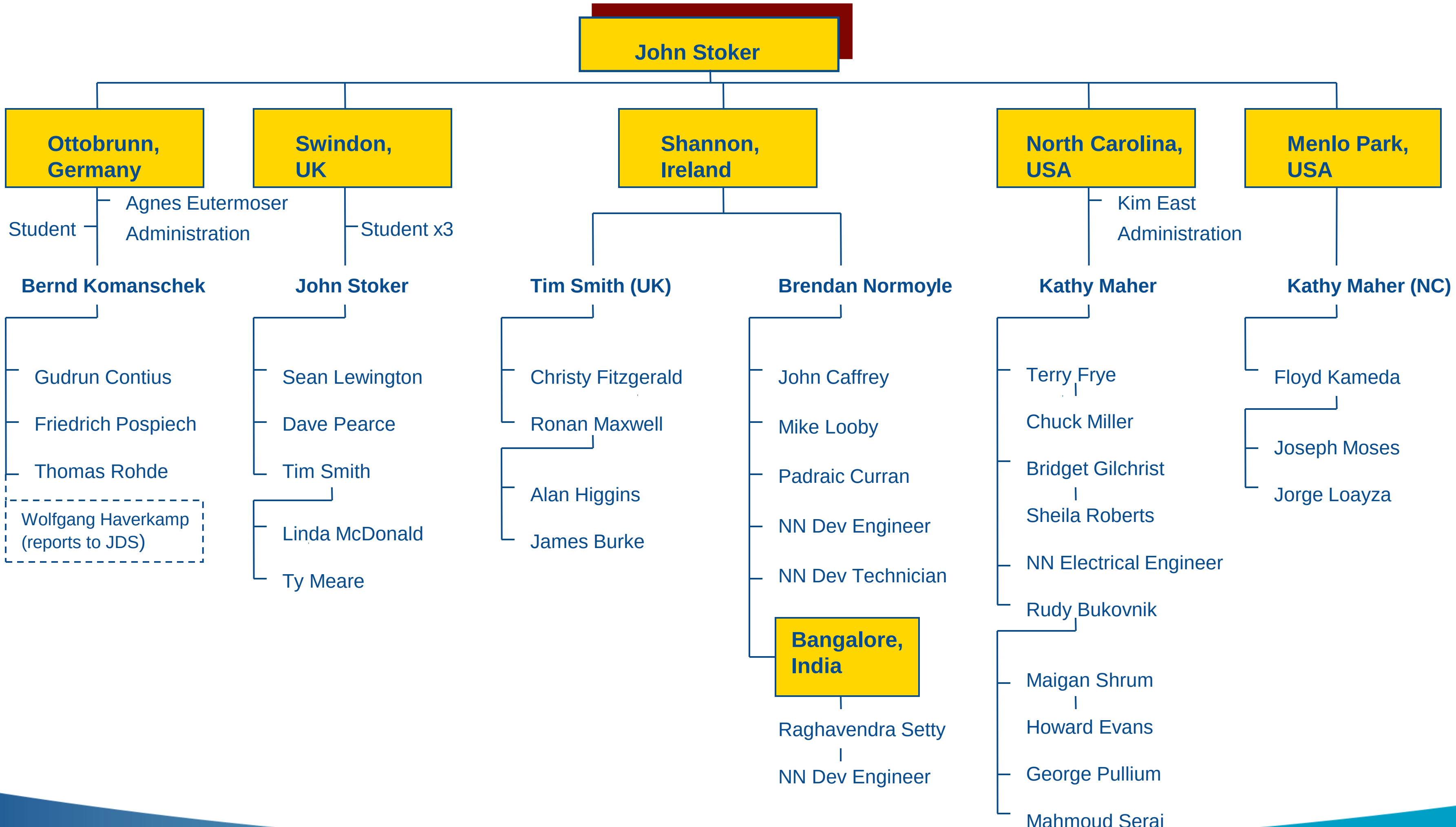
tyco Electronics

17 January, 2024

Energy Materials

Energy Products R+D Organisation



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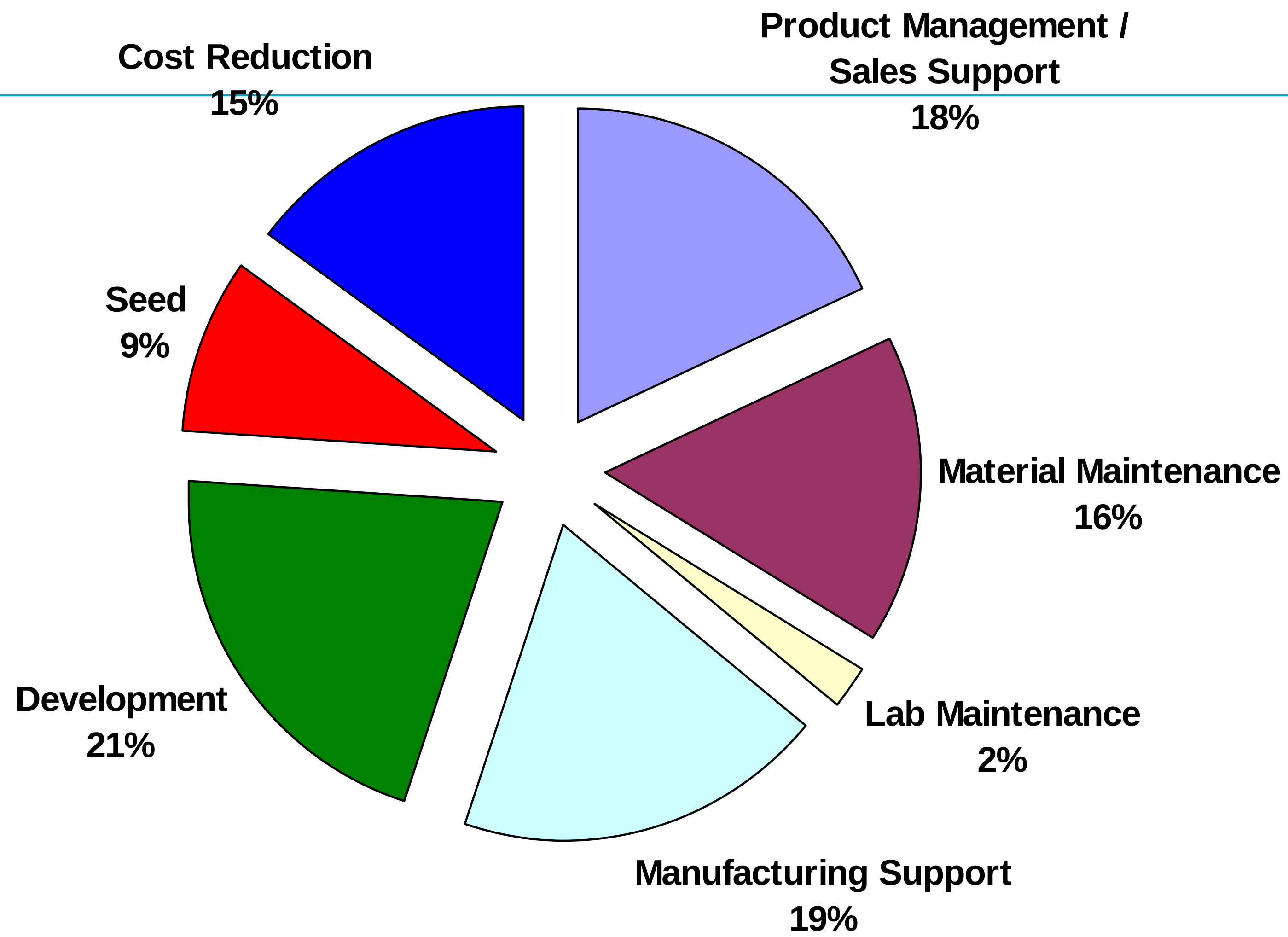
Materials & Processes Resources- Current Split

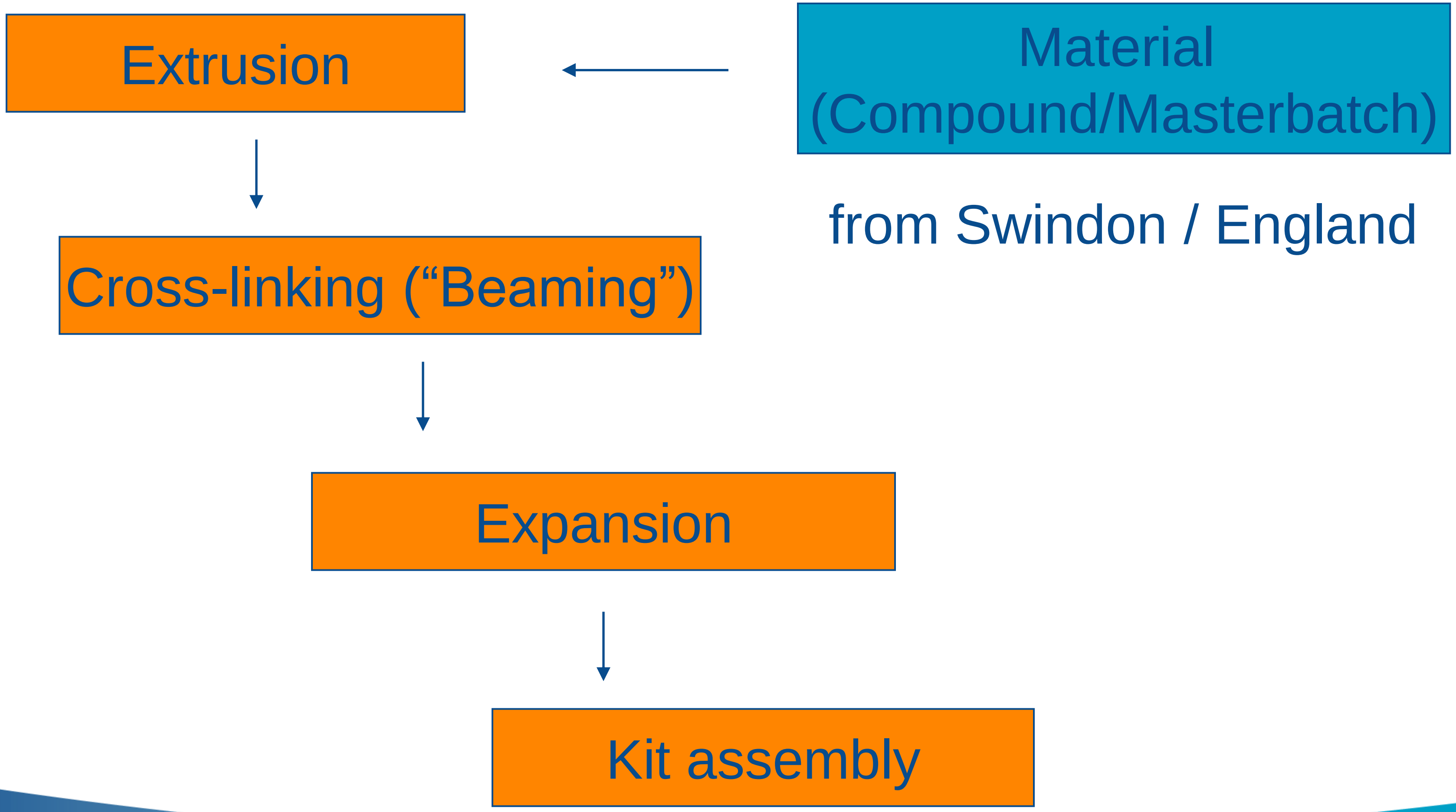


Presentation Summary.

- Fundamentals
- - Processing
- - Polymers / Elastomers
- - Cross-linking and elastic memory
- - Fillers and Additives
- Energy Materials
- - Overview
- - Anti-tracking materials
- - Stress-grading materials
- Materials Team Contacts
- Feedback Quiz

Manufacturing heat-shrinkable tubes

Process Flow Chart



Compounding & Mixing

The Material

Masterbatch: A concentrate; contains all additives, color pigments, process aids etc. bound in a polymer matrix. The manufacturer uses small amounts and adds it to the base polymer.

Advantage: The manufacturer does not need to touch dusty or liquid substances by himself.

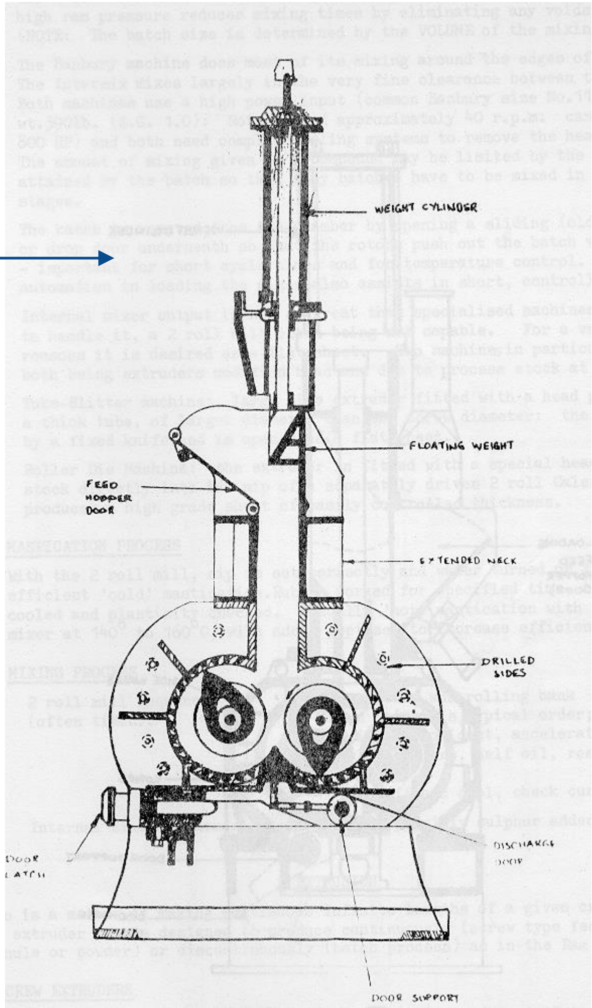
=> CLEANLINESS !

Polymer Processing

- Types of polymer processing :
  - Compounding Processes
    - Batch Mixers
    - Continuous Mixers
  - Conversion Processes
    - Extrusion
    - Injection Moulding
    - Blow Extrusion and Moulding
    - Thermoforming

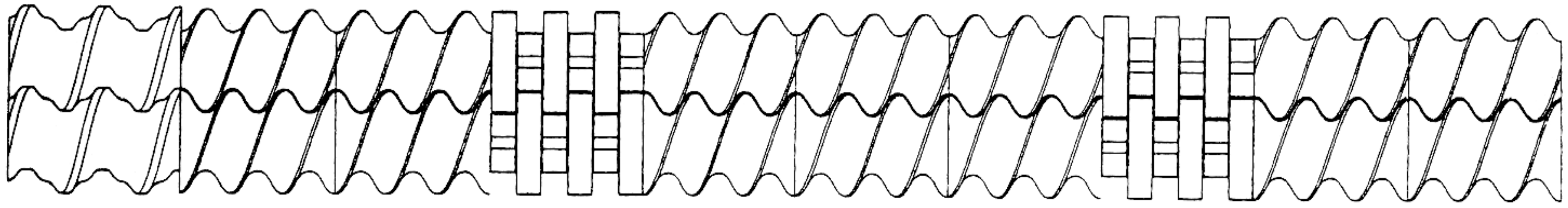
Polymer Processing

- Batch Mixer
  - Internal Mixer
  - Sigma / Z-Blade Mixer
  - 2-Rollen Mill



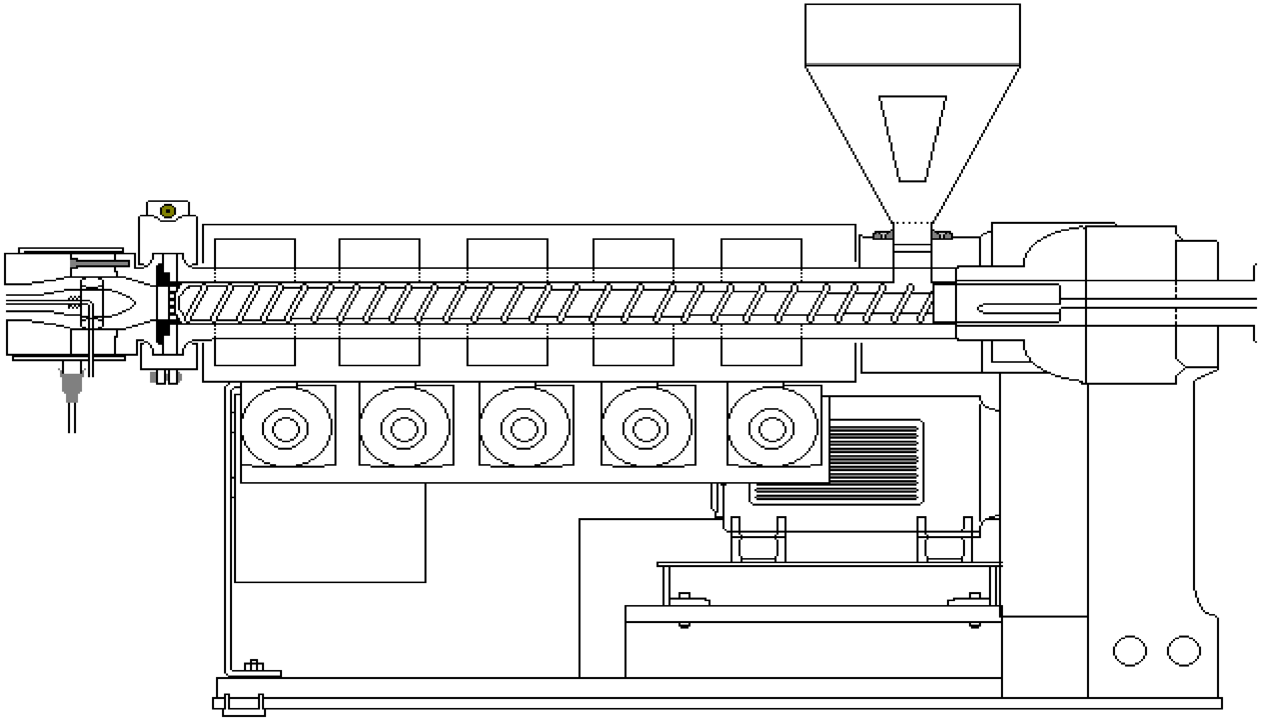
Polymer Processing

- Continous Mixer
  - "Buss" Co-Kneader
  - "Farrel" continous Mixer (FCM-type)
  - Double-Screw-Extruder



Polymer Processing

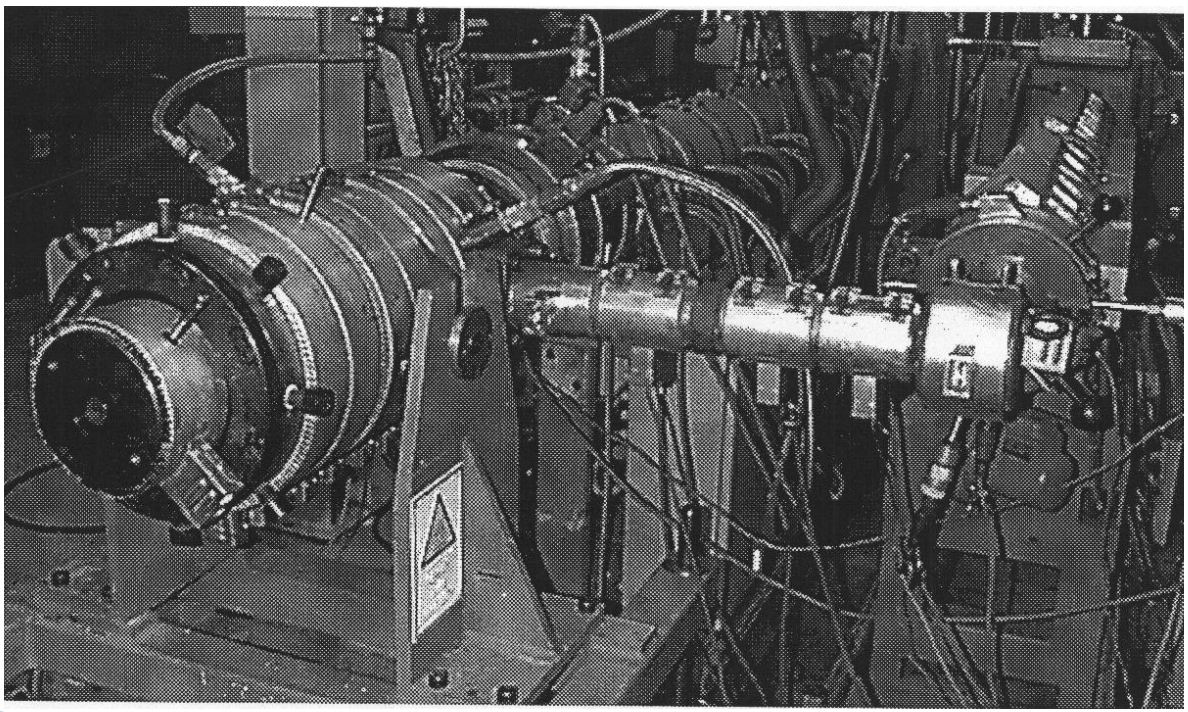
Extrusion

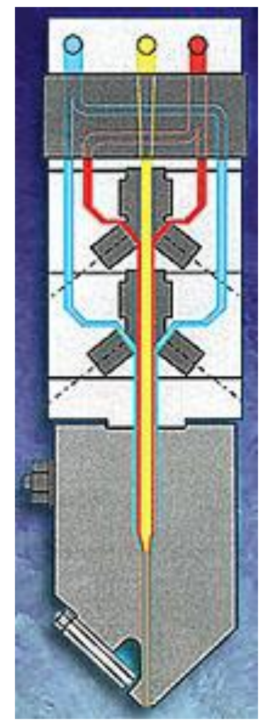


Tube Extrusion in Ottobrunn

Co-extrusion: **Two different layers of plastic-melt come together in a specially designed head at the end of the main extruder.**

Usually a bigger extruder is the main extruder and a smaller one the "Co".





Bsp.
Example of a design for production of multi layer foils.

Tube Extrusion in Ottobrunn

Some Numbers:

Tube extrusion on 7 Extrusion lines

> 2500 t Compound usage per year

- 42 Product families
- 40 different Compounds
- 338 different tubes
>> Wall thickness from 0,8 mm to 18,8 mm
>> Inner diameter from 1,5 mm to 135 mm

- > 10 000 Kilometer tube produced / year

- Shipping of > 2 000 000 Kits / year

How to cross-link ?
Which machines and processes do we use ?

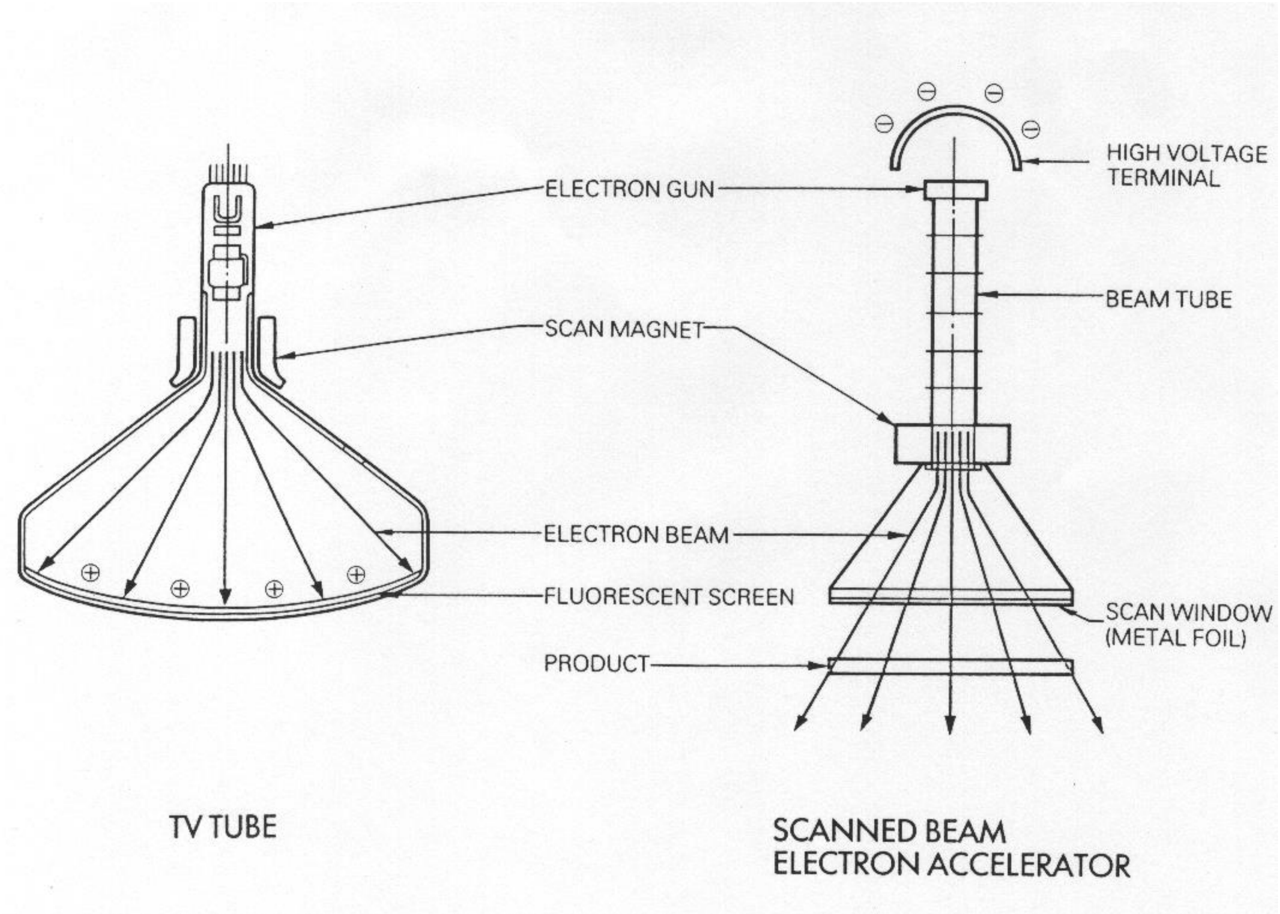
„Linear electron accelerator"   !

- Ottobrunn beam is a linear electron accelerator; build by
  RDI, New York, USA

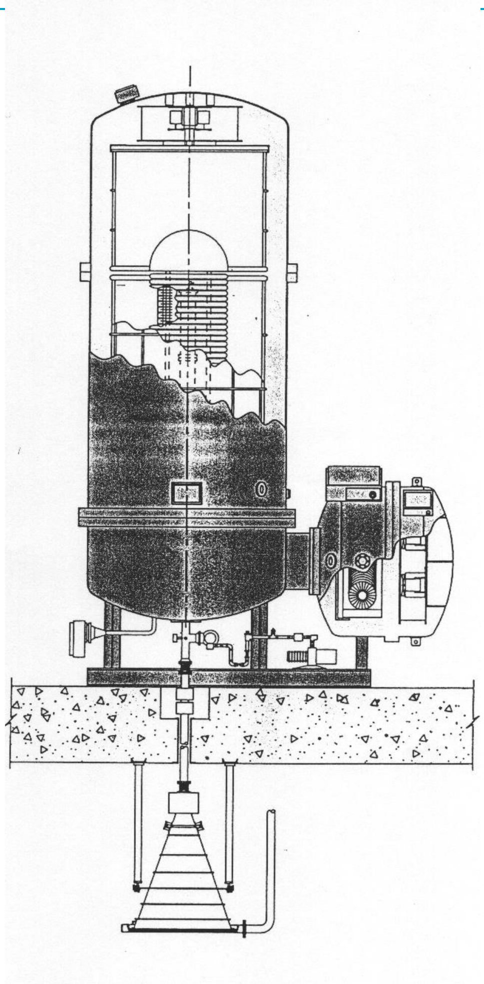
Functional principle is VERY similiar to a TV:

- heatable metalspiral, which emits electrons.
- vacuumtube
- electrons are accelerated by a difference of voltage
- unlike to a TV the electrons do not stop at a screen; instead
they penetrate a very thin titan foil which seals the accelerator tube

Working principle of an electron accelerator !



Electron Accelerator



Facts:

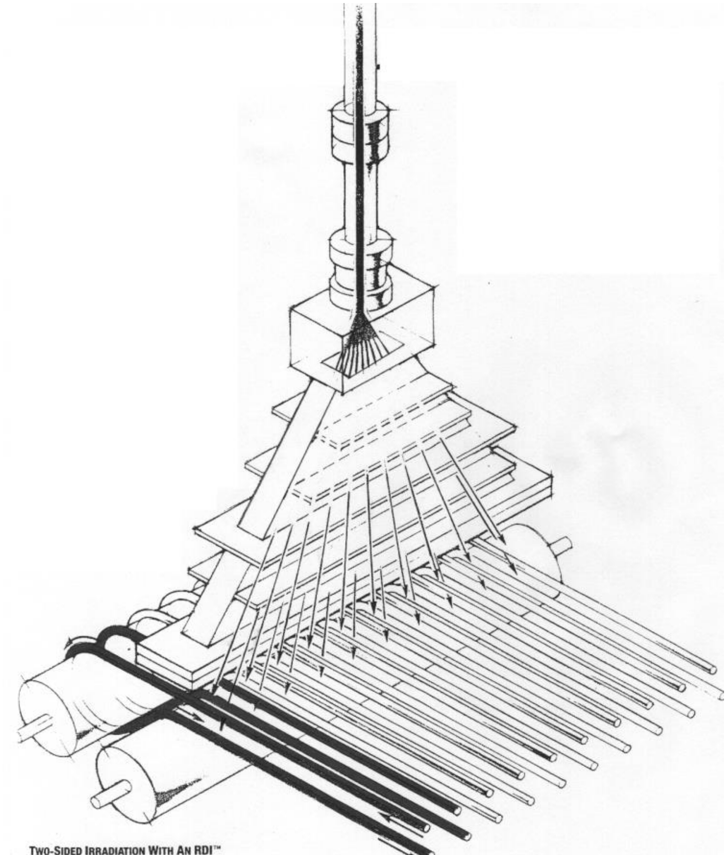
A TV work with ~25 kV; enough voltage to accelerate the electrons so they can produce a picture on the screen, but not enough power that they could come out of the screen.

Voltage range of the EA from 500 kV to 5 MeV.
Electrons accelerated with a voltage of 5 MeV gain a speed of 99,6% of LIGHTSPEED (~ 300 000 km/s) !!!

Such electrons are VERY POWERFUL!

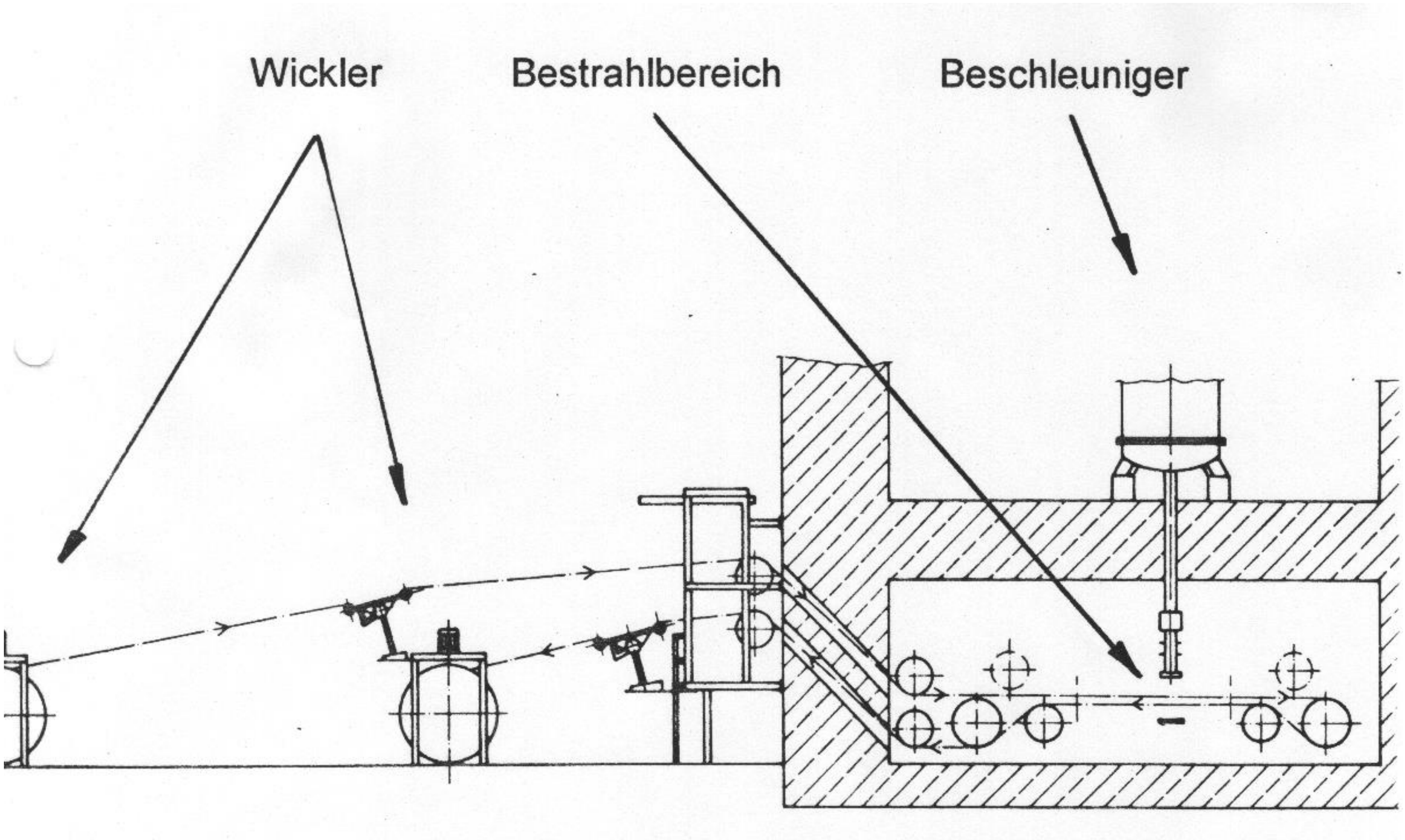
With impact to the molecules of the plastic they lose this energy and convert it into heat.

Spreading of the electron beam and beaming the tube



Two-Sided Irradiation With An RDI™ Dynamitron® Electron Beam System

Sectional drawing of the beaming site in Ottobrunn



Manufacturing of heat-shrink tubes in Ottobrunn

Expansion:

During the expansion process beamed tubes become hot until they weaken (NOT melt). Heating is done by a bath of GLYCERINE or MICROWAVES.

When the tube is weak it is stretched by vacuum or pressure to the diameter that is delivered to the customer. This diameter is fixed by cooling.

Manufacturing heat-shrink tubes in OB

Tube - Expansion:

General:

- Capacity: 9 Expansion-Lines

>> 6 Glycerin Linear-Expander
>> 1 Glycerin Rolltank-Expander
>> 2 Microwaves-Expander

Differences:

>> The way the product is heated
>> The way the product goes through the heating tank.
>> Expansion-tooling

Manufacturing heat-shrink tubes in OB

Tube - Expansion:

Heating by Glycerin:

- Heating by heat transfer from the hot Glycerine to the tube

==> heat gradient from outside to inside of the tube

- for expansion needed temperature: 85 - 145°C

==> depends on the melting point of the base polymer

>> HVOT: 83°C
>> WCSM: 108°C
>> MWTM: 130°C

Failures that could occur during expansion:

- if tubes are expanded with a lower temperature than stated, failures in terms of quality could happen

>> Eccentricity

>> „Cold“ stretching of the tube:

- high “snap back” (Diameter and Length)
- Deforming of the cut edges
- “Banana”-shape and dents

Manufacturing of heat-shrink tubes in OB

Tube - Expansion:

Heating the product by Microwaves:

- there is no temperature gradient because the heating takes place directly in the material:

= = > microwaves penetrate into the material and lose their energy
which is converted into heat. The plastic becomes warm.

- Why don‘t all plastics become warm by using microwaves ???
==> there must be special molecules into the polymer matrix that can "Swing"
>> plastics with Dipolcharakter: HVOT, ATOX
>> Filler (example Carbon Black): MWTM, SCTM, WCSM

Manufacturing of heat-shrink tubes in OB

Tube-Expansion:

Advantage Microwave-Expansion:

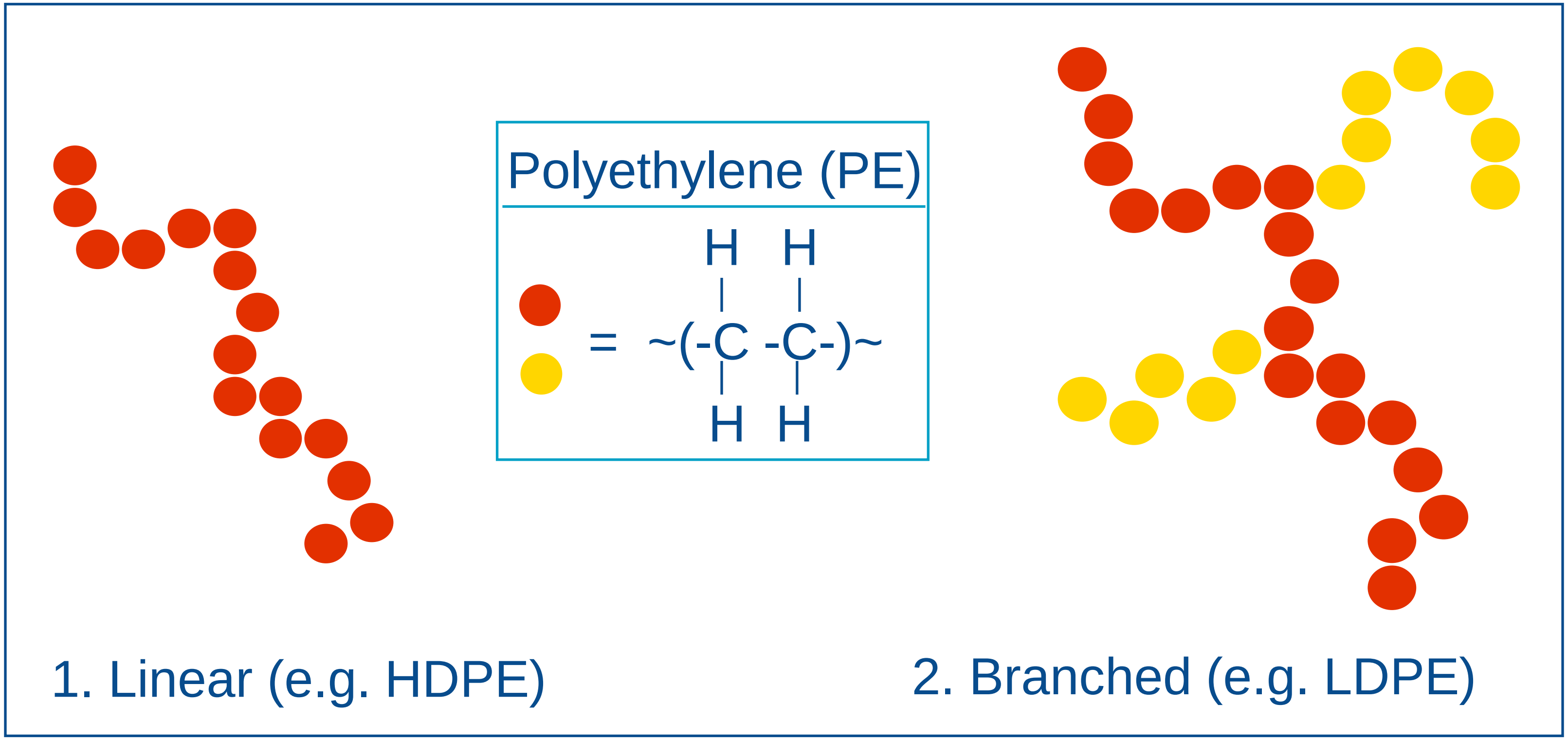
- no temperature gradient ==> less stress in the product
- no influence on the surface by the Glycerine
- lower costs for production and service
==> Cost of Glycerin (500 EUR/Barrel + dumping)
==> ~ 90 % less use of energy

Disadvantages:

- only suited for tubes with diameter less than 40 mm
- not all materials are suited

Polymers/Elastomers

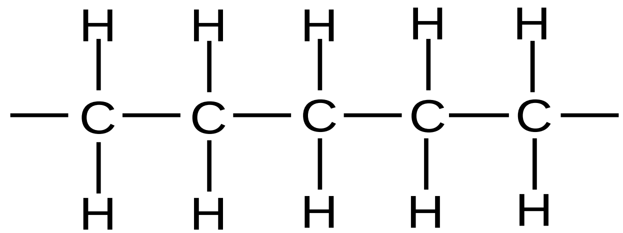
- What is a polymer?



Properties of polymers

Chemical Composition

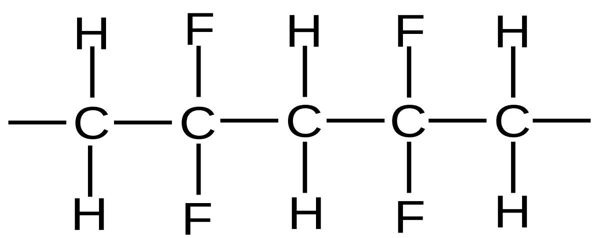
soft to hard, unbreakable,
(MWTM)



Polyethylen(PE)

weich bis hart,
unzerbrechlich,
löslich in einer Vielza
von Lösungsmitteln
(MWTM)

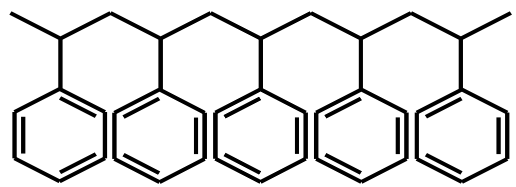
hard, tough, unbreakable,
superior chemical resistivity
(OBTF)



Polyvinylidenflourid (PVDF)

hart, zäh,
unzerbrechlich,
hervorragende chem.
Beständigkeit
(OBTF)

hard, breakable,
(plastic spoons and forks,
joghurtbeaker)



Polystyrol (PS)

hart,
zerbrechlich
(z.B. Geodreiecke,
Joghurtbecher,
Wegwerfbestecke)

Definition: Polymer

Polymers are materials, who...

- consist out of *Makromolecules*

and

- are made by modifying natural materials

or

- made by sythesis out of primary raw materials like oil , coal or silicium.

Macromolecular Products

natural products	modified natural products	synthetic products
• Wood • Caoutchouc • Cotton • Silk	• Bakelit • Rubber • Vulcanfiber	• Polyethylen (PE) • Polyvinylchlorid (PVC) • Polyvinylidenfluorid (PVDF) • Silicones

Composition of synthetic polymers

Plastics are made from following basic chemical **elements**:

- **Carbon (C)**
- **Hydrogen (H)**
- **Oxygen (O)**

Sometimes there will be also nitrogen, sulphur, fluor and chlor.
The Silicones are made mainly from silicium (Si).
All these basic chemical elements are part in coal, chalk, water, air oil and quarz-sand.
Basic molecules for manufacturing sythetic polymers are refined mostly from crude oil.

Categories of Polymers

Thermoplastics	Duroplastics	Elastomers
• more soft • warm ductile • deforming is reversible • polymer chains are „Spaghetti“-like composed	• hard and refractory • temperature stable • not ductile • cannot melt • unsoluble • polymer chains are crosslinked in all directions (3D)	• elastic • can swell • chain are widely crosslinked, molecular composition like a net

From basic molecules to a synthetic polymer !

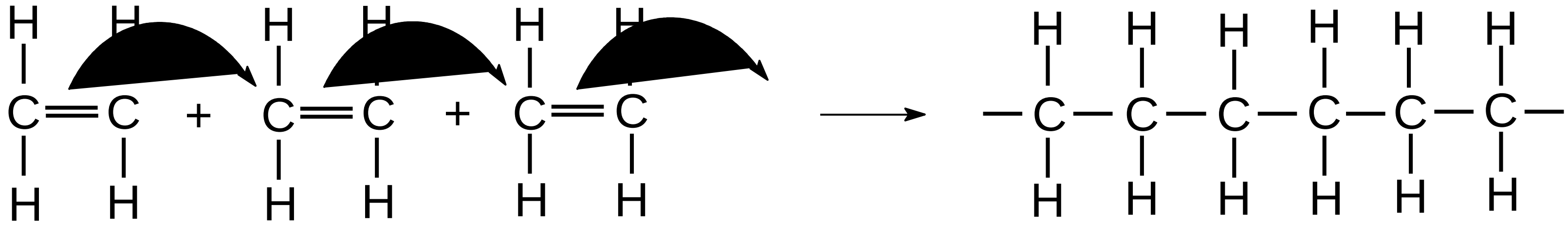
By chemical reaction monomeres are linked to each other and polymeres (long chains of many linked monomeres) are formed.

There are 3 ways to do this chem. reaction:

- polymerisation
- polycondensation
- polyaddition

This new polymeres do have completely different properties than the single monomeres !

From basic molecules to a synthetic polymer !



Ethylen
Monomer

Polyethylen
Ausschnitt aus der Kette
Polymer

By a suitable start reaction a doublebond between two carbon atoms is broken.

A chainreaction repeat this many times and forms a long polymerchain.

This reaction stops when all monomeres are used up.

Above example shows a POLYMERISATION.

Properties of synthetic polymers

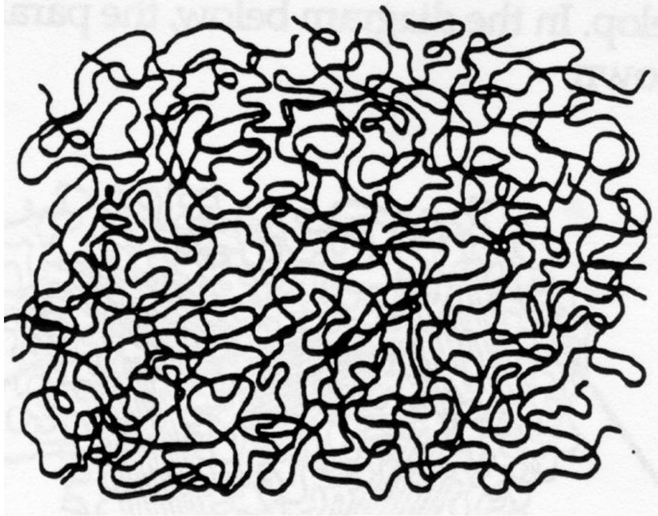
To characterize the properties of a synthetic polymer there are a lot of numbers, values and categories.

All numbers can be categorized in one of the following groups:

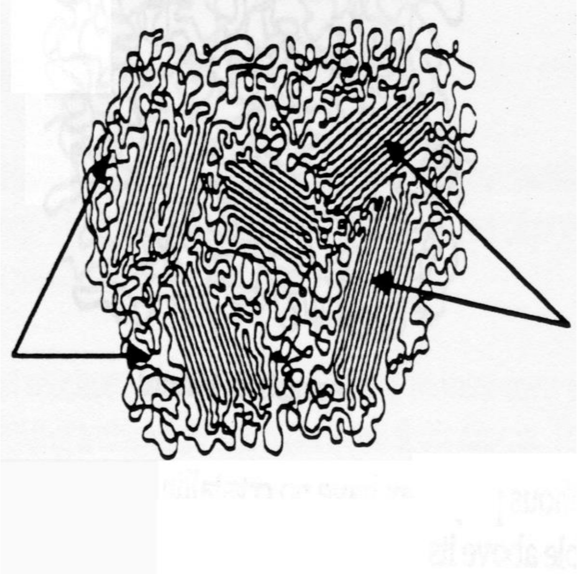
- chemically/physically (chem. resistivity, melting point, density, ...)
- mechanically (tensile strength, ultimate elongation, hardness, ...)
- electrically (conductivity, dielectric strength, volume resistivity...)

But how can we influence the properties of polymers ?

Amorphous and Semi-crystalline



Amorphous areas

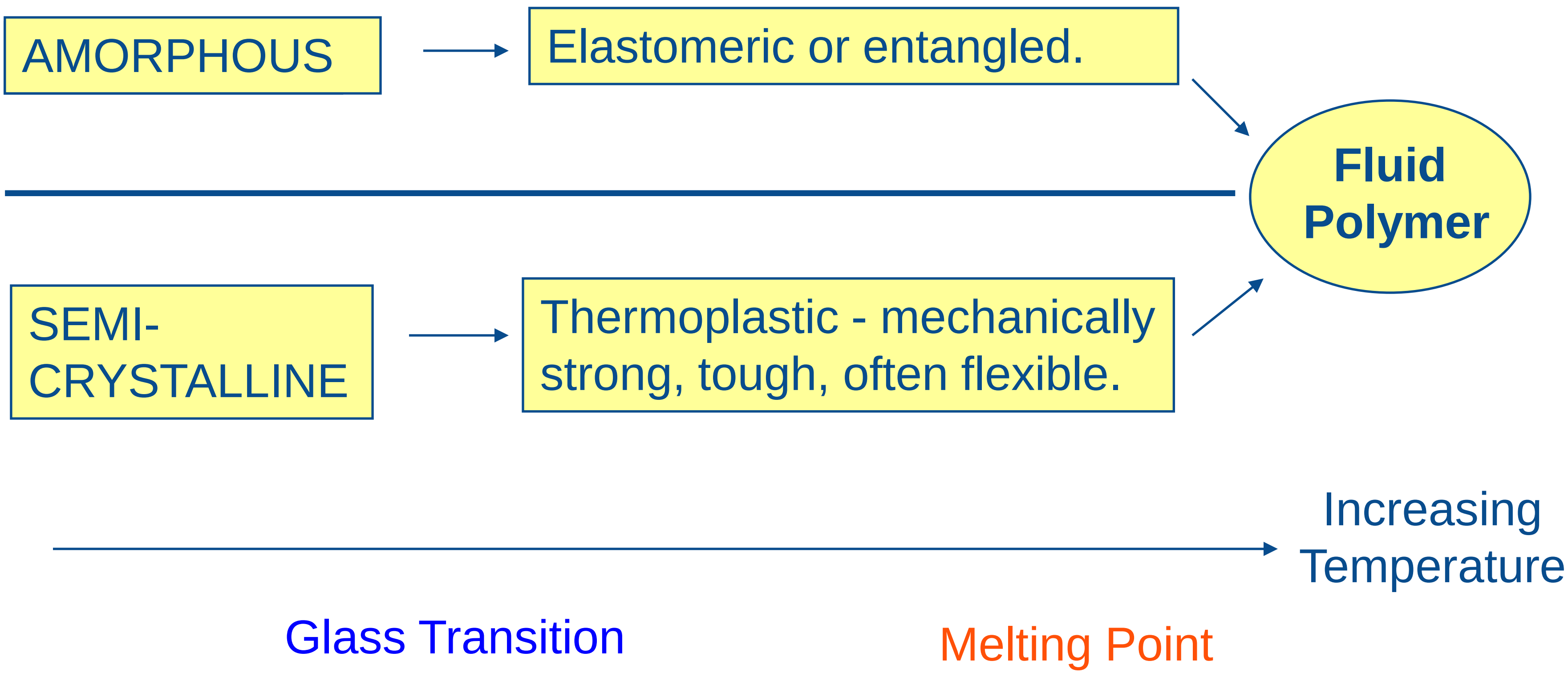


Crystalline areas

Amorphous

Semi-crystalline

Phase Transitions



Polymer Properties

- Mechanical Properties
    - ❑ Physical properties
- Electrical Properties
    - ❑ Volume & surface resistivity
    - ❑ Tracking & erosion resistance
- Chemical Properties
    - ❑ Thermal stability
    - ❑ Ultraviolet resistance

Why does a heat-shrinkable tube shrink ?

A heat-shrinkable tube shrinks when it is heated.........

- and does not melt (!), because the material is cross-linked **!**

- because the polymer chains were stretched (expanded) AFTER the material was cross-linked. The “frozen” and stretched chains become moveable by the heat supply and can now snap back.

→ **What** is cross-linking ?
→ **Why** cross-linking ?
→ **How** to cross-link ?
→ **What** machines and processes are used ?

Cross-linking and Elastic Memory

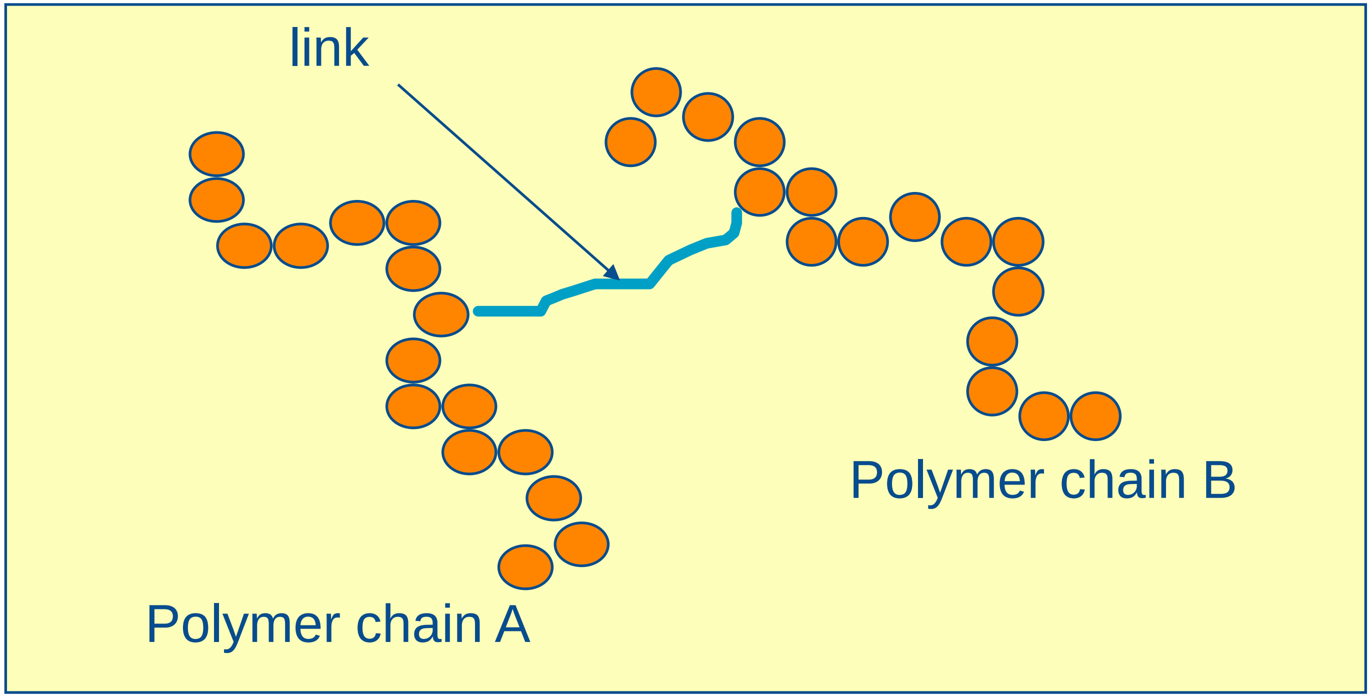
- Why cross-link polymers?

  - **'Elastic Memory' effects for heat shrink products.**
  - Increased strength and toughness.
  - Increased environmental, solvent and chemical resistance.
  - Improved mechanical performance.
  - More stable electrical properties.
  - Improved thermal performance.

What does “cross-linked” mean ?

Cross-linking is building a 3 dimensional network between the single polymer chains by connecting the chains !

- Visual idea of cross-linking



How to cross-link ?

A) **Cross-linking by beaming** (physical)

-> **Electronbeam** !!!
-> Electromagnetic Rays

B) **Chemical Cross-linking**

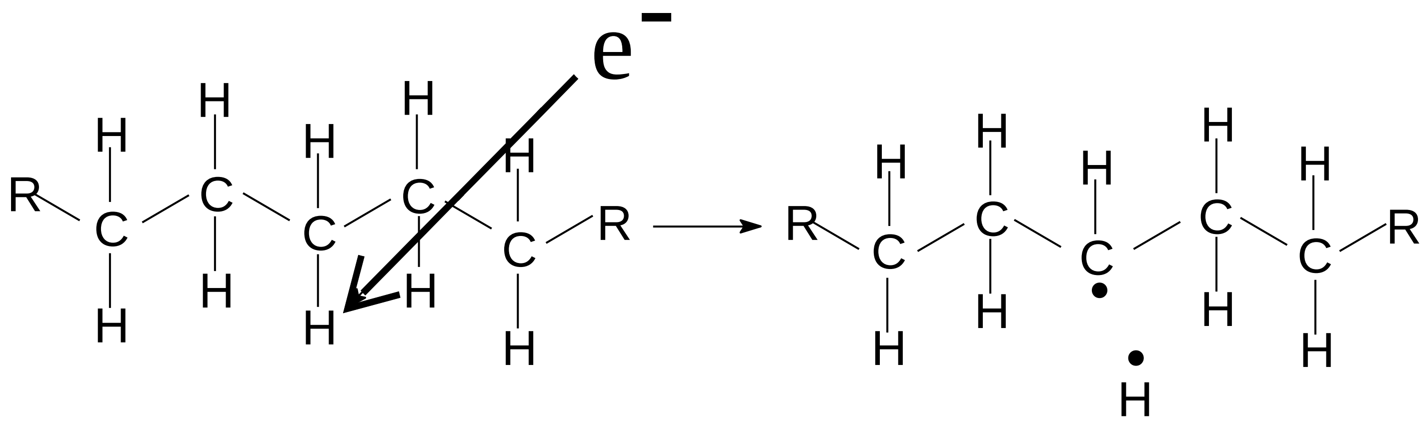
- Vulkanisation (carbon chains are cross-linked by using sulphur.)
-> Goodyear 1839 (Tires made from natural-rubber)
- Cross-linking by peroxides
- Cross-linking by Silanes

Cross-linking and Elastic Memory

- Methods of cross-linking :

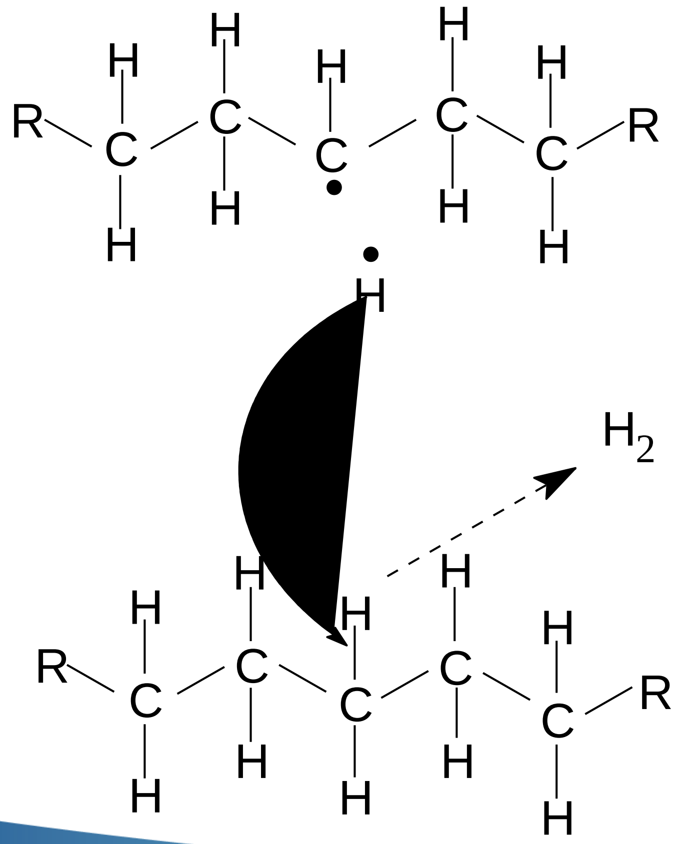
Radiation	Chemical
▪ light ▪ X-ray ▪ **gamma-rays (e.g. Cobalt 60)** ▪ **electron [beta]** **- (e.g. electron beam)** ▪ alpha-rays (He-cores) ▪ neutrons	▪ **peroxide (e.g. Dicup)** ▪ **silicone addition cure** ▪ amine (e.g. epoxy) ▪ Sulphur (vulcanisation) ▪ other reactive groups

Cross-linking with electrons by example of PE



An energy rich (fast) electron destroys the bond between a carbon atom and a hydrogen atom.

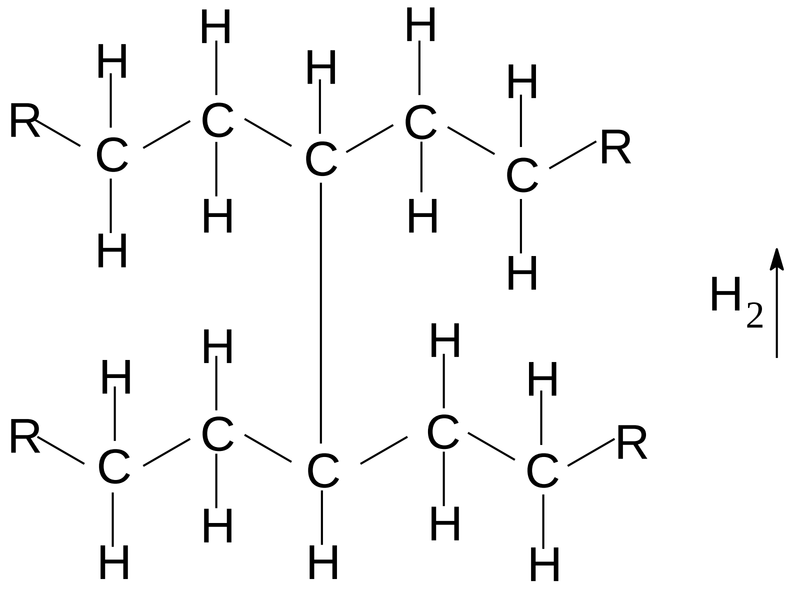
Cross-linking with electrons by example of PE



The loose and very reactive hydrogen atom breaks another bond open between carbon and hydrogen in a neighboured chain.

The single hydrogen atoms combine with hydrogen gas and disappear.

Cross-linking with electrons by example of PE

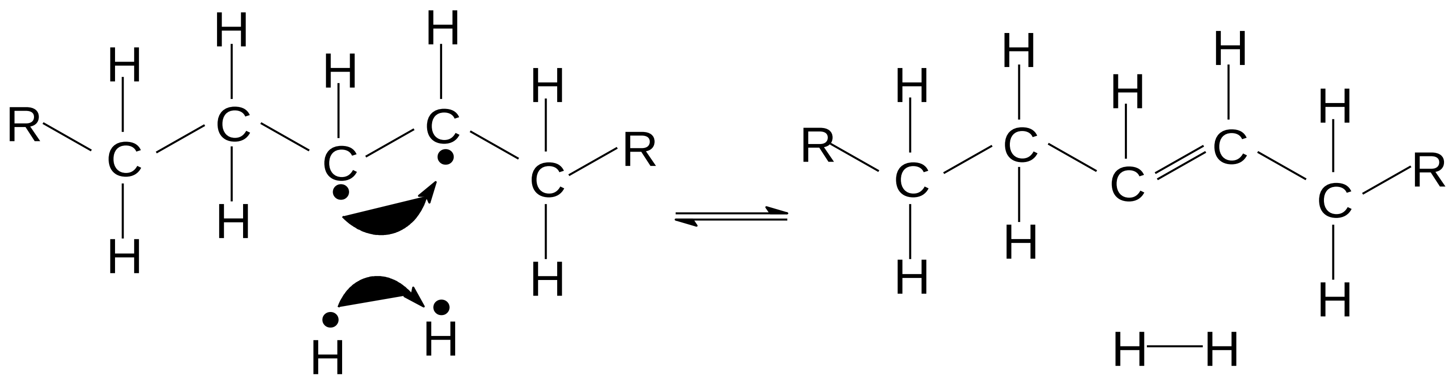


The polymer chains combine.

Chains that where “ loose” before are now bound together (CROSS-LINKED)!

Cross-linking with electrons by example of PE

Side reaction A:

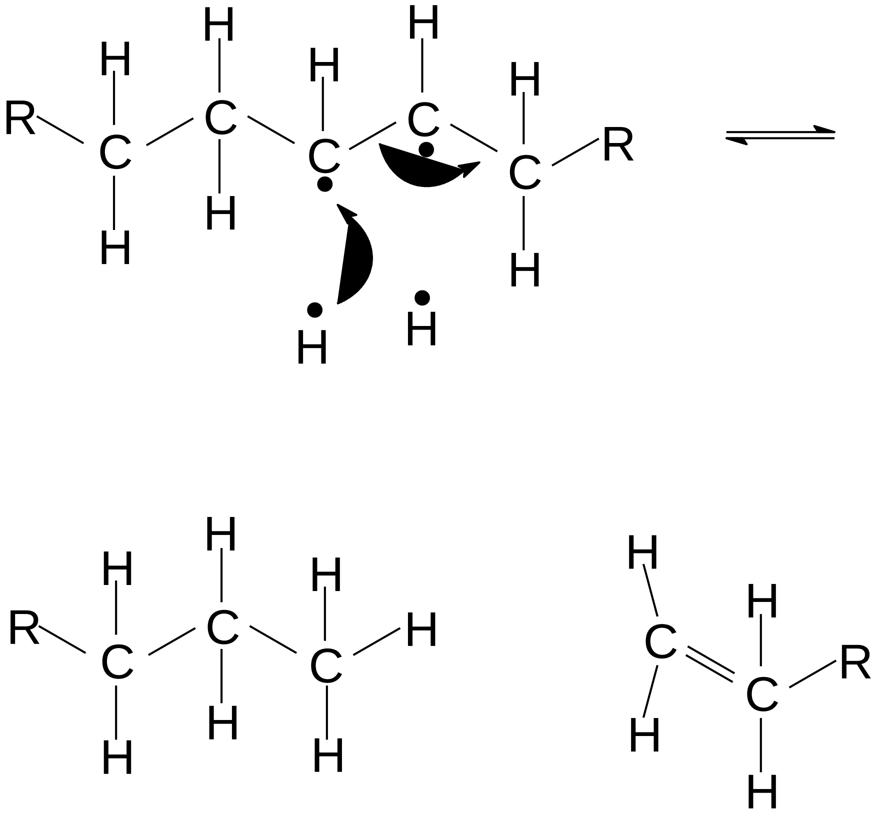


Forming a “double” -connection

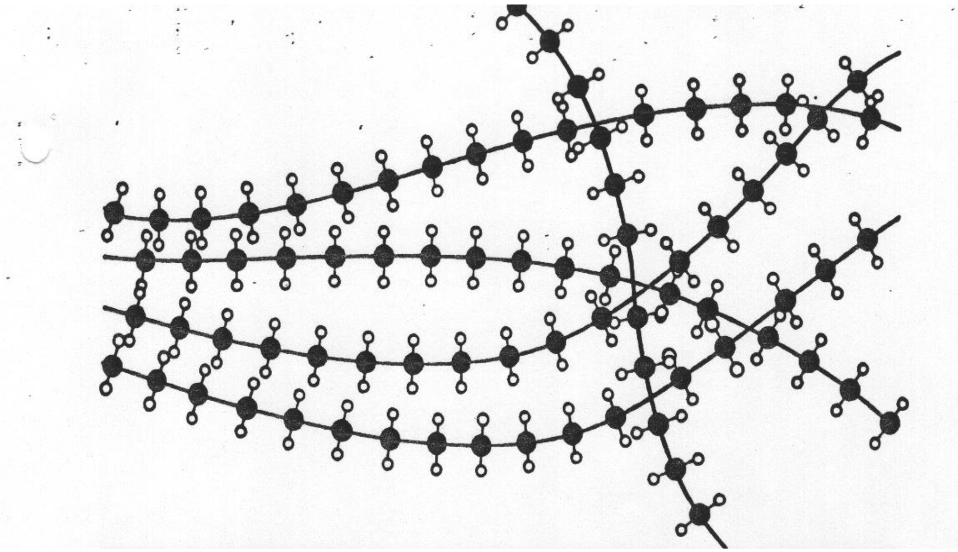
Cross-linking with electrons by example of PE

Side reaction B:

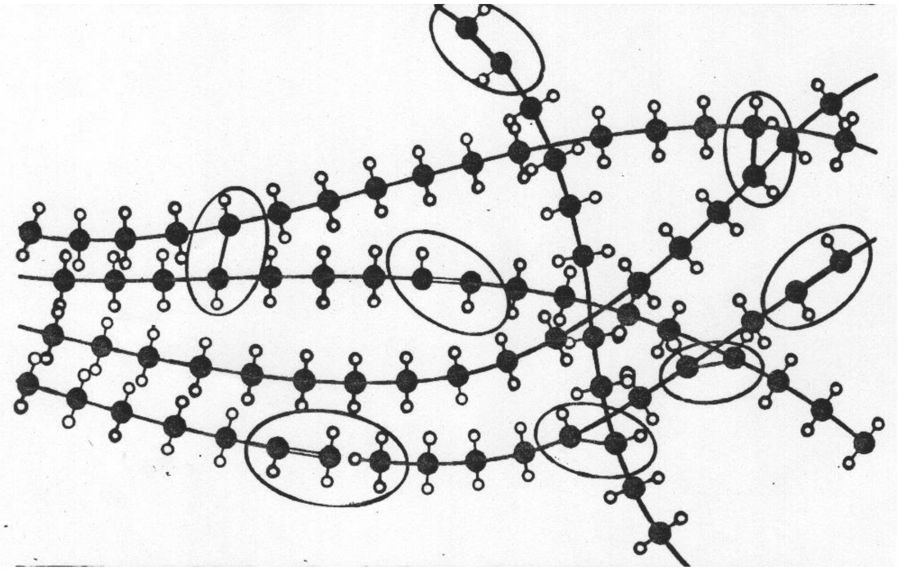
“Breaking” of a chain



Cross-linking with electrons by example of PE



Polyethylene molecule chain before Cross-linking by electron beam



Polyethylene molecule chain after Cross-linking by electron beam

Fillers / Additives for Polymers / Elastomers

- **What are fillers / additives, and why are they used?**

Additives are chemicals blended with polymers during a compounding operation. They are used to modify and enhance the physical and chemical properties of the polymers, extend service life and improve the processability.

Fillers / Additives for Polymers / Elastomers

Iron Oxide

Uses;
- Pigment
- UV screen
- Anti-tracking

Other Fillers

Uses;
- Cost reduction
- UV screen
- Reinforcement

Carbon Blacks

Uses;
- Conductivity
- UV screen
- Reinforcement
- Pigment

Thermal Stabilisers

Uses;
- Thermal withstand
- Long term aging

Polymer

Process Aids

Uses;
- Dispersion
- Process speed
- Surface finish

UV Stabilisers

Uses;
- UV absorber
- Long term aging

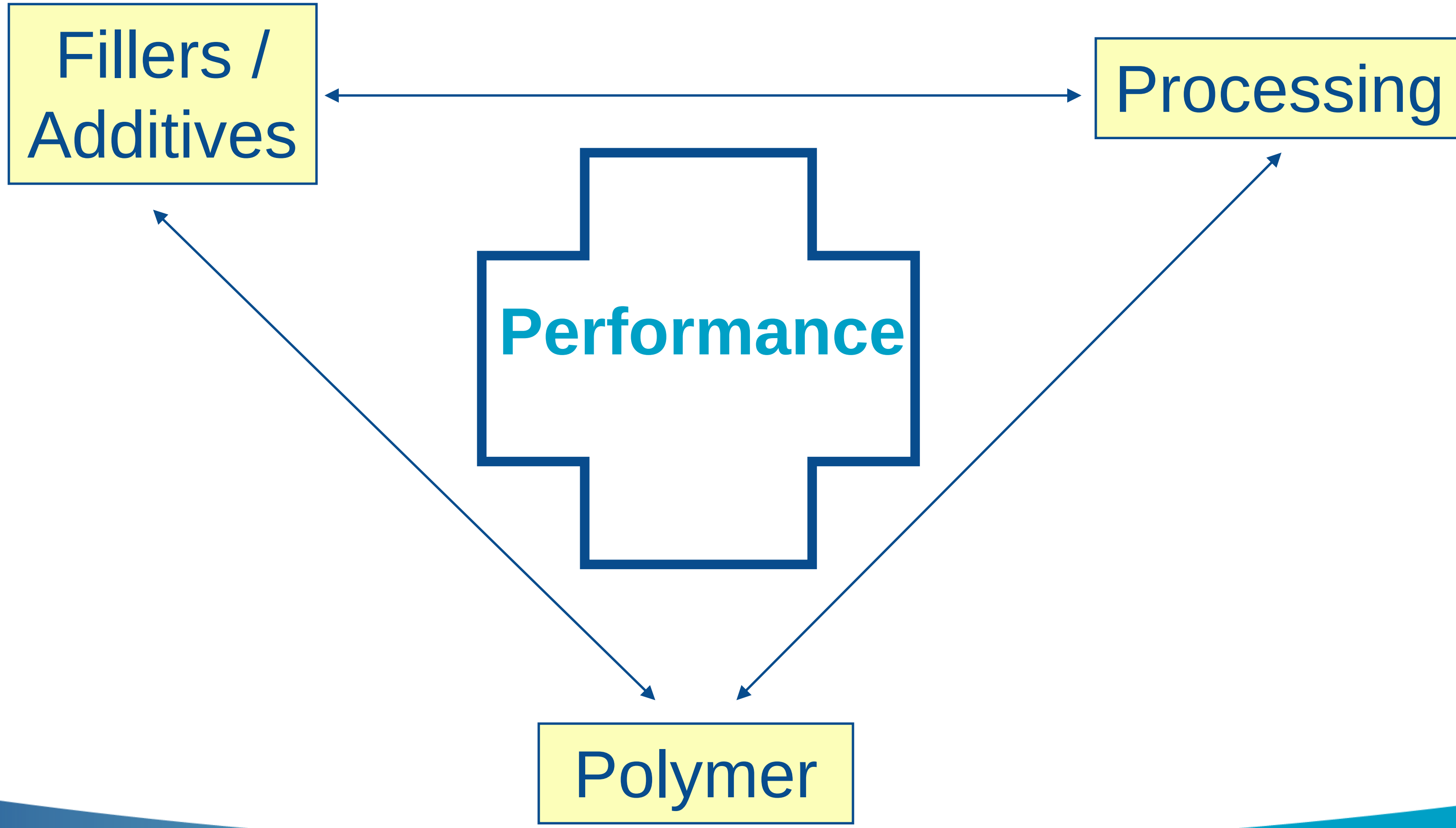
Oils

Uses;
- Filler acceptance
- Dielectric strength
- Viscosity modifier

Anti-Tracking Fillers

Uses;
- Anti-tracking
- Flame retardant

Overall Product Performance



Testmethods and Specifications

Testing and measuring is done by........

- Qualitycontrol (QC)
- „Materials Group“ (PPS)
- „Product Management“ (Application)

Testmethods and Specifications

Qualitycontrol takes care and measures, if product parameters are in spec. Product parameters are:

1) Dimensions

2) mechanical properties (tensile strength, ultimate elongation)
- level of crosslinking
- shrinking performance

3) electrical properties (z.B. conductivity, volume resistivity)

Testmethods and Specifications

„Materials-Group" checks **ALL** material properties

of a product when:

- product is a new development
- Requalifikation is needed

(example: replacement of one or more raw materials)

- if there are any other problems

Testmethods and Specifications

„Product-Management" examines and tests all products under real conditions and to international standards !

Example:
- salt-fog-chamber-Test
- leakage current test
- various tests according Cenelec

etc.

Testmethods and Specifications

Testing and measuring according to:

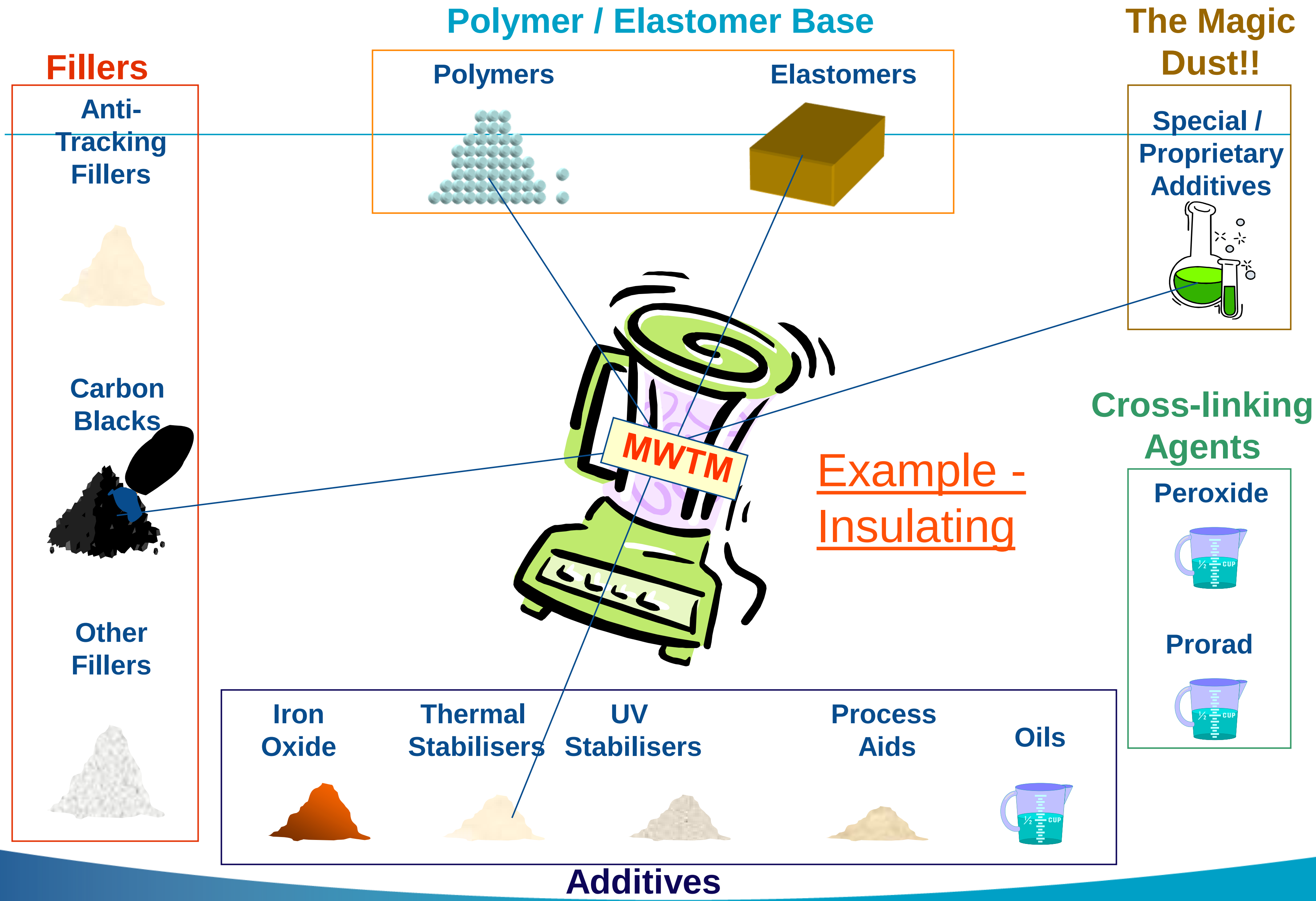
- DIN (Deutsche Industrie Norm)
- VDE (Verein deutscher Elektrotechniker)
- ASTM (American Standard for Testing and Measurement)
- BS (British Standard)
- IEEE (Institute of Electrical and Electronics Engineers)
- IEC (International Electrotechnical Commission)
- EATC bzw. ESI
- CENELEC
- specific customer request

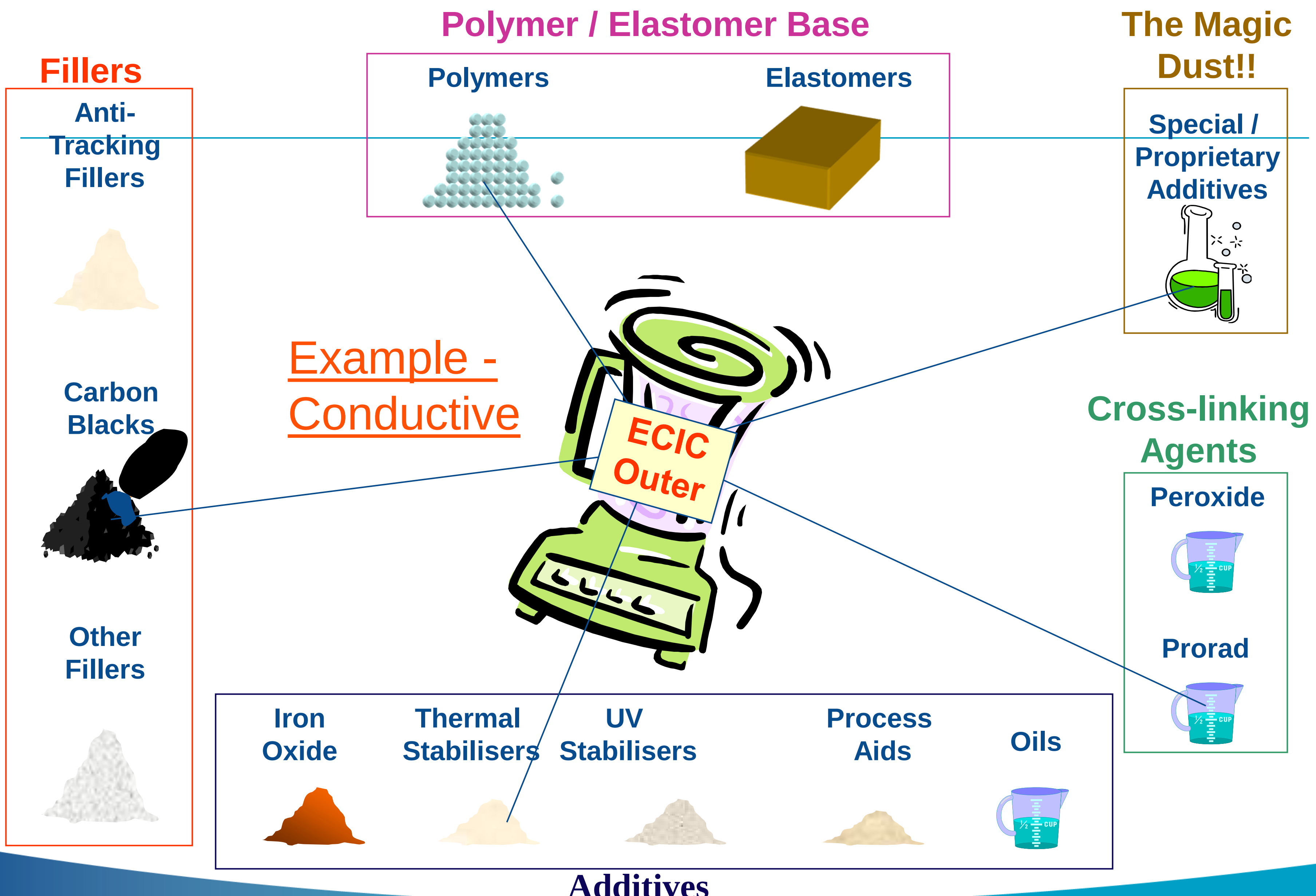
Part of a typical PPS (**P**ower **P**roducts **S**pecification):

Test	Spec. Clause	Quality Assurance	Requirement S.I. Units	Requirement Imperial Units
Tensile Strength	4.3	Product Acceptance	15 MPa min.	2160 PSI min.
Ultimate Elongation	4.3	Product Acceptance	400% min.	400% min.
Density	4.5	Product Acceptance	(1.25-1.35) g/cm^3	(1.25-1.35) g/cm^3
Accelerated Ageing 168 hrs. at (150±2)°C - Tensile Strength - Ultimate Elongation	4.9	Qualification	 15 MPa min. 400% min.	 2160 PSI min. 400% min.
Thermal Endurance	4.11	Qualification	110°C min.	110°C min.
Low Temperature Flexibility 4 hrs. at -(40±3)°C	4.12	Qualification	No cracking	No cracking
Dielectric Strength 1.5 mm/0.06 inch wall 3 mm/0.12 inch wall	4.30	Qualification	 200 kV/cm min. 140 kV/cm min.	 500 V/mil min. 350 V/mil min.
Volume Resistivity	4.31	Qualification	1 x 10^{13} Ohm cm min.	1 x 10^{13} Ohm cm min.
Dielectric Constant	4.32	Qualification	5.0 max.	5.0 max.

Energy Materials

- Insulating
- Conductive
- Semi-conductive (stress grading)
- Anti-tracking
- Sealing (mastic & adhesives)
- Oil Barrier
- Void Filling


Polymer / Elastomer Base
Polymers
Elastomers
The Magic Dust!!
Special / Proprietary Additives
Fillers
Anti-Tracking Fillers
Carbon Blacks
Other Fillers
MWTM
Example - Insulating
Cross-linking Agents
Peroxide
Prorad
Iron Oxide
Thermal Stabilisers
UV Stabilisers
Process Aids
Oils
Additives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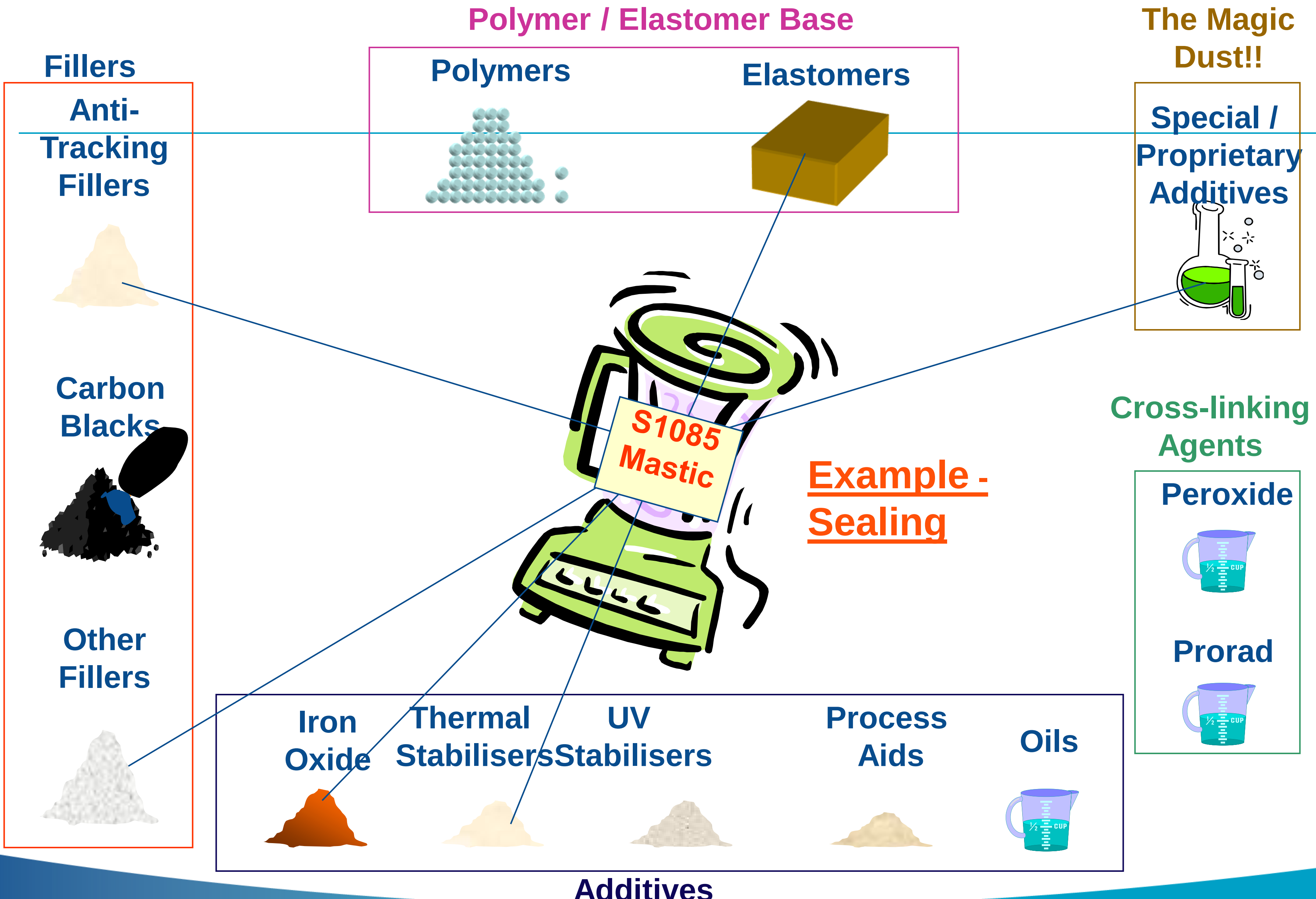
UV Stabilisers
Process Aids
Oils
Additives


Polymer / Elastomer Base
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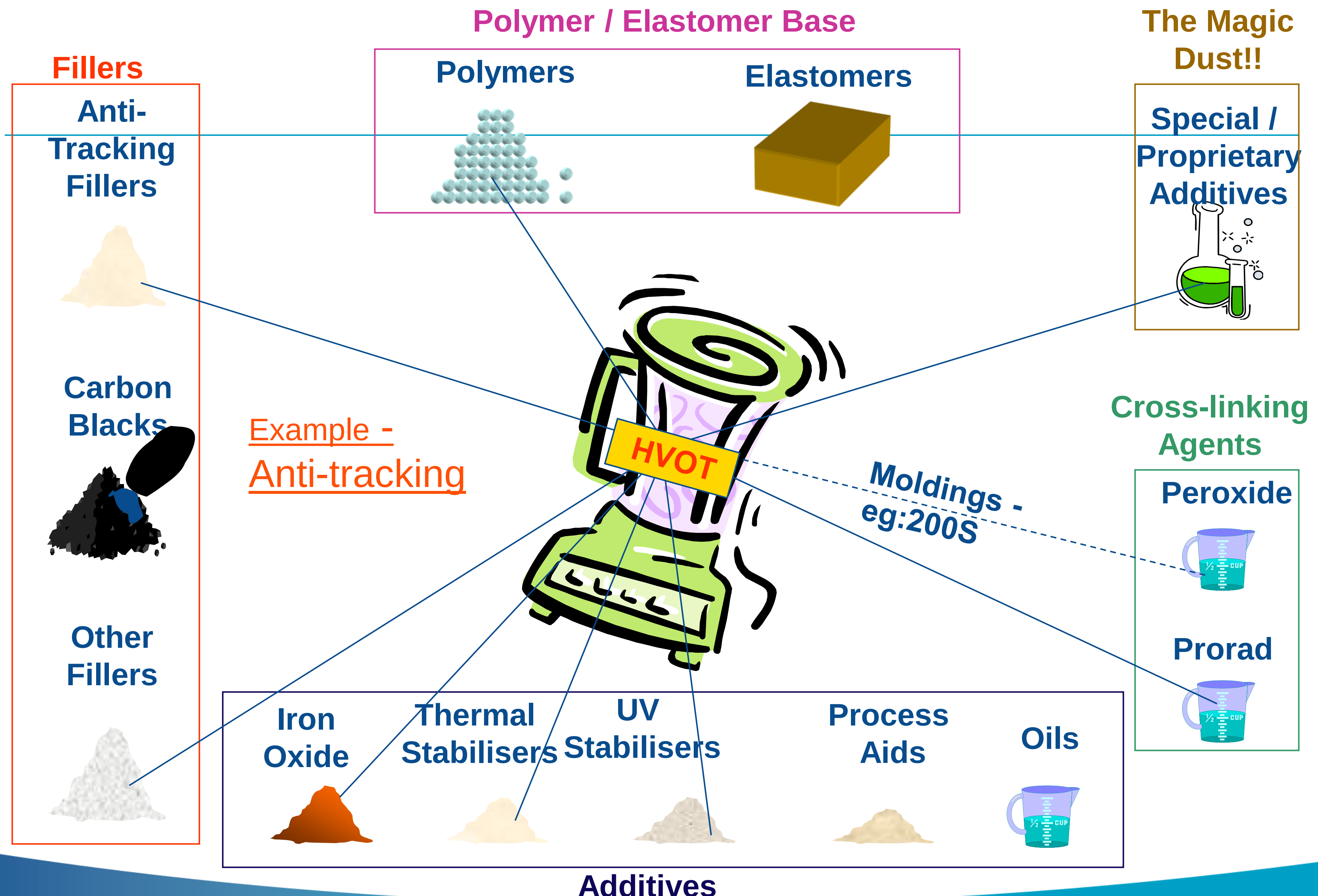
Special / Proprietary Additives
S1085 Mastic
Carbon Blacks
Cross-linking Agents
Example - Sealing
Peroxide
Prorad
Other Fillers
Iron Oxide
Thermal Stabilisers
UV Stabilisers
Process Aids
Oils
Additives

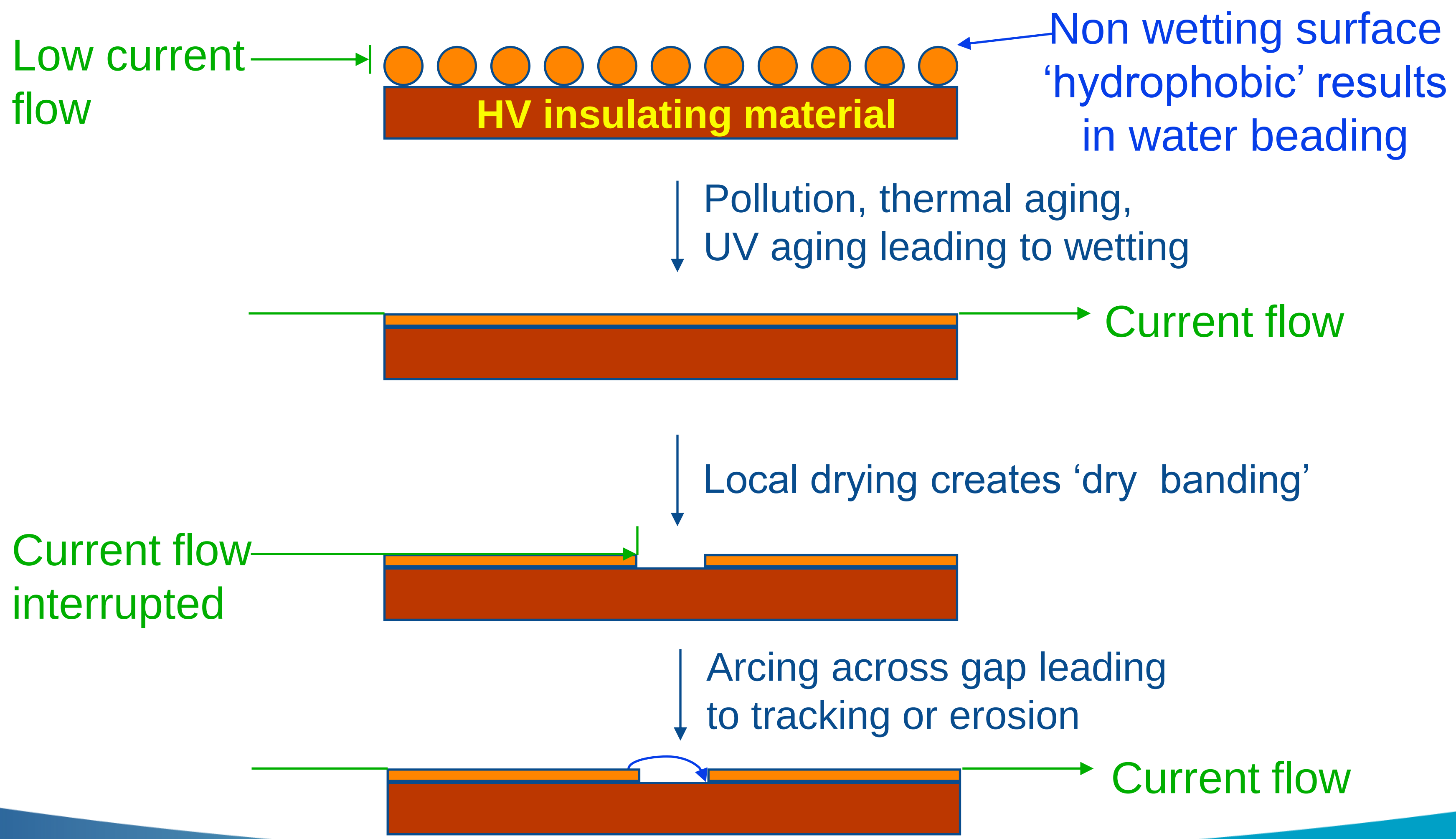
Requirements Of Polymeric Anti-Tracking Materials

Critical parameters :

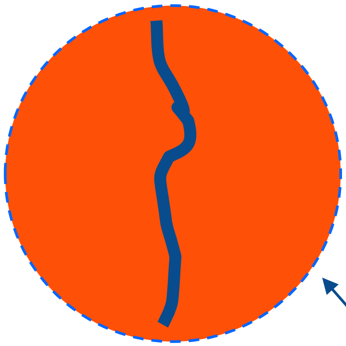
- Outstanding long term weatherability
- Tough and impact resistant
- Function in polluted environments
  - Non tracking and low erosion rates
  - Non wetting (hydrophobic) is an advantage, but not essential

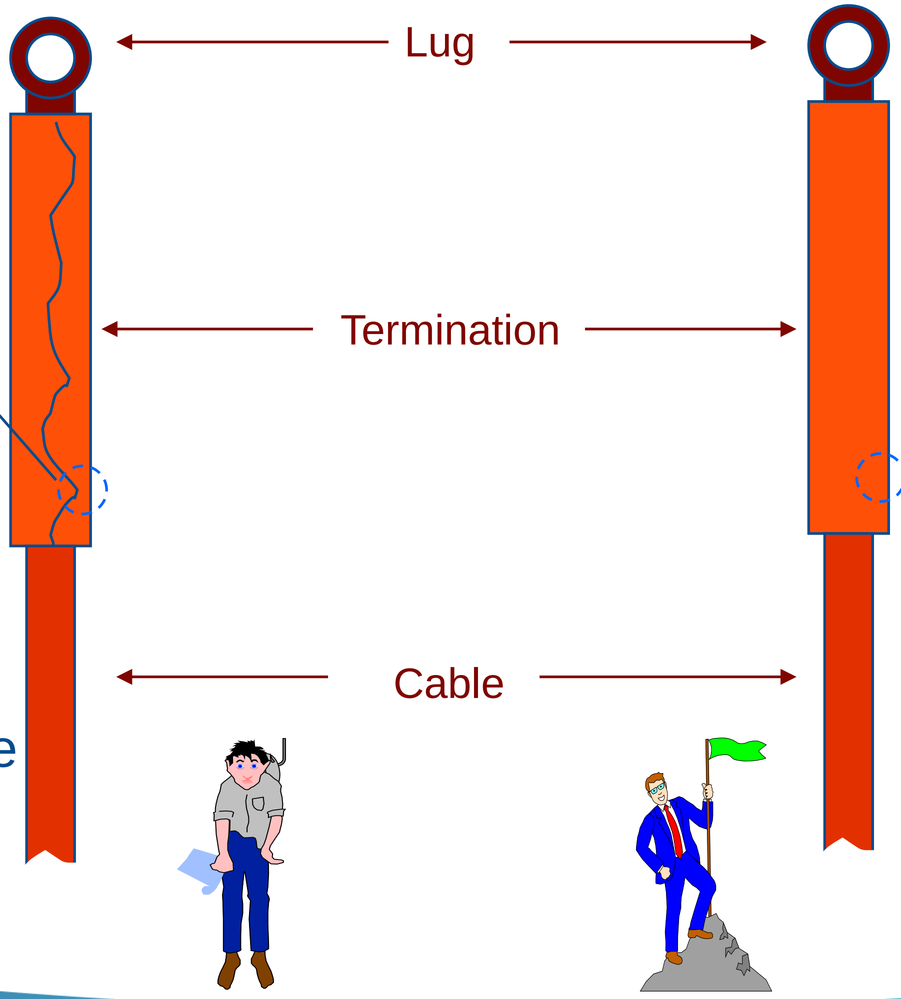

Polymer / Elastomer Base
Polymers
Elastomers
The Magic Dust!!
Special / Proprietary Additives
Fillers
Anti-Tracking Fillers
Carbon Blacks
Other Fillers
Example -
Anti-tracking
HVOT
Moldings - eg:200S
Cross-linking Agents
Peroxide
Prorad
Iron Oxide
Thermal Stabilisers
UV Stabilisers
Process Aids
Oils
Additives

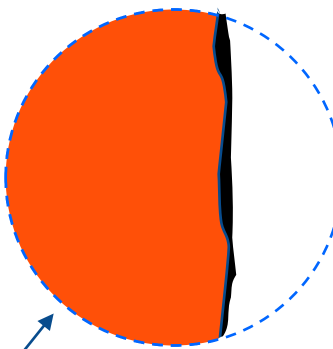
Hydrophobicity And Loss Through Aging / Pollution



What Is Tracking And Erosion?







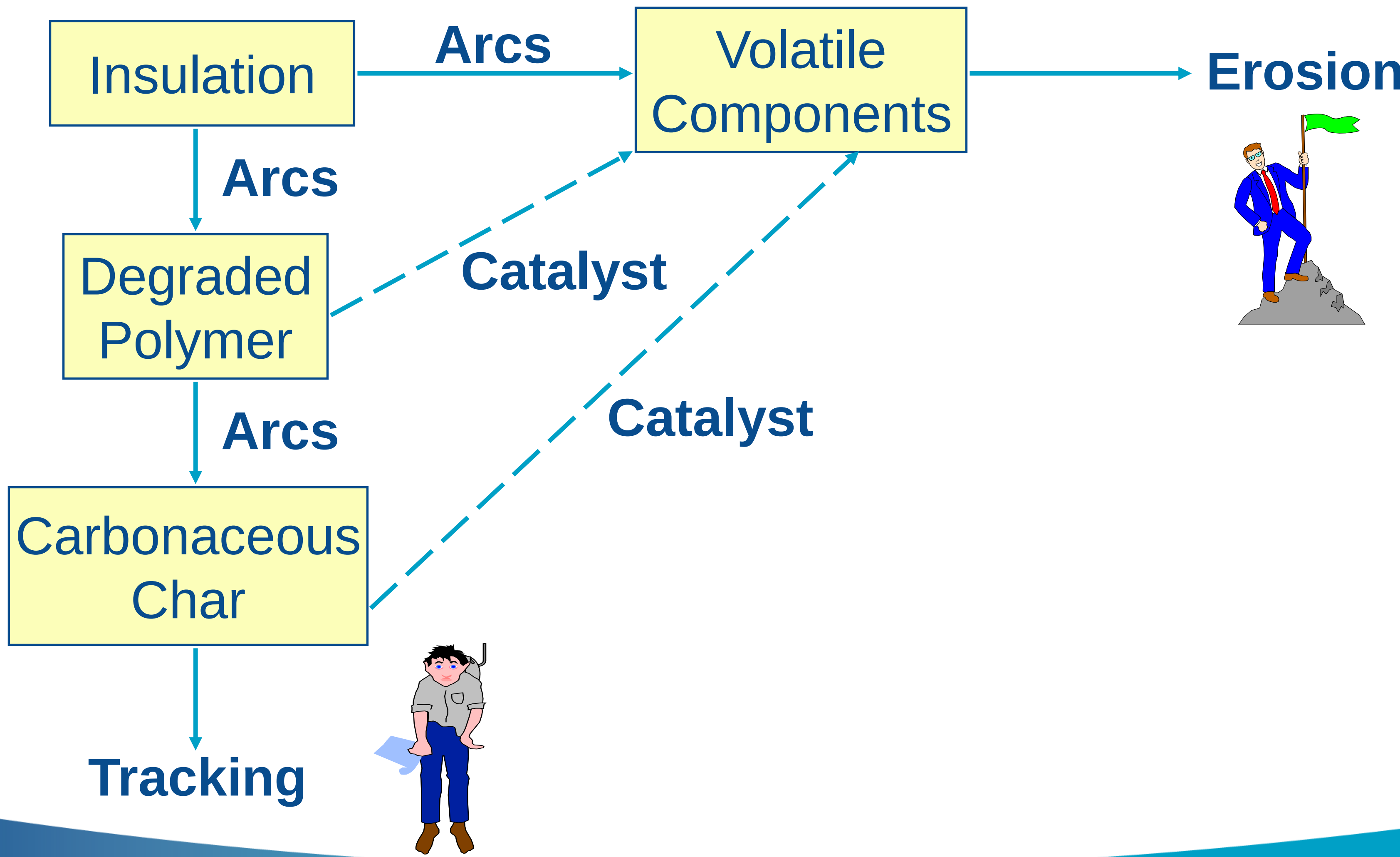
Tracking

- Rapid process
- Conductive path
- Short product life

Erosion

- Slow process
- No conductive path
- Longer product life

Material Behaviour Under Arcing Conditions

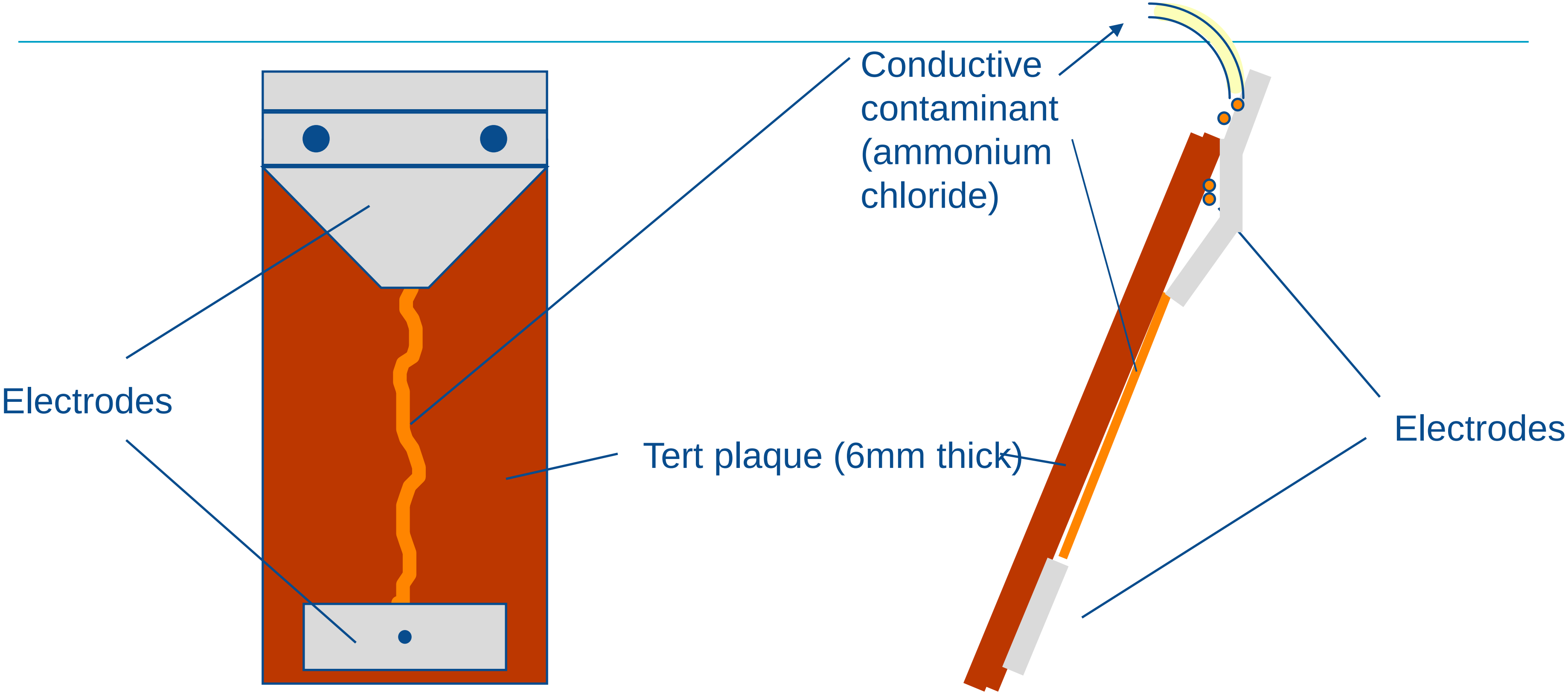


Accelerated Material Test Methods

Key screening tests:

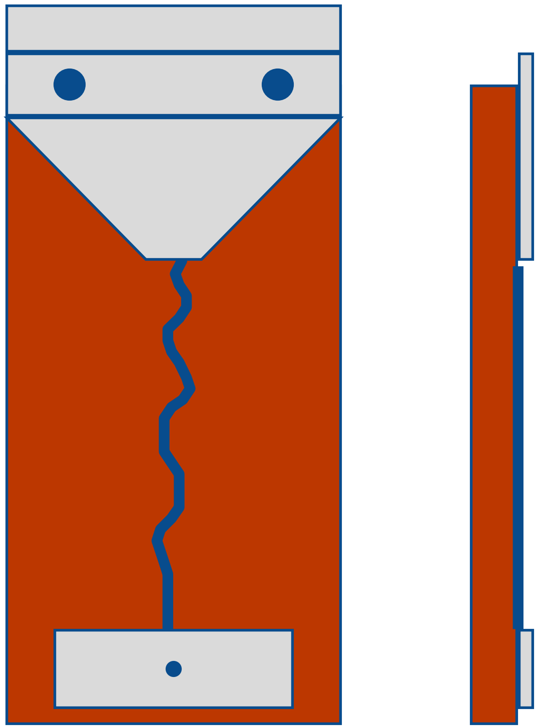
- TGA analysis
- Tracking and Erosion Resistance Test (TERT)
- Aging tests
  - UV resistance
  - Thermal aging
- Field assessments in high UV and heavily polluted areas

Tracking and Erosion Resistance Test (TERT)



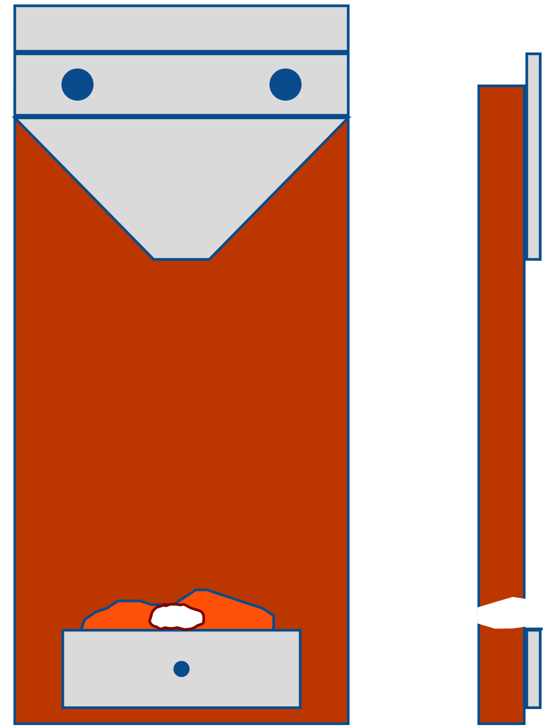
Two tert tests :
- Step test: Voltage is increased each hour and contaminant rate increased periodically
- Constant Voltage test: Voltage and contaminant flow rate maintained for set time

TERT - Key Failure Mechanisms



Sample - Front View   Side View

Tracking failure
(rapid process)



Sample - Front View   Side View

Erosion failure
(slow process)

Anti-Tracking Properties Through Aluminium Tri Hydrate

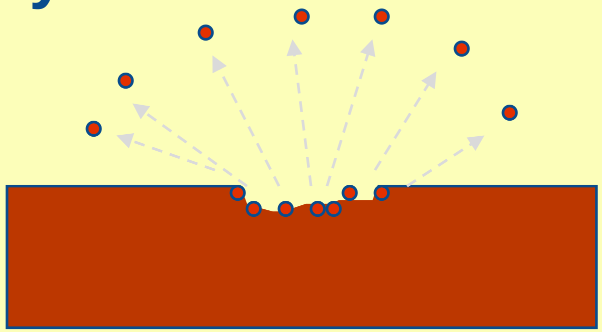
1. Chemical action:

$Al_2O_3.3H_2O$ + $3C$

↓

$3CO$ + Al_2O_3 + $3H_2$

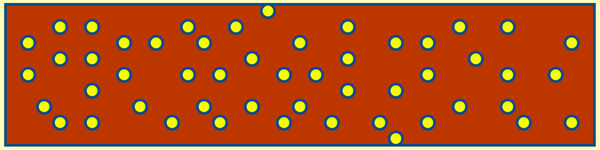
2. Physical action:



$Al_2O_3.3H_2O$ → Steam

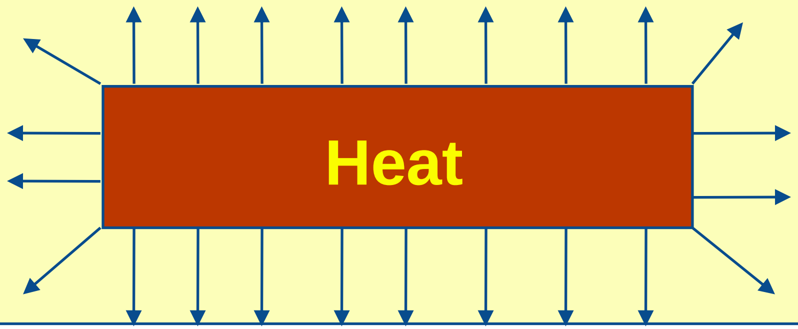
3. Volume effect

The amount of fuel (polymer) is reduced by adding ALTH



4. Thermal effect

Endothermic reaction keeps polymer cool



tyco Electronics

Mechanism Of Iron Oxide

Iron oxide acts as a UV screen and an additional catalyst for oxidation of the char (anti-tracking properties) in silicone materials

Examples of reaction;

$$Fe_2O_3 + C \rightarrow 2FeO + CO$$

$$Fe + O_2 + 2C \rightarrow Fe + 2CO$$

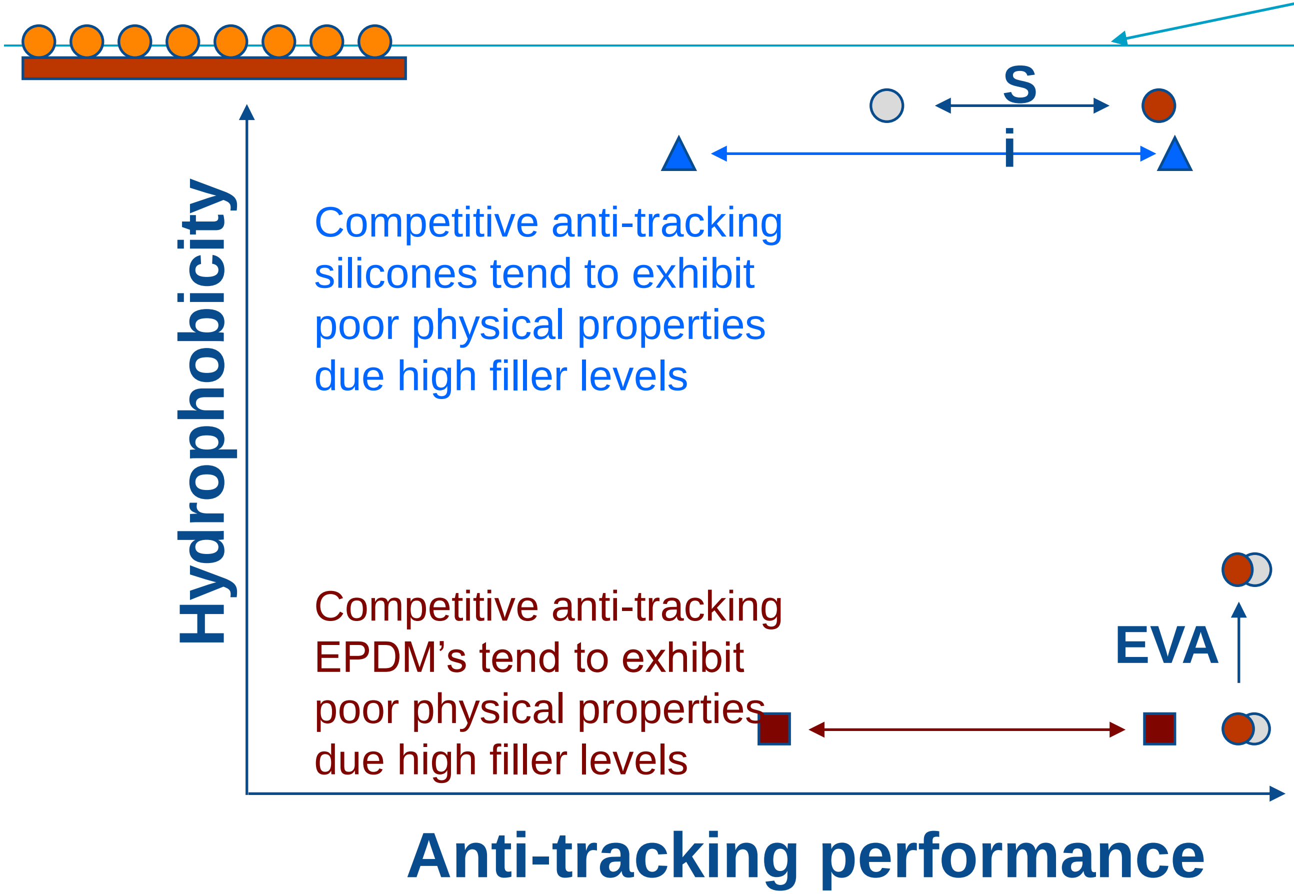
$$3Fe + C \rightarrow Fe_3C$$

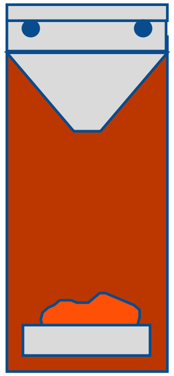
$$Fe_2O_3 + 3C \rightarrow 2Fe + 3CO$$

$$Fe_2O_3 + 11C \rightarrow 2Fe_3C + 9CO$$

Material Comparison

Raychem anti-tracking silicones exhibit good physical properties due to proprietary fillers used at low loadings





○ Raychem materials
▲ Competitive Silicones
■ Competitive EPDM's

Base Polymer Tracking Resistance

In general conduction (tracking) is facilitated by a combination of the following factors :

- Chain formation
- Aromaticity
- Conjugation
- Ionic Charge Centers
- Interaction Of Adjacent Charged Zones

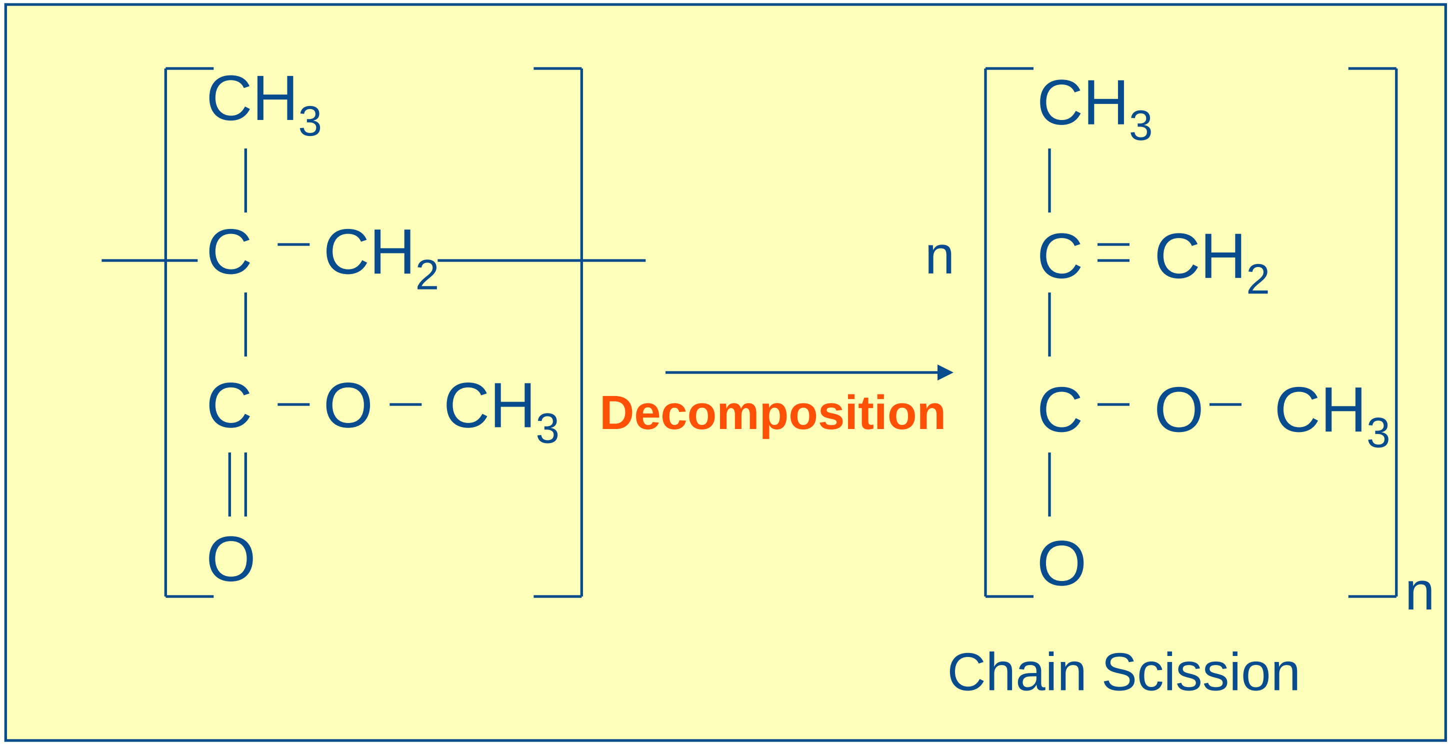
Base Polymer Tracking Resistance

	Dust-Fog (hours)
Polyvinyl chloride	0.3
Polystyrene	0.9
Polyvinyl acetate	1
Polyethylene	33
Poly methyl methacrylate	162
Polytetrafluoroethylene	600

Tracking performance is associated with a materials tendency to form a conductive char residue on decomposition.

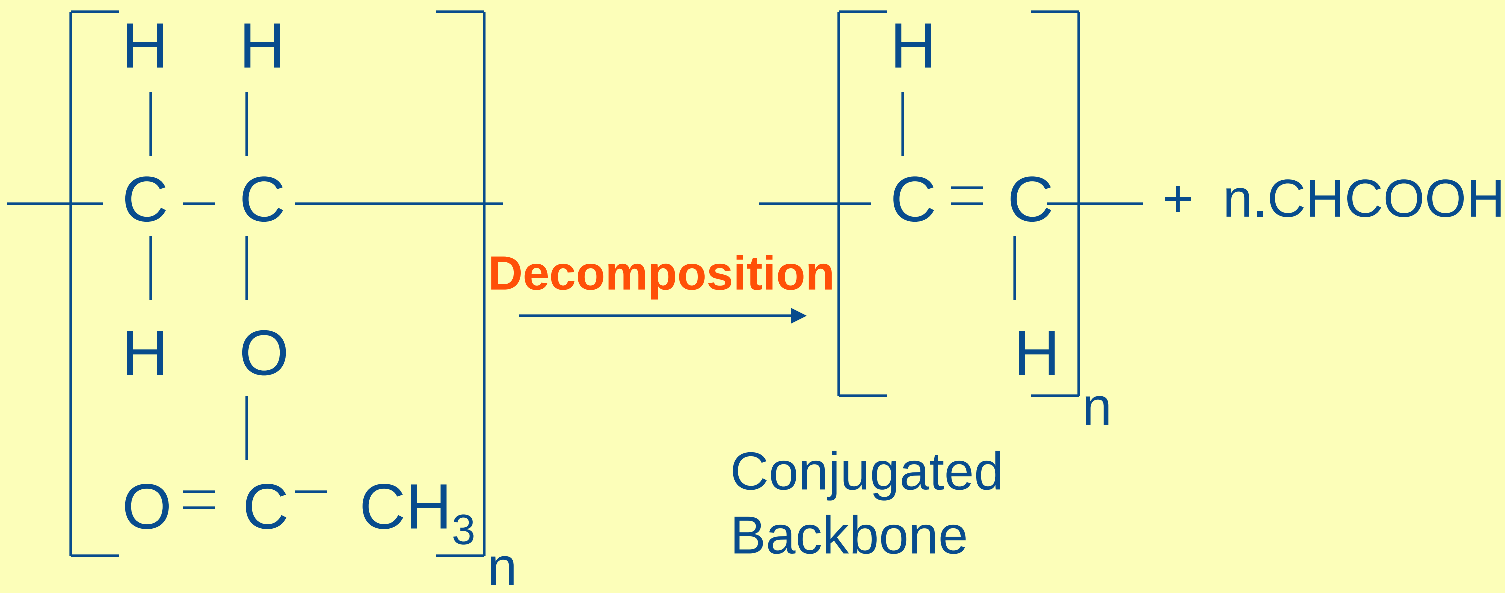
Example Of A Track Resistant Polymer

PMMA



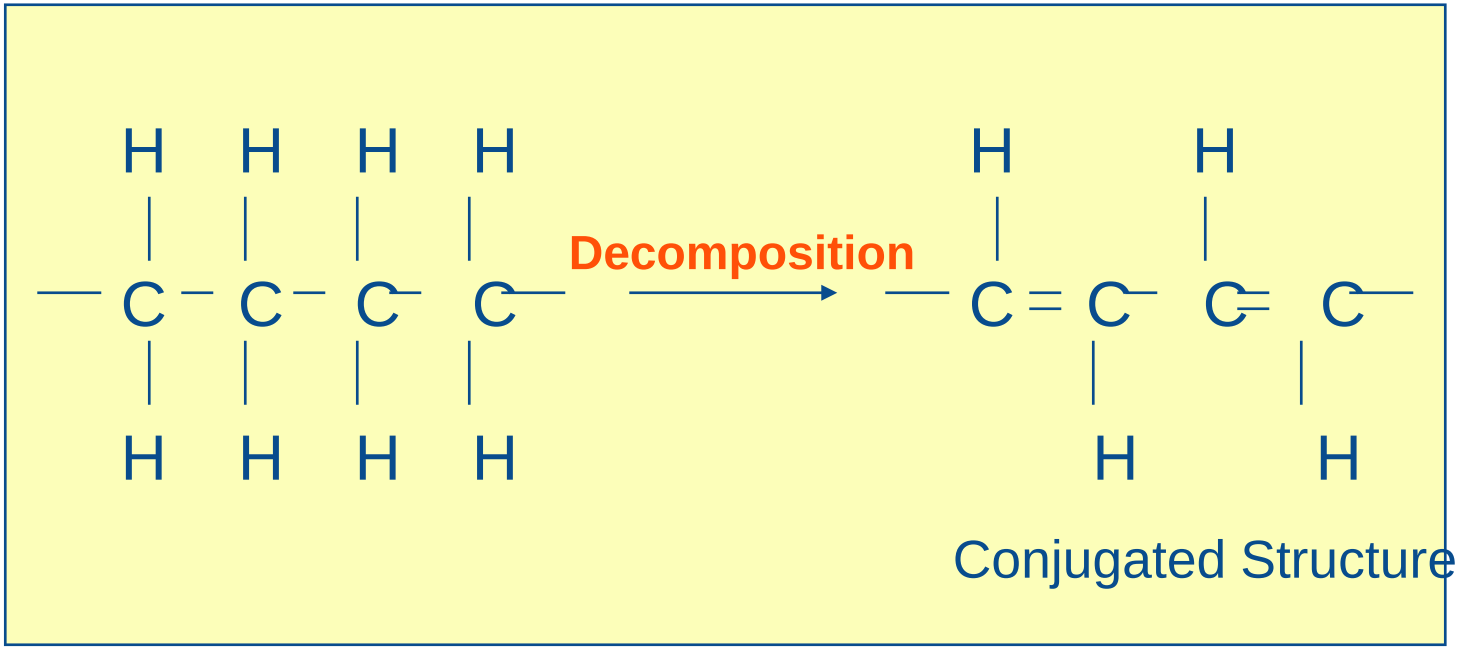
Example Of A Track Prone Polymer

EVA (Base polymer used for HVOT)

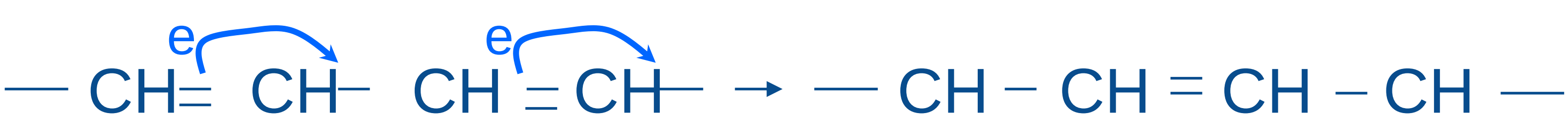


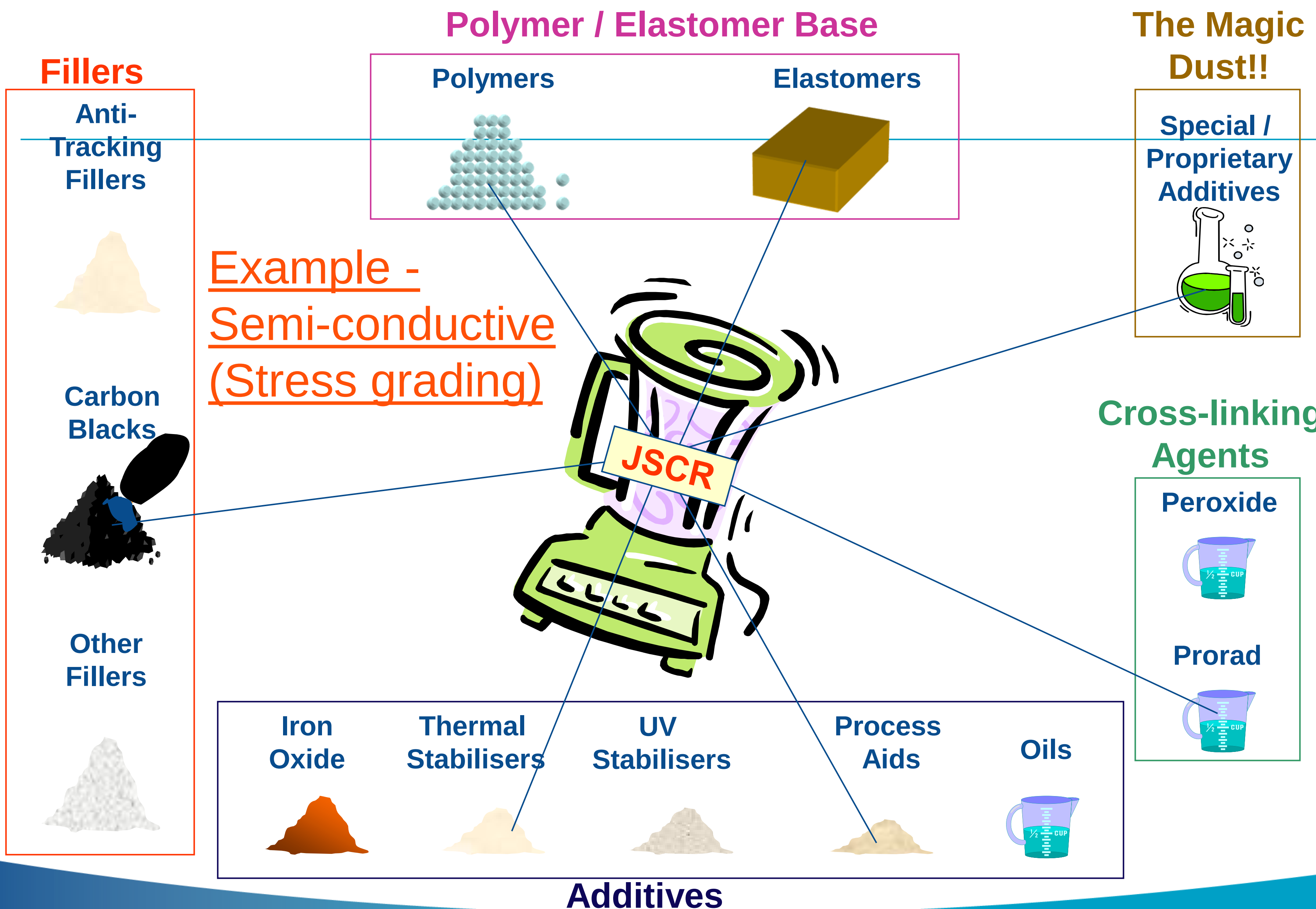
Example Of A Track Prone Polymer

PVC



Conduction occurs via electron transfer :

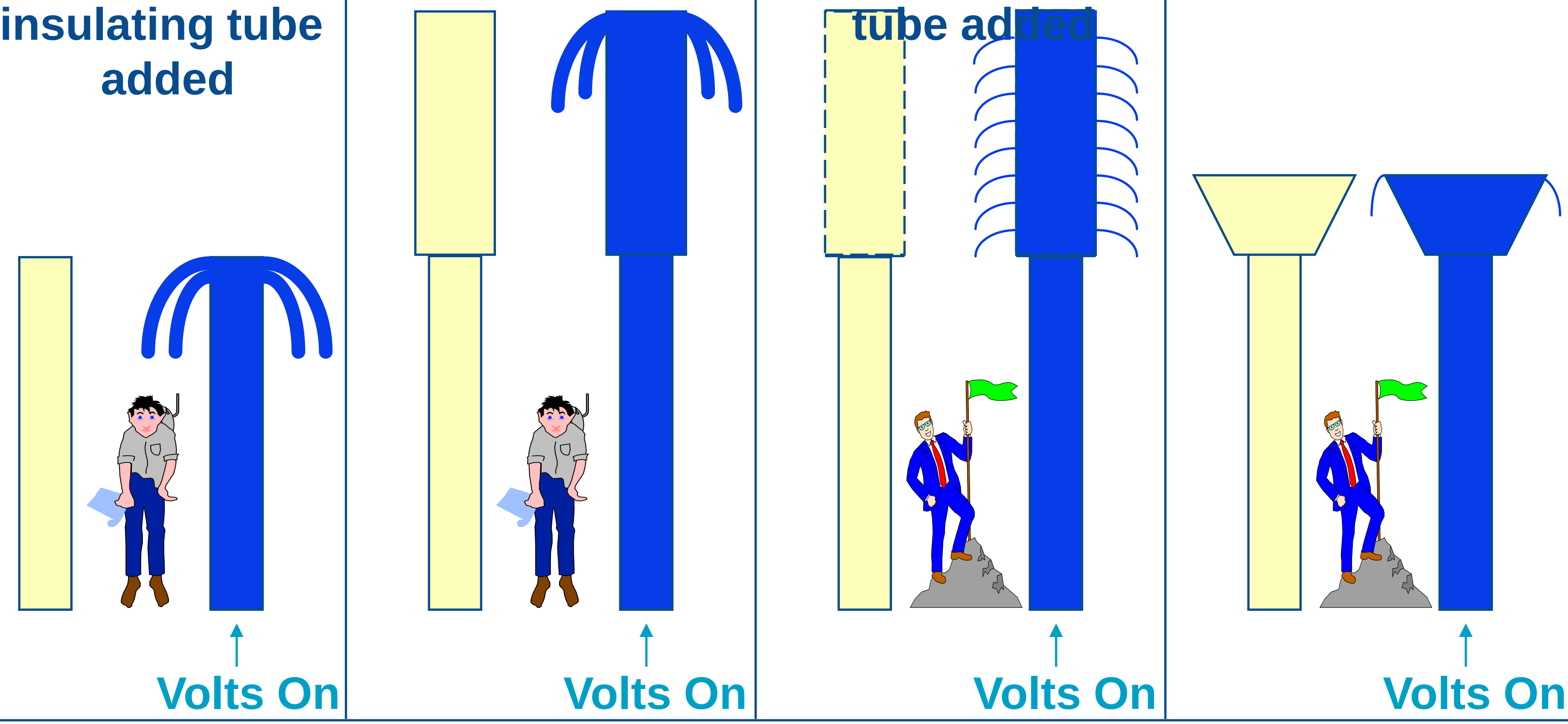




Polymer / Elastomer Base
Polymers
Elastomers
The Magic Dust!!
Special / Proprietary Additives
Fillers
Anti-Tracking Fillers
Carbon Blacks
Other Fillers
Example - Semi-conductive (Stress grading)
JSCR
Cross-linking Agents
Peroxide
Prorad
Iron Oxide
Thermal Stabilisers
UV Stabilisers
Process Aids
Oils
Additives

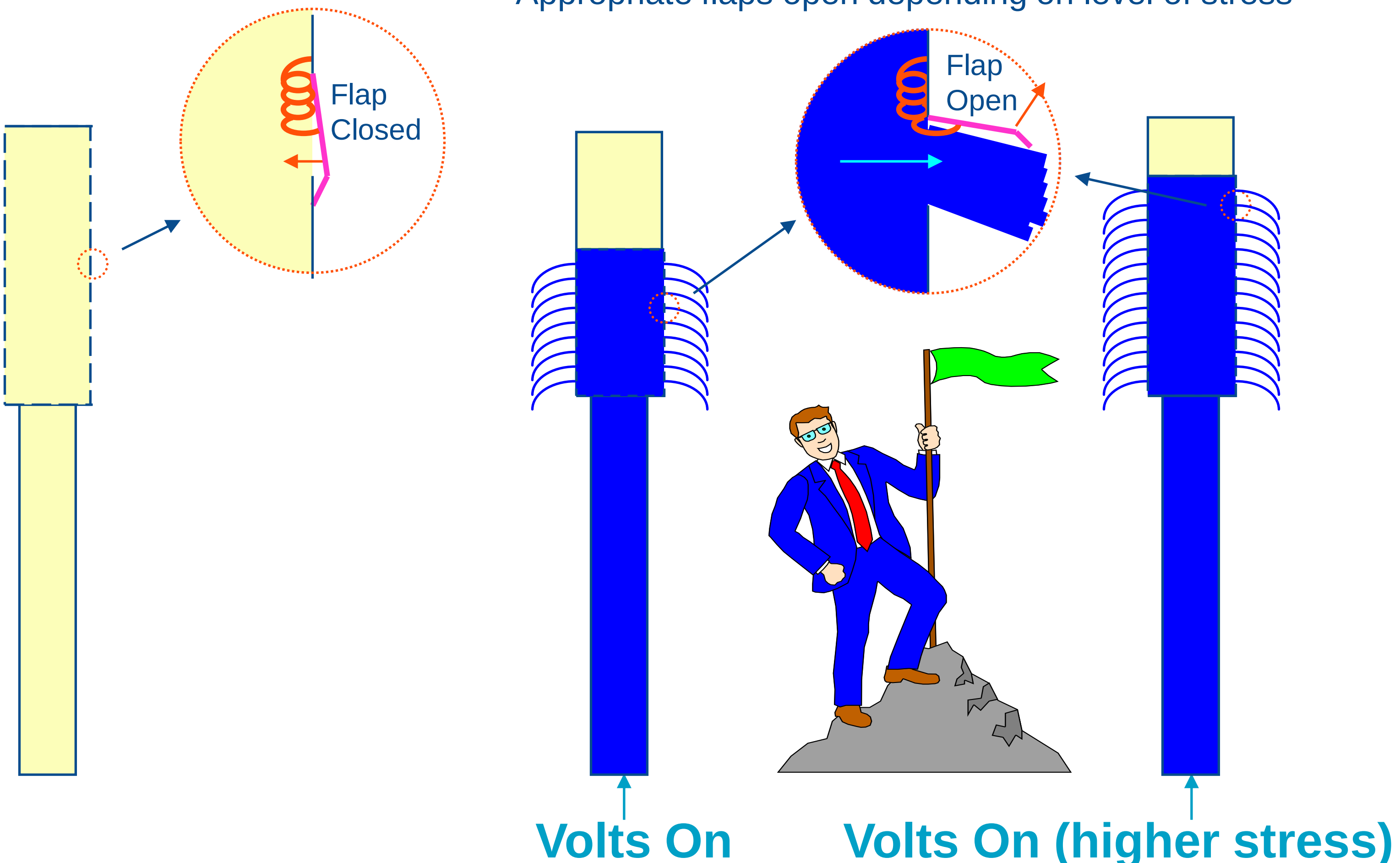
Stress Control And Material Selection

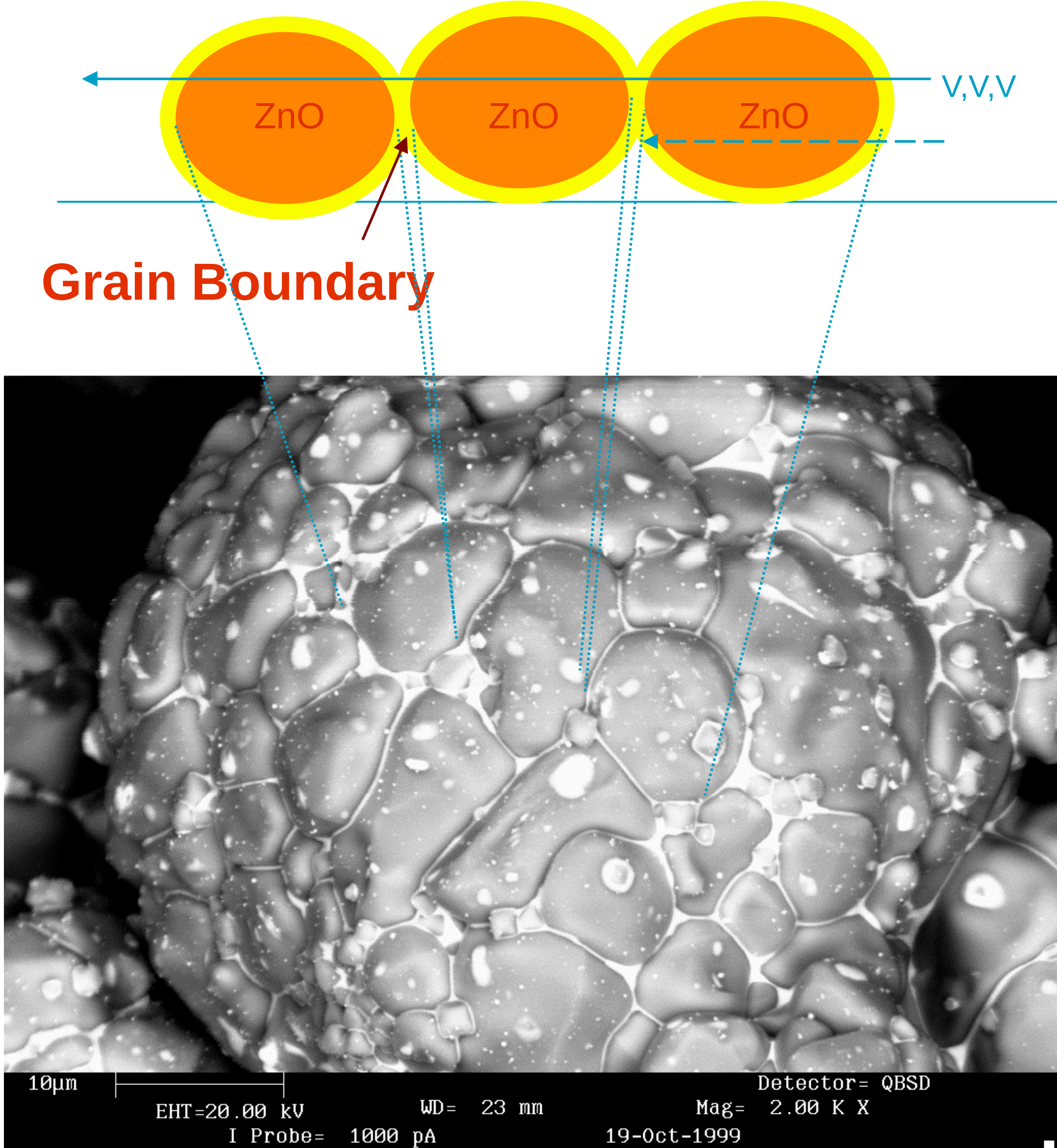
Untreated screen cutback or if insulating tube added	If conductive tube added	If semi - conductive tube added	If stress cone is added



New Energy Stress Control - Uniterm

Model: Spring loaded flap closed when no / low stress
Appropriate flaps open depending on level of stress

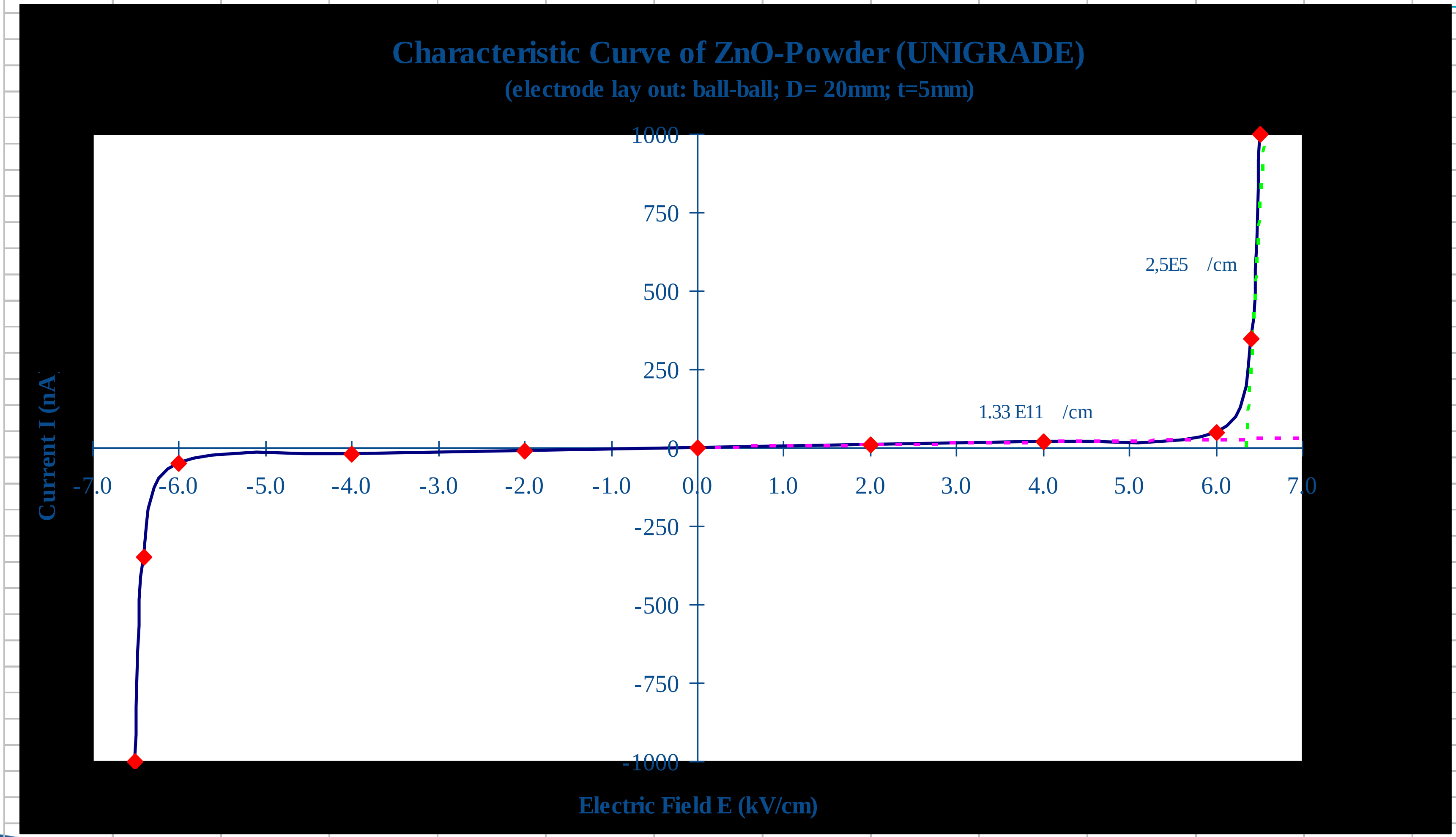




Switching Behaviour

- When under low electrical stress the ZnO grains are conductive and the grain boundaries are insulating
- At a threshold electrical field, the boundary layers become conductive
- This is a reversible process
- Switching threshold depends on number of boundaries (size of grains)

Electrical Switching Behaviour



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