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The chemistry of fire and fire suppression

Royale Underhill
Group Leader, Materials Identification and Analysis
Dockyard Laboratory
DRDC Atlantic Research Centre

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Canada

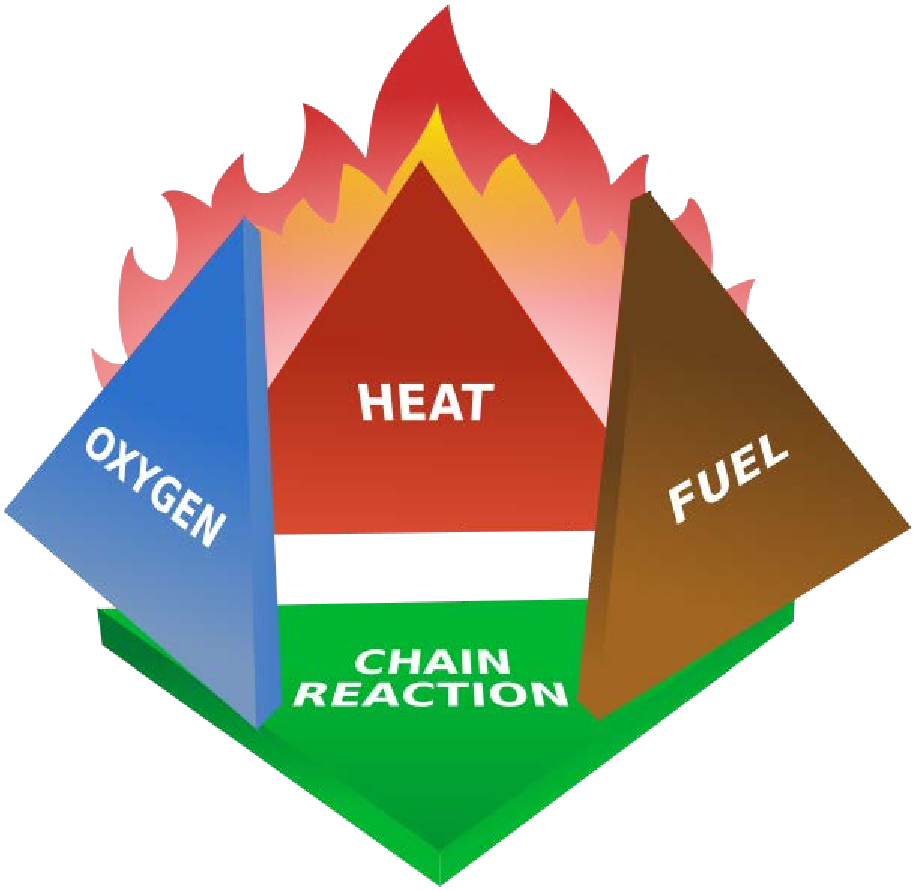
Outline

- Fire Chemistry
  - Fire tetrahedron, ignition, pyrolysis and combustion, quenching
- Case Study – fire investigation
- Damage Control
  - Fire retardant materials
    - Case Study – making polyureas fire resistant
  - Firefighting
    - Automated
    - Manual

Inorganic salts change the colour of the flame

RCN Damage Control School

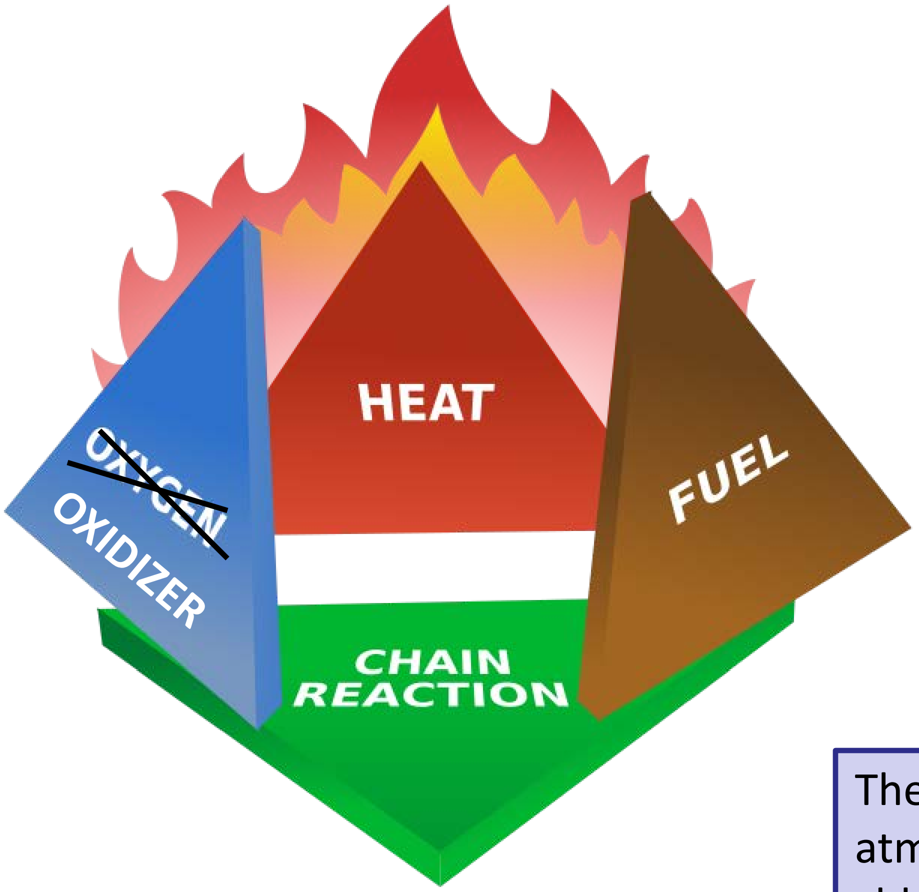
The fire tetrahedron



- Combustion is an exothermic, self-sustaining chemical reaction involving a solid, liquid or gas-phase fuel, its oxidation (usually by atmospheric oxygen), and the emission of energy in the form of heat and light.[1]
- A flame is a chemical reaction in the gas-phase.

1. "Chemistry of Fire", what-when-how: In Depth Tutorials and Information, on http://what-when-how.com/forensic-sciences/chemistry-of-fire

The fire tetrahedron



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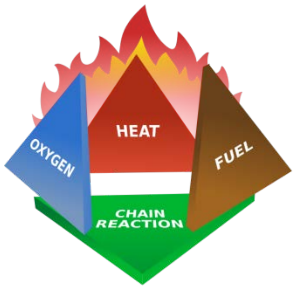
- A flame is a chemical reaction in the gas-phase.

The oxidizer can be something other than atmospheric O_2, examples include nitrates, chlorates and peroxides

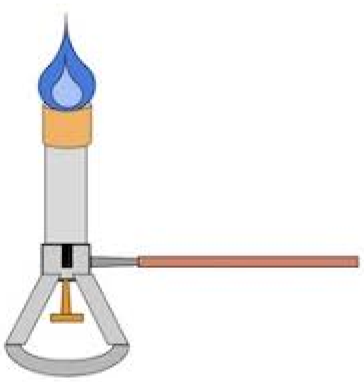
1. "Chemistry of Fire", what-when-how: In Depth Tutorials and Information, on http://what-when-how.com/forensic-sciences/chemistry-of-fire

Combustion (1)

- Combustion is the chemical reaction that sustains a fire



Heat of combustion



$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g) + \Delta H_c$$

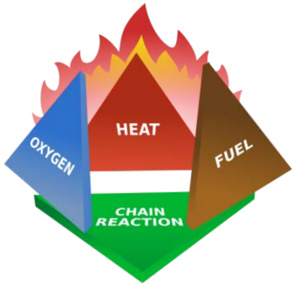
(complete)

Hess's law:

$$\Delta H_c = -\left(\sum \Delta H_{f,products} - \sum \Delta H_{f,\ reactants}\right)$$

Combustion (2)

- Combustion is the chemical reaction that sustains a fire



Heat of combustion

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g) + \Delta H_c$$

(complete)

Soot

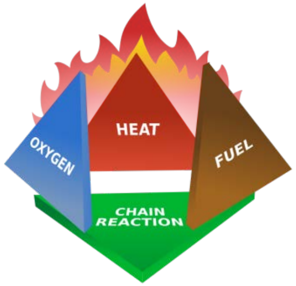
$$6CH_4(g) + 9O_2(g) \rightarrow 2CO_2(g) + 2CO(g) + 12H_2O(g) + 2C(s) + \Delta H_c$$

(incomplete)

limited control over the supply of reactants, and removal of products

$$\Delta H_c = -\left(\sum \Delta H_{f,products} - \sum \Delta H_{f,\ reactants}\right)$$

Combustion (3)



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(complete)

$$6CH_4(g) + 9O_2(g) \rightarrow 2CO_2(g) + 2CO(g) + 12H_2O(g) + 2C(s) + \Delta H_c$$

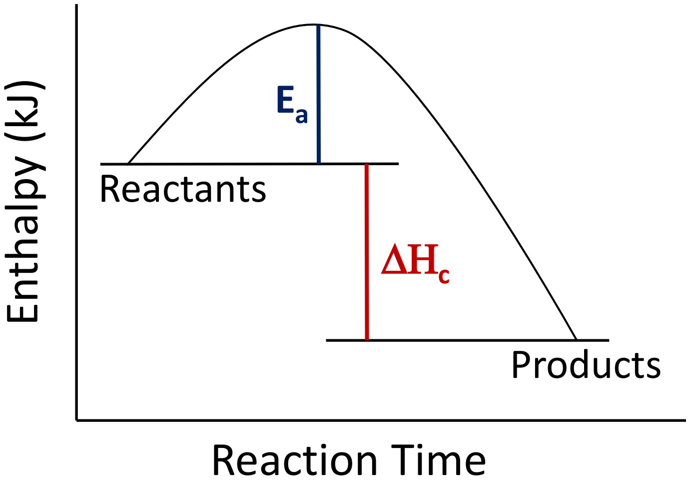
(incomplete)

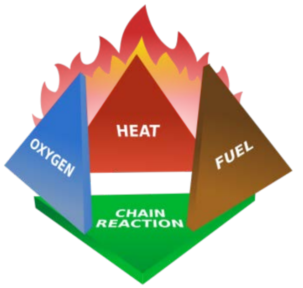
The reaction mechanisms occurring in a flame are complex, and involve free radical chain reactions (OH•, H•, R•)

Ignition

- Overall the reaction gives off heat (ΔH_c) but,
- An activation energy (E_a) is needed to start combustion (an ignition source)
  - Friction
  - Electricity (e.g. lightening, static spark)
  - Focused light (e.g. laser)

Photo credit:
http://allphotoz.blogspot.com





Pyrolysis

- Combustion occurs in the gaseous state, in the flame… what happens if your fuel is a solid?

PYROLYSIS

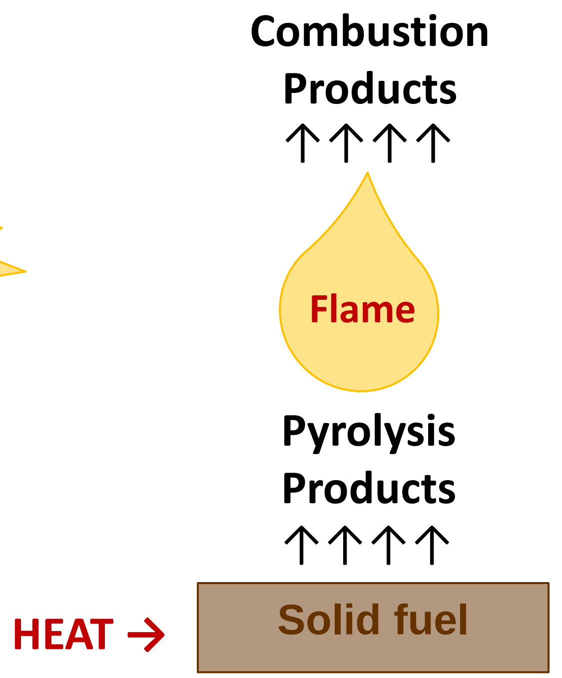
$$6C_{10}H_{15}O_7(s) + E_a \xrightarrow{\text{decomposition}} C_{50}H_{10}O(s) + CH_2O(g)$$

Cellulose

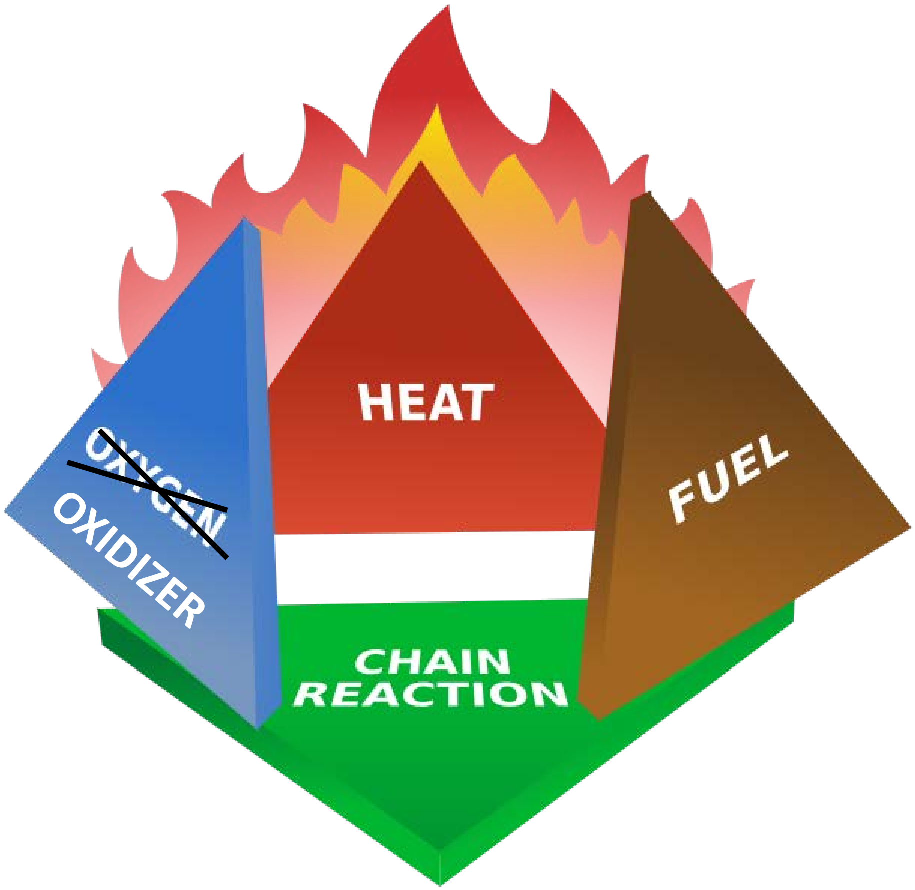
Soot

then COMBUSTION

$$CH_2O(g) + O_2(g) \rightarrow CO_2(g) + H_2O(g) + \text{heat}$$

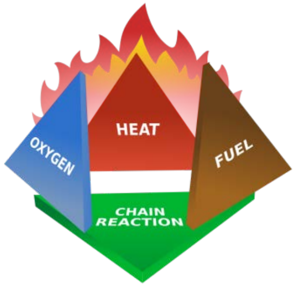


Quenching fire



- In order to put a fire out, you must remove one of the components:
  - Cool (remove heat)
  - Starve (remove fuel)
  - Smother (remove oxidizer)

Quenching fire – cooling



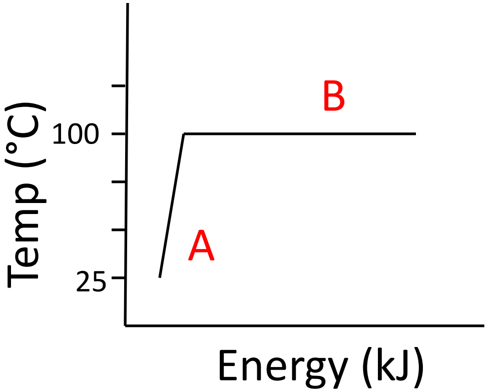
- Water sprinklers – liquid-to-gas phase change absorbs heat:

$$H_2O(l) \rightarrow H_2O(g)$$

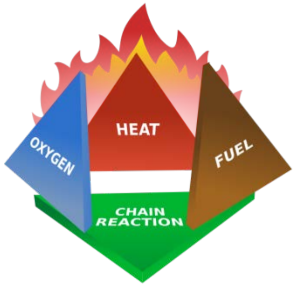
$$C_{water} = 4.18\ J/g°C$$

$$\Delta H_{vap} = 40.67\ kJ/mol$$

- Eg. If you douse a fire with 2L of water starting at 25°C (1 atm):
  - A: raising the temp of the water to 100°C takes 626kJ
  - B: liquid to gas phase takes 4474kJ
  - Total energy absorbed = 5100kJ



Quenching fire – cooling



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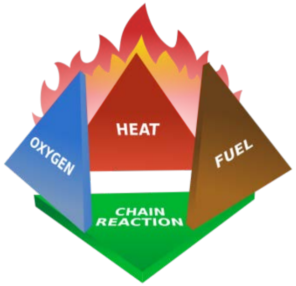
  - A: raising the temp of the water to 100°C takes 626kJ
  - B: liquid to gas phase takes 4474kJ
  - Total energy absorbed = 5100kJ

  - **(enough to put out 325g cellulose burning)**

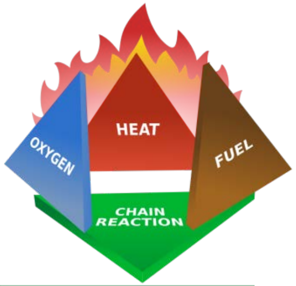
Quenching fire – starvation



- Controlled burn (letting a fire “burn itself out”)
- Mechanical dispersion (rakes, shovels, etc.)
- Water jet

Photo Credit: Australian firefighting service

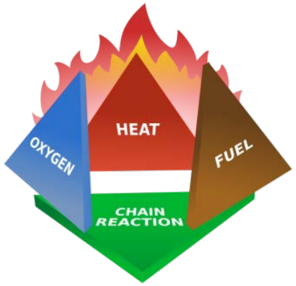
Quenching fire – smothering



- Separate the fuel from the oxidant
  - Blanket
  - Inert Sand/Dirt
  - Foam – has a lower density than a liquid fuel (eg. oil, gasoline), sits on the surface acting as a chemical blanket.
    - separates fuel from flames
    - stops flammable vapour from escaping the surface

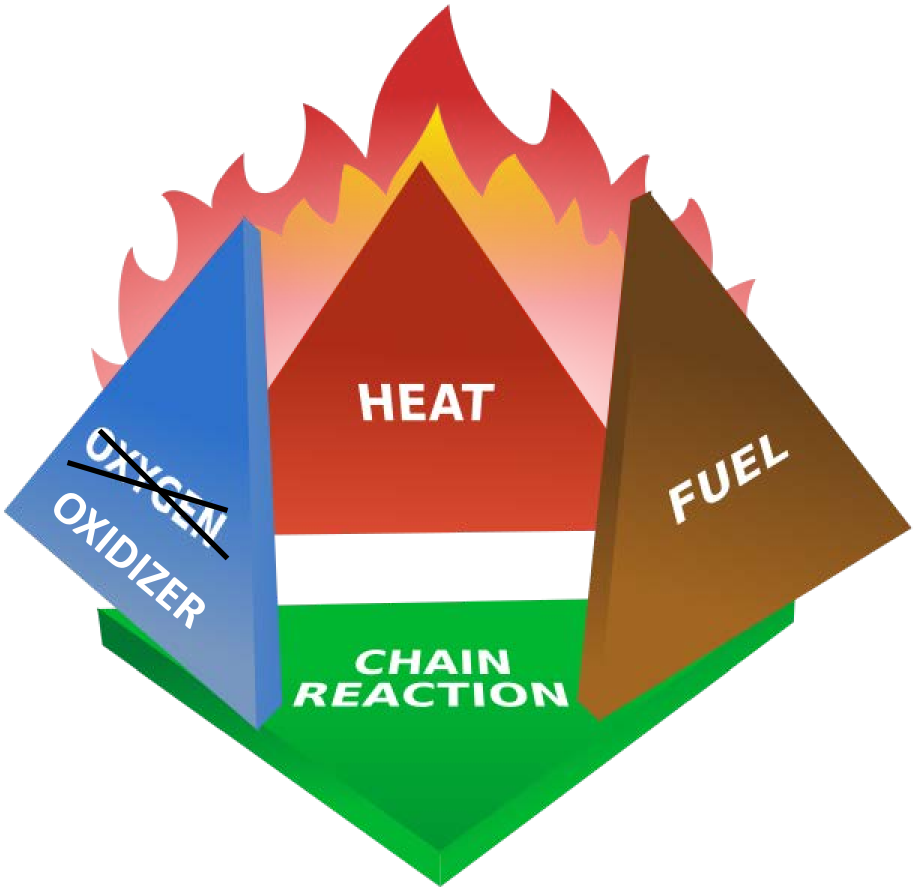
Photo Credit: Fire Apparatus Magazine

Quenching fire – smothering



- Displace the oxidant
  - CO_2 fire extinguisher – denser than air (1.1 g/L), forming a blanket over fuel
  - Water mist systems

Quenching fire



- In order to put a fire out, you must remove one of the components:
  - Cool (remove heat)
  - Starve (remove fuel)
  - Smoother (remove oxidizer)
  - Break the chain reaction

Quenching fire – break the chain reaction

- Halon = 1211 $BrCF_3$ (bromo-trifluoromethane) or 1301 $BrClCF_2$ (bromo-chloro-difluoromethane)
- Used as a "clean agent" – an electrically non-conducting extinguishing agent that does not leave a residue upon evaporation
- Works in concentrations as low as 7%, doesn't displace O_2

$$BrCClF_2 + \text{heat} \rightarrow Br\bullet + \bullet CClF_2$$

$$Br\bullet + \bullet H \rightarrow H\text{–}Br$$

$$\bullet CClF_2 + \bullet R \rightarrow R\text{–}CClF_2$$

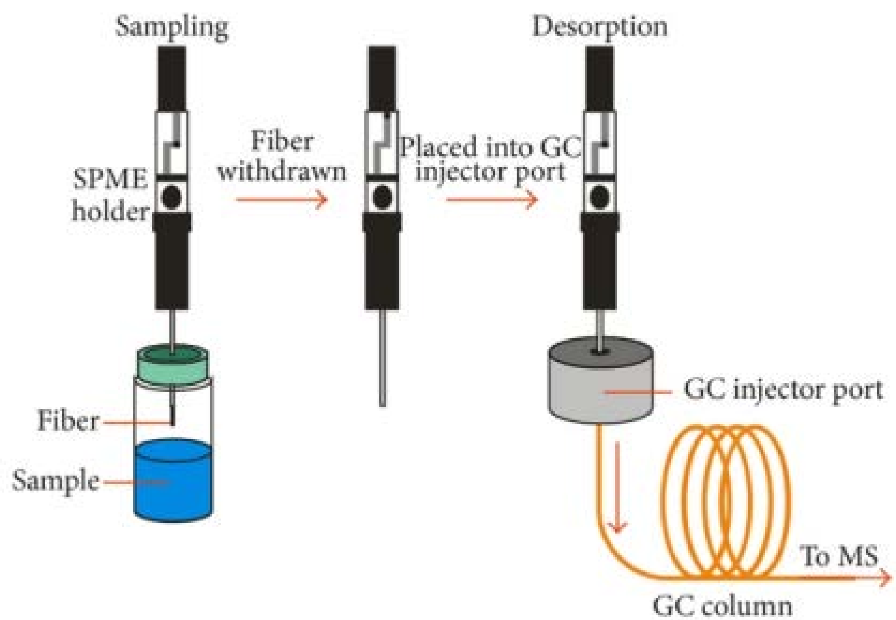
Radicals in flame from combustion reaction

Case Study – Fire Investigation (background)

- A minor fire incident happened in the evening hours when there were minimum personnel around. When the firefighters arrived there was:
  - A melted 5 gal. pail labeled “Ameroid MSD-PAK”, containing packets
  - An empty blackened 1 gal. metal container, the lid was found next to it covered in a “sticky grey residue”
  - The most affected area (burn marks, soot) was around a breaker panel
- Questions:
  - Was this an electrical fire? or something else?
  - How do you determine cause when everything appears to be destroyed in the fire?

Case Study – Fire Investigation (analytical techniques)

- Breaker Panel – Radiography (X-ray)
  - Wiring intact
- Fire pattern –
  - originated at the floor level
- Metal container – Head space analysis (SPME)
  - Trimethyl benzene and dichlorobenzene
- Metal lid – Radiography (X-ray)
  - Cap AND neck of container fused together
- Grey residue – pH and XRD
  - pH 12
  - $Ca(ClO)_2$

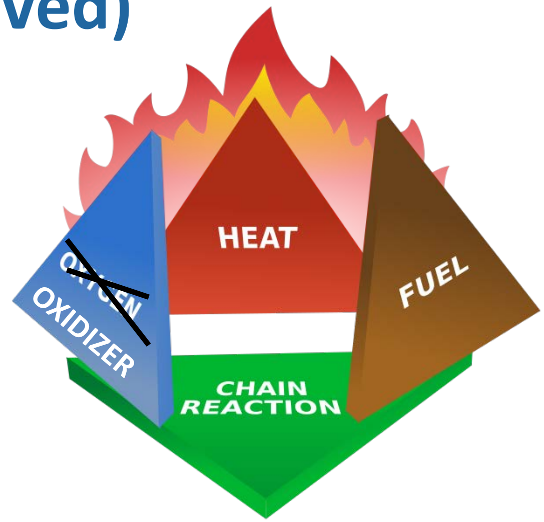


Case Study – Fire Investigation (solved)

- $Ca(ClO)_2$ tablets are used to disinfect wastewater. They are a strong oxidizer.
- (1) grease or diesel;

  (2) Ameroid MSD-PAKs

  (contain starch as a filler)
- The oxidation reaction of hypochlorite with organic solvents is extremely exothermic
- Oxidation reaction between the hypochlorite and the solvents provided chain reaction



Conclusions

- Organic solvents and oxidizing agent were incorrectly stored next to each other.
- The oxidation reaction provided the heat needed to ignite the fire.
- The starch provided fuel to sustain the fire.

Damage Control

"In navies and the maritime industry, **damage control** is the emergency control of situations that may cause the sinking of a watercraft."

-- wikipedia (Jan 16, 2019)

- Damage control = structural stability, flooding, and firefighting

Photo Credit:
RCN Damage Control School

How do you control damage?

REduce risk (of a fire starting)

REsist damage (by firefighting)

REstore seaworthiness (ability to float and move)

STIMarine.com

Firesecurity.com

StatX.com

DSPAflameguard.com

Photo Credit:
RCN Damage Control School

How do you control damage?

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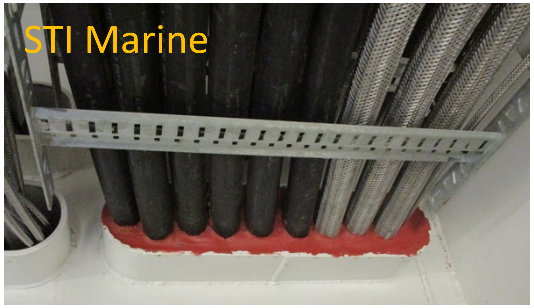
Fire Retardant Materials



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REduce Risk (Fire Retardant Materials)

- Many of the materials around us are organic, and have varying degrees of flammability (eg. coatings, cable sheathing, polymeric insulation)
- Fire Retardant Material Strategies:
  - Cooling:
    - Metal hydroxides ($Al(OH)_3$, $Mg(OH)_2$): decompose endothermically

$$2Al(OH)_{3(s)} \rightarrow Al_2O_{3(s)}, + 3H_2O_{(g)} \quad \Delta H=+1.3kJ/g$$

  - Interrupt combustion reaction:
    - Halogenated compounds (Br & Cl): produce radicals on heating
  - Insulation/isolation:
    - Phosphorous: promotes char formation
    - Crosslinking: promotes char formation
    - Borates: intumescence and promote char

*Intumescent: a material that swells on heating, providing an insulative barrier and off-gasing H_2O

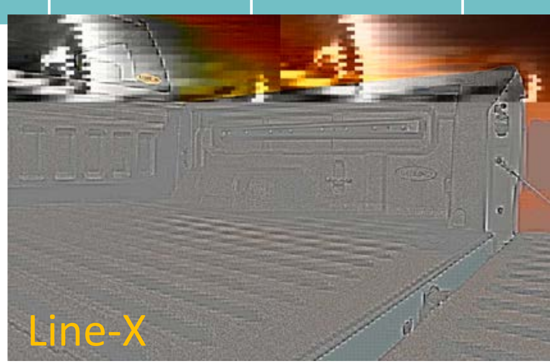
Case Study – Fire resistant polyureas (motivation)

- Problem: New threats to vehicles, ships, buildings
- Challenge: Find lightweight, low cost technology to improve protection (retrofit)

Case Study – Fire resistant polyureas (background)

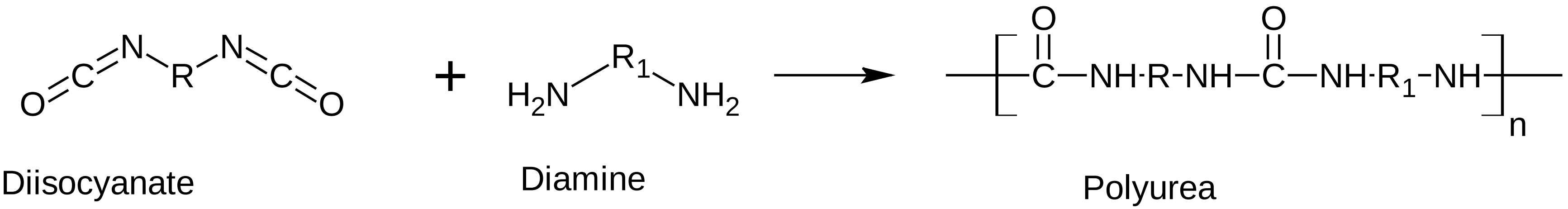
- An Explosion Resistant Coating (ERC) is a thick elastomeric coating designed to mitigate blast/ballistic /fragmentation

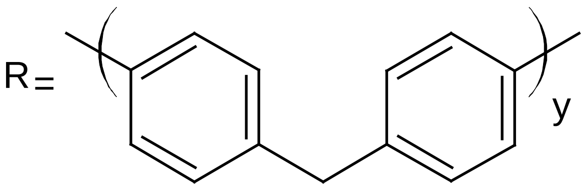
	Time to Ignition (s)	Peak HRR (kW/m²)	Smoke Factor (X10³kW/kg)	Peak mass loss rate (g/m²s)
Base Polyurea	21	1252	657	44
US mil Standard	150	65	7	N/A

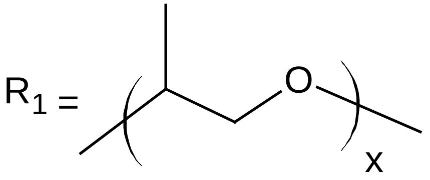


https://coatings.rhinolinings.com/applications/military-blast-mitigation/76

Case Study – Fire resistant polyureas (chemistry)







- Tailorable properties
- 2-part synthesis
- Fast reaction kinetics

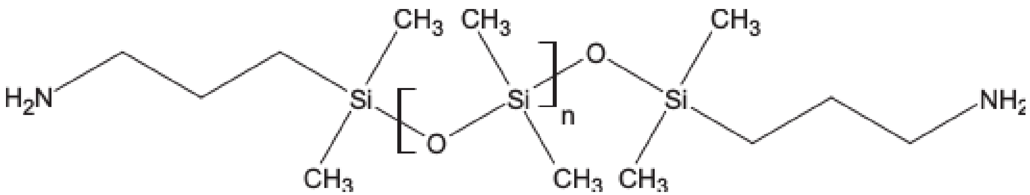
Underhill, et al. “Development of polyureas with improved fire resistance”, J. Fire Sciences, 31(3) 211-226, 2012.

Case Study – Fire resistant polyureas (backbone substitution #1)

- **Phosphorous or Siloxane**
  - Silicon, a direct substitution for carbon in the polymer chain
  - Phosphorous can act as a fire retardant, as well as substituting for carbon

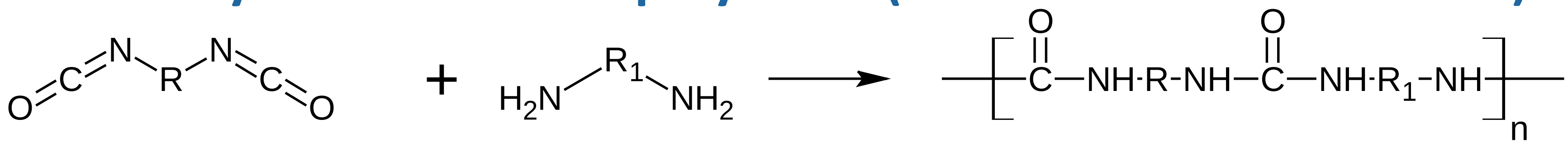
	Time to Ignition (s)	Peak HRR (kW/m^2)	Smoke Factor ($X10^3 kW/kg$)	Peak mass loss rate (g/m^2s)
Base Polyurea	21	1252	657	44
US mil Std	150	65	7	N/A
P	11	286	256	21
Si	14	542	433	23
P+Si	16	352	245	23

- a phosphate containing diisocyanate prepolymer
- a diamine terminated siloxane
- both



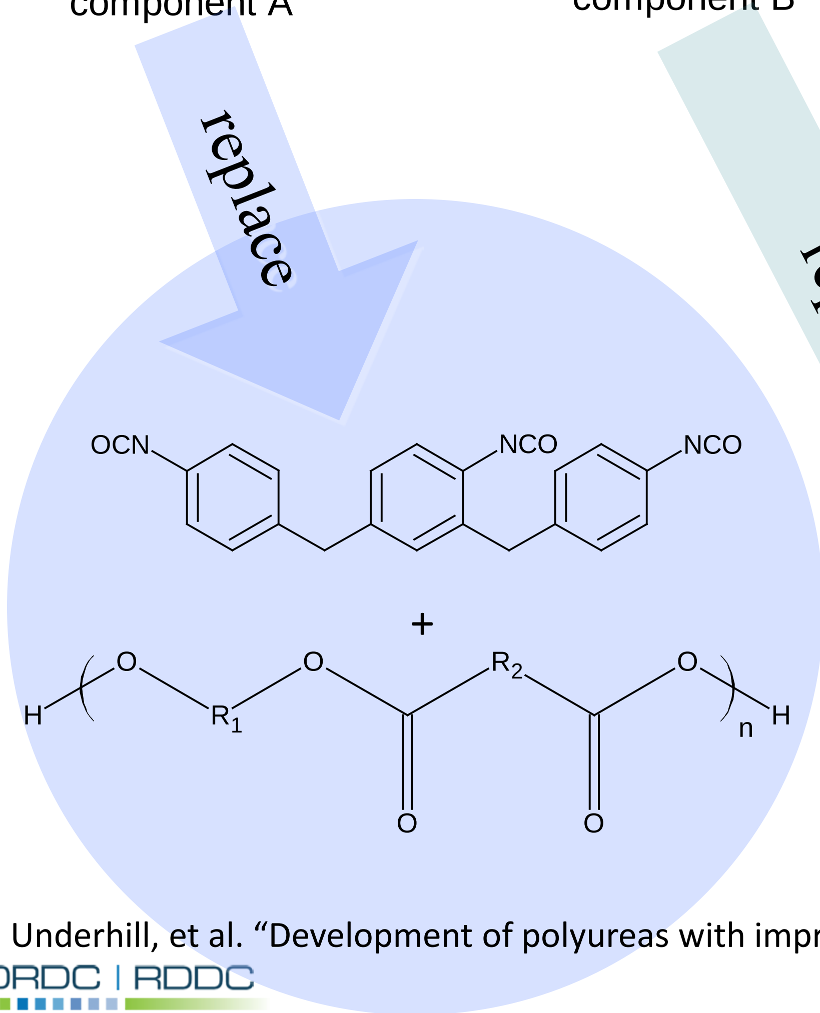
Underhill, et al. “Development of polyureas with improved fire resistance”, J. Fire Sciences, 31(3) 211-226, 2012.

Case Study – Fire resistant polyureas (backbone substitution #2)

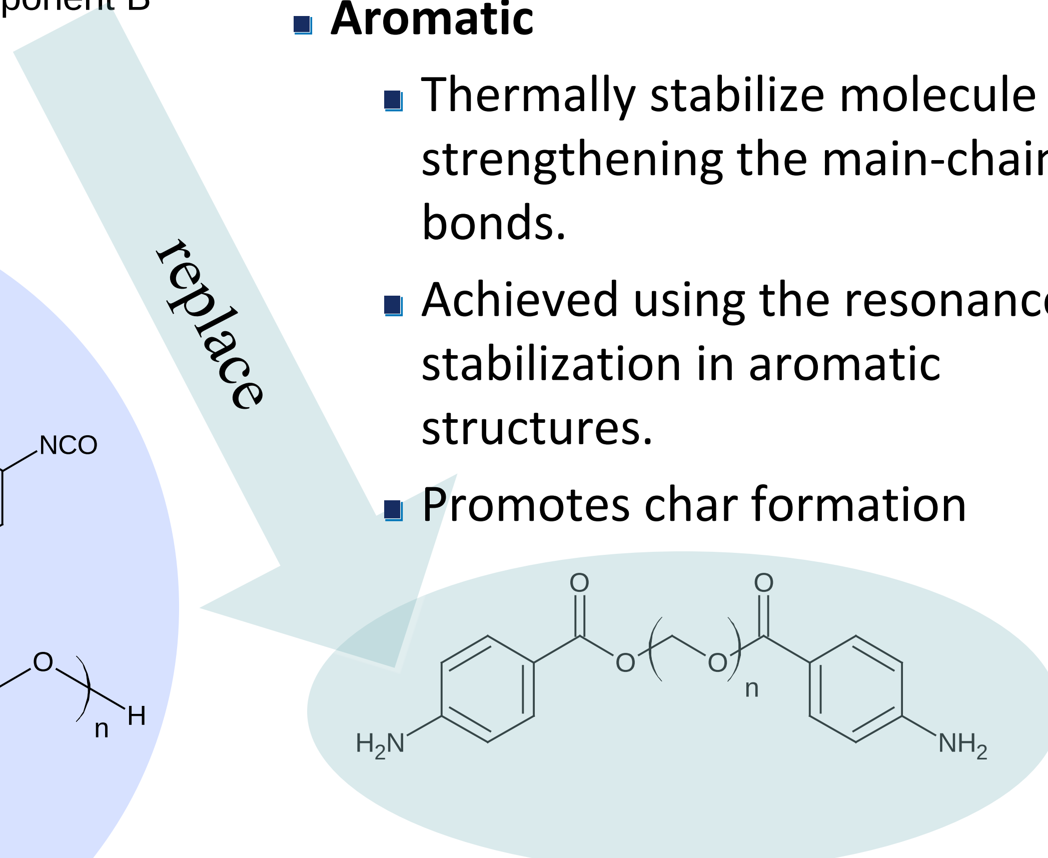


component A

component B



- **Aromatic**
  - Thermally stabilize molecule by strengthening the main-chain bonds.
  - Achieved using the resonance stabilization in aromatic structures.
  - Promotes char formation



Underhill, et al. "Development of polyureas with improved fire resistance", J. Fire Sciences, 31(3) 211-226, 2012.

Case Study – Fire resistant polyureas (backbone substitution #2)

	t_{ign} (s)	Peak HRR (kW/m^2)	Smoke Factor ($\times 10^3$ kW/kg)	Peak Mass Loss Rate (g/m^2s)
US Mil Std	150	60	6.5	n/a
Base polyurea	21	1252	657	44
P+Si	16	352	245	23
Ar1	27	977	483	43
Ar2	26	882	438	43
Ar3	**27**	449	227	30
Ar4	27	494	305	31
Ar5	33	642	274	33
Ar6	30	599	294	28
Ar7	36	997	562	42
Ar8	33	1006	571	43

Underhill, et al. “Development of polyureas with improved fire resistance”, J. Fire Sciences, 31(3) 211-226, 2012.

Case Study – Fire resistant polyureas (flame-retardant additives)

- **Flame-retardant additives**
  - Minerals: Cloisite 30B clay, Zeolite 3A, Talc, Polyhedral oligomeric silsesquioxanes (POSS)
  - Phosphates: Ammonium polyphosphate (APP), Na_3PO_4, $Ca_3(PO_4)_2$
  - Zinc borate (Firebrake^{TM})
  - $Al(OH)_3$
  - $(NH_4)_2SO_4$
- A combination of fire-retardant additives optimizes the desired properties.

Case Study – Fire resistant polyureas (flame-retardant additives)

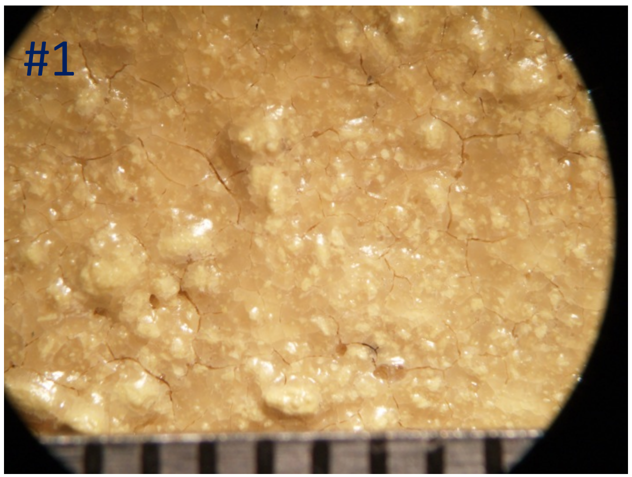
	t_{ign} (s)	Peak HRR (kW/m^2)	Smoke Factor (x 10^3 kW/kg)	Peak Mass Loss Rate (g/m^2s)
US Mil Std	150	60	6.5	n/a
Base polyurea	21	1252	657	44
P+Si	16	352	245	23
P+Si+FRA1	15	302	135	17
P+Si+FRA2	15	222	103	12
P+Si+FRA3	12	208	90	12
P+Si+FRA4	13	164	55	10
P+Si+FRA5	15	202	76	11
P+Si+FRA6	10	450	280	22
P+Si+FRA7	11	205	81	12
P+Si+FRA8	14	200	83	11

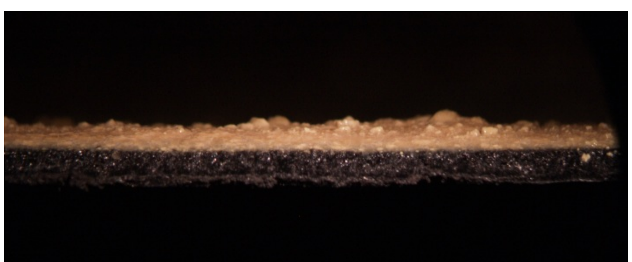
Filler combo:
$Ca_3(PO_4)_2$
$(NH_4)_2SO_4$
APP
talc

Underhill, et al. "Development of polyureas with improved fire resistance", J. Fire Sciences, 31(3) 211-226, 2012.

Case Study – Fire resistant polyureas (ignition barrier coatings)

- Coating #1: polyphenylene based polymer
- Coating #2: polymer modified gypsum based paint





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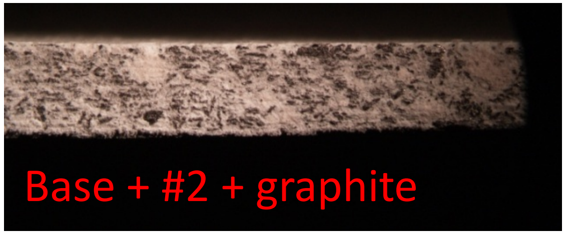
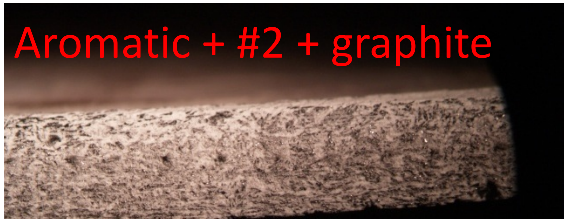
Case Study – Fire resistant polyureas (ignition barrier coatings)

	t_{ign} (s)	Peak HRR (kW/m^2)	Smoke Factor (x 10^3 kW/kg)	Peak Mass Loss Rate (g/m^2s)
US Mil Std	150	60	6.5	n/a
Base polyurea	21	1252	657	44
P+Si	16	352	245	23
Ar3	27	449	227	30
IBC4 (Base + #2 + graphite)	701	50	3	21
IBC10 (Aromatic + #2 + graphite)	560	22	0	17





Underhill, et al. "Development of polyureas with improved fire resistance", J. Fire Sciences, 31(3) 211-226, 2012.

Case Study – Fire resistant polyureas (Conclusions)

- Examined the effects of:
  - change in backbone chemistry (P, Si, Ar)
  - fillers
  - surface coatings
- A combination of all three methods resulted in two formulations that met US military specification for materials in enclosed spaces

	t_{ign} (s)	Peak HRR (kW/m^2)	Smoke Factor ($x\ 10^3$ kW/kg)	Peak Mass Loss Rate (g/m^2s)
US Mil. Spec.	150	60	6.5	n/a
IBC4 (Base + #2 + graphite)	701	50	3	21
IBC10 (Aromatic + #2 + graphite)	560	22	0	17

How do you control damage?

RE duce risk (of a fire starting)

RE sist damage (by firefighting)

RE store seaworthiness (ability to float and move)

StatX.com

StatX.com

DSPAflameguard.com

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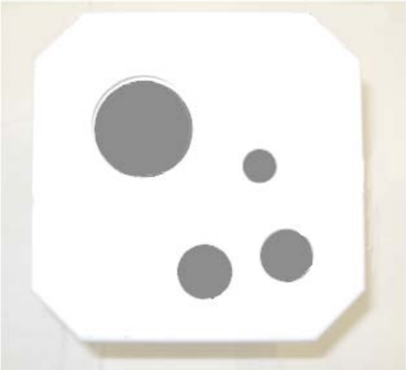
REsist Damage – Automation

- Fire-fighting must be achieved through solutions that require fewer crew members utilising healthy and environmentally-sound products.



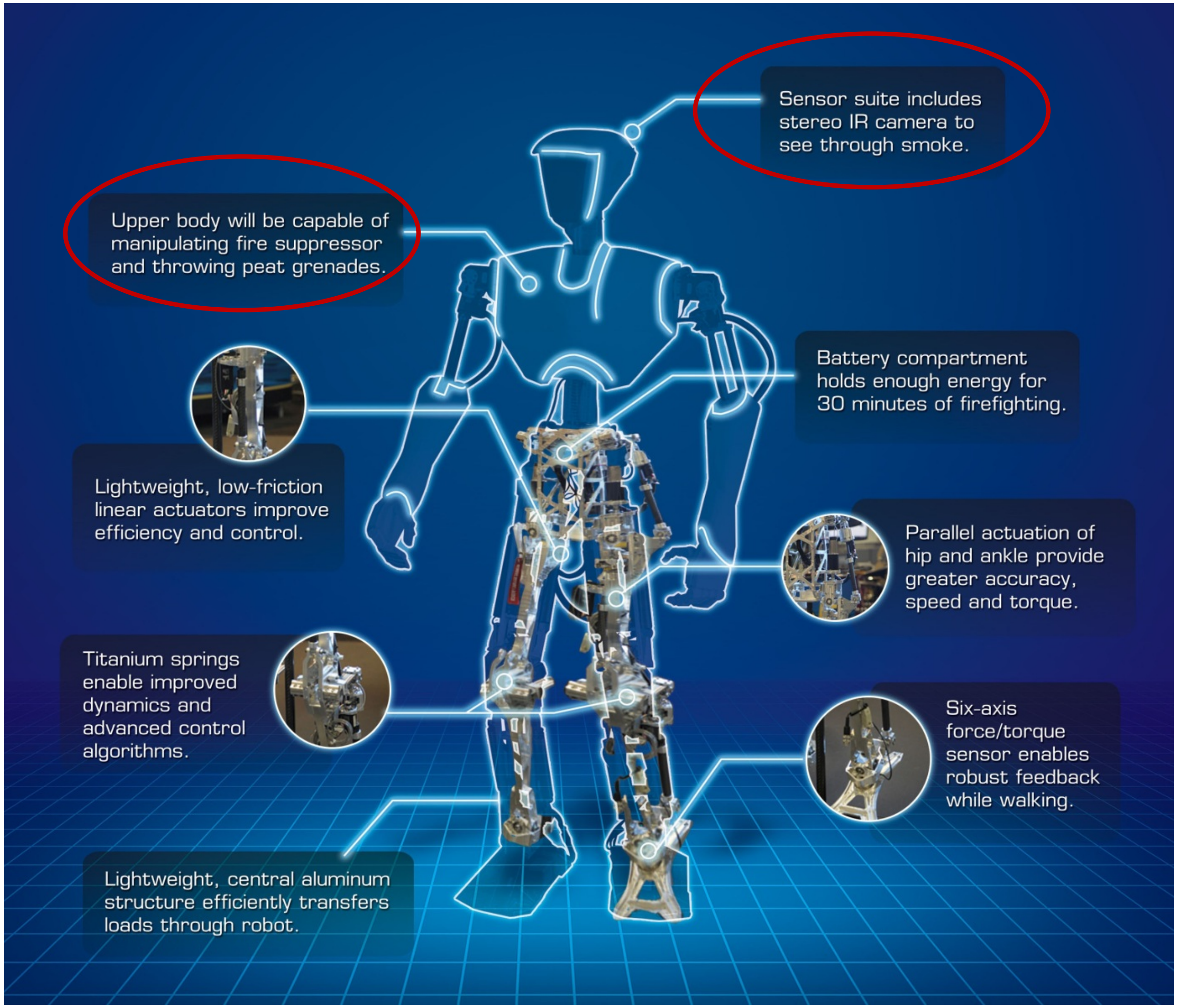
UV
NIR
Microphone
Visible (camera)

multisensor

aerosol

- A number of technologies are being explored (eg. Smart valves, ventilation control)
- Chemistry plays a role:
  - In early detection of fire – making better sensors
  - In developing better fire suppression systems – aerosols, additives for water mist systems

REsist Damage – The future of automation



https://blog.robotiq.com/saffir-the-firefighting-robot

- Shipboard Autonomous Firefighting Robot (SAFFiR):
  - move autonomously throughout the ship
  - interact with personnel
  - fight fires

Photo credit: US Naval Research Laboratories, Virginia Tech, University of Pennsylvania

REsist Damage – Manual Firefighting

- Even with automation, fighting fires still needs human interaction
- Chemistry plays a role:
  - Developing better materials for damage control personnel clothing
    - Eg. Aerogels or phase change materials – gear that is cooling
    - Eg. Silver nanoparticle – gear that reflects heat
    - Eg. fibre-reinforced bismaleimide composites – PPE that is strong as well as insulating
  - Developing better fire fighting technologies
    - Eg. Silica nanoparticle foams – to blanket a fire

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Conclusions

- Combustion (fire) is a complex chemical process.

- Firefighting technologies are as complicated as the fires they fight. They must continue to adapt to address the changes in the construction materials we use, the environmental regulations, and the changes in number of people available to fight fire.

- Firefighting technologies must draw on materials, research and understanding from a variety of fields to accomplish one mission: to more effectively fight fires and save lives.


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Questions?

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SCIENCE, TECHNOLOGY AND KNOWLEDGE FOR CANADA'S DEFENCE AND SECURITY

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