

Sustainable pMDI filling and Flammable Propellant Handling

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Reducing Propellant Emissions During The Filling Process

Purging vs. Vacuum Crimping

Why is it Necessary to Purge the Can?

Purging is used to expel the air from the can prior to crimping the valve.

If the can is not purged

This air can cause the following problems:-

- Increase the pressure in the can as it is compressed into the head space
- A temperature increase will cause hydraulic expansion of the product and increased pressure rise
- This pressure will decrease as the can is used and the liquid level goes down
- Any impurities in the air will be trapped in the can for the life of the product
- The formulation could react with the O₂ content

So it is best to remove the air!



Air is present in un crimped can



Crimp seals air in can



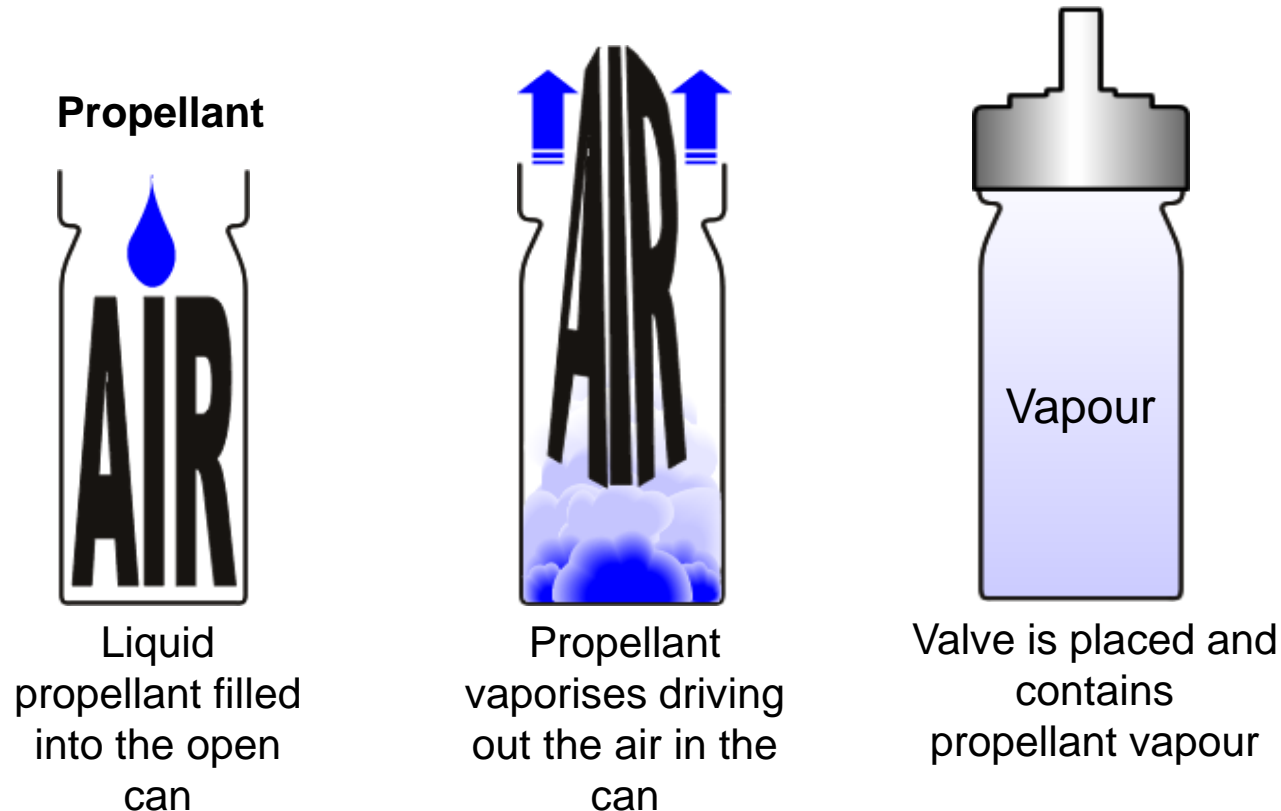
When product filled through valve into sealed can air is compressed into head space

Different Methods of Purging

Propellant Purging into the Open Can

This purging method is typically used for two stage filling where through valve purging cannot be used.

The propellant can be in either the liquid or vapour phase for this process though the liquid phase is most common



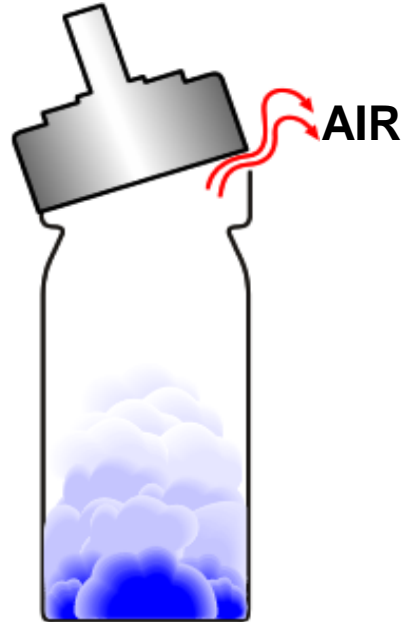
Propellant Purging Through the Valve

This purging method is used for single stage or dual filling where no product is filled into the open can

The propellant is pumped at high pressure in its liquid phase to a purge metering system



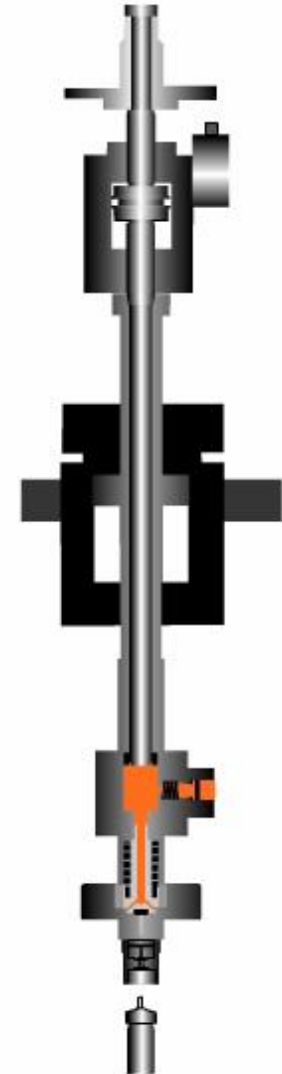
Liquid propellant filled
through uncrimped
valve into can



Propellant vaporizes
lifting valve and forcing
air from the can



When valve crimped,
propellant vapour is
sealed in can



Gas Loss/Usage During HFA Propellant Purging

Both open can and through valve purging use propellant to remove the air from the can
The propellant is dispensed from a purge metering unit with a 0.7cc capacity metering chamber

The full capacity is not generally used so I will assume 0.5cc of liquid HFA for this calculation

As only the residual vapour remains in the can after the purge process is complete i.e. no liquid, the following losses occur during production with this method:-

Batch Size	Volume per Can (ml)	Volume per Batch (ml)	Volume per Batch (l)
1,000	0.5	500	0.5
10,000	0.5	5,000	5
50,000	0.5	25,000	25

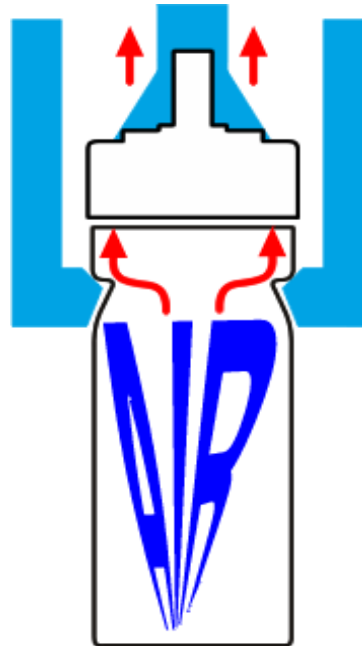
Annual Production Volume	Volume per Can (ml)	Volume per Year (l)
2,500,000	0.5	1,250
10,000,000	0.5	5,000
50,000,000	0.5	25,000

Vacuum Crimping as an Alternative to Purging

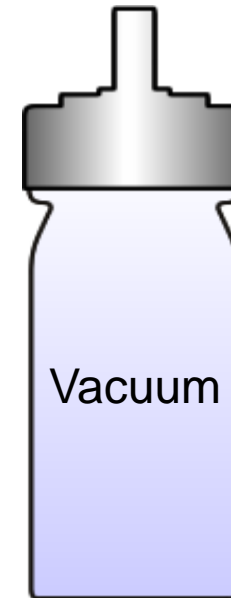
To prevent this gas loss we can change the purging process and remove the air from the can using vacuum
This process has zero propellant emissions.
It is done as part of the crimping operation:-



Vacuum bell
descends onto can
sealing around neck



Valve is lifted from
can and vacuum
is pulled to expel air



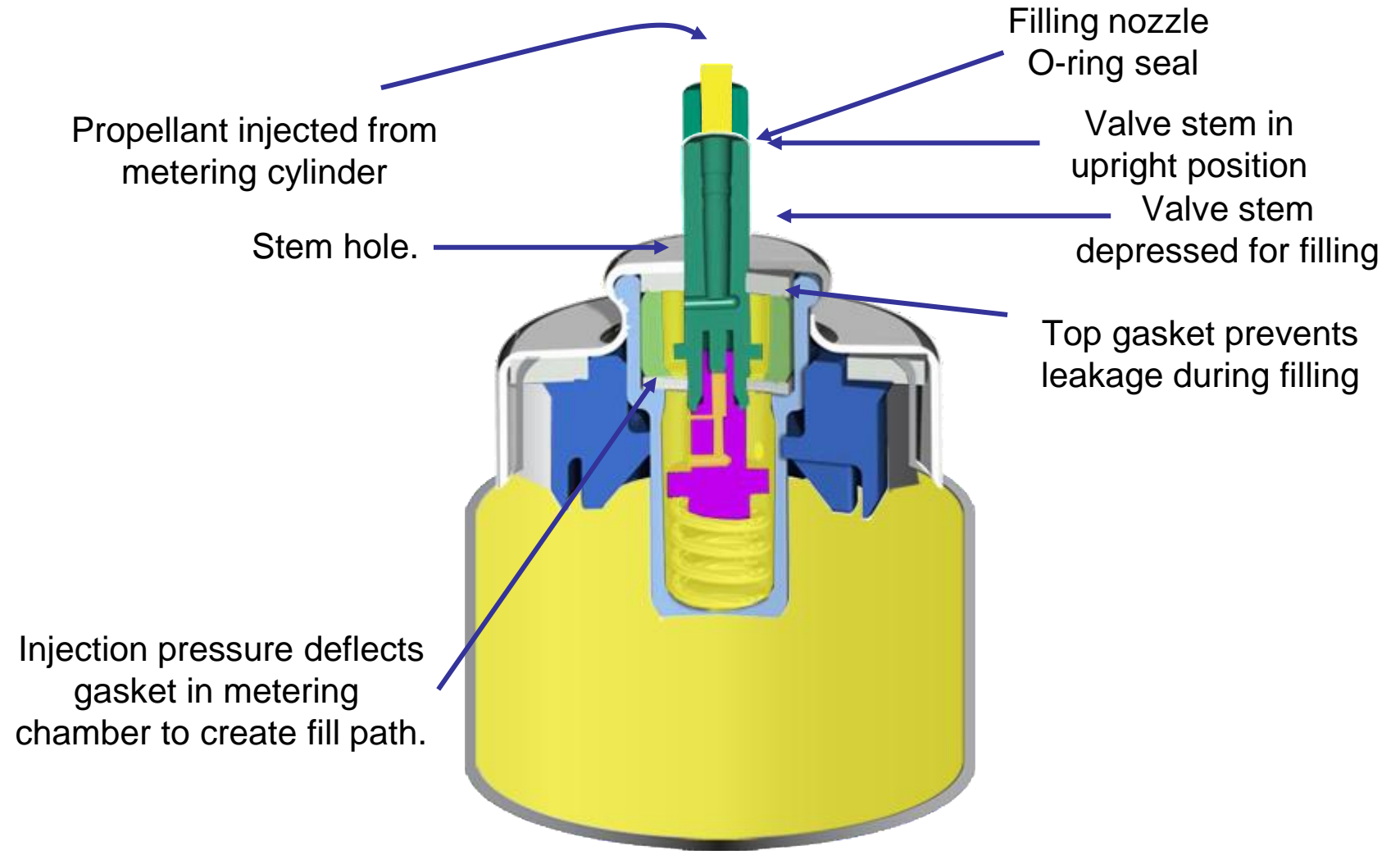
Valve is placed back
and crimped sealing
vacuum in the can

Recovering Propellant Losses During filling

Pressure Filling Through the Valve

Filling the Valve

There is never a direct path from the contents of the can to the valve stem, so how do we fill it?



Gas Loss During Filling

Because the product/propellant is filled in its liquid phase under high pressure into the can, there is residual product/propellant in the valve stem and filling nozzle after the fill process is complete

This vaporises and is lost when the filling head releases from the valve



Calculating the Gas Loss

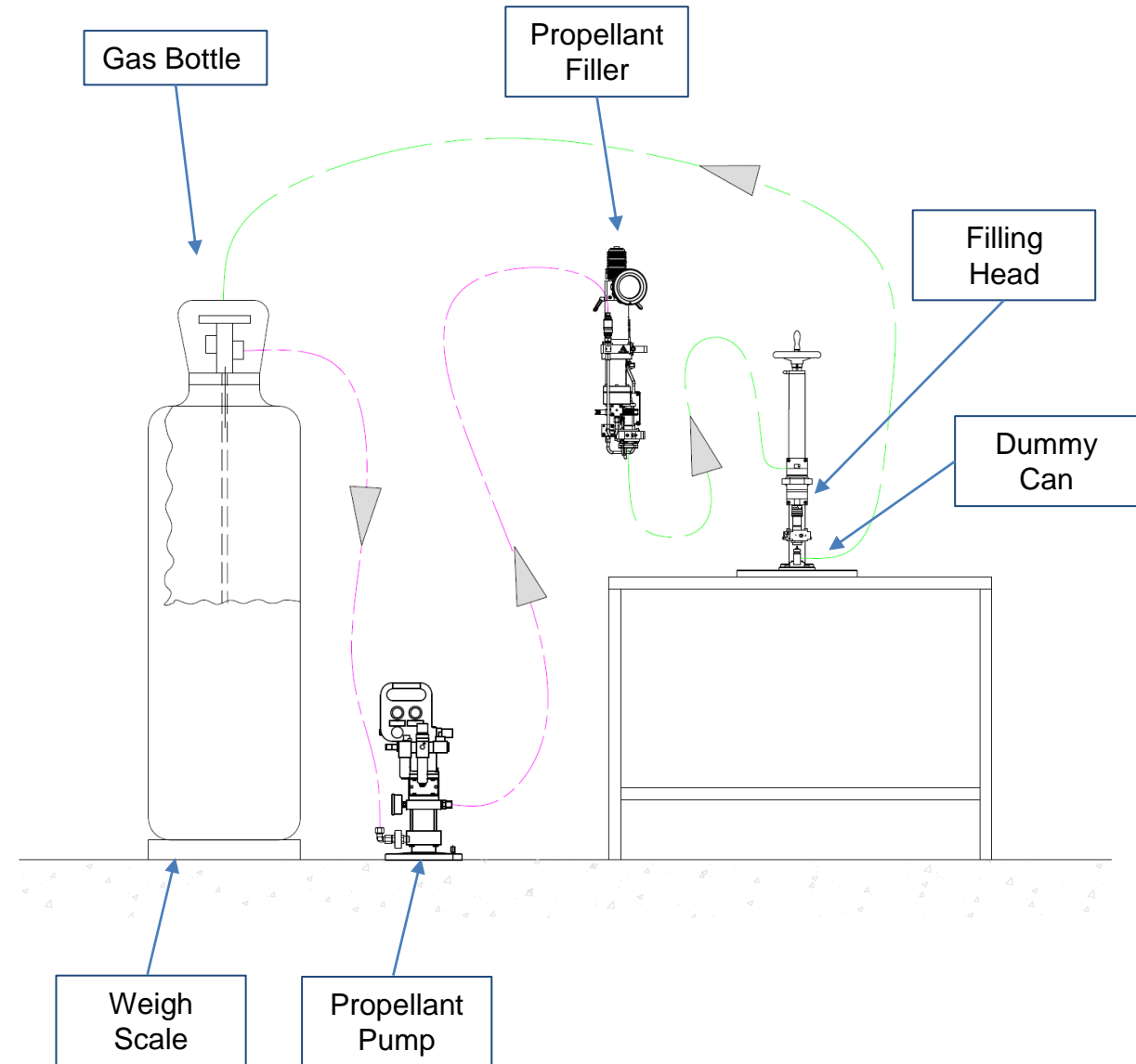
The gas loss will vary with different valve types, nozzle arrangements, filling speeds, products etc. but a theoretical loss can be calculated

To calculate the loss we need to work out the volume in the valve stem and the internal volume of the filling nozzle after the shut off

To confirm these calculations, and generate some actual gas loss figures, I thought it would be a good idea to adopt a practical approach as well

We set up a test rig which filled a dummy can with a pMDI valve crimped to it in a closed loop system

The system filled the same can and valve with propellant a pre-set number of times and each time the can was filled the propellant was returned to the cylinder. Therefore, the only way propellant could be lost from the system was during the filling process.



Gas Loss Calculations

The following tables show the theoretical gas loss calculations compared to the actual losses recorded on the test rig

Theoretical Calculations				Practical Test		
Valve	Part	Part Number	Internal Volume (mm ³)	Number of Fills	Loss from System (ml)	Loss per Fill (ml)
Valve A	Stem		13.085			
	Insert kit	X2043-0007-390-001	2.356			
	Filling Head	X2043-0007-020/018	27.833			
	Total (mm ³)		43.274			
Total (ml)			0.043	200	10	0.05
Valve B	Stem		31.416			
	Insert kit	X2043-0007-360-079	4.712			
	Filling Head	X2043-0007-020/018	27.833			
	Total (mm ³)		63.961			
Total (ml)			0.064	50	4	0.08

Gas Loss Calculations

Here are the gas loss amounts during production

Valve A			
Batch Size	Volume per Can (ml)	Volume per Batch (ml)	Volume per Batch (l)
1,000	0.05	50	0.1
10,000	0.05	500	1
50,000	0.05	2,500	3
Annual Production Volume	Volume per Can (ml)	Volume per Year (l)	
2,500,000	0.05	125	
10,000,000	0.05	500	
50,000,000	0.05	2,500	

Valve B			
Batch Size	Volume per Can (ml)	Volume per Batch (ml)	Volume per Batch (l)
1,000	0.08	80	0.1
10,000	0.08	800	1
50,000	0.08	4,000	4
Annual Production Volume	Volume per Can (ml)	Volume per Year (l)	
2,500,000	0.08	200	
10,000,000	0.08	800	
50,000,000	0.08	4,000	

Propellant Recovery

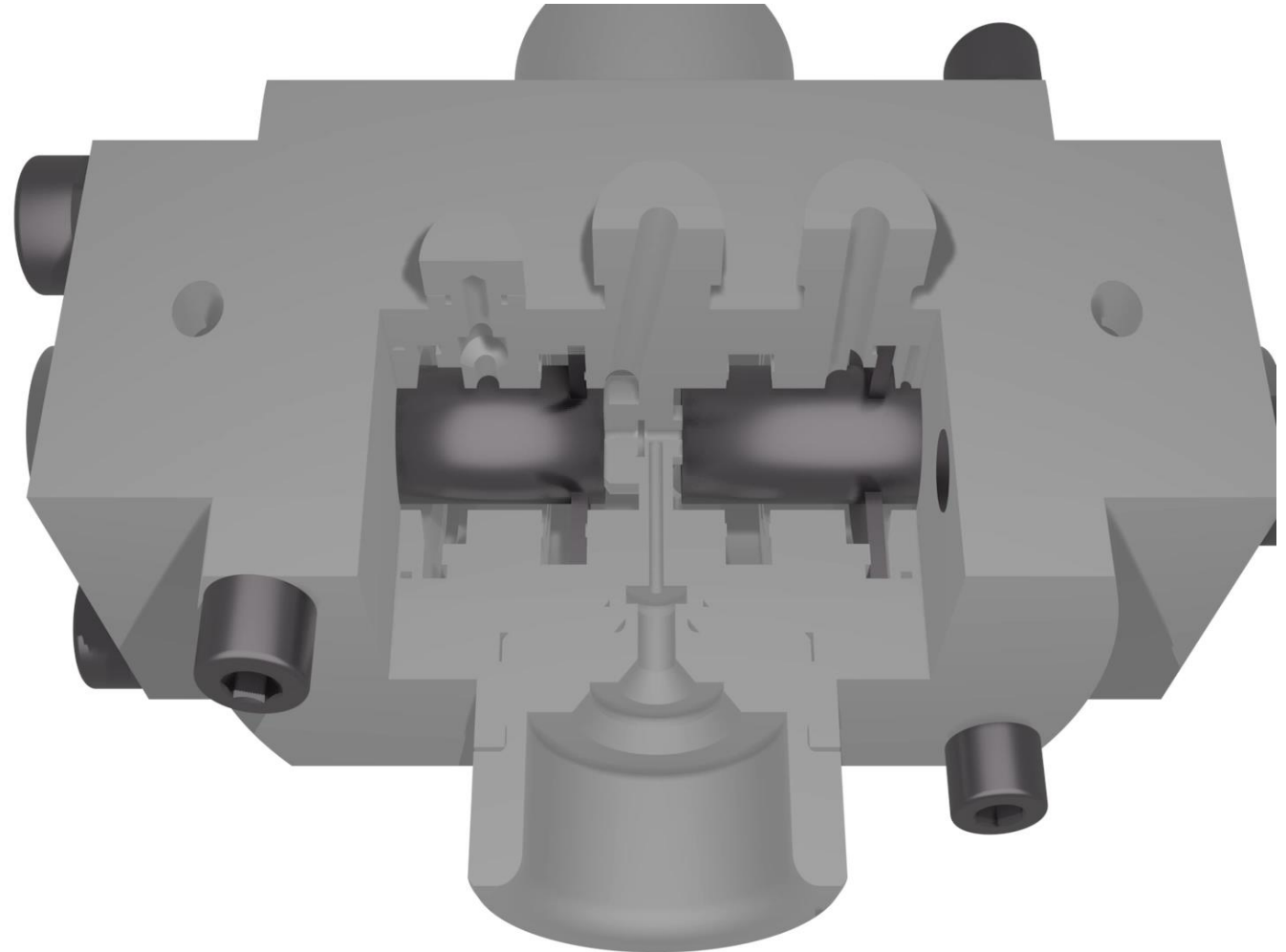
These figures do not amount to as much as the through valve purging but are still losses that can be recovered

To do this we can use a variation of our aspirator nozzle

The aspirator nozzle has two sides

One side carries out the filling operation and the other sucks away the fill residue to ensure a clean fill with no contamination

The residue recovered by the aspirator side can be directed to a propellant recovery device, through filters if needed and re-compressed into waste cylinders for recycling.



New Low GWP Propellants

New Low GWP Propellant from a Filling Perspective

There are two propellant being considered as alternatives to HFA
Their properties from a filling and handling perspective are as follows:-

Propellant	Vapour Pressure (bar g)	Flammable	LEL	UEL	Boiling Point	Vapour Density
1234ze	3.4 @ 21°C	No	N/A	N/A	- 19°	4
152a	5.0 @ 25°C	Yes	3.7%	18%	- 24°C	2.4

Both these propellants can be easily handled on new equipment and installations
Existing installation cannot/may not be possible, even with 1234ze, due to the flammability

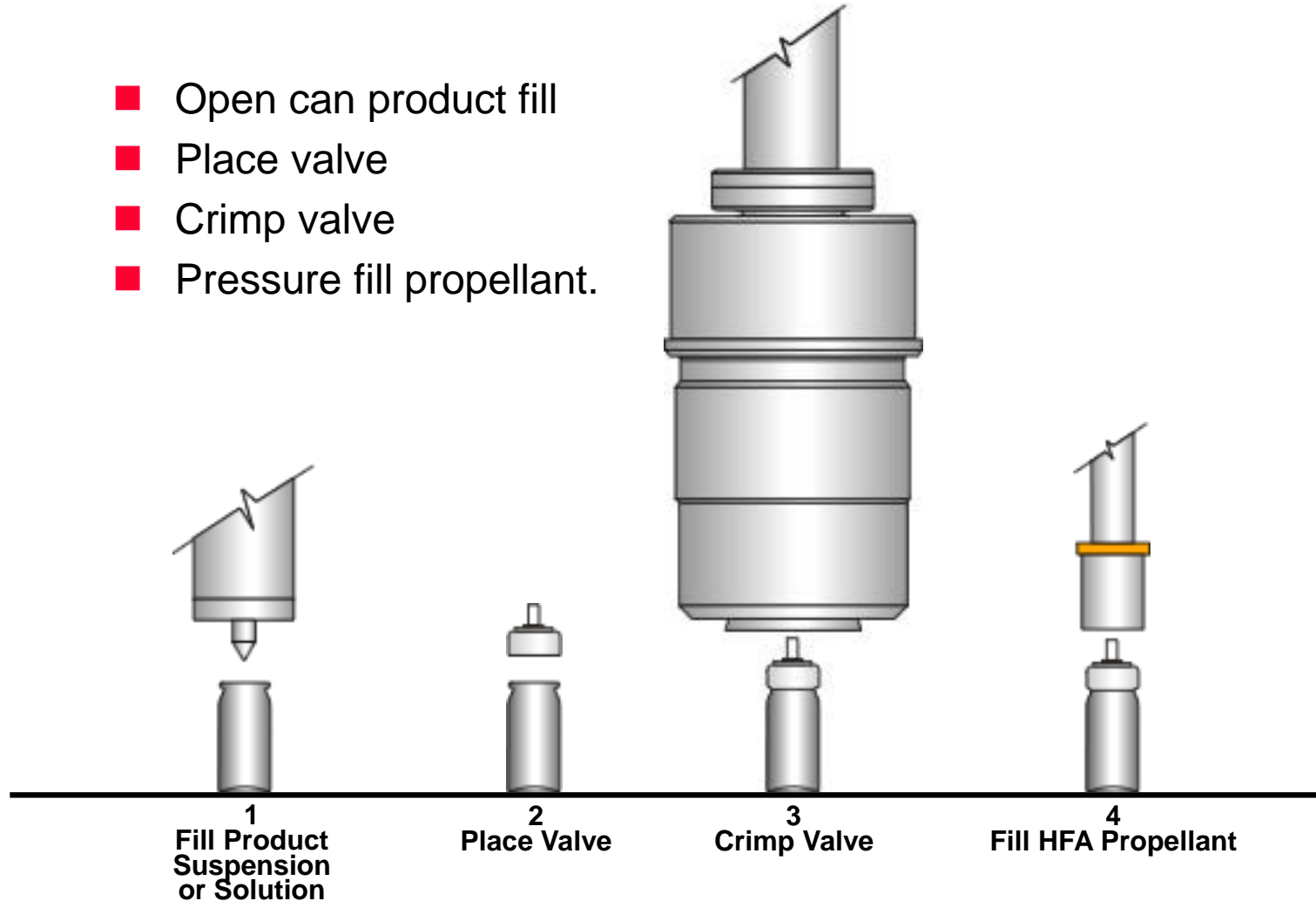
There is conflicting data on the flammability of 1234ze
If we looked at the properties chart considering a higher temperature then it will look like this ..

Propellant	Vapour Pressure (bar g)	Flammable	LEL	UEL	Boiling Point	Vapour Density
1234ze	3.4 @ 21°C	Yes (>30°C)	7%	9.5%	- 19°	4
152a	5.0 @ 25°C	Yes	3.7%	18%	- 24°C	2.4

New Propellant Filling Processes

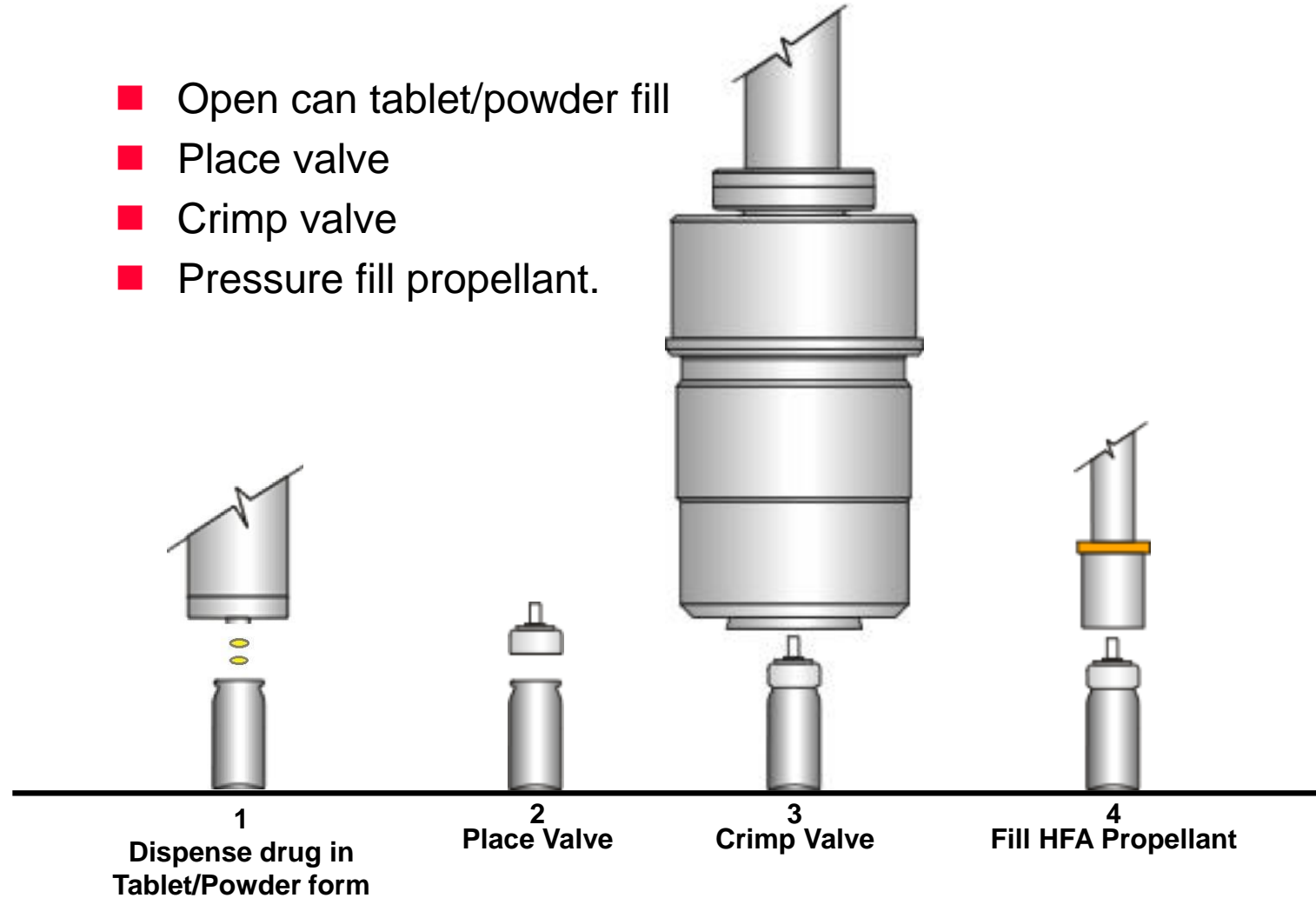
Two Stage Filling

- Open can product fill
- Place valve
- Crimp valve
- Pressure fill propellant.

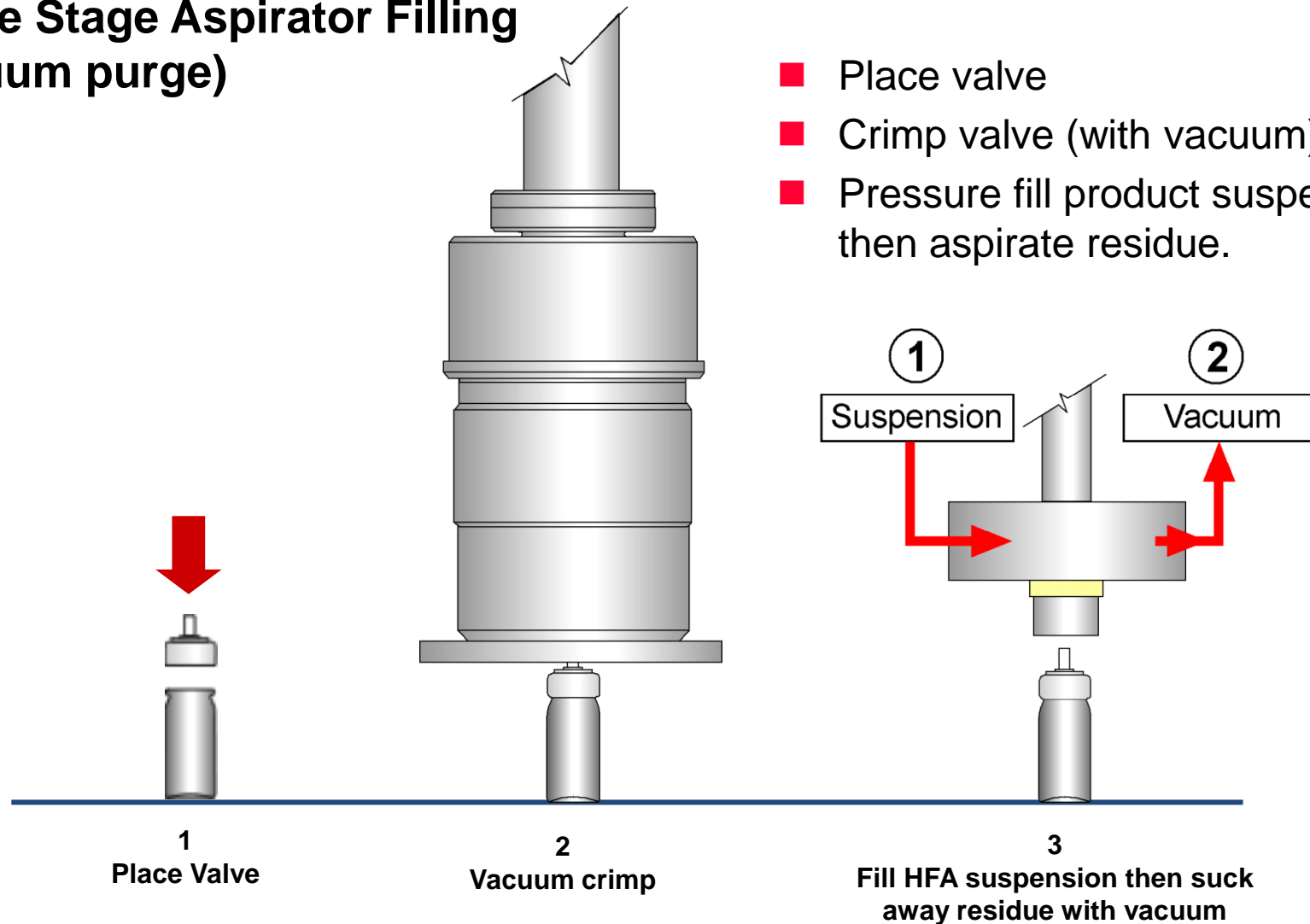


Two Stage Filling with Tablet/Powder

- Open can tablet/powder fill
- Place valve
- Crimp valve
- Pressure fill propellant.



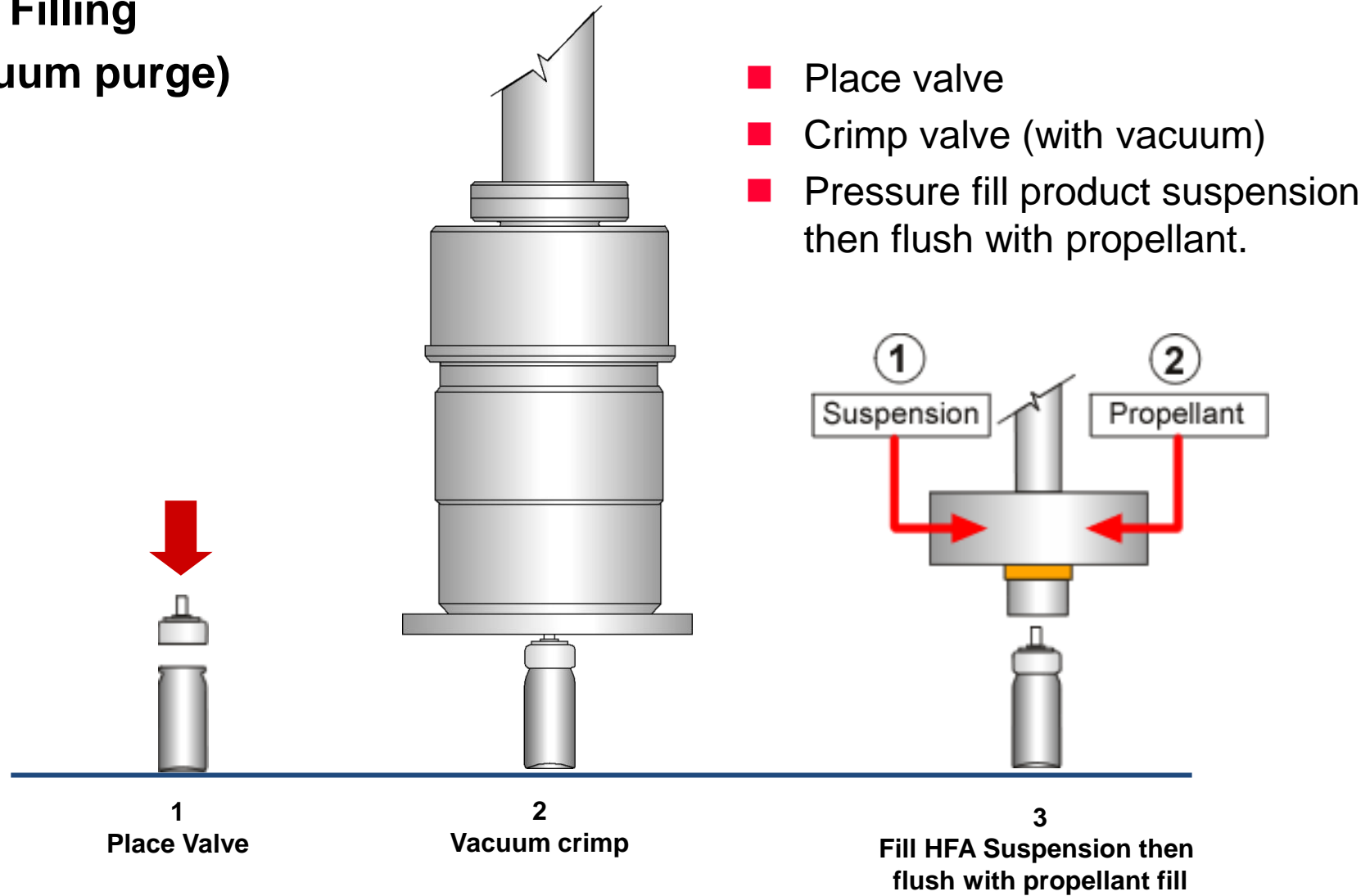
Single Stage Aspirator Filling (vacuum purge)



- Place valve
- Crimp valve (with vacuum)
- Pressure fill product suspension then aspirate residue.



Dual Filling (vacuum purge)



Handling Flammable Propellants

Filling Flammable Propellants

The aerosol industry has safely filled flammable propellants, in considerably larger volumes than will be required for pMDIs, for over 60 years

In the UK over 1.5 billion aerosols were filled in 2019, the majority with flammable propellants (propane/butane blends)

This is 50% higher than the estimated annual worldwide production for pMDIs

All of these aerosols were filled safely with no accidents

But, we are in a transition period so must be careful

2019 BAMA FILLING FIGURES

Primary product category	Secondary product category	Total 2019	Total 2018	% change 2018 to 2019
Insecticide sprays	Insect repellents and flea spray	4,248	3,662	16.00%
Paints and lacquers	Automotive, household, clear varnish and decorative	25,368	23,080	9.91%
Household products	Air fresheners – dry and wet, including room and fabric fresheners	183,010	193,483	-5.41%
	Polish – including all furniture polishes, dusting aids etc.	17,421	17,210	1.23%
	Shoe and leather treatment sprays and mousses	3,704	2,708	36.76%
	Starches, fabric finish sprays – including iron aid sprays	4,792	3,888	23.25%
	Oven cleaners	649	1,578	-58.87%
	Hard surface cleaners – including bathroom and kitchen mousses	14,100	11,561	21.96%
	Other household products – including rug and upholstery cleaners, water repellents, DIY, lubricants, window glass cleaners, etc.	38,462	41,632	-7.61%
Personal care products (toiletries)	Shaving soaps, creams, lathers and gels	157,887	164,995	-4.31%
	Haircare products – including mousse products, sprays, lacquers, glitter sprays, etc.	125,765	138,173	-8.98%
	Perfumes and colognes	10,214	10,100	1.13%
	Deodorants/body sprays – liquid based products, not containing powder actives	327,995	322,677	1.65%
	Antiperspirants	484,206	478,582	1.18%
	Other personal care products – including insect repellents, shower gels, hand lotions, talcs, depilatories and feminine products	15,567	17,299	-10.01%
	Suntan and artificial bronzing products	5,078	5,026	1.03%
Medical and pharmaceutical products	Other medical and pharmaceutical products – including over the counter (OTC) and prescription products	26,160	23,105	13.22%
Veterinary and pet care products	Flea sprays and all veterinary over the counter (OTC) and prescription products	678	5,615	-87.93%
Automotive products	All products designed for the car or cycle – EXCEPT paints and lacquers	23,050	34,996	-34.14%
Industrial aerosols	All products designed for industrial use	35,199	38,156	-7.75%
Food products	Not including pet products or medicines	0	0	
Miscellaneous	Products not recorded elsewhere – including novelty products such as artificial snow, silly string, custard pie sprays, glitter etc.	17,507	29,370	-40.39%
TOTAL		1,521,058	1,566,896	-2.93%
Break down by can type – volume millions (%)				
Total tinplate cans		660 [43%]	687 [44%]	
Total aluminium cans		861 [57%]	880 [56%]	

Filling Flammable Propellants

There are UK and International standard for filling aerosols with flammable propellants

The British Aerosol Manufacturers Association (BAMA) publish these for the UK and the European Aerosol Federation (FEA) for Europe

There are other national guides to cover other countries including the USA

They all follow the same basic principles:-

Risk Assessment – conduct a Risk Assessment to identify areas where flammable propellant can be released

Certified Equipment – use only equipment certified for the zones defined in the risk assessment

Containment – contain the propellant to prevent it from spreading

Extraction – provide single pass extraction to remove the propellant vapours to a safe place

Detection – install gas detectors to detect the propellant and take appropriate action

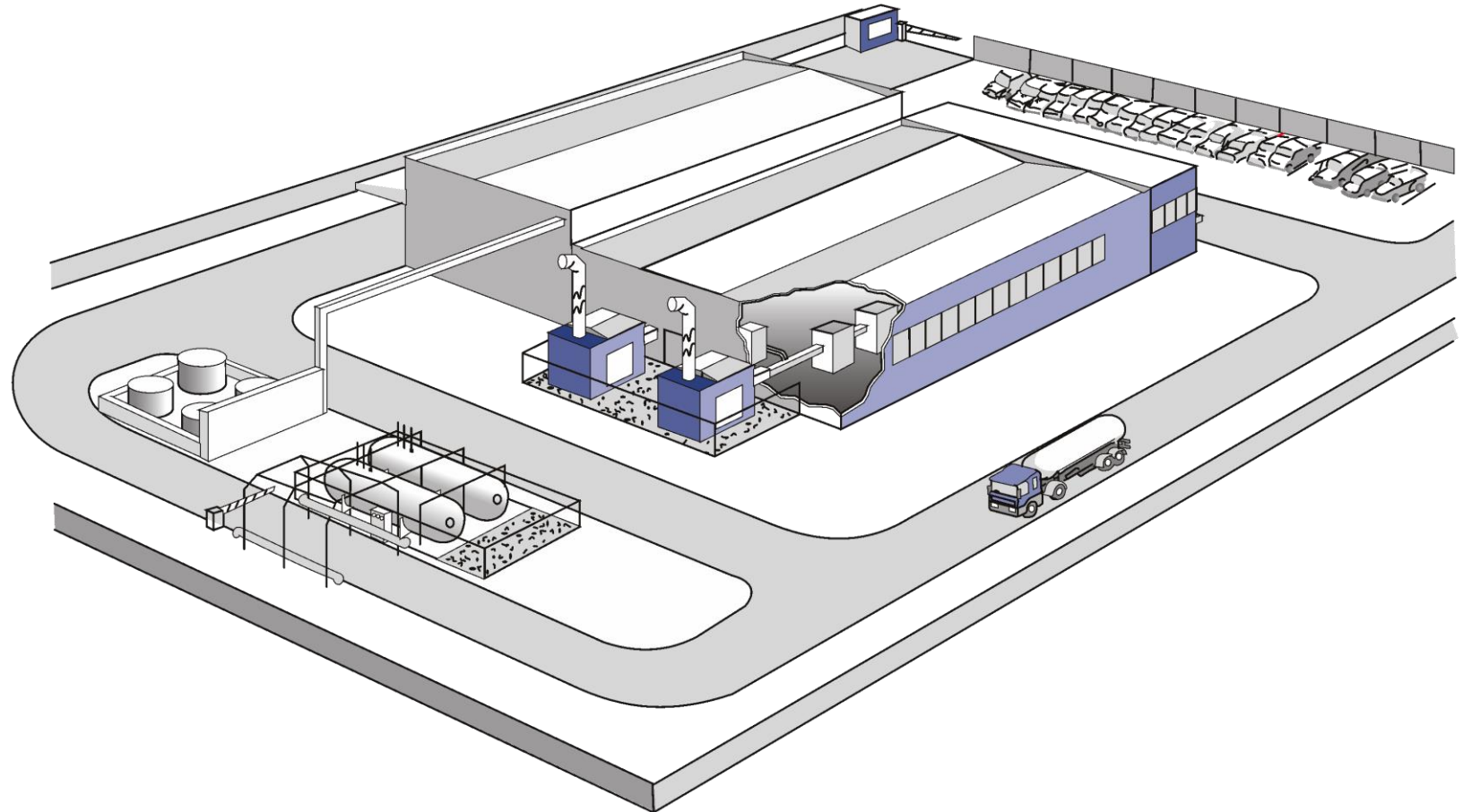
Isolation – provide a means to isolate the propellant in the event of a leak (detection)



Risk Assessment

Risk Assessment

The hazardous areas are identified by carrying out a risk assessment of all the aerosol filling activities on the site.



ATEX Flammable Zone Classifications

Zone 0

A place in which an explosive atmosphere consisting of a mixture with air of dangerous substances in the form of gas, vapour or mist is present continuously or for long periods or frequently.

Zone 1

A place in which an explosive atmosphere consisting of a mixture with air of dangerous substances in the form of gas, vapour or mist is likely to occur in normal operation occasionally.

Zone 2

A place in which an explosive atmosphere consisting of a mixture with air of dangerous substances in the form of gas, vapour or mist is not likely to occur in normal operation, but if it does occur, will persist for a short period only.

UL Classes For Ignitable substance

Class 1 Flammable gas, vapours and liquids

Class 2 Combustible dusts

Class 3 Ignitable fibres and flyings

UL Classes For Ignitable substance

Divisions go further in classifying how often the flammable or explosive substances are likely to be present under normal operating conditions

Division 1 Flammable substances are continually present or are likely to exist under normal operating conditions

Division 2 Flammable substances are not likely to exist under normal operating conditions

ATEX Zone 1 - Class 1, Div 1

Within the primary enclosure of aerosol filling machines and mixing vessels

In and around the suspension mixing vessel(s)

In any bins containing cans rejected from the filling line

Within the secondary enclosure of aerosol filling machines and mixing vessels (NFPA)

ATEX Zone 2 - Class 1, Div 2

Within the secondary enclosure of aerosol filling machines and mixing vessels

Within propellant storage tank farms

At the water stress test bath

One metre (three feet) in any direction of all Class 1, Div 1 zones

Non-Hazardous Areas

Any area not zoned

These zones not definitive and the risk assessment should identify local conditions that might affect the diffusion of any gas, vapour or haze due to spillage or leakage

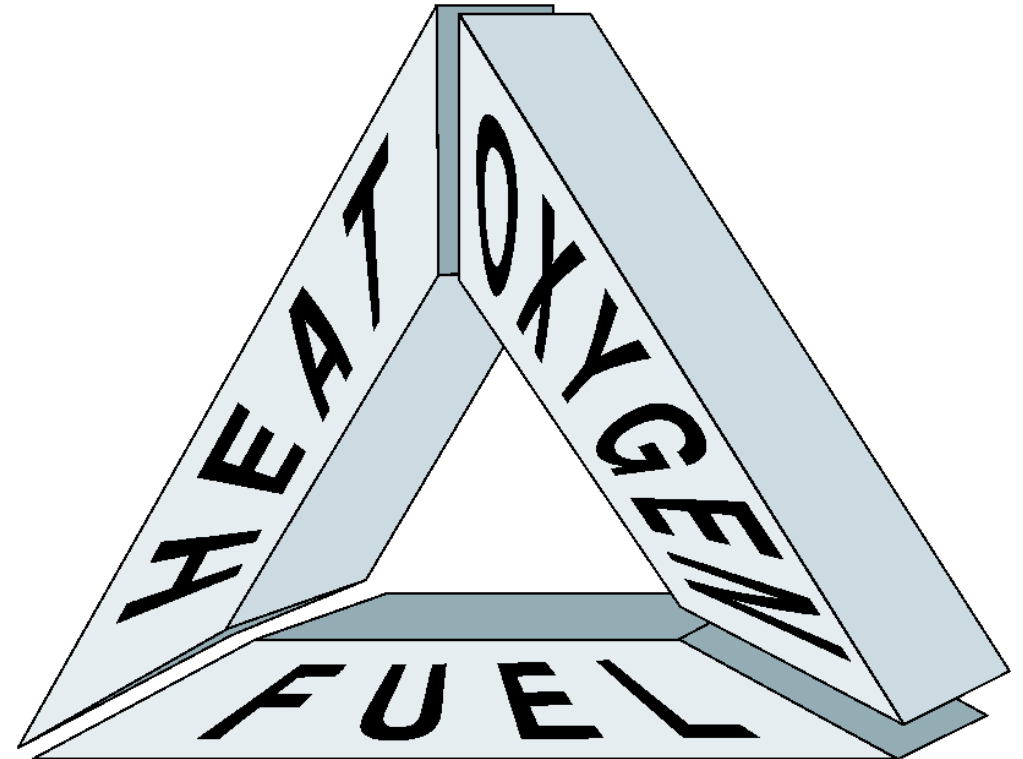
Equipment used in any area identified as a hazardous zone in the risk assessment should be suitably rated and certified.

Certified Equipment

Why do we need certified equipment?

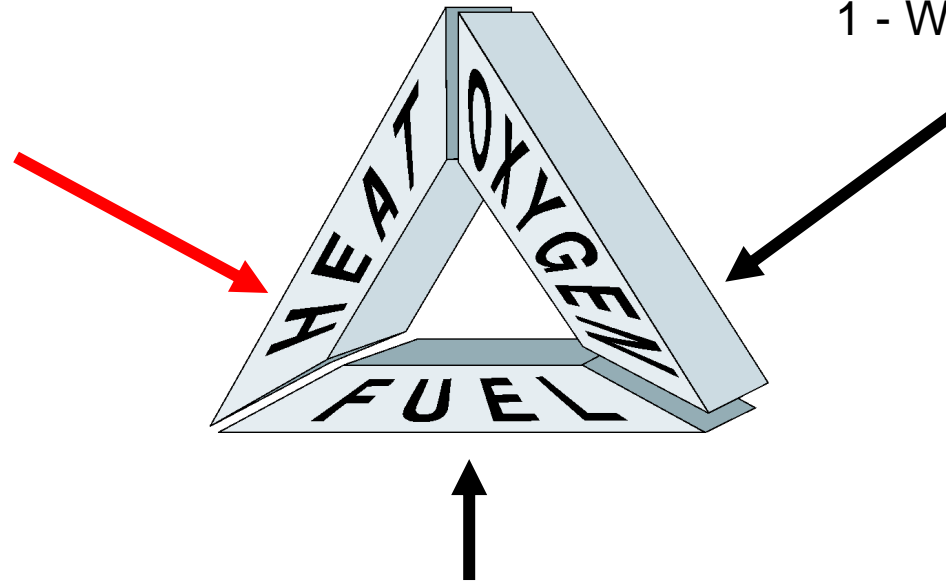
Triangle of Fire

To create a fire you need Oxygen, Fuel and Heat
Heat in some form is the source of ignition
Fire cannot exist if one side of the triangle is missing



In the MDI filling room ...

3 - We certainly don't want this.



1 - We will have this

2 - We may have this in vapour or liquid form

How Do We Eliminate Heat?

By only using electrical and mechanical equipment certified in the category for use in the relevant zone

Also by:-

Controlling discharge of static electricity by earthing throughout and using conducting conveyors

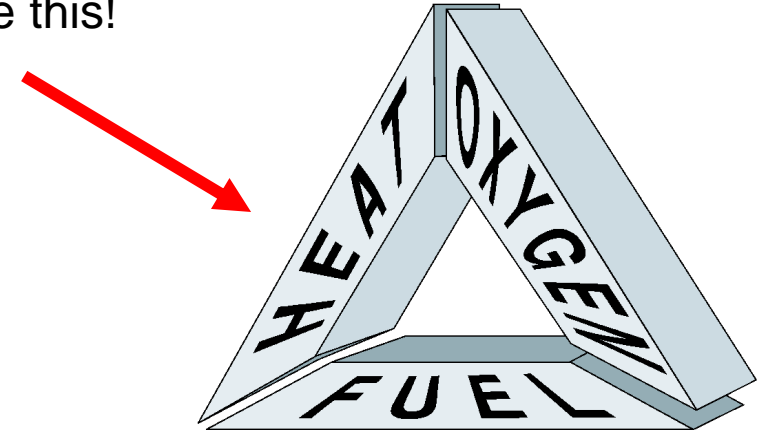
Wearing clothing which does not generate a static charge

Restricting general access and preventing non-certified electrical equipment being taken into the area

Avoiding the mechanical striking of sparks with incorrect footwear, rusty tools on aluminium or faulty rotating impellers

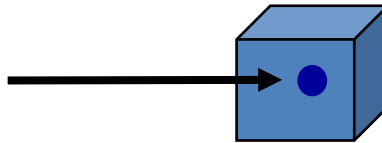
Using a permit to work system for special maintenance and repair.

We eliminate this!



Containment

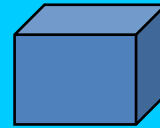
**A liquid
leak of
1 litre**



**Will expand into
324 litres of
vapour.**

It must not be allowed to reach an ignition source

It must be contained, diluted and extracted to a safe place.



Which, mixed with air will form a flammable vapour cloud of 1,905 to 6,480 litres in volume

Containment

It is therefore essential to provide a containment enclosure around any machine or piece of equipment where propellant is likely to be to stop it from spreading

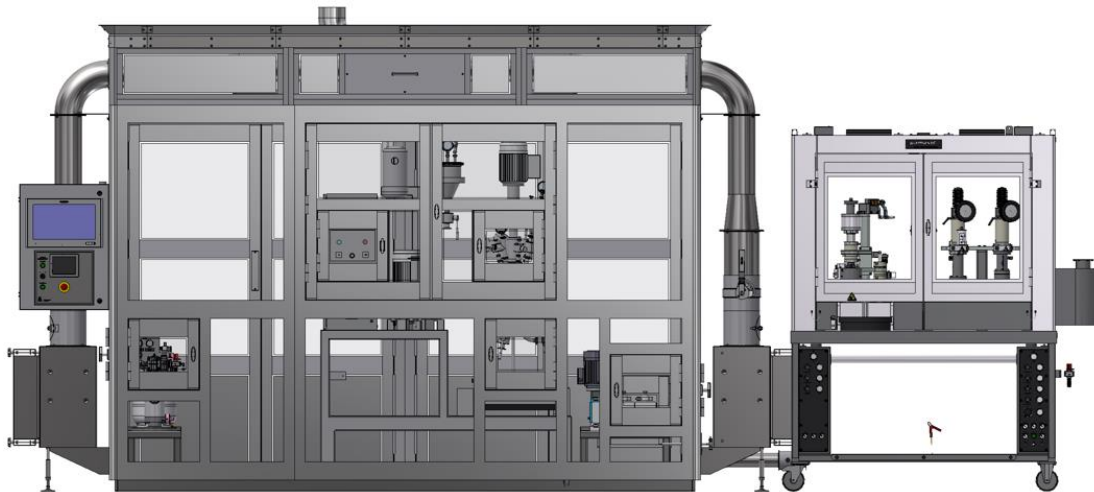
It can then be contained, collected, detected and extracted to a safe place

These containment enclosures must be fitted around mixing vessel systems as well as the filling machines

A primary enclosure is fitted around the filling heads and mixing vessel

A secondary enclosure is required for higher speed filling lines or mixing vessel capacities

The secondary enclosure is made with damage limiting construction and is commonly known as the gassing room.



Extraction and Ventilation

Flammable Propellant Vapour

152a and 1234ze vapour is heavier than air

Leaking vapour will therefore fall to the ground and flow like water

It will travel down slopes or stairs

Down drains and along gullies

It doesn't disperse easily - it accumulates in pits or depressions - and can form a flammable mixture with air far away from the source of leakage

And it has no odour

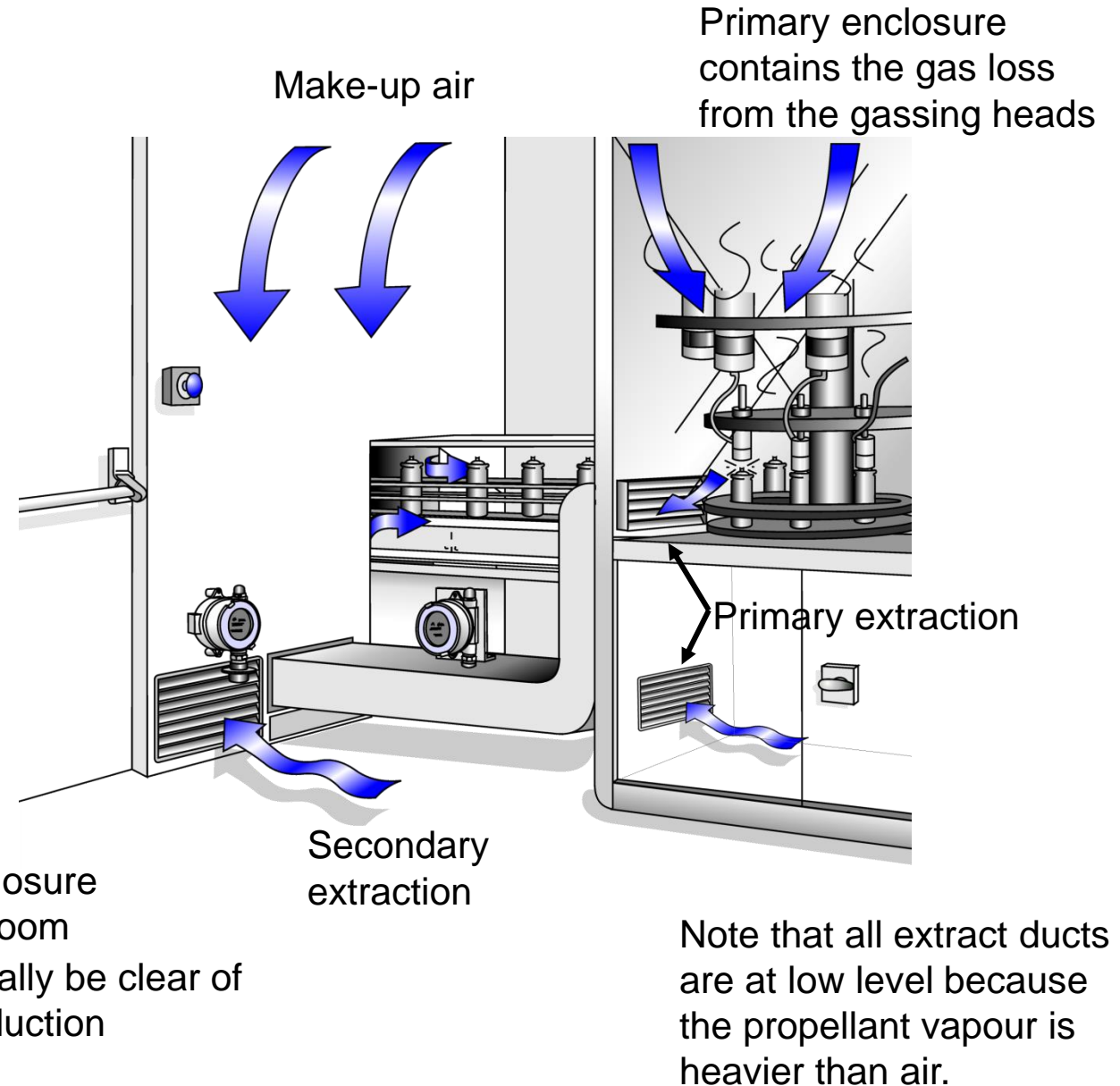


Extraction and Ventilation

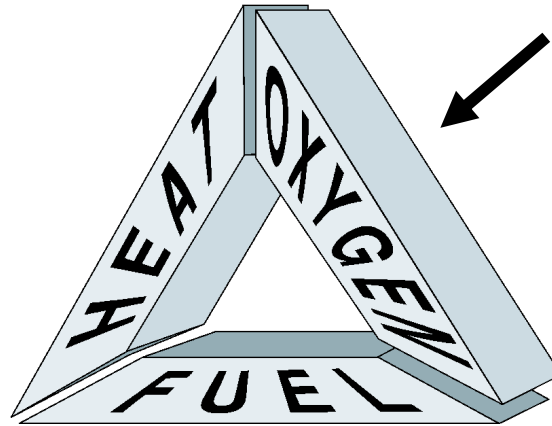
Extraction must therefore be provided in the containment enclosures to continually remove any propellant vapour from the manufacturing process and prevent the build up of a flammable atmosphere

These extraction positions will be at low level where the propellant vapour will collect

Typically 50 air changes per hour are required in the primary enclosure during normal running conditions and this will increase to 100 air changes to boost the extraction if a high level of vapour is detected.



Back to the Triangle of Fire ...



We will have this, so we might as well introduce more to dilute the concentration to below the LEL

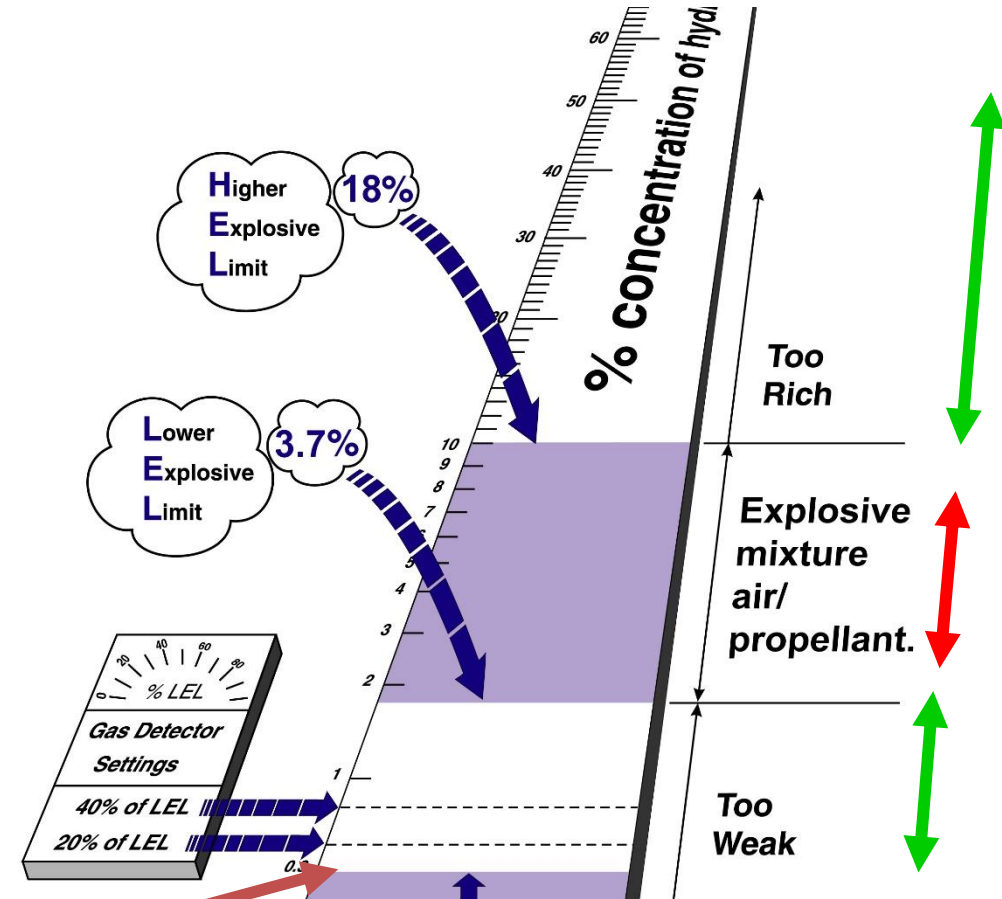
↑
We minimise this and contain and extract it to a safe place.

Detection

Flammable Range

This shows the mixture of 152a propellant with air required to make a flammable atmosphere

We need to keep well below the 3.7% mixture at all times during the filling and handling processes to ensure safe operation



Ideally keep below this line which is 15% of the LEL

Gas Detection Action Chart

Gas detectors work by detecting the gas levels and monitoring the percentage of the lower explosive limit (LEL) in the different areas

The detectors are linked to the control system and different actions carried out depending on the percentage of the LEL reached

An action chart for the safety system similar to this is produced

Gas detectors must be regularly tested and calibrated for the gas that is being used.

Key: O = Normal operation X = Action required		Remove Manufacturing System Healthy signal from Process Vessel System	Close Propellant 152a Supply Valve 1	Stop Propellant 152a Supply Pump	Open Propellant 152a Supply Valve 2	Disable / Close Propellant 152a Supply Valve 2	Close Mixing Vessel Outlet / Return Valves	Stop Process System Tandem Diaphragm Pump	Close HFA Conditioning Vessel Outlet Valve	Stop Process System Propellant Pump	Stop Process System Mixing Vessel Mixer	Request Extract Fan Boost	Signal to External System	Alarm displayed on HMI	Beacon (G/R)
Item	Condition														
1	No fault conditions - Normal operation	O	O	O	O	O	O	O	O	O	O	O	O	O	G
2	Gas level 20% LEL or above in Lab	O	O	O	O	X	X	X	X	X	O	X	O	X	R
3	Gas level 50% LEL or above in Lab	O	O	O	O	X	X	X	X	X	X	X	X	X	R
4	Gas level 20% LEL or above in Propellant Storage	O	X	X	O	O	O	O	O	O	O	O	O	X	R
5	Gas level 50% LEL or above in Propellant Storage	O	X	X	O	O	O	O	O	O	O	O	X	X	R
6	Emergency Stop Activated	X	X	X	O	X	X	X	X	X	X	X	O	X	R
7	Process Vessel Safety Relay Healthy signal lost	X	O	O	O	X	X	X	X	X	X	O	O	X	R
8	Loss of power to control system	X	X	X	O	X	X	X	X	X	X	O	O	-	-
9	Filler compressed air pressure low / off for time	O	O	O	O	X	X	X	X	X	O	O	O	X	R
10	Automatic valve position fault in Lab	O	O	O	O	X	X	X	X	X	O	O	O	X	R
11	Automatic valve position fault in Propellant Storage	O	X	X	O	O	O	O	O	O	O	O	O	X	R
12	Gas detection system fault	O	X	X	O	X	X	X	X	X	X	O	O	X	R
13	MDI Manufacturing System enclosure open (for a time)	O	O	O	O	X	X	X	X	X	O	O	O	X	R
14	Extraction System Healthy signal lost	X	O	O	O	X	X	X	X	X	X	O	O	X	R
15	Fire Alarm Healthy signal lost	X	X	X	O	X	X	X	X	X	X	O	O	X	R
16	Propellant storage manual valve closed	O	X	X	O	O	O	O	O	O	O	O	O	-	-
17	Propellant storage manual valve intermediate position	O	X	X	O	O	O	O	O	O	O	O	O	X	R
18	152a Propellant Top-up pushbutton pressed whilst other process system valves are open	O	O	O	X	O	O	O	O	O	O	O	O	-	-
19	152a Propellant Top-up valve position fault	O	X	X	O	O	O	O	O	O	O	O	O	X	R

Isolation

Isolation Valves and Controls

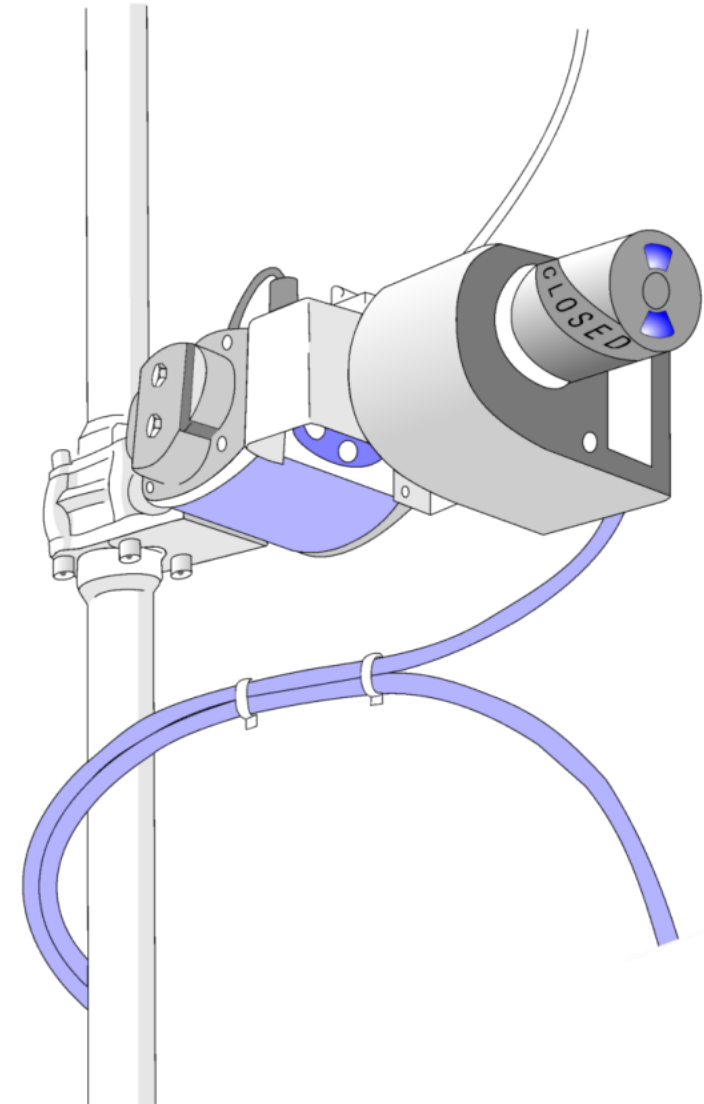
Supply of flammable propellant should only be turned on when it is required for filling and safe to do so. Automatic propellant isolation valves and remote pump controls are installed to provide this safety feature

If a high level of propellant vapour is detected the control system will shut off all propellant supplies to prevent any more entering the containment enclosure

This is an essential part of the safety system

The automatic propellant isolation valves will be closed if ...

- The machine is not being used
- The extract system is not running
- Gassing room or enclosure doors are open
- An emergency stop is pressed
- The fire alarm is activated
- Gas level is >40% in the primary enclosure or >20% in the secondary area
- The machine stops for a time due to queue/backup control
- The machine is stopped manually
- A loss in propellant pressure is detected
- Explosion suppression is activated
- And so on



Additional Safety Systems

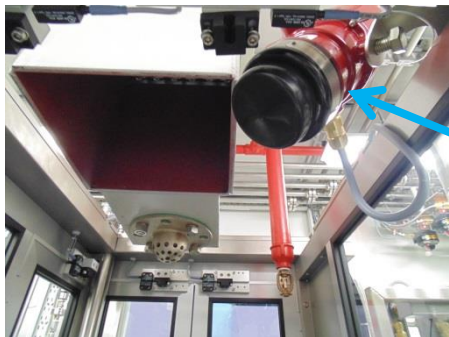
Depending on the outcome of the risk assessment additional safety systems can be installed on the filling line and in the gassing room

Fire Suppression Equipment

A Fire Suppression system can be installed in the filling area. It is there to actuate in the unlikely event of all the safety systems failing and a fast fire or explosion commencing

Sensors are positioned to cover both Primary and secondary areas. They need to see both Ultra Violet and Infra Red radiation before confirming presence of fire

When a fire is confirmed, High Rate Discharge water fire extinguishers will actuate within approximately 50 milliseconds to stop the fast fire before it develops



Primary
UV/IR
sensor



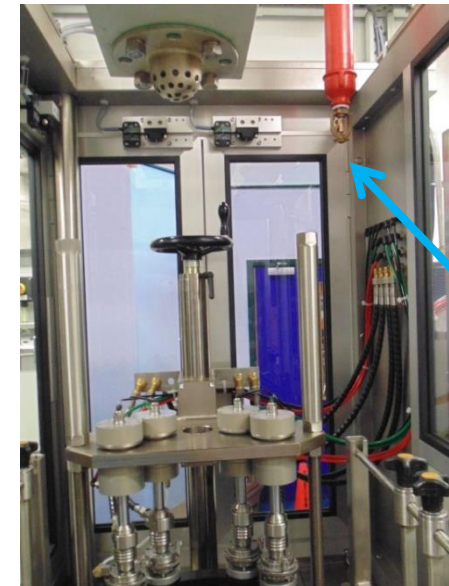
Secondary
HRD
extinguishers

Sprinkler Installation

Sprinkler pipework and heads can be installed to continue extinguishing (and may treat any burns) if a fire persists or re-ignites after the Fire Suppression system has actuated

This pipework should be connected to the site sprinkler system

It is normal to install a 'dry pipe' system to the gassing room in locations where ambient temperatures are expected to drop below the freezing point of water; however, it should be noted that dry pipe systems can take up to 60 seconds longer than wet pipe systems to actuate



Sprinkler
nozzle in
secondary
zone

Sprinkler
nozzle above
filling heads in
primary zone.



Filling Flammable Propellants – pMDI Laboratory Scale



Filling Flammable Propellants – Production Scale

152a Production Line

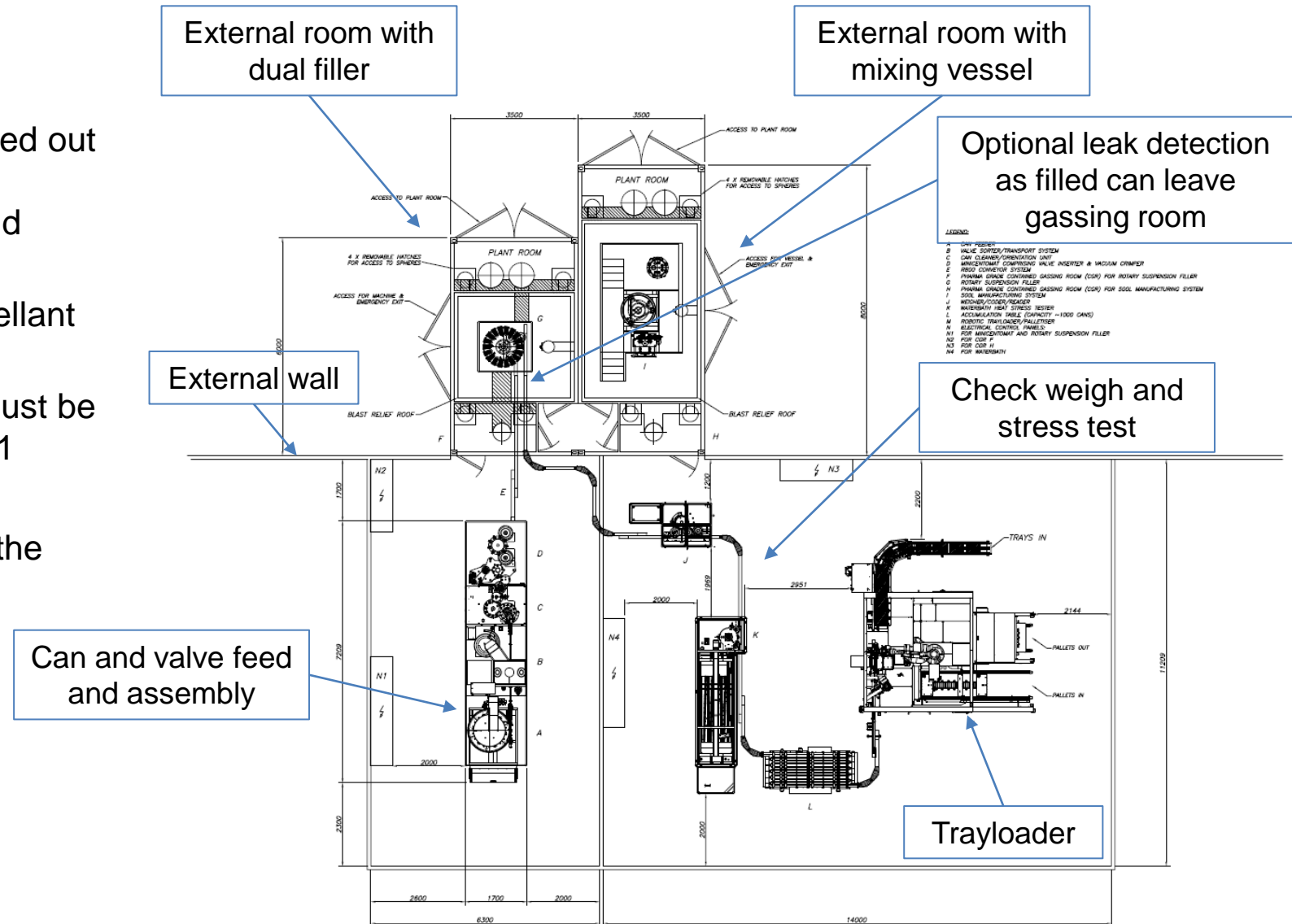
In a production environment, flammable propellant filling and handling must be carried out in a purpose build external room with the necessary classification, safety systems and controls

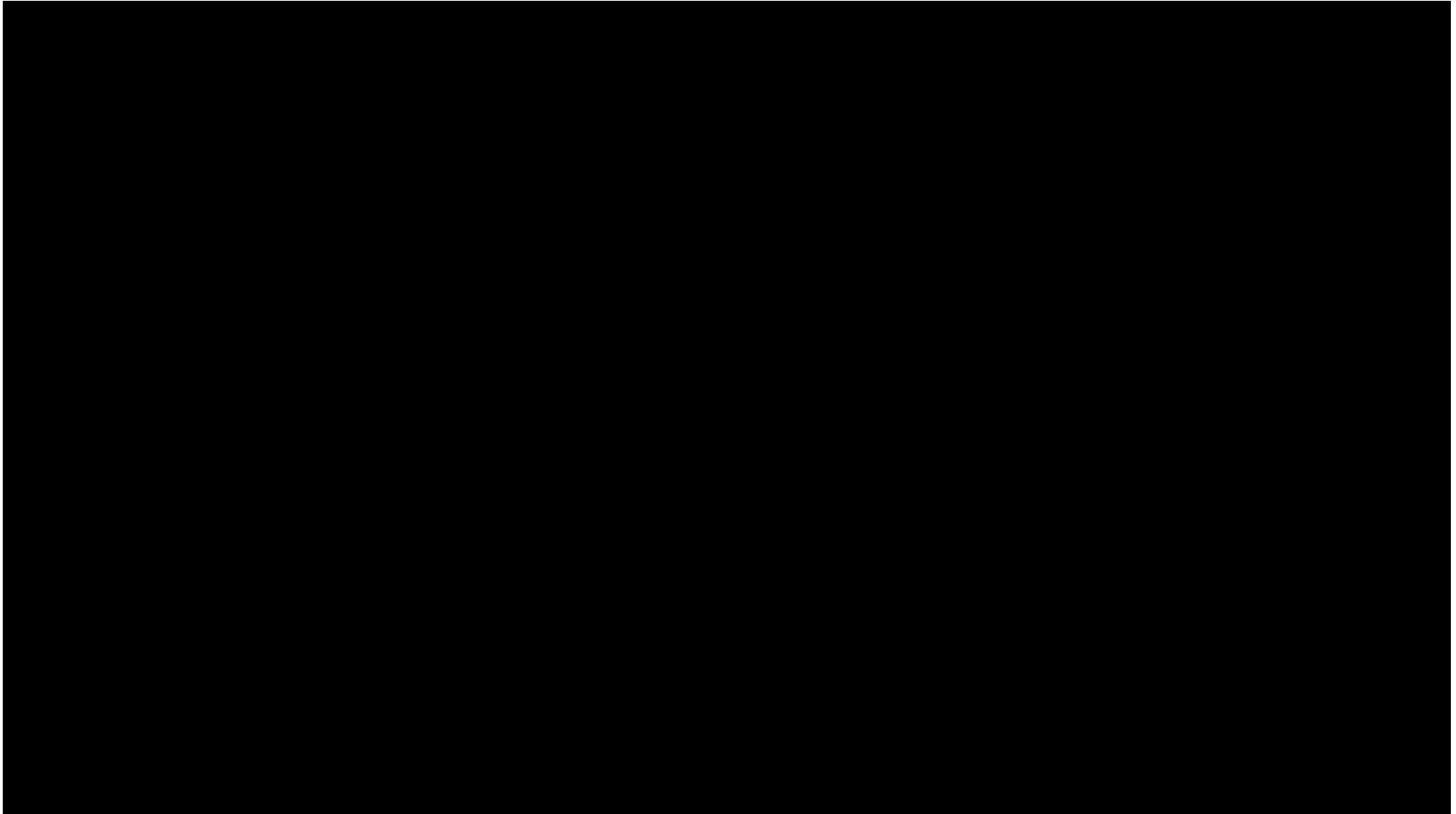
This is because of the high volume of propellant being used

The mixing vessels and filling equipment must be classified as ATEX zone 1, UL Class 1 Div 1

Existing equipment cannot be used

The other operations can be carried out in the facility as normal





pMDI Filling Safety Guide

As previously mentioned, there are many existing safety guides for filling 1” aerosols in the cosmetic, household and industrial aerosol industry

However there are specific processes and requirements in the pharmaceutical pMDI filling application that are not considered in the existing guides

DH Industries, Koura and Recipharm are therefore collaborating to produce a Flammable Propellant Safe Handling guide for the Pharmaceutical Industry

The intention is to provide a concise guide to factors to consider at each stage of the product development and manufacturing process

It will be largely based on existing Standards and Guidance but tailored to suit the pMDI manufacturing processes

Watch this space!

Thank You

For your attention

Please visit our web site www.dhi.co.uk for further information



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