

The Evolution of Formulations of PVC Compounds for Cables in the Context of a Non-toxic Environment

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Abstract: This paper examines the evolution of poly(vinyl chloride) compounds used in cable manufacturing, focusing on the key drivers for replacing hazardous chemicals in PVC or PVC-based compounds with halogen-free alternatives, particularly concerning additive issues and fire performance. The environmental benefits of PVC are emphasized, along with advancements in reducing smoke and acidic effluents during fires. The paper highlights the role of stringent European Union regulations and directives, such as RoHS, REACH, and CPR, in driving the development of more sustainable PVC formulations. Furthermore, it explores the creation of new low-smoke, low-acidity compounds for cables that incorporate advanced flame retardants, smoke suppressants, and acid scavengers, demonstrating how these compounds meet and exceed fire safety standards in terms of heat release, smoke production, and toxicity of the effluents. Additionally, it addresses common misconceptions, including the belief that modern PVC cables still contain hazardous additives, cannot be recycled, and produce dense black smoke and toxic emissions, making them less sustainable than halogen-free alternatives. The findings support the conclusion that PVC remains a viable and often superior option for cable applications in today's increasingly competitive and environmentally conscious market, mainly due to its sustainability and adaptability to stricter fire safety regulations.

1. Introduction

Poly(vinyl chloride) (PVC) has been a cornerstone material in the cable industry for decades, recognized for its exceptional durability, flexibility, cost-effectiveness and easy installation. In recent years, however, the focus has shifted towards enhancing PVC's environmental and fire safety aspects, driven by both regulatory requirements and growing public awareness of sustainability and safety. It is important to note that the PVC associations and manufacturers have often taken proactive measures, implementing changes well before regulatory requirements. This paper provides a comprehensive analysis of the factors that influenced the evolution of PVC compounds for cables since the 1990s, strongly emphasizing which problematic ingredients have been phased and the new ones introduced, which increase the fire performances, reduce smoke production and acidity in fires. Furthermore, the paper addresses common misconceptions, such as the belief that PVC combustion leads to significant emission of toxic effluents, which can hinder the continued and expanded use of PVC in cable applications.

2. Regulatory Drivers for Substitution and impact on formulations

2.1. The Role of RoHS and REACH in Material Substitution

The European Union promoted the restrictions of some harmful substances in Electrical and Electronic Equipment (EEE) by issuing the Directives 2002/95/CE (RoHS 1), 2011/65/EU (RoHS 2), and (EU) 2015/863 (RoHS 3) between 2003 and 2015, Fig. 1. [1-3]. The aim was to help the sustainable recycling of waste from Electrical and Electronic Equipment (WEEE), prohibiting the use of the harmful substances contained in them and therefore reducing problems related to their

handling according to Directive 2002/96/EC and 2012/19/EU (last consolidated version dated 13/04/2024) [4,5]. PVC cables involved were cords and internal wiring of white goods, house appliances, mobile phones, computers, televisions, lamps, photovoltaic panels, and medical devices. In 2015, thanks to RoHS 3, the low molecular weight plasticizers such as Di Ethyl Hesi Phthalate (DEHP or trivially DOP), Di Iso Butyl Phthalate (DiBP), Di Butyl Phthalate (DBP) and Butyl Benzyl Phthalate (BBP) were also added to the negative list. These listings affected the evolution of the EEE formulations, involving many other kinds of cable (energy, communication, signal, and control, for example, but extending to many others) thanks to the proactive action of the PVC value chain. Tables 1-3 show the progress from the 1990s TM1 jacket formulation to the 2017 one, with non-classified ingredients imparting the same properties according to the product standard EN 50363-4-1 requirements. [6] Similarly, the actions from the European Parliament and Council Regulation (EC) No 1907/2006 (Regulation Evaluation, Authorization, and Restriction of Chemicals or REACH) have been crucial in driving material substitution within PVC compounds for cables. [7]

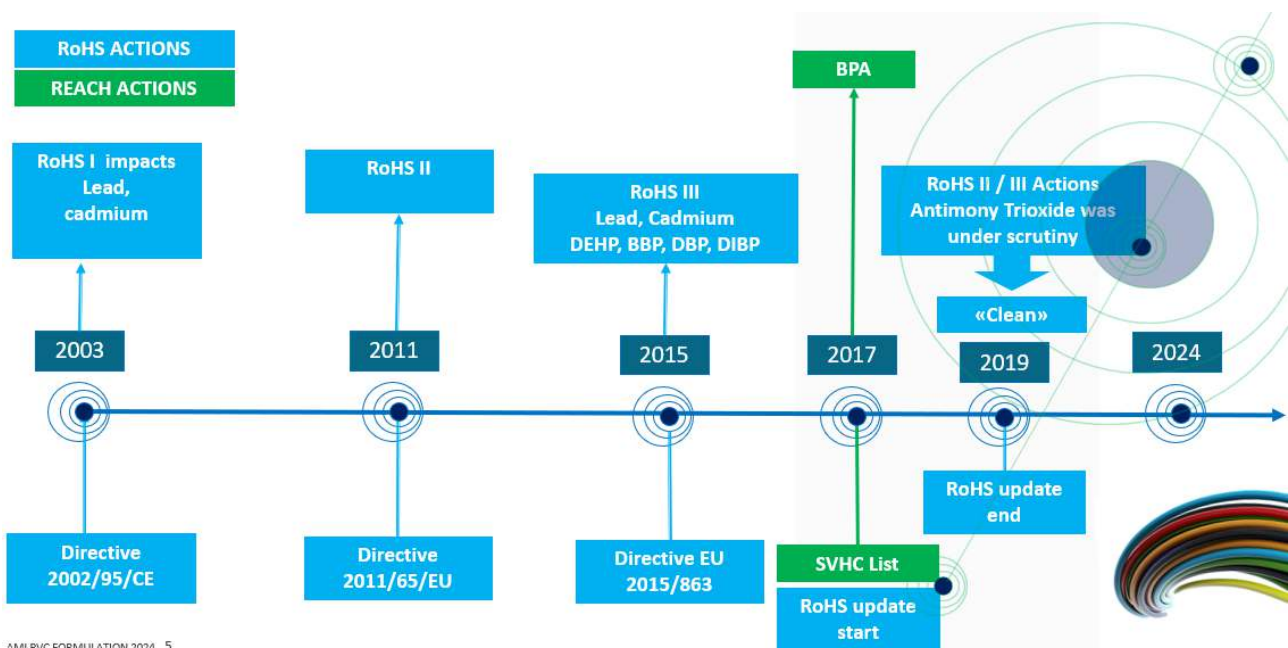


Figure 1: Timeline of the actions from Directives / Regulations affecting PVC cable compound composition from 2003 – 2020.

The first target was the Bis Phenol A (4,4'-isopropylidenediphenol or BPA), an antioxidant utilized, among others, in various plastics, as the monomer in polycarbonate and additive in thermal paper. It was listed in the Substance of Very High Concern (SVHC) list in 2017 and 2018 because it is toxic for reproduction and has endocrine-disrupting properties to the environment and human health. Its use has been restricted in thermal paper in 2017, and an Assessment of Regulatory Needs (ARN) is still ongoing to evaluate the need for further regulatory actions. [8] As happened to Pb, Cd, and low molecular weight plasticizers through RoHS, the value chain proactively banned BPA before any authorization or restriction action from ECHA, starting from plasticizers and stabilizers down to compounds and masterbatches, with non-toxic alternatives. All this shows how the PVC industry, in response to these regulations and directives, has not only complied but also has proactively sought to exceed their requirements, demonstrating a commitment to environmental stewardship and human health.

2.2 Evolution of the formulation in the period 2000 – 2015. Substitution of Hazardous Additives.

Traditionally, lead-based stabilizers were used in PVC formulations for cables, providing exceptional thermal stability, aging, and weathering, among other characteristics. However, in response to lead's environmental and health risks highlighted in Section 2.1, the industry has successfully transitioned to calcium-zinc stabilizers, which deliver comparable performance without the associated toxicity. Similarly, phthalates like DEHP (Di Ethyl Hexyll Phthalate), DIBP (Di Iso Butyl Phthalate), DBP (Di Butyl Phthalate), and BBP (Butyl Benzyl Phthalate), which were once widely used as plasticizers, have been replaced by alternatives such as DINP (Di Iso Nonyl phthalate) and DIDP (Di Iso Decyl phthalate), which are safer and maintain the flexibility, mechanical and aging properties, thermal stability, and durability required by the product standards. Tables 1 and 2 show this evolution from 1990s formulations to 2017, which includes the substitution of BPA with phenolic antioxidants, such as pentaerythritol tetrakis(3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate), CAS n. 6683-19-8, or octadecyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate, CAS n. 2082-79-3.

Table 1: TM1 1990s formulation before RoHS (a) and properties (b)

1990s TM1 FR Jacket / FR Rz (ITA)	phr
S PVC K 70	100,0
DEHP	46,0
MCCP (45 % – 52 %) Chlorine	10,0
CaCO ₃	70,0
Antimony Trioxide	4,0
BPA	0,2
Stabilizer Lead Based	7,0
Stearic acid	0,3
TOT	237,5

Table 1a

1990s TM1 FR Jacket	EN 50363-4-1
Density [g/CC]	1,504
Hardness [Shore A]	84
Tensile Strength [MPa]	14,0
Elongation at break [%]	265
LOI [%O ₂]	30
Lead [% w/w]	1,39
ATO [% w/w]	1,68
BPA [% w/w]	0,08
MCCP [% w/w]	4,21
DEHP [% w/w]	19,30

Table 1b

Table 2: a TM1 2017 formulation after RoHS 3 and BPA in SVHS (a) and properties (b)

TM1 FR Jacket Lead Free FR Rz (ITA)	
S PVC K 70	100,0
DEHP → DINP (BPA free)	49,0
MCCP	10,0
CaCO ₃	76,0
Antimony Trioxide	4,0
BPA → IX 1010	0,2
Lead Based → Stabilizer CZ	5,0
FT Wax	0,3
TOT	244,5

Table 2a

TM1 FR Jacket Lead Free	EN 50363-4-1
Density [g/CC]	1,511
Hardness [Shore A]	85
Tensile Strength [MPa]	13,3
Elongation at break [%]	260
LOI [%O ₂]	31
Lead [% w/w]	0,00
ATO [% w/w]	1,64
BPA [% w/w]	0,00
MCCP [% w/w]	4,09
DEHP [% w/w]	0,00

Table 2b

This proactive approach to material substitution emphasizes the PVC industry's ability to adapt and innovate under regulatory pressures, ensuring that PVC cables remain a top choice for a wide range of applications.

2.3. Recycling Challenges for Consuming PVC Cable compounds before 2015

Using recyclates (recycled materials) and feedstock derived from renewable sources in PVC compounds is a crucial strategy for reducing a product's carbon footprint (PCF) and aligning with circular economy principles without compromising the final product's durability. Incorporating both into production processes helps minimize the demand for fossil feedstock, often involving energy-intensive extraction, processing, and long transport routes, thereby reducing greenhouse gas emissions. In a circular economy, the goal is to create a closed-loop system where products and materials are reused, remanufactured, or recycled back into the production cycle, thus contributing to sustainability and environmental stewardship. Adopting recyclates and renewable feedstock in the final product is a key strategy in achieving this vision, helping the PVC value chain to meet stringent environmental regulations and enhance the overall sustainability of its products. That is crucial for a) competing with halogen-free compounds when, for example, utilities request environmental product declaration (EPD) as an entry-level condition for purchasing cables and b) to counterbalance the misconceptions claiming that PVC is not a sustainable polymer. Ref. 9 gives some examples of how using recyclates can help the sustainability of the PVC cable compound.

In any case, three main problems occur when cable manufacturers try to use recyclates and bio-based additives in cables:

- 1) Bio-based additives must maintain the primary characteristics of cable compounds. They should prevent migration to the surface or other cable parts that could impact the mechanical properties of nearby insulation or jackets. These additives should provide similar thermal stability, processability, durability, aging, and insulation properties as the original compounds, and they should not alter their color. [9]
- 2) Recyclates from mechanical recycling processes (Fig. 2) often have unknown compositions, moreover, post-consumption scraps coming from demolition waste. Recyclates are produced by a mix of milled jackets, beddings, and compounds from dismantling the out-of-specification or post-consumption cables (in Italy, called friendly "floreale" because they are composed of a variety of pieces of different colors, Fig. 2a). Their use can significantly impact the main properties of the cable, such as insulation properties or thermal stability, even at low concentrations. As a result, only a tiny fraction of close-loop recycling from post-consumption recyclates is used and only in less demanding cable compounds. On the contrary, post-industrial scraps of known composition can be used even in more demanding cable compounds. However, the most applied is an open-loop recycling system using these recyclates in other items.
- 3) Handling materials with hazardous legacy additives requires careful consideration to ensure identification, sorting, safe management, and disposal.

This third is the most significant challenge facing the PVC industry, mainly due to the presence of lead and DEHP. While no longer used in new formulations, these substances persist in cables produced before 2015, complicating the recycling process. Recycling is the fundamental background of circular economy policies in the European Union (EU). Despite this, the Regulation

(EU) n. 2018/2005 [10] and 2023/923 [11] limit DEHP and lead content in PVC articles to 0.1% w/w. If we want to recover scraps in EEE, we must also respect the limits indicated in RoHS. That highlights the current need to manage these legacy additives, which can be found in Floreale from post-consumption cables. When floreale is extruded with stabilizers, lubricants, and pigments (if needed), the intermediate, aka the recyclate (Fig. 2b), can be then diluted in less demanding compound cables or used in undercoat for hoses or the bottom layer of roofing membranes.

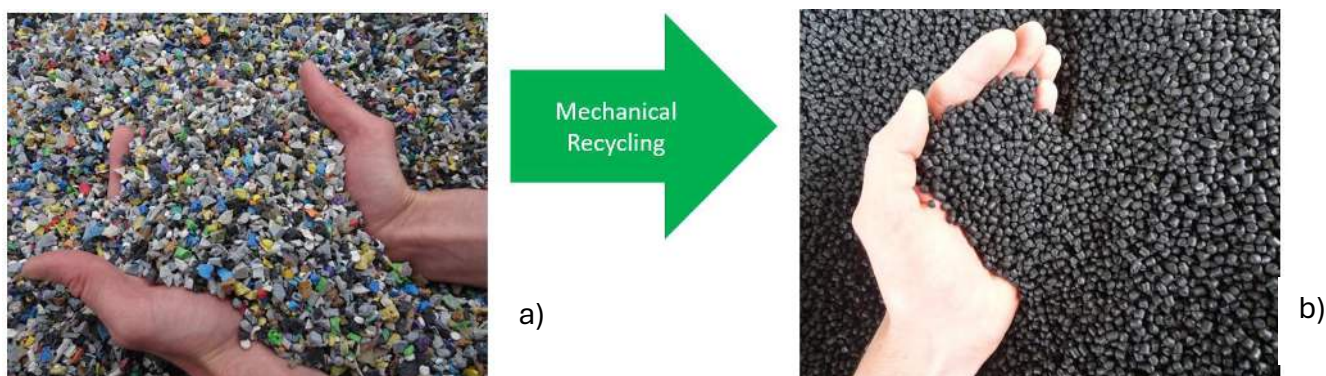


Figure 2: Floreale (a) and how it is mechanically recovered in recyclates by "recyclers" (b).

Since 2020, Regulation (EU) No. 2018/2005 has banned using articles containing more than 0.1% DEHP. Additionally, Regulation (EU) No. 2023/923 grants a two-year derogation for PVC-P containing more than 0.1% lead. Therefore, after May 28, 2025, recyclers will be prohibited from placing recyclates with lead levels exceeding this limit on the market. This situation highlights a conflict between EU circular economy policies and REACH regulations, revealing that solutions for trapping legacy additives in durable articles are viewed as more hazardous than incineration or landfilling. According to these regulations, innovative recycling solutions must be developed and implemented for post-consumption cables.

2.4. New Recycling solutions

Despite these challenges, the PVC industry has significantly progressed in developing advanced recycling technologies. Mechanical recycling, the most common method, involves grinding PVC scraps into tiny particles that can be stabilized and reprocessed even 10 times. However, hazardous additives require sophisticated sorting and cleaning processes to ensure that the recycled material meets the requirements of the Regulations. In this, portable XRF detection systems for lead and cadmium are evaluated as the most used "static" apparatuses carrying on solid and repeatable methods capable of detecting them at very low concentrations, using portable XRF test apparatuses according to Ref. 12. This enables the easy in situ detection of cables containing lead, cadmium, bromine, and other elements. However, DEHP detection requires laboratory analysis using gas chromatography-mass spectrometry (GC-MS) or high-performance liquid chromatography (HPLC). The use of the dynamic methods of detection and sorting scraps containing DEHP, MCCP, and lead and cadmium are under development by Phoenix srl through XRF and NIR technologies, as described in Refs 13 and 14. Chemical recycling is an emerging technology based on dissolving PVC compounds in a specific solvent, separating fillers and non-soluble additives, precipitation and cleaning of PVC resin, separating it from legacy additives, and producing recycled PVC resin. In the past, Vinyloop technology was developed in Ferrara (Italy) by Solvin, but the project was closed in 2017. In 2024, Inovyn announced the project's restarting, offering the potential recovery of virgin, clean, and partially stabilized PVC

resin for various applications, including cables. [15] This innovation represents a significant advancement in pursuing a circular economy because even post-consumption PVC cable scraps containing legacy additives could be treated, recovering the resins. Figures 3 and 4 display the flowchart of the PVC cable process, showing the inventory analysis of the LCA study reported in Ref. 9, which indicates the flow of energy, materials, and environmental impacts from cradle to grave, with landfill, incineration, or recycling as fate. The last one impacts the final product's PCF by reducing the use of fossil-based feedstock, energy consumption, production of waste, and emission to air and soil. In all this, must be considered the fact that the new compounds contain substances with a lower environmental impact. It must be highlighted that dynamic or static systems of detection and sorting in mechanical recycling based on NIR or XRF and chemical recycling can be adjusted for new incoming legacy additives from new updates of REACH or RoHS.

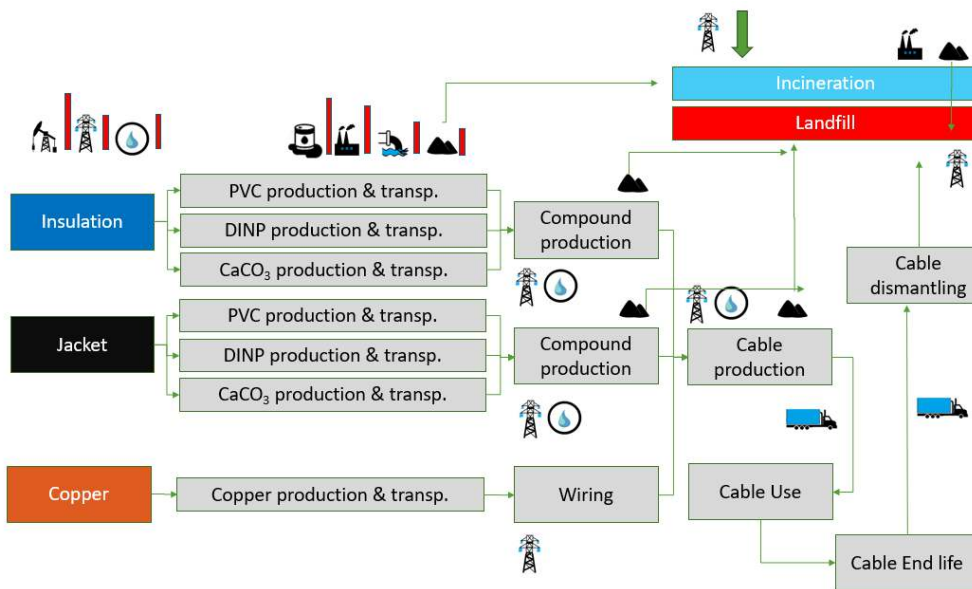


Figure 3: Flowchart of cable manufacturing from the cradle to the grave (Incineration and landfill) [9]

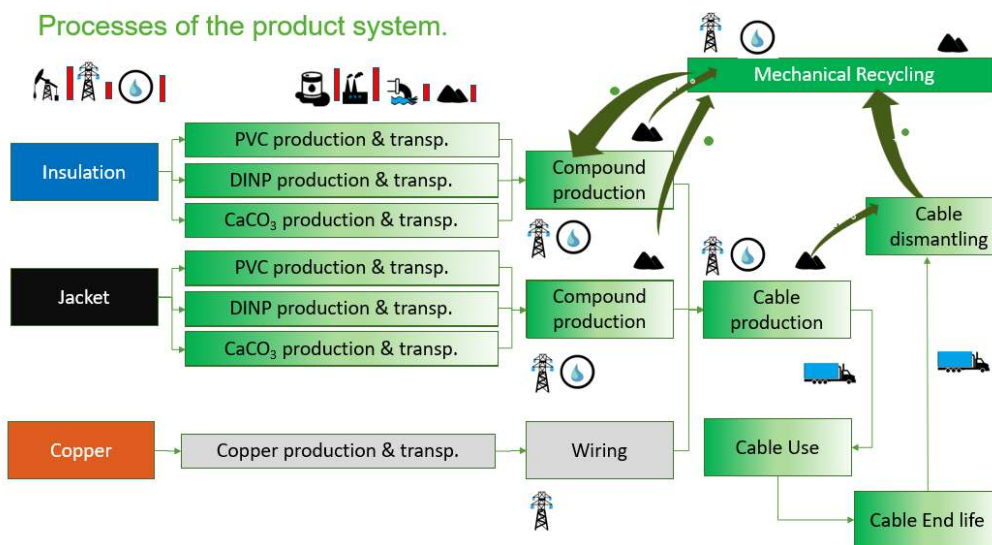


Figure 4: Flowchart of cable manufacturing from the cradle to the grave (Recycling Process) [9]

2.5. New target substances. Actual and possible scenarios

Which other substances can be the next target of REACH, RoHS, or other incoming directives/regulations? Figure 5 gives the last regulatory actions involving also PVC cable compounds.

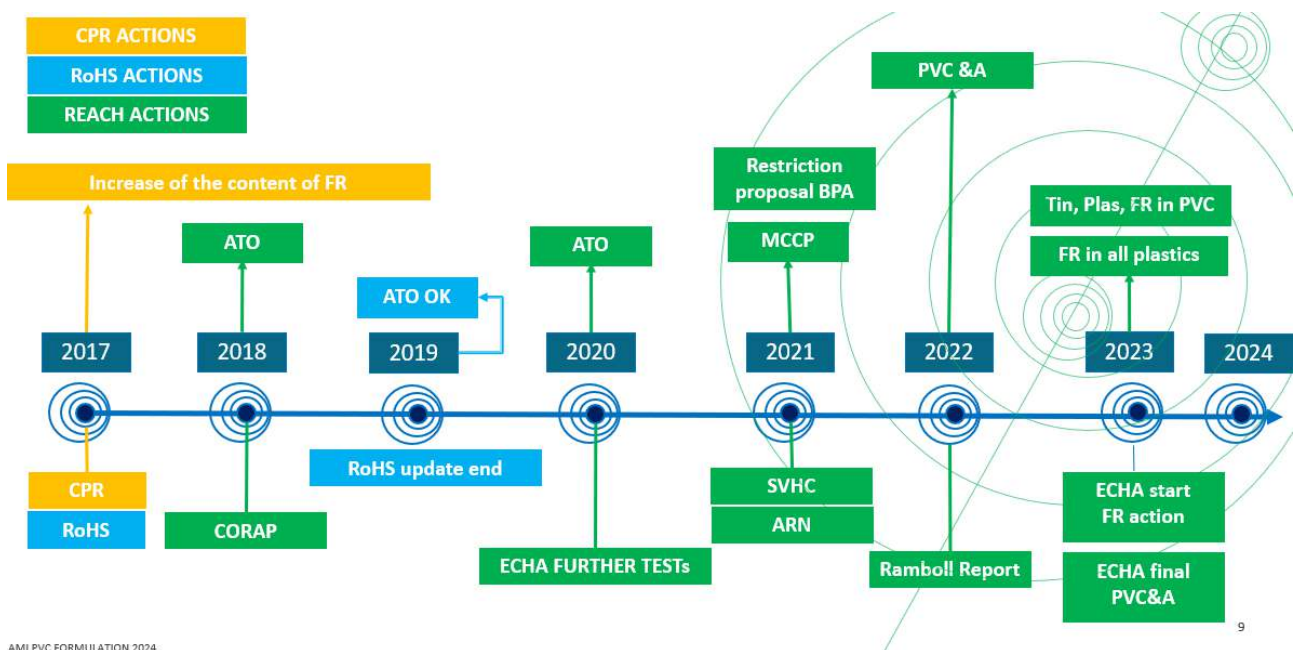


Figure 5: Timeline of the series of Directives / Regulations affecting PVC cable compound composition from 2017 to 2024.

The Regulation (EU) n. 305/2011 (Construction Product Regulation, or CPR) entered into force in 2017, [16] severely impacted cable formulation compounds by increasing the concentration of flame retardants due to issuing more stringent and severe standards for testing fire performances. The result was the introduction of flame-retardant fillers less used in the past, such as magnesium hydroxide (MDH) and aluminum tri hydroxide (ATH), and the increase of ATO and zinc borate (ZBO) concentrations (Tables 3a and b).

Table 3: a TM1 2017 formulation after CPR (a) and properties (b)

TM1 Jacket a.t. EN 50363-4-1 and R16 a.t. EN 50363-0 Annex 1 (ITA)	Original	New one
S PVC K 70	100,0	100,0
DINP	49,0	49,0
MCCP	10,0	10,0
Chlorinated Esters	0,0	0,0
CaCO ₃	76,0	26,0
Brucite	0,0	50,0
ATO	4,0	5,0
Zinc Borate	0,0	5,0
IX 1010	0,2	0,2
Stabilizer CZ	5,0	5,0
FT Wax	0,3	0,5
TOT	244,5	250,7

Table 3a

TM1 Jacket a.t. EN 50363-4-1 and R16 a.t. EN 50363-0 Annex (ITA)	Original	New one
Density [g/CC]	1,511	1,509
Hardness [Shore A]	85	86
Tensile Strength [MPa]	13,3	13,0
Elongation at break [%]	260	258
LOI [%O₂]	31	34
Lead [% w/w]	0,00	0,00
ATO [% w/w]	1,64	1,99
Zinc Borate [% w/w]	0,00	1,99
Brucite [% w/w]	0,00	19,94
BPA [% w/w]	0,00	0,00
MCCP [% w/w]	4,09	3,99
DEHP [% w/w]	0,00	0,00

Table 3b

The regulatory evolution depicted in Fig. 5 shows that probably the next substance candidates to be phased out could be antimony trioxide (ATO) and medium-chain chloroparaffins (MCCP). ATO was entered into the CORAP list in 2018 and evaluated as a possible H350 substance (carcinogenic by inhalation) by Bua in 2020. [17] In 2020, ECHA asked registrants for further tests to confute the Bua report. Tests are ongoing and should become available in 2025. MCCP entered in SVHC list in July 2021 [18]. They are used to increase flame retardancy and for lowering the cost of non-flame retarded PVC-P compounds, including cheaper cable compounds, and for a variety of other applications, moreover in the southern EU countries. A less extensive use in the northern EU countries makes it a typical issue of nations such as Italy, Spain, and Portugal. Although the SVHC list is just a parking lot of the candidate substances to be authorized or restricted, today, most cable manufacturers in the EU southern countries are substituting MCCP proactively with the formulations indicated in Table 4.

Table 4: a TM1 2017 with and without MCCP (a) and properties (b)

TM1 Jacket a.t. EN 50363-4-1 and R16 a.t. EN 50363-0 Annex 1 (ITA)	Original	New one A MCCP free	New one B MCCP free
S PVC K 70	100,0	100,0	100,0
DINP	49,0	54,0	49,0
MCCP	10,0	0,0	0,0
Chlorinated Esters	0,0	0,0	10,0
CaCO ₃	26,0	20,0	26,0
Brucite	50,0	56,0	50,0
ATO	5,0	6,0	5,0
Zinc Borate	5,0	5,0	5,0
IX 1010	0,2	0,2	0,2
Stabilizer CZ	5,0	5,0	5,0
FT Wax	0,5	0,1	0,5
TOT	250,7	246,3	250,7

Table 4a

TM1 Jacket a.t. EN 50363-4-1 and R16 a.t. EN 50363-0 Annex 1 (ITA)	Original	New one A MCCP free	New one B MCCP free
Density [g/CC]	1,509	1,529	1,509
Hardness [Shore A]	86	86	86
Tensile Strength [MPa]	13,0	12,4	13,0
Elongation at break [%]	258	245	258
LOI [%O₂]	34	34	34
Lead [% w/w]	0,0	0,0	0,0
ATO [% w/w]	1,99	2,44	1,99
Zinc Borate [% w/w]	1,99	2,03	1,99
Brucite [% w/w]	19,94	22,74	19,94
BPA [% w/w]	0,00	0,00	0,00
MCCP [% w/w]	3,99	0,00	0,00
DEHP [% w/w]	0,00	0,00	0,00

Table 4b

Finally, Table 5 gives the adjustment in the formulation due to the presence of ATO-free flame retardants.

Table 5: FR TM1 ATO based and free (a) and properties (b)

TM1 Jacket a.t. EN 50363-4-1 and R16 a.t. EN 50363-0 Annex 1 (ITA)	Original	New one ATO free
S PVC K 70	100,0	100,0
DINP	49,0	49,0
MCCP	0,0	0,0
Chlorinated Esters	10,0	10,0
CaCO ₃	26,0	20,0
Brucite	50,0	70,0
ATO free FR	0,0	10
ATO	5,0	0,0
Zinc Borate	5,0	0,0
IX 1010	0,2	0,2
Stabilizer CZ	5,0	5,0
FT Wax	0,5	0,5

Table 5a

TM1 Jacket a.t. EN 50363-4-1 and R16 a.t. EN 50363-0 Annex 1 (ITA)	New one ATO free	New one ATO free
Density [g/CC]	1,509	1,529
Hardness [Shore A]	86	87
Tensile Strength [MPa]	13,0	12,8
Elongation at break [%]	258	259
LOI [%O₂]	34	33
Lead [% w/w]	0,00	0,00
ATO [% w/w]	1,99	0,00
Zinc Borate [% w/w]	1,99	0,00
Brucite [% w/w]	19,94	28,42
BPA [% w/w]	0,00	0,00
MCCP [% w/w]	0,00	0,00
DEHP [% w/w]	0,00	0,00

Table 5b

3. Enhancing Fire Performance and Reducing Acidic Smoke in PVC Compounds

3.1. Advanced Fire Safety Regulations and PVC's Response. The impact of CPR

Fire safety is a vital concern in designing and manufacturing cables and PVC compounds for cables, particularly in applications such as building and construction (B&C), where the risk of fire can be elevated and its consequences catastrophic. In the EU, CPR has been issued to guarantee that construction products (CP) permanently installed in buildings are "safe" to be marketed and used in B&C. In construction works, "safe" intends that CP must be designed, produced, installed, used, and disposed considering the seven basic requirements of CPR (see Annex I in Ref. 16), which ensure the health and safety of persons and the environment throughout the entire life cycle of the product. CP must meet performance standards among seven basic requirements, particularly fire safety, energy efficiency, and structural integrity. For example, cables permanently installed in B&C must have a harmonized classification in reaction to fire. Aca, B1ca, B2ca, Cca, Dca, Eca, and Fca (this last one is less performant) have been adopted as main classes and take into consideration flame spread (FS) and heat release. Additional classes are assessed to complete the fire hazard profile of the article: smoke production (s_{1a} , s_{1b} , s_2 , and s_3 , this last one less performant), flaming droplets (d_0 , d_1 , and d_2 , this last one less performant) and acidity (a_1 , a_2 , and a_3 , this last one less performant). [19] Installing the cables in B&C depends on the fire risk of the location with the logical approach of "more performant classes in high fire risk locations" and is ruled by the national laws and codes of the countries in the EU. It must be highlighted that CPR has driven the issue of more severe technical standards and requirements for testing CP, which challenged the industry to enhance the fire behavior of insulation, bedding, and sheathing materials. All these implied the increase of flame-retardant levels in all halogen-based or -free compounds for meeting the best classification in reaction to fire. Also, the quantity of smoke suppressants and anti-dripping additives improved. While halogen-free flame-retardant (HFFR) compounds are the preferred choice for achieving the highest classification for acidity and smoke production, significant research has been conducted to reduce the release of hydrogen chloride (HCl) from PVC compounds used in cables without compromising the heat release and smoke production, to remain competitive with HFFR solutions. [20-30] In this, the role of flame retardants, smoke suppressants, and acid scavengers play a crucial role in developing new PVC compounds for cables with better fire performances. [31,32]

3.2. Flame Retardants, Smoke Suppressants, Acid Scavengers, and the new low smoke acidity compounds and their heat release.

PVC's inherent flame retardancy is primarily due to the release of HCl during combustion, which acts as a radical inhibitor, preventing the propagation of flames. Flame retardants such as ATO, ZnBO, MDH, and ATH are usually combined into PVC formulations to further enhance this property. By forming antimony trichloride (SbCl_3) during combustion, ATO significantly enhances the flame-retardant effect by lowering the flame's energy and improving the material's reaction to fire. [33] Additionally, incorporating other flame retardants like MDH, ATH, and incipient Lewis acids [34], smoke production can decrease at levels comparable with HFFR. [26] Another class is acid scavengers, which play a crucial role in reducing the HCl release and dropping the acidity of the effluents. Recent research funded by PVC4cables has focused on reducing the acidity of smoke produced during PVC combustion, an area that should be under revision in modern fire safety science. That research started in 2013 in Italy, when some cable compound manufacturers figured out how to reduce smoke acidity without compromising the main properties of the cable and some fire performances, such as smoke and heat release. The HCl scavenging, in fact, affects the ability of PVC to poison the flame and create a protective char [24], forcing the researchers to find other routes to get both back. Today, we know that these compounds provide cables with extremely low heat release and flaming dripping, easily reaching classes B_{2ca} and d_0 . [26-32,34] The acidity has been reduced (pH 3.80, Conductivity 1.6 microS/mm), [34] but it does not meet the values for achieving the a_2 or a_1 additional classification for acidity at 950 °C. However, they reach almost the class a_1 performing the test by applying the heating regime of EN 60754-1 (40 min to 800°C and an additional 20 minutes at 800°C). [35] These are called "low smoke acidity compounds" and show remarkable properties in terms of reaction to fire, smoke production, flaming droplets, and acidity. [26,34]

3.3. Does PVC release black, dense, thick smoke?

The smoke issue is a typical misconception used against PVC often mentioned in HFFR brochures or some internet videos comparing, in pseudo-scientific experiments, the smoke released from PVC and HFFR cables, usually the worst and cheapest PVC in the market and the best HFFR of the research. When smoke suppressants are introduced in PVC compound for cables, smoke production is remarkably reduced. In Ref. 26, low smoke acidity compounds were used for producing an FG16OR16 cable, a not harmonized Italian cable according to CEI UNEL 35318, [36] which was tested according to EN 50399 [37] and EN 61034-2, [38] reaching the classification s_{1b} . In Fig. 6, [26], the yellow curve shows the transmittance values of a low smoke acidity compound compared to an HFFR according to EN 61034-2.

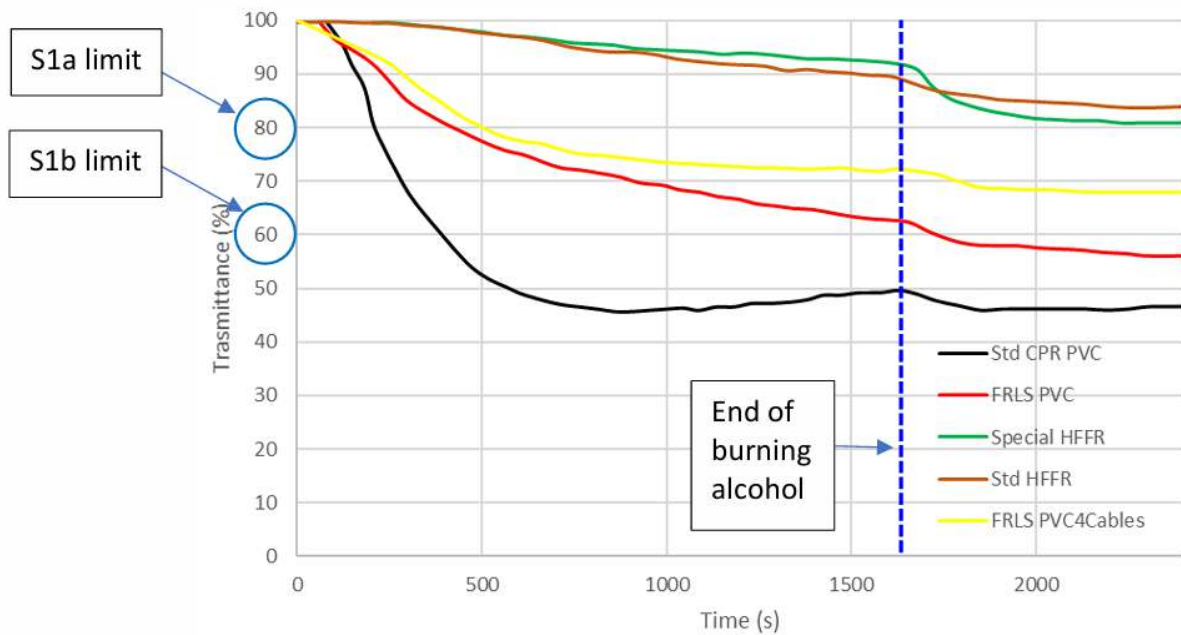


Figure 6: EN 61034-2 smoke density measure for assessing the classes s1a and s1b. [26]

The figure indicates that the low smoke acidity cable not only reaches a remarkable smoke classification (S_{1b}) but even a standard CPR cable, according to CEI UNEL 38318, easily meets the S_2 classification. That is because the severe EN 50399 requires more charring agents in the cable compound, reducing flaming dripping and the FS and remarkably dropping the smoke production. If we observe the red curve, which represents a FRLS (Flame Retardant Low Smoke) PVC cable commonly found in the Russian market but also common in India, [39], as FRLSH where H stands for halogen, Ukraine, and several other countries in the Far and Middle East, it reaches almost the class S_{1b} .

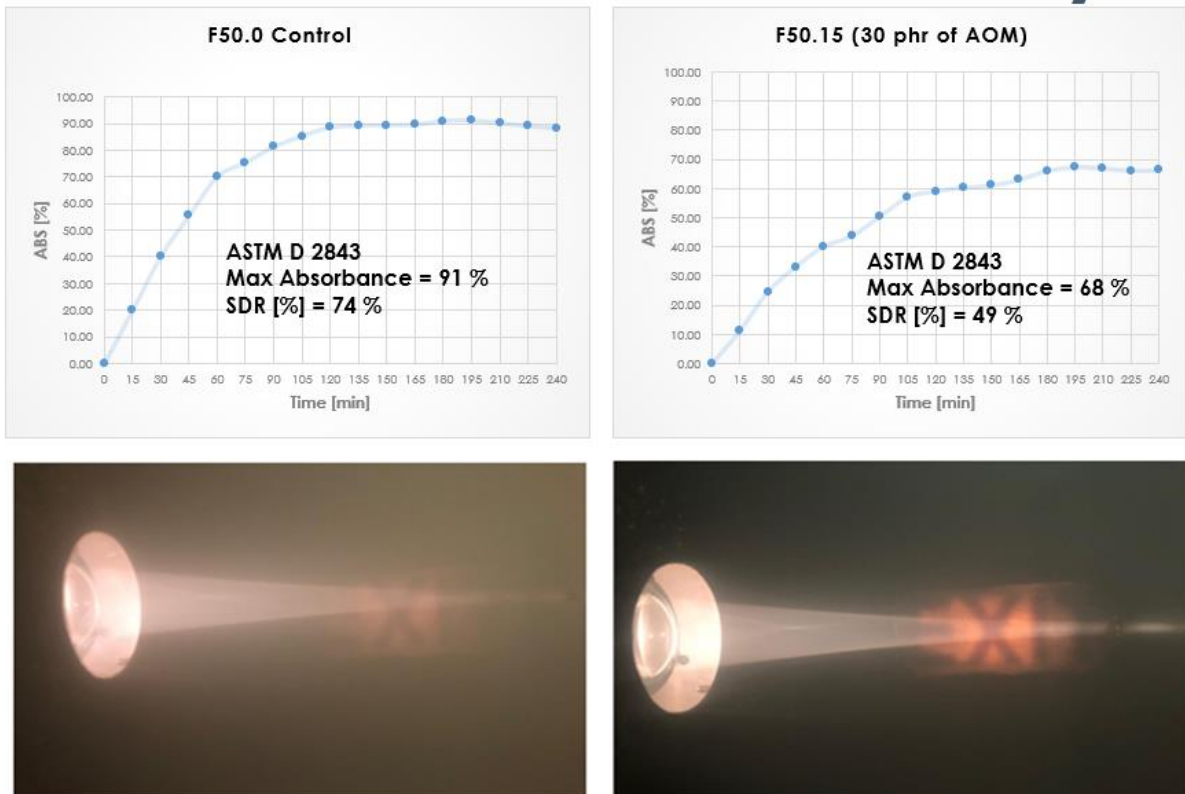


Figure 7. [28] Compounds for PVC jacket Plenum grade vs. standard PVC compound for cable without smoke suppressants. Smoke density Rating [%] according to ASTM D 2843. [40] The plenum compound is much below 60 % SDR.

Furthermore, it must be highlighted that PVC is the premium choice for producing plenum jackets according to NFPA 262, [41] famous for their extremely low smoke production and heat release. Plenum cables are laid down in plenum spaces in high-rise buildings (including skyscrapers), where standard cables can give an increased risk of spreading flames and smoke flooring by flooring, trapping people in a nightmare fire scenario. Plenum cables were developed at the end of the 1970s after a fire (with no casualties and fatalities) in the Twin Tower North in 1975. The report following the fire revealed the critical issues in using standard cables for these kinds of locations. Plenum cables are tested through the Steiner Tunnel, ASTM E 84 [42], one of the most critical standards for evaluating reaction to fire in terms of FS and smoke production. Currently, no HFFR is on the market capable of meeting all requirements of NFPA 262, failing them mainly in FS requirements. Fig.7 shows the performance of standard PVC cable compound versus plenum grade in terms of smoke, indicating the strong smoke suppression thanks to the potent flame retardants and smoke suppressants commonly used in this compound grade.

All this evidence demonstrates how the notion that "PVC cables produce dense and thick smoke" is a misconception often used in some HFFR marketing brochures or videos to promote products with higher costs and lower productivity, which cannot effectively compete in price with PVC compounds. [43]

3.3. Focus on Smoke Acidity Reduction

Acid scavengers have been developed to trap HCl evolving in the gas phase, effectively reducing smoke acidity in low-smoke acidity compounds. However, they cannot reach the additional

classification for acidity, a_2 and a_1 , performing the standard EN 60754-2 [44] at temperatures over 935°C, where acid scavengers fail. Studies, such as those by Bassi et al. (2023) [25] and Chandler et al. [45], showed that the temperature and heating rate influence the efficiency of these scavengers in combustion. In fact, at the typical pre-flashover temperatures, less than 600 °C / 650 °C, these scavengers are highly effective, significantly dropping the acidity of the effluents. In contrast, they fail to scavenge HCl at the typical temperatures of a fully developed fire (more than 650°C) because they cannot compete in velocity with the HCl release. However, here, the "big toxic killer in smoke" is CO, which is released at its lethal concentrations by every polymer despite its chemical nature (20 % w/w of their weight) [46] and drives tenability before flashover [47,48]. Therefore, EN 60754-2, performed at temperatures between 935 °C and 965 °C in isothermal, is useless and should be revised, introducing heating regimes more similar to the condition of the growing stage of the fire, where the HCl evaluation could have a sense in fire science for whom thinks that HCl could impede a safe escape and where flame retardants are usually tested, (Figures 7-11, and the comments in there).

Fire Scenario number 1: 3 minutes between ignition and flashover (the point of non-return)

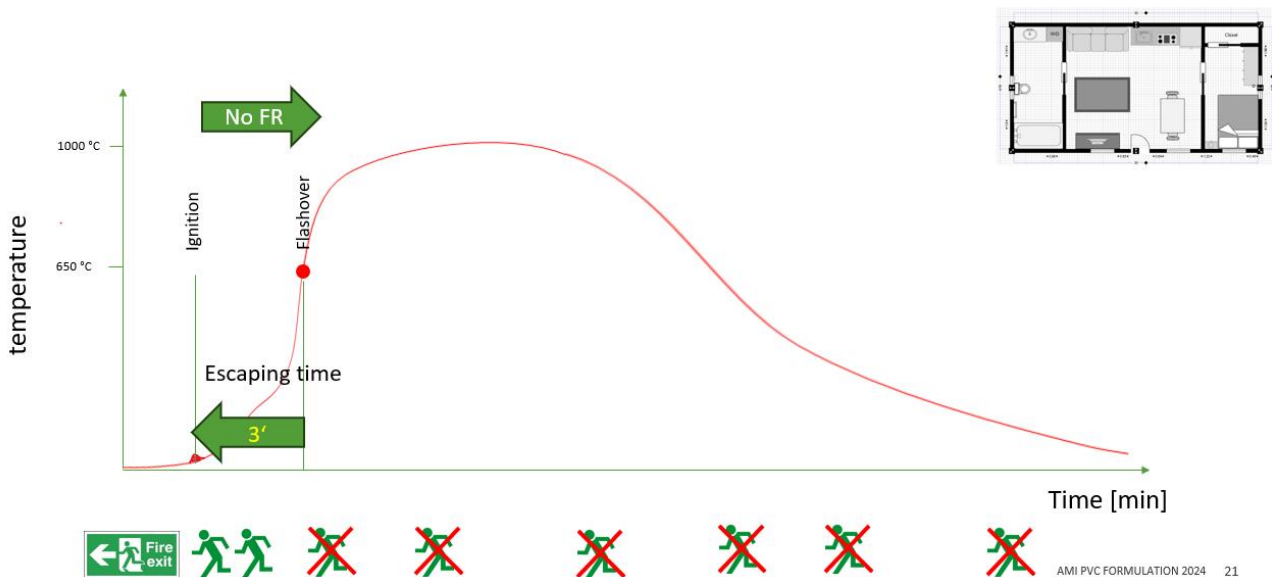


Figure 7: Typical evolution of temperature in a compartment fire in case of presence of non-flame retarded items. Escaping time of just 3 minutes, given by a quick flashover, which brings the fire to its fully developed stage with temperatures over 650 °C. This scenario can cause lots of fatalities.

Fig. 7 represents the typical evolution of a simple compartment fire where articles in there are not flame retarded, and the location goes flashover quickly. Stages, temperatures, and heat fluxed are well described in Ref. 49. Refs 49 and 50 also provide the incidental heat fluxes that must be utilized at cone calorimetry according to the typical temperatures reached in different stages of a fire scenario. This kind of scenario can cause lots of fatalities also depending on how many fire exits are available, the presence of active fire protection systems such as fire alarms, smoke detectors, and fire suppression devices, if the people involved have low levels of mobility and alertness, for example, individuals who require assistance with ambulation. Furthermore, fire scenarios are more complicated than a compartment fire because they can involve more locations where fire can be in different stages. Tenability is influenced mainly by temperatures, visibility, narcoleptic substances, and oxygen levels. Figs 8 and 9 show the effect of flame retardants on the evolution of a fire in a compartment. Flashover is delayed as much as the efficiency and concentration of flame retardants increase and this reduces the number of fatalities. However,

other variables can affect the time to escape. For instance, smoke production affects visibility (Figures 9 and 10), so using smoke suppressants is crucial.

Fire Scenario number 2: 10 minutes between ignition and flashover (the point of non-return)

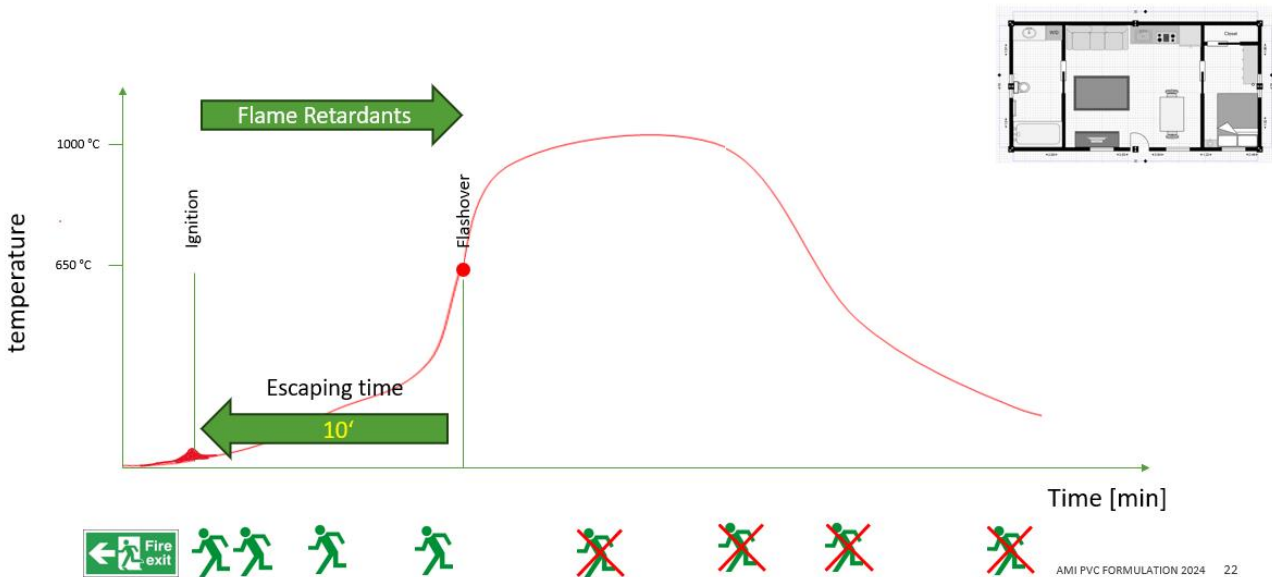


Figure 8: flame retardants in items change the temperature profile of a compartment fire. In this scenario escaping time reaches 10 minutes, increasing the probability of escaping safely from the fire scenario.

Fire Scenario number 4: 15 minutes between ignition and flashover (the point of non-return), dense smoke

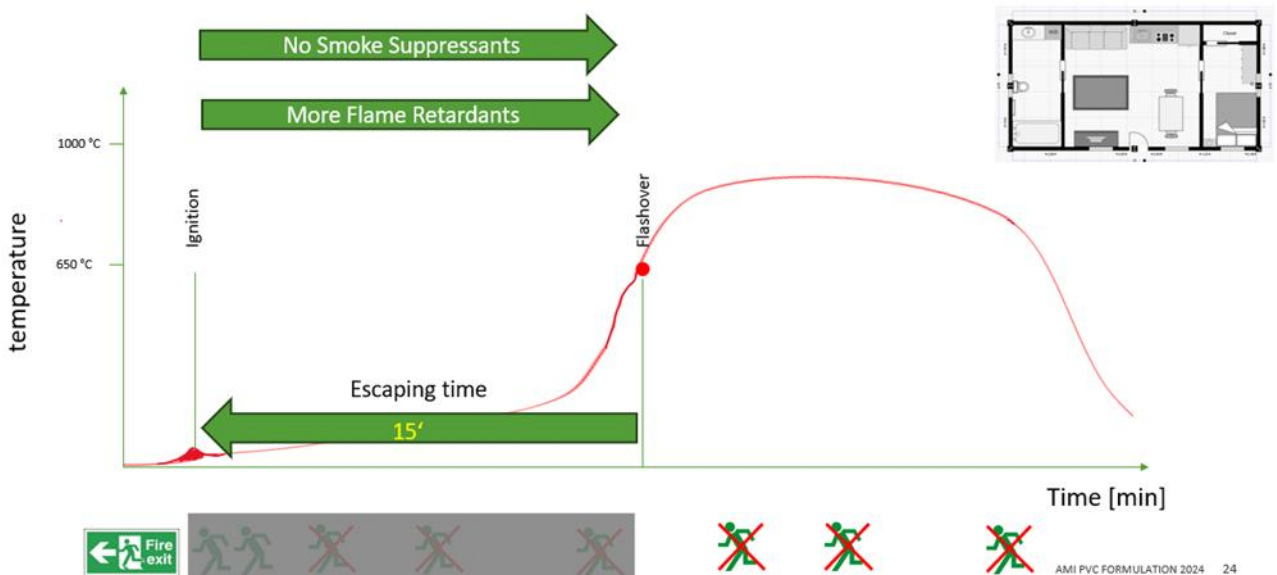


Figure 9: more (or more performant) flame retardants in items change the temperature profile of a compartment fire, further giving fewer fatalities. However, tenability limits can be determined by the presence of smoke or narcoleptic substances.

However, even with smoke suppressants, narcoleptic substances can affect tenability (Fig. 10). CO drives tenability in pre-flashover fires, and most fire scientists claim that HCl is a secondary parameter in fire safety. Specifically, "Declarations" of acid gas emissions are not associated with fire hazard." [46]

Fire Scenario number 5: 15 minutes between ignition and flashover (the point of non-return), no dense smoke

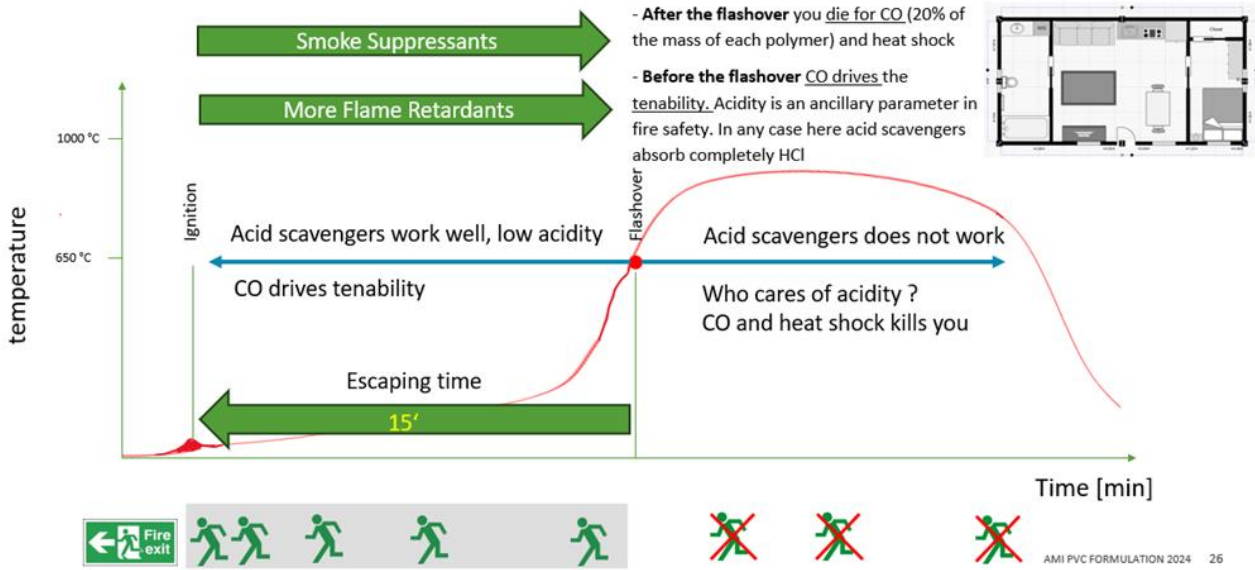


Figure 10: With smoke suppressants in items more probability of a safe escape is reached. However, despite low smoke production, CO drives tenability, while HCl at these temperatures can be easily scavenged and reduced by acid scavengers at extremely low levels.

Nonetheless, at the typical temperature of pre-flashover fires, HCl can be easily trapped by acid scavengers commonly found in low-smoke acidity compounds [25,26,34 and the references there]. In contrast, acid scavengers fail at temperatures over 935°C according to EN 60754-2, representing the typical temperature of post-flashover fires. (Fig. 11)

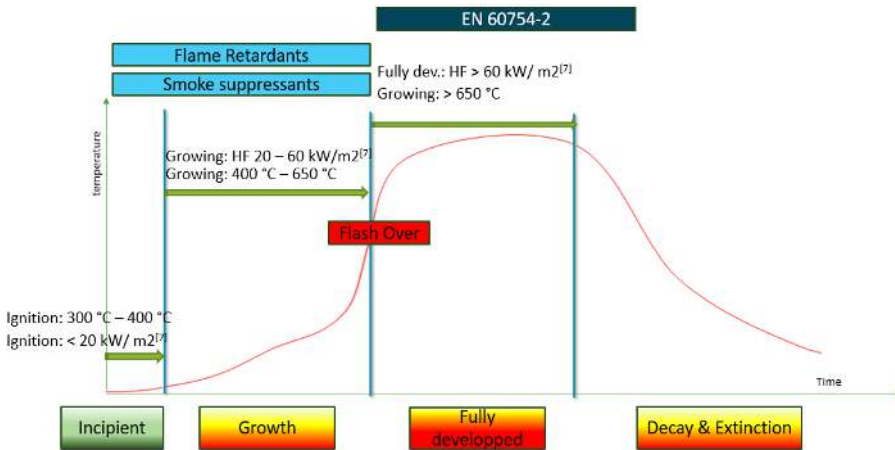


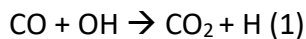
Figure 11: Typical stages, temperatures, and heat fluxes of a compartment fire. [49-50] EN 60754-2 temperature profile (935°C – 965°C, isothermal) can be reached only in the fully developed stage of a fire.

Furthermore, it must be highlighted that HCl decays and does not travel far from where it originated. [46] This aspect should be considered even in fire scenarios where some locations go to flashover, and the released gasses can reach escaping people, affecting their tenability and impeding them from escaping safely.

3.4. CO is the "big killer toxic in smoke": the contribution of cable PVC compounds

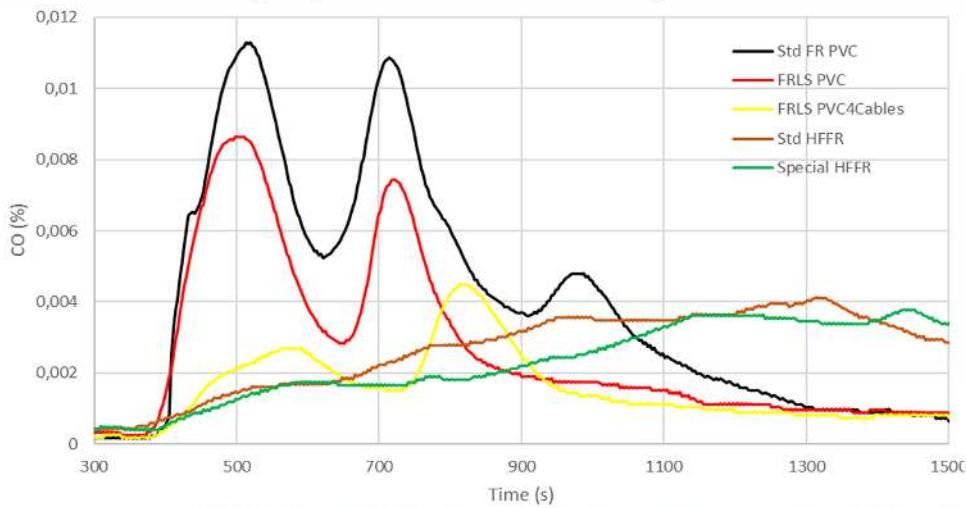
Research by Camillo Cardelli in 2022 [26] performed EN 50399 utilizing also specific sensors for detecting the concentration of CO and CO₂. It clearly showed that the CO released by PVC cables decays in time (Fig. 12a). In contrast, CO from HFFR increases (Fig. 12a). Specifically low smoke acidity cables (FRLS PVC4cables) showed an extremely low production of CO, better in kinetic and concentration than HFFR. (Figs. 12 b and 13) The genial experiment was designed by those scientists better to understand the release of the main intoxicant, CO, considering the standardized conditions of EN 50399. This standard was developed according to CPR by choosing a flame energy of 20.5 kW, which matches the typical temperatures of pre-flashover fires. This condition of measuring CO emission is completely different from the current bench scale standards, such as ISO 19700, issued for assessing the toxicity of effluents [51], which gives a complete combustion of the test specimen.

What chemistry is behind the CO contribution from PVC compounds for cable? There is, obviously, the partial combustion of organic species in the compounds, and the CO quote coming from the main flame-retardant action is in the gas phase of HCl. HCl starts a series of chain reactions that scavenge the radical H and OH in the flame, lowering its energy. Specifically, during the combustion of organic substances, the more energetic reaction is given by reaction 1, where CO is oxidized to CO₂.



Without halogens, it releases lots of energy, while the scavenging of OH by chlorine impedes reaction 1 and, at the same time, increases the content of CO in smoke. Some fire scientists claim reaction 1 to prove that PVC emits more CO than halogen-free,[52] performing the bench scale test ISO 19700 on unknown composition PVC cable compounds. Usually, in a real fire scenario, HCl decays [46], and this should make the CO decay as depicted in Fig. 12a. Another effect is related to the presence of flame retardants itself in PVC compounds and strictly linked to how much it performs in terms of reaction to fire. If PVC compound burns less, it releases less smoke and generates less CO, and also this aspect is not considered in the bench scale tests for assessing the toxicity. Guillaume et al. well highlighted this aspect in Ref. 47, where, in a real-scale fire test, most of the CO was generated much before the emission of HCl, which starts later because PVC articles, even without flame retardants, are usually much more fire-performant than furnishing commonly found in houses. Despite the good performances of standard PVC articles, low smoke acidity compounds bring more advantages. In fact, if the reaction in equation 1 occurs in the presence of potent acid scavengers, as in low-smoke acidity compounds, there is not enough HCl to quench reaction 1, and radical OH more likely consumes CO. This explains why low-smoke acidity cables release even less CO of the best HFFR tested in Ref 26. (Fig. 13)

FR(LS) PVC vs HFFR compounds: CO evolution

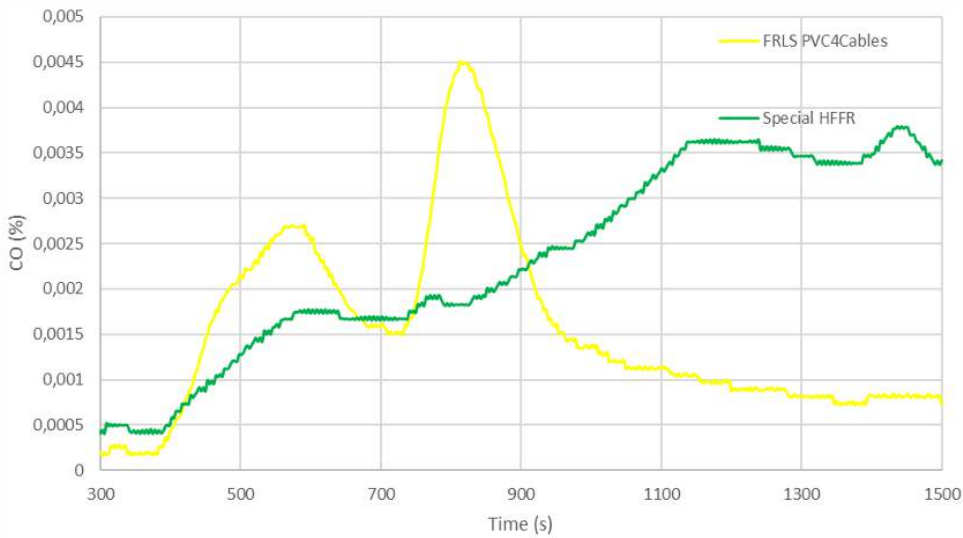


Emission of CO is faster and higher for FR PVC, and lower for FR LS PVC which have low CO emission like HFFR cables. HFFR cables release more CO in the 2nd half of the burning test.

⇒ Emission of CO is the most relevant parameter of smoke toxicity

CO emission

(a)



(b)

Figure 12: CO [%] (t) emission from different PVC and HFFR cables (a). (b) focus on low smoke acidity cable (FRLS PVC4 cable, yellow line) and the best HFFR (green line) [26]

it originated. CO travels fast and far from where the fire originated, involving the area not involved by flames used to escape the fire scenario.

One of the most pervasive misconceptions is the belief that the combustion of PVC inevitably leads to the formation of large amounts of smoke, and, sometimes on the Internet, some videos comparing smoke emission of PVC and HFFR cables are offered as scientific evidence claiming that PVC is unsuitable to be used in enclosed spaces. Often, they forget to mention that PVC is a premium choice in manufacturing Plenum cable jackets in the US market, which are outstanding in terms of smoke emission, developed for those locations where smoke can be a considerable problem for escaping, such as skyscrapers and tall buildings with plenum spaces full of energy, and telecommunication cables. With suitable additives, PVC emits as much smoke as standard HFFR cables. [26]

Furthermore, our competitors claim that the smoke produced by PVC cables is toxic and corrosive and hinders safe evacuation during a fire. At the typical temperature below flashover, Cardelli experiments in Ref. 26 have shown that the generation of CO from PVC cables combustion decays, and we know that chemically this is due to the decay of HCl, as stated in Ref. 46. According to Ref. 26, standard FRLS PVC cable compounds, widely used in confined spaces, produce the same amount of CO as standard HFFR. (Fig. 13, red line) Low smoke acidity cable compounds, FRLS PVC4cables, perform even better than the top-rated HFFR, as shown in Figure 13 (yellow vs. green curve). We believe that these evaluations in medium-scale fire tests are more significant than those we can obtain in bench-scale tests such as ISO 19700, which cannot consider fundamental aspects such as HCl decay and the fact that less article burns less toxic smoke it emitted.

Nevertheless, another scenario should be taken into consideration. Figure 14b clearly shows a typical fire scenario (number 6) where one room goes to the flashover, and the smoke and effluents like CO and HCl (if PVC items are contained) can spread everywhere in other locations not yet reached by flames and putting at risk the people evacuating from flames. In those conditions, even low smoke acidity cables could emit HCl, which in any case will decay, bringing less contribution to CO generation. However, CO should be the biggest intoxicant in the surroundings, affecting the tenability of the people involved in the fire scenario, considering that experiments performed in the past confirmed that HCl decays and travels not far from where a fire originated. [46, 51] This aspect could definitely be clarified by performing a large-scale fire test. Several small-scale test methods are employed to measure smoke and toxic fire effluent components, ISO 19700 and EN 60754 series. However, the assessment of smoke and fire hazards is generally not a scalable process, meaning that data from small-scale tests often represent only a limited approximation of real fire scenarios. Large-scale test methods offer a more accurate correlation to combustion conditions commonly found in real fire scenarios. [54]

6. Conclusion

The evolution of PVC compounds for cable manufacturing is a story of innovation, adaptation, and resilience. Driven by regulatory pressures, market demands, and a commitment to sustainability, the PVC industry has continually improved its products, ensuring that PVC remains a top choice for cable applications. The substitution of hazardous materials with safer alternatives, the enhancement of fire behavior and smoke suppression, and the ongoing efforts to reduce the environmental impact of PVC production are all evidence of the industry's dedication to excellence.

Despite the challenges posed by misinformation, including misconceptions about smoke density and toxicity and the complexities of recycling, PVC has proven itself to be a superior material, offering unmatched benefits in terms of safety, performance, and environmental sustainability. As the industry continues to innovate and adapt to new challenges, PVC is poised to remain at the forefront of cable manufacturing for years to come.

The PVC industry has responded to these misconceptions by investing in research and public education. Studies funded by industry groups, such as PVC4Cables, have demonstrated that modern PVC cables with low smoke acidity can perform comparably to, and in some cases better than, halogen-free alternatives. These findings challenge the notion that PVC is inherently less safe and highlight the importance of using scientifically accurate data to inform regulatory and consumer decisions.

By continuing to communicate through authoritative information the benefits of PVC, including its superior fire performance and reduced environmental impacts, the industry and academia can help shift perceptions and reinforce PVC's position as a safe, reliable, and sustainable material for cable applications.

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