IV REUNIÓN NACIONAL DE DIOXINAS, FURANOS Y COMPUESTOS ORGÁNICOS PERSISTENTES RELACIONADOS

Alicante, 26-28 Junio 2013

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IV Reunión Nacional de Dioxinas, Furanos y COPs

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EFFECT OF THE METAL IN THE PRODUCTION OF POLLUTANTS DURING THE DECOMPOSITION OF TWO TYPES OF ELECTRIC WIRES

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Introduction

The wire and cable industry manufactures a wide range of products that support a multitude of applications. Some of the major markets are communication cables, power and cable wire, automotive wiring, control and signal cables, and building wiring. Generally wires differ in conducting and isolation materials. The classic conductor material has been copper but aluminium is also used frequently today.

Many wire insulation and covering compositions contain materials, such as lead, halogenated compounds and other compounds, that impart electrical insulation and fire performance properties. Specifically, fire retardants are used to avoid the propagation of fire. One of the most frequently used types of fire retardant, Halogenated Flame Retardants (HFRs), have been proven to be a hazard to human life and environment, which has led to regulations on their use with the ultimate goal of removing them from the market.

There is not extensive information about the emissions from thermal degradation processes of electric wires in oxidative atmosphere, and less in the presence of conductive metal[1-4]. The present work aims to extend the information in this issue providing the basis for the analysis of environmental impact and development of new products, with special interest in the effect of the metal on the decomposition and the predictable differences between PVC and halogen-free wires.

Materials and methods

Electrical Wires

Supplied by General Cable, Co., two kinds of commercial cables have been employed in this work. The first one is a common wire (designed as P),with PVC cover and reticulated polyethylene as insulation. The second one is a special fire-resistant and halogen-free wire (designed as H). Figure 1 shows the scheme of electrical wire, the composition of the two materials used and the weight percentage of each part. As we can see in Figure 1, the material used in the cover (or jacket) of the halogen free wire is a mixture of polyethylene, a thermoplastic elastomer and aluminium trihydroxide (PE-TPE-ATH). Elemental analysis of the wires and some more details can be found in a previous work[5]. To ensure the homogeneity, the samples were crushed (1-3 mm) using a laboratory blender by DINKO, 8010 model (DINKO, Barcelona, Spain).
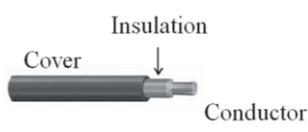
Part	PVC cable (P) wt. %	Halogen free cable (H) wt. %
1 (Cover)	P1: PVC, 41 %	H1: Thermoplastic polyolefin (PE-TPE-ATH), 36 %
2 (Insulation)	P2: Reticulated polyethylene, 9 %	H2: Silicone rubber, 20 %
3 (Conductor)	P3: Copper, 50 %	H3: Copper, 44 %

Figure 1.Scheme of the electrical cables, their composition (supplied by manufacturer) and % weight of each part.

In order to study the effect of the presence of copper during the decomposition, for each kind of wire two different samples were prepared: one consisting of the plastic parts, named P1+P2 and H1+H2, and the other one representing the entire wire named P1+P2+P3 and H1+H2+H3, where P3 and H3 refers to the metal (see Figure 1).

Experimental system

Experiments were performed in a moving tubular reactor which consists in a quartz tube (10 mm wide), were the material is introduced uniformly along. This tube is introduced in a horizontal furnace, maintained at the desired temperature, at constant velocity using a horizontal actuator.

More details of the equipment can be found elsewhere[6-7]. In all runs the temperature of the oven was 700 ºC. Synthetic air was introduced parallel to the sample, with gas flowing at 300 mL/min (measured at 1 atm and 20 °C).

The outlet gas stream was sampled to analyze semivolatile compounds such as PAHs, ClPhs and ClBzs, PCDD/Fs, and dioxin-like PCBs. Emitted gases were collected using poliaromatic Amberlite® XAD-2 resin as sorbent (Supelco, Bellefonte, USA) placed at the outlet of the furnace during the whole experiment. Before the decomposition runs, a control containing no sample was carried out using the same experimental conditions (blank).

Amberlite® XAD-2 resin was extracted in toluene by Accelerated Solvent Extraction (ASE-100, Dionex-Thermo Fisher Scientific Inc., California, USA) and the extracted solution was divided as follows: approximately 30 wt. % was employed to analyze PAHs (US-EPA 8270D method), ClPhs and ClBzs; the rest (over 70 wt. %) was used for the analysis of PCDD/Fs and "dioxin-like" PCBs (EPA 1613 and 1668A methods).

Results and discussion

Table 1 shows the results on the emission of PAHs for the four runs done in the laboratory reactor. Note that these results are expressed in mg/(kg of consumed material), i.e., considering only the plastic fractions in the basis; if the whole weight is considered in the weight base, emission of runs P1+P2+P3 and H1+H2+H3 will be approximately halved (composition is shown in Figure 1). In the first column (Table 1) we can see the results for the combustion of the halogen free wire with no metal, the second column corresponds to the presence of metal, and third and fourth columns are the ones obtained with the PVC wire.

The main PAHs emitted in all cases are naphthalene and acenaphtylene. It seems, in both cases, that the presence of metal reduces the production of this kind of pollutants,

Table 1. Emission of 16 EPA priority PAHs in the four runs performed (emission/kg plastic fraction).

Compound	H1+H2 mg compound/kg consumed material	H1+H2+H3	P1+P2 mg compound/kg consumed material	P1+P2+P3
naphthalene	142.6	102.8	410.0	39.8
acenaphthylene	54.8	42.4	113.3	3.83
acenaphthene	2.26	2.35	6.61	nd
fluorene	nd	4.86	34.1	0.71
phenanthrene	19.1	13.7	89.1	3.37
anthracene	2.29	1.25	13.0	nd
fluoranthene	6.01	4.86	28.8	0.93
pyrene	12.7	10.8	36.2	0.67
benzo(a)anthracene	1.19	0.90	5.48	0.20
chrysene	3.50	3.07	10.6	0.73
benzo(b)fluoranthene	nd	nd	nd	nd
benzo(k)fluoranthene	4.69	5.80	13.0	nd
benzo(a)pyrene	1.94	2.85	1.39	nd
indeno(1.2.3-cd)pyrene	1.14	1.09	0.43	nd
dibenz(a.h)anthracene	nd	nd	nd	nd
benzo(g.h.i)perylene	2.69	3.13	2.08	nd
Total	**255.14**	**199.9**	**764.37**	**50.2**

Table 2. Total emission of chlorobenzenes (ClBzs) and chlorophenols (ClPhs) in the four runs performed (emission/kg plastic fraction).

	H1+H2 mg compound/kg consumed material	H1+H2+H3	P1+P2 mg compound/kg consumed material	P1+P2+P3
ClBzs	0.051	0.044	0.444	20.8
ClPhs	12.1	13.5	43.0	141.9

probably due to the catalysis of cracking reactions that produces low molecular weight compounds. Also, it is possible that the presence of metal catalyses chlorination reactions as will be presented later. The emission of each of the species shown in Table 1 is decreased almost in the same proportion for each one of the wires, being approximately an 80 % of the emission in the absence of the metal in the case of halogen-free wire, and a 6 % in the case of PVC wire.

The total emission of ClBzs and ClPhs is presented in Table 2. For both kind of compounds the formation is much more important for the PVC wire, and is enhanced in the presence of metal. This would explain, at least partly, the decrease in PAHs shown before. Transformation of PAHs to chlorinated species has been already reported[8] at temperatures between 300 and 1000 ºC.

Both wires present a much higher emission of ClPhs than ClBzs. Furthermore, the highest chlorobenzene emission is in the mono-chlorobenzene species, and 3,4-dichlorophenol in the case of chlorophenols. Chlorinated phenols are known to be the most prone direct precursors of the formation of PCDD/Fs congeners, and these are among the most abundant aromatic compounds found in municipal solid waste incineration emissions. On the other hand, many authors have confirmed the formation of chlorinated compounds and dioxins, both in gas and solid phases, from phenols when there is an oxidative atmosphere and in the presence of copper chloride.

Figure 2 presents the distribution of the congeners contributing to the toxicity of the PCDD/Fs emission in the four experiments, with H and P wires in the presence or absence of metal. Data in Figure 2 has been calculated by using I-TEQ factors and normalizing the contribution of each congener to the total toxicity.

Some points should be noted. On the one hand, the distribution of congeners depends on the material but rarely on the presence of metal. In this sense, the major contribution to the total toxicity is from 2,3,7,8-tetrachlorodibenzofuran in the case of H wire and 2,3,4,7,8-pentachlorodibenzofuran in the combustion of PVC. On the other hand, it is important to note that in the runs performed, furans contribute much more to the toxicity than dioxins. Specifically, congener 2,3,4,7,8-pentachlorodibenzofuran has been found to be the most represented in industrial incinerators emissions[9]. Another work[10] determined the concentrations and profiles of PCDD/Fs, PCBs and polybrominated diphenyl ethers (PBDEs) in the ambient air of an e-waste dismantling area, in the southeast of China; and they found that congener 2,3,4,7,8-pentachlorodibenzofuran contributed dominantly to the total I-TEQs in all the samples analyzed.

Concerning the total toxicity, not the congener distribution, the values obtained for halogen free wire were 65 pg WHO/g in the case of no metal (sample H1+H2) and 61 pg WHO/g in the presence of the metal (sample H1+H2+H3); for PVC wire the emission was 5690 pg WHO/g in the run performed without metal (P1+P2), and 33840 pg WHO/g in the presence of the metal (P1+P2+P3). In this way, it is clear that halogen-free wire does not produce a high amount of these pollutants, independent of the presence or absence of metal. On the other hand, PVC wire emission is almost 100 times the one observed in H wire, and there is a great increase in the presence of the copper metal. Note that the level of PCDD/Fs emission is expressed in pg/g that is one million times lower than the results presented for PAHs, ClBzs and ClPhs.
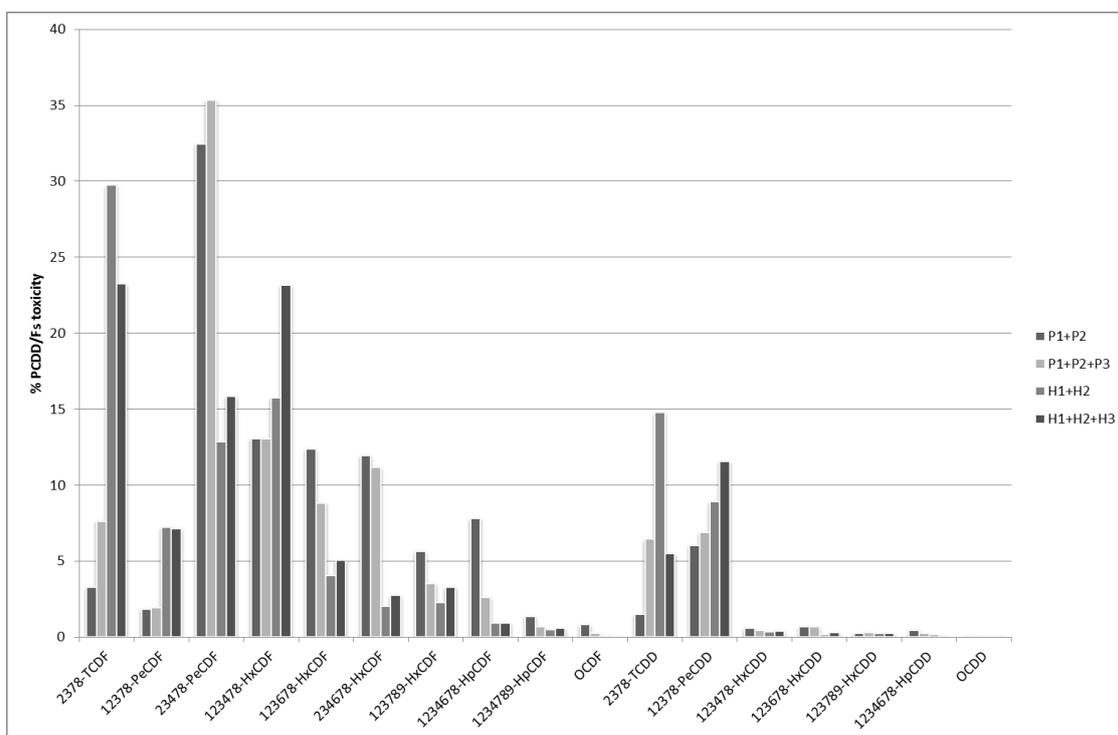

Figure 2. Toxic congener profiles in the emission of PCDD/Fs for H (halogen-free) and P (PVC) wires.

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