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Industrial Chemistry Department "Toso Montanari"

Master's Degree Course

## **Industrial Chemistry**

Class LM-71 – Science and Technologies of Industrial Chemistry

Characterization of PVC compounds and evaluation of their fire behavior focusing on the comparison between EN 60754-1 and EN 60754-2 in the assessment of the smoke acidity

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## **ABSTRACT**

The Regulation (EU) No 305/2011 CPR (Construction Product Regulation, CPR) [1] lays down harmonized conditions for marketing construction products in the European Union (EU). One of the seven basic requirements of the CPR is safety in case of fire; therefore, construction products must meet certain specific requirements in terms of reaction- to-fire. Tests, requirements, marking, controls, etc. on construction products must be the same in all EU countries, starting with the harmonized classification in terms of reaction- to-fire. Construction products also include cables in permanently installed in buildings. The product standard EN 50575 [2] defines how cables are managed from their production to placing them on the market according to the CPR (test, classification, controls, marking etc.). The technical standard EN 13501-6 [3], on the other hand, provides the reaction- to-fire classifications for cables, the technical standards to be performed and the requirements that must be achieved to obtain a specific class or an additional class of reaction- to-fire.

Two technical standards have been compared in the research: EN 60754-1 [4] and EN 60754-2 [5].

EN 60754-2 is the standard to be used for the determination of the additional classification for acidity in cables. EN 60754-1 on the other hand is a standard used specifically for PVC cables outside the CPR regulation. Both technical standards use the same type of tube furnace but with different heating regimes and temperatures. Considering the mechanism by which acid scavengers in PVC cable compounds trap hydrochloric acid (HCl) and evaluating the experimental data, the expectation is to obtain clear evidence on how the different heating conditions and temperatures adopted by the two standards affect the amount of released HCl during combustion. The technical standard IEC 60754-3, based on ion chromatography, has been used to check which substances have an impact on the smoke acidity. Finally, the influence of acid scavengers on flame retardancy and smoke emission has been evaluated.

## 1 PVC

### 1.1 INTRODUCTION

PVC is the third most important plastic material produced in Europe, following polyethylene (PE) and polypropylene (PP) [6]. Additives are added to the PVC resin for processing it into semi-finished products known as compounds and/or finished articles. Articles can be rigid (PVC-U) or flexible (PVC-P). Everyday articles and special articles made up of PVC can be found in homes, cars, offices, hospitals, etc. The largest consumption is in building and construction, involving for example electrical cables, window profiles, rolling shutters, gutters, pipes and rigid fittings, flooring, wall coverings, roofing, hoses etc.

Nevertheless, because of its versatility, PVC is also used extensively in technical and food packaging, pharma, transportation, electrical and electronic equipment, telecommunication and IT, clothes, fashion, etc. Figure 1 provides the PVC resin consumption by application in the EU in 2019.

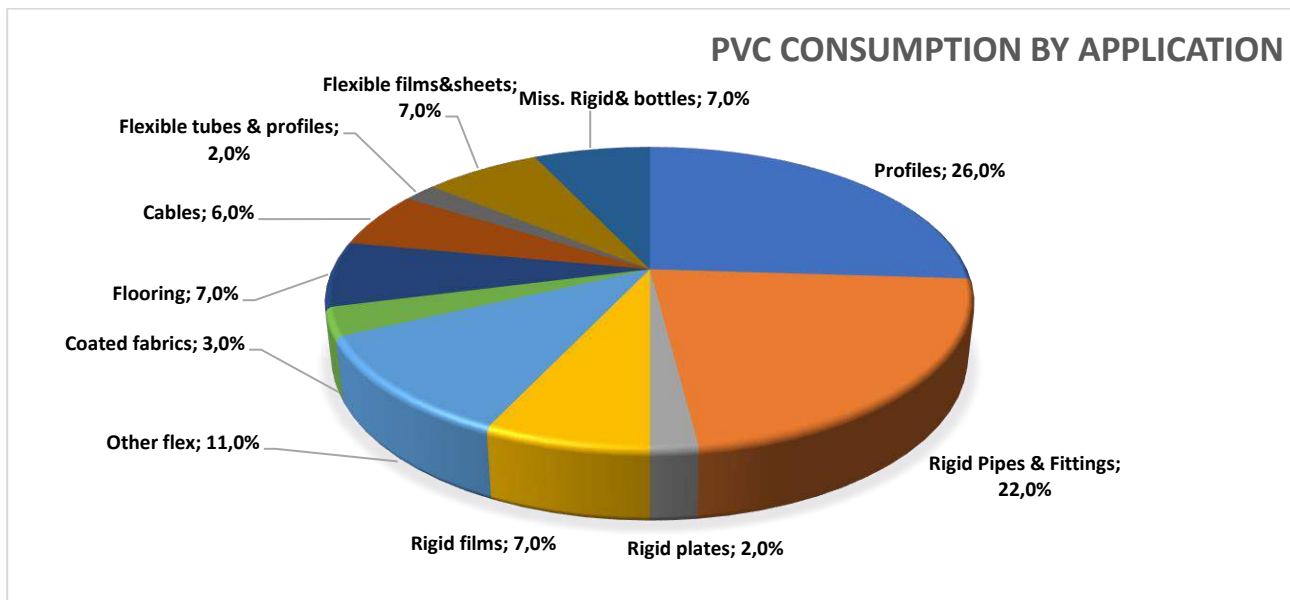


Figure 1: PVC resin consumption per article in the EU in 2019 (EU 27 + CH + NO: 2019), Plastic Europe, unpublished report

One of the uses of PVC compounds is in electrical cables as insulation, jacket, and bedding.

When they burn, PVC cable compounds release HCl and therefore the smoke becomes acidic. The concentration of released HCl in the gas phase depends on the additives present in PVC compounds,

such as fillers, plasticizers, flame retardants, acid scavengers, etc. Measured by EN 60754-1 the HCl concentration in PVC cable compounds can vary between 5 % and 26%. It is a matter of fact that the gaseous HCl released during combustion of PVC compounds decays quickly in the surrounding environment, further reducing the amount of HCl present in the gas phase, and it is a common knowledge that the "big toxic killer in smoke" is actually the carbon monoxide (CO) [7,8,9]. However, the acidity developed during the combustion of cables in a fire can cause irritation of the respiratory tract and, according to some researchers, it can generate panic and incapacitate people in the fire scenario [10]. But most of the fire scientists do not consider the assessment of smoke acidity to be a life-saving "measure" in a fire. There are other "measures" that must be performed in articles to assess their fire performances and to understand if the fire can turn into a large one no longer controllable (after the point of no return known as "flashover"). Among these, the measure of the heat released from the article (Total Heat Release - THR), the rate at which it is released (Heat Release Rate - HRR), particularly the maximum peak of the heat release curve (pHRR) and the density of the smoke are of extreme importance [7,11,12]. The "reduction" of heat release and smoke production in the articles is achieved using special additives called flame retardants and smoke suppressants [13] and it allows the people involved in the fire to escape unharmed before the development of the "flashover" without being trapped by dense smoke. For these reasons, in many countries the smoke acidity is not a measure taken in consideration in fire risk assessments.

In the EU with the CPD in 2006 [14] and then with the entry into force of the CPR in 2017, the additional classification for acidity has been introduced in cables (and only in cables), and a high smoke acidity precludes the usage of PVC cables in specific locations such as railways, tunnels and car parks, subways, health and entertainment facilities, data centers etc. Therefore, in the past [15] but also recently [16], efforts have been made to create compounds with a low smoke acidity and to produce PVC cables capable of reaching low acidity classes. It is hoped that these low smoke acidity PVC cables will be able to compete with halogen-free flame retardant cables (HFFR), a class of cables made with compounds not containing halogenated polymers or halogenated flame retardants. In order to understand why PVC cables release HCl in a fire, it is necessary to provide information on the synthesis of PVC, its degradation and its stabilization.

## **1.2 PVC SYNTHESIS**

PVC is a halogenated polymer having the structure in figure 2:

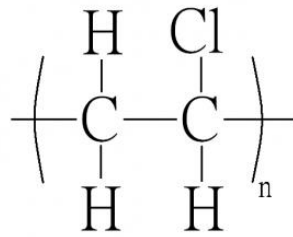


Figure 2: PVC structure.

and it can be produced industrially by three different steps.

The first step involves the use of a chlor-alkali electrochemical cell for the production of NaOH and Cl<sub>2</sub>. Approximately 30% of all the worldwide Cl<sub>2</sub> produced by this process is used for the synthesis of PVC [17].

The second step is the synthesis of the actual polymerization monomer from ethylene dichloride (EDC): vinyl chloride (VCM).

The third step is the radical polymerization of VCM. The product resulting from polyaddition consists of approximately 400-1000 monomer units, mostly arranged in an atactic structure and therefore responsible for the amorphous structure of PVC.

The synthesis of PVC involves a polyaddition reaction between the monomers, which can be carried out using different polymerization techniques [17]:

- Bulk polymerization
- Emulsion polymerization
- Suspension polymerization

Bulk polymerization does not use solvents, suspending agents or emulsifiers but only involves the use of the monomer which, as the reaction proceeds, forms the insoluble polymer in the monomer that has not reacted yet.

Emulsion polymerization involves the use of an emulsifying agent that creates micelles in which the polymerization of the monomer takes place.

Suspension polymerization consists of keeping the monomer dispersed in water through stirring and the presence of surfactants; with the addition of the initiator, each drop of monomer

polymerizes separately and is transformed into a polymer bead, which is recovered by filtration and drying. The consumption rates of the different types are as follows:

- PVC by bulk polymerization accounts for about 8% of the total consumed. Given the type of synthesis, it has very good dielectric properties and a good clarity.
- Emulsion PVC accounts for approximately 12% of the total amount consumed. It has a very fine particle size ( $d=0.1\ \mu\text{m}$ ) and is used for special processes such as coating to produce items such as wallpaper and vinyl flooring, among others.
- Suspension PVC is used in most PVC articles (80% of the total consumed). Cables, window profiles, technical profiles, pipes, etc. are produced using this type of PVC.

### 1.3 PVC THERMAL DEGRADATION

When PVC is processed at high temperatures, it degrades because of the presence of structural irregularities in the polymer chain: the main ones are allylic chlorides and tertiary chlorides [18,19]. From these defects, a cage reaction called zip elimination is initiated starting from 70°C / 80°C and it brings the formation of polyene sequences, the release of HCl, the progressive color darkening and an increase in the viscosity and temperature of the melt during processing. Two types of secondary reactions can also occur from the polyene sequences:

- Crosslinking of the polymer matrix (via intermolecular Dies-Alder cyclization and Friedel-Craft alkylation). These reactions lead to a further deterioration of the color of the compound and an increase in the viscosity of the polymer melt and consequently a high temperature rise.
- Benzene emission through intramolecular reactions between cis-trans sequences (emission of approximately 1 mole of benzene per 100 moles of HCl).

Three mechanisms have been proposed so far to describe the PVC thermal degradation

- radical
- six-center concerted
- ionic

The first PVC degradation hypotheses claimed radical mechanisms as responsible for degradation and they were proposed in the 1950s by Arlman [20], Stromberg [21] and Winkler [22].



Radical mechanisms have been superseded due to different considerations:

- it is not possible to demonstrate the presence of radicals during thermal degradation of PVC at temperatures below 200°C [23];
- zip elimination is a selective mechanism not taking in consideration the non-selectivity of radical species [23, 24];
- they do not demonstrate the catalytic activity that HCl has on PVC degradation, indeed Arlman, trying to defend his model, concluded that it simply did not exist at all [25].

The six-center concerted mechanism was first proposed by Amer and Shapiro in 1980 and subsequently modified by Bacaloglu and Fisher [23].

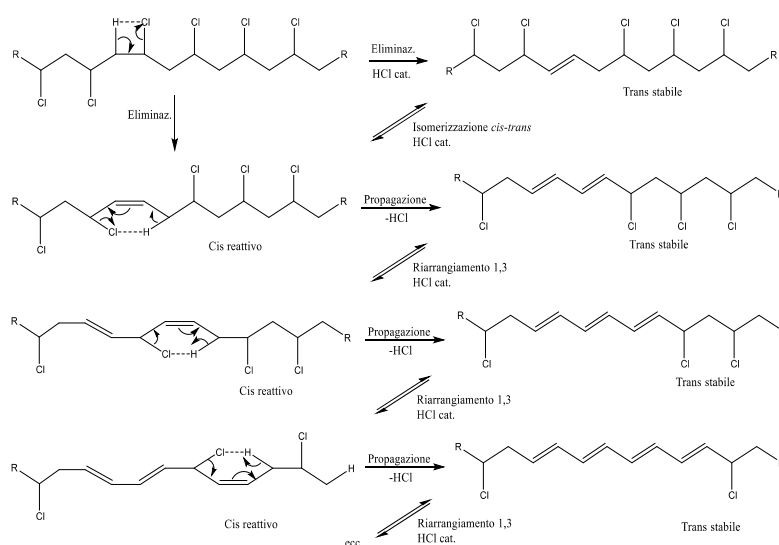


Figure 3: six-center concerted mechanism

As can be seen from Figure 3, the mechanism is quite complex and it is based on the initial randomly formation of a double bond in the polymer chain followed by a HCl elimination. HCl itself or Lewis acid can catalyze the reaction through a six-center intermediate. Once the diene is obtained, HCl reacts with the chain to give a 1,3 rearrangement, a six-center transition state that provides a new elimination, lengthening the chain of conjugated polyenes. This chain reaction can continue until HCl disappears: its elimination blocks the 1,3 rearrangements, and the chain remains in the stable trans configuration.

The experimental evidence supporting this reaction mechanism is twofold: primarily, the catalytic activity of HCl is demonstrated, and secondly it provides also an explanation for the selectivity of the zip elimination.

The mechanism proposed by Bacaloglu and Fischer was dismantled through various demonstrations by Starnes in the 1990s and early 2000s [24, 26, 27, 28]. Starnes in turn proposed the ionic mechanism. To date, the ionic mechanism is actually the most accepted by the scientific community [18,19,29].

The ionic mechanism involves the formation of ionic pairs distributed randomly throughout the polymer chain, but particularly involving allylic chlorides, due to the weakness of their bond. These ionic pairs result in the creation of a carbocation coupled to a chloride ion. This is followed by the elimination promoted by the Cl attack to methylene hydrogens with the formation of a double bond and the elimination of HCl. This mechanism can form up to 14-20 polyene sequences before stopping [27].

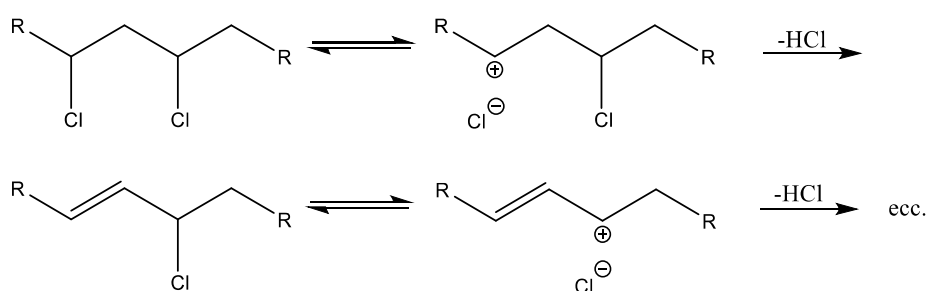


Figure 4: ionic mechanism.

HCl reactivates the 'dead' polyene sequences, creating cationic polyenyl radicals [27], which are able to generate other radicals elsewhere in the chain or in neighboring chains by extraction of the methylene hydrogens. By elimination, new allylic chlorides are created from which degradation continues by the ionic mechanism. Therefore, the reactivation of dead polyene sequences extends the degradation catastrophically throughout the polymer matrix [27].

As HCl does, Lewis acids also catalyze the degradation of PVC. The formation of polyene sequences and the consequent cross-linking reactions change the color of the polymer to yellow, red and

then brown and exponentially increase its viscosity and temperature during the process. For this reason, a category of additives called thermal stabilizers is of primary importance in PVC.

#### **1.4 PVC THERMAL STABILISERS**

In order to be processed at process temperatures and transformed into articles, PVC needs to be mixed to various additives such as thermal stabilizers, lubricants, plasticizers, fillers, process aids, etc.

Plasticizers are substances added to make PVC flexible by lowering the glass transition temperature ( $t_g$ ) below the service temperature of the article. The most important are phthalates, trimellitates, citrates, adipates, terephthalates, benzoates, and epoxy esters.

Lubricants are added to help the processing of the PVC compound. The most common are polyethylene waxes, Fischer-Tropsch waxes, some carboxylic acids such as stearic and oleic acids, some carboxylic acid esters, etc...

The typical filler used in PVC compound is  $\text{CaCO}_3$ , but also flame retardants fillers such as  $\text{Al}(\text{OH})_3$ , and  $\text{Mg}(\text{OH})_2$  can be used. Flame retardants such as  $\text{Sb}_2\text{O}_3$ , medium-chain chlorinated paraffins (MCCP), brominated compounds, zinc borate, etc. can also be added.

UV adsorbers (benzophenones and benzotriazoles) and pigments such as titanium dioxide and carbon black, as well as pigmenting the article, are added to improve the weatherability of outdoor articles.

Thermal stabilizers have the aim of slowing down the thermal degradation of PVC and they consist of primary and secondary stabilizers. In some cases, the action of "primary" and "secondary" stabilizers can be provided by a single molecule.

Primary stabilizers consist of a group of substances that can replace allylic chlorides, establish a stronger bond with the carbon atom and "inhibit" the zip-elimination in its initial stages [18,19].

Secondary stabilizers are a group of substances that absorb HCl, deactivate Lewis acids, repair polyene sequences and trap the radicals responsible for creating new defects.

Based on the chemistry of the primary stabilizer, stabilizers can be divided into:

- Tin stabilizers
- Lead stabilizers
- Cadmium stabilizers

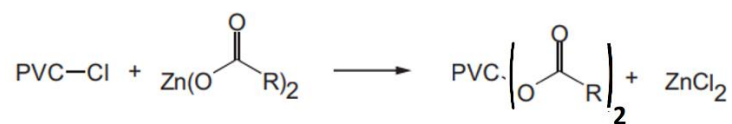
- Barium-zinc stabilizers
- Calcium-zinc stabilizers
- Organic stabilizers

Tin stabilizers are organotin compounds and recently some of them are under investigation by ECHA (European Chemicals Agency) for their reproductive toxicity; in the coming years one of the possible scenarios could be their complete elimination from the EU market. Lead stabilizers are made up of lead salts such as tribasic lead sulphate, dibasic lead phthalate, dibasic lead phosphite, etc. [17]. In 2003, the Directive 2002/95/EC (RoHS I) [30] banned the use of lead stabilizers in formulations for Electrical and Electronic Equipment (EEE), leading to the elimination of these stabilizers from all kinds of PVC cables. In December 2015, ESPA (the European PVC Stabilizers Producers Association) completed the substitution of lead-based stabilizers in the European market, as the final step of the “VINYL 2010, the voluntary commitment of the PVC industry” agreed by the manufacturers in 2000 [31]. Thanks to Vinyl 2010, cadmium-based stabilizers were also phased out in 2001 (in EU15) and 2007 (in EU27) [31].

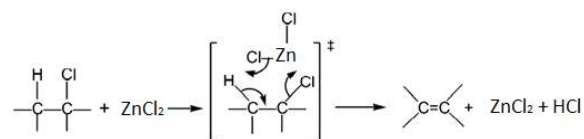
Calcium Zinc, Barium Zinc and Organic Stabilizers are currently the only ones with a future perspective in the EU. Especially COS (Calcium Zinc and Calcium Organic solid stabilizers) are the most innovative solutions for the thermal stabilization of PVC.

As an example, the stabilization mechanism in PVC of the calcium stearate - zinc stearate pair is shown below. Zinc stearate is the primary stabilizer which replaces labile chloride groups (Figure 5, reaction **a**). In doing so, by replacing two allylic chlorides, it produces two molecules of  $\text{ZnCl}_2$ . Zinc stearate also acts as an acid scavenger giving  $\text{ZnCl}_2$  (Figure 5, reaction **d**). The  $\text{ZnCl}_2$ , formed in reactions **a** and **d**, catalyzes the degradation of PVC according to reaction **b**. Calcium stearate (reaction **e**) is able to deactivate both  $\text{ZnCl}_2$  and  $\text{HCl}$  by neutralizing their catalytic actions on the degradation of PVC and producing  $\text{CaCl}_2$  which is a weak Lewis acid. Through the reaction **e** zinc stearate is “regenerated” and therefore it can continue its action as primary stabilizer.

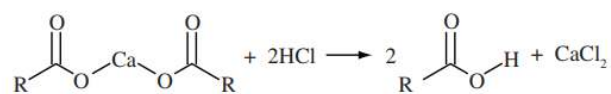
**a**



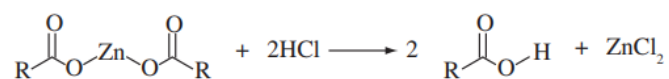
**b**



**c**



**d**



**e**

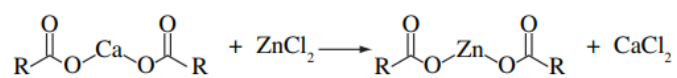
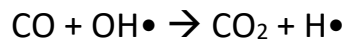
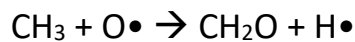
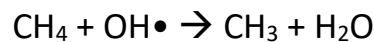
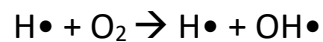


Figure 5: stabilization mechanism of PVC of the calcium stearate-zinc stearate pair.

## 2 POLYMERS IN A FIRE

### 2.1 FIRE BEHAVIOR OF POLYMERS

Polymers, when exposed to a source of heat of enough magnitude, tend to degrade and decompose releasing volatile substances. These substances mix with the surrounding air and, if the temperature is high enough and if they reach a critical concentration, they ignite the flame. The flame is fueled by radicals such as  $\text{H}\bullet$  and  $\text{OH}\bullet$  [17] which are the main responsible for the exothermicity of the chain reactions involved such as the oxidation of CO to  $\text{CO}_2$ . Figure 6 shows the radical reactions present in a hydrocarbon flame which is a good approximation of what happens when polymers burn.



*Figure 6: radical reactions.*

The ignition can occur spontaneously (auto-ignition) or due to the presence of an external source such as a spark or a flame (flash-ignition). If the temperature reached during combustion is equal to or higher than the polymer degradation temperature, a self-propagating or sustained combustion is achieved.

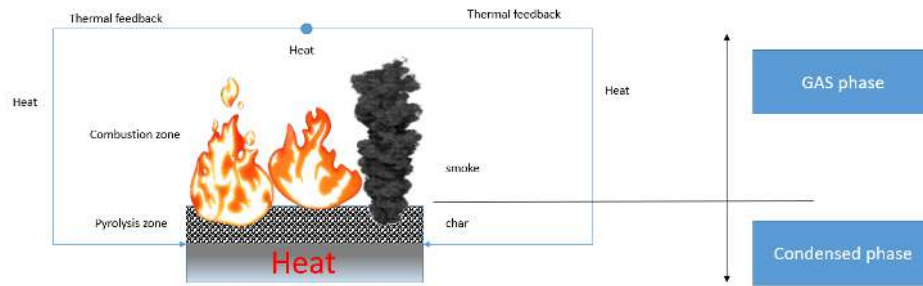


Figure 7: self-powered combustion cycle.

A fire can be ignited by either plastics or other combustible materials such as wood and paper present in a location. Plastics are present in fixed articles such as cables, panels, flooring, linear insulation for pipes, wall coverings, etc., or in non-fixed articles such as furniture, draperies, carpets, mattresses, appliances, etc. All these articles containing plastics, if not properly flame retarded, contribute to the spread of fire.

Four stages can be observed in a fire development in a compartment:

- *Incipient*: in this stage the combustion is not stable yet.
- *Growth*: after ignition, the fire begins to spread within the compartment and the temperature increases. In this stage the fire is still controllable and extinguishable. People can escape safe and sound from fire scenario.
- *Fully developed*: at “flashover”, when temperature reaches 500 °C – 600 °C, all articles in the compartment, more or less simultaneously, start burning due to the sudden combustion of gases released by the pyrolysis of materials. In this phase the temperature rises quickly, the fire spreads throughout the compartment in a noticeably short time, and the fire enters in the fully developed stage. Now the fire is no longer controllable and extinguishable.
- *Decay*: it is the final part of a fire. Here the thermal emission decreases due to exhaustion of the fuel and the temperature begins to drop. When the room temperature drops below 300°C the fire can be considered extinguished.

T(°C)

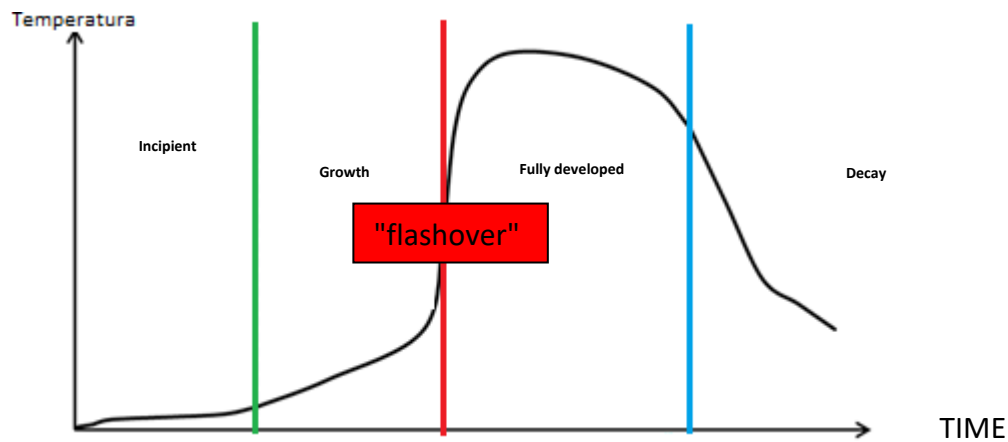


Figure 8: four stages of the fire development in a compartment.

As pointed out, after the "flashover" we no longer have the possibility to extinguish the fire, but only to prevent its spread to surrounding areas. The greatest number of victims occurs when fires become too large and reach this point of no return, hence the need to use flame retarded materials, that will delay the "flashover" giving people a chance to get out unharmed, becomes of primary importance [17].

## 2.2 TEST AND REQUIREMENTS

In a fire risk assessment, the selection of the right materials in terms of fire performance is a key factor. The fire behavior of materials is outlined by the following parameters:

- Ignitability, ease of ignition
- Ease of extinction
- Flammability
- Flame spread
- Heat release
- Tendency to produce smoke and give obscuration
- Smoke Toxicity and acidity.

### Ignitability, ease of ignition

If a material requires high energy (and therefore high temperature) to generate the ignition of a flame (ease of ignition) it will contribute less to the fire. One of the many small-scale tests that can be used to evaluate ease of ignition is cone calorimetry (ASTM E 1354, ISO 9660) in evaluating TTI



(Time To Ignition), which is the time a material exposed to an energy source takes to have a sustained combustion. Among plastics, PVC and many PVC compounds have the highest TTI values [17].

### Ease of extinction

If a material ignites but has a high tendency to extinguish the flame, it will contribute less to the spread of the fire. One of the many small-scale tests that can be used to evaluate the ease of extinction is the oxygen index (ASTM D 2863).

The oxygen index (LOI) is defined as the minimum oxygen concentration, expressed its volumetric percentage in a nitrogen-oxygen mixture, that supports flaming combustion of a material. Table 1 shows LOI values of the most common plastics, highlighting that PVC has one of the highest values of oxygen index among polymers.

Table 1: LOI value for the most common plastics.

POLYMERS	LOI [%O <sub>2</sub> ]
FEP	96
PTFE	95
C-PVC	70
PVC	45
PC	26
NYLON 6.6	25
WOOL	25
EVA	19
PP	18
PE	17

Table 2: LOI value for PVC formulations.

PVC 100, STAB 3, DIDP X (phr)	LOI [%O <sub>2</sub> ]
0	45
30	28
50	24
100	20

Simplifying the composition of air as a 79/21 nitrogen-oxygen mixture, all plastics having a LOI lower than 21 are able to propagate flame to air.

PVC has an inherent flame retardancy thanks to the presence of Cl in the polymer able to delay the development of flames: for this reason, the PVC LOI value is very high and it is about 45 %O<sub>2</sub>.

Using general purpose plasticizers (GPP) such as phthalic esters, the LOI values are considerably lower as can be seen in Table 2. Therefore, it is crucial to use flame retardants and smoke suppressants in the flexible PVC compound.

### Flammability

Flammability is the ability of a material to burn with a flame [32]. Once a flame is ignited, the greater the flammability of a material, the greater its contribution to the fire. On the small scale, one of the most widely performed test to measure "flammability" is UL 94 series. The test is carried out on a standardized specimen of a certain thickness by igniting the flame with a bunsen burner using procedures and requirements described in [30]. PVC compounds easily achieve the more stringent UL94 ratings on thinner thicknesses [17].

### Flame Spread

If a material tends to spread the "flame front" away from the source of the fire, it contributes to the spread of the fire to surrounding areas [17]. The dynamics by which flame propagation can occur can be physical (e.g., the shape and geometry of a particular article) or chemical (e.g., its tendency to extinguish or conversely to promote the formation of burning droplets).

There are a lot of tests to evaluate the flame spread depending on the articles needed to be evaluated. For example, in EN 50399 [33] a vertically-mounted bunched cables are burned to assess their tendency to spread the "flame front", due to their length and the fact that, passing from one location to another, cables can spread the fire on a large scale. Properly flame retarded PVC compounds have a low tendency to spread flames.

### Heat Release

Heat release is the thermal energy developed by combustion [32]. When a material burns, the heat released and the rate at which it is released contributes to the increase the temperature in the surrounding environment and ignite the flame to nearby materials. The measurement of a material's heat release rate (HRR), the peak of the HRR curve (pHRR), the time at which the peak is reached, and the total heat release (THR) are therefore key parameters to predict how large a fire can become [17]. All these quantities can be measured using the cone calorimeter (ASTM E 1354, ISO 5660) which is one of the most complete tools for assessing fire performances of materials. The sample receives a specific heat flux and it ignites with a spark igniter. The combustion products are collected by an exhaust hood and conveyed into a pipeline where they are analyzed. From the rate of oxygen consumption as result of combustion, the rate of heat release can be determined [34]. In

addition to heat, other measures are time to ignition (TTI), time to end (TTE), total smoke production (TSP), smoke production rate (SPR), the peak of SPR curve (pSPR), and with special sensors even the amount of CO<sub>2</sub>, CO and HCl emitted.

#### *Tendency to produce smoke and give obscuration*

The dense smoke released by a material in a fire is dangerous, because it may obscure escape routes, thus delaying the escape of people from the fire scenario and impeding the firefighters to rescue persons trapped in the fire. Dense smoke, therefore, increases the time required for escaping safe and sound from the fire scenario. There are many standards for measuring smoke density (ASTM D 2843, ASTM E 1354 etc.). The most widely used instrument is the NBS chamber (ASTM E 662, ISO 5659) [35]. This instrument measures the specific optical density of smoke generated from a generally flat plastic sample (up to 25 mm thick) that is vertically exposed to a radiant heat source in an enclosed chamber with or without the use of a pilot flame. A sensor measures the density of smoke collected during combustion of the specimen. PVC compounds, without smoke suppressants, have a great tendency to produce dense, dark smoke, especially if antimony trioxide is used as a flame retardant.

#### *Smoke toxicity and acidity*

Most fire fatalities are caused by fires that have passed the flashover point, i.e., small fires that have become too large to be extinguished [17]. Surprisingly, most victims die not for burns but because of smoke inhalation of particulate matter obstructing the respiratory tract and moreover toxic substances inhaled during combustion. Smoke toxicity can be measured using fractional effective dose (FED) [17], which is proportional to the concentration and toxic potential of individual substances released during combustion.

It is known, however, that after flashover each polymer emits about 20% of its weight as CO [7,8,36,37,38] and it is statistically proven that 2/3 of fire deaths are mainly due to CO inhalation and thus CO is actually the main cause to deaths or intoxication as a result of smoke aspiration during a fire [8].

The main source of smoke acidity are halogenated polymers. When PVC burns, it releases HCl through the zip-elimination and this makes the smoke acidic. According to some researchers, the

acidity of the fumes can cause panic and inability to leave the fire scenario [11] and HCl coming from small fires can attack electronic devices nearby.

Nevertheless, most of fire scientists think that smoke acidity is a secondary parameter to heat release and smoke density [17], because of the difficulty in predicting the real concentration of HCl in gas phase due to its tendency to decay over time. Generally, the amount of gaseous HCl in "real" fires scenario is much less than the theoretical amount that can be developed. This is because HCl is absorbed by the same fillers contained in the compound, washed away by water released in the fire, and retained by the surfaces of many materials present in the fire scenario such as cement, gypsum, and carbon residues. The dynamics of release of HCl during the combustion of PVC articles is also quite peculiar. Due to their difficulty in igniting, low heat release and low tendency to spread the flame, PVC articles often burn after other more flammable articles have already begun to develop smoke, heat, and gases such as CO and CO<sub>2</sub> [43]. This particular dynamic shows how CO often reaches lethal concentrations when HCl levels are still completely negligible. Thus, the amount of released HCl does not compromise the tenability, which is greatly affected by CO, but also by heat, temperature, and smoke [43].

### **2.3 FIRE BEHAVIOUR OF PVC COMPOUND**

As seen in the previous chapters PVC compounds has very good fire performance in terms of its difficulty to ignite, its tendency to extinguish, the low heat release, the low flammability. Even PVC-P with the right additives can further improve fire performance and significantly reduce smoke, achieving extremely high performance in some cases better than PVC-U [17]. But the weak point remains smoke acidity. Unfortunately, the secret of its high fire performance lies in the fact that PVC releases HCl, which is the "responsible" in poisoning the flame and helping to create a carbonaceous layer during combustion in the presence of particular substances called "charring agents".

In fact, during its combustion PVC releases HCl and HCl traps H• e OH• radicals, the main responsible of the flame development [39]. The following is the mechanism of action of HCl, resulting from the combustion of PVC:

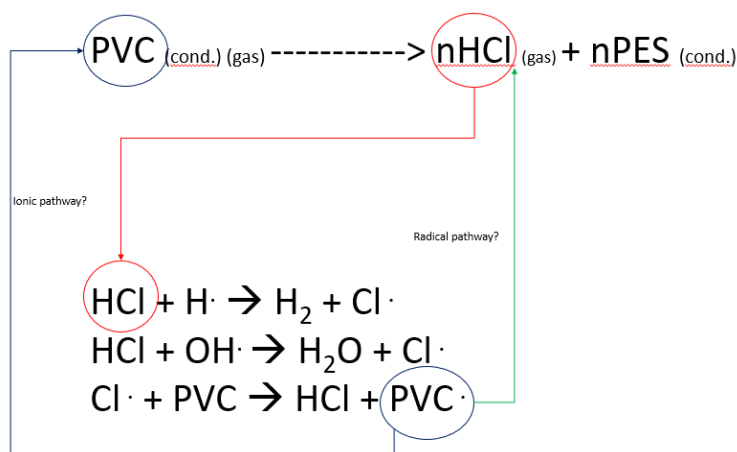


Figure 9: HCl action mechanism. PES = Polyene Sequences

Many smoke suppressants used in PVC are incipient Lewis acids reacting with HCl to create potent Lewis acids [40]. Lewis acids formed during combustion not only catalyze PVC degradation by promoting zip-elimination, but also promote intermolecular cross-linking reactions (Diels-Alder and Friedel-Craft) of polyene sequences.

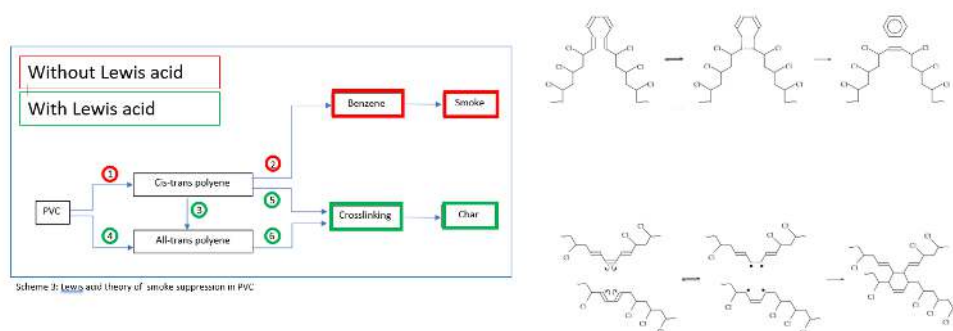


Figure 10: PVC degradation scheme.

Cross-linked matrices promote the formation of a char that inhibits the formation of flames, smoke and burning droplets.

Figure 10 shows the degradation pattern of PVC in the presence or absence of Lewis acids within the formulation. As reported above, Lewis acids catalyze the degradation of PVC leading to the formation of trans-polyene sequences (green pattern in Figure 10) promoting intermolecular cross-linking reactions (Diels-Alder and Friedel-Craft) and bringing to a char formation [40]. In contrary, in the absence of Lewis acids (red pattern in Figure 10) intramolecular reactions are promoted and this stimulates benzene and smoke production.

## 2.4 FLAME RETARDANTS AND SMOKE SUPPRESSANTS FOR PVC

As mentioned, PVC is an inherently flame-retardant polymer but, the addition of certain additives such as general-purpose plasticizers increase the tendency to "burn" and promote smoke production.

In order to retard the flame in a plastic material, there are two types of approaches: the *physical approach* and the *chemical approach*. Some additives act more in the condensed phase or the gas phase, and consequently you can formulate mixtures operating mainly as smoke suppressants or as flame retardants.

Figure 11 shows the possible modes of action of flame retardants and smoke suppressants in the gas or condensed phase.

Table 3 shows the mechanism of action of some flame retardants and smoke suppressants in the market.

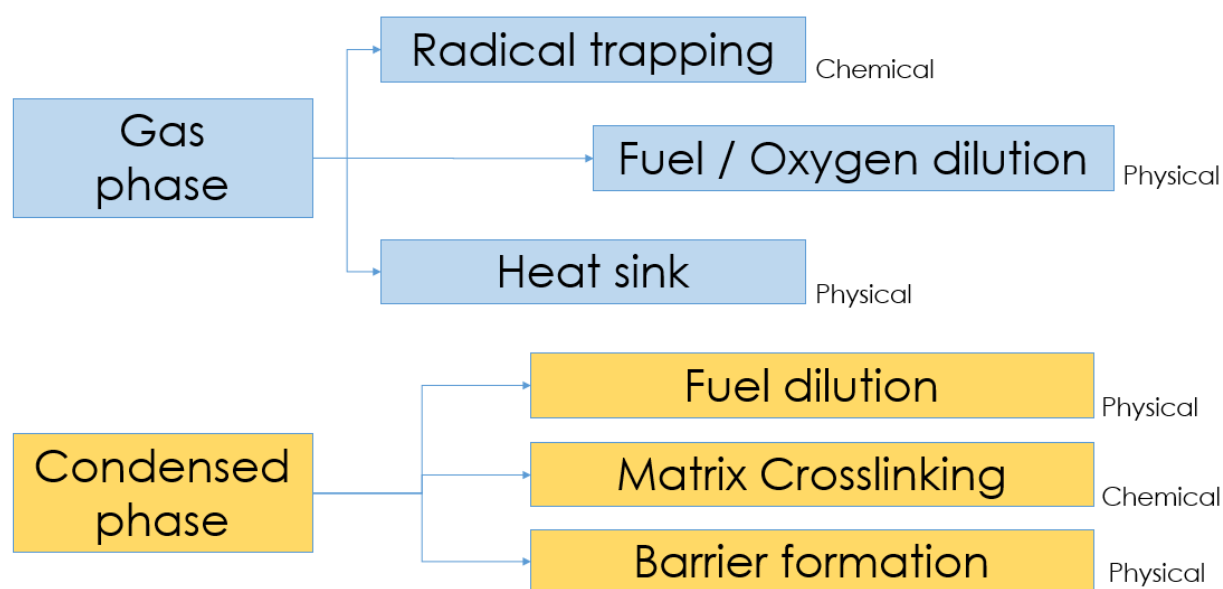


Figure 1: possibility of action of flame retardants and smoke suppressants.

Table 3: mechanism of actions of the main smoke suppressants and flame retardants.

ADDITIVE	Action	OPERATION	PROBLEMS
<b>Antimony Trioxide</b> <b>(ATO) - <math>\text{Sb}_2\text{O}_3</math></b>	<i>Gas phase</i> <ul style="list-style-type: none"> <li>RADICAL TRAPPING</li> </ul>	Synergy with PVC Cl.	Does not protect polymer surface and prevents CO to $\text{CO}_2$ oxidation.
<b>Chloroparaffins</b>	<i>Gas phase</i> <ul style="list-style-type: none"> <li>RADICAL TRAPPING</li> </ul>	Increased Cl concentration to increase synergy with ATO.	Lower the thermal stability of the compound.
<b>Lewis acids</b> <b><math>\text{MoO}_3</math></b> <b><math>\text{ZnO}</math></b> <b><math>\text{Zn}_3(\text{PO}_4)_2</math></b>	<i>Condensed phase</i> <ul style="list-style-type: none"> <li>CHAR FORMATION</li> </ul>	Cross-linking of polyene sequences following Dies-Alder and Friedel Craft catalyzed by Lewis acids.	They lower the thermal stability of the compound, some are colored and prevent the transparency of the part.
<b>Organophosphates</b>	<i>Gas phase</i> <ul style="list-style-type: none"> <li>RADICAL TRAPPING</li> </ul> <i>Condensed phase</i> <ul style="list-style-type: none"> <li>CHAR FORMATION</li> </ul>	They act both in the condensed phase, (phosphoric acid catalyzes char formation and dilutes the fuel) and in the gas phase (PO- and HPO-radicals act as scavengers of hot radicals). Depending on whether they operate in the condensed or gas phase they act as smoke suppressants or flame retardants.	Their effect is synergistic with other additives but they cannot be used individually.
<b>Copper Compounds</b>	<i>Condensed phase</i> <ul style="list-style-type: none"> <li>CHAR FORMATION</li> </ul>	Reductive coupling.	Green/blue color preventing transparency.
<b>Metal hydroxides</b> <b><math>\text{Mg}(\text{OH})_2</math></b> <b><math>\text{Al}(\text{OH})_3</math></b>	<i>Gas phase</i> <ul style="list-style-type: none"> <li>Heat removal</li> </ul> <i>Condensed phase</i> <ul style="list-style-type: none"> <li>Fuel dilution</li> <li>Physical barrier</li> </ul>	Heat absorption is due to the fact that the degradation of these additives is an endothermic reaction, which produces water vapour that dilutes the combustible gases. In addition, these additives form an oxide patina that provides protection to the material.	

## 2.5 ACID SCAVENGERS

To understand how HCl scavenging occurs in the condensed phase, it is necessary to understand how PVC and PVC compounds degrade during combustion. Thermogravimetry in isothermal conditions or with various heating ramps is a technique used by several research groups to understand the mechanism by which the degradation of PVC or PVC compounds occurs.

The degradation of pure PVC has been studied with thermogravimetric techniques by several research groups and in the scientific community the most accepted model is the two-stage claimed by Wu [41].

The degradation of a PVC compound will be much more complex because some additives are present. Some of them can interact with the released HCl, or may evaporate and/or decompose influencing the thermogravimetric curves in a pattern that is often difficult to understand. For example, the formula in Table 4 shows the degradation indicated by the TGA-FTIR of Figures 12 and 13. In the first step, between 223°C and 323°C, the following gasses are released:

- HCl comes from zip elimination
- CO<sub>2</sub> from the reaction between HCl and CaCO<sub>3</sub>
- Aromatic hydrocarbons from the pyrolysis of PVC
- DINP plasticizer evaporating at 230°C.

The second step is due to the char decomposition through the emission of volatiles mainly alkyl hydrocarbons. The last step concerns a massive emission of CO<sub>2</sub> due to the decomposition of CaCO<sub>3</sub>: by means of the ratio of the areas under the peaks, it is possible to know how much CaCO<sub>3</sub> has reacted with HCl and when it is degraded.

*Table 4: typical PVC compound for cable.*

Formulation (phr)	
PVC	100
DINP	50
Stabilizer	5
CaCO <sub>3</sub>	90



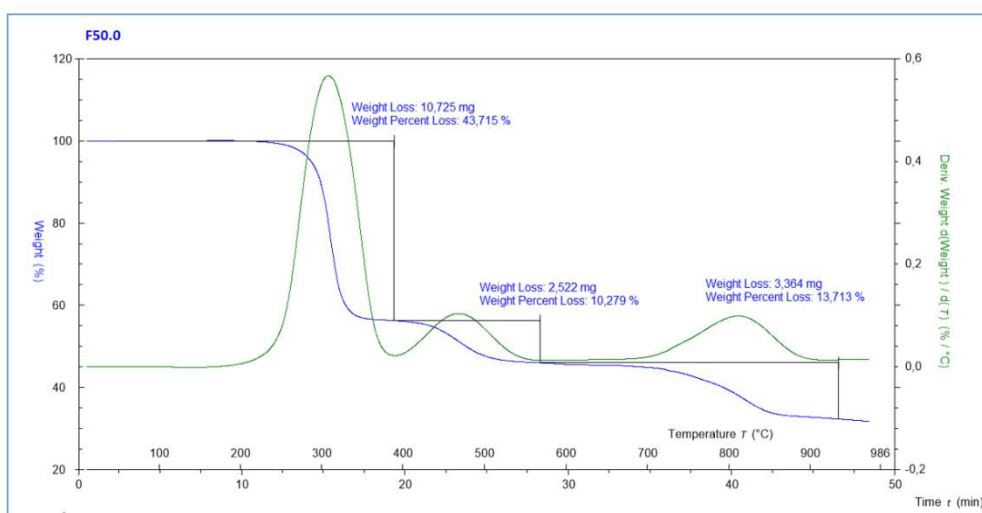


Figure 11: TGA of the table 3 PVC formulation.

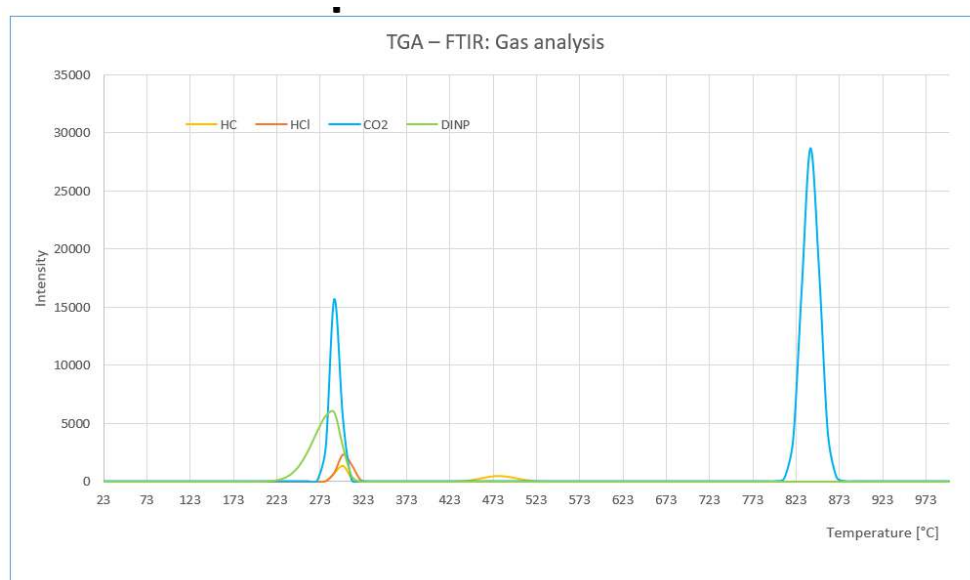


Figure 12: TGA-FTIR of table 3 PVC formulation.

A good acid scavenger, which performs well under EN 60754-1 and EN 60754-2, must therefore absorb as much HCl as possible throughout the PVC combustion process, in a temperature range between 250°C and 360°C and it should give stable reaction products between 360 °C up to the maximum temperature of the performed test (e.g., 810 °C in EN 60754-1 and 965 °C in EN 60754-2).

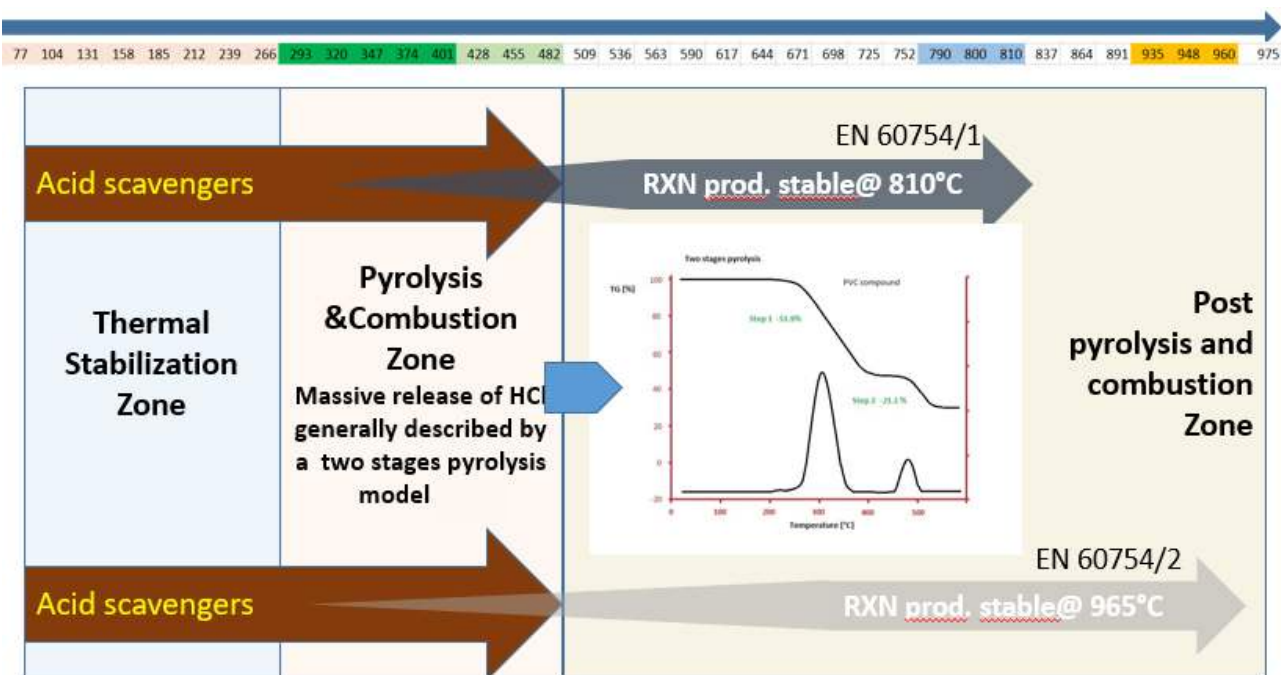


Figure 14: acid scavenger action.

The reactions involved in the HCl scavenging are often quite complicated to be well understood and they consist of a series of HCl “transfer” between the various actors involved in the scavenging process. Understanding how acid scavengers interact one each other and with the polymer matrix is the key element to improve the efficiency of the HCl scavenging process.

Acid scavengers are divided into two classes:

1. Acid scavengers typically used as thermal stabilizers in PVC (metal soaps, alkali and alkaline earth metal hydroxides, hydrotalcites, zeolites, hydrocalumites, etc.).
2. Acid scavengers typically used as HCl absorbers at high temperatures.

This last class of additives removes HCl from smokes coming from PVC compounds combustion. These additives are mixtures of acid scavengers acting synergistically to trap HCl in a temperature range from 200°C up to 1000°C, preventing its release in the gas phase during the combustion of the compound.

The simplest examples of high-temperature acid scavengers are fine calcium carbonates, which have always been used in PVC to produce low smoke acidity compounds destined to specific locations. Low smoke acidity cables are for example required in oil offshore platforms, according to specific supply procurements of Exxon, Eni, Agip, etc. and in some national standards.

Other acid scavengers are formulas containing two or more high temperature acid scavengers that work synergistically and with the polymer over a wide temperature range. These mixtures are generally proprietary formulas of cable or cable compound manufacturers, who have opened up research areas aimed at reducing the smoke acidity coming from the combustion of the article, in order to open up new market segments.

### **3 CABLES**

#### **3.1 PVC IN CABLES**

An electrical cable is a tool designed to transport energy and information. There are different kinds of cables: power, signal and control, telecommunications, railway, mining, automotive, etc...

It is made up of an electrical conductor that consists of a set of one or more twisted wires and covered with one or more layers of material acting as insulator. Cables may have beddings, armoring and shields, and an outer protection called sheath.

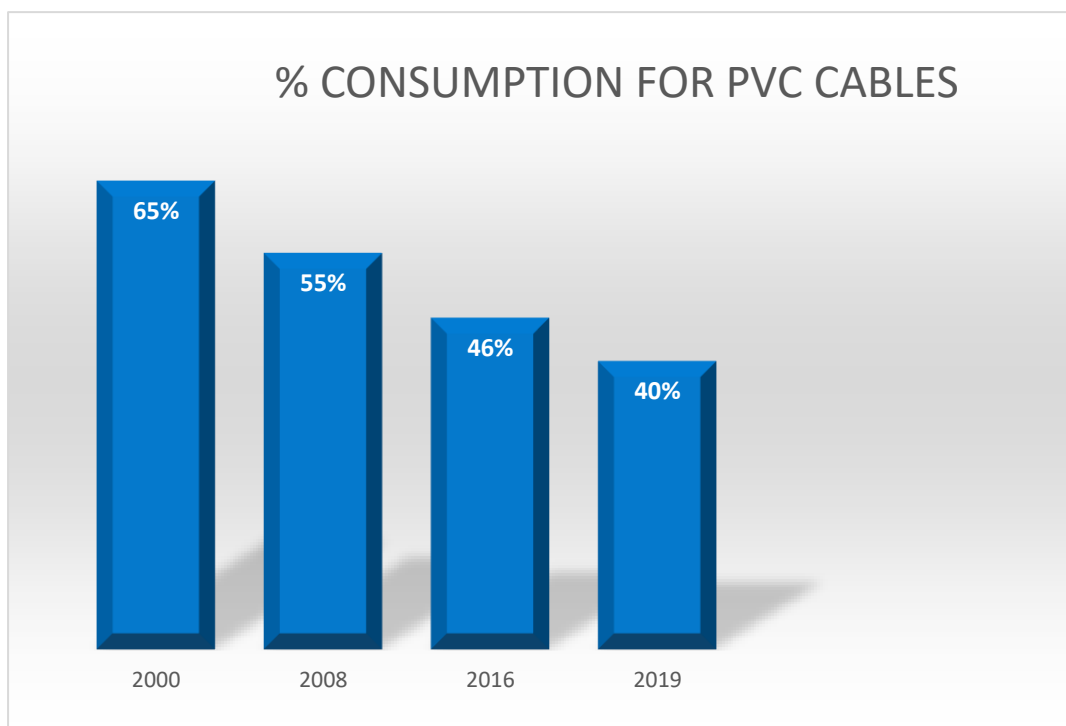


*Figure 2: an electrical cable.*

In almost all electrical cables, metals with a very low electrical resistivity (e.g., copper or aluminum) are used for the conductor wires. The thickness of the conductor varies depending on the current carrying capacity and whether greater resistance to mechanical stress or greater flexibility is required; they can also be spirally twisted, flattened or shaped. Insulation and sheathing can be produced from various thermoplastic and thermosetting polymeric materials (PVC, HEPR, NBR, XLPE, PE, CPE chloroprene, fluorinated polymers, silicones, nylon, etc.).

Among these, the plastic material that is not only the most widely used but also guarantees the best cost/performance ratio and versatility is PVC. As regards the sustainability of PVC material in cable formulations, it is important to highlight that the entire PVC value chain has been working over the last 10 /20 years to make not only production but also products more sustainable [31, 42].

Despite this, in recent decades there has been a significant decrease in the use of PVC for both electrical and telecommunication cables due to the use of materials that do not produce acid smokes called halogen free. The graph below shows the decrease in consumption (in percentage) of PVC compound for cables compared to other polymers [44].



*Graphic 1: % consumption of PVC compounds for cables.*

### 3.2 CPR AND PVC CABLES

The CPR (Construction Product Regulation) [1] is a European regulation (Regulation EU n.305/2011) that lays down harmonized conditions for the marketing of construction products and it replaced Council Directive 89/106 / EEC (Construction Product Directive, CPD) in 2017. The objective of the CPR is to ensure the free movement of construction products in the European Union by adopting a harmonized technical language capable of defining performance and essential characteristics for minimizing risks to persons and goods. The construction products must therefore satisfy seven requirements ([1] Annex I of the CPR), including safety in case of fire. Point two of Annex I of the CPR reports as follows:

*“The construction works must be designed and built in such a way that in the event of an outbreak of fire:*

- *the load-bearing capacity of the construction can be assumed for a specific period of time;*
- *the generation and spread of fire and smoke within the construction works are limited;*
- *the spread of fire to neighboring construction works is limited;*
- *occupants can leave the construction works or be rescued by other means;*
- *the safety of rescue teams is taken into consideration.”*

The key elements of the CPR for ensuring safety in the event of fire are a harmonized classification of construction products in terms of their performance in the event of fire, the presence of common standards and requirements, the use of the same control procedures by the competent authorities, the presence on the finished product of a CE marking which implies a declaration of performance (DoP), without which the CE marking cannot be affixed. Electrical cables are considered building and construction products and the CPR has 'activated' two technical standards:

- EN 50575 is a product standard “specifying reaction- to-fire performance requirements, test and assessment methods for electric cables used for the supply of electricity and for control and communication purposes”;
- EN 13501-6 defines classes and additional classes, standards and requirements to obtain them.

All cables for fixed installations in buildings (energy, communication and optical) must therefore be classified according to EN 13501-6. There are 7 classes for reaction- to-fire, identified by the

subscript "ca" (cables) according to their decreasing performance: Aca, B1ca, B2ca, Cca, Dca, Eca, Fca.

Table 5: classes for reaction- to-fire according to EN 13501-6.

Decreasing performance

Class	Test	Requirements
A <sub>ca</sub>	EN ISO 1716	PCS ≤ 2,0 MJ/kg
B1 <sub>ca</sub>	EN 50399	FS ≤ 1,75 m THR 1200s ≤ 10 MJ Peak HRR ≤ 20 kW FIGRA ≤ 150 W/s H ≤ 425 mm
B2 <sub>ca</sub>	EN 60332 1-2	
C <sub>ca</sub>	EN 50399	FS ≤ 2,0 m THR 1200 s ≤ 30 MJ PEAK HRR ≤ 60 kW FIGRA ≤ 300 W/s
D <sub>ca</sub>	EN 60332 1-2 EN 50399	H ≤ 425 mm THR 1200s ≤ 70 MJ PEAK HRR ≤ 400 kW FIGRA ≤ 1300 W/s
E <sub>ca</sub>	EN 60332 1-2 EN 60322 1-2	H ≤ 425 mm
F <sub>ca</sub>	EN 60322 1-2	H > 425 mm

In addition to the main classification shown in the (Table EN 13501-6), there are also the following additional classes:

- s = smoke density evaluation. It varies from s1a, s1b, s2 and s3 with decreasing performance
- d = flaming droplets evaluation. It varies from d0 to d2 with decreasing performance
- a = acidity evaluation. It varies from a1 to a3 with decreasing performance.

Therefore, the CPR provides harmonized classification for cables in the EU. In Italy, according to CEI UNEL 35016, there are four types of classification for cables in terms of fire performance.

Table 6: Italian classification for fire performance cables according to CEI UNEL 35016.

CPR Class	Additional classes	Who?
B2ca	s1a d1 a1	LSZH
Cca	s1b d1 a1	LSZH
Cca	s3 d1 a3	PVC
Eca	none	PVC

On the basis of a fire risk assessment carried out in accordance with the internal laws and codes of each European countries, the cables are chosen according to the rule "higher fire risk", "higher performance cable". Table 7 from [42] gives some indications for the choice of cables depending on where they are to be placed.

Table 7: cables classes according to the locations.

<b>HIGHLY FREQUENTLY INTERCHANGE PLACES</b>		<b>RAILWAYS</b>
<ul style="list-style-type: none"> <li>▪ Railway and maritime stations</li> <li>▪ Subways</li> <li>▪ Terminals</li> </ul>	HIGH RISK	
<b>TRANSPORT AND COMMUNICATION</b>		<b>GALLERIES AND PARKING LOTS</b>
<ul style="list-style-type: none"> <li>▪ Railways</li> <li>▪ Railway tunnels with a length of more than 1,000 m</li> <li>▪ Road tunnels with a length exceeding 500 m</li> <li>▪ Garages</li> </ul>	HIGH RISK	
<b>HEALTH FACILITIES</b>		<b>HEALTH</b>
<ul style="list-style-type: none"> <li>▪ Hospital and nursing homes with hospitalisation</li> <li>▪ Assisted residences for the elderly and disabled</li> <li>▪ Rehabilitation facilities</li> </ul>	MEDIUM RISK	
<b>ENTERTAINMENT, SHOW AND CULTURE</b>		<b>ENTERTAINMENT</b>
<ul style="list-style-type: none"> <li>▪ Cinemas, theatres, discos</li> <li>▪ Sports centres and gyms</li> <li>▪ Museums, galleries, exhibition spaces</li> <li>▪ Exhibition areas</li> <li>▪ Libraries</li> <li>▪ Shopping centres</li> </ul>	MEDIUM RISK	
<b>SCHOOLS</b>		<b>SCHOOLS</b>
<ul style="list-style-type: none"> <li>▪ School buildings of every order and degree</li> </ul>	MEDIUM RISK	
<b>HIGH BUILDINGS</b>		<b>HIGH BUILDINGS</b>
<ul style="list-style-type: none"> <li>▪ Buildings for civil use with fire-fighting &gt; 24 m to 28 m</li> <li>▪ Companies and offices with over 300 people</li> </ul>	MEDIUM RISK	
<b>ACCOMMODATION FACILITIES</b>		<b>HOTELS</b>
<ul style="list-style-type: none"> <li>▪ Hotel, motel, guesthouses</li> <li>▪ Tourist villages, holiday homes, campgrounds</li> <li>▪ Student accommodation</li> <li>▪ Holiday farms and bed &amp; breakfast</li> </ul>	MEDIUM RISK	
<b>RESIDENTIAL BUILDINGS</b>		<b>RESIDENCE</b>
<ul style="list-style-type: none"> <li>▪ Houses and residential buildings &lt; 24 m to 28 m</li> <li>▪ Small companies, professional offices</li> <li>▪ Shops, bars and restaurants</li> </ul>	LOW RISK	

### 3.3 ADDITIONAL CLASSIFICATION FOR ACIDITY

According to CPR, EN 60754-2 is the standard to be used for the determination of the additional smoke acidity class for cables. On the other hand, EN 60754-1 is a standard used specifically for PVC cables outside the CPR regulation.

Performing EN-60754-2, a small quantity of the PVC cable is burnt in a furnace tube in isothermal conditions at a temperature chosen between 935°C and 965°C as shown in Figure 16. The fumes are then collected in two bubbling devices containing double deionized water. The solutions are brought to 1 L volume and pH and conductivity measurements are carried out.

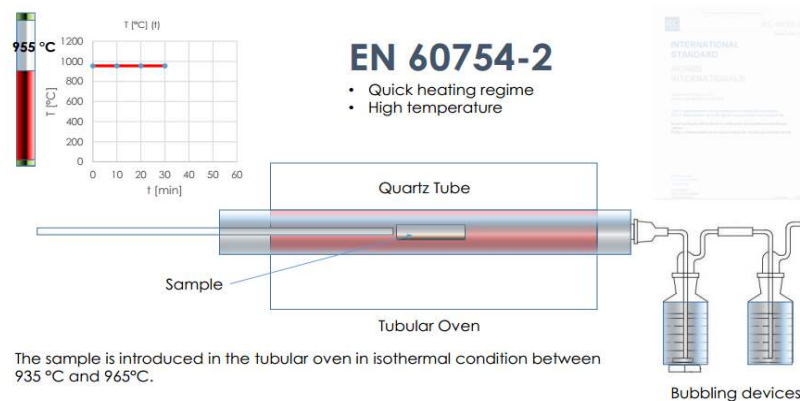


Figure 16: EN 60754-2.

The classes of smoke acidity are the following:

- Class a1: pH > 4.3, Conductivity [mS/mm] < 2.5
- Class a2: pH > 4.3, Conductivity [mS/mm] < 10
- Class a3: pH ≤ 4.3, Conductivity [mS/mm] ≥ 10.

Performing EN 60754-1, a small quantity of PVC cable is burnt with a heating ramp (40 min until a temperature of 800°C is reached) and then that temperature is held for further 20 min, as shown in Figure 17. The fumes are then collected in two bubbling devices containing a 0.1 N NaOH solution, and the smoke acidity assessment is performed by a titration to determine the mg of hydrogen halide per gram of compound. The titration doses HCl and HBr (without being able to distinguish between them) and it is only suggested for acidity values greater than 5 mg/g, below which it becomes inaccurate. In the case of the presence of F, it is necessary to complete the analysis with other standards such as IEC 60684-2 [55].



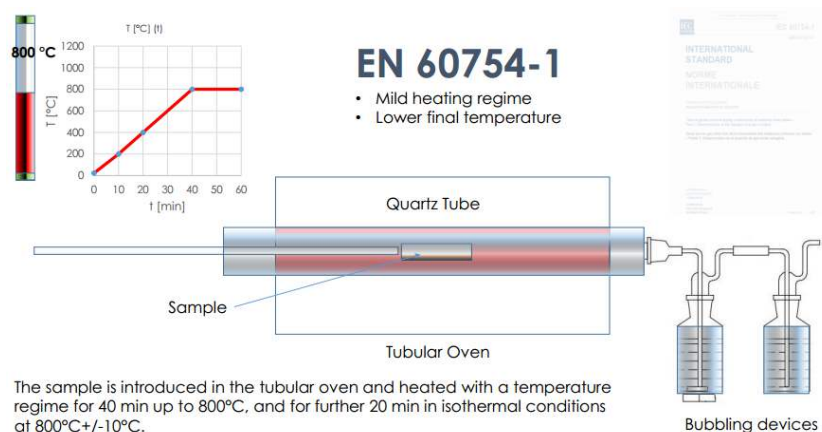


Figure 17: EN 60754-1.

The Figure 18 shows the IEC 60754-3. It has the heating conditions as EN 60754-2. The only difference is that the smokes collected by the bubblers are analyzed by ion chromatography (IC) using the method specified in ISO10304-1. F, Cl and Br can therefore be determined separately.

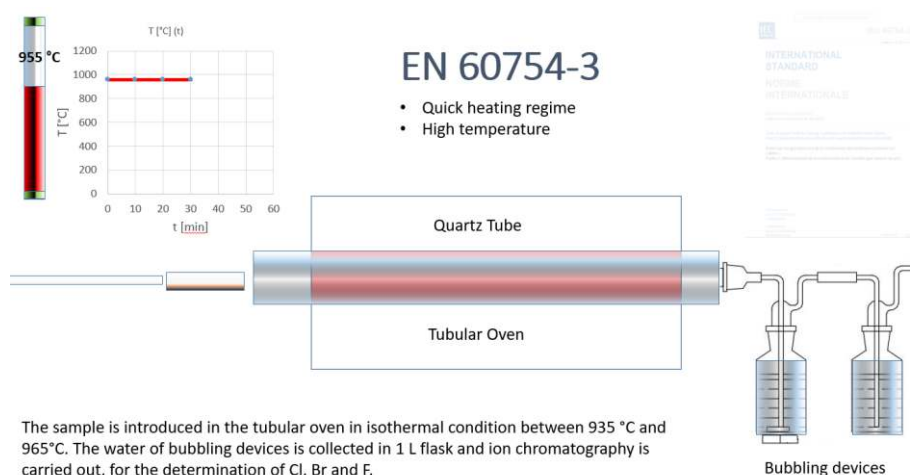


Figure 18: EN 60754-3.

#### 4 PURPOSE OF THE THESIS

Over a period of time from 2013 to 2020, the “Gruppo Italiano Compound per Cavi” (GICC, a research group that brings together the major Italian PVC compounders), with the support of “Istituto Giordano” (a research company, avant-garde in its experimentation, certification, planning and training), “PVC Forum Italia” (the association that brings together the Italian PVC supply chain) and PVC4cables (EVCM's platform dedicated to the PVC cables supply chain) compared the two technical standards, measuring the smoke acidity of a series of PVC compounds for cables and some PVC cables. The data were presented in a series of conferences held between 2017 and 2020 [16].

GICC highlighted that by performing EN 60754-2 with the temperature profile of EN 60754-1, test samples with acid scavengers gave higher pH values and lower conductivity values. The difference between the EN 60754-2 and EN 60754-1 values depends on the mechanism of action of the used acid scavengers. If acid scavengers are absent or not efficient, the differences are almost zero; otherwise, when strong acid scavengers are present, the differences are huge. In fact, EN 60754-2 has no heating ramp and it is performed at very high temperatures: this prevents the acid scavenger to interact strongly with HCl. In contrary, EN 60754-1 has a heating ramp and it is performed at lower temperatures: this gives to acid scavengers more time to trap HCl in the condensed phase, as it normally happens in a real fire scenario, where temperatures do not reach instantaneously 955°C.

The aim of the thesis is:

- to verify the impact of some acid scavengers on the main properties of PVC compounds for cables and on fire performances;
- to verify the difference between EN 60754-1 and EN 60754-2 by measuring smoke acidity of some cable compounds in isothermal condition at 955 °C as in EN 60754-2 and with a heating ramp as in EN 60754-1.

The reason for this hypothesis is that acid scavengers - contained in PVC compounds to absorb HCl - need time to react with gaseous HCl. The presence of a heating ramp and lower temperatures in EN 60754-1 gives a slower kinetics of HCl release and this means a lower smoke acidity measured in EN 60754-1 than in EN 60754-2. The confirmation of the hypothesis in the experimental part and the previous researches will hopefully be the preliminary step to consider the possibility to start an

advocacy procedure – held by the PVC manufacturers associations – with the aim to modify the EN 60754-2 standard with the introduction of a heating ramp and a lower test temperature; in fact, cables classified a3 with EN 60754-2 and - re-tested with EN 60754-1 - were found to be in class a2 [16].

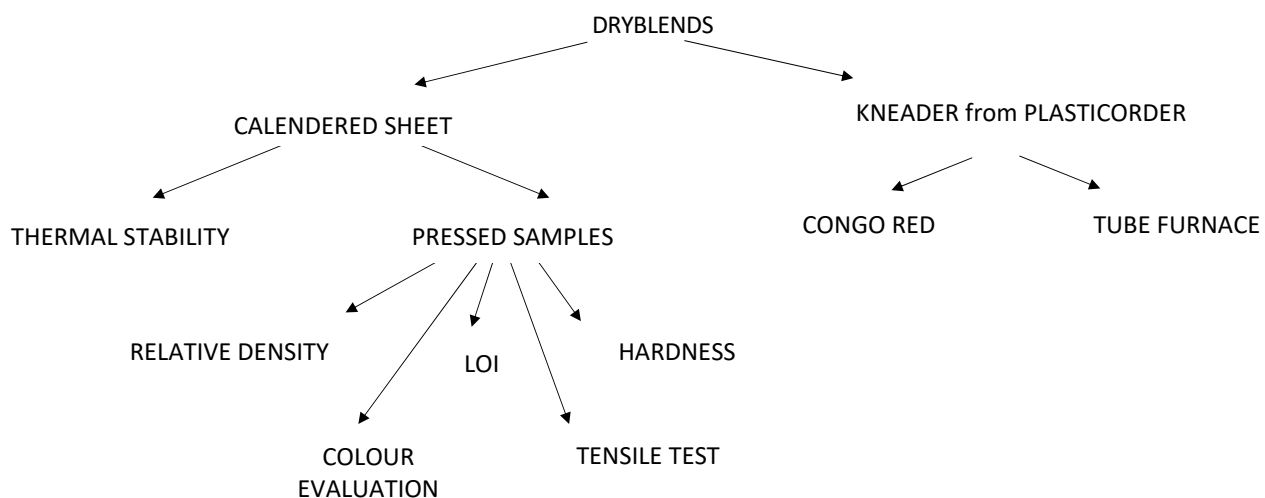
## 5. RESULTS AND DISCUSSION

### 5.1 DRY BLENDS AND SAMPLES PREPARATION

Based on formulations already known in Reagens S.p.A, 10 different dry blends were prepared and are shown in Table 8. Dry blends were prepared in Grindomix for 3 minutes at 1200 rpm. Figure 19 shows schematically the necessary steps for the analysis to which the dry blends were subjected.

*Table 8: dry blends formulations.*

	REA1	REA2	REA3	REA4	REA5	REA6	REA7	REA8	REA9	REA10
PVC K70	50	100	100	100	100	100	100	100	100	100
DINP	50	50	50	50	50	50	50	50	50	50
ESBO	2	2	2	2	2	2	2	2	2	2
IX 1010	0,1	0,1	0,1	0,1	0,1	0,1	0,1	0,1	0,1	0,1
STABILIZER	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0
Antimony Trioxide		3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0
CaCO3 medium particle size			90							
CaCO3 fine particle size				90						
CaCO3 ultra fine particle size					90				90	90
Acid Scavenger 1						90				
Mg(OH) <sub>2</sub>							90		30	
Al(OH) <sub>3</sub>								90		30



*Figure 19: scheme for preparing specimens from dry blends.*

## 5.2 SAMPLE CHARACTERIZATION

### 5.2.1 HARDNESS TEST



*Figure 20: Instrument used for hardness testing.*

The hardness of elastomers and elastic rubber polymers is determined by the test method according to technical standards ISO 7619-1 and ASTM D2240.

Shore A hardness test is performed with a truncated cone indenter with an angular opening of the cone of  $35^\circ$ . In this test method, the depth at which a spring-loaded indenter enters the material is calculated, responding differently depending on the hardness. In particular, the shallower the indentation depth, the greater the hardness. The measurement is taken at 15".

The specimens subjected were prepared by cutting out the pressed material to obtain squares of size 4x4 cm, with a thickness of 6 mm. The instrument used was a manual digital hardness tester (Gibitre Instrument) as shown in Figure 20.

*Table 9: average hardness values [ShA, at 15 seconds] and relative deviation standard obtained (average of 12 measurements).*

	REA1	REA2	REA3	REA4	REA5	REA6	REA7	REA8	REA9	REA10
Shore A	80	81	87	88	88	92	90	88	89	90
Dev. Std.	0,22	1,19	0,56	0,4	0,95	0,55	0,37	0,52	1,24	1,42

The addition of fillers and flame retardants fillers contributes to the increase the hardness of the plastic material in equal measure, and the hardness's of REA3 – REA10 are significantly different from REA1 and REA2 which, as shown in Table 8, do not contain any kind of filler.

### **5.2.2 TENSILE TEST**

The tensile test (or uniaxial tensile test) is a materials characterization test consisting in subjecting a standard-sized specimen of a material to an initially zero uniaxial load  $F$ , that is increased to a maximum value up to material failure.

The tensile test is used to determine several characteristics of the material under examination, including Young's modulus ( $E$ , defined as the ratio between stress and strain), load at failure, and percent elongation at failure. Figure 21 shows the instrument used (H10KS HOUNSFIELD dynamometer). The ISO 527-1 standard has been performed with specimen type 1A.



*Figure 21: Tensile Test Instrument.*

Figure 22 shows the specimens before and after the test.



*Figure 22: Test specimens before and after tensile test.*

Table 10 shows the results of the tests performed in the laboratory. The values obtained are the average of the 8 measurements made for each sample.

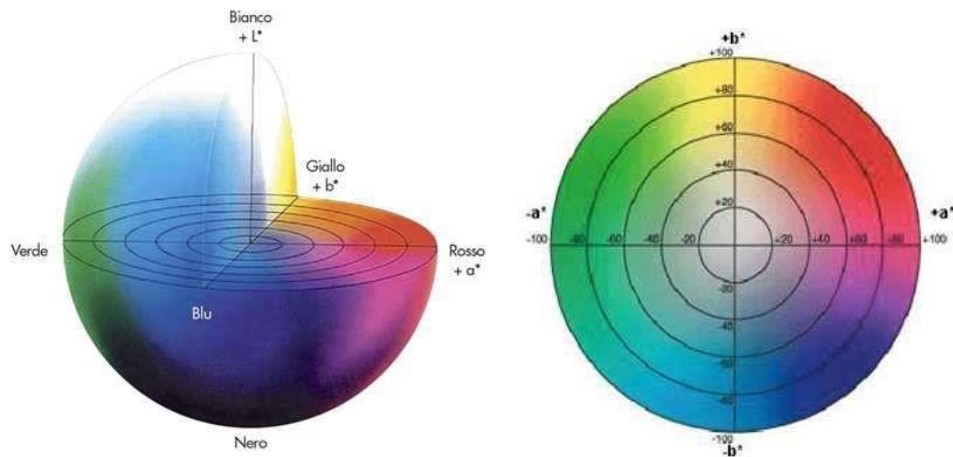
*Table 10: Experimental results of tensile test and relative deviation standard.*

	REA1	REA2	REA3	REA4	REA5	REA6	REA7	REA8	REA9	REA10
Tensile strength [N/mm <sup>2</sup> ]	20,3	19,5	13,7	13,2	12,7	12	13,3	12	10,6	10,2
Deviation standard	0,28	0,32	0,17	0,23	0,20	0,26	0,07	0,07	0,16	0,28
Elongation at break [%]	463	439	309	322	258	208	253	283	175	174
Deviation standard	10,63	19,88	13,02	18,85	10,75	5,55	8,87	7,17	8,14	19,3

As expected, the fillers' addition makes the material less elastic, "harder" and "fragile", i.e., with lower tensile strength and less elongation at break.

### 5.2.3 COLOUR EVALUATION

For the evaluation of the initial color of plastic materials, a colorimetric analysis was carried out using the X-Rite QA2000 colorimeter. With this instrument it is possible to identify numerically the color through three values belonging to the CIE color space ( $L^*a^*b^*$ ).



*Figure 23: Graphical representation of the colorimetric space.*

$L^*$  indicates brightness, expressed as a percentage (0 for black and 100 for white),  $a^*$  and  $b^*$  are the values indicating the color directions, ranging from green ( $-a^*$ ) to red ( $+a^*$ ) and from blue ( $-b^*$ ) to yellow ( $+b^*$ ), respectively.

The results obtained from colorimetric analysis of the 10 samples are shown in Table 11:

Table 11: Colorimetric analysis results.

	REA1	REA2	REA3	REA4	REA5	REA6	REA7	REA8	REA9	REA10
L*	70,14	91,25	88,36	88,96	80,63	63,78	55,98	88,11	68,51	78,53
a*	0,61	-0,06	1,38	1,57	2,67	8,32	7,19	1,16	4,82	2,88
b*	14,42	5,8	8	9,51	7,2	15,17	3,8	7,61	4,59	7,38



Figure 24: Test specimens of calendered dry blends.

Focusing on the impact on color, the filler affecting more the initial color is  $\text{Mg}(\text{OH})_2$ . From Figure 24 we can see that REA7 has a color shifted to brown.

REA1, without any filler, is transparent, while REA2, having  $\text{Sb}_2\text{O}_3$  (ATO), is opaque. Among all the specimens, the one with the best in initial color is REA8 with  $\text{Al}(\text{OH})_3$ .

## 5.2.4 RELATIVE DENSITY



Figure 25: equipment for measuring relative density.

Relative density can be determined in several ways. Solid bodies that have a density greater than that of water are weighed first in air and then in water under conditions of complete immersion. Relative density is obtained by dividing the weight in air by the decrease in weight of the immersed body based on Archimedes' principle.



For each sample, three measurements were made in air and three in water under fully underwater conditions. Table 12 shows the results obtained.

*Table 12: Average of the relative density values obtained (from the average of three measurements).*

	REA1	REA2	REA3	REA4	REA5	REA6	REA7	REA8	REA9	REA10
Density [g/mL]	1,237	1,269	1,552	1,546	1,526	1,484	1,513	1,509	1,581	1,582

### 5.2.5 PLASTICORDER

The plasticorder is an instrument measuring the torque (viscosity) of a plastic material as function of time and temperature. Following ASTM D 2538, a known amount of dryblend is poured inside the thermostated chamber of the instrument through a quick-loading chute, a ram is placed into the chute and a weight is added. Inside the 50 cm<sup>3</sup> chamber, the compound is subjected to heat and shear stress by two internal roller-style blades rotating at a given rate.



*Figure 26: The plasticorder used (Brabender Plastograph EC + Mixer W50).*

The graph obtained plotting the torque [Nm] as a function of the elapsed time is called plastogram.

Figure 27 shows some plastograms of the compounds in Table 8: the graphs show the points A, B and X discussed below.

Each curve is characterized by a peak of maximum, i.e., the zone where the torque has the maximum value, when the operator loads the dryblend and then the ram and the weight (point A), by a point of minimum torque (B) corresponding to the initial stages of gelation, followed by a point of relative

maximum (X), representing the end of dryblend gelation. The fusion time is given by the difference between the time at X and the time at A.

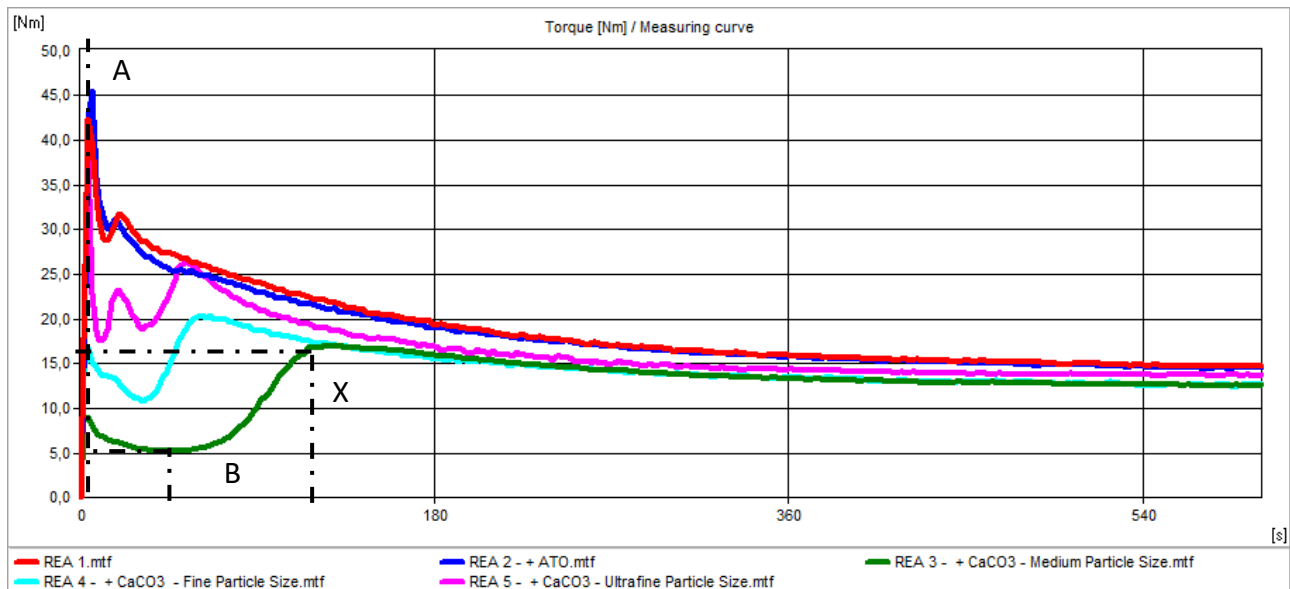


Figure 27: Most significant plastograms for the 10 compounds; test conditions 160°C-64g-30 rpm-10 min.

The plastograms of REA1 and REA2 are practically identical being free of fillers and differing only in the presence of ATO.

As the fillers increase in the compound, the density of the plastic material increases (Table 12) and the plasticorder roller mixing chamber becomes emptier delaying the gelation, as confirmed by the curves of REA3, REA4 and REA5 compared to REA1 and REA2.

Figure 27 also shows that, for the same quantity of the filler, the gelation time of the material is a function of the particle size of the filler. In particular, the finer the particles, the greater the friction they impart to the compound and the earlier the gelation. In fact, the REA5 formula, based on ultrafine calcium carbonate, has a shorter gelation time than the medium and fine particle size calcium carbonate curves.

## 5.3 HIGH TEMPERATURE AND FIRE BEHAVIOUR TESTS

### 5.3.1 INSTRUMENTATION AND METHODS

#### 5.3.1.1 WERNER-MATHIS OVEN

With a Werner Mathis Oven (Figure 28), we can evaluate the initial color, color hold, and long-term thermal stability of a PVC compound.

The test specimens are introduced at 200°C in the oven and they are moved outward at a rate of 0.5 cm every 120 seconds.

The specimens used for this test have characteristic dimensions and are derived from calendered dry blends prepared at 160°C for 3 minutes.



*Figure 28: Werner-Mathis Oven.*

#### 5.3.1.2 LOI

The LOI (Limiting Oxygen Index), as defined in the ASTM D 2863 technical standard, represents the minimum concentration of oxygen (expressed as a percentage volume in an oxygen - nitrogen mixture) necessary to maintain the combustion of a material (initial temperature of 23°C ± 2°C) under specified test conditions.

The ASTM D 2863 technical standard has been performed to measure LOI using an FTT (Fire Testing Technology Limited, Oxygen Index Tester) instrument.

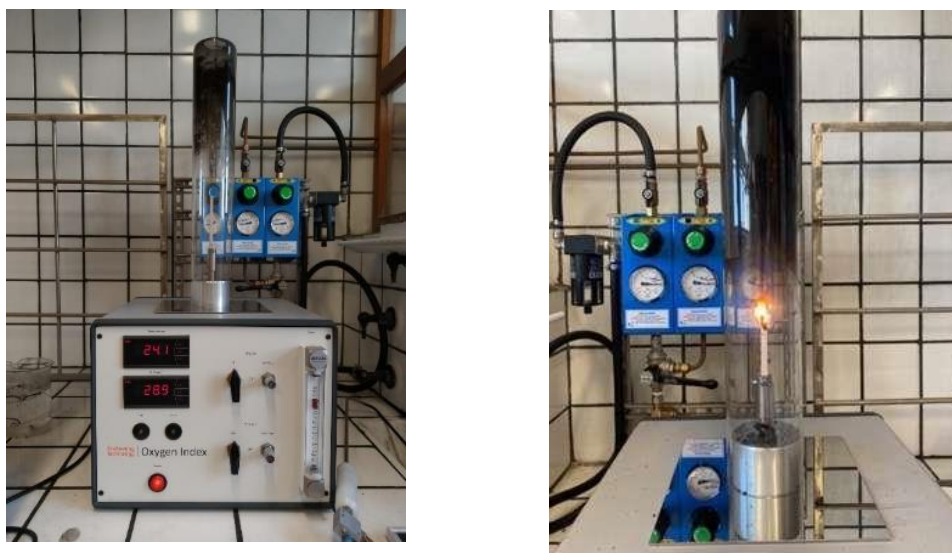
A plastic specimen of specific dimensions (in Figure 29) is vertically placed in a glass column in which a normalized mixture of oxygen/nitrogen flows. The top end of test specimen is ignited, and the combustion behavior of the specimen is observed by determining the period and extent of burning.

By testing a series of different samples at different oxygen concentrations, the minimum amount of oxygen, i.e., the LOI, is determined.

*Figure 29: Standard type IV specimen for LOI.*



NOTE: the dimensions of the test piece are defined in the technical standard ASTM D2863; in the present case the dimensions of type IV are: length = 10.5 cm; width = 6.2 cm; thickness 3 mm)



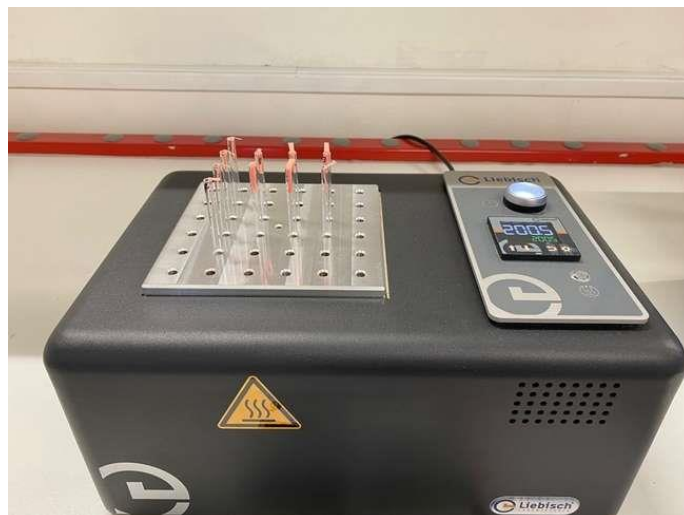
*Figure 30: left: instrument used to measure LOI; right: specimen during the test.*

From an operational perspective, we first proceed with the calibration of LOI test apparatus (gas calibration in terms of concentration and flow) then we measure the LOI of an internal standard and then we perform the test for the samples under examination.

### **5.3.1.3 THERMAL STABILITY**

The thermal stability of PVC compounds is measured according to the technical standard EN 60811-405 (called Congo Red Test) usually used in the electrical cable industry. It consists in determining

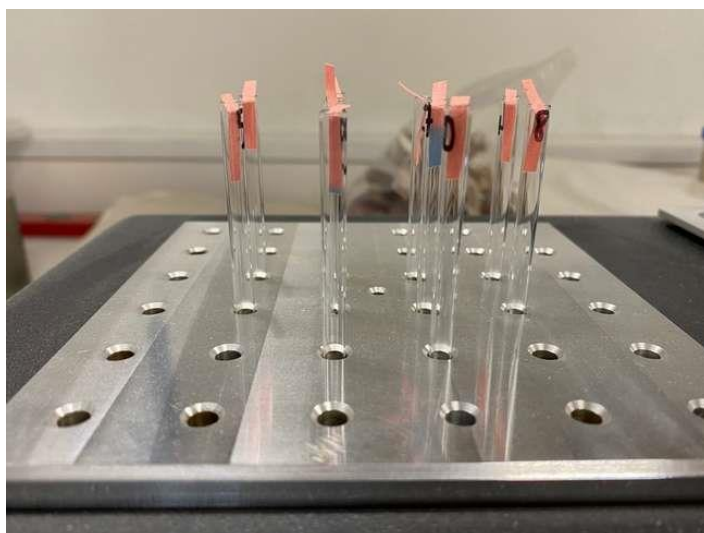
the time to shift of a congo red paper following the emission of HCl. The used instrument is a Liebisch block thermostat, Liebisch Labortechnik LT-PVC-210-36-5.



*Figure 31: Instrument used to measure the red congo value.*

An amount of sample ( $50 \pm 5$  mg) is placed inside a glass tube and placed in the block thermostat (Figure 31) at  $200 \pm 0.5$  °C. The congo red paper is placed at the top end of the tube and it turns blue when the PVC begins to release HCl.

The congo red value is the time elapsed between the start of the test and the time when the congo red paper turns blue.



*Figure 32: Block thermostat and map change from red to blue.*

#### 5.3.1.4 TUBE FURNACE

When PVC compounds burn, they release hydrochloric acid (HCl) as main the combustion product, making the fumes acidic. The tube furnace is one of the most widely used instruments to assess the smoke acidity during the combustion of a sample at high temperature.

The tube furnace is produced by S.A. ASSOCIATES (Halogen Acid Gas Generation Test apparatus) and has dimensions according to EN 60754 series. Temperature profiles and air flow are set in a touch screen control panel and temperatures are confirmed with a calibrated thermocouple.



*Figure 33: Tube furnace according to EN 60754 series.*

From an operational point of view, the plastic sample is cut into small, homogeneously sized pieces to avoid passivation during combustion. It is then weighed in an analytical balance ( $1,000 \pm 0.001$ ) g and placed on a ceramic combustion boat (Figure 34) which is then manually inserted into the furnace. For each sample the general method of EN 60754-2 has been applied, therefore the results reported in Tables 16, 17, 18, 19, 20, 21, 22 and Graphic 2 and 3 are a mean of a set of measurements having a coefficient of variation of  $\pm 5\%$ .





*Figure 34: ceramic combustion boat according to EN 60754 series.*

Two series of measurements of 10 compounds of Table 8 have been carried out: for the first series EN 60754-2 was faithfully applied, setting an isothermal temperature profile at 950 °C, for the second series setting the heating profile according to EN 60754-1. In both series the fumes have been collected in two bubbling devices containing double deionized water. The water is filtered through a pleated filter and brought to volume inside a 1L flask. From the filtered solution aliquots are taken for the following measurements:

- pH measurement (by pH meter) and conductivity measurement (by conductivity meter) to assess the amount of HCl present;
- Ion Chromatography (IC) to evaluate which anions contribute to pH and conductivity.
- Inductive Coupled Plasma (ICP) to assess which cations contribute to conductivity.

Solid residues have been analyzed by SEM-EDX microscopy and FTIR-ATR spectroscopy to qualitatively evaluate the carbonaceous residue.

### **5.3.2 ANALYSIS OF RESULTS**

The results obtained for the tests described in the previous section are shown below.

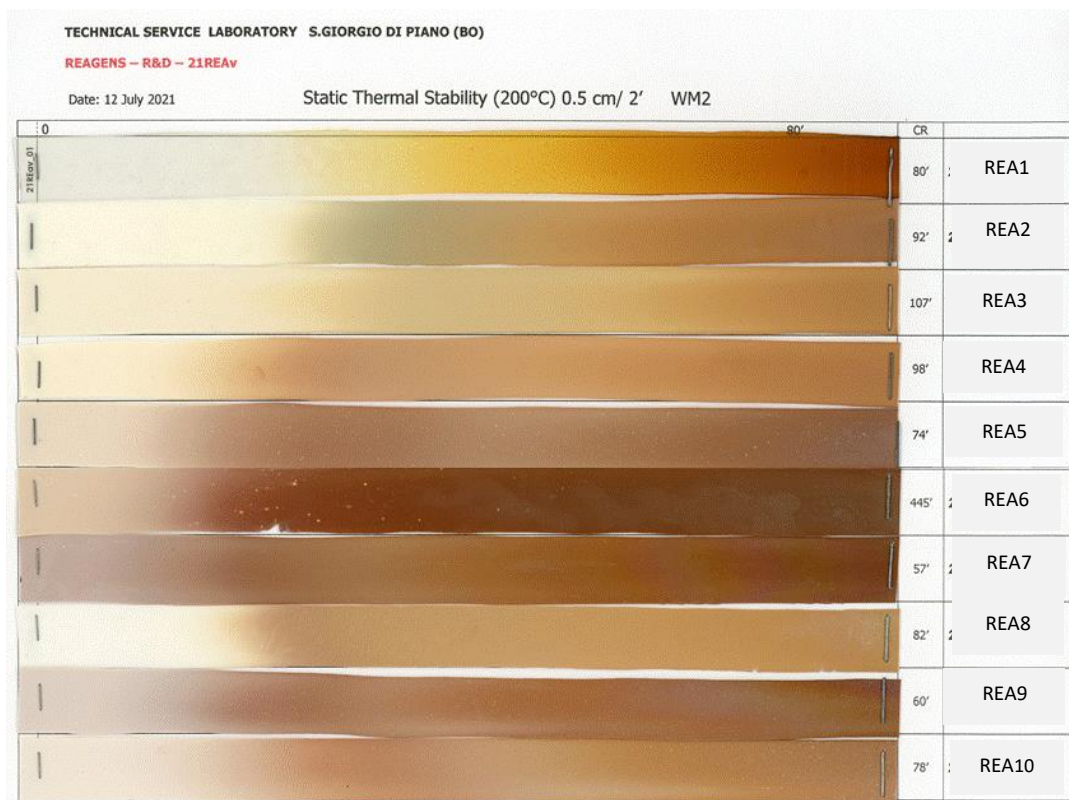


Figure 35: Thermal stability test results, performing Werner – Mathis Oven.

Table 13: congo red values (average of three measurements).

	REA1	REA2	REA3	REA4	REA5	REA6	REA7	REA8	REA9	REA10
C.R @ 200°C	80'	92'	107'	98'	74'	445'	57'	82'	60'	78'

Table 14: LOI values ( $\pm 1\%$ ) assessed using the procedure described in ASTM D 2863.

	REA1	REA2	REA3	REA4	REA5	REA6	REA7	REA8	REA9	REA10
LOI (%O <sub>2</sub> )	25	29	28	27	22	23	35	34	24	25

Table 15: residue analysis (SEM and FTIR).

	EN 60754-1		EN 60754-2	
	Found Elements from SEM/EDX	Found substances from IR	Found Elements from SEM/EDX	Found substances from IR
REA1	-	-	-	-
REA2	-	-	-	-
REA3	Ca, Cl	CaCl <sub>2</sub>	Ca, Cl	CaCl <sub>2</sub> , CaCO <sub>3</sub>
REA4	Ca, Cl	CaCl <sub>2</sub>	Ca, Cl	CaCl <sub>2</sub> , CaCO <sub>3</sub>
REA5	Ca, Cl	CaCl <sub>2</sub>	Ca, Cl	CaCl <sub>2</sub>
REA6	n.a.	n.a.	n.a.	n.a.
REA7	Mg	MgCl <sub>2</sub>	Mg	MgO
REA8	Al	Al <sub>2</sub> O <sub>3</sub>	Al	Al <sub>2</sub> O <sub>3</sub>
REA9	Ca, Cl, Mg	MgCl <sub>2</sub> , CaCl <sub>2</sub>	Ca, Cl, Mg	CaCl <sub>2</sub> , MgO
REA10	Ca, Cl, Al	CaCl <sub>2</sub> , Al <sub>2</sub> O <sub>3</sub>	Ca, Cl, Al	CaCl <sub>2</sub> , Al <sub>2</sub> O <sub>3</sub>



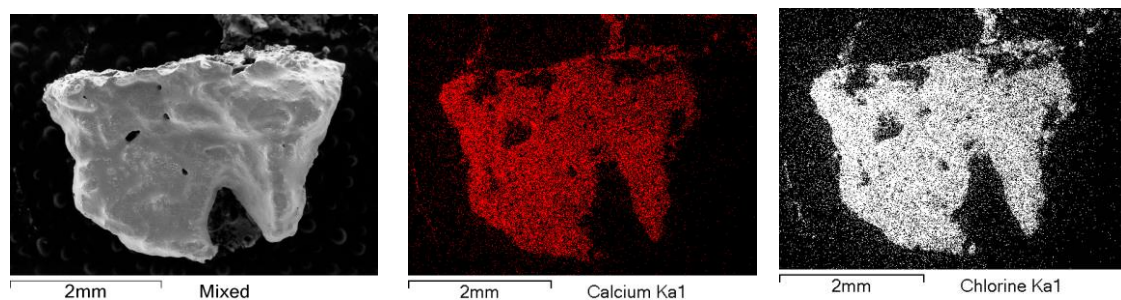
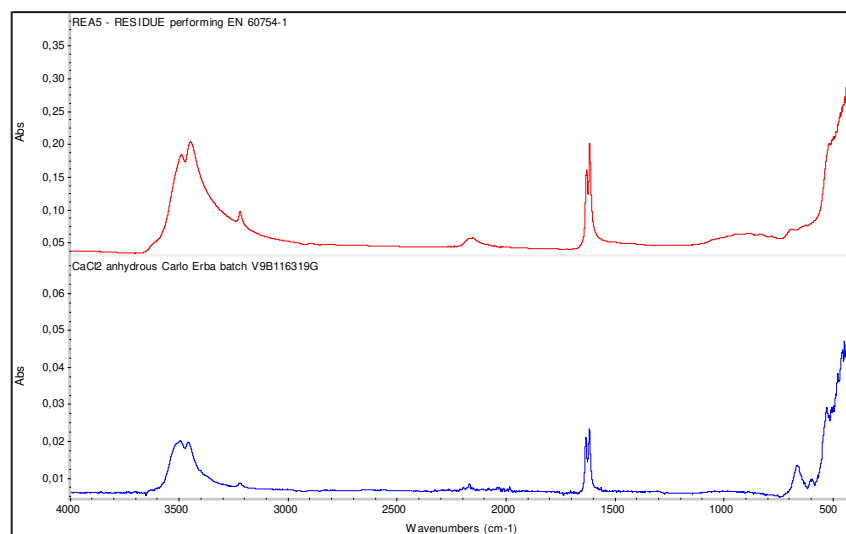
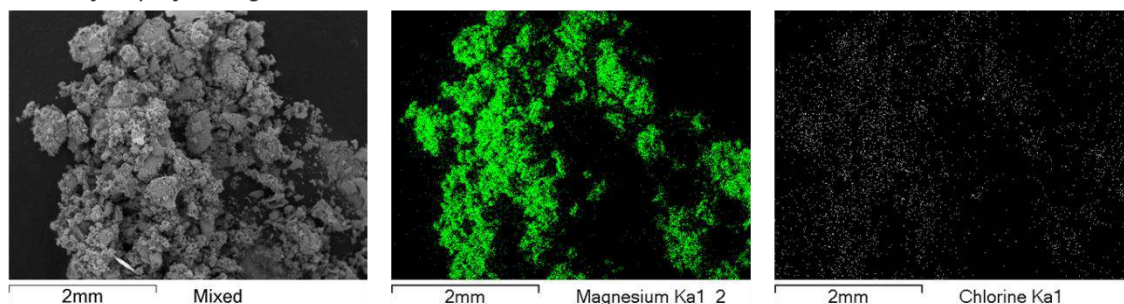


Figure 36: Top, IR spectrum of the residue (red profile) for REA5 after EN 60754-1 compared to standard  $\text{CaCl}_2$  (blue profile). Bottom, distribution of the main elements highlighted at EDX for REA5 after EN 60754-1.

REA7 after performing EN 60754-1



REA7 after performing EN 60754-2

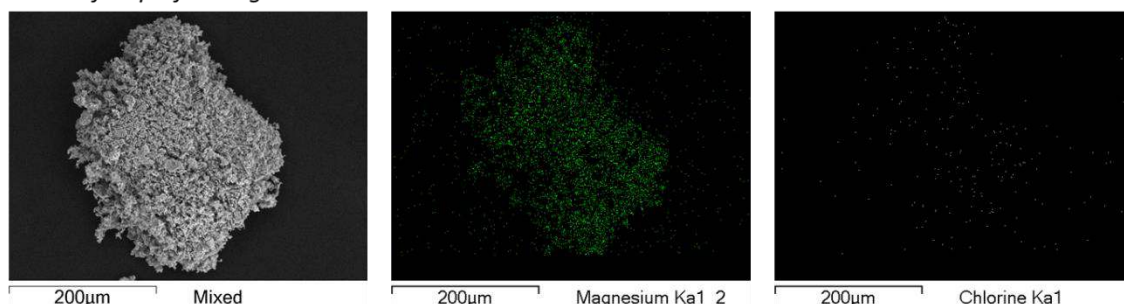


Figure 37: Distribution of the main elements highlighted at EDX for REA7 performing EN 60754-1 (top) and EN 60754-2 (bottom).

Table 16: pH comparison between EN 60754-2 and EN 60754-1.

pH	REA1	REA2	REA3	REA4	REA5	REAv6	REA7	REA8	REA9	REA10
EN 60754-2	2,1	2,1	2,7	2,8	2,7	2,9	2,4	2,4	3	3
EN 60754-1	2,2	2,3	2,6	2,9	3,2	4,2	2,5	2,4	3,7	3,4

Table 17: Conductivity comparison between EN 60754-2 and EN 60754-1.

Conducibilità µS/mm	REA1	REA2	REA3	REA4	REA5	REAv6	REA7	REA8	REA9	REA10
EN 60754-2	368,3	360,3	107	85,2	102,6	69,2	223,4	226,6	51,6	60,5
EN 60754-1	359,7	328,5	105,7	70,1	31,1	3,8	180,7	205,2	11,8	25

Table 18: pH and conductivity performing EN 60754-1.

EN 60754/1	REA1	REA2	REA3	REA4	REA5	REAv6	REA7	REA8	REA9	REA10
pH	2,2	2,3	2,6	2,9	3,2	4,2	2,5	2,4	3,7	3,4
K (µS/mm)	359,7	328,5	105,7	70,1	31,1	3,8	180,7	205,2	11,8	25

The main objective of the analysis is to highlight the properties imparted to the compounds by the various additives, focusing mainly on the smoke acidity measurements and trying to understand which acid scavengers are able to capture HCl more efficiently.

Tests performed at the tube furnace show that EN 60754-2, at temperatures above 900 °C and without a heating ramp, flattens the measurements by leveling out the differences in smoke acidity among different acid scavengers (Table 16 and 17). On the contrary, using the temperature profile of EN 60754-1, there is a slowing down of HCl emission and this allows to better view how the different acid scavengers work. Table 18 shows that REA1 has the highest smoke acidity values among all the formulations. From the Table 14, it is also observed that REA1, not containing any flame retardant, gives a very low oxygen index (25 %O<sub>2</sub>). When 5 phr of ATO (REA2) are added, no significant change in pH and conductivity values is observed, due to the fact that there are no acid scavengers, while the LOI rises to 29 %O<sub>2</sub>. This because Sb<sub>2</sub>O<sub>3</sub> has all the stoichiometric HCl available to yield gaseous SbCl<sub>3</sub>, capable to trap OH· and H· radicals feeding the flame (flame poisoning). Being heavier and thus staying longer in the flame, SbCl<sub>3</sub> is able to impart more flame retardance than HCl. In fact, the LOI increases from 25 in REA1 to 29 in REA2.

Comparing with REA2 the REA3 and REA4 data, containing medium and fine particle size CaCO<sub>3</sub> respectively, we can deduce that CaCO<sub>3</sub> slightly reduces LOI (Table 14), and it has an impact on pH and conductivity depending on its particle size (Table 18). This is due to the high-temperature acid scavenger nature of CaCO<sub>3</sub>, which removes some HCl from the gas phase and makes it no longer available to generate SbCl<sub>3</sub>. If then we move to ultrafine particle size CaCO<sub>3</sub>, a lower smoke acidity is observed compared to REA2, REA3 and REA4 (Table 18), obviously followed by a drop in LOI (22 %O<sub>2</sub> in Table 14). This is due to the fact that ultrafine particle size calcium carbonate has a high surface area making it a more efficient acid scavenger at high temperature than the previous ones. Ultrafine particle size CaCO<sub>3</sub>, by capturing gaseous HCl more quickly:

- gives less acidic fumes;
- inhibits the mechanism of flame poisoning, reducing the flame retardance;
- impedes the char formation, yielding more smokes, even in presence of smoke suppressants.

Regarding this last point, previous studies [16] show that, scavenging HCl, the formation of ZnCl<sub>2</sub> is inhibited and consequently also the yield of carbonaceous residue gets down contributing to the production of smoke. Further evidences that CaCO<sub>3</sub> behaves as an acid scavenger in the condensed phase are the FTIR-ATR and SEM-EDX analyses of the residue in combustion boats shown in Table 15 and Figure 36, which highlight the presence of calcium dichloride.

The same decrease in LOI followed by a further reduction in smoke acidity is also evident in the REA6, containing a very strong acid scavenger at high temperatures. In this case we can also observe a pretty high thermal stability according to EN 60811-405 (Table 13).

REA7 and REA8 have the highest LOI values of the series. Such values can be explained considering that both  $\text{Mg}(\text{OH})_2$  and  $\text{Al}(\text{OH})_3$  are excellent flame retardants, acting through a physical mechanism. In fact, releasing water through an endothermic decomposition, they

- absorb heat
- dilute the flame
- create a physical barrier of magnesium oxide and alumina.

Their contribution to smoke acidity is different. In particular,  $\text{Al}(\text{OH})_3$  does not react with HCl (Table 15, 18). In fact, being inert in the temperature range "explored" by the two standards, it has one of the highest smoke acidities. On the contrary from the Table 15 we can see that  $\text{Mg}(\text{OH})_2$  or MgO reacts with HCl forming  $\text{MgCl}_2$ , which however is not stable and slowly decomposes into MgO and HCl in temperatures between 450°C and 550°C. This explains why, though  $\text{Mg}(\text{OH})_2$  is capable to react with HCl, the smoke acidity is high (Table 18). The residue in the combustion boat of REA7 performing EN 60754-1 still contains Mg and Cl signals as shown in Figure 37 and Table 15. This suggests that, under milder heating conditions, not all  $\text{MgCl}_2$  decomposes into MgO and HCl. On the contrary, performing EN 60754-2, in the combustion boat the SEM identifies only the Mg coming from MgO (Figure 37 and Table 15).

Comparing REA9 with REA5, we see that the former has 30 phr of  $\text{Mg}(\text{OH})_2$ . Acting as flame retardant REA9 has a higher LOI than REA5 (Table 14). In addition, REA9 has significantly lower smoke acidity than REA5 and REA7 (Table 18). This is due to the synergism between the two acid scavengers,  $\text{Mg}(\text{OH})_2$  and ultrafine particle size  $\text{CaCO}_3$ . In fact  $\text{MgCl}_2$ , coming from the reaction between  $\text{Mg}(\text{OH})_2$  / MgO with HCl, decomposes between 450°C-550°C, releasing HCl with a slow kinetic. Then the free HCl is captured more efficiently by ultrafine particle size  $\text{CaCO}_3$ , yielding  $\text{CaCl}_2$ , a substance stable at temperatures above 960°C.

REA10 contains ultrafine particle size  $\text{CaCO}_3$  and a flame retardant ( $\text{Al}(\text{OH})_3$ ). Therefore, an increase in LOI is observed in REA10 compared to REA5, while we have just a slight decrease in terms of

smoke acidity, which can be considered within the fluctuations of the measurement itself (Table 18).

Ion chromatography (IC) analysis was used to assess which anions in the bubbling devices contribute to pH and conductivity (Table 19). Conversely, ICP was used to assess which cations contribute to conductivity (Table 20).

Table 19: IC analysis results.

EN 60754-1	REA1	REA2	REA3	REA4	REA5	REA6	REA7	REA8	REA9	REA10
Cl	348,14	150,22	64,47	60,81	23,44	2,98	173,64	192,44	10,33	25
F	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
Br	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
NO <sub>3</sub> <sup>-</sup>	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
NO <sub>2</sub> <sup>-</sup>	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
SO <sub>4</sub> <sup>2-</sup>	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
PO <sub>4</sub> <sup>3-</sup>	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
EN 60754-2	REA1	REA2	REA3	REA4	REA5	REA6	REA7	REA8	REA9	REA10
Cl	166,21	169,95	98,70	70,94	97,07	64,05	206,06	197,12	42,81	62,05
F	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
Br	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
NO <sub>3</sub> <sup>-</sup>	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
NO <sub>2</sub> <sup>-</sup>	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
SO <sub>4</sub> <sup>2-</sup>	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
PO <sub>4</sub> <sup>3-</sup>	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD

Table 20: ICP analysis results.

EN 60754-1	REA 1	REA2	REA3	REA4	REA5	REA6	REA7	REA8	REA9	REA10
Ca	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
Mg	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
Al	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
Sb	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
Zn	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
EN 60754-2	REA 1	REA2	REA3	REA4	REA5	REA6	REA7	REA8	REA9	REA10
Ca	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
Mg	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
Al	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
Sb	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
Zn	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD

Analysis of the data shows that the most concentrated species are Cl<sup>-</sup> and the resulting H<sup>+</sup>, while all other cations and anions are in negligible concentrations. Assuming a complete dissociation of HCl into H<sup>+</sup> and Cl<sup>-</sup>, the pH is easily derived from the Cl<sup>-</sup> concentration. Tables 21 and 22 show that the

pH values calculated by IC are quite in line with those measured with the pH meter, indicating that the contribution to the pH of other species is zero.

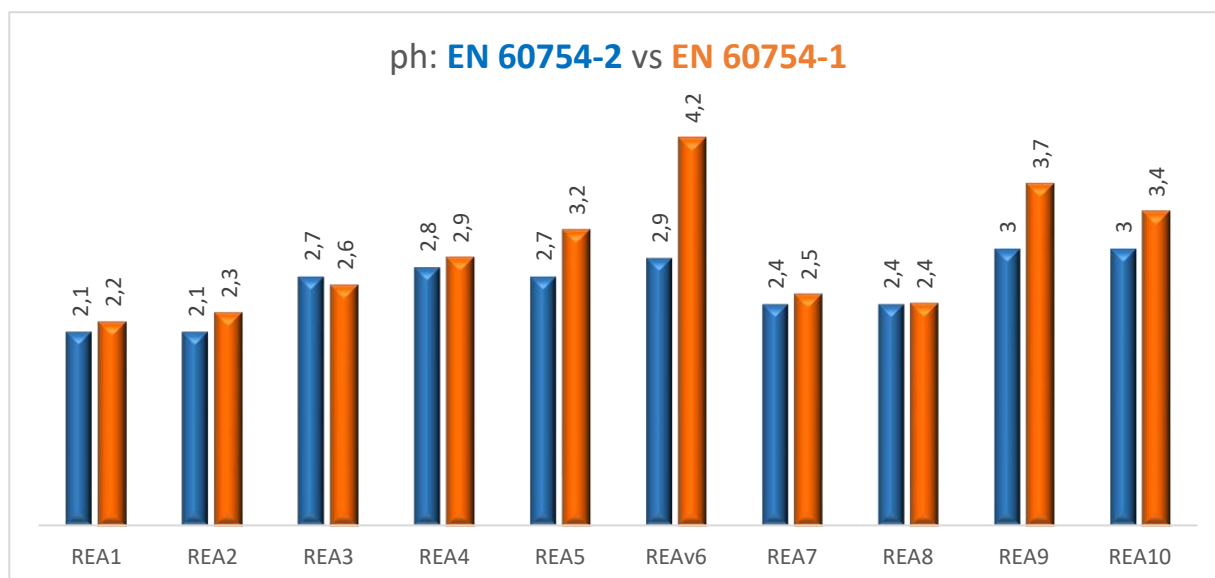
*Table 21: Comparison of measured pH vs. calculated pH by CI per EN 60754-1.*

EN 60754-1	REA1	REA2	REA3	REA4	REA5	REAv6	REA7	REA8	REA9	REA10
pH	2,2	2,3	2,6	2,9	3,2	4,2	2,5	2,4	3,7	3,4
pH from IC	2	2,4	2,7	2,8	3,2	4,1	2,3	2,3	3,5	2,8

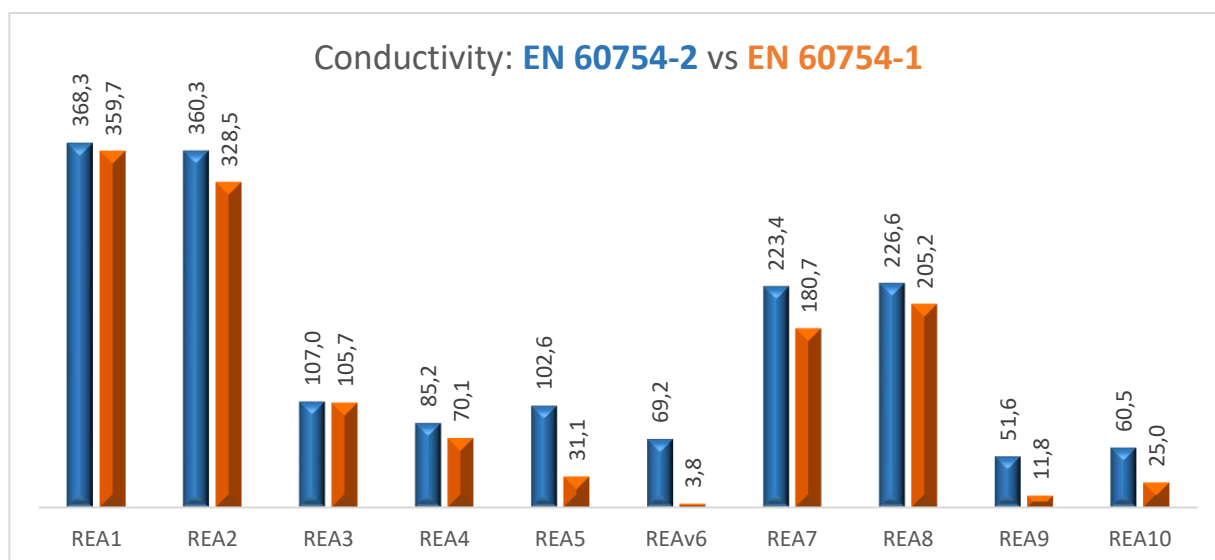
*Table 22: Comparison of measured pH vs. calculated pH by CI per EN 60754-2.*

EN 60754-2	REA1	REA2	REA3	REA4	REA5	REAv6	REA7	REA8	REA9	REA10
pH	2,1	2,1	2,7	2,8	2,7	2,9	2,4	2,4	3	3
pH from IC	2,3	2,3	2,6	2,7	2,6	2,7	2,2	2,3	2,9	2,8

Graphs 2 and 3 and Tables 16 and 17 show the comparison of the smoke acidity results with EN 60754-2 and EN 60754-1. Without strong acid scavengers typically used to get down the smoke acidity in PVC compounds, the pH and conductivity data are similar (REA1, REA2, REA3, REA4).



*Graph 2: pH measured according to EN 60754-1 and EN 60754-2.*



Graph 3: measured conductivity ( $\mu\text{S/mm}$ ) according to EN 60754-1 and EN 60754-2.

In contrary, in the presence of strong acid scavengers, there are obvious differences. They are due to the kinetics of HCl release (REA5, REA6 and REA9). The presence of a heating ramp and lower temperatures (EN 60754-1) slows down the HCl evolution, allowing the acid scavengers to perform their function more efficiently.

A clear example is the difference in smoke acidity in REA6, where the very strong acid scavenger present gives the possibility to reach with part 1 a pH value of 4.2 and a conductivity of 3.8  $\mu\text{S/mm}$ , which is close to class a2, according to CPR.

EN 60754-2 is therefore much more severe because it does not have a heating ramp and is performed at higher temperatures than EN 60754-1. The reason lies in the kinetics of HCl emission that in isothermal conditions at 950°C is very fast and inhibits the action of acid scavengers used to reduce the acidity of the fumes. On the other hand, in the presence of a heating ramp like the one provided for EN 60754-1, the evolution of HCl is slow and this allows the acid scavengers to efficiently trap the HCl in the solid phase, preventing the production of acid fumes.

## 6 CONCLUSIONS

The main purpose of the project has been to demonstrate the clear difference between the smoke acidity values obtained carrying out EN 60754-1 and EN 60754-2. The results obtained are very explicative and show that EN 60754-2 is much more severe as it does not have a heating ramp and is performed at higher temperatures than EN 60754-1.

It is hoped that this research will be useful to start an advocacy procedure by PVC manufacturers' associations to amend EN 60754-2 with the introduction of a heating ramp and a lower test temperature.



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