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Drum Burst due to Runaway Reaction and the Limits of MOC

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Daily operations and equipment failures may require slight process changes which in many cases are carried out without any effect on safety. But sometimes unknown hazards are hidden beyond those slight changes.
Even if a company has a well implemented Management of Change protocol, the evaluation of every single process change may be difficult to assess in detail as a balance between time available and analysis depth has to be achieved, therefore assessment is made with information and knowledge available in the spot. In this sense, even if the evaluation is done, the knowledge available may lead to neglect hazards.
In this paper, an example of a slight process change is presented which lead to a runaway reaction and a drum burst. Hopefully no injures had to be blamed and only damages on the area where the drum burst had to be considered.
A solvent and a process reactant were mixed for a too long time inside a drum due to a pump failure leading to a different operation during the dosing of reactants into the reactor.
The change was evaluated according the MOC and available criteria by plant operator, shift leader and production chemist on duty, without identifying any significant hazard thus allowing the chance to be carried on.
Investigations later revealed that a hazardous exotherm reaction was present at temperatures close to ambient temperature between the reactant and the solvent.
This case is an example of an unknown by the operational workforce – known only by experts and the fact that experts may not be systematically involved in the assessment of slight process changes due to the time available to carry out operations.
Beside the analysis and explanation of the accident, the aim is to define measure to prevent similar incidents to take place; therefore lessons learned allow defining some recommendations related to MOC management which can be applied to any company helping to unhide hazards and make the knowledge available to people carrying out operations in the field.

1. Description of the operations

At this point, the operation as designed is presented, then the process modification and its reasons are explained and, finally, the incident and its consequences are described.

1.1 Intended operation

During a chemical synthesis process, Sulphuryl Chloride is used as reactant in an intermediate step.
This substance is received in drums, which are handled in groups of 4 on a pallet. The normal production size requires 4 drums to be dosed into the reactor.
Dosing of Sulphuryl Chloride is done by using a dip pipe introduced in the drum and pump sucking out the substance and pumping it to the reactor.
The pumping rate is limited in order to control the exotherm released during the reaction and keep a low reactant accumulation. In this sense, the dosing time for each drum was set to 2 hours, meaning that the dosing operation of Sulphuryl Chloride lasts around 8 hours per batch.
When no more Sulphuryl Chloride could be pumped out from the drum, and in order to rinse the few litters remaining inside, 20L of Xylene were introduced in the drum without stopping the dosing pump to the reactor.

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Operational details at this step are important. As the drums had two orifices on the top, the bigger orifice was used to introduce the dip pipe sucking out the Sulphuryl Chloride while the smaller one was used to pump in the 20L of rinsing Xylene.
Once the 20L of Xylene had been introduced and no more liquid could be pumped out, the drum was considered as completely used and therefore closed and handled as a dirty drum for disposal.

1.2 Process deviation

When the dosing of Sulphuryl Chloride started on the day of the incident, it was noticed that the pump used to transfer the Xylene for rinsing was not running well. As the reparation could not be done immediately, the situation was assessed and the process was modified as described next.
With only one pump in operation, it was decided that once no more Sulphuryl Chloride could be sucked out from a drum, the transfer would be stopped and then dosing pump would be used to introduce the 20L of Xylene into the almost empty drum, after which it would be immediately closed. The drums with the Sulphuryl Chloride and Xylene mixture would remain closed until the last drum was charged; at this moment the pump woud be used to transfer to the reactor the rinsing mixture in all 4 drums.
When the process modification was evaluated, it was thought that is was safer to keep the Sulphuryl Chloride diluted with Xylene in an almost empty drum than just leaving a few litres of pure reactant inside. A reason considered at that moment was that Xylene, besides being used for rinsing, was as well the main solvent in the reaction mass and, therefore, it was thought that no reactive hazards would be present in the mixture resulting from diluting a few litres of Sulphuryl Chloride with the process solvent.

1.3 Incident

Proceeding as described above, the Sulphuryl Chloride in three drums was completely transferred and all three were filled with 20L of Xylene and closed.
While the fourth drum was being dosed to the reactor, meaning that the other 3 drums were on the same pallet, closed and only containing the leftover of Sulphuryl Chloride and rinsing Xylene, the operators noticed that the second drum (in order of dosing) was becoming pressurized. A clear deformation could be observed on that drum.
Initially, operators attempted to carefully loosen the cap and release the pressure, but as the attempts were not successful they decided to stop the transfer on the fourth drum and evacuate the area.
A few minutes after the zone was evacuated, the drum exploded.
The other two empty drums were blown apart, remaining only in the pallet the last drum, which was full, and fortunately did not suffer any damage causing a leak.
The incident resulted in no personal injuries. Neither fire nor major spill was reported. Damages were limited to the pallet and neighbouring drums as well as some equipment in the loading area, such as piping for local vapour exhaust and transfer pipes.

2. Reactivity of Sulphuryl Chloride

According to the description of the incident, it was obvious that the reactivity of Sulphuryl Chloride had probably played a clear role on the event. In this sense, and as already mentioned above, the fact that the mixture between the reactant and the solvent could show a dangerous behavior was unknown at that time by the company.

2.1 Amount of Sulphuryl Chloride

In order to assess the reactive behaviour, the mixture composition is initially estimated.
In first place the amount of Sulphuryl Chloride remaining inside the drum once it is considered as empty is estimated. To do so, next considerations were made:

A. Drum was tilted when empty, but this operation depends on the skills of the operator, the tilting degree and the time during which the drum is hold in a tilted position. According to experience it is considered reasonable to assume that a thin layer of 0.5 cm of liquid remains inside the drum when it is declared empty. The amount of substance that this layer represents in a 55 cm diameter drum with a chemical having a density of 1.67 (g/cm^3) at 20ºC is 1,19L or 1983g.
B. The configuration of the piping caused that once the dosing pump was stopped a small amount of substance was drained back to the drum. The estimation made by considering the layout of the system lead to a result of around 3 litres of liquid able to flow back to the drum. A volume of 3 L in a substance with a density of 1.67 (g/cm^3) at 20ºC represents a mass of 5010 g.

Therefore, a total amount of around 7kg of Sulphuryl Chloride (4.2L) could remain in the drum when the 20L of Xylene were introduced for rinsing.

Considering a density of Xylene of 880 (kg/m^3) at 20ºC the mass of Xylene added with rinsing purposes is 17.6 kg.
As a result a mixture with a concentration of 28.5% w/w of Sulphuryl Chloride in Xylene was obtained after introducing the rinsing solvent in each empty drum.

2.2 Reactivity with water

Nevertheless, it is well known that Sulphuryl Chloride reacts violently with water releasing gas, therefore the presence of water was investigated in relation with the incident.
At this point the operations and experience acquired while handling this substance are of importance. According to operational experience, when the relative humidity is high, Sulphuryl Chloride drums rapidly generate fumes when opened. This behaviour is caused due of the reactivity of the substance with moisture contained in the air.
Being aware of this behaviour, on the day of the incident it was decided that the drums would be closed immediately after charging the rinsing Xylene. According to the explanations of operators, when this operation was performed no fumes were observed and no water was present at the loading station.
Moreover, as the reaction with water is very fast and violent, in case that water could have entered the drum, the reactivity would have been observed much earlier. The explosion occurred around 4h after charging the drum contents into the reactor, introducing the Xylene for rinsing and closing it.
Finally, it is reasonable to consider that the drum was tightly closed since when the pressurization started it was not possible to open it.

2.3 Reactivity with organics

As can be found in literature, although Sulphuryl Chloride is supplied in galvanised drums they may be unsafe and lead to unintended reactivity with this substance.
It is known that Sulphuryl Chloride can chlorinate many active organics, including aromatics, ketones and probably esters. This will release sulphur dioxide and hydrogen chloride, a fairly soluble gas, which will react with zinc and iron to produce hydrogen, an insoluble gas, and zinc or iron chlorides, both catalysts for many reactions.
As mentioned before, the reactive potential of Sulphuryl Chloride often involves gas generation, moreover documentation available describing the reactivity of this substance with organics and galvanised drums, triggers the suspicion that it is not a safe process condition to store Sulphuryl Chloride with Xylene in a galvanised drum for an extended period of time (a few hours).

2.4 Experimental tests

Finally, thermal stability tests were done by means of DSC in order to investigate and confirm the suspicions on the potential exothermal behaviour of a mixture between Sulphuryl Chloride and Xylene.
To do so, mixtures of Sulphuryl Chloride and Xylene at different concentrations were investigated in both stainless steel and gold crucibles.
As a summary next table shows the most relevant results obtained for a mixture with a concentration of 25% w/w of Sulphuryl Chloride in Xylene:

Table 1: DSC 25% w/w Sulphuryl Chloride in Xylene. Gold Crucible

Variable	Value	Unit	Comments
Crucible Material	Gold	--	
Left Peak Temperature	147.01	ºC	
Peak Temperature	190.68	ºC	
Right Peak Temperature	205.50	ºC	
Heat Released	102.59	J/g	Normalised value

Table 2: DSC 25% w/w Sulphuryl Chloride in Xylene. Stainless Steel Crucible

Variable	Value	Unit	Comments
Crucible Material	Stainless Steel	--	
Left Peak Temperature	107.09	ºC	
Peak Temperature	176.37	ºC	
Right Peak Temperature	195.40	ºC	
Heat Released	139.77	J/g	Normalised value

3. Pressure build up

As a rule of thumb, it is considered in practice that the bursting pressure of a standard 220L metallic drum is 7 to 10 bar.
Reactions related to Sulphuryl Chloride may easily release gas; nevertheless in a DSC test the pressure evolution inside the cell is not available.
In first place, as the mixture showed to have a certain exothermal behaviour, it is evaluated if the adiabatic temperature rise could lead to the drum pressurisation due to the vapour pressure exclusively due to the substances present in the mixture.

3.1 Vapour pressure

Considering the composition of the mixture in the drum and the liquid heat capacity of the substances, the resulting mixture heat capacity is around 1.6 kJ/(kg·ºC), which, linked to a heat release around 140 J/g and considering adiabatic conditions would lead to a maximum temperature increase of around 88ºC.
Considering that the operation was being done at ambient temperature, the final temperature inside the drum would be around 105ºC.
In figures 1 and 2 the vapour pressure curves as a function of temperature are respectively shown for Sulphuryl Chloride and o-Xylene. As can be seen, at a temperature around 105ºC, and considering the typical bursting values considered for a 220L drum, the vapour pressure alone would have not been able to cause the incident with the consequences observed.

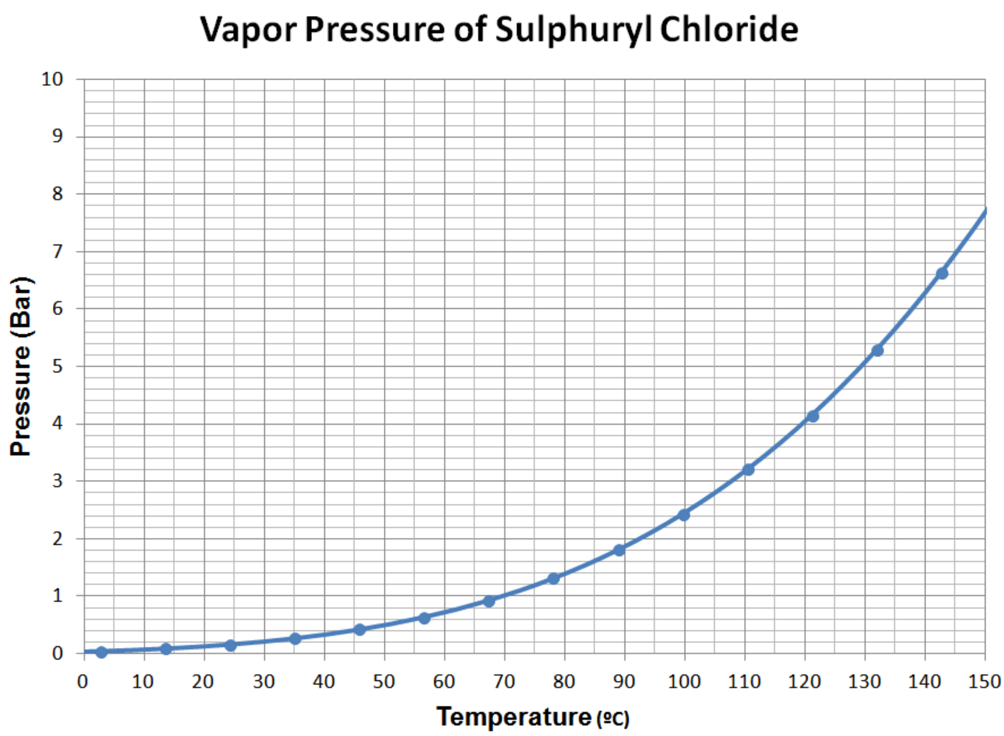

Figure 1: Vapour pressure curve of Sulphuryl Chloride

3.2 Reaction gases

In all potentially considered unintended reactions of Sulphuryl Chloride, the gases generated are hazardous for the health and the environment, therefore the operation of opening a pressurized drum with this substance inside it is considered as very dangerous.
As well, as the pressure rise rate and the current pressure inside the drum are unknown during this type of events, it should be considered that the drum may burst at any time, and therefore, staying close to it or trying to do some actions on the drum is not considered as a safe behaviour.

3.3 Bursting a Drum

In order to reach a pressure of 10bar inside a 220 L drum, considering ideal gas behaviour and 22.4 L per mol, around 100 moles of gas are required.
In this sense, when Sulphuryl Chloride decomposes, it may generate 2 moles of gas per mol of Sulphuryl Chloride. Considering that Sulphuryl Chloride has a molecular weight of 134.97 (g/mol), the amount of Sulphuryl Chloride required to generate 100 moles of gas is approx. 6750 g or 4 L.
This calculation does not aim to conclude that the reaction involved in the accident was the decomposition of Sulphuryl Chloride, but only to show that the amount of Sulphuryl Chloride required to pressurise an empty drum is not very large and could be achieved easily with only a few litres of substance.

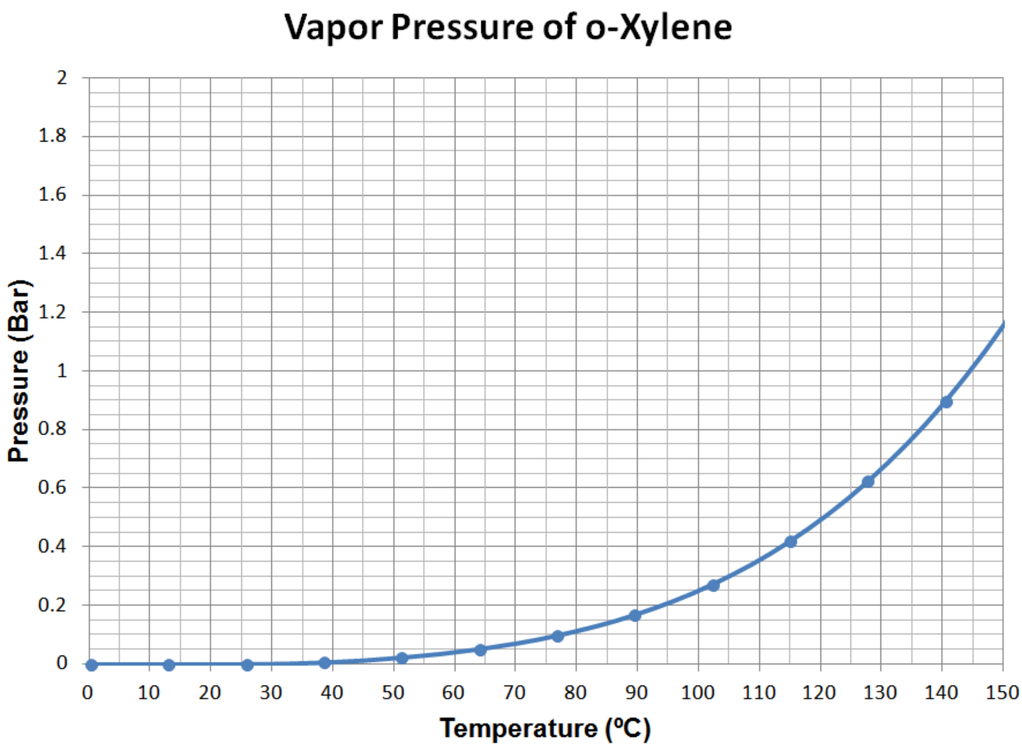

Figure 2: Vapour pressure curve of o-Xylene

4. Management of Change

In terms of Management of Change (MOC) the protocol was applied as defined in the safety management system, but the problem laid on the knowledge available at the time of evaluating the situation.
The assumption that a reactant is stable when mixed with a solvent lead to the wrong conclusion that the mixture between Xylene and Sulphuryl Chloride would not represent a reactive hazard if kept at room temperature for an extended process time.
Lessons in this sense were introduced indicating that in case of a longer process time, the stability of the chemical mixture should be carefully evaluated and a more in depth information review should be performed in front of a similar situation.
The instability of Sulphuryl Chloride when handled in metal drums as well as its reactivity with aromatic substances could be found in literature, but these sources were not checked. In this sense a more detailed specification of required resources to be considered while investigating reactive hazards was also defined.

5. Conclusions

To start with conclusions related with this incident, it should be said in first place that the evaluation of a process deviation requires always an in depth and detailed review, otherwise, process hazards may remain unidentified leading to dangerous process conditions.
In this sense MOC protocols are very important and they should also be as detailed as possible, showing required information sources, people to involve and hazards to be evaluated.

The fact that a hazard is known will not prevent that we continue learning from accidents as long as it remains unknown for us. In this sense, prevent dealing with know/unknowns should a clear target in any safety management system.

In relation with the incident itself and its consequences, as Sulphuryl Chloride is used in many chemical processes involving different types sectors, the information contained in this report and the incident that took place may be useful for any company handling or using this substance in its processes.

Finally, during the accident investigation it was also shown how important is to have a minimum testing capacity in site. Screen equipment such as a DSC brings a solid basis on the assessment of thermal stability of chemical mixtures. In this case the DSC was made to late, as it was made to investigate an incident, which brings us back to realise how important is to have good MOC procedures.

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