New formulations and test comparison for the classification of PVC cables under EU regulation n° 305/2011 for construction products

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Cable Group Italy

- The research on new formulations has been performed by Cable Group Italy.
- The group was born in 2013 and it gathers some of the biggest Italian PVC Compounders.
- The aim of the research is the development of new formulations for cables with better performances in term of flame retardancy, smoke suppressant properties and smoke acidity.
- The project is called B2ca.

B2ca Project

1 • Evaluation of PVC cables on the market before CPR.

2 • R&D for getting improvements on compounds on lab scale tests.

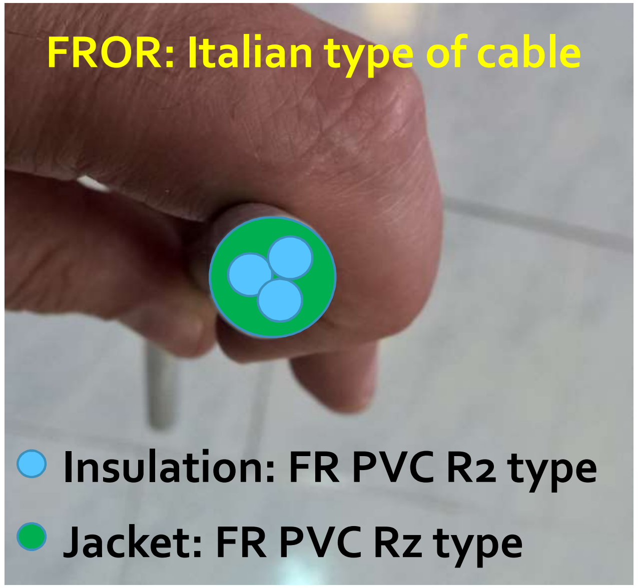
3 • Evaluation of the new generation of cables.

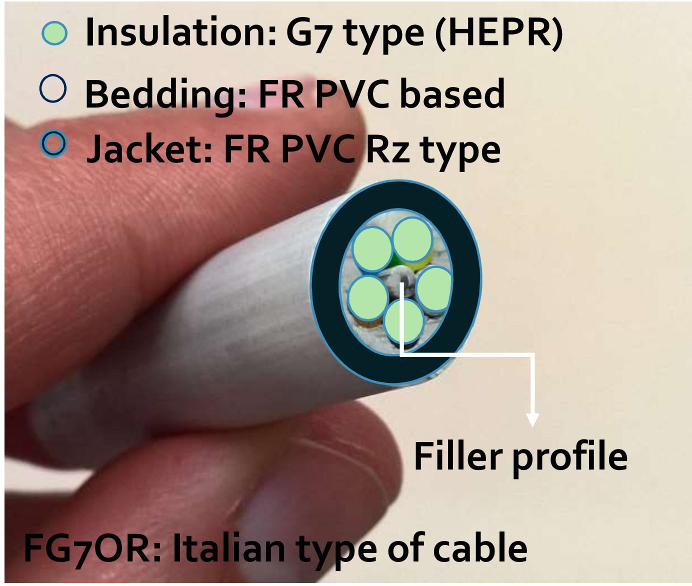
The target?

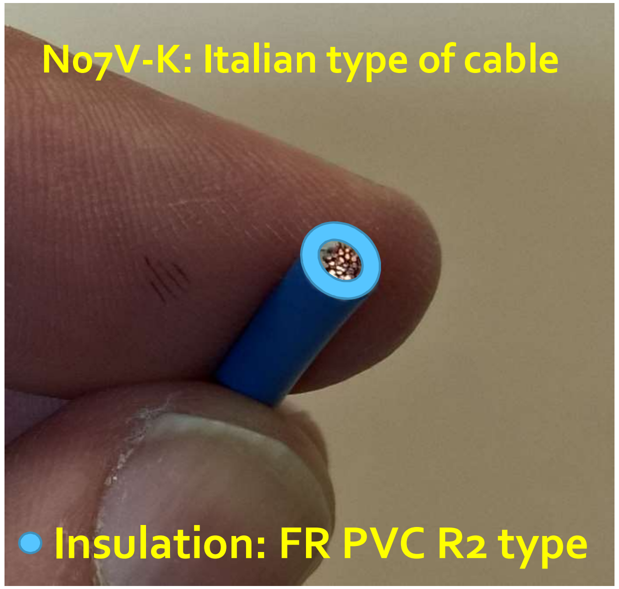
- Classification B2ca and the best possible subclasses.

1 Evaluation of the cables on the market before CPR

As starting point several kinds of CPD cables have been tested with new CPR rules.





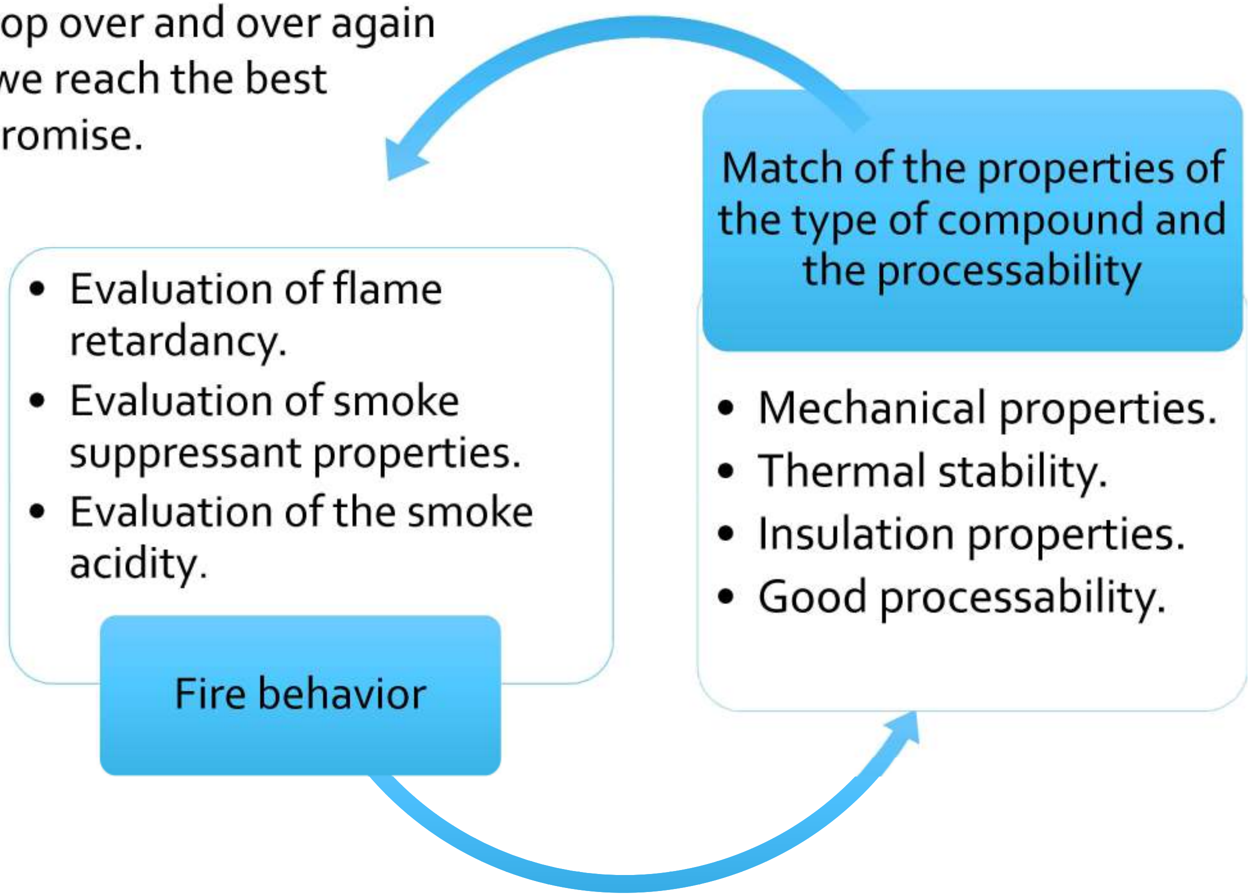


Type	Class	Smoke	Droplets	Acidity
FG7OR	Dca	S2	d1	a3
FROR	Cca	S2	d0	a3
N07V-K	Dca	S2	d0	a3

2 Lab scale tests

R&D for getting improvements on lab scale tests on specific types of compounds.

We loop over and over again until we reach the best compromise.



More than 100 compounds have been tested according to the following technical standards.

2 Lab scale tests

Technical standards performed in term of:

- Fire behavior
- Cone calorimetry (ISO 5660 – 1)
- Oxygen index (ASTM D 2863)
- Smoke Density Rate (ASTM D 2843)
- Smoke acidity (EN 60754 part 1 and 2)

- Type of compound a.t. the technical standard
- Tensile strength & Elongation @ break before and after aging (EN 60811-501, EN 60811-401, ISO R 527 -1 and -2)
- Water absorption (EN 60811-402)
- Thermal Stability (EN 60811-405)
- Insulation properties
- Other properties a.t. specific technical standard of type of compound

2 Lab scale tests

Comparison of some critical physical properties

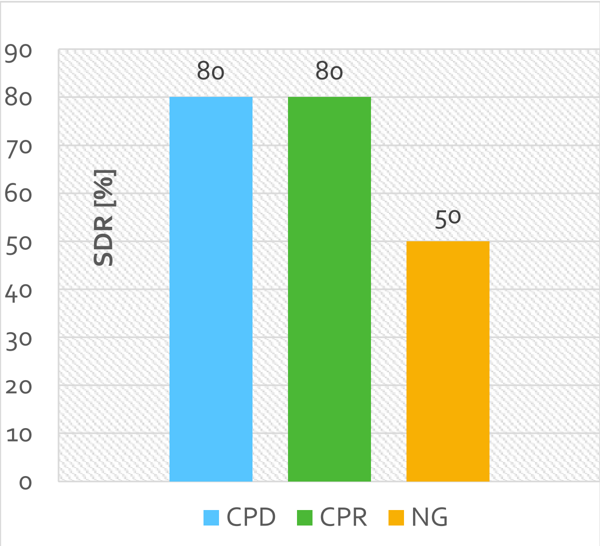
Standard CPD/CPR compound vs next generation compound (NG):

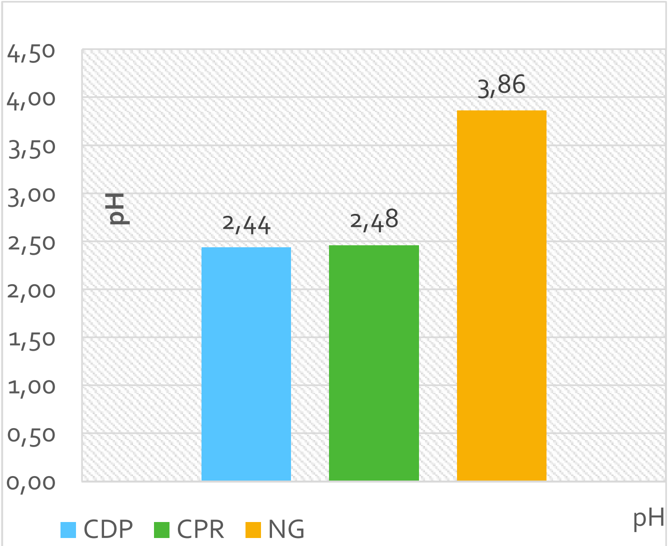
TM1 Jacket	CPD Compound	CPR Compound	Next Generation
Tensile strength [N/mm²]	13,5	13,5	12,5
Elongation @ break [%]	250	250	220
LOI [%O2]	31	34	31
SDR [%]	80	80	50
pH	2,44	2,48	3,86
Conductivity [µS/mm]	151,7	145,7	5,9

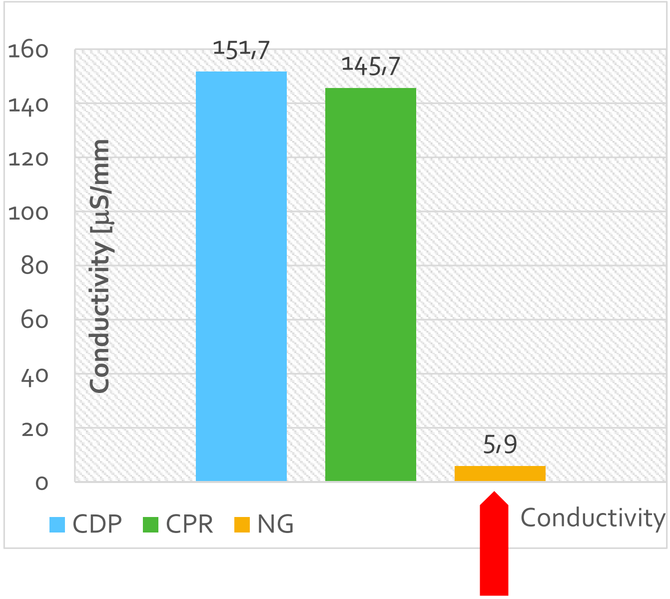
2 Lab scale tests

Comparison of some critical physical properties

Standard CPD/CPR compound vs next generation compound (NG):







SMOKE DENSITY
ASTM D 2843

SMOKE ACIDITY
EN 60754 2

3 Tests on cables

Production and classification of the cables

Evaluation of fire performances a.t. CPR. Standard performed:

- EN 60332-1-2 (Vertical flame propagation on single cable)
- EN 50399 (Vertical flame propagation on bunched cables)
- EN 61034-2 (Smoke density in 27 m^3 chamber)
- EN 60754-2 (Test on gases evolved during combustion of materials from cables)
- Part 2: Determination of acidity (by pH measurement and conductivity)

3 Tests on cables

Production and classification of the cables

- All tests required by specific standard of the cable
- Processability

Match of cables' characteristics a.t. specific standard.

Tests a.t. CPR

- THR, HRR, FIGRA, FS, SPR : EN 50399
- TSP, SPR: EN 61034-2
- Flaming Droplets: EN 50399
- Smoke acidity: EN 60754-2

- Identification of Classes
- B2ca, Cca, Dca, Eca or Fca
- Identification of Subclasses
- S1a, S1b, S2, S3
- d0, d1, d2
- a1, a2, a3

Classification of the cable

3 Tests on cables: what we did

Performances: CPD vs CPR cables

CPR Cables	Class	Smoke	Droplets	Acidity
FG16OR16	Cca	S2	d0	a3
FROR	B2ca	S2	d0	a3
FS17	Cca	S1	d0	a3

CDP Cables	Class	Smoke	Droplets	Acidity
FG7OR	Dca	S2	d1	a3
FROR	Cca	S2	d0	a3
N07V-K	Dca	S2	d0	a3

3 Tests on cables: next plan

Performances: CPR vs New Generation cables

Next step will be the evaluation of cables with new compounds

New Cables	Class	Smoke	Droplets	Acidity
FG16OR16	B2Ca	S1	do	a2

CPR Cables	Class	Smoke	Droplets	Acidity
FG16OR16	Cca	S2	do	a3

But the most difficult task will be the reduction of smoke acidity

FOCUS ON SMOKE ACIDITY

Technical standards a.t. CPR

EN 60754-2

- Tubular Oven at fixed temperature ranging b/w 935°C up to 960°C
- Determination of pH and conductivity
- Requirements 1 for class a2: pH > 4,3, Conductivity [µS/mm] < 10
- Requirements 2 for class a1: pH > 4,3, Conductivity [µS/mm] < 2,5
- The requirement 1 defines what is an Halogen Free

The method used 4 PVC before CPR

EN 60754-1

- Tubular Oven at temperature ranging b/w 790°C up to 810°C
- Temperature regime
- Determination of mg of halogens in 1 g of compound

ACID SCAVENGING THEORY

°C

23	50	77	104	131	158	185	212	239	266	293	320	347	374	401	428	455	482	509	536	563	590	617	644	671	698	725	752	790	800	810	837	864	891	935	948	960	975

Acid scavengers

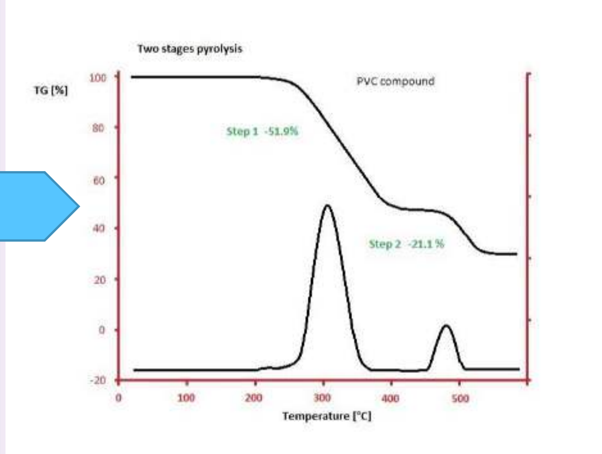
EN 60754/1

RXN prod. stable@ 810°C

Thermal Stabilization Zone

Pyrolysis &Combustion Zone

Massive release of HCl generally described by a two stages pyrolysis model [1],[2]



Uncharted Zone

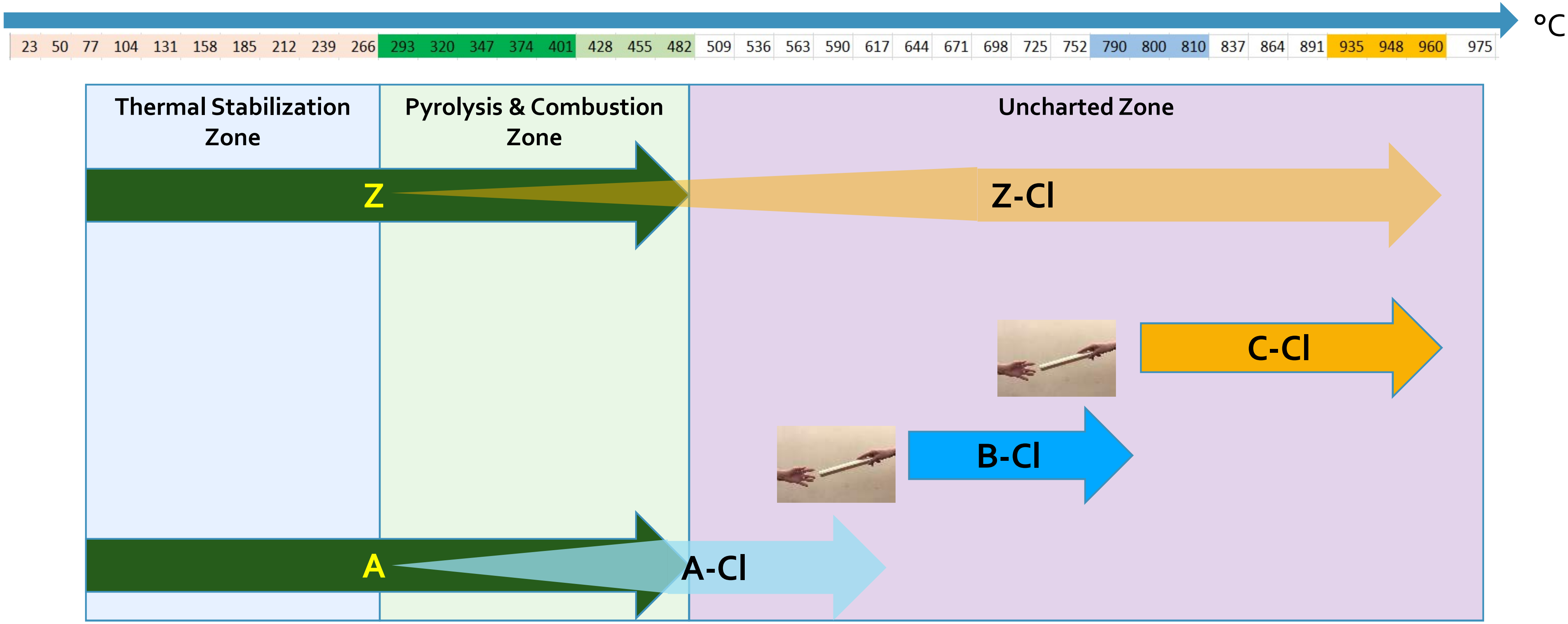
EN 60754/2

Acid scavengers

RXN prod. stable@ 960°C

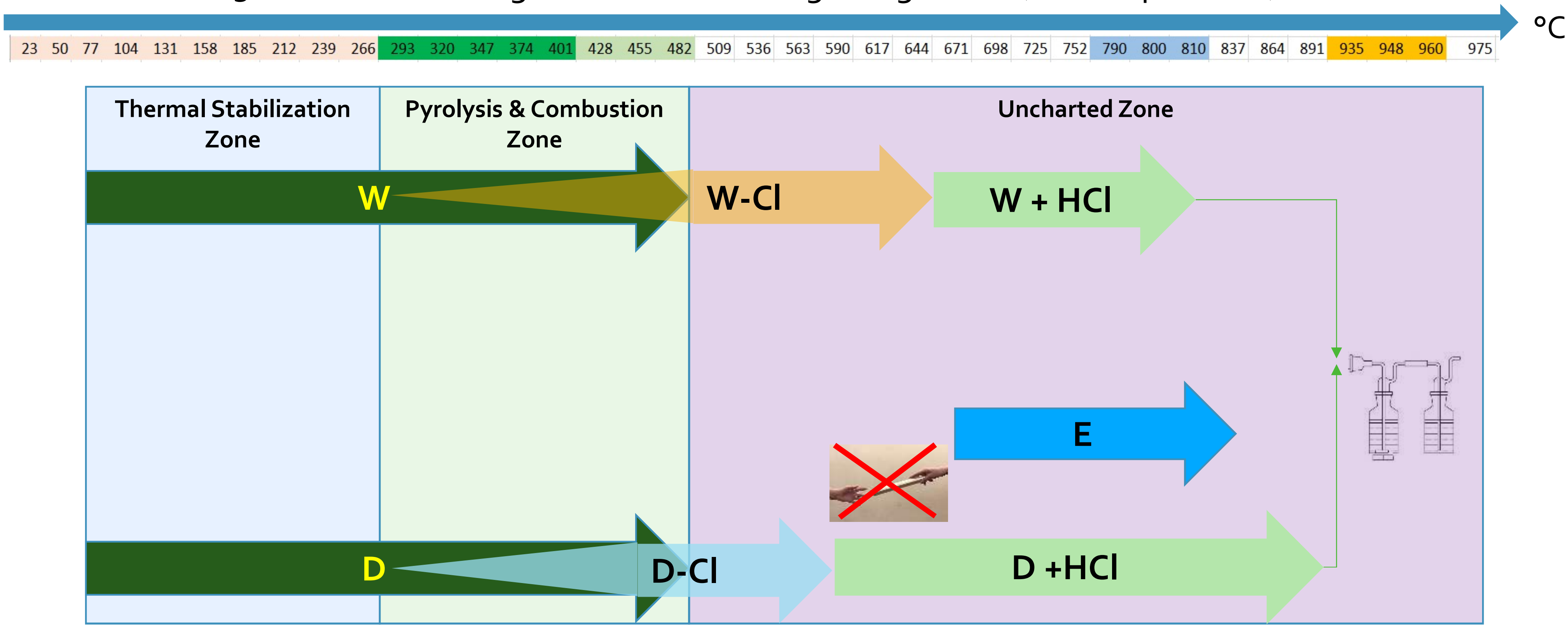
Single vs Multiple Step reaction

- Single step reaction: Z is stable up to pyrolysis zone and it creates Z-Cl stable up to the test temperature.
- Multiple step reaction: A, stable up to pyrolysis zone, reacts with HCl giving A-Cl; A-Cl decomposes but a «team mate» is ready to get the HCl and so on up to the test temperature (relay race scheme).



Multiple Step vs Single Step reaction

- Failure case 1: W-Cl decomposes making free HCl before reaching the test temperature.
- Failure case 2: D-Cl decomposes making free HCl before the formation of E.
- Failure case 3: The Acid Scavengers are too slow in getting HCl in (Kinetic problem).



Acid scavenging theory: inert substance

- $Al(OH)_3$ starts the decompositions b/w 180°C and 200°C, releasing water. It acts as heat sink, it dilutes the flame, it dilutes the polymer and plasticizers, it creates a char of Al_2O_3 [3].
- From acid scavenging point of view $Al(OH)_3$ is useless due to its chemical inertia.

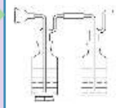
°C

23	50	77	104	131	158	185	212	239	266	293	320	347	374	401	428	455	482	509	536	563	590	617	644	671	698	725	752	790	800	810	837	864	891	935	948	960	975

Thermal Stabilization Zone	Pyrolysis & Combustion Zone	Uncharted Zone

$Al(OH)_3$ / Al_2O_3

Al_2O_3 + HCl

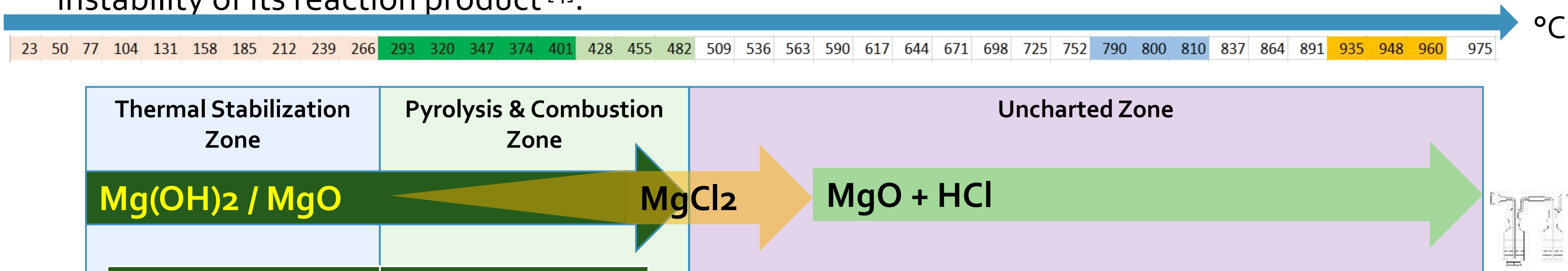


RM	phr
PVC S K70	100
$Al(OH)_3$	80
DINP	50
STAB	5

LOI	28 [%O2]
pH	2,22
Conductivity	212 µS/mm

Acid scavenging theory: ineffective substance

- $Mg(OH)_2$ starts the decompositions b/w 300°C and 320°C, releasing water. It acts as heat sink, it dilutes the flame, it dilutes the polymer and plasticizers [3].
- From acid scavenging point of view in a single step reaction $Mg(OH)_2$ is ineffective due to the instability of its reaction product [4].

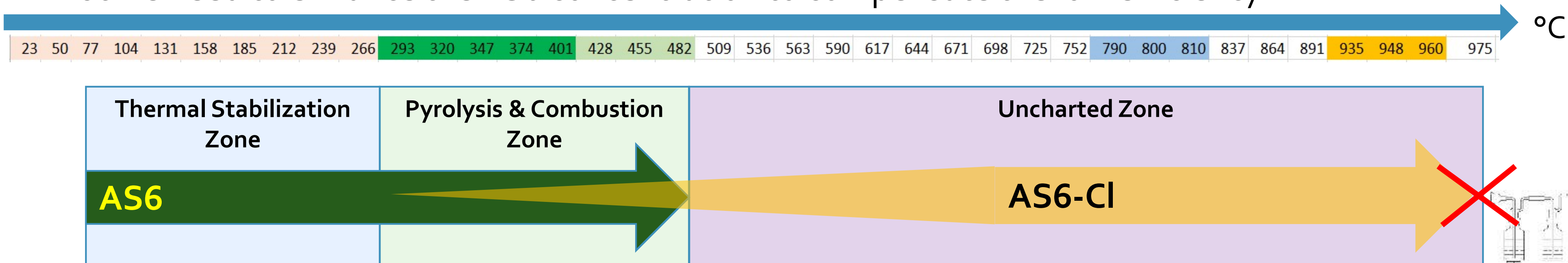


RM	phr
PVC S K70	100
$Mg(OH)_2$	80
DINP	50
STAB	5

LOI	28 [%O2]
pH	2,27
Conductivity	188 µS/mm

Acid scavenging theory: good acid scavenger

- AS6 is stable along the pyrolysis and combustion zone and it reacts efficiently with HCl, trapping it in a reaction product.
- Its reaction product is stable up to the maximum temperature required by EN 60754-2.
- But we need to enhance the AS6 concentration to compensate the low efficiency.



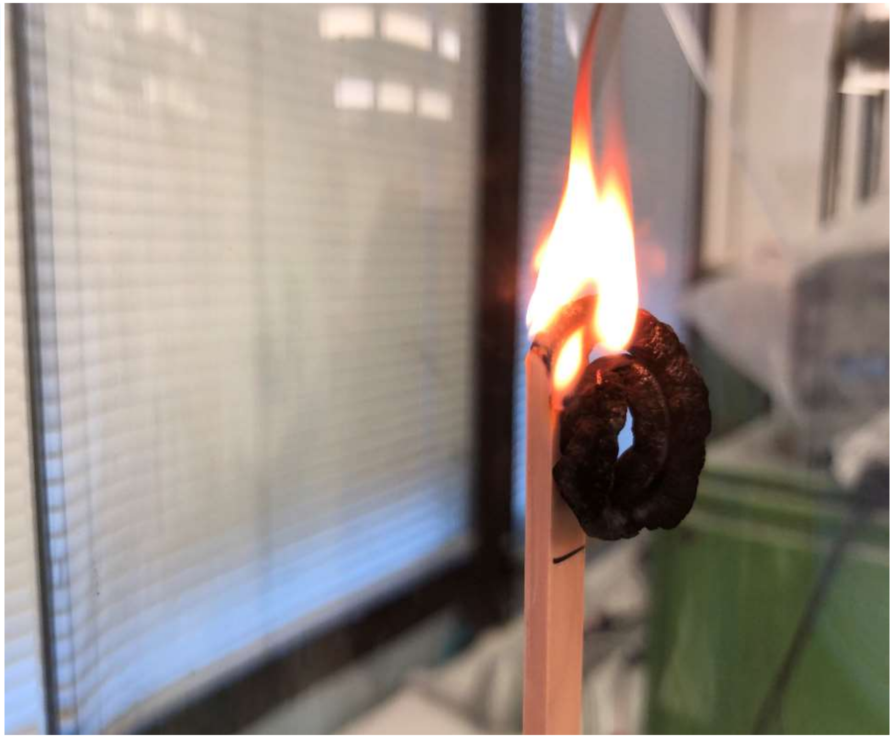
RM	phr
PVC S K70	100
AS6	120
DINP	50
STAB	5

LOI	25 [%O2]
pH	3,98
Conductivity	4,4 µS/mm

But what happens to the flame retardancy?

If most of HCl is scavenged, the intrinsic flame retardancy of PVC is switched off

RM	phr
PVC S K70	100
$CaCO_3$	90
MDH ($Mg(OH)_2$	0
DINP	50
STAB	5
ATO (Sb_2O_3)	0
pH	2,59
Conductivity	107,2 µS/mm
LOI	23 %O_2



But what happens to the flame retardancy?

- Sb_2O_3 works totally in gas phase. Sb_2O_3 creates $SbCl_3$ acting as a "quencher" of radicals feeding the flame.[5] But AS-1B scavenges all HCl, and Oxygen Index drops down to 23 %O2.
- Even if we double the Sb_2O_3 quantity we have no effect at all.

RM	phr	RM	phr	RM	phr
PVC S K70	100	PVC S K70	100	PVC S K70	100
$CaCO_3$	60	AS-1B	123	AS-1B	123
MDH	30	MDH	30	MDH	30
DINP	50	DINP	50	DINP	50
Stabilizer	5	Stabilizer	5	Stabilizer	5
ATO	5	ATO	5	ATO	10
pH	2,63	pH	4,12	pH	4,03
Conductivity	99,3 µS/mm	Conductivity	3,20 µS/mm	Conductivity	4,00 µS/mm
LOI	32 %O2	LOI	23 %O2	LOI	23 %O2

But what happens to the flame retardancy?

$$Sb_2O_3 \ _{(cond.)} + 6HCl \ _{(gas)} \text{---------->} 2SbCl_3 \ _{(gas)} + 3H_2O \ _{(v)}$$

$SbCl_3 + H^* \rightarrow HCl + SbCl_2^*$
$SbCl_2 + H^* \rightarrow HCl + SbCl^*$
$SbCl + H^* \rightarrow HCl + Sb^*$
$Sb^* + OH^* \rightarrow SbOH$
$SbOH^* + H^* \rightarrow SbO^* + H_2$
$SbO^* + H^* \rightarrow SbOH$

Complete inhibition of the quenching of the «hot radicals» feeding the flame and flame retardancy drops down.

In absence of AS-1B we have the formation of $SbCl_3$ and the quenching mechanism is active.

AS-1B prevents the formation of $SbCl_3$.

But what happens to the flame retardancy?

- Ammonium Octamolybdate (AOM) works mainly in condensed phase: decomposes b/w 287 °C and 370 °C to MoO_3 [6] ; it reacts with HCl creating MoO_2Cl_2 a powerful Lewis acid promoting the formation of a char barrier between gas and condensed phase[7],[8].
- AS-1B, interfering with the char creation mechanism of AOM, inhibits totally its flame retardancy.

RM	phr
PVC S K70	100
CaCO3	60
AOM	30
DINP	50
Stabilizer	5
ATO	3
pH	2,43
Conductivity	155,2 µs/mm
LOI	38 %O2

RM	phr
PVC S K70	100
AS-1B	123
AOM	30
DINP	50
Stabilizer	5
ATO	3
pH	4,13
Conductivity	2,88 µs/mm
LOI	23 %O2

RM	phr
PVC S K70	100
AS-1B	123
AOM	53
DINP	50
Stabilizer	5
ATO	3
pH	4,08
Conductivity	3,12 µs/mm
LOI	24 %O2

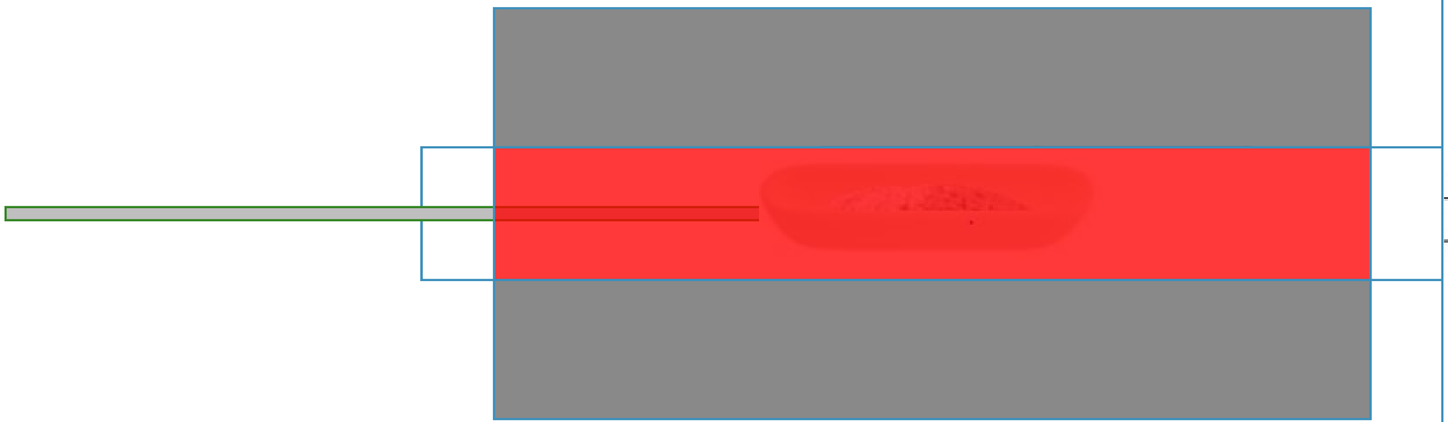
But what happens to the flame retardancy?

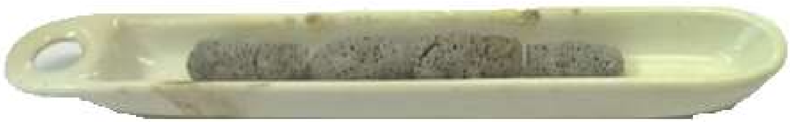
- The only way to recover flame retardancy is the reduction of AS-1B.
- So we need other routes for getting back the lost flame retardancy.

RM	phr	RM	phr	RM	phr
PVC K70	100	PVC K70	100	PVC K70	100
AS-1B	123	AS-1B	100	AS-1B	60
AOM	30	AOM	53	AOM	53
DINP	50	DINP	50	DINP	50
Stabilizer	5	Stabilizer	5	Stabilizer	5
ATO	3	ATO	3	ATO	3
pH	4,13	pH	3,05	pH	2,76
Conductivity	2,88 µs/mm	Conductivity	37,8 µs/mm	Conductivity	72,9 µs/mm
LOI	23 %O2	LOI	26 %O2	LOI	32 %O2

Focus on technical standards used

EN 60754-1: used before CPR





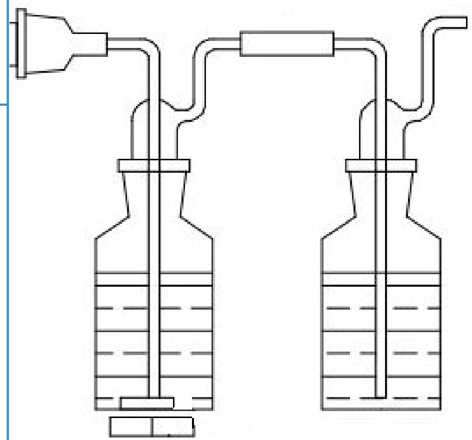
From 23°C to 800 +/-10 °C @ 20°/min

Advantages

"800 °C" ensure a higher number of stable substances.

We can use easily multiple steps reactions, enhancing synergism b/w substances.

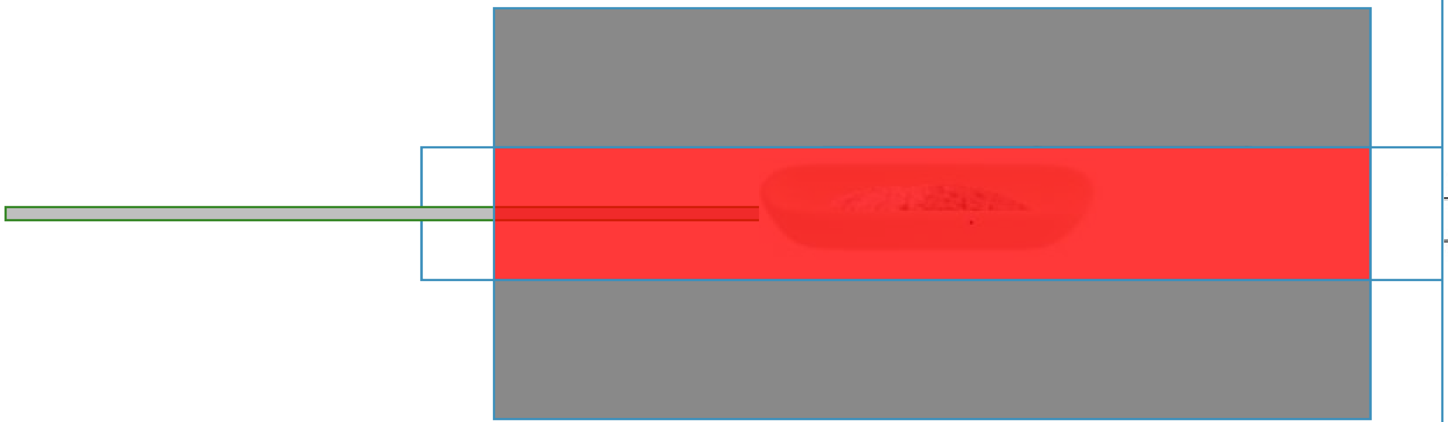
With a temperature ramp acid scavengers have more time to trap the evolving HCl.

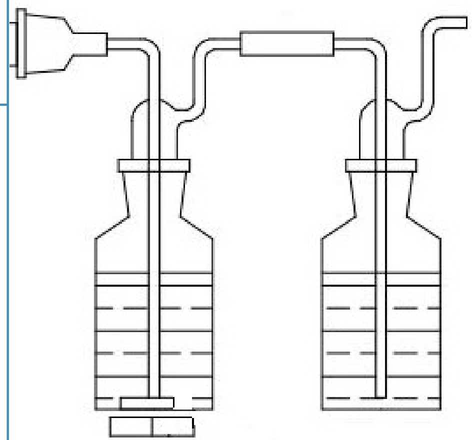


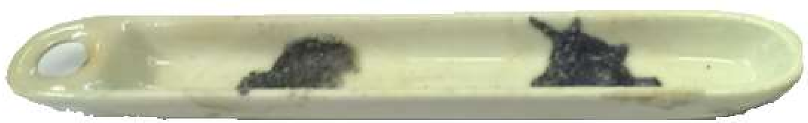
In term of temperature and ramp it is more similar to a real fire scenario.

Focus on technical standards used

EN 60754-2: a.t. CPR







Fixed b/w 935°C and 960°C

Disadvantages

A higher temperature gives a smaller number of stable substances.
The decomposition makes free HCl again.

Without temperature ramps acid scavengers have no time to trap the evolving HCl efficiently.

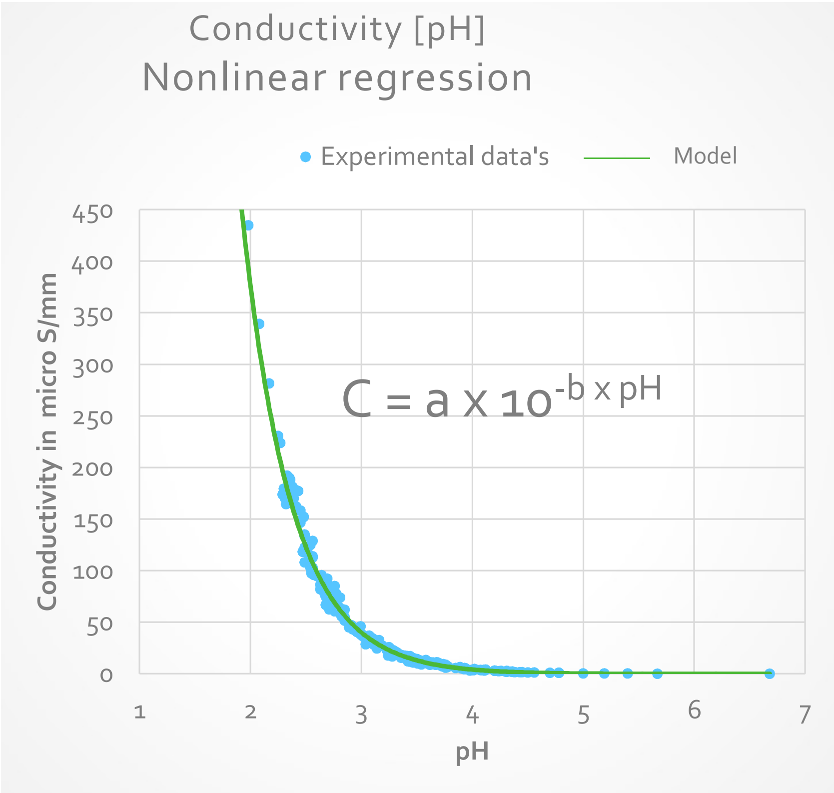
Differences in numbers

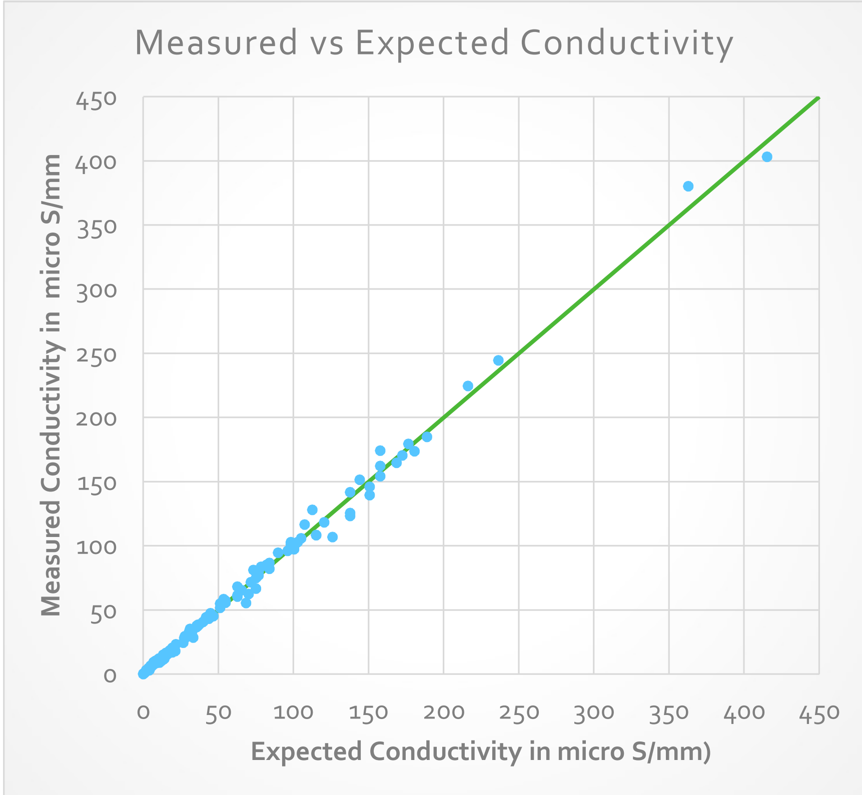
- We tested the same compound with the two standards EN60754-1 and EN 60754-2.
- The EN60754-1 is performed with its temperature regime and 800°C as final temperature, but, instead of the mgs of halogens in 1 gram of compound, pH and Conductivity are measured.
- That to permit a comparison b/w EN 60754-1 and EN 60754-2, focusing on the effect of the ramp and the final temperature on data's.
- In all tests the EN 60754-1 gives higher values of pH e lower values of conductivity. The gap depends on the mechanism of action of used acid scavengers and on the presence of sources of labile Cl.

	EN 60754 part 2			EN 60754 part 1		
Formulation Code	pH	Conductivity [µS/mm]	H^+ [mol/L]	pH	Conductivity [µS/mm]	H^+ [mol/L]
54	3,54	10,4	$2{,}88 \times 10^{-4}$	4,00	3,80	$1{,}00 \times 10^{-4}$
90	3,75	7,10	$1{,}78 \times 10^{-4}$	4,24	3,00	$5{,}75 \times 10^{-5}$
91	2,46	140,0	$3{,}47 \times 10^{-3}$	2,65	90,4	$2{,}24 \times 10^{-3}$
94	3,52	13,5	$3{,}02 \times 10^{-4}$	4,07	3,90	$8{,}51 \times 10^{-5}$

Relationship b/w pH and conductivity

In in the bubbling devices the stronger electrolyte is always HCl.
Pyrolysis and combustion of PVC jackets by TGA/FTIR shows the main presence of HCl, CO_2 and H_2O[2].





So no other volatile substance can affect conductivity driven only by the presence of HCl.

Conclusions: why PVC Cables[9]

- PVC can obtain the highest fire reaction results compared with any thermoplastic material: it can reach the Euroclass B-s1-d0;
- PVC is self-extinguishing and has intrinsically a high potential to resist ignition sources: it does not contribute, or only minimally contributes, to the generation and spread of a fire;
- PVC irradiates only a minimum amount of heat; this means a minimum contribution to heat diffusion;
- Hydrogen Chloride (HCl) contained in the smoke is highly irritating but provides an immediate signal of the development of the fire, acting as an escape alarm;
- No irreversible damage to the building structure can be caused by the release of hydrogen chloride in the event of a fire.

Thank you for your attention

Thanks to:

- Cable Group Italy
- PVC Forum Italia www.pvcforum.it
- PVC4cables www.pvc4cables.org

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PVC4CABLES
www.pvc4cables.org