The project class B2ca
How formulations can influence the PVC cables fire behavior

PVC FORUM ITALIA: CABLES GROUP
How formulations can influence the PVC cables fire behavior

- Cables Group Italy
- The project class B2ca
- Fire performances of old and new cables
- Focus on smoke acidity
- The importance of R&D
- Conclusions

Introduction
Cables Group Italy

• The group was born in 2013 with the aim to develop new formulations for cables with better performances in terms of flame retardancy, smoke suppressant properties and smoke acidity.

• The project was called B2Ca.
B2ca PROJECT

• The project is divided in 3 steps

  1) Evaluation of the cables on the market before CPR
  2) R&D for getting improvements on compounds on lab scale tests
  3) Evaluation of the new cables on CPR basis

• The target?

Classification B2ca and the best possible on subclasses
1) Evaluation of the cables on the market before CPR

Several kinds of cables have been tested with new CPR rules.
1) Evaluation of the cables on the market before CPR

Several kinds of cables have been tested with new CPR rules.
1) Evaluation of the cables on the market before CPR

Classes and subclasses according to CPR

<table>
<thead>
<tr>
<th>Type</th>
<th>Class</th>
<th>Smoke</th>
<th>Droplets</th>
<th>Acidity</th>
</tr>
</thead>
<tbody>
<tr>
<td>FG7OR</td>
<td>Dca</td>
<td>S2</td>
<td>d1</td>
<td>a3</td>
</tr>
<tr>
<td>FROR</td>
<td>Cca</td>
<td>S2</td>
<td>do</td>
<td>a3</td>
</tr>
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</tbody>
</table>
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

- Evaluation of flame retardancy.
- Evaluation of smokes suppressant properties.
- Evaluation of the smoke acidity.

- Mechanical properties.
- Thermal stability.
- Volume resistivity.
- Good processability.

Match of the properties of the type of compound and the processability.
More than 70 compounds have been tested according to the following technical standards
2) Lab scale tests: Technical standards performed

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

**Type of compound**
- Tensile strength & Elongation @ break before and after aging
- Water absorption
- Insulation properties
- Etc....
- a.t. specific technical standard of type of compound
2) Lab scale tests:
Comparison of some critical physical properties

<table>
<thead>
<tr>
<th>OLD COMPOUNDS</th>
<th>NEW COMPOUNDS</th>
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<tbody>
<tr>
<td>• SDR %: [75 – 85] %</td>
<td>• SDR %: [55 – 65] %</td>
</tr>
<tr>
<td>• pH: [2.50 – 2.80]</td>
<td>• pH: [3.50 – 3.90]</td>
</tr>
<tr>
<td>• Conductivity: [100 – 220]μS/mm</td>
<td>• Conductivity: [10 – 28] μS/mm</td>
</tr>
</tbody>
</table>
2) Lab scale tests:

Comparison of some critical physical properties: SDR % mean values
2) Lab scale tests:

Comparison of some critical physical properties: pH mean values

![Bar chart comparing pH values for OLD and New samples. The OLD sample has a pH of 2.65, and the New sample has a pH of 3.75.]
2) Lab scale tests:

Comparison of some critical physical properties: conductivity mean values

![Graph showing conductivity comparison between OLD and New samples.](image)
3) Tests on cables
Production and classification of the cables

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

Verifying the match of cables’ characteristic a.t. specific standard.

Performing the tests a.t. CPR

• THR, HRR, FIGRA, Burn length;
• TSP1200, SPR
• Droplets
• Smoke acidity
• 27 CM chamber test

Identification of the 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

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 m³ chamber)
- EN 60754-2 (Test on gases evolved during combustion of materials from cables – Part 2: Determination of acidity (by pH measurement and conductivity))
### FIRE PERFORMANCES: OLD AND NEW CABLES

Comparison b/w old and new cables

<table>
<thead>
<tr>
<th>New Cables</th>
<th>Class</th>
<th>Smoke</th>
<th>Droplets</th>
<th>Acidity</th>
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</thead>
<tbody>
<tr>
<td>FG16OR16</td>
<td>Cca</td>
<td>S₂</td>
<td>d₀</td>
<td>a₃</td>
</tr>
<tr>
<td>New code of FGyOR</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>FROR</td>
<td>B₂ca</td>
<td>S₂</td>
<td>d₀</td>
<td>a₃</td>
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FIRE PERFORMANCES: OLD AND NEW CABLES

We improved the flame retardancy reaching the class B2ca for some kinds of cables.

We verified a quite better performance in term of dripping in comparison to the Halogen Free systems.

But we have to get better values in terms of smoke density and smoke acidity.

So other sets of lab scale tests are scheduled to reach the new targets.

The most difficult task is the reduction of smoke acidity.
FOCUS ON SMOKE ACIDITY

Technical standards a.t. CPR

• EN 60754-2
• Tubolar Oven at fixed temperature ranging b/w 935°C up to 960°C
• Determination of pH and conductivity

The method used 4 PVC before CPR

• EN 60754-1
• Tubolar Oven at temperature ranging b/w 790°C up to 810°C
• Determination of mg of halogens in 1 g of compound
• Temperature ramp
To understand the differences b/w the two standards we need to introduce the theory of acid scavenging for the reduction of smoke acidity
ACID SCAVENGING THEORY

- **Stabilization zone**: Acid scavengers active until PVC is still alive.
- **Pyrolysis**: Massive release of HCl.
  - **Stable reaction products with HCl**: 810°C for EN 60754-1.
  - **Single step RXN**
  - **Multiple steps RXN**
- **Uncharted Zone**: Stable reaction products with HCl: 960°C for EN 60754-2.
  - **FOCUS ON SMOKE ACIDITY**
    - Chlorinated aromatic hydrocarbons
    - Loss of HCl
Acid scavenging theory: inert substance

ATH starts the decompositions b/w 180°C and 200°C, releasing water. It acts as heat sink, dilutes the flame, dilutes the polymer and plasticizers, creates a char of Al₂O₃[^3].

From a AS point of view ATH is ineffective due to the chemical inertia of Al₂O₃.

[^3]: Mass release of HCl 1,2

Al(OH)₃

Stabilization zone

Pyrolysis Massive release of HCl 1,2

Al₂O₃

Al₂O₃

<table>
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<tr>
<th>MM</th>
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<tbody>
<tr>
<td>PVC K70</td>
<td>100</td>
</tr>
<tr>
<td>ATH</td>
<td>80</td>
</tr>
<tr>
<td>DINP</td>
<td>50</td>
</tr>
<tr>
<td>STAB</td>
<td>5</td>
</tr>
</tbody>
</table>

| LOI   | 28 [%O₂] |
| pH    | 2,22      |
| Conductivity | 212 µs/mm |
Acid scavenging theory: ineffective AS

MDH starts the decompositions b/w 300°C - 320°C, releasing water. It acts as heat sink, dilutes the flame and as dilutes the polymer / plasticizers [3].

From AS point of view in single step reaction MDH is ineffective due to the instability of its reaction product [4].
Acid scavenging theory: efficient AS

AS5 is stable up to PVC is still alive 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

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<td>80</td>
</tr>
<tr>
<td>DINP</td>
<td>50</td>
</tr>
<tr>
<td>STAB</td>
<td>5</td>
</tr>
<tr>
<td>pH</td>
<td>3.11</td>
</tr>
<tr>
<td>Conductivity</td>
<td>30.1 µs/mm</td>
</tr>
</tbody>
</table>
EN 60754-1: used before CPR

Advantages

“800 °C“ mean a higher number of stable substances

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

With temperature ramps the acid scavengers have more time to trap the evolving HCl

From 23°C to 800 +/-10 °C
@ 20°/min

FOCUS ON SMOKE ACIDITY
EN 60754-2: a.t. CPR

Fixed b/w 935°C and 960°C

Disadvantages
- Higher temperature means a smaller number of stable substances
- Decomposition makes free HCl again
- Without temperature ramps the acid scavengers have no time to trap the evolving HCl efficiently
Differences in numbers

We tested the same compound with the two standards

**EN 60754-2**

- **pH:** 3.54
  
- Conductivity [µS/mm]: 10.4

**EN 60754-1**

- **pH:** 4.00
  
- Conductivity [µS/mm]: 3.8

The concentration of protons is 3 times higher in EN 60754-2

**FOCUS ON SMOKE ACIDITY**
Relationship b/w pH and conductivity

In in the bubbling devices the stronger electrolyte is always HCl
The importance of R&D in PVC

Last «adjustments» were at the end of 90’s for ROhS requirements

After 2008 an impoverishment of LV formulations is evident

HFFR eroded more and more market to PVC

Case history: Plenum cables in USA (NFPA 262): R&D permitted the production of compounds with a quite high flame retardancy with low smoke emissions, avoided the banishment of PVC from plenum conduits
Conclusions

The aim of the R&D is the innovation of the cables formulations

The new horizons of our R&D will be focused on the use of new additives, enhancing further the performances of cables formulations
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References

[1] Two-Stage Pyrolysis Model of PVC,

Edward D. Weil, Sergei Levchik and Paul Moy. Journal of Fire Sciences 2006; 24; 211

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[4] A Thermal Analysis of the Production of Anhydrous MgCl₂:
G. J. Kipouros, Donald R. Sadoway
THANK YOU

PVC FORUM ITALIA: CABLES GROUP

PVC forum: Cable Group Italy
www.pvcforum.it
info@pvcforum.it