Safe Use of Phosgene and Triphosgene in the Fine Chemicals Industry

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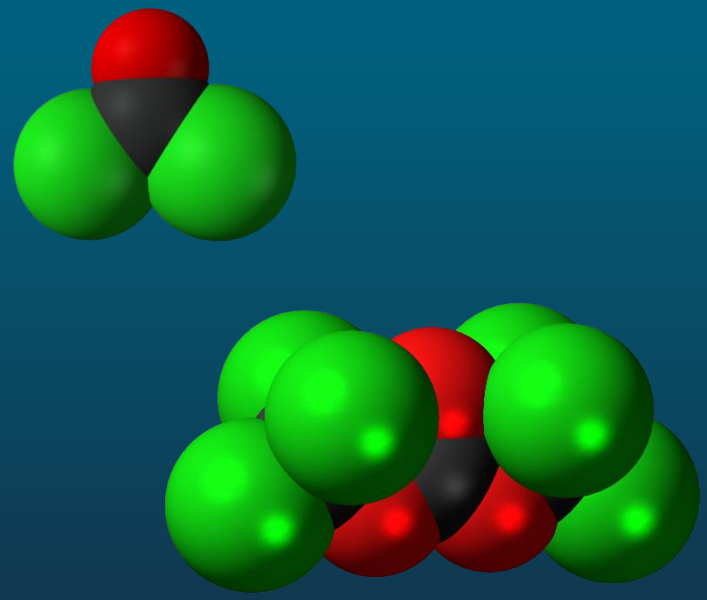
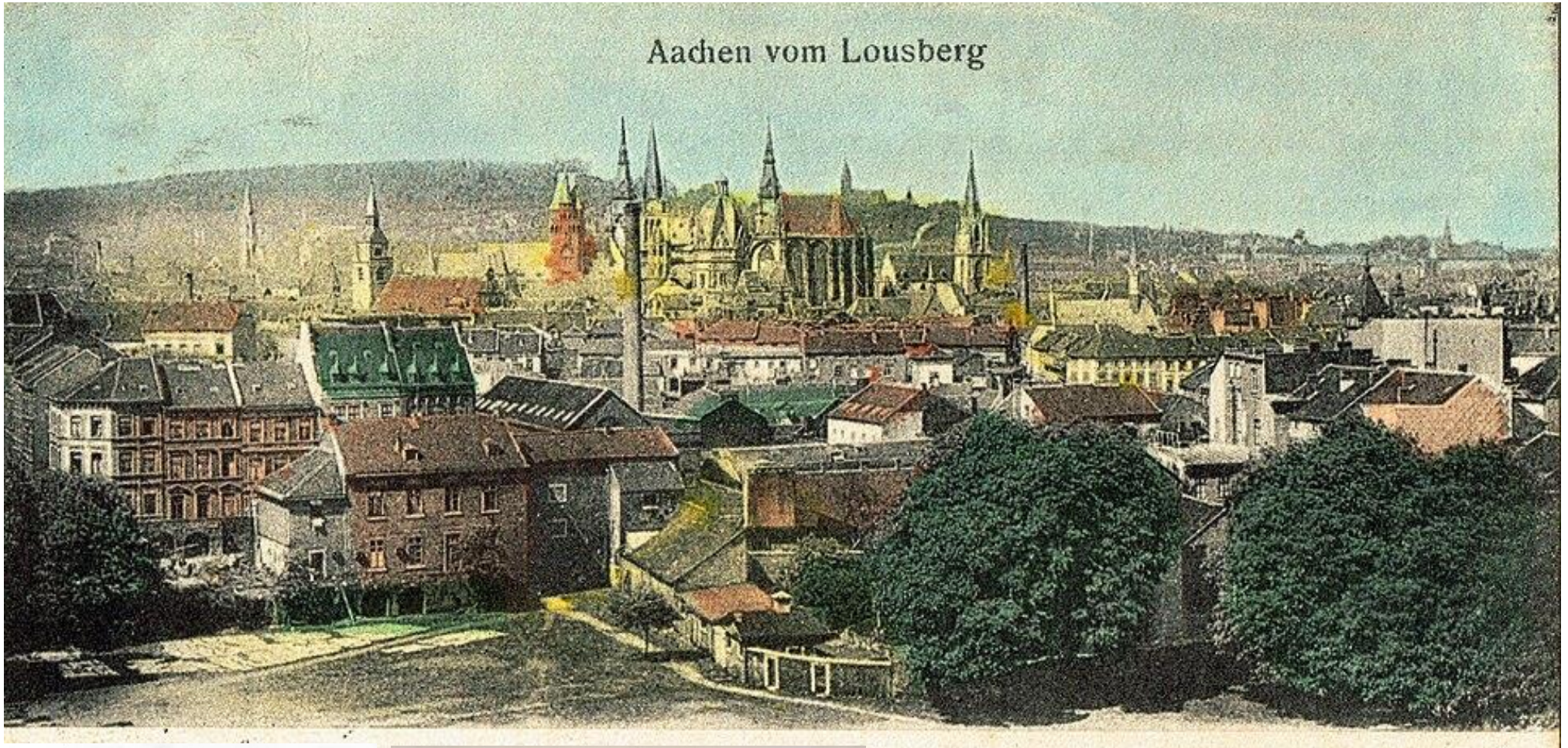
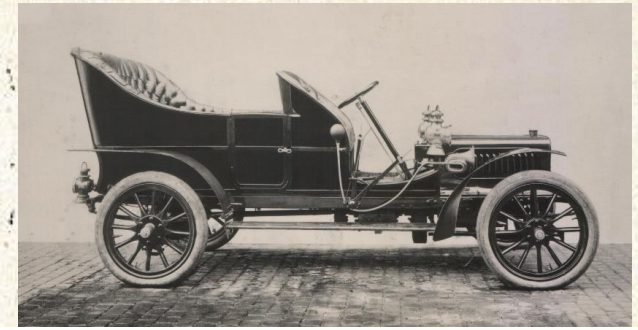






Photos:wikimedia commons,

Life has significantly changed due to polymers, agrochemicals and drugs

Photos:wikimedia commons, Bayer, Covestro

Phosgenation

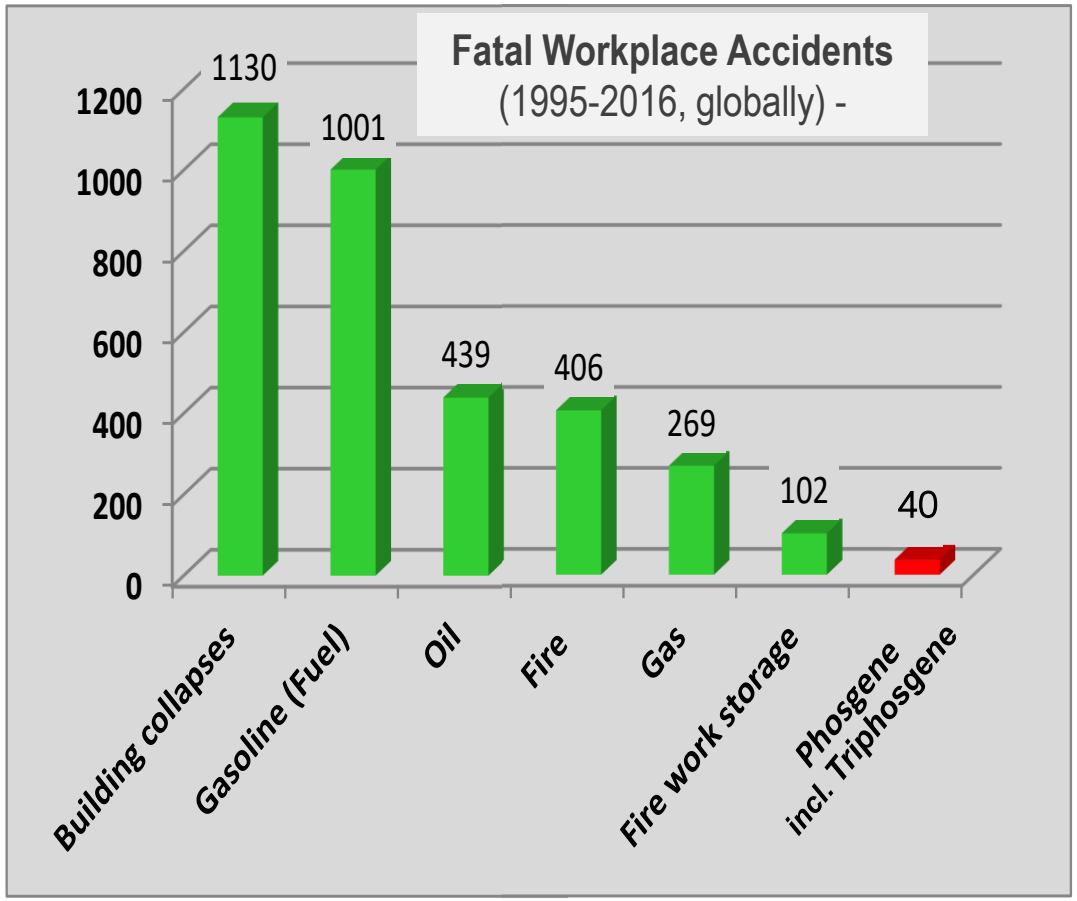
A key technology

Phosgene

Photos: wikimedia commons, Bayer, Covestro, Capt. Frank Hurley

Phosgene Incidents

"Ranking"



- Despite the low number of accidents, the public reacts very sensitively to phosgene
- Stigma and fear (poisonous gas, chemical weapon, World War I) create a very negative image of the very valuable synthesis building block phosgene
- In case of an incident, we have to expect:
  - non-factual reporting
  - influence on permits

Source: IHS/IRS Chemical, DWCP/Gilbert International list, International Isocyanate Institute, Internet market research data, public company websites

Phosgenation

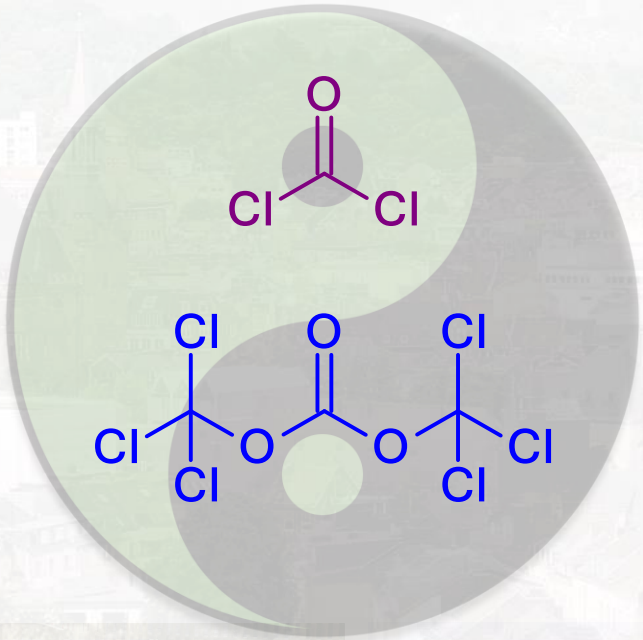
Phosgene & Triphosgene (BTC)

Enable highly efficient production

- mild conditions
- high yields (selectivity!)
- positive by-product profile
- inexpensive reagents

Triphosgene

- advertised as “safer phosgene”
- no phosgene generator required
- “only” solid, handling



Phosgene & Triphosgene are highly toxic

Phosgene

- stigmatized due to WW1 (ca. 100 years ago!)
- permit situation
- public perception

Triphosgene

- low vapor pressure – but significant exposure possible!
- safety profile depends on quality
- sublimation & high lipophilicity
- misleading literature (!)

* BTC = Bis(trichloromethoxy) carbonate (BTC, triphosgene); “Yin&Yang: https://en.wiktionary.org/wiki/yin-yang; https://creativecommons.org/licenses/by-sa/3.0/

Phosgenation

Triphosgene (BTC), Literature

… Darüber hinaus ergeben sich aber be[illegible]ten mit Tri-
phosgen weitere überraschende V[illegible]ann Triphos-
gen z.B. ohne Zersetzung bei[illegible]tilliert
werden. Es tritt ausserd[illegible]konzen-
trierter Schwefelsäu[illegible]e auf. We-
gen seiner gerin[illegible]phosgen sogar
ohne Benutzu[illegible]benenfalls in offe-
nen Anlagen v[illegible]

H. Eckert; (1984); DE 3440[illegible]

Dangerous, not acceptable!

…Furthermore, the use of t[illegible]gene has surprisingly additional advantages. For example, triphosgene can be distilled without decomposition at 203 – 207 °C. There is almost no reaction with conc. sulfuric acid or cold sodium hydroxide solution. **Due to the low volatility triphosgene can be used without a fume hood and, were applicable, in open plant equipment.** …

Triphosgene (BTC)

Literature

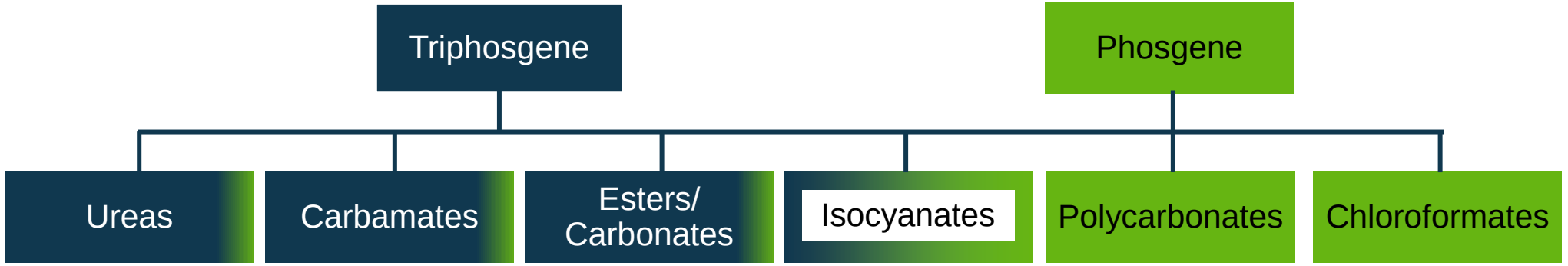
What is AI telling us?

Example: Copilot

Misleading!

Phosgenation

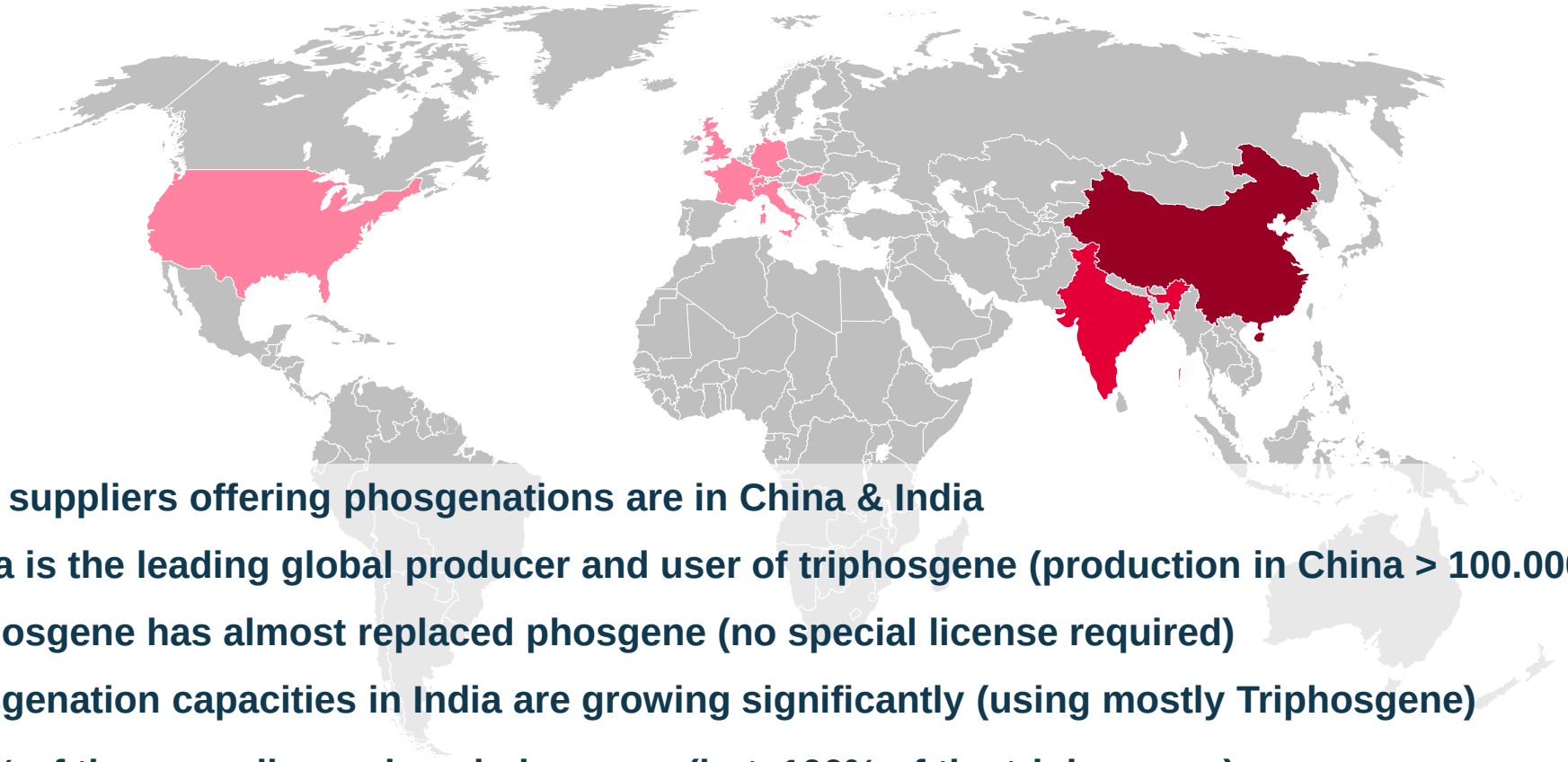
Triphosgene vs. phosgene



- **Phosgene is the preferred reagent for large-scale polymer production (>90% of annual phosgene use)**
- **Triphosgene is the reagent of choice in the fine chemical industry**
- **Reactions involving triphosgene always produce phosgene!**

Phosgene Industry

Fine chemicals



- **Most suppliers offering phosgenations are in China & India**
- **China is the leading global producer and user of triphosgene (production in China > 100.000 t/a)**
- **Triphosgene has almost replaced phosgene (no special license required)**
- **Phosgenation capacities in India are growing significantly (using mostly Triphosgene)**
- **< 10% of the annually produced phosgene (but 100% of the triphosgene)**
- **Ca. 50 % of fatal phosgene incidents are linked to the fine chemical industry**

Phosgene Industry

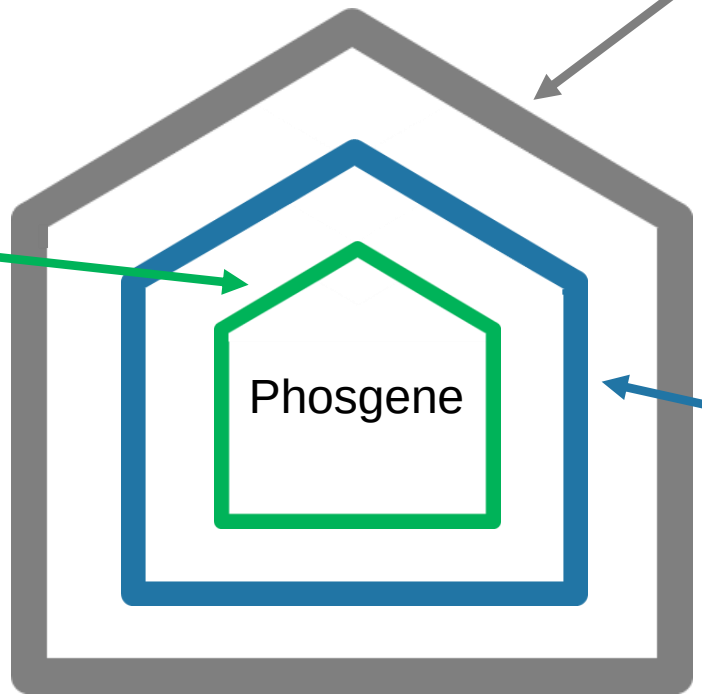
General Safety Concept

Emergency response

(3rd barrier: reaction)

Primary Measures

(1st barrier: prevention)



Secondary Measures

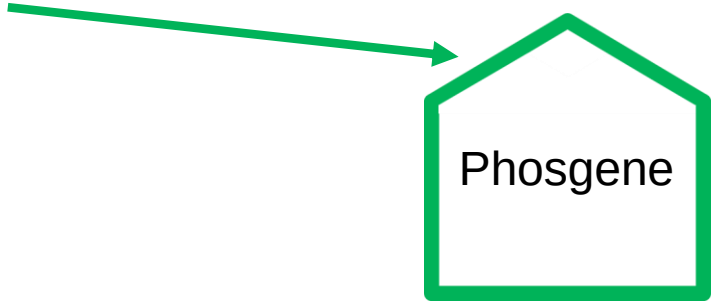
(2nd barrier: mitigation)

Phosgene Industry

General Safety Concept

Primary Measures

(1st barrier: prevention)



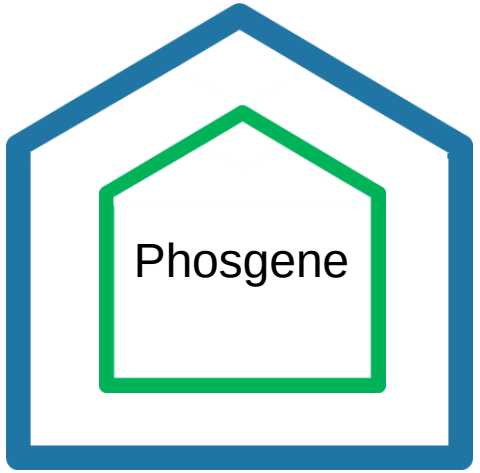
- Very tight, state of the art equipment
- Systematic safety/risk analyses (HAZOP, …)
- Regulations/documentation of organization and responsibilities (periodic inspections, systematic maintenance plans, …)
- SOP & specific training
- Safety information (MSDS)

- Minimized hold-up
- Local phosgene production
- MOC selection (no glass equipment)
- Decomposition system
- Valves and pumps with secondary sealing
- No hoses, no screwed connections
- Proper process monitoring

Phosgene Industry

General Safety Concept

- Containment or Fully Jacketed set-up or Steam-Ammonia-System
- Continuous ambient air monitoring
- Suitable respiratory protection
- Phosgene badges (= dosimeter!)

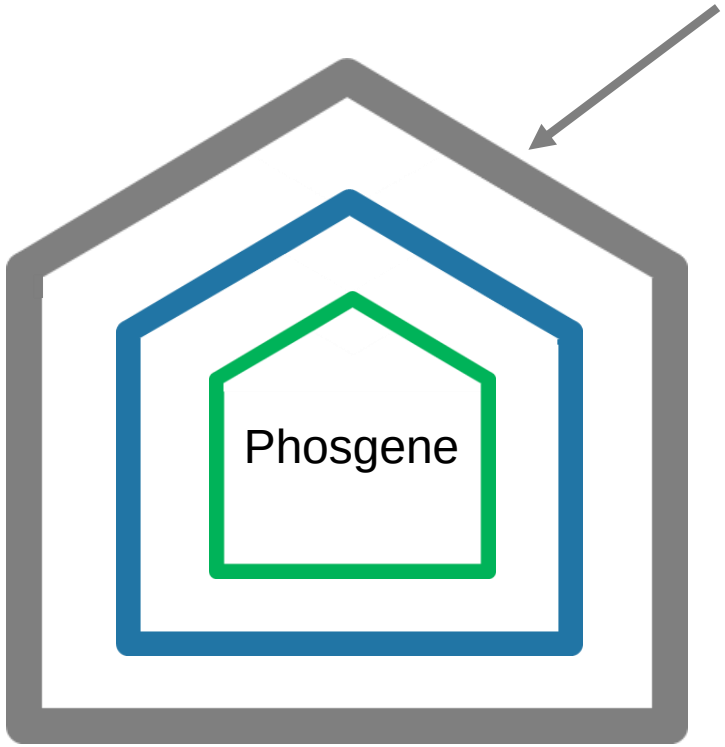


Secondary Measures

(2nd barrier: mitigation)

Phosgene Industry

General Safety Concept



Emergency response

(3rd barrier: reaction)

- Fire brigade, paramedics, ...
- Emergency response plan (training, medical measures, cooperation with hospital, ...)
- Networking (e.g. Phosgene Safety Exchange meetings)

Phosgene Industry

Outsourcing – experiences & observations

// **HSE & performance indicators**	// Reports are normally good, incl. valid ISO 9001 & 14001 certifications
// **Documentation**	// Normally proper documentation
// **Phosgene emission**	// No negative track record observed
// **Appearance**	// Very clean sites (with a lot of freshly painted or newly insulated equipment)
// **Correlations**	// Audit/visit dates sometimes correlate with a maintenance shut-down

Phosgenation, Outsourcing

Lessons learned

// **HAZOP**	sometimes with significant gaps
// **Know-How (technic, safety, material properties)**	• between excellent to limited • Triphosgene use: risks are sometimes underestimated!
// **Detectors**	normally installed, check of alarm levels recommended
// **Phosgene badges**	sometimes “optimized” use
// **SOP´s and MSDS**	• normally available (local language, reading ability of personnel?) • Triphosgene use: normally incomplete or even wrong MSDS
// **Local hazards**	important to check (e.g. monkeys, ...)

Phosgenation, Outsourcing

Lessons learned

// **PPE***	accessibility & use not always sufficient
// **Emissions**	should be checked
// **Safe haven concept**	To be verified
// **Corrosion**	technical equipment and infrastructure should be checked
// **Maintenance**	check blind flanges, gaskets and valves as far as possible
// **Hoses**	occasionally braided hoses might be a topic
// **Electrical installation**	check for proper wiring, insulation and grounding

* Personal Protective Equipment

Phosgenation, Outsourcing

Lessons learned

- **Mitigation measures** — check for completeness and suitability
- **Ventilation concept** — discuss location, suction capacity and, containment (where applicable)

- **Process control system** — ranges from high quality to basic functionality (“no frills”)
- **Sensors** — mostly only basic setup (temperature, pressure, flow, ...)

Summary

- **Safe handling of Phosgene and Triphosgene is possible**
- **There is a tendency of underestimating the risks of Triphosgene**
- **Triphosgene is as toxic as Phosgene → safety concept: Phosgene concept + solid handling & storage!**
- **The literature is sometimes misleading or even poses safety risks; AI based information* or “WIKI” can´t replace expert knowledge**

- **There are reputable CMO companies in the market – but also some highly problematic!**
- **A standard HSE audit might not provide the necessary insights (technical experience in phosgenations and local expertise is a need!)**

CMO: Custom / Contract Manufacturing Organisation

Thank you 🙂