Phenolic resins

Thermosetting resins obtained by polycondensation of phenols with aldehydes in the presence of acid or basic catalysts with removal of water molecules.

Two main families (RESOLS and NOVOLACS) obtained from different:

- formaldehyde / phenol ratio

- solution pH

- reaction temperature

Phenolic resins are the first commercial plastics introduced in 1909 under the name of bakelite.

Phenol and Formaldehyde

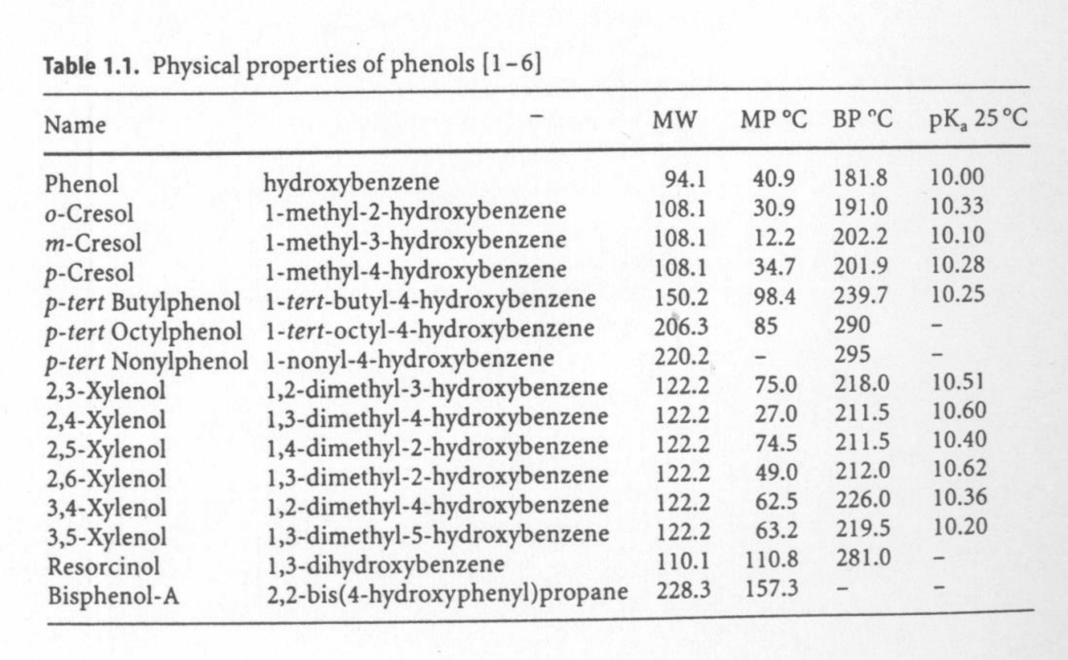
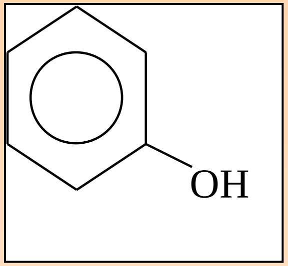


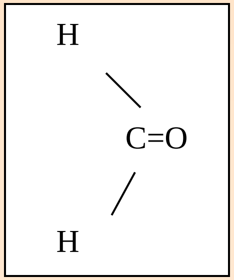
Table 1.1. Physical properties of phenols [1–6]

Name	–	MW	MP °C	BP °C	pK_a 25 °C
Phenol	hydroxybenzene	94.1	40.9	181.8	10.00
o-Cresol	1-methyl-2-hydroxybenzene	108.1	30.9	191.0	10.33
m-Cresol	1-methyl-3-hydroxybenzene	108.1	12.2	202.2	10.10
p-Cresol	1-methyl-4-hydroxybenzene	108.1	34.7	201.9	10.28
p-*tert* Butylphenol	1-*tert*-butyl-4-hydroxybenzene	150.2	98.4	239.7	10.25
p-*tert* Octylphenol	1-*tert*-octyl-4-hydroxybenzene	206.3	85	290	–
p-*tert* Nonylphenol	1-nonyl-4-hydroxybenzene	220.2	–	295	–
2,3-Xylenol	1,2-dimethyl-3-hydroxybenzene	122.2	75.0	218.0	10.51
2,4-Xylenol	1,3-dimethyl-4-hydroxybenzene	122.2	27.0	211.5	10.60
2,5-Xylenol	1,4-dimethyl-2-hydroxybenzene	122.2	74.5	211.5	10.40
2,6-Xylenol	1,3-dimethyl-2-hydroxybenzene	122.2	49.0	212.0	10.62
3,4-Xylenol	1,2-dimethyl-4-hydroxybenzene	122.2	62.5	226.0	10.36
3,5-Xylenol	1,3-dimethyl-5-hydroxybenzene	122.2	63.2	219.5	10.20
Resorcinol	1,3-dihydroxybenzene	110.1	110.8	281.0	–
Bisphenol-A	2,2-bis(4-hydroxyphenyl)propane	228.3	157.3	–	–

PHENOLS are a family of aromatic compounds with the hydroxyl group -OH bound directly to the aromatic ring. They are colorless solids and behave as weak acids.



FORMALDEHYDE is a very reactive aliphatic aldehyde. It is a colorless gas with a pungent smell



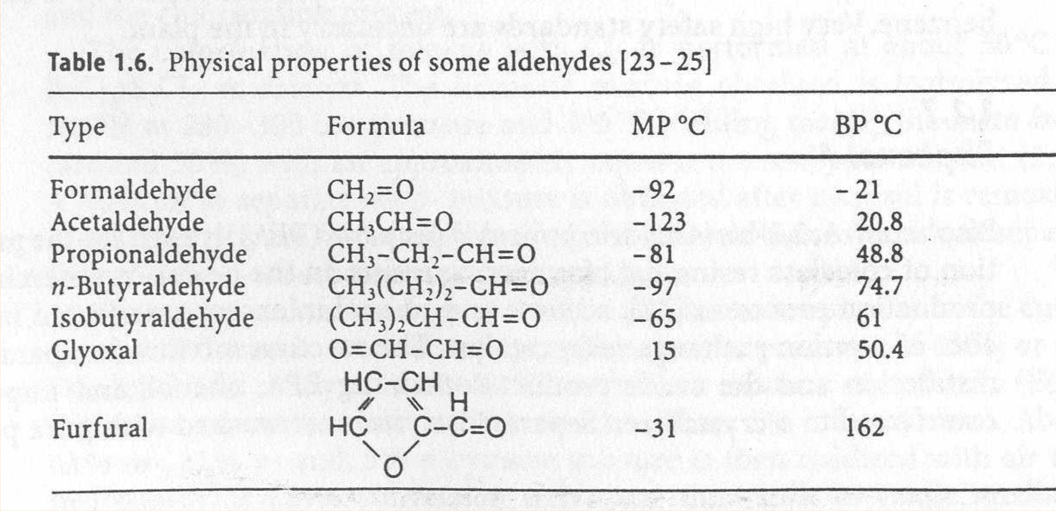
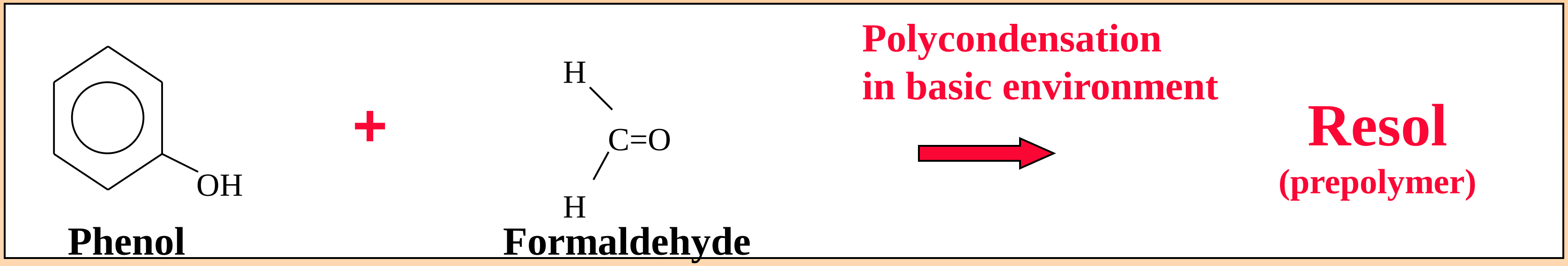


Table 1.6. Physical properties of some aldehydes [23–25]

Type	Formula	MP °C	BP °C
Formaldehyde	$CH_2{=}O$	–92	–21
Acetaldehyde	$CH_3CH{=}O$	–123	20.8
Propionaldehyde	$CH_3{-}CH_2{-}CH{=}O$	–81	48.8
n-Butyraldehyde	$CH_3(CH_2)_2{-}CH{=}O$	–97	74.7
Isobutyraldehyde	$(CH_3)_2CH{-}CH{=}O$	–65	61
Glyoxal	$O{=}CH{-}CH{=}O$	15	50.4
Furfural	HC–CH HC C–C=O H O	–31	162

Phenolic resins: RESOL

Polycondensation with excess of formaldehyde $\frac{\text{formaldehyde}}{\text{phenol}} > 1 \quad (1.2-3)$



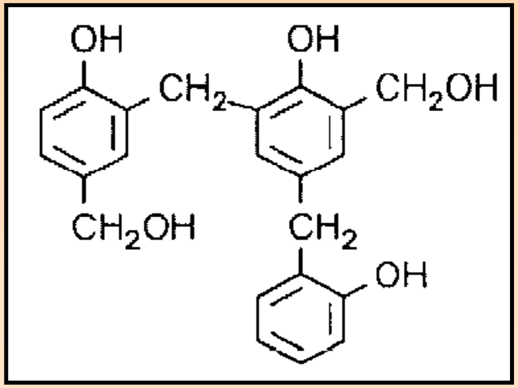
Phenol

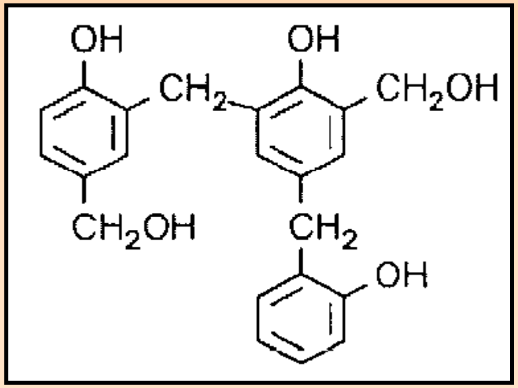
Formaldehyde

Polycondensation in basic environment

Resol

(prepolymer)





Curing at $T \geq 120°\ C$

Crosslinked polymer + H_2O

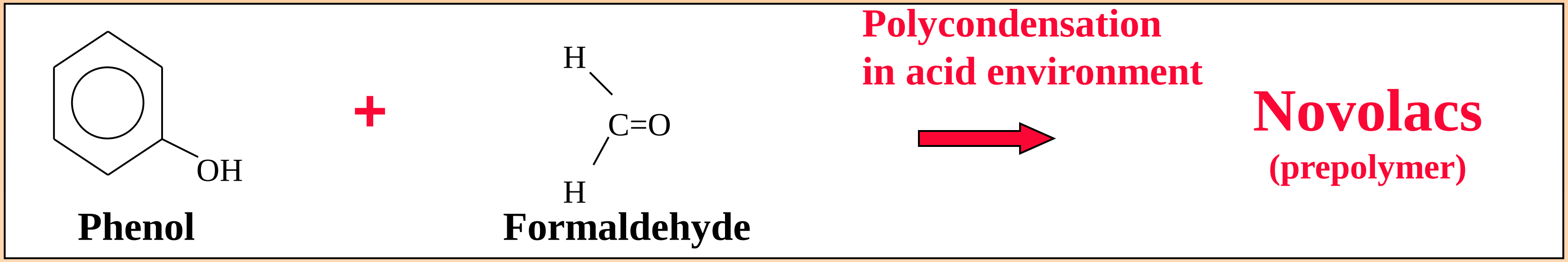
Uncured RESOL:

- **M_w= 500-5000 g/mol**
- **liquid (Suitable as composite matrix)**

•crosslinking without hardeners

Phenolic resins: NOVOLAC

Polycondensation at low formaldehyde content $\frac{\text{formaldehyde}}{\text{phenol}} < 1 \quad (0.75-0.85)$



Phenol

Formaldehyde

Polycondensation in acid environment

Novolacs

(prepolymer)

Curing at $T \geq 160^\circ$ C with hexamethylenetetramine (HEXA)

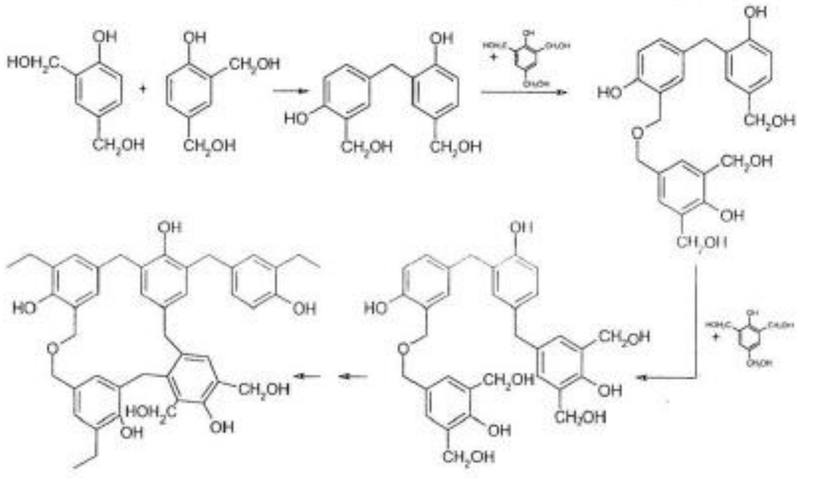
Crosslinked polymer + H_2O

Uncured Novolac:

- **lower molecular weigth than resols**
- **solid (not suitable as composite matrix)**
- **crosslinking with hardeners (hexamethylenetetramine)**

Phenolic resins: Resoles and Lignin

Crosslinking by polycondensation



phenolic resin - artificial network based on condensation of methylolated phenol

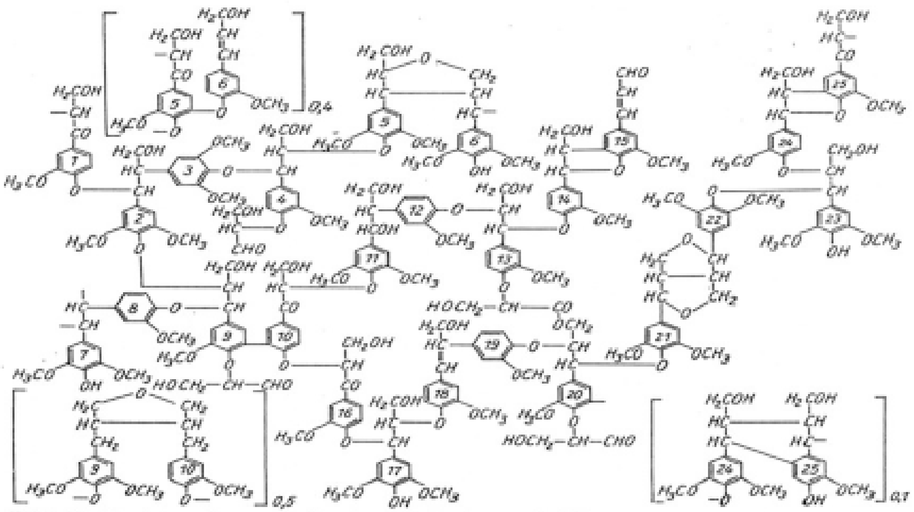


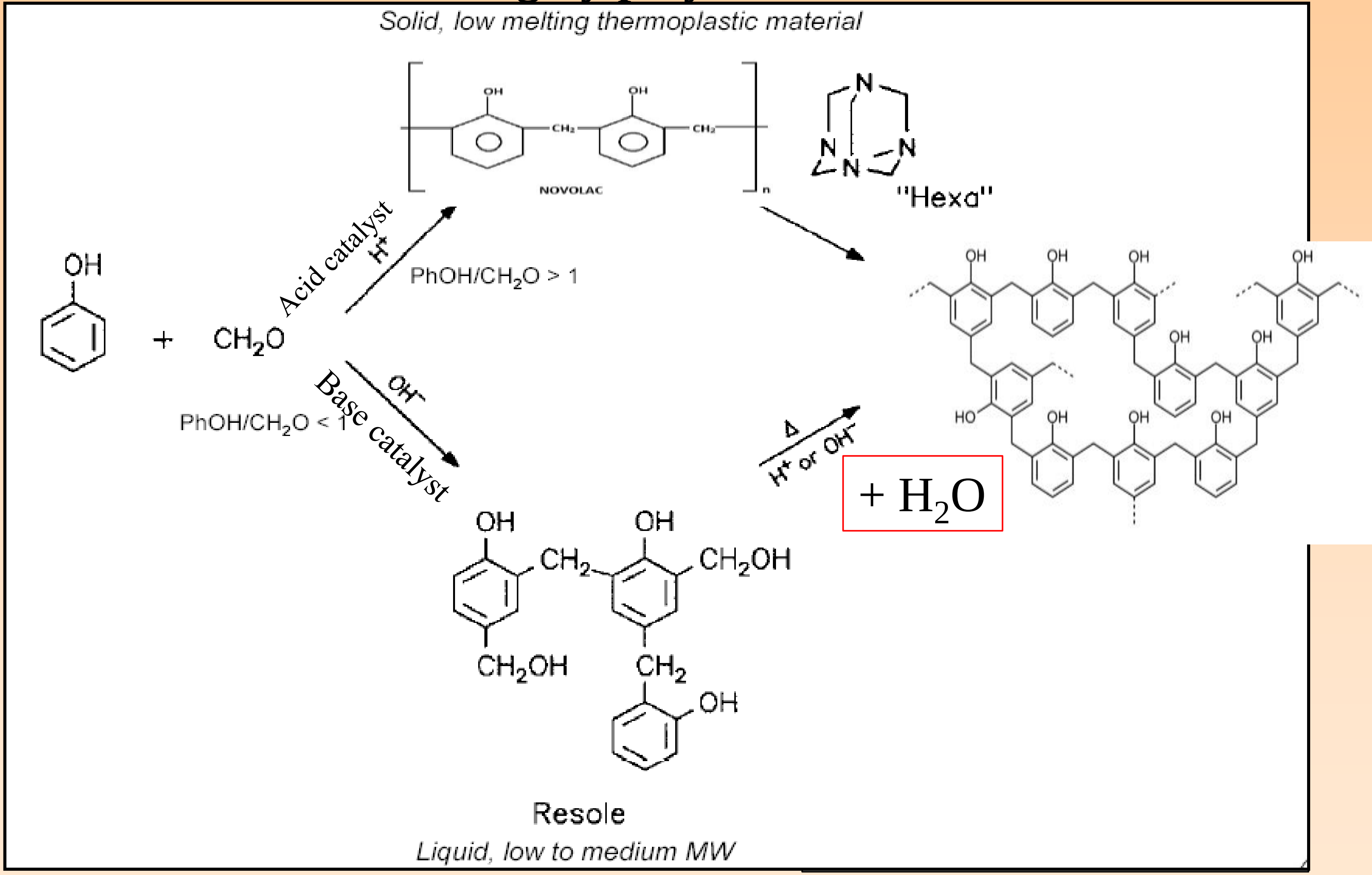
Bild 48. Strukturschema des Buchenholzlignins nach Nimz

Lignin is 15%-25% of wood

lignin – natural network molecule based on phenolic units

Phenolic resins: synthesis and curing

Crosslinking by polycondensation



Phenolic resins: properties

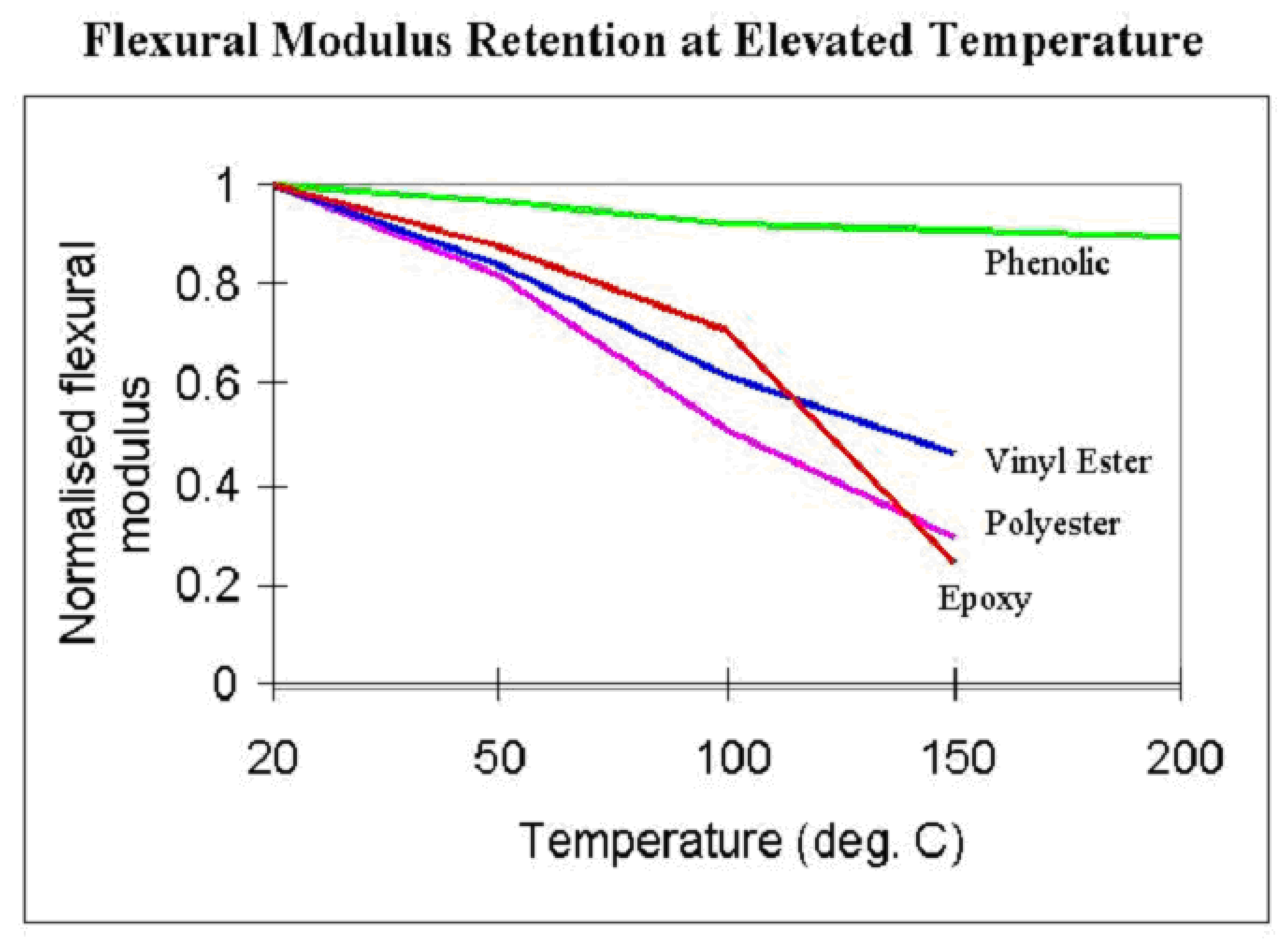
Benefits :

- **Good thermal resistance (HDT=200-260° C)**
- **Good dimensional stability (even at high temperature)**
- **High creep resistance**
- **High adhesion properties**
- **Good chemical resistance**
- **High hardness**
- **High compression strength**
- **Good electric insulator**
- **Low flammability and smoke generation**
- **Low moisture absorption**
- **Low cost**

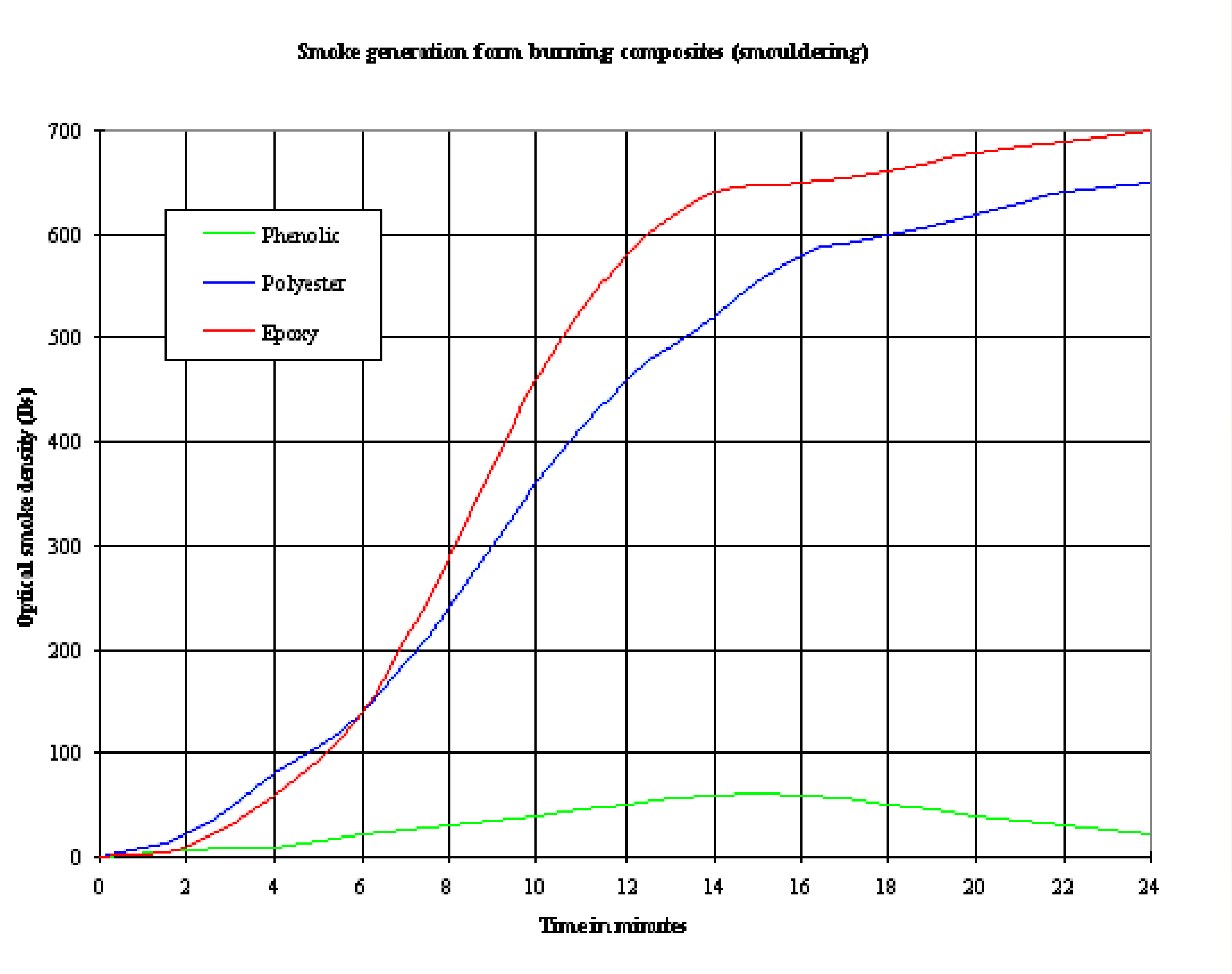
Drawbacks:

- **Production of by-products (Water) during the polycondensation**
- **Instability to UV radiation**
- **Low strain at break**

Phenolic resins: mechanichal properties



Phenolic resins: fire resistance



Ds a quantity inversely proportional to optical transmittance, accounting for calibration and geometry of the experimental set up

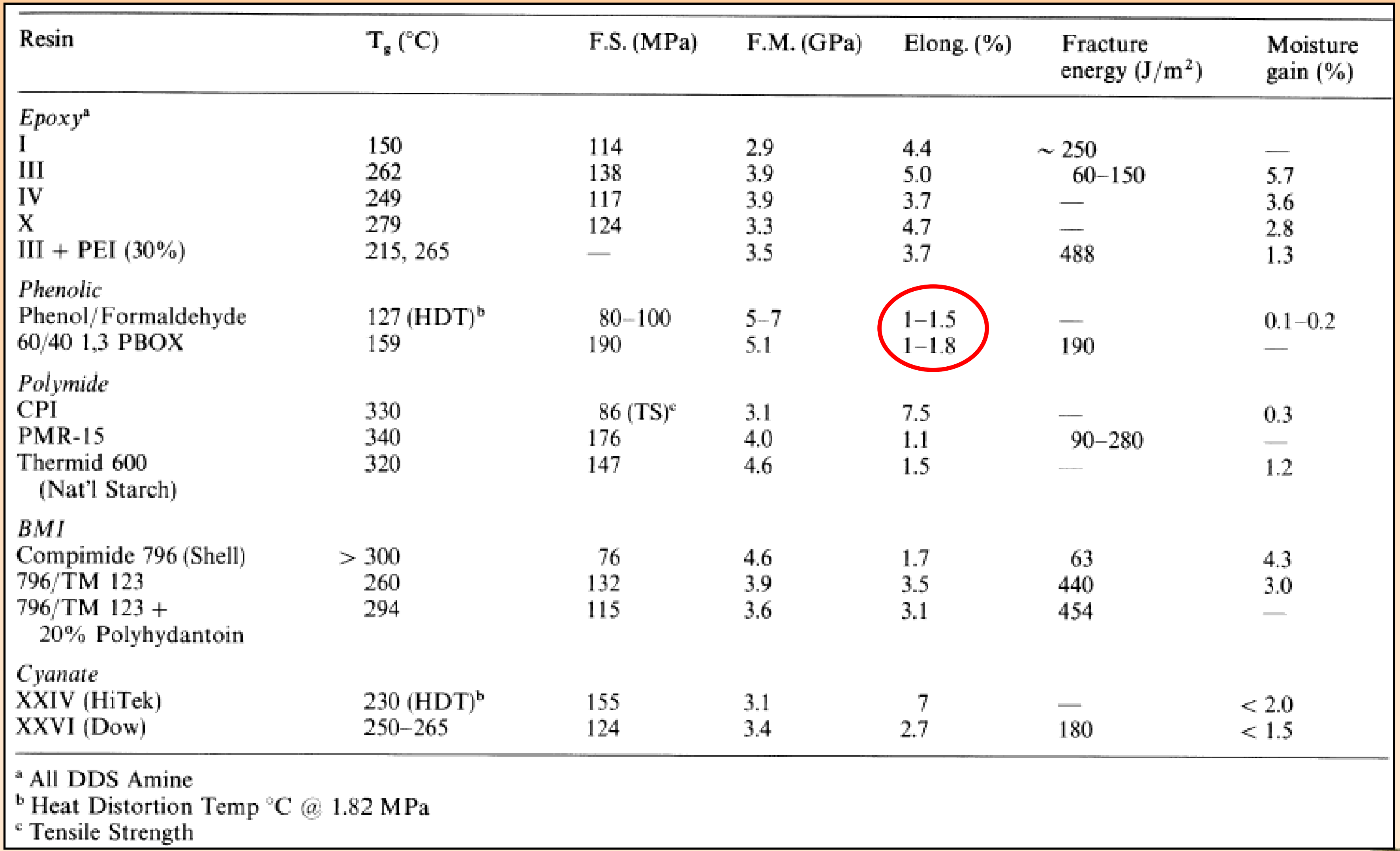
Phenolic resins: applications

- **Almost 50% of the applications is in the field of thermoforming adhesives for plywood.**

- **Heat resistant materials**
  - Thermally insulating panels
  - High temperature resistant composites
  - Automotive components
- **Fire resistance properties**
  - Marine and off-shore applications
  - Inner and outer panels for railway vehicles
  - Electrical applications
  - Inner panels for aircrafts
  - Heat shields for nozzles and aerospace applications

- **Composites resistant to corrosive or acid environments**
- **Industrial laminates reinforced with glass fabrics**

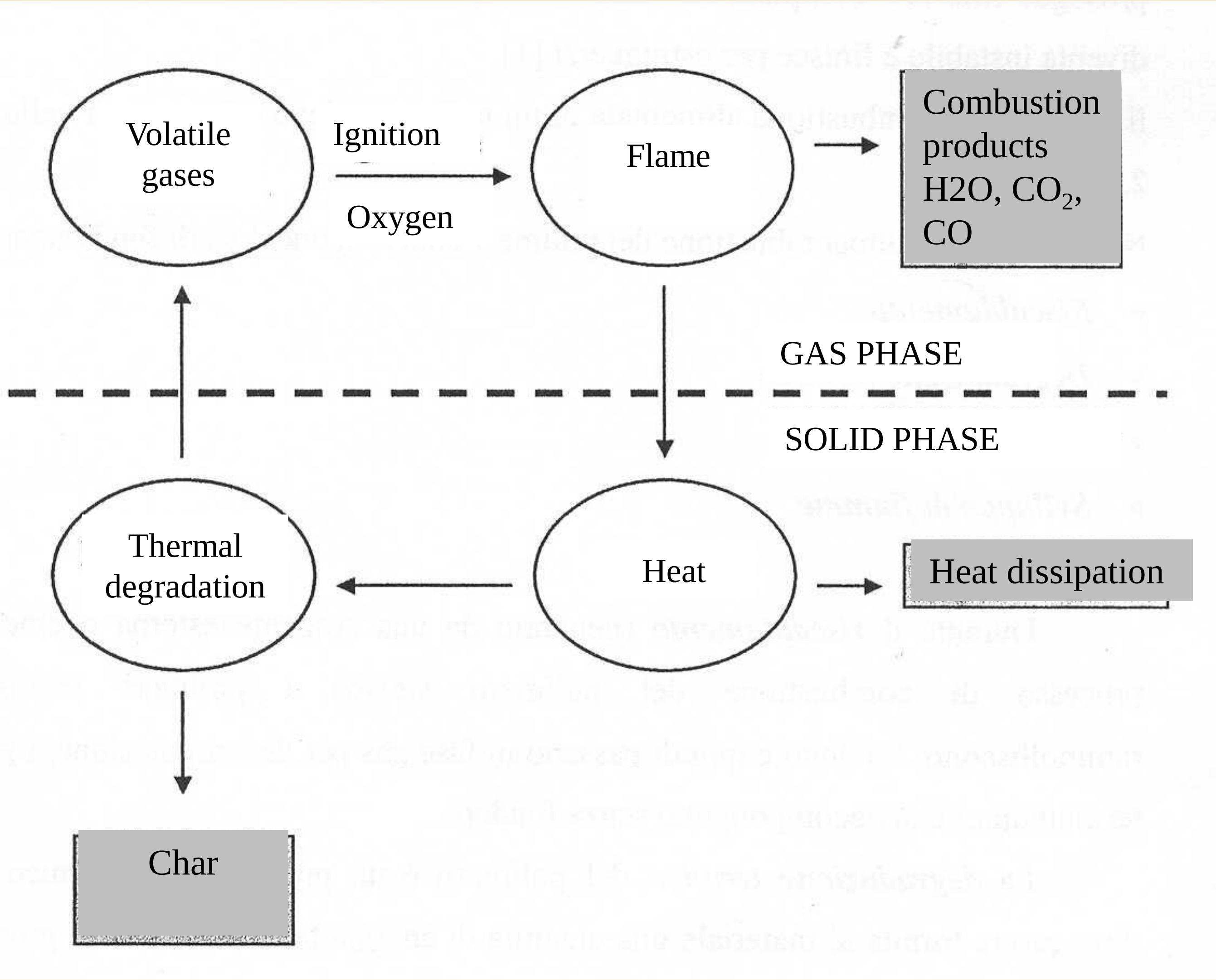
Thermosetting matrices: property comparison



Resin	T_g (°C)	F.S. (MPa)	F.M. (GPa)	Elong. (%)	Fracture energy (J/m²)	Moisture gain (%)
Epoxy[a]						
I	150	114	2.9	4.4	~ 250	—
III	262	138	3.9	5.0	60–150	5.7
IV	249	117	3.9	3.7	—	3.6
X	279	124	3.3	4.7	—	2.8
III + PEI (30%)	215, 265	—	3.5	3.7	488	1.3
Phenolic						
Phenol/Formaldehyde	127 (HDT)[b]	80–100	5–7	1–1.5	—	0.1–0.2
60/40 1,3 PBOX	159	190	5.1	1–1.8	190	—
Polymide						
CPI	330	86 (TS)[c]	3.1	7.5	—	0.3
PMR-15	340	176	4.0	1.1	90–280	—
Thermid 600 (Nat'l Starch)	320	147	4.6	1.5	—	1.2
BMI						
Compimide 796 (Shell)	> 300	76	4.6	1.7	63	4.3
796/TM 123	260	132	3.9	3.5	440	3.0
796/TM 123 + 20% Polyhydantoin	294	115	3.6	3.1	454	—
Cyanate						
XXIV (HiTek)	230 (HDT)[b]	155	3.1	7	—	< 2.0
XXVI (Dow)	250–265	124	3.4	2.7	180	< 1.5

[a] All DDS Amine
[b] Heat Distortion Temp °C @ 1.82 MPa
[c] Tensile Strength

Combustion cycle in polymers



Volatile gases

Ignition

Oxygen

Flame

Combustion products H_2O, CO_2, CO

GAS PHASE

SOLID PHASE

Thermal degradation

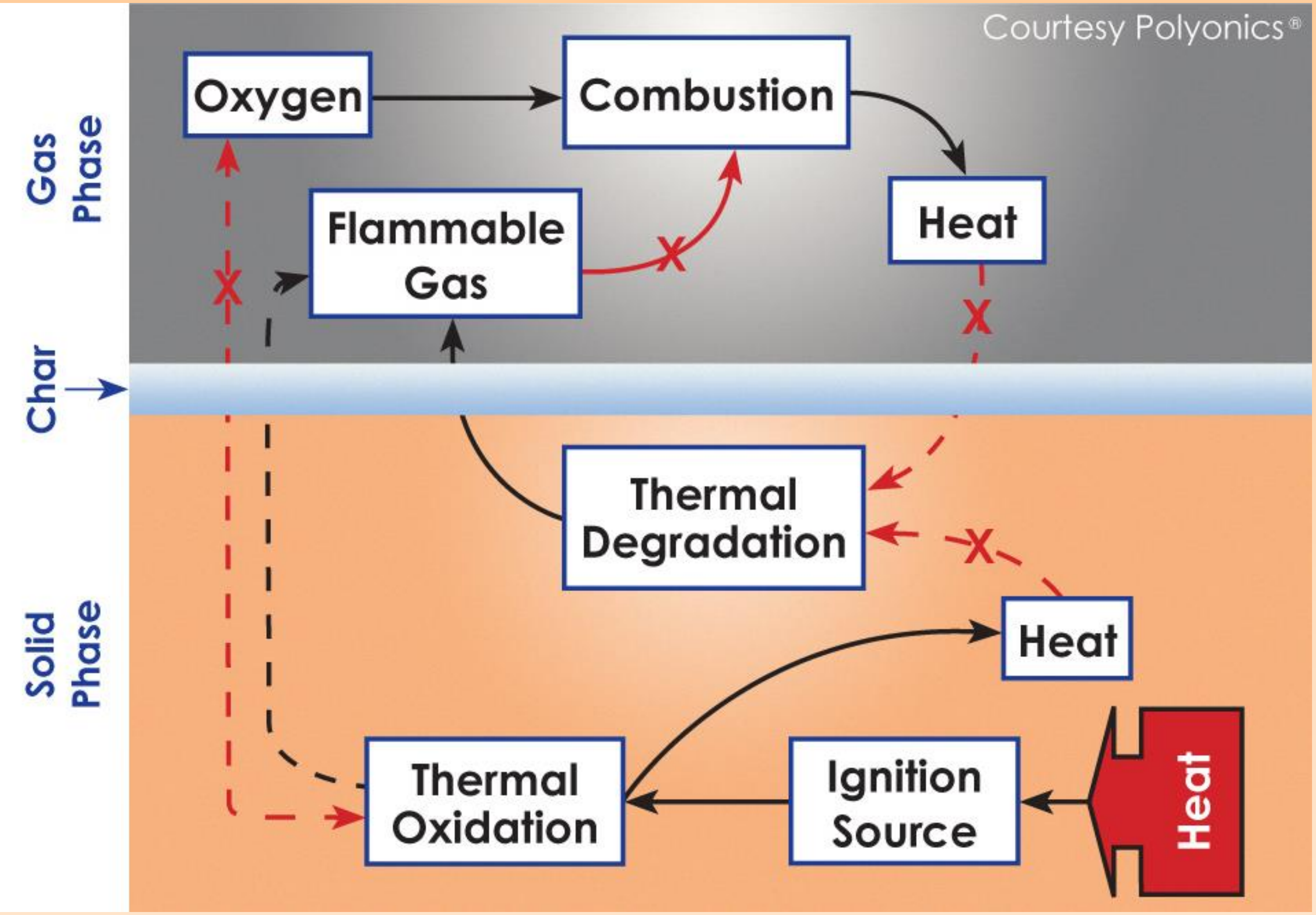
Heat

Heat dissipation

Char

Heating ⇒ Thermal degradation ⇒ Ignition of volatiles ⇒ Flame development

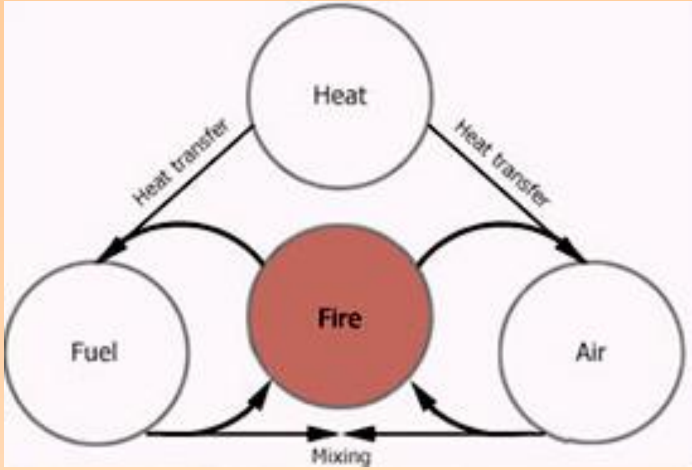
Combustion cycle in polymers



Heating ⇒ Thermal degradation ⇒ Ignition ⇒ Flame development

Heat causes thermal degradation of polymers which in turn generates flammable gasses (fuel).
Burning occurs when this fuel combines with oxygen in the presence of an ignition source.
The process generates additional heat and gases creating a self-sustaining burn cycle.

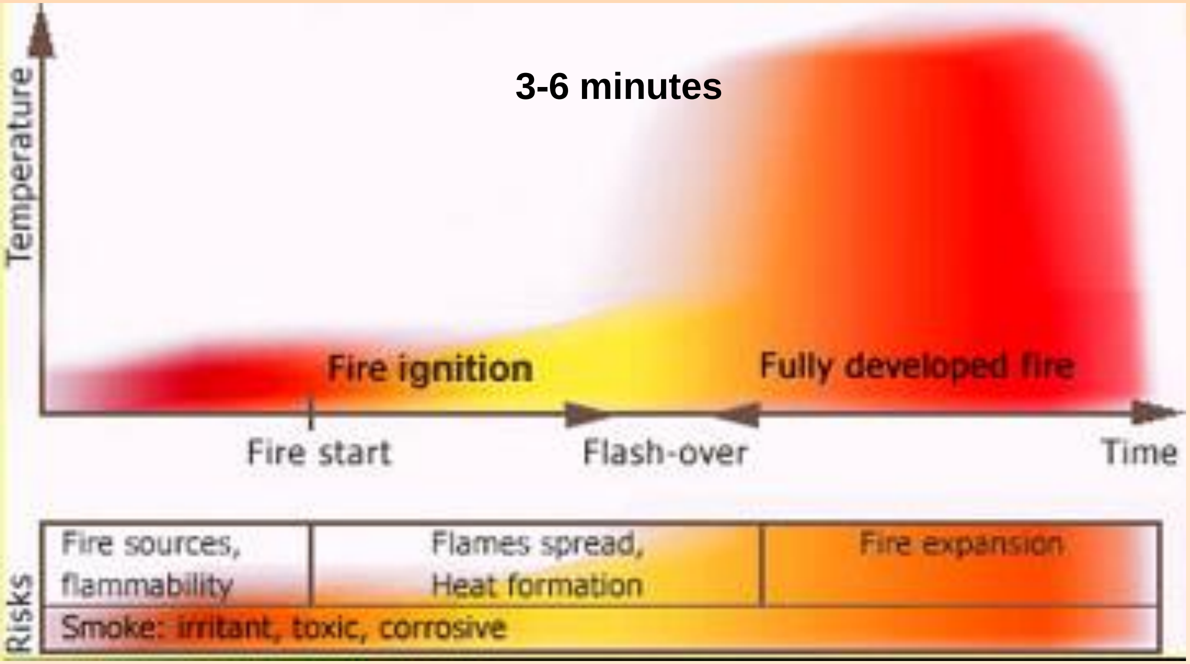
Fire development



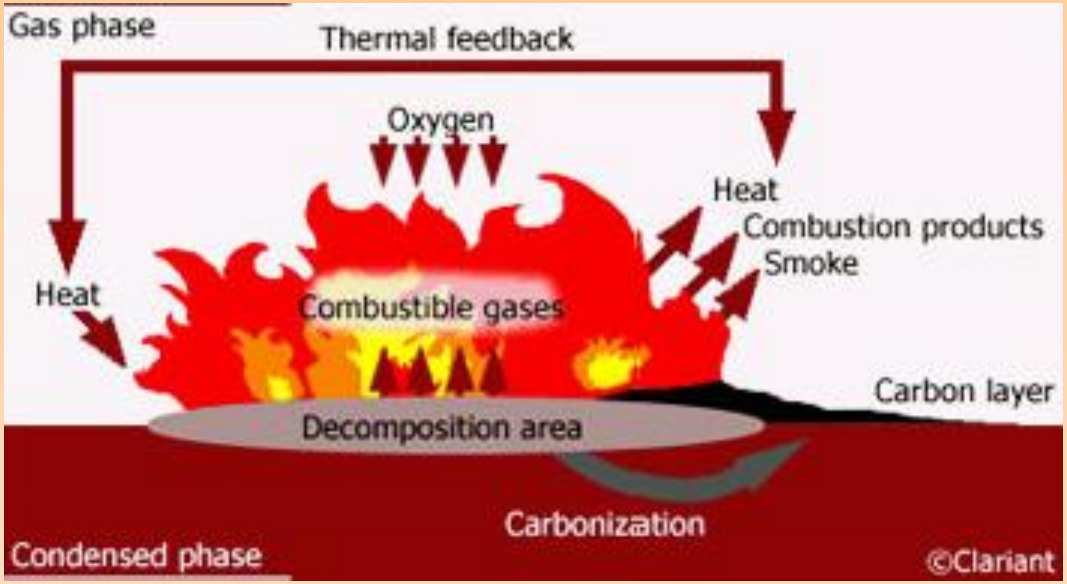
A combustion process need 3 components :

- **Fuel**, influences the combustion according to its intrinsic and extrinsic properties.
- **Oxidizing** (oxigen), necessary for the oxidation-reduction reaction.
- **Energy**, can be transferred to the fuel through radiation, flame or spark.

A fire is thus the macroscopic shape of a more complex process.



Combustion of polymers



Any polymer can give rise to redox processes of combustion accompanied by release of heat and light emission.

By heating a polymer
at T>T thermal degradation

↓

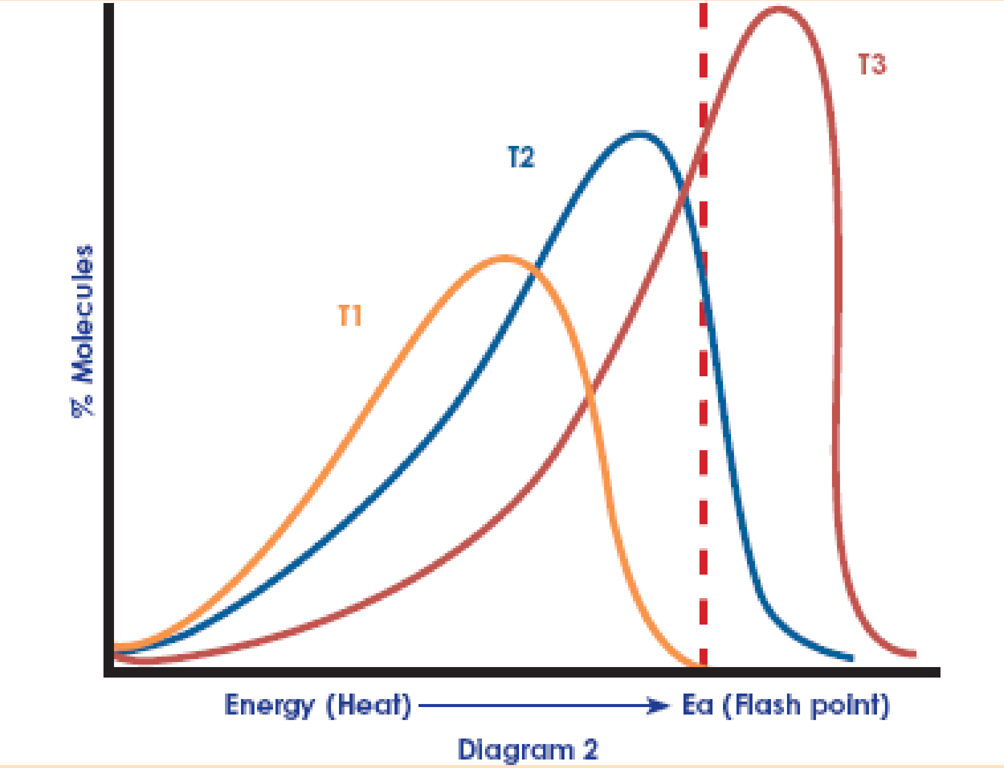
gaseous fuels are products that are mixed with the air

- If the composition of the gaseous mixture is within its flammability limits (ratio of fuel to comburent) , fire can start for ignition.

- The combustion continues until the heat supplied to the material is sufficient to support its thermal degradation at a speed higher than that necessary to feed the flame (powered combustion). Otherwise, the flame becomes unstable and eventually become extinct .

- Flame retardants prevent chemical reactions in the flame or create a carbonized layer (char) on the surface which prevents contact between the fuel and oxygen in the air.

Combustion in polymers: role of temperature in gas phase



At temperature (T1) very few of the molecules have enough energy (activation energy Ea) to burn. Adding more heat raises the temperature to (T2) causing more molecules to have enough energy to become fuel and burn.

At (T3), the majority of molecules have become fuel and a sustainable fire is likely.

<u>Conversely, if the temperature can be lowered from (T3) to (T1), the fire will self extinguish</u>.

Flame retardants

They act both at the physical and chemical level:

Physical mechanisms:

- *Cooling* of polymer and developed gases
- *Dilution* with not combustible gases

- Chemical mechanisms :

- *Reaction in the gaseous phase*: they interrupt or change the normal combustion reactions allowing a considerable reduction of the flame temperature.
- *Reactions in the condensed phase*: they slow the thermal degradation of the polymer and act as a barrier between polymer and gas by limiting the oxygen-polymer contact.

They are grouped according to the chemical element that provides their effectiveness. The most important elements are bromine, chlorine, phosphorus, aluminum, magnesium and nitrogen.

Halogenated flame retardants

They act by interrupting the radical reactions of the combustion.

Halogenated retardant HX (X=Cl, Br)

$$H^* + HX \longrightarrow H_2 + X^*$$

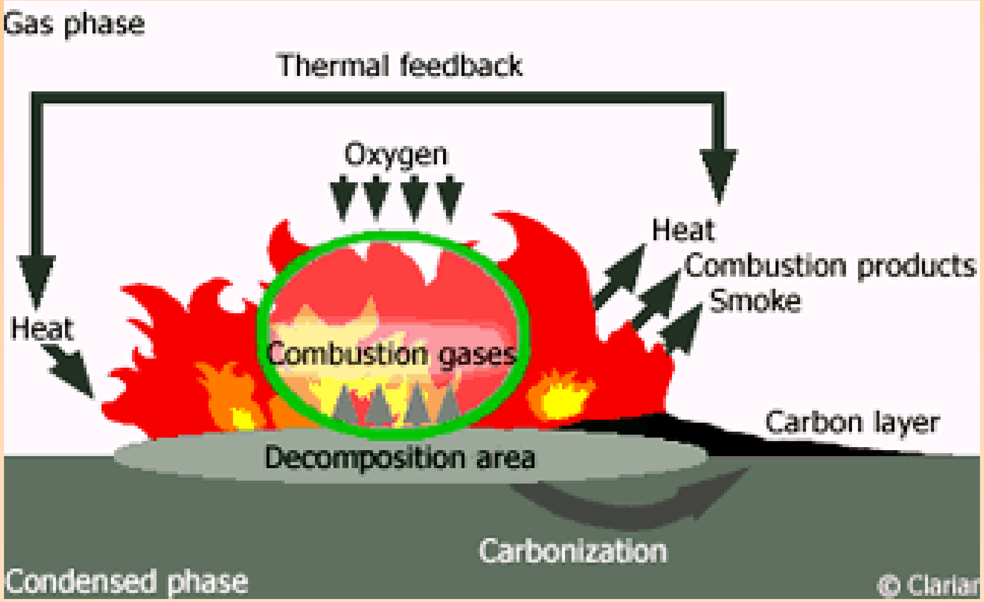
$$OH^* + HX \longrightarrow H_2O + X^*$$

- **The hydrohalic acid is continuously regenerated by the reaction between the products RH of degradation of the polymer and the radicals X***

$$X^* + RH \longrightarrow HX + R^*$$

- **The most common halogenated compounds are bromide and chloride based.**
- **They are dangerous because they develop toxic fumes (containing also HBr)**

Halogenated flame retardants



Bromine (Chlorine)

Acting principle: interruption of the radical chain mechanism of the combustion process in the gas phase:

1. Release of halogen radicals

$$\mathrm{R - X} \longrightarrow \mathrm{R^* + X^*}$$

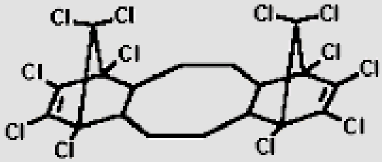
2. Formation of halogen hydroxides (HX)

$$\mathrm{RH + X^*} \longrightarrow \mathrm{HX + R^*}$$

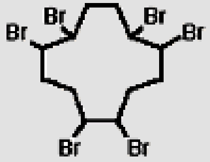
3. Neutralization of energy-rich radicals

$$\mathrm{HX + H^*} \longrightarrow \mathrm{H_2 + X^*}$$

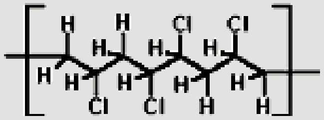
$$\mathrm{HX + OH^*} \longrightarrow \mathrm{H_2O + X^*}$$



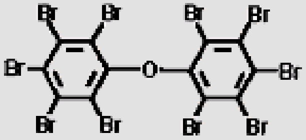
Dedecachloropenta-cyclooctadecadiene (dechlorane)



Hexabromo-cyclodedecan

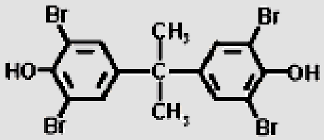


Chlorinated paraffins

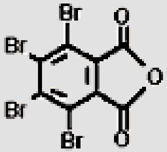


Decabromodiphenylether

Further product examples:



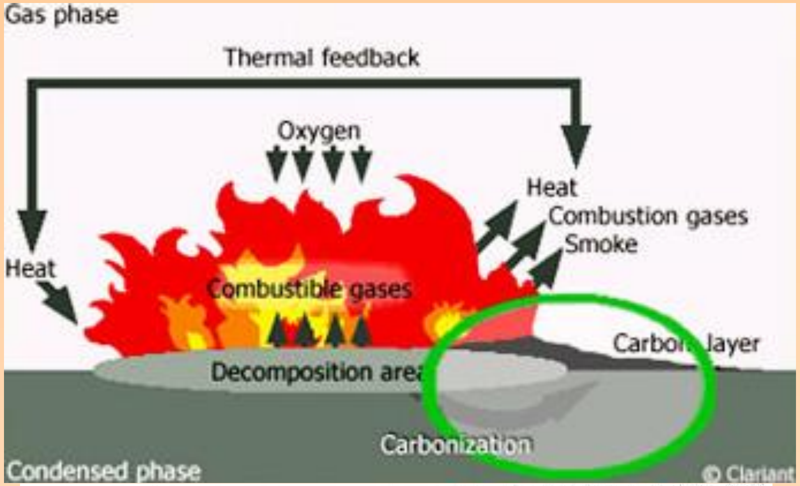
Tetrabromobisphenol A (TBBA)

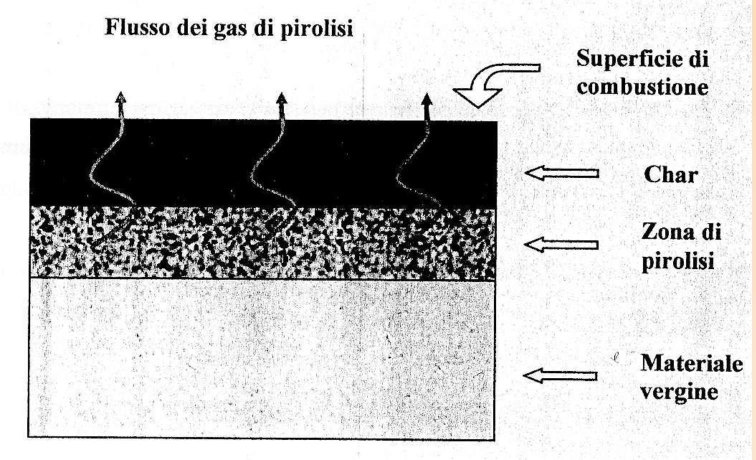


Tetrabromophthalic acid anhydride

Phosphorus based flame retardants

The phosphorus compounds give rise to phosphoric or polyphosphoric acid, which through pyrolysis of the polymer, leads to the formation of char, which constitutes a barrier to the attack of oxygen and heat and reduces the amount of combustible gases that reach the surface of the polymer.





Acting principle: formation of a solid surface layer of phosphorus compounds:

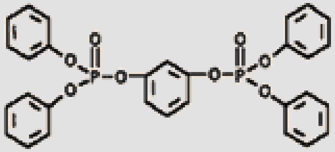
$$(NH_4PO_3)_n \xrightarrow[-\ n\ NH_3]{>250°C} (HPO_3)_n$$

$$P_{rot} \xrightarrow{O_2} P_4O_{10} \xrightarrow{H_2O} (HPO_3)_n$$

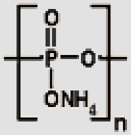
Formation of a protective layer by the production of polyphosphoric acid and carbonization, e.g. by release of water.

$$(HPO_3)_n + C_x(H_2O)_m \longrightarrow [\text{"C"}]_x + (HPO_3)_n x\ mH_2O$$

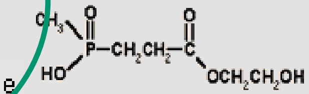
Further examples :



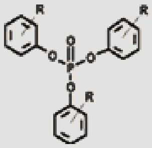
Resorcinol diphosphoric acid tetraphenyl ester (RDP)



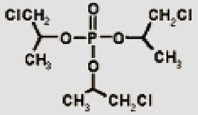
Ammonium polyphosphate (APP)



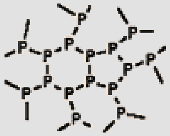
Phosphine acid derivatives



Triaryl phosphates



Trichloropropylphosphate (TCPP)



Red phosphorus

Metal hydroxides based flame retardants

They decompose by endothermic reaction that removes heat from the flame.

Aluminium TriHydroxide (ATH) e magnesium hydroxide degradate at about 220 ° C e 300 ° C.

From this decomposition, water and the corresponding oxide, which contributes to the properties of char, are produced.

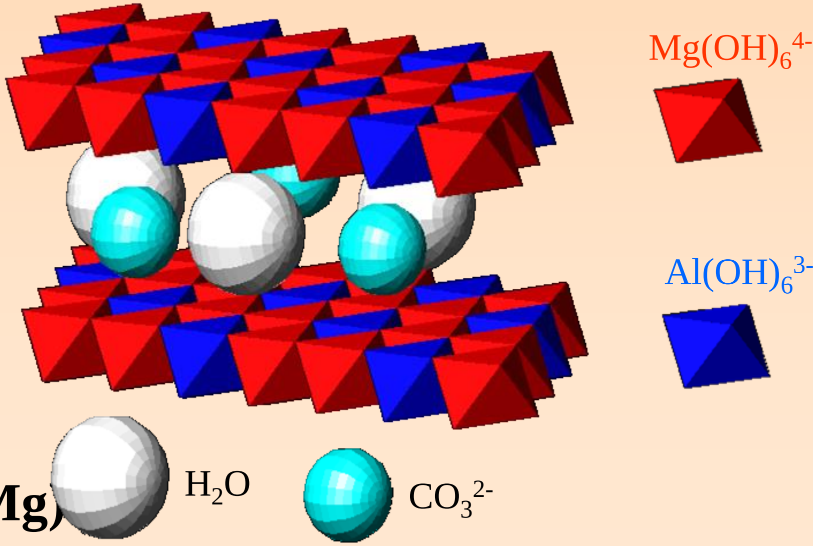
$$2Al(OH)_3 \rightarrow Al_2O_3+3H_2O-\Delta H$$

$$Mg(OH)_2 \rightarrow MgO+H_2O-\Delta H$$

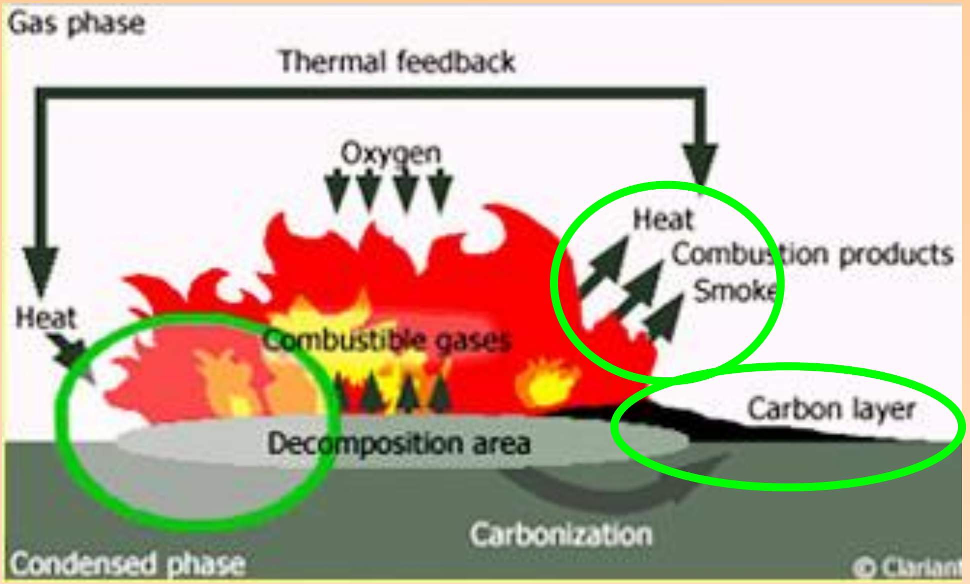
Other molecules are:

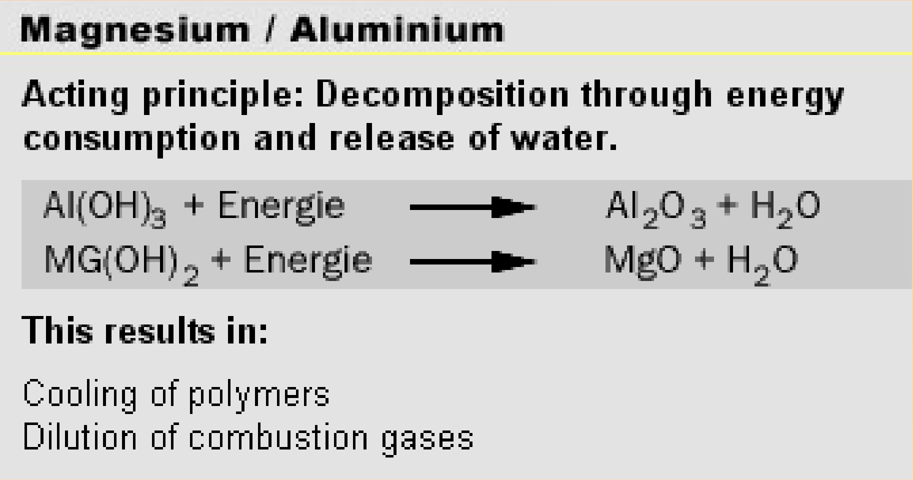
- boehmites AlOOH

- hydrotalcites (layered hydroxides of Al and Mg)



Metal hydroxides based flame retardants





Magnesium / Aluminium

Acting principle: Decomposition through energy consumption and release of water.

$Al(OH)_3$ + Energie $\longrightarrow$ $Al_2O_3 + H_2O$

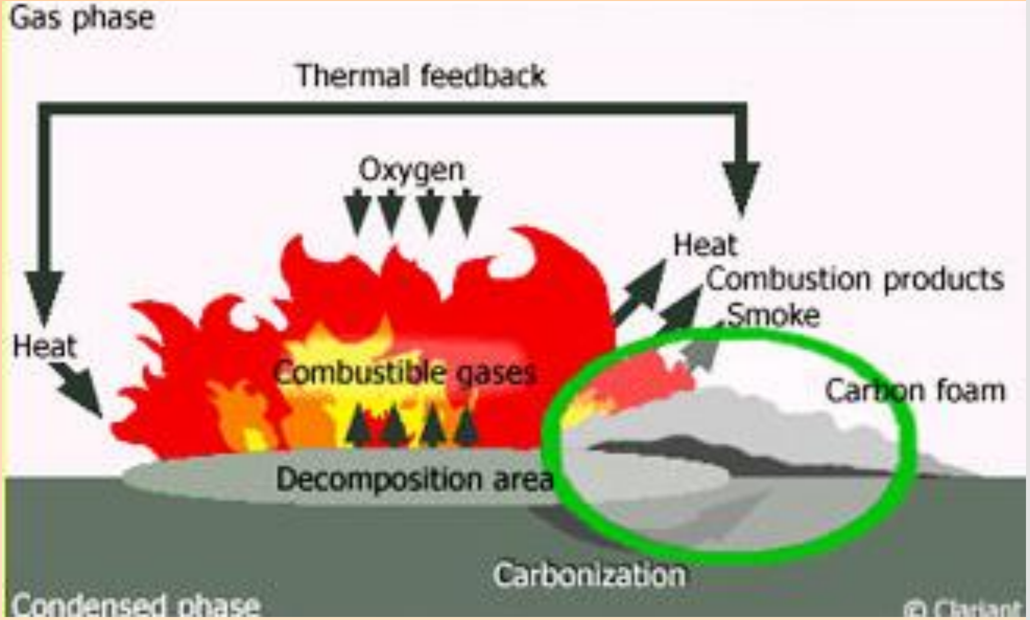
$MG(OH)_2$ + Energie $\longrightarrow$ $MgO + H_2O$

This results in:

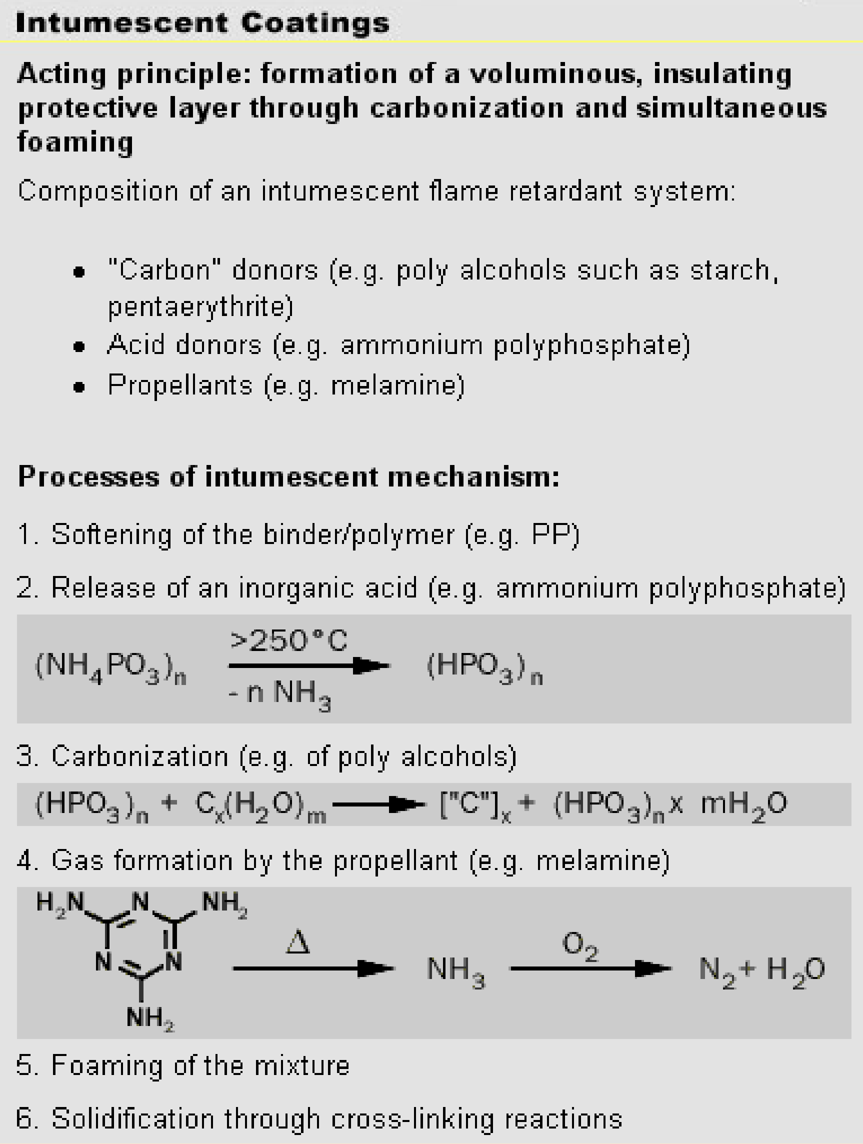
Cooling of polymers
Dilution of combustion gases

- They decompose by an endothermic reaction that removes heat from the flame.
- They produce water that dilutes combustible gases gas phase.
- They produce Alumina which increases the volume of char
- Aluminium TriHydroxide (ATH) e magnesium hydroxide degrade at about 220-300 ° C.

Intumescent Coatings



Steel beams treated with intumescent fire protective coating, before and after test fire heat application



Intumescent Coatings

Acting principle: formation of a voluminous, insulating protective layer through carbonization and simultaneous foaming

Composition of an intumescent flame retardant system:

- "Carbon" donors (e.g. poly alcohols such as starch, pentaerythrite)
- Acid donors (e.g. ammonium polyphosphate)
- Propellants (e.g. melamine)

Processes of intumescent mechanism:

1. Softening of the binder/polymer (e.g. PP)
2. Release of an inorganic acid (e.g. ammonium polyphosphate)

$$(NH_4PO_3)_n \xrightarrow[-\,n\,NH_3]{>250\,°C} (HPO_3)_n$$

3. Carbonization (e.g. of poly alcohols)

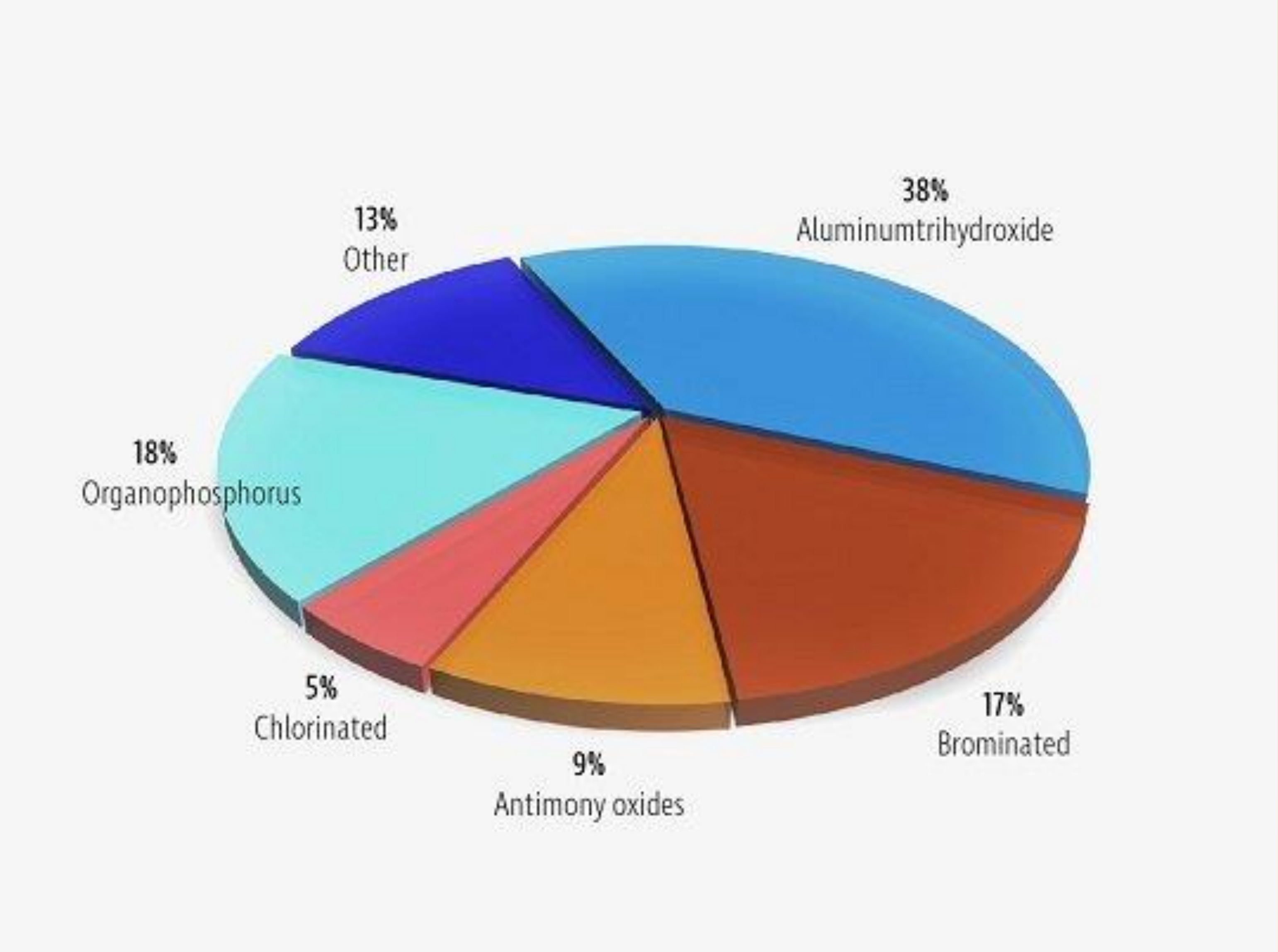
$$(HPO_3)_n + C_x(H_2O)_m \longrightarrow [\text{"C"}]_x + (HPO_3)_n x \ mH_2O$$

4. Gas formation by the propellant (e.g. melamine)

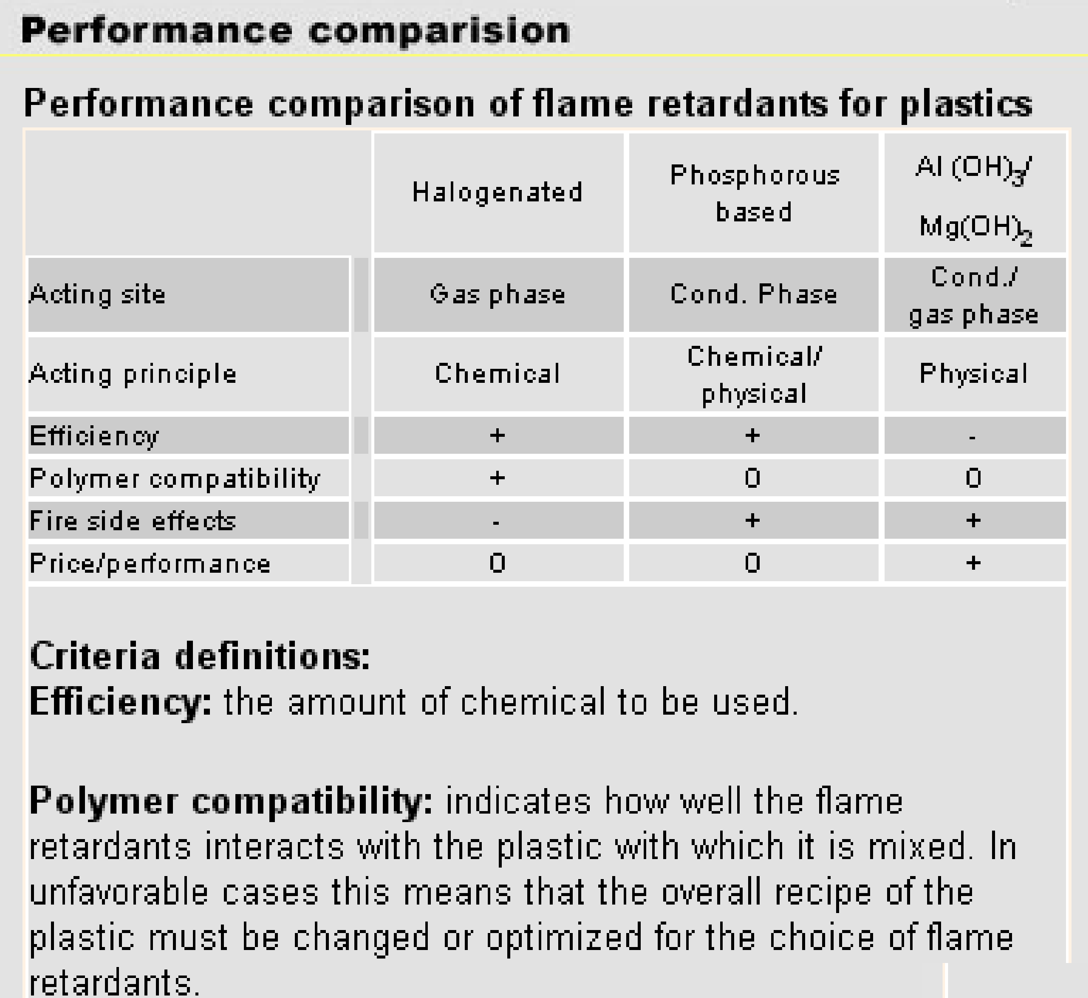
$$\xrightarrow{\Delta} NH_3 \xrightarrow{O_2} N_2 + H_2O$$

5. Foaming of the mixture
6. Solidification through cross-linking reactions

Flame retardants



Flame retardants: performance comparison



Performance comparision

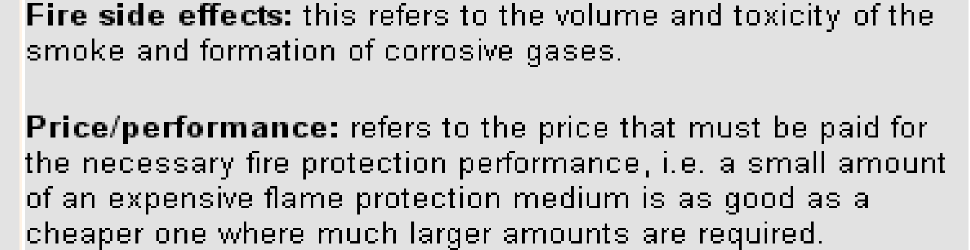
Performance comparison of flame retardants for plastics

	Halogenated	Phosphorous based	$Al(OH)_3$/ $Mg(OH)_2$
Acting site	Gas phase	Cond. Phase	Cond./ gas phase
Acting principle	Chemical	Chemical/ physical	Physical
Efficiency	+	+	-
Polymer compatibility	+	0	0
Fire side effects	-	+	+
Price/performance	0	0	+

Criteria definitions:

Efficiency: the amount of chemical to be used.

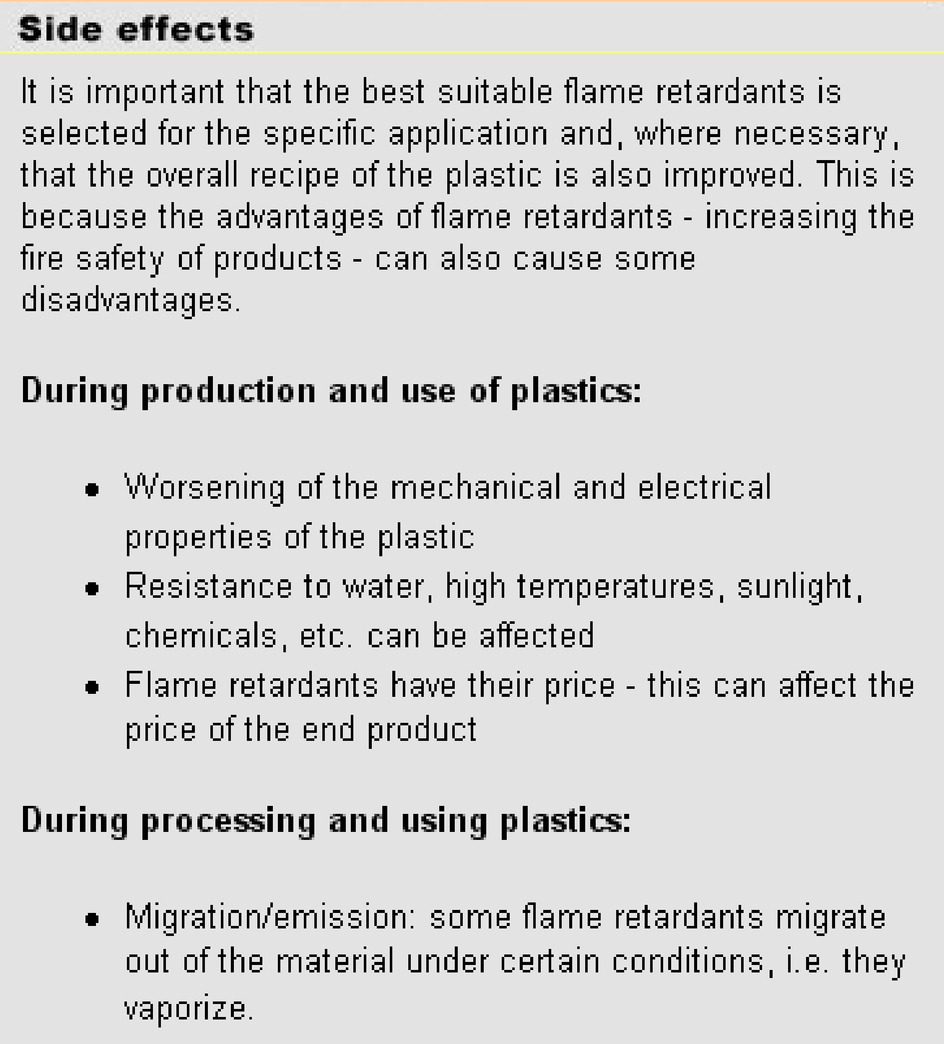
Polymer compatibility: indicates how well the flame retardants interacts with the plastic with which it is mixed. In unfavorable cases this means that the overall recipe of the plastic must be changed or optimized for the choice of flame retardants.



Fire side effects: this refers to the volume and toxicity of the smoke and formation of corrosive gases.

Price/performance: refers to the price that must be paid for the necessary fire protection performance, i.e. a small amount of an expensive flame protection medium is as good as a cheaper one where much larger amounts are required.

Flame retardants: performance comparison



Side effects

It is important that the best suitable flame retardants is selected for the specific application and, where necessary, that the overall recipe of the plastic is also improved. This is because the advantages of flame retardants - increasing the fire safety of products - can also cause some disadvantages.

During production and use of plastics:

- Worsening of the mechanical and electrical properties of the plastic
- Resistance to water, high temperatures, sunlight, chemicals, etc. can be affected
- Flame retardants have their price - this can affect the price of the end product

During processing and using plastics:

- Migration/emission: some flame retardants migrate out of the material under certain conditions, i.e. they vaporize.

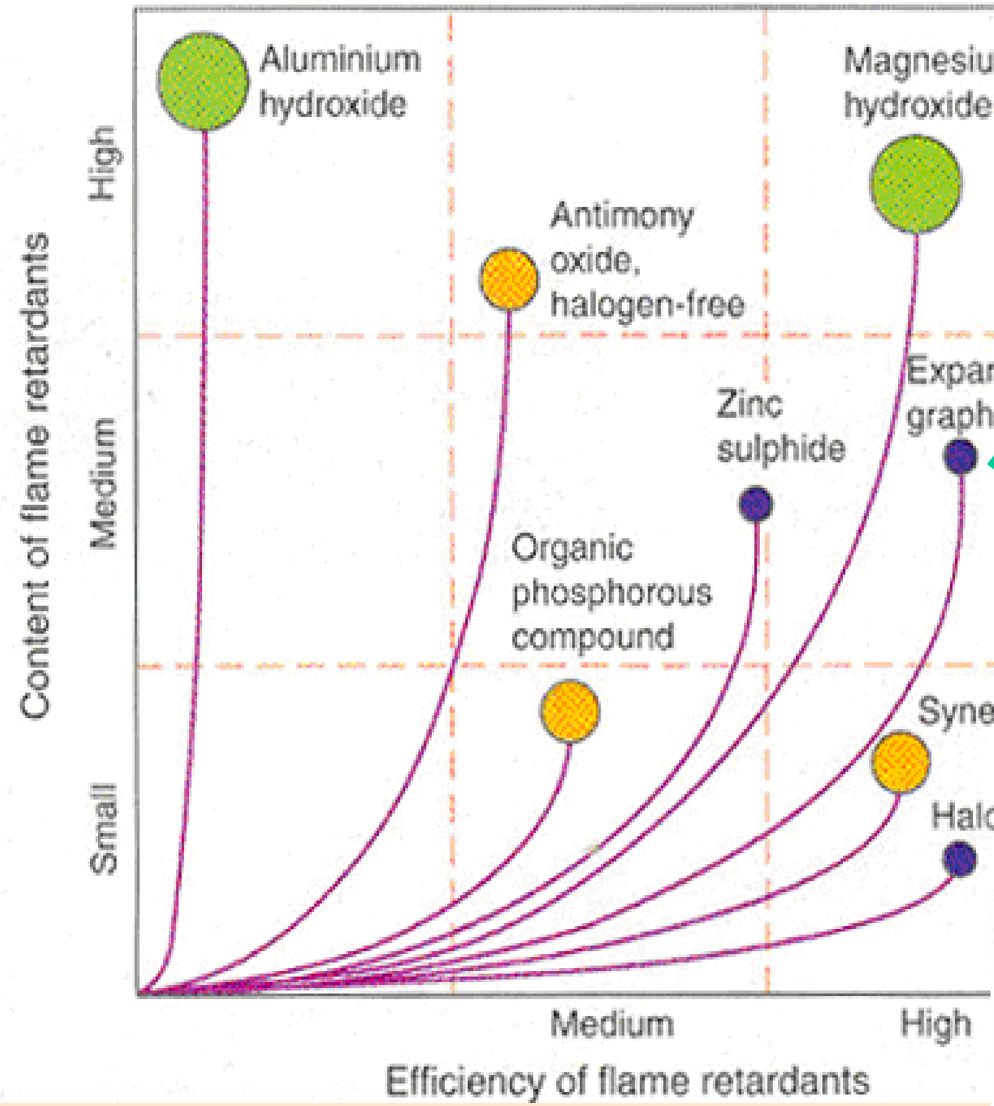
During processing and using plastics:

- Migration/emission: some flame retardants migrate out of the material under certain conditions, i.e. they vaporize.

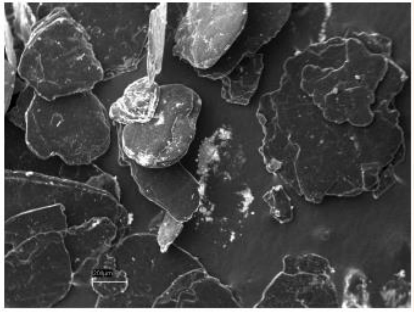
During recycling or disposal:

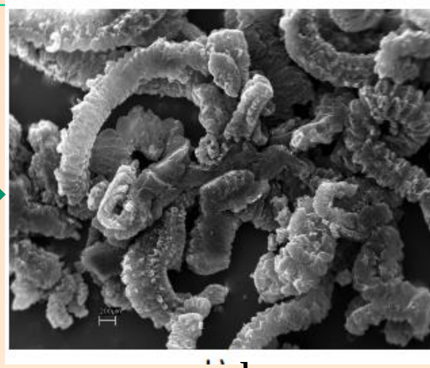
- Possible release of toxic decomposition products
- Separate processing may be required for halogenated products
- Corrosive fire gases may be produced by halogenated products

Flame retardants: property comparison

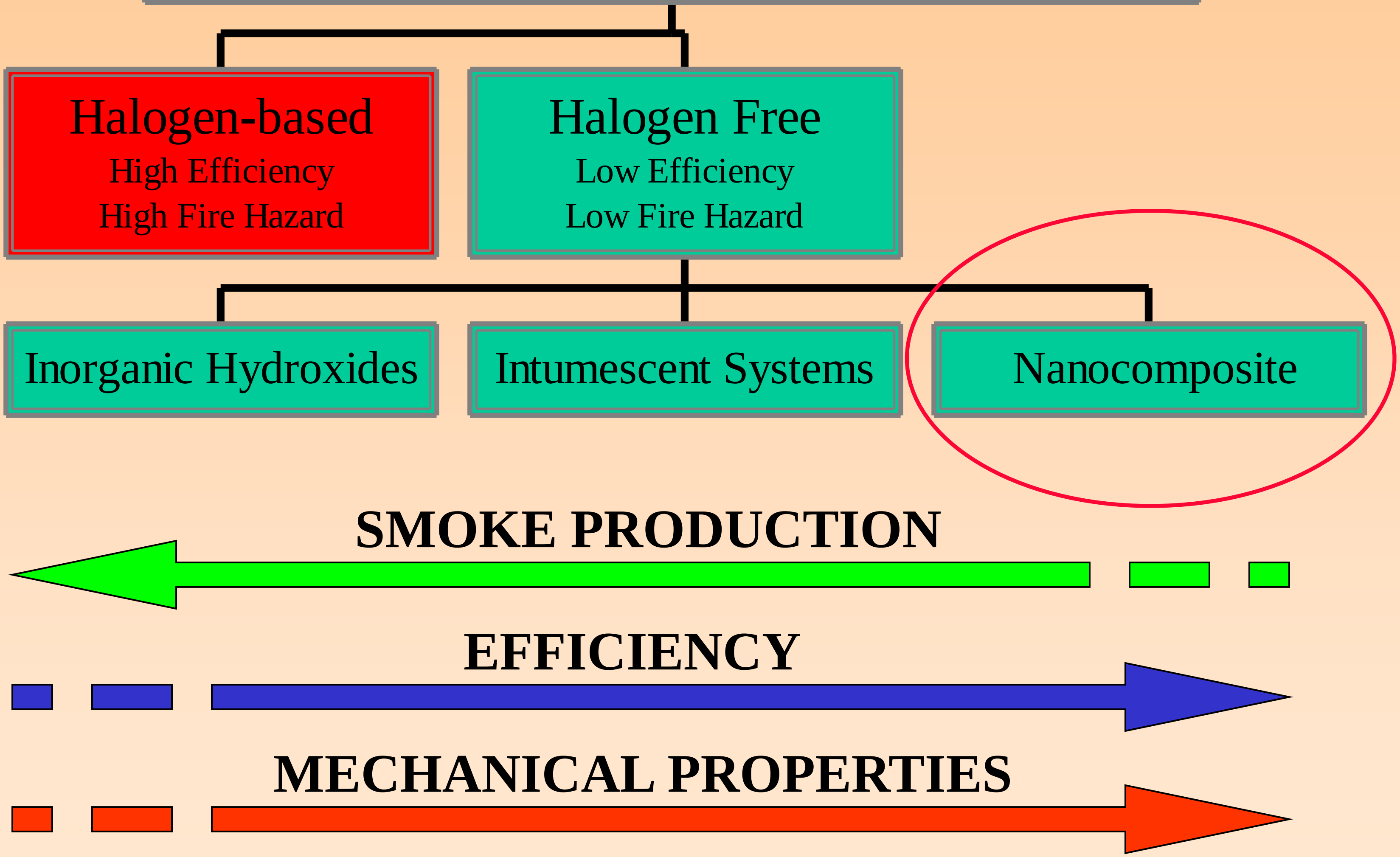


Expandable graphite=graphite layers intercalated by sulfuric acid (a). Upon heating the acid decomposes producing SO_3 determining a huge expansion (b)


a


b

Flame Retardant Systems



Halogen-based
High Efficiency
High Fire Hazard

Halogen Free
Low Efficiency
Low Fire Hazard

Inorganic Hydroxides

Intumescent Systems

Nanocomposite

SMOKE PRODUCTION

EFFICIENCY

MECHANICAL PROPERTIES

Fire resistance: measurement methods

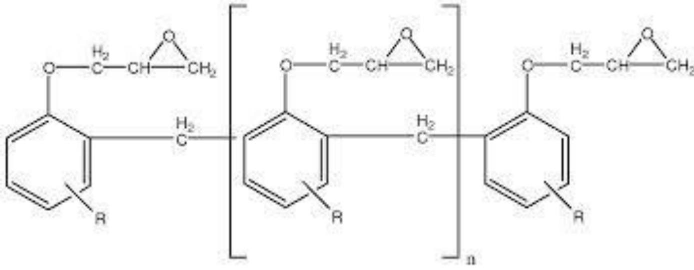
- cone calorimeter
  - heat release and smoke analysis of 100x100 mm specimens subjected to radiant heat
- flame propagation (for example UL 94)
  - burning rate and flame retardant behaviour of horizontal or vertical specimens after start of combustion
- oxygen index
  - amount of oxygen, in a mixture with nitrogen, able to ensure the combustion of a vertical polymer specimen (after start of combustion) under steady conditions, defined by the standard

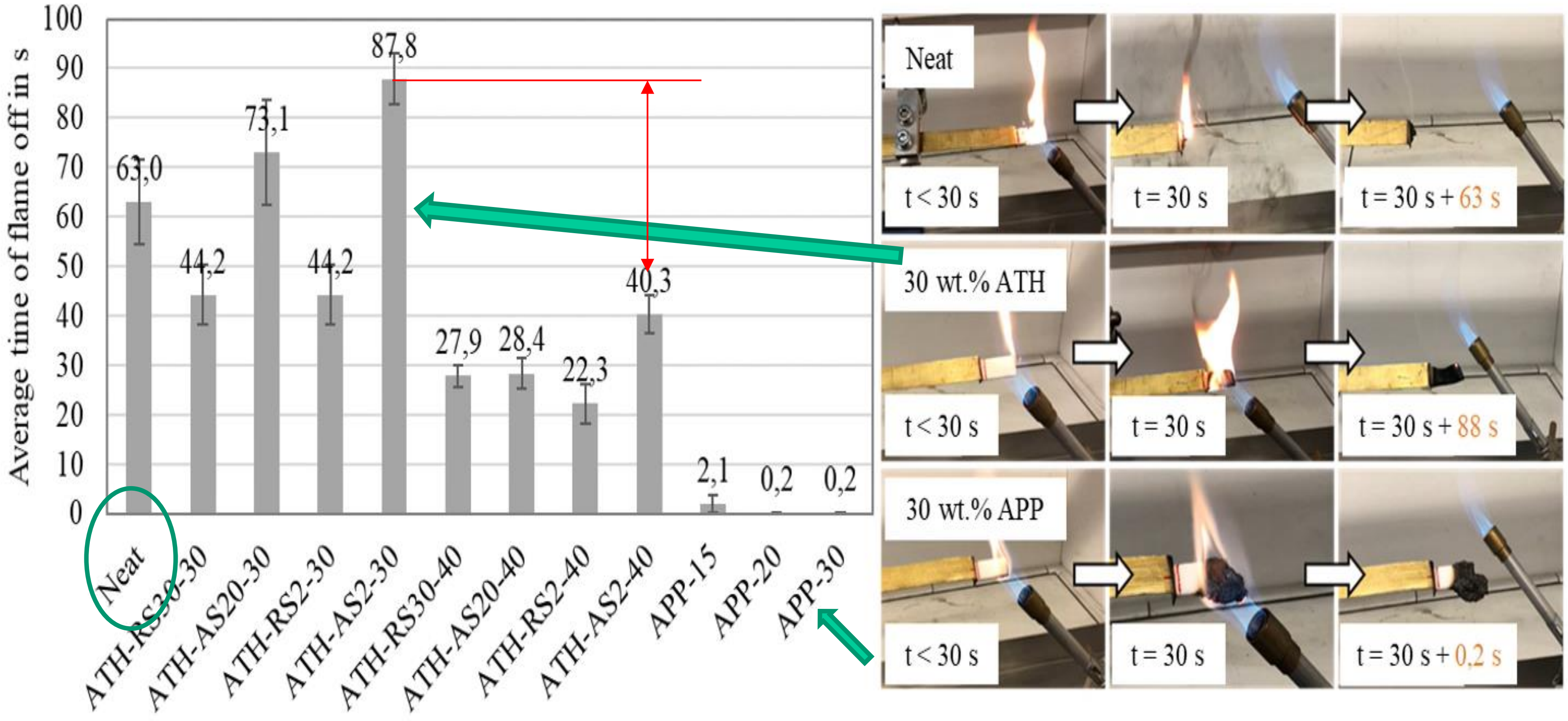
Horizontal burning (UL94) test of epoxy foams

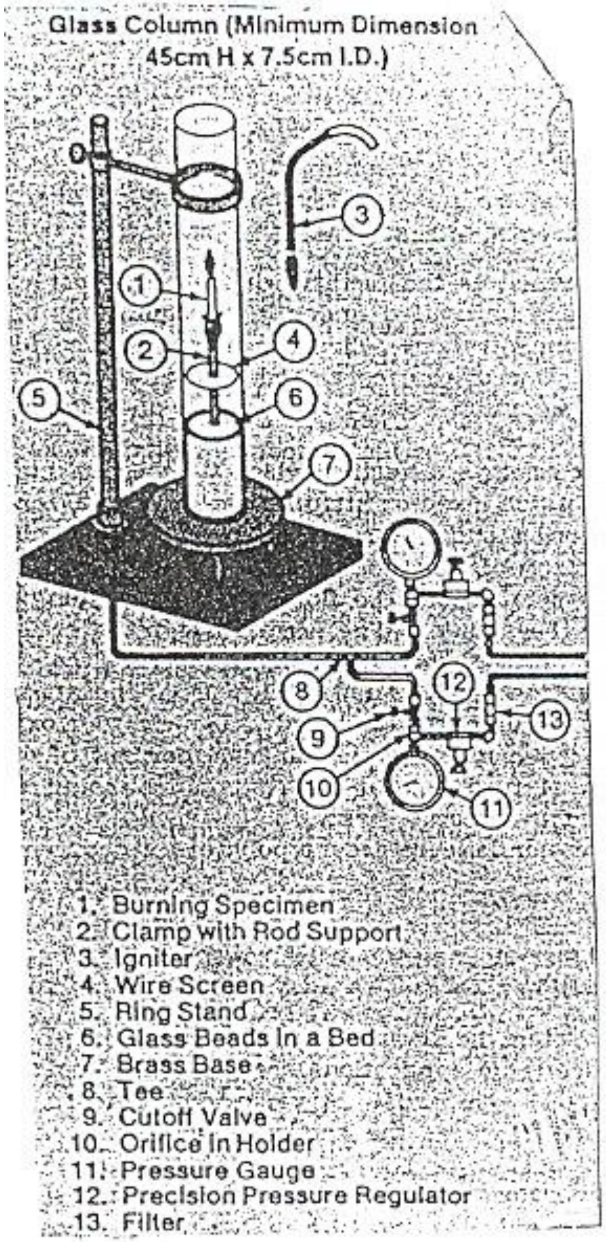
Materials: Epoxy Novolac+ Isophorone diamine

Flame retardans:

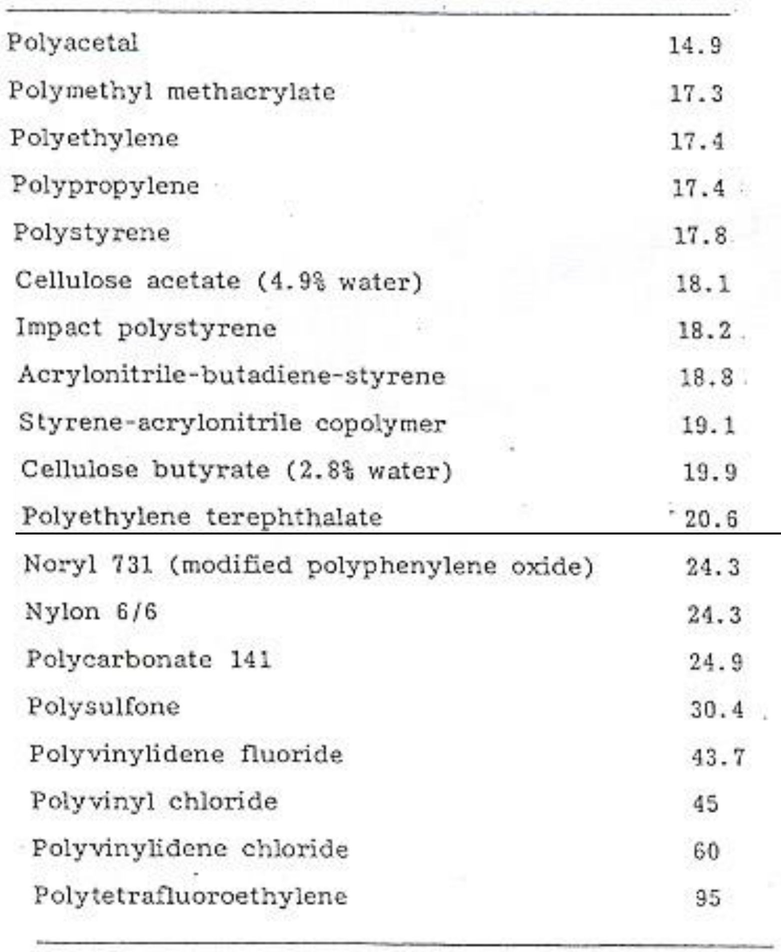
- AP (ammonium polyphosphate) 15, 20 and 30wt%
- ATH 30 and 40wt%
- Ignition time = 30s







L'apparecchiatura per la misura
dell indice dell'ossigeno



polymer	Oxygen index
Polyacetal	14.9
Polymethyl methacrylate	17.3
Polyethylene	17.4
Polypropylene	17.4
Polystyrene	17.8
Cellulose acetate (4.9% water)	18.1
Impact polystyrene	18.2
Acrylonitrile-butadiene-styrene	18.8
Styrene-acrylonitrile copolymer	19.1
Cellulose butyrate (2.8% water)	19.9
Polyethylene terephthalate	20.6
Noryl 731 (modified polyphenylene oxide)	24.3
Nylon 6/6	24.3
Polycarbonate 141	24.9
Polysulfone	30.4
Polyvinylidene fluoride	43.7
Polyvinyl chloride	45
Polyvinylidene chloride	60
Polytetrafluoroethylene	95

Not burning in air

L'indice dell'ossigeno per
diversi polimeri senza
ritardanti alla fiamma

Ablation

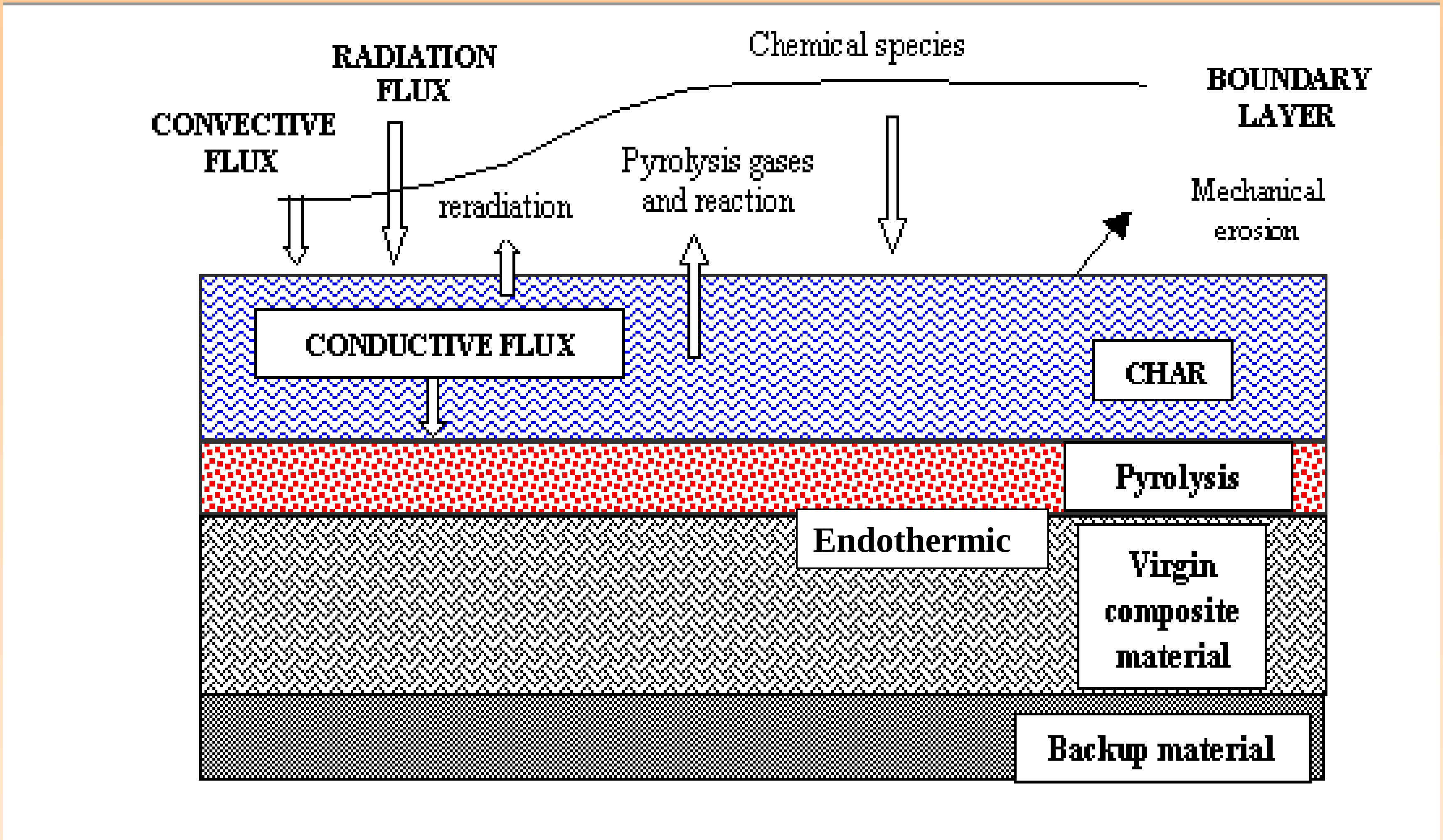
Loss of material from an exposed surface, usually due to the action of a flow of hot gases in motion, which occurs through various mechanisms, such as melting, evaporation, pyrolysis, combustion and mechanical erosion .

The wide range of heating conditions that must be followed during ablation restricts the use to materials that meet specific criteria. These criteria include controlled recession of the surface, heat transfer to the substrate, reliability of the shielding.

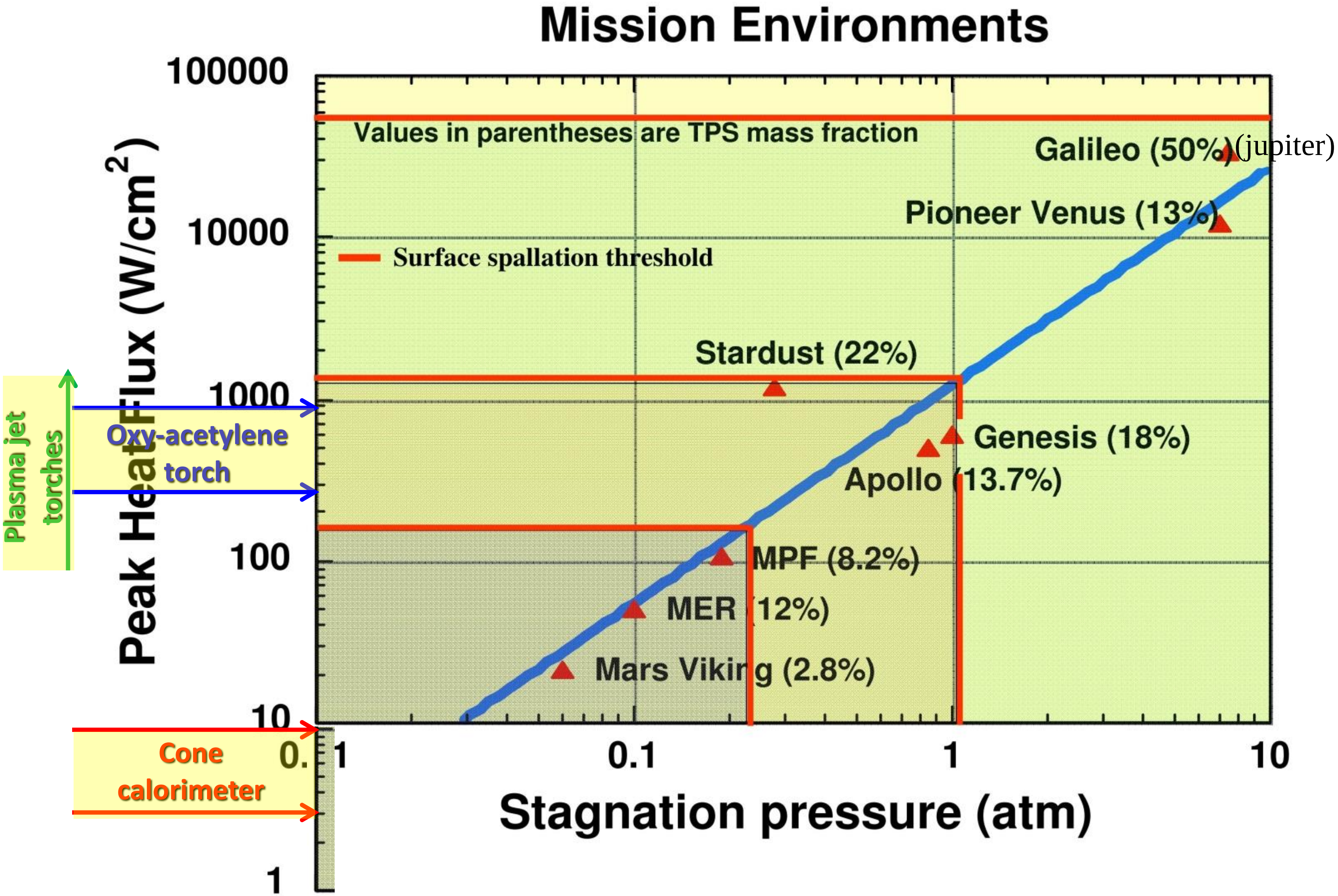
The mechanisms mainly responsible for the ablative behavior of the resins are pyrolysis with char formation and oxidation: the degradation of thermosetting polymers indeed gives rise to gaseous products and a solid residue. In particular, if the polymer contains mainly carbon in the chain, carbon based char will be formed while, with polymers containing Si-O bonds, the char will be silica based: these layers of porous and rigid char are not uniform and often contain irregular cracks due to the shrinkage that accompanies the process

The reaction of thermal degradation must be endothermic in non-oxidizing conditions. The ablative material during decomposition behaves as a heat sink capable of absorbing the incident heat flow (heat shields for the re-entry from space or coating of rocket nozzles).

Structure of a material as a result of pyrolysis and char formation



Heat fluxes and mass fraction of a Thermal Protection system



Ablation measured in Galileo mission

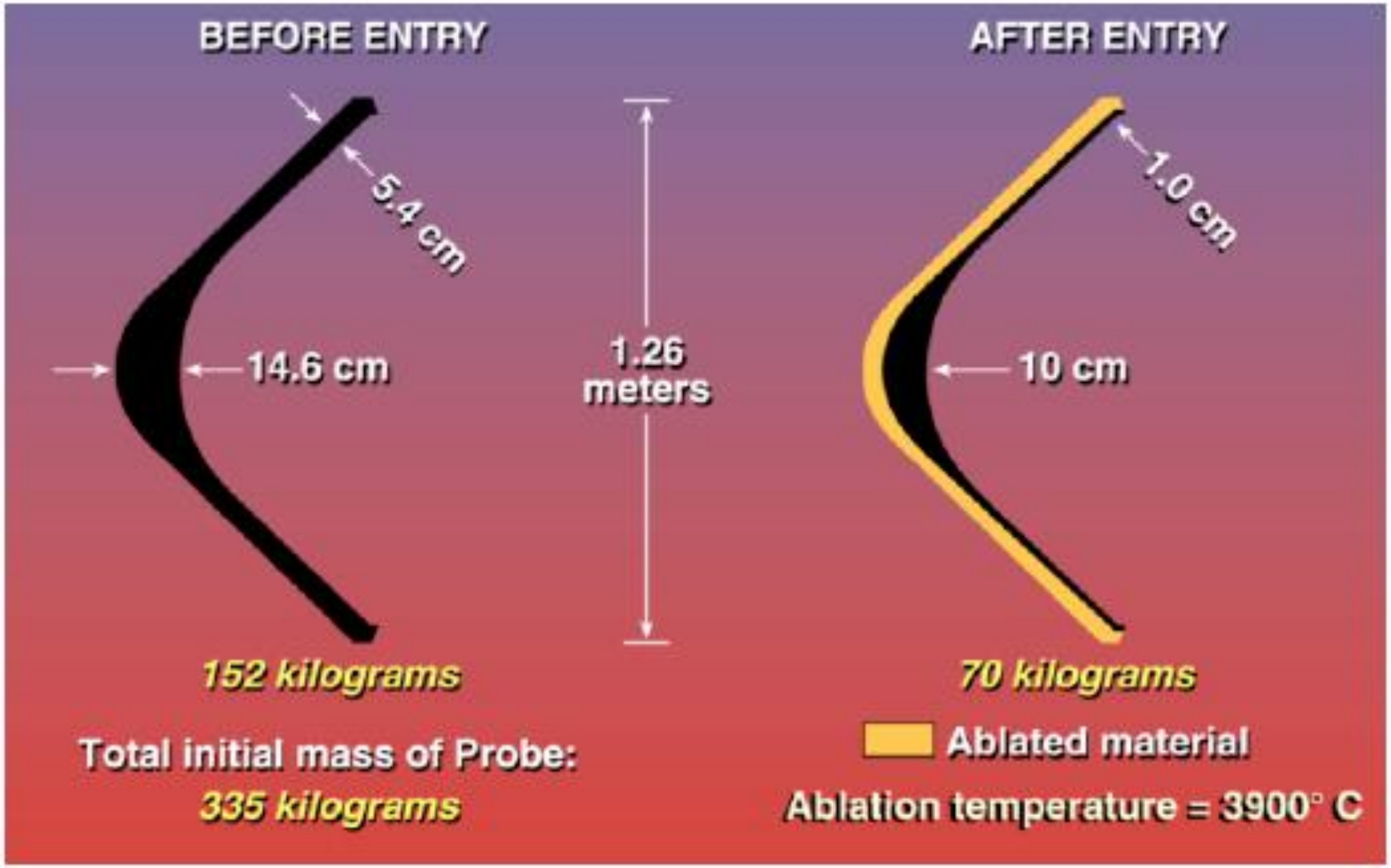
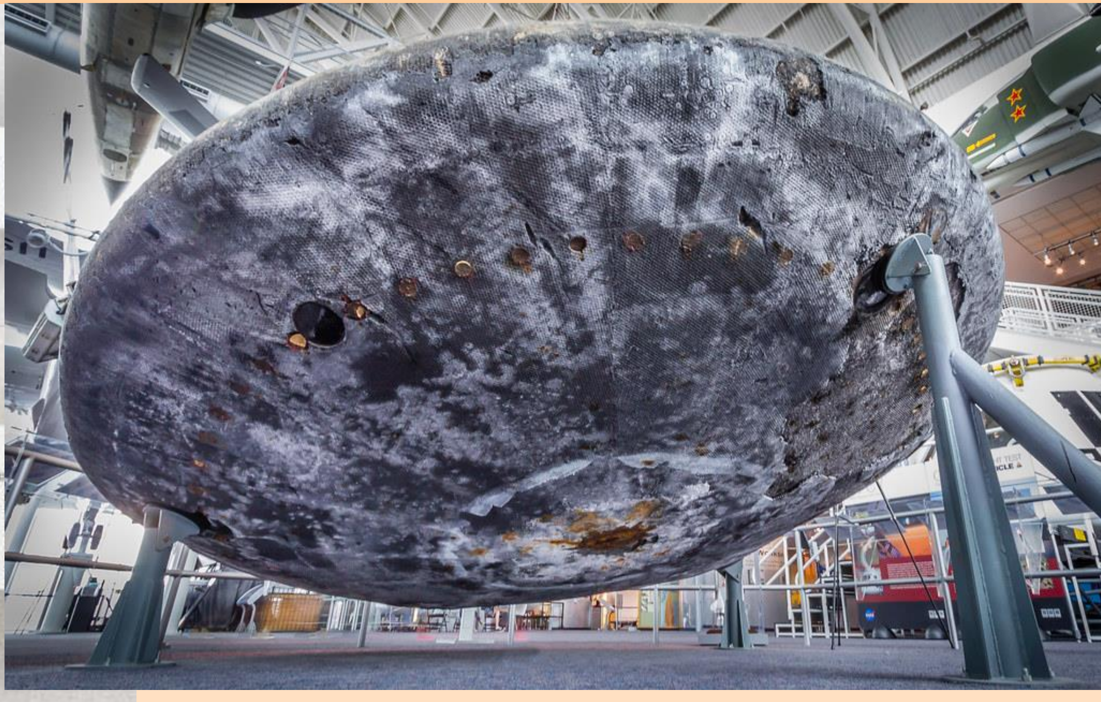


Fig. 8 Galileo probe heat shield ablation

The Galileo mission was launched in October 1989 and one probe successfully entered the Jovian atmosphere in December 1995.

Ablative materials used in Apollo Missions



Avcoat Phenolic composite. Density 500 kg/m^3
Test of specimens with oxy-acetylene torch
Top: before testing. Bottom after testing
A phenolic honeycomb with filled cells is clearly present

Heat shield of Apollo 12 command module

Ablative materials: our experience

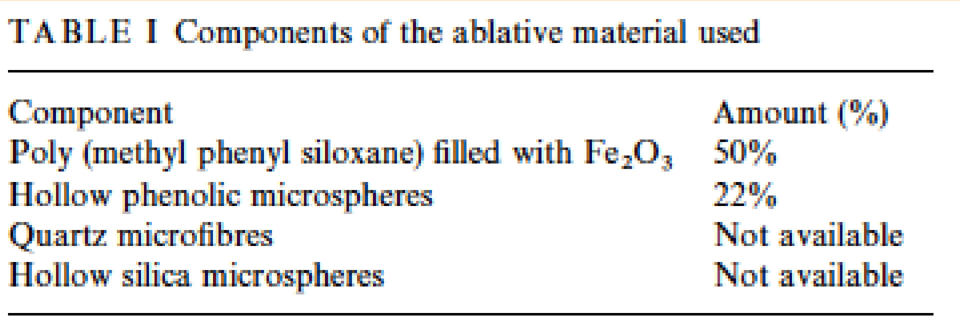
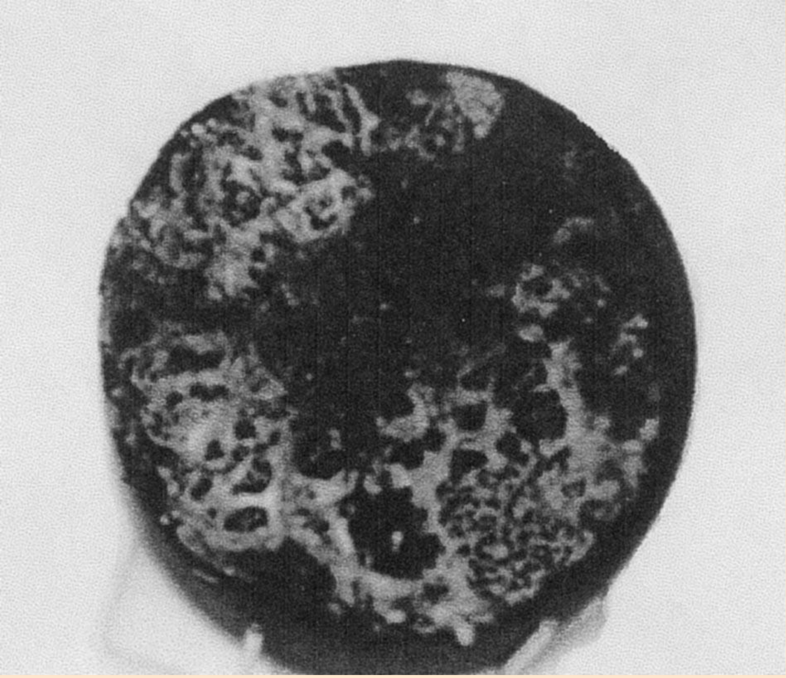


TABLE I Components of the ablative material used

Component	Amount (%)
Poly (methyl phenyl siloxane) filled with Fe_2O_3	50%
Hollow phenolic microspheres	22%
Quartz microfibres	Not available
Hollow silica microspheres	Not available

Ablative used to fill Nomex honeycomb



Test of specimens with oxy-acetylene torch

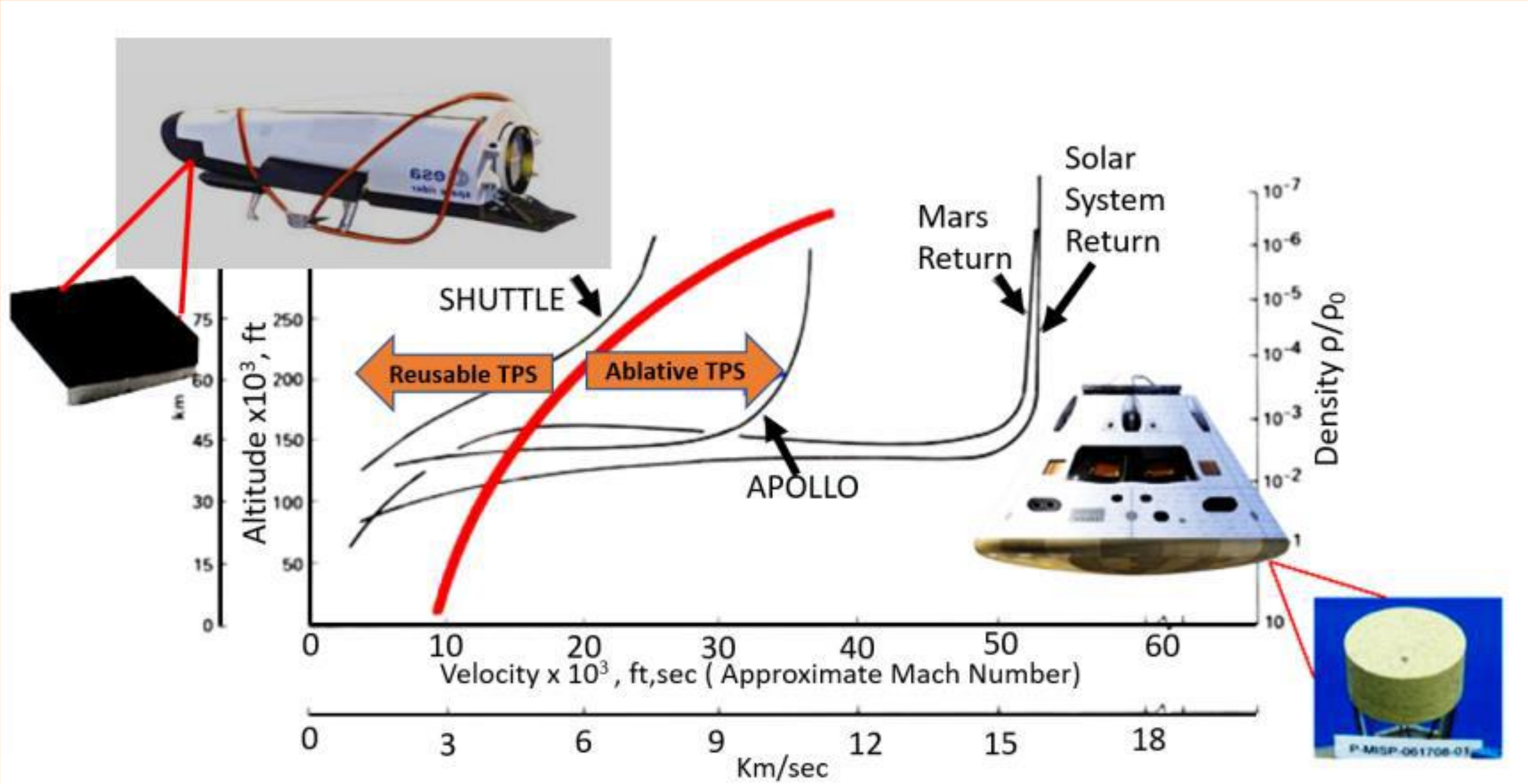
JOURNAL OF MATERIALS SCIENCE 33 (1998) 3137 3143

Ablative materials and composites: Mars 2020 Perseverance rover aeroshell

Structure (diameter 4.5 m): Cyanate ester/carbon fibres
Heat shield: tiled Phenolic Impregnated Carbon Ablator

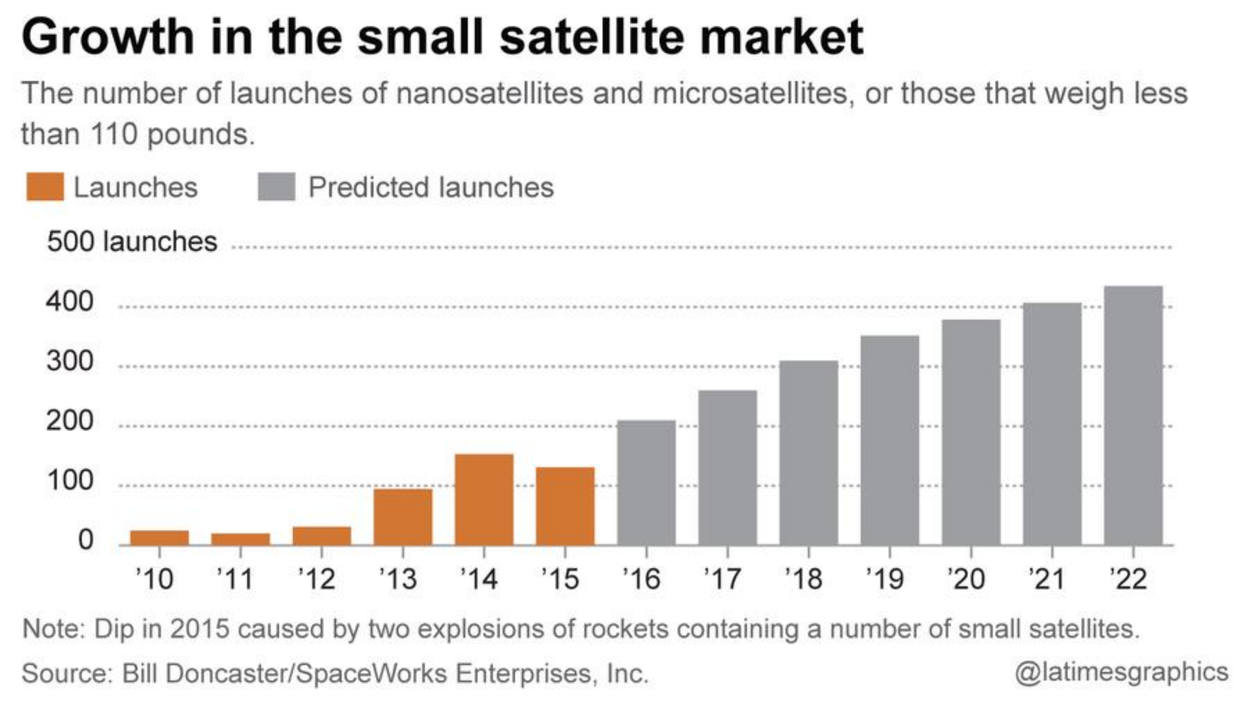
Ablative materials and reusable heat shields

- Carbon/carbon composites are used up a to re-entry velocity of 9 km/s (i.e. Space Shuttle) . Reusable protection systems rely on radiating away the thermal energy obtained during reentry. So, they have high emissivity and low thermal conductivity
- Ablative materials are used above 9 km/s (i.e. Apollo)



The space economy

The space sector is a very profitable market


Growth in the small satellite market

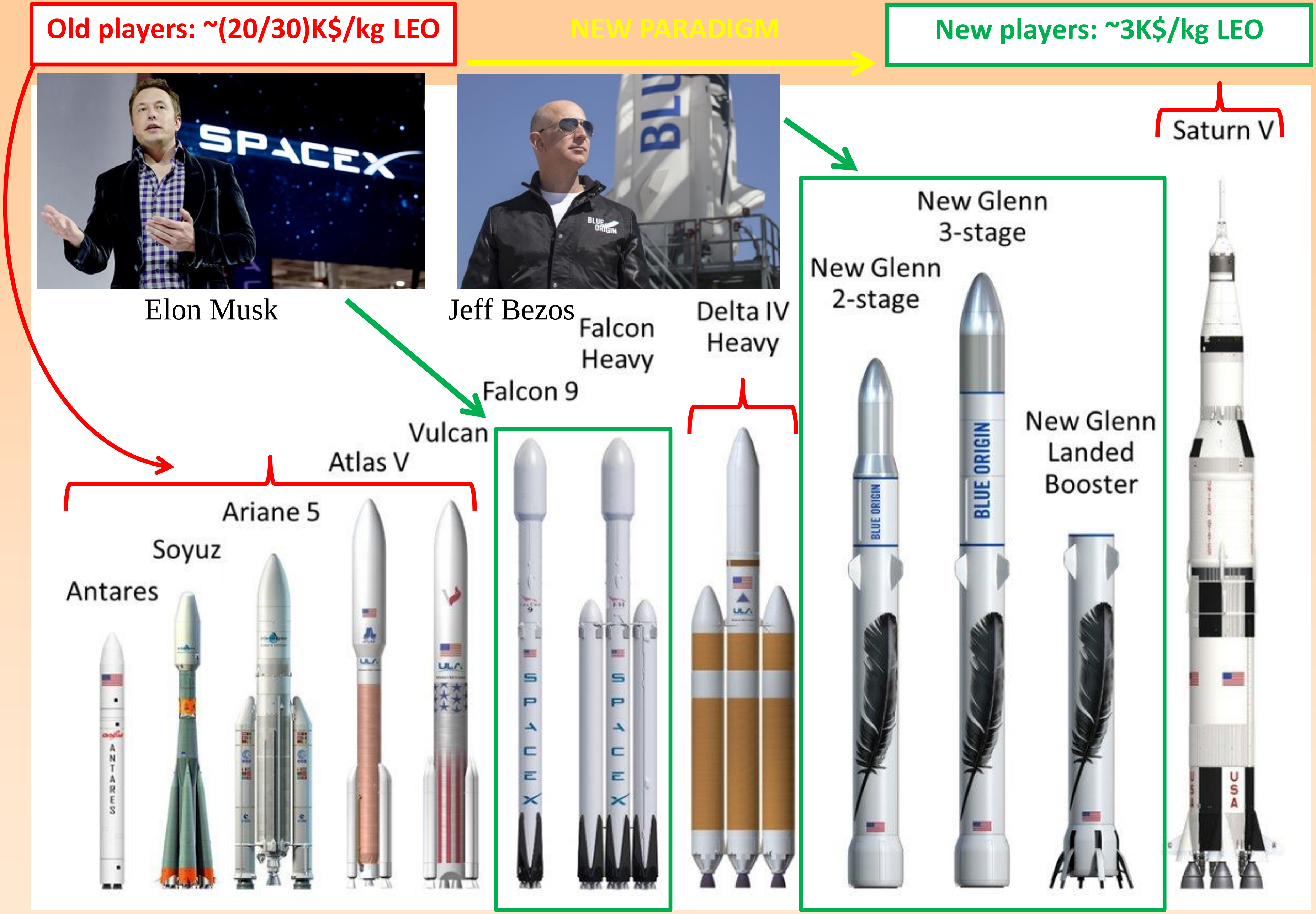
The number of launches of nanosatellites and microsatellites, or those that weigh less than 110 pounds.

Note: Dip in 2015 caused by two explosions of rockets containing a number of small satellites.

Source: Bill Doncaster/SpaceWorks Enterprises, Inc. @latimesgraphics

Nano- and micro-satellites (from 1 to 100 kg) which have been made economically feasible by micro-electronics and new materials, also represent a huge opportunity. The nano- and micro-satellite market is grown from $US 0.7 billions in 2014 to $US 1.9 billions in 2019.

The space economy for Low Earth Orbit (LEO) launcher



Old players: ~(20/30)K$/kg LEO

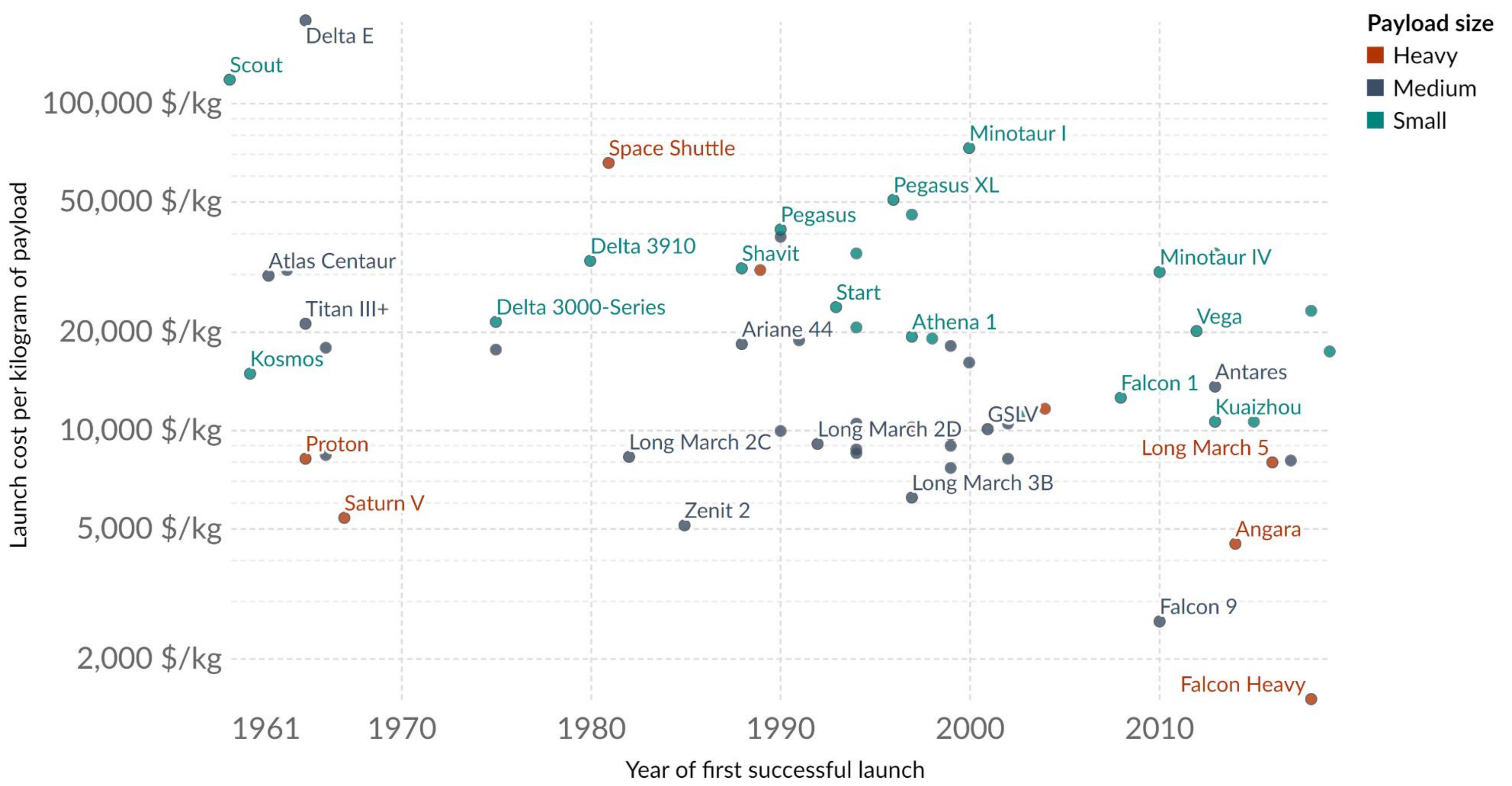
NEW PARADIGM

New players: ~3K$/kg LEO

Cost of space launches to low Earth orbit

Cost to launch one kilogram of payload mass to low Earth orbit[1] as part of a dedicated launch. This data is adjusted for inflation.

Our World in Data



Geostationary Equatorial Orbit (GEO) (30.000 km) costs 30.000 $/kg using conventional rockets and 6000 with Falcon launcher

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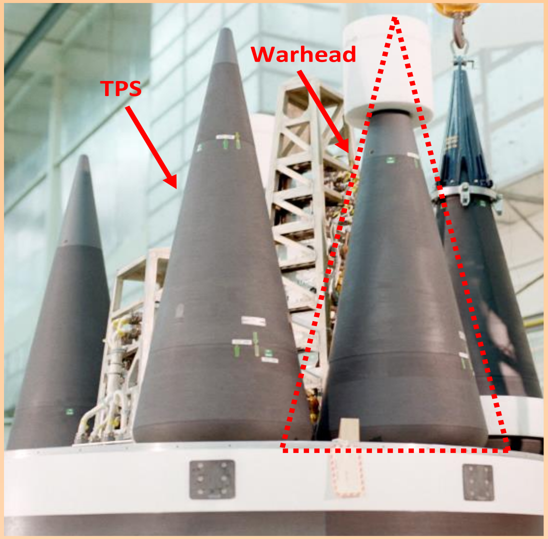
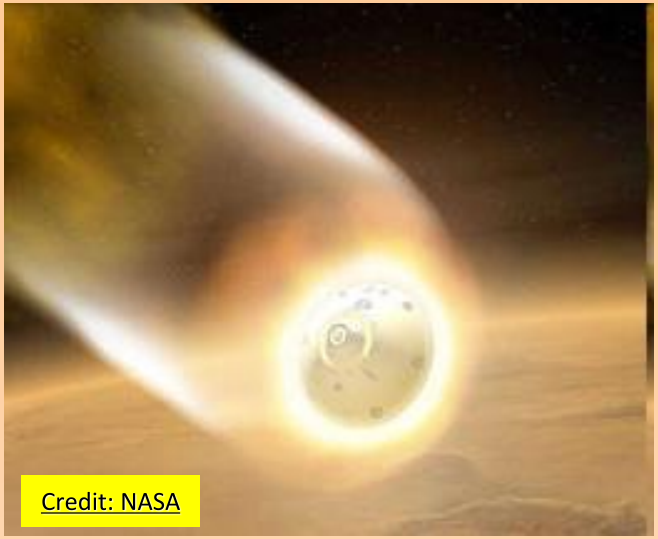
[1] **Low Earth orbit:** A low Earth orbit (LEO) is an orbit around Earth with a period of 128 minutes or less (making at least 11.25 orbits per day). Most of the artificial objects in outer space are in LEO, with an altitude never more than about one-third of the radius of Earth.

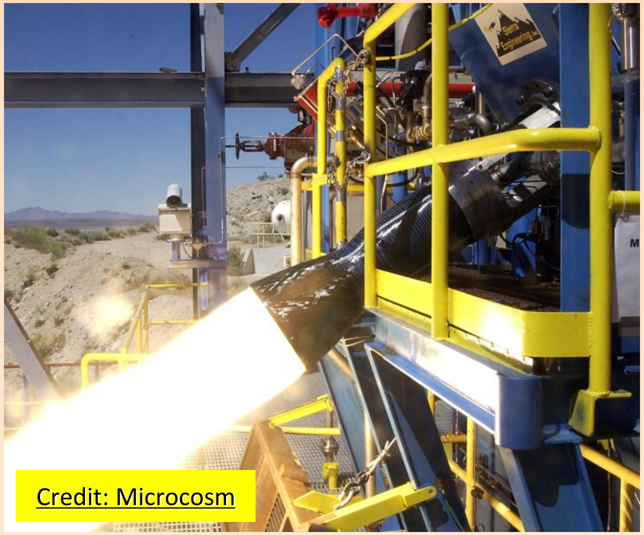



Credit: NASA

Ablatives are used to produce the heat shields of space vehicles as well as passively cooled rocket engines


Credit: Orbital-ATK


Credit: NASA


Credit: Microcosm