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

Abstract: a new generation of PVC compounds for cables with very low values of smoke acidity have been developed, with the aim to reduce the emission of hydrochloric acid (HCl) due to the combustion of cables in case of fire. The use of several acid scavengers, capable to react quickly with HCl, trapping it in the ashes, and blocking its release in gas phase, have been evaluated. Two technical standards have been performed, EN 60754/1 and EN 60754/2, and the results have been compared, in order to understand if the presence of a temperature regime or different test temperatures can affect the measurements. The theory of acid scavenging in condensed phase at high temperature is introduced, describing the impact of acid scavengers on common flame retardants and smoke suppressants additives.

Gianluca Sarti [a]***, Marco Piana*** [b]

[a] *Cable Group Italy.* [b] *PVC Forum Italia*

Keywords: acid scavengers, PVC, cables, smoke acidity

1. Introduction

Smokes coming from a fire involving PVC cables contain HCl an irritant and water soluble gas. Its diffusion in a fire scenario can give incapacitation and hinders a safe escape [1], [2], but it is a matter of fact that the concentration of HCl decays quickly, thanks to the absorption by walls, ceilings, panels and other objects involved in the fire and even by fillers present in compounds used for manufacturing cables [3]. For reducing the acidic smokes a new generation of PVC compounds has been developed by Cable Group Italy. The group was born in 2013 and it gathers some of the biggest Italian PVC Compounders. The research project is called B2Ca.

2. B2Ca Research Project

In 2013 a set of old generation of CPD[1] cables have been tested with the new incoming CPR[2] rules [12] for evaluating classes and subclasses. The results are reported in table 1.

Type	Class	Smoke	Droplets	Acidity
FG7OR	Dca	s_2	d_1	a_3
FROR	Cca	s_2	d_0	a_3
N07V-K	Dca	s_2	d_0	a_3

Table 1: classes and subclasses obtained by a set of old CPD cables tested with the new CPR rules. The cables are typical low voltage Italian cables.

Type	Class	Smoke	Droplets	Acidity
FG7OR	Cca	s_2	d_0	a_3
FROR	B2ca	s_2	d_0	a_3
N07V-K	Cca	s_1	d_0	a_3

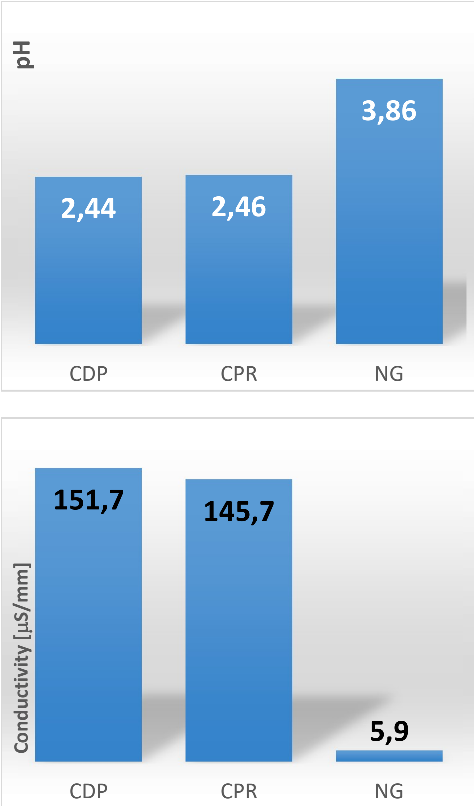
Table 2: new cables manufactured with new compounds, much more performant in term of fire performances and smoke suppressant properties.

The reached classes were poorer than expected and the risk to lose market share forced the modification of the formulations, improving the fire performances of compounds and achieving much more performing CPR classes. Table 2 shows this improvement, making clear that B2Ca class is easily to be reach with PVC compounds. Obviously the most difficult task has been the reduction of acidic smokes, therefore a new generation of compounds have been developed with the aim to reduce smoke acidity.

[1] Construction Products Directive (CPD): Directive 89/106/CEE

[2] Construction Products Regulation (CPR): Regulation (EU) N. 305/2011

As shown in picture 1 the new generation (NG) reached a pH 3.86 and a conductivity less than 6 μS/mm, values never achieved by PVC compounds with all characteristics needed for manufacturing TM1 and TM2 jackets.



Picture 1: smoke acidity in term of pH and conductivity according to EN 60754/2. Comparison between CPD, CPR and NG compounds.

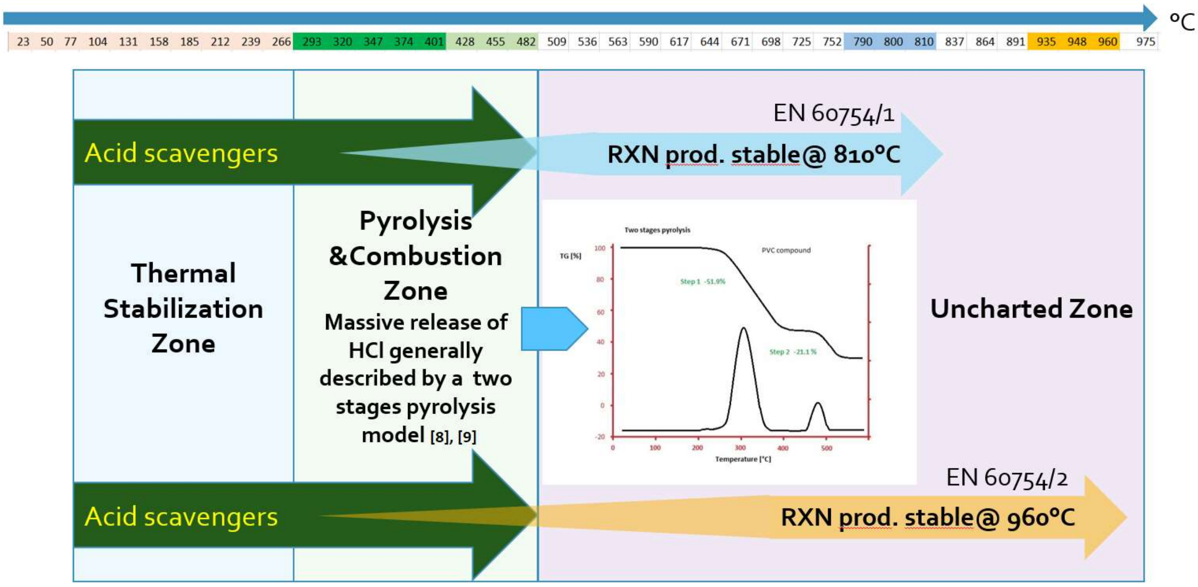
3. Acid scavenging at high temperature in condensed phase

To understand how we can reduce smoke acidity, we need to know how acid scavengers work at high temperature in trapping HCl in condensed phase. The picture 2 shows the main zones through which PVC compound passes during heating process bringing to combustion and calcination.

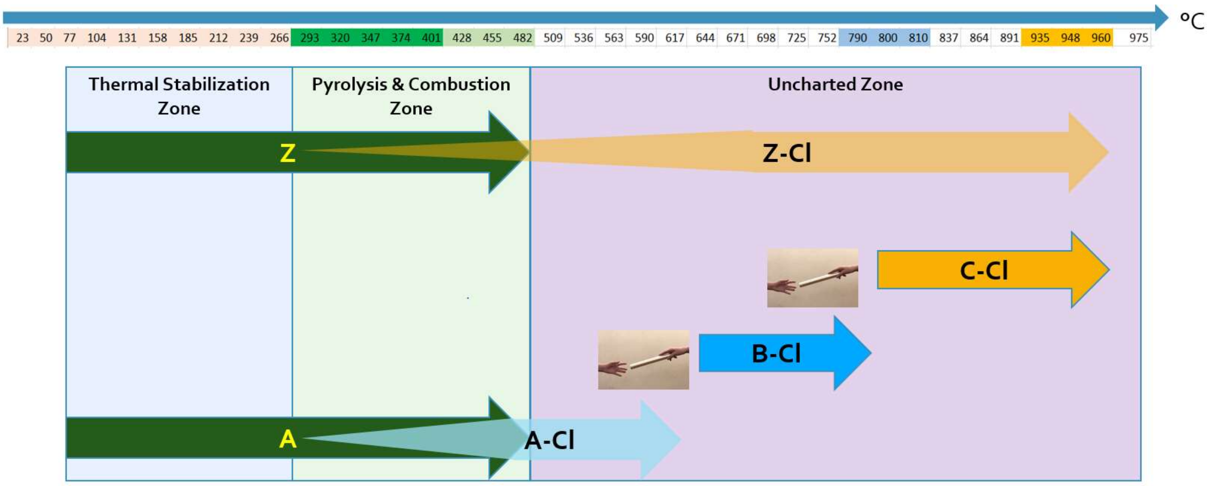
The key of success in a smoke acidity test is trying to figure out how acid scavengers behave in the "zones" indicated in picture 2, before, after and during the pyrolysis and combustion of PVC compound. Some substances are inert and others decompose, increasing the acidic smokes [4].

Therefore acid scavengers should be alive and active along the stabilization and combustion zone and they must create stable reaction products up to the maximum temperature according to the performed standard (i.e. 810 °C for EN 60754/1 and 960 °C for EN 60754/2). If not, their action will fail and HCl will evolve easily in gas phase with no chance to be trapped in the ashes. The interaction between HCl and acid scavengers can pass through a single step or a multiple step reaction. In single step reaction the acid scavenger reacts with HCl, fixing it in a stable reaction product up to the test temperature. In multiple step reaction two or more acid scavengers "cooperate" helping one each other through a relay race scheme. Like in a "relay race" the first teammate hands off the relay baton (HCl) to a second teammate and so on until the test temperature has reached (picture 3). This cooperation permits to enhance the efficiency of HCl scavenging. The speed of evolution of HCl influences a lot the behavior of acid scavengers. HCl is a gas and acid scavengers are solid substances trying to seize it. So they must be particularly quick in their interaction with HCl before it flies away. Consequently the test temperature and the presence or absence of temperature regime are the main causes affecting the "efficiency" of acid scavenging. It should be pointed out that this concept was highlighted in the past by other research teams. In fact Chandler and others made the same considerations performing measurements with furnace tubes tests in 1987 [5]. Picture 4 shows the decrease of efficiency of an acid scavenger as temperature increases and table 3 the difference between the results achieved with EN60754/1 and EN60754/2. The data's show clearly that, in presence of strong acid scavengers, commonly used in PVC for getting down smoke acidity, EN 60754/2 is more severe than EN 60754/1. The difference can be high or low depending on the action mechanism of used acid scavenger. With no acid scavenger obviously the difference becomes smaller, and that is what happens in most of the old generation of standard PVC compound for cables.

Another phenomenon found making thousands and thousands of measurements is that HCl is always the driving force of conductivity and so pH and Conductivity stay strongly linked in a mathematical relationship [4]. We can assume that other substances can evaporate, but their impact on conductivity is always slight and negligible.



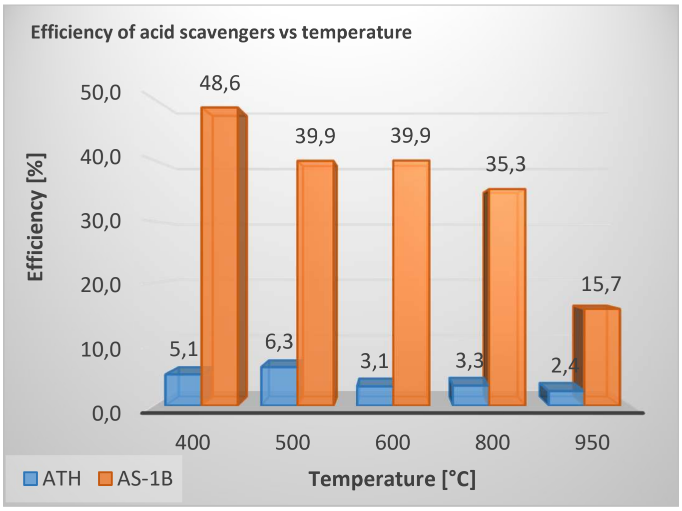
Picture 2: main identified zones: thermal stabilization zone where stabilizers act; pyrolysis and combustion where matrix burns; uncharted zone or "post pyrolysis and combustion zone" where no organic substances are present. The first stage is due to the massive release of HCl and it starts at 220 °C – 250 °C and it ends at 360 °C. After this point all HCl is in gas phase if acid scavengers are not present.



Picture 3: single step reaction vs multiple step reaction: A-Cl is unstable and decomposing needs a teammate capable to get HCl back.

	EN60754/2			EN60754/1			
Compound code	**pH**	**Conductivity [µS/mm]**	**[H$^+$] [mol/L]**	**pH**	**Conductivity [µS/mm]**	**[H$^+$] [mol/L]**	**[H$^+$]$^{EN60754-1}$/[H$^+$]$^{EN60754-2}$**
54	3.54	10.4	2.88×10^{-4}	4.00	3.80	1.00×10^{-4}	2.9
90	3.75	7.1	1.78×10^{-4}	4.24	3.0	5.75×10^{-5}	3.1
91	2.46	140.0	3.47×10^{-3}	2.65	90.4	2.24×10^{-3}	1.5
94	3.52	13.5	3.02×10^{-4}	4.07	3.9	8.51×10^{-5}	3.6

Table 3: comparison between EN60754/1 and EN 60754/2. EN60754/1 has been performed with pH and conductivity measurements for giving a comparison with EN60754/2. Temperature regime follows the indications of EN 60754/1. Last column gives the ratio between the molar concentrations of protons found with EN60754/1 and EN60754/2. **91** is a TM1 CPR compound showing smaller difference in comparison to **54**, **90** and **94**, TM1 compounds containing strong acid scavengers.



Picture 4: efficiency decay of acid scavenger AS-1B and ATH as temperature increases: after 800° the drop of efficiency is quite severe.

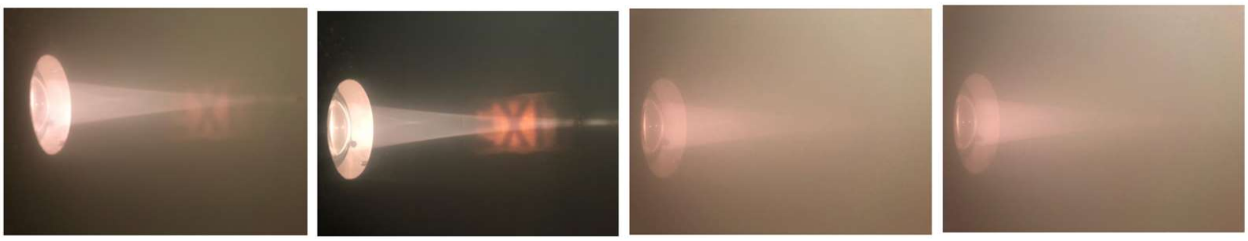
	F0	F1	F2	F3	F4	F5	F6
PVC	100	100	100	100	100	100	100
DINP	50	50	50	50	50	50	50
$CaCO_3$	90	60	60	60	60	60	60
$Mg(OH)_2$	0	30	30	30	0	30	30
Stabilizer	5	5	5	5	5	5	5
AS-1B	0	0	123	123	0	123	123
Sb_2O_3	0	5	5	10	3	3	3
AOM	0	0	0	0	30	30	53
LOI [O_2%]	23	32	23	23	38	23	24
pH	2.59	2.63	4.12	4.03	2.43	4.13	4.08
Conductivity [µS/mm]	107.2	99.3	3.2	4.0	155.2	2.88	3.12
SDR [%]	n.a.	n.a.	n.a.	71	57	84	81

Table 4: set of formulations for evaluating the impact of acid scavenger on flame retardancy and smoke suppressant properties. LOI has been performed according to ASTM D 2863 and smoke density rating according to ASTM D 2843.

4. Impact of acid scavengers on flame retardancy and on smoke suppressant properties

Acid scavengers interfere with the flame retardant mechanism in gas phase and in condensed phase, inhibiting the flame retardancy and smoke suppressant properties of PVC compounds. Tables 5 shows the impact of a powerful acid scavenger, AS-1B, on flame retardancy of Sb_2O_3 (ATO) and on flame retardancy and smoke suppressant properties of Ammonium Octa Molybdate (AOM). If we introduce AS-1B, all chlorine is trapped as chloride in condensed phase, preventing the formation of $SbCl_3$ in gas phase and stopping the formation of the “quenching scheme” of “hot radicals” feeding the flame [6]. That causes a dramatic dropping down of Oxygen Index (LOI) to 23 %O_2 and if we double the quantity of ATO the LOI remains stuck at 23 % O_2 (F1-F3).

Furthermore the scavenging of chlorine interferes with the charring mechanism of some smoke suppressants. AOM works in condensed phase and the key of its success is the formation of MoO_2Cl_2, a powerful Lewis Acid promoting the PVC crosslinking during the combustion [7]. Consequently, scavenging most of HCl, the formation of MoO_2Cl_2 is inhibited and the char



A B C D

Picture 5: smoke chamber according to ASM D2843: view on “EXIT” label at 120 seconds. It shows clearly how AOM smoke suppressant properties are inhibited by the presence of a strong acid scavenger.

cannot be formed. Then the flame retardancy drops down and smoke rises up. Smoke density rating passes from 71 % in F3, it drops down to 57 % in F4 and it rises up again (F5, F6) as the acid scavenger is introduced in the formulation. Better of any number the picture 5 shows the impact on smoke generation. **A** is the formulation without AOM, **B** has 30 phr of AOM, **C** 30 phr of AOM and a powerful acid scavenger inhibiting its action, **D** 53 phr of AOM and the same quantity of acid scavenger.

5. Conclusions

In these last years, innovation in PVC formulations has been made through a strong research aiming to improve fire performances of PVC compounds for cables. Recently E. Boccaleri and others [10], [11] studied the Use of POSS-Based nanoadditives for Cable Grade PVC, exploring their effect on thermal stability and evaluating their impact on HCl emission. PVC response in fires and fire risk tables have been reported by M. Piana and others [12], showing the positive aspects of PVC compounds for cables in term of performances and costs.

It is well established that PVC compounds for cables can obtain the highest fire reaction results compared with any other thermoplastic material, reaching easily B2Ca class, and d0 and S1a subclasses. The reasons stay in the following considerations:

1. PVC is self-extinguishing and has intrinsically a high potential to resist ignition sources. It does not contribute, or it only minimally contributes, to the generation and spread of a fire;
2. PVC irradiates only a minimum amount of heat and this means a minimum contribution to heat diffusion;
3. PVC tends to create a solid char during the combustion preventing the flame dropping. This property is intrinsically better than any other thermoplastic material and some specific additives called “charring agents”, like zinc, molybdenum and copper compounds, can emphasize this aspect, reducing incredibly the spread of fire and the emission of black dense smokes [6], [12], [13].

HCl contained in the smoke is highly irritating but not only it provides an immediate signal of the presence of the fire, acting as an escape alarm, but it decays quickly with no damage to the building structures or to environment in large scale fires [3].
In conclusion in this article Cable Group Italy has shown how the new generation of PVC compounds for cables emits acidic smokes 25 time less in comparison to CPD or CPR compounds, reaching results close to 4.00 phr and with a conductivity less than 6 μS/mm, results never got before with PVC compound for cables.

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