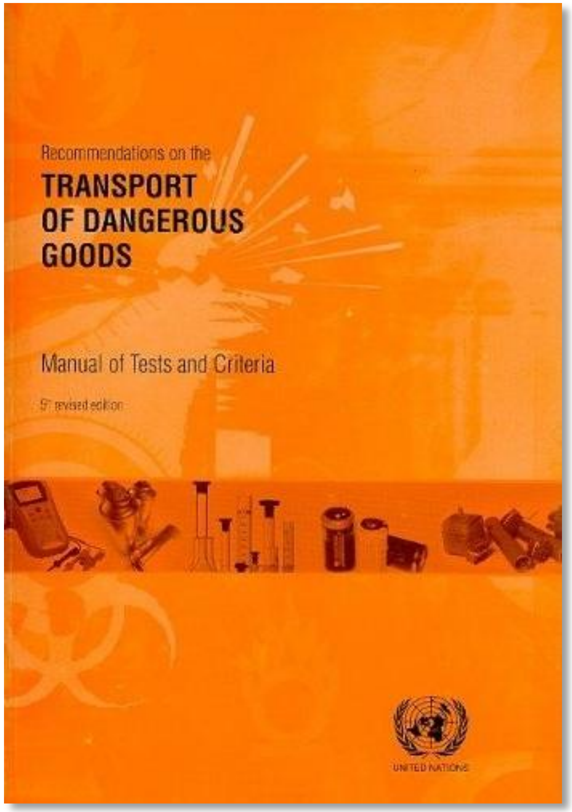
Minimum Ignition Energy (MIE)

	MIE in Air (mJ)
Acetylene	0.017
Diethyl Ether	0.190
Ethylene	0.070
Hydrogen	0.016
Methane	0.210
Propane	0.250

Ref: Plant/Operations Progress (Vol. 11, No. 2), April, 1992

Plant/Transportation (UN/DOT) Testing

- Class 4 Classification Testing
  - Division 4.1, Flammable Solids
  - Division 4.2, Self-Heating Substances
  - Division 4.3, Dangerous When Wet Material
- Class 5 Classification Testing
  - Division 5.1, Oxidizing Solids
- Impact and Friction Sensitivity Testing
- Self Accelerating Decomposition Temperate (SADT)



Plant/Transportation (UN/DOT) Testing

- Other flammability based safety data in a SDS
- Section 14 – Transportation
  - Transportation class has information about if a material is flammable and how fast it burns (Class 4 Div. 4.1)
  - Can it self-heat or is it pyrophoric (Class 4 Div. 4.2)
  - Is it dangerous when wet? (Class 4 Div. 4.3)
  - If the material is an oxidizer (Class 5 Div. 5.1) it can accelerate combustion of other materials

- Tests are fairly standard and universally accepted.

Characterize the Explosion Potential of a "Powder Material"

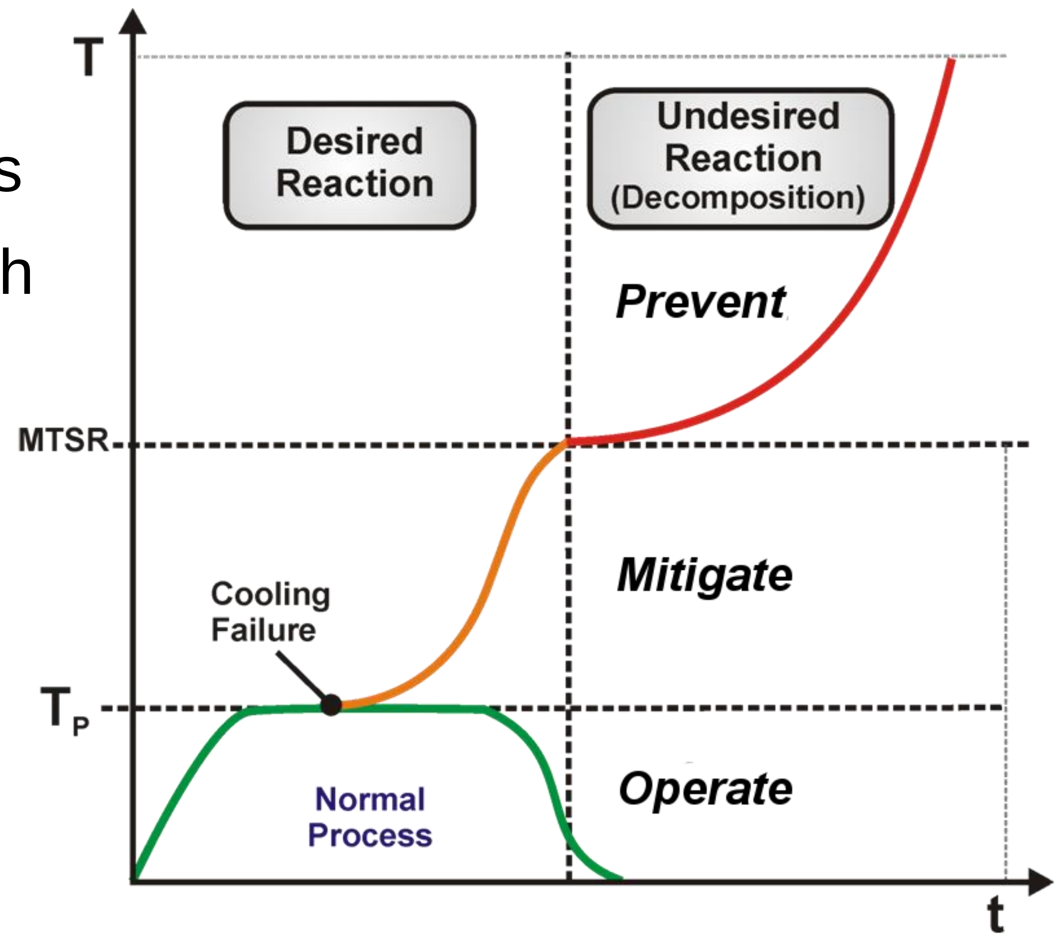
- Explosion severity – violence of the explosion
  - K_{St} – Dust deflagration index
  - P_{max} – Maximum explosion overpressure
  - $(dP/dt)_{max}$ – Maximum rate of pressure rise
- Ignition sensitivity – ease of ignition
  - MIE – Minimum ignition energy
  - MEC – Minimum explosible concentration

Dust Explosibility data

- Information not required for solids and powders or solids that can become dusts
- Slight differences between European methods and ASTM
- Values change with particle size distribution, shape and moisture content
- Data you include may not reflect the end-users hazard risk
- If you include the data in the SDS remember to indicate:
  - Test method
  - Units of measurement

Thermal Hazards Testing

- Reactive Chemistries
- Data-driven approach
- Three goals
  - Operation
  - Prevention
  - Mitigation



The Tools of Thermal Hazards Testing

Accelerating Rate Calorimeter (ARC)

Advanced Reactive System Screening Tool (ARSST™)

Vent Sizing Package 2 (VSP2™)

Differential Scanning Calorimeter (DSC)

Thermal Activity Monitor (TAM)

Thermal Hazards Testing
Operation

- Understand and design the desired process chemistry
- Key Tools: RC1, ChemiSens, µRC
- Determine
  - Heat generation rates
  - Heat of mixing
  - Heat of dissolution
  - Adiabatic temperature rise (due to desired reaction)
  - Heat capacity of reaction mass

Source: Mettler Toledo

Thermal Hazards Testing

- Determine critical safety parameters to avoid unintended reactions
- Key Tools: DSC, TAM, TGA, ARSST, VSP2, C80
- Determine
  - Onset temperature
  - Time to maximum rate (TMR)
  - 24 hour adiabatic decomposition temperature
  - Critical temperature of a vessel
  - Self-accelerating decomposition temperature (SADT)

To Conclude

- Flammability and thermal stability characteristics of a material is not necessarily an intrinsic parameter
- It is an artifact of the test methodology
- Since this variability exists it is very important to include method data in Section 9
- If method information is not there for physical and chemical data you wish to use in Section 9 – consider it with a grain of salt
  - Ask supplier for a test report