



Pyrophoric material



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A pyrophoric material is a liquid or solid that, even in small quantities and without an external ignition source, can ignite within 5 minutes after coming in contact with air

Example pyrophoric materials include alkali metals and many organometallic compounds such as alkyl magnesiums, alkyl zincs, and of course pyrophoric iron sulfide. Nickle carbonyl in some catalysts



Chemistry of Pyrophorics



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Pyrophoric compound + oxygen (typically air) Oxide of the compound + heat

Sometimes with several intermediate reaction steps

Can be very reactive or very slow to react

Can vary with conditions, humidity, temperature, particle size, degree of disbursement in air, etc.

Bottom line: pyrophoric can be a very elusive and tricky animal to recognize and capture until it bites you



Conditions required to form pyrophoric iron sulfide



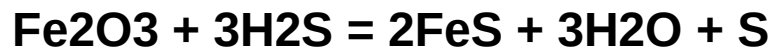
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H₂S concentration > 1% (can form at lower concentrations but typically not in concentrations that are a concern)

Iron scale or rust (FeS)

Less than a 1:1 ratio of oxygen to H₂S (some oxygen is required to form the rust but if insufficient oxygen is present the reaction with H₂S

cannot go to completion)





Where pyrophorics have been known to form in refinery equipment



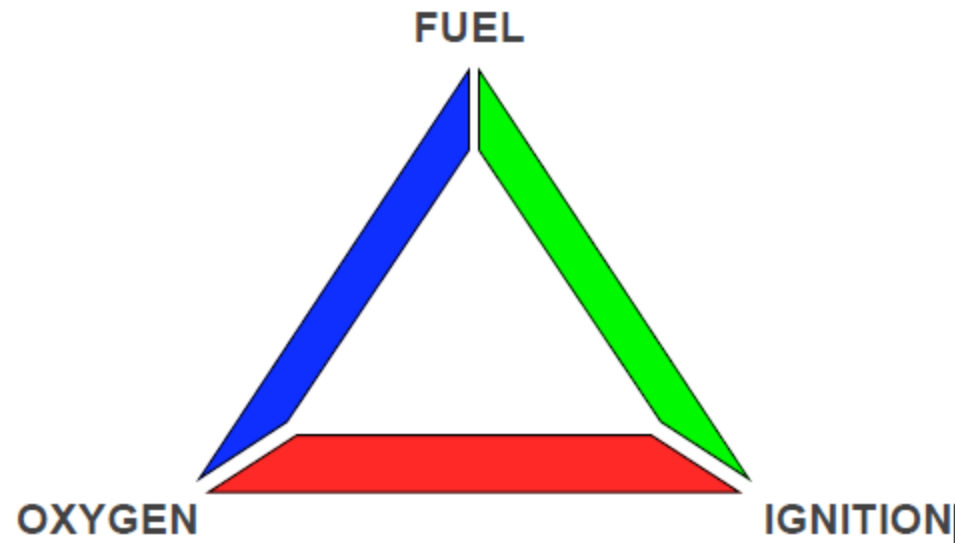
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- Crude oil tanks
- Asphalt tanks
- Sour water tanks
- Vessels in sour service such as coke drums, distillation columns, inlet separators, pig receiver / launchers
- Reactors
- API Separators
- Marine tankers and barges
- Portable tanks and tote bins

Pyrophorics and the Fire Triangle



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Example 1



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- Cargo was light crude with low, sufficient vapors to reduce oxygen
- levels to near zero
- High humidity accelerated rust and formation of pyrophoric iron sulfide
- As crude cargo was off loaded, the normal inerting with engine
- exhaust was halted
- Air was allowed to enter causing the pyrophoric iron sulfide to react,
- heat up, and ignite
- Fortunately, the vapor space was relatively small so the damages were slight and there were no injuries

API Separator explosion.

- An API Separator in an upstream producing facility is in operation in a sour producing area
- The separator is gas blanketed to prevent oxygen from getting inside
- Pyrophoric iron sulfide forms inside the separator
- The separator is taken out of service for maintenance
- No washing or chemical neutralization is performed prior to opening the separator
- Air enters, a pyrophoric reaction takes place, igniting residual hydrocarbon inside the separator

- Most effective method is chemical neutralization before opening the equipment; potassium permanganate solution (typically around a 1% solution, circulate and check for color)
- Keeping the deposits and scale wet until it can be safely removed to a remote area and allowed to dry
- Maintain a constant air ventilation to ensure there is plenty of oxygen to allow the reaction to go to completion, preventing the formation of the pyrophoric intermediates
- Replace components that contain sulfur compounds
- Use nitrogen or other inert gases to keep oxygen out (obviously difficult and adds hazards of its own)
- Quickly move scale and potential pyrophoric deposits to a remote area and monitor in case ignition does occur