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A HEATED TUBE FURNACE TEST FOR THE EMISSION OF ACID GAS FROM PVC WIRE COATING MATERIALS: EFFECTS OF EXPERIMENTAL PROCEDURES AND MECHANISTIC CONSIDERATIONS

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Abstract—This work has investigated the mechanism of the reactions involved in the thermal breakdown of PVC wire coating materials and their effect on the conditions under which a test for measuring acid gas emission in a fire should be carried out. Simultaneous thermal analytical procedures were used to model the combustion reactions. The efficiencies of the calcium carbonate, used as a filler, in retaining acid gas, were calculated both from thermal analysis data and from tube furnace data. This allowed some of the deficiencies of the test procedure to be singled out. It has been found that the most important parameters which need to be controlled include: the temperature, the extent of soot formation and the humidity.

INTRODUCTION

When organic materials are burnt, they release a multitude of combustion products, some of which may be corrosive. In particular, halogen-containing materials may release a certain proportion of their halogen content as hydrogen halides.

When poly(vinyl chloride) (PVC) is heated above 300°C, it decomposes thermally and yields, as one of its first products, hydrogen chloride, as a result of thermal dehydrochlorination:

$$\sim H_2C\text{–}CHCl\sim \rightarrow \sim H\text{–}C{=}C\text{–}H\sim + HCl.$$

Various test methods have been proposed for measuring properties related to the corrosivity of the smoke from polymeric materials [1–11]. Although some of the procedures actually measure corrosivity, others are designed to determine the amount of acid gas emitted by the product being tested, using the assumption that smoke corrosivity can be related directly to acid gas emission. This assumption is inadequate because other combustion products, including carbon (soot), can have corrosive effects.

In particular, one of the test procedures being used [1–3] measures the amount of acid gas being produced after combustion of a sample in a tube furnace at high temperature. The present work is geared towards the development of a test protocol which will relate to the actual conditions that the test intends to model. For that purpose, an investigation was carried out which addresses two issues:

(a) the effects of changes in experimental procedures on test results and on test reproducibility, and

(b) the mechanism of the reactions occurring during the combustion process.

EXPERIMENTAL

Tube furnace test

The tube furnace used for this experiment is 225 mm long and 45 mm in diameter (ID), and contains a 490 mm long quartz tube, the heated zone of which has a diameter of 43 mm (OD) and a length of 200 mm. The outlet and inlet ends of the quartz tube have been narrowed down to 25 mm (OD), for the inlet (150 mm long), and to 14 mm (OD), for the outlet (100 mm long). The furnace temperature is controlled by a variable power transformer and measured with a chromel/alumel type K thermocouple. The area downstream from the furnace is maintained at a temperature above 100°C to avoid deposits of water or of HCl.

The porcelain sample boat used is a Coors No. 60032 (part No. 11005) which is almost 60 mm long (sample area *ca* 50 mm). The platinum sample boat is a specially-constructed 14 mm long rectangular-based (14 × 11 mm) straight-walled (6 mm high) boat. The sample boat is held, and advanced, by a holder, consisting of two pieces of quartz tubing welded together: a length of 60 mm of 14 mm OD tubing, in which the boat is placed, and a longer length of 5 mm OD tubing, for handling from outside the furnace. The boat holder passes through an O-ring seal, at the inlet end of the combustion tube, for advancement of the sample boat into the furnace. A thermocouple wire can be introduced through the narrow quartz tube, with the junction at the seal between the two tubes, to measure furnace temperature close to the sample boat. For some experiments, the 14 mm OD tube was cut in such a way that the top of the sample boat is exposed (uncovered experiments).

The sample boat is advanced in numerous small steps over a period of 30 min to reach the centre of the furnace. The boat is held at that position for a further 30 min. Both the air and the sample enter the furnace from the same end.

The combustion products are trapped in 200 cm^3 of demineralized water contained in a gas washer bottle fitted with a glass frit, to disperse the gas bubbles into the liquid and to trap solids. It is generally acknowledged that this method will collect all the HCl that reaches the aqueous phase. The air flow rate used is 100 cm^3/min. The acid gas produced is determined either by titration with NaOH, using a glass electrode with an end point set at pH of 5.3, or by using a chloride ion selective electrode (Orion model 94-17B, with a double junction reference electrode and an Orion model 701A digital voltmeter).

Three types of materials were used for the trapping of soot particles: platinum screens, porcelain saddles and a ceramic fibre (Fiberfrax B6, four circles, 6 mm thick). They were all inserted into the outlet end of the combustion tube, within the heated zone, in order that the soot could be trapped and burnt off.

Coil test [11]

A small amount of sample (*ca* 70–80 mg) is placed in a porcelain boat (Coors No. 60028) and heated with a coil of Nichrome resistance wire wrapped around it: 9 mm diameter, 20 mm length). A current of 2.5 A, at 12.5 V voltage (corresponding to a measured temperature of 350°C), is applied for 5 min, followed by 5 min cooling. The acid gas emitted is collected in demineralized water, which is also used to wash the walls of the vessel, after removal of the charred sample. No undecomposed polymer remains in the residue.

Thermal analysis

A Netzsch STA 409 simultaneous thermal analyzer, associated with a Hewlett–Packard 86B computer by means of an HP 3421B data acqusition unit, was used for all thermoanalytical experiments. The air flow rate was set at 50 cm^3/min for all experiments. All experiments were carried out with sample sizes of 20–25 mg, using crucibles made of alumina.

Isothermal runs were carried out by introducing the sample with the crucible in a pre-heated furnace, according to a specially-developed procedure. The furnace is preheated to achieve a steady sample temperature as desired. A clean empty crucible is then used to zero the hot thermal balance. This crucible is removed from the thermal balance and replaced by another crucible, which has been preweighed, filled with porcelain chips and the thermal balance is returned to the desired temperature. This establishes the total weight for use by the data acquisition unit and for the background. The sample is introduced into the clean empty crucible making sure that the total weight (crucible + sample) is identical (± 0.1 mg) to that of the crucible containing porcelain chips. The thermal balance is now arrested, the furnace is raised, the crucibles are switched, the thermal balance disarrested and the furnace lowered into place. The entire operation of crucible switching can be carried out, by an experienced operator, in 15 sec, while the balance stops swinging, after disarrest, in 7.5 sec. In this way one or two points are printed (printing of weight data on strip chart occurs every 4 sec) before weight loss is first recorded. The data acquisition unit is paused after total weight is established and before the thermal balance is arrested; it is restarted immediately after balance disarrest.

For some experiments "wet air" was used. In such cases, the air from the cylinder was bubbled through a gas washer tube filled with demineralized water prior to entering the thermal balance.

Calcium chloride experiments

Several experiments were carried out with analytical grade hydrated calcium chloride in the thermal balance. In all of them, the salt was heated, at a heating rate of 10°C/min, up to 900°C, and then held at that temperature until a constant weight was reached, at a flow rate of 50 cm^3/min of air (dry or wet).

One experiment was carried out in which 0.520 g of $CaCl_2$ was heated in the large porcelain sample boat in the tube furnace, with a flow of 100 cm^3/min of dry air. The sample boat was inserted gradually, to drive off the water of hydration, until a temperature of >750°C was achieved, after 40 min. In another 10 min the temperature was raised to 900°C, where it was kept for 2 hr. The outflowing gases were bubbled through a hydrogen peroxide solution (0.8%). H_2O_2 will trap any chlorine present and convert it into chloride. Both pH titration and a chloride ion selective electrode were used to measure the amount of chloride ion in the solution, after boiling off any H_2O_2 remaining.

Table 1. Composition of poly(vinyl chloride) samples (wt %)*

	C3†	SN23
Chlorine content	22.8	25.5
Plasticizer	20.5	14.8
$CaCO_3$ filler	39.3	33.8
Non-Ca residue‡	0.7	4.4

*Proportion of major components only, does not add up to 100%.

†Composition measured by tetrahydrofuran/methanol separation, and by other standard analytical procedures.

‡Amount of inorganic calcium-free material remaining after calcination.

Materials

All materials used were PVC compounds with proprietary compositions which could be used for electric wire insulation purposes. Materials C3 and B were supplied by Carlew Chemicals Ltd and by BFGoodrich Canada Inc., respectively, to the Canadian Standards Association for development of an acid gas analysis test; materials SN8, SN9, SN22, SN23 and SN24 were prepared by the BFGoodrich Co., Geon Vinyl Division, for the development of a different test method for acid gas analysis, viz. the Coil method [11]. Materials SN22, SN23 and SN24 are of similar composition but contain increasing levels of $CaCO_3$. An approximate analysis of C3 was made by various analytical methods, including a standard tetrahydrofuran/methanol separation procedure [12]. Table 1 presents details of the composition of the two PVC compounds used for most of the experiments.

RESULTS

Figure 1 shows a comparison made between the two methods used for analysis of acid gas evolution, viz. NaOH titration or ion selective electrode titration. It is evident from the distribution of experimental data around a straight line of slope 1.0 that both methods of analysis produce totally equivalent results.

Table 2 presents the results of the experiments carried out to measure acid gas emission in the tube furnace equipment; Table 3 presents results for some experiments carried out in the coil method. It is clear that there can be a large degree of variability in the results, depending not only on the method used but also on the exact conditions of the experiment. In particular, the emission of acid gas, as measured by the tube furnace procedure, will increase if the tem-

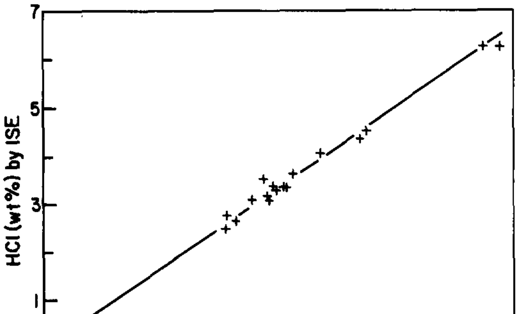

Fig. 1. Comparison of two methods for measuring acid gas emission: ion selective chloride electrode (ISE) and pH titration.

Table 2. Furnace tube results

Experiment	Sample	Temperature (°C)	HCl (wt % sple)	Residue (wt % sple)	Soot	Conditions
8*	C3	900	2.97		Abundant	Cov. 2″ porc. boat
3*	C3	900	3.32		Abundant	Cov. 2″ porc. boat
9*	C3	900	3.20		Abundant	Cov. 0.5″ Pt boat
10*	C3	900	3.43		Abundant	As 9 + Pt screens
11*	C3	900	4.51		1/4 amt	As 9 + porc. screens
12†	C3	900	4.60		None	As 1 + ceramic fibre
13†	C3	900	6.28	31.4	None	As 12 but uncovered
14†	C3	900	3.22	32.2	None	Uncov. Pt bt + cerm. fibre
15†	C3	900	3.13	32.3	None	As 14
16†	C3	900	6.51	24.8	None	As 14 with wet air
1*	C3	800	2.60		Abundant	Cov. 2″ porc. boat
6*	C3	800	2.61		Abundant	Cov. 2″ porc. boat
17†	C3	800	2.76	31.0	None	As 14
COIL 3	C3	650‡	1.5		N.A.	N.A.
4*	SN23	900	3.55		Abundant	Cov. 2″ porc. boat
7*	SN23	900	3.94		Abundant	Cov. 2″ porc. boat
21†	SN23	900	3.94	37.2	None	As 14
2*	SN23	800	3.47		Abundant	Cov. 2″ porc. boat
5*	SN23	800	3.29		Abundant	Cov. 2″ porc. boat
20†	SN23	800	3.26	37.0	None	As 14
COIL 12	SN23	650‡	2.9		N.A.	N.A.
18†	B	900	9.71	25.4	None	As 14
19†	B	900	12.35	21.0	None	As 14 with wet air
COIL 1	B	650‡	8.2		N.A.	N.A.
23†	SN8	900	29.01		1/4 amt	Covered 2″ porc. boat
26†	SN8	900	26.40	10.2	None	As 14
25†	SN8	800	25.90	13.7	None	As 14
22†	SN8	650	25.35		Trace	Covered 2″ porc. boat
28†	SN9	900	18.09		1/4 amt	Covered 2″ porc. boat
30†	SN9	900	16.55	22.8	None	As 14
29†	SN9	800	16.11	24.6	None	As 14
27†	SN9	650	15.98		Trace	Covered 2″ porc. boat

*0.7 g sample; †0.35 g sample; ‡equivalent temperature.

perature is higher and if there is water present in the atmosphere. Experiments carried out at 650–700°C and above (Table 2) show that the levels of acid gas emission increase with temperature. Another parameter, the importance of which is less immediately apparent, is the formation of soot. When soot is formed, it will adsorb HCl and, consequently, the level of HCl subsequently measured is slightly lower than would be the case if all the soot had been burnt off.

The size of the sample boat can also have a strong effect on the quantity of HCl found; a smaller boat will result in better temperature distribution and more efficient retention of HCl. Figure 2 shows the temperature profile within the furnace, making clear the very large temperature gradient found at the upstream end of the furnace. Therefore, a large boat will result in very uneven heating of the sample, in the initial stages of the reaction.

A calculation can be made from the results obtained for HCl emitted, as to the efficiency of the $CaCO_3$ used in the PVC compound. The reaction which takes place between the HCl and the $CaCO_3$ filler is:

$$2HCl + CaCO_3 \rightarrow CaCl_2 + CO_2 + H_2O,$$

The formula to be used is, thus:

$$\text{Efficiency} = \frac{\begin{array}{c}[\text{mol HCl present in 100 g}\\ -\text{ mol HCl emitted by 100 g}]\end{array}}{2 \times \text{mol Ca present in 100 g}} \times 100$$

Table 3. Coil test results

Experiment	Sample	HCl wt % sample
Coil 1	B	8.2
Coil 2	B	8.2
Coil 3	C3	1.5
Coil 4	C3	2.2
Coil 5	C3	2.0
Coil 6	C3	1.9
Coil 8	SN8	24.4
Coil 9	SN8	25.1
Coil 10	SN9	16.0
Coil 11	SN9	15.0
Coil 12	SN23	2.9
Coil 13	SN23	2.7

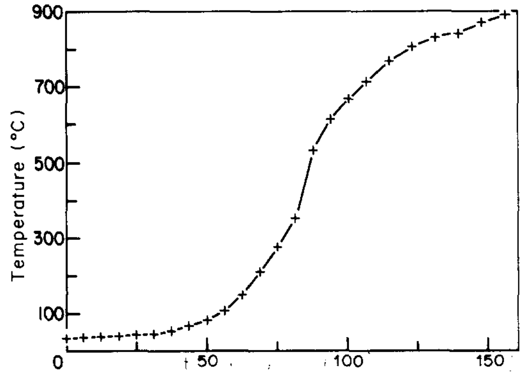

Fig. 2. Distance–temperature trace in the tube furnace used.

where:

mol HCl emitted = (wt % HCl emitted/M_w HCl);

"mol HCl present in 100 g" is the number of moles of HCl which would correspond to the chlorine contained in 100 g of original PVC compound; "mol Ca present in 100 g" is the number of moles of $CaCO_3$ present in 100 g of original PVC compound and "wt % HCl emitted" is the wt % of HCl emitted from the burnt compound, as shown in Tables 2 and 3. Table 4 presents the results of these calculations, for all the experiments reported in Tables 2 and 3.

Tables 5–10 present the results of the thermoanalytical experiments carried out at a fixed temperature of 700, 800 or 900°C, in dry air (labelled 700D, 800D and 900D) or in air saturated with water vapour (wet air, labelled 700W, 800W and 900W). Each column of each of these Tables presents the results, in chronological order, of the one or more experiments carried out on the corresponding compound. The preliminary experiments were only taken up to the end of the rapid weight loss stages. Thus, three weight loss stages occur within a very short period (< 10 min), the first of which is over within less than 30 sec. Those experiments designated L were run for several hours, at least overnight.

Table 4. Efficiency of HCl retention by calcium carbonate filler in acid gas emission test

Sample	Experiment	HCl emission (wt %)	Efficiency (%)
C3	1	2.60	73
C3	3	3.32	70
C3	6	2.61	73
C3	8	2.97	71
C3	9	3.20	71
C3	10	3.43	70
C3	11	4.51	66
C3	12	4.60	66
C3	13	6.28	60
C3	14	3.22	70
C3	15	3.13	71
C3	16	6.51	59
C3	17	2.76	72
C3	Coil	2.20	74
C3	Coil	1.51	76
C3	Coil	1.97	75
C3	Coil	1.86	75
SN23	2	3.47	92
SN23	4	3.55	92
SN23	5	3.29	93
SN23	7	3.94	90
SN23	20	3.27	93
SN23	21	3.95	90
SN23	Coil	2.86	95
SN23	Coil	2.67	96

Table 11 presents the results of thermoanalytical experiments where the samples were heated using a gradual temperature rise of $10°C\,min^{-1}$. The total weight loss for either sample C3 (*ca* 62 wt %) or sample SN23 (*ca* 57 wt %) during gradual heating is of the same order as that during the first three weight loss stages under any of the other (isothermal) conditions, particularly in the latter runs, where the sample was left in the thermobalance for many hours. Furthermore, introducing water into the atmosphere, during gradual heating, has virtually no effect on the thermoanalytical results.

At the end of these three weight loss stages, the residue will continue losing weight very slowly when it is heated further for very long periods. At least one experiment was carried out under each of the six isothermal conditions for the two main compounds investigated, viz. C3 and SN23. These were the experiments used to calculate the fourth weight loss, which occurred over a period of only a few hours at 900W, but over a period of more than 60 hr at 700D. It is clear from these results that the use of high temperatures and/or of wet air will affect both the amount and the chemical composition of the residue finally obtained. This can be seen by comparing the results of the isothermal runs with those in Table 11, at a heating rate of $10°C\,min^{-1}$. Further heating at 700°C in dry air has a relatively small effect on the residue: there is an additional weight loss of only *ca* 6 wt % for C3. However, when the atmosphere is saturated with water or when the temperature is 800 or 900°C, the additional weight loss is *ca* 17 wt % for C3.

Table 5. STA runs at 700°C in dry air*†

	C3	SN22	SN23	SN24
Total wt loss (%) (after 3 stages)	65.8–65.7 62.7L–63.6L	65.3–68.8 63.0	61.9–59.8L	55.1
1st loss (wt %)	50.4–50.6 47.4L–47.4L	41.6–43.1 39.1	42.1–39.7L	36.5
Average rate (%/min)	168–145 119L–119L	104–144 130	140–99L	146
2nd loss (wt %)	9.9–9.0 11.0L–10.9L	15.1–17.0 16.3	11.8–12.2L	11.5
Average rate (%/min)	20–18 15L–20L	30–28 23	21–20L	23
3rd loss (wt %)	5.5–6.0 4.3L–5.3L	8.7–8.6 7.6	8.0–7.9L	7.1
Average rate (%/min)	0.6–0.8 0.6L–0.8L	1.7–1.2 1.3	1.1–1.3L	1.2
4th loss (wt %)	5.8L–7.2L		9.2L	
Average rate (%/hr)	0.1L–0.1L		0.1L	
Total wt loss (%) (after 4 stages)	68.5L–70.9L		69.1L	

*Various runs under the same conditions are reported successively in each column; †L: long runs.

Table 6. STA runs at 700°C in wet air*†

	C3	SN22	SN23	SN24
Total wt loss (%) (after 3 stages)	65.8–65.7 63.9L	70.3–66.1	61.8–61.4 58.4L–60.4L	55.8
1st loss (wt %)	50.5–49.8 47.6L	46.5–44.9	42.4–40.4 39.4L–40.9L	36.9
Average rate (%/min)	126–100 127L	93–150	106–101 113L–117L	123
2nd loss (wt %)	10.3–11.6 10.9L	13.1–12.4	11.8–12.8 10.9L–12.9L	11.9
Average rate (%/min)	19–18 17L	26–24	24–26 22L–19L	24
3rd loss (wt %)	4.9–5.3 5.4L	10.7–9.3	7.6–8.2 8.1L–6.6L	6.9
Average rate (%/min)	0.8–0.7 0.8L	1.3–1.1	1.0–1.2 1.1L–0.9L	1.0
4th loss (wt %)	16.1L		19.8L–17.5L	
Average rate (%/hr)	0.2L		0.4L–0.6L	
Total wt loss (%) (after 4 stages)	80.0L		78.2L–77.8L	

*Various runs under the same conditions are reported successively in each column; †L: long runs.

Table 7. STA runs at 800°C in dry air*†

	C3	SN22	SN23	SN24
Total wt loss (%) (after 3 stages)	63.5–62.0L	71.1	60.8–60.5L 63.6L	56.1
1st loss (wt %)	44.4–48.0L	49.7	42.5–42.9L 42.8L	37.7
Average rate (%/min)	178–192L	248	170–143L 143L	151
2nd loss (wt %)	16.0–9.7L	12.4	11.2–10.8L 13.7L	11.5
Average rate (%/min)	27–28L	41	45–36L 39L	38
3rd loss (wt %)	3.0–4.3L	9.0	7.1–6.8L 7.1L	6.9
Average rate (%/min)	0.5–1.2L	1.4	1.1–1.3L 1.5L	0.9
4th loss (wt %)	18.8L		18.2L 16.0L	
Average rate (%/hr)	1.0L		0.7L 0.8L	
Total wt loss (%) (after 4 stages)	80.8L		79.3L 79.6L	

*Various runs under the same conditions are reported successively in each column; †L: long runs.

Table 8. STA runs at 800°C in wet air*†

	C3	SN22	SN23	SN24
Total wt loss (%) (after 3 stages)	61.3L	68.8–68.8	57.3–61.7L 62.5L	55.8
1st loss (wt %)	46.7L	47.5–48.6	43.1–41.3L 41.6L	40.1
Average rate (%/min)	187L	190–194	172–165L 167L	160
2nd loss (wt %)	10.8L	11.9–11.3	11.1–12.0L 12.8L	10.9
Average rate (%/min)	27L	34–32 23	32–40L 37L	36
3rd loss (wt %)	3.9L	9.3–8.5	3.1–8.4L 8.0L	4.9
Average rate (%/min)	1.0L	1.2–1.4	0.7–1.2L 1.3L	1.0
4th loss (wt %)	18.7L		17.6L	
Average rate (%/hr)	2.7L		2.4L	
Total wt loss (%) (after 4 stages)	80.0L		80.0L	

*Various runs under the same conditions are reported successively in each column; †L: long runs.

Table 9. STA runs at 900°C in dry air*†

	C3	SN22	SN23	SN24
Total wt loss (%) (after 3 stages)	64.0–61.7L	69.8	61.7–57.1L	56.4
1st loss (wt%)	51.0–49.2L	48.5	38.5–40.0L	41.6
Average rate (%/min)	170–197L	194	192–200L	208
2nd loss (wt %)	8.1–8.5L	11.7	17.0–10.5L	7.9
Average rate (%/min)	33–34L	58	42–70L	40
3rd loss (wt %)	4.8–4.0L	9.7	6.3–6.6L	6.9
Average rate (%/min)	0.7–1.4L	1.4	1.4–2.1L	0.7
4th loss (wt %)	19.8L		20.8L	
Average rate (%/hr)	1.9L		2.0L	
Total wt loss (%) (after 4 stages)	81.3L		77.9L	

*Various runs under the same conditions are reported successively in each column; †L: long runs.

Another interesting comparison is between the weight lost in the first stage in the isothermal runs and that lost in those runs with a 10°C min^{-1} heating rate. The average weight loss for the isothermal runs is *ca* 8 wt % greater than that for the runs with gradual heating, both for C3 and for SN23.

The residue remaining after the long thermoanalytical experiments does not contain any $CaCO_3$; this is all destroyed and converted into calcium oxide, as becomes clear from the results of the thermoanalytical experiments with commercial $CaCO_3$ (Table 11).

It was decided to carry out experiments with calcium chloride, under the same conditions as the experiments performed with the PVC compounds, in order to obtain a better understanding of the behaviour of the residues from combustion or thermal decomposition of the PVC compounds.

A thermoanalytical experiment was carried out, with hydrated $CaCl_2$ in wet air: it was heated at 10°C min^{-1} up to 900°C and then maintained at that temperature until a constant weight was reached. Figure 3 shows that $CaCl_2$ dehydrates endothermally ($\Delta H = 96$ kJ/g) at a temperature range of 118–175°C (21.5% wt loss). It then, when heated gradually, maintains its weight until a temperature of over 850°C, i.e. until soon after the calcium salt melts ($\Delta H = 16$ kJ/g, at 772°C), when it slowly, and exothermally, loses weight ($\Delta H = -103$ kJ/g, 33.9% wt loss, average reaction rate *ca* 26%/hr).

When the same thermal decomposition is carried out in dry air, the dehydration occurs, not sur-

Table 10. STA runs at 900°C in wet air*

	C3	SN22	SN23	SN24
Total wt loss (%) (After 3 stages)	62.5L	65.3	60.3L	55.1
1st loss (wt %)	48.1L	44.5	41.7L	40.6
Average rate (%/min)	192L	178	208L	162
2nd loss (wt %)	9.6L	11.7	10.9L	8.2
Average rate (%/min)	32L	47	55L	33
3rd loss (wt %)	4.8L	8.9	7.7L	6.3
Average rate (%/min)	1.5L	1.8	2.0L	1.7
4th loss (wt %)	17.8L		18.2L	
Average rate (%/hr)	3.6L		6.6L	
Total wt loss (%) (after 4 stages)	80.3L		78.5L	

*L: long runs.

Table 11. STA runs at heating rate of 10°C/min in air

	C3D	C3W	SN23D	$CaCO_3$D	$CaCO_3$W
Total wt loss (%)	61.2	60.6	57.2	42.3	44.2
1st loss (wt %)	39.0	39.6	33.4	42.3	44.2
Temp. range (°C)	258–360	248–360	263–360	650–780	620–825
Max. Rate (%/min)	9.8	9.2	10.8	6.1	5.6
Temp. max rate (°C)	297	315	300	772	773
DTA area (kJ/g)	−32.80	−29.33	−29.85	−116.23	−123.26
2nd loss (wt %)	11.8	11.6	12.1		
Temp. range (°C)	360–490	360–490	360–490		
Max. Rate (%/min)	2.5	2.0	2.5		
Temp. max rate (°C)	440	435	425		
DTA area (kJ/g)	−7.75	−4.70	−9.86		
3rd loss (wt %)	10.4	9.4	11.6		
Temp. range (°C)	490–650	490–650	490–625		
Max. Rate (%/min)	1.7	1.4	2.4		
Temp. max rate (°C)	580	565	540		
DTA area (kJ/g)*	−162.22	−146.67	−229.27		
$T_{1\%}$ (°C)	262	256	269	650	620

*Both PVC compounds have an additional DTA peak with areas corresponding to −0.28, −2.73 and −0.82 kJ/g respectively.

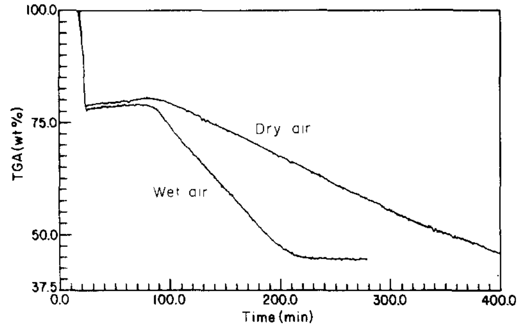

Fig. 3. Wt % of original sample remaining after thermogravimetric experiments with hydrated calcium chloride in an atmosphere of wet air and in one of dry air.

prisingly, at virtually the same temperature (between 115 and 170°C; $\Delta H = 89$ kJ/g). Once again the material melts at 772°C without having lost weight after dehydration. Of more interest, however, is the fact that the anhydrous $CaCl_2$ loses weight, immediately after melting (at a temperature above 870°C), at a constant rate of *ca* 7%/hr. Furthermore, the weight loss for this stage varied, in the various experiments carried out, between 30.5 and 46.7% wt. Figure 3 shows that this reaction continues for a very long period at a surprisingly constant rate. Visual observation showed no residue inside the crucible. It was found, however, that there was ample evidence of $CaCl_2$ deposits at slightly cooler surfaces, in the vicinity of the crucible, inside the thermal balance and, partially, on the crucible assembly itself. It is clear, therefore, that, the variable weight loss for the final stage is a function of the localization of these $CaCl_2$ deposits (i.e. they are weighed, if they remain on the crucible support, which is much cooler than the crucible itself). On reheating the crucible, with its contents, no melting occurred at the temperature corresponding to $CaCl_2$, indicating that no free $CaCl_2$ remained.

An experiment carried out with $CaCl_2$ and dry air in the tube furnace showed that a significant proportion of the chlorine content of the salt is given off. Measurement of the chloride present in the aqueous solution showed that 3.65×10^{-3} mol were present (identical results from chloride electrode and pH titration). This amount of chloride corresponds to 51.6% of the chlorine initially present in the salt. The total weight loss during the experiment was 47.0 wt %. This result is consistent only with partial oxidation to form calcium oxide and chlorine and partial volatilization of $CaCl_2$.

Table 12 shows the calculations of the efficiency of the $CaCO_3$ filler from thermoanalytical experiments. In this case, although the efficiency is related to the same chemical reaction, it is calculated from the amount of residue rather than from the amount of HCl emitted, as was the case for the data in Table 4. Assuming that the calcium has not volatilized, the equation to be used here is:

$$\begin{aligned}\%\,\text{Ca residue} &= \text{mol Ca present in } 100\,\text{g}\\ &\quad \times \{(\text{efficiency}/100 \times M_w\,\text{CaCl}_2)\\ &\quad + [(100 - \text{efficiency})/100]\\ &\quad \times M_w\,\text{CaO}\}\end{aligned}$$

where "% Ca residue" is the wt % of calcium compounds (either $CaCl_2$ or CaO) present in the residue and "mol Ca present in 100 g" has been defined before.

The residue remaining after thermal analysis contains not only $CaCl_2$ and CaO but also some calcium-free products. It becomes necessary, therefore, to define this additional residue. Here "% non-Ca residue" is the wt % of non-combustible inorganic residue into which the components of the original PVC compound other than $CaCO_3$ will be transformed after combustion. Thus:

$$\begin{aligned}\%\,\text{Ca residue} &= 100 - \%\,\text{wt lost}\\ &\quad - \%\,\text{non-Ca residue}\end{aligned}$$

Table 12. Efficiency of retention of HCl by calcium carbonate filler in thermal analysis

		After 3 stages			After 4 stages	
Sample	STA	Wt loss (wt %)	Efficiency (%)	Average (%)	Total loss (wt %)	Final efficiency (%)
C3	700D	62.7	67		68.5	41
C3	700D	63.6	63		70.9	29
C3	700W	63.9	62		80.0	0
C3	800D	62.0	71	68	80.8	*
C3	800W	61.3	74		80.0	0
C3	900D	61.7	72		81.3	*
C3	900W	62.5	68		80.3	0
C3	10°C HRD	61.2	74	76		
C3	10°C HRW	60.6	77			
SN23	700D	59.8	91		69.1	41
SN23	700W	58.4	98		78.2	0
SN23	700W	60.4	88		77.8	0
SN23	800D	60.5	87	88	79.3	*
SN23	800D	63.6	70		79.6	*
SN23	800W	62.5	76		80.0	0
SN23	900D	57.1	105		77.9	*
SN23	900W	60.3	88		78.5	0
SN23	10°C HRD	57.2	104	104		

*Efficiency cannot be calculated.

Using the above two equations it is then possible to calculate the efficiency of the $CaCO_3$ as:

$$\begin{aligned}\text{Efficiency} = \{&[(\%\text{ Ca residue} \times 100)/\\ &\text{mol Ca present in } 100\text{ g}]\\ &-(100 \times M_w\,\text{CaO})\}\\ &\times [1/(M_w\,\text{CaCl}_2 - M_w\,\text{CaO})]\end{aligned}$$

A comparison of the results in Tables 12 and 4 shows that the average efficiency at the end of the three weight loss stages for C3 (viz. 68%) is very similar to the efficiency of those tube furnace experiments where the conditions were optimized, i.e. experiments number 14 and 15 (70%). However, by the time that all the weight is lost, the efficiency has dropped to zero, except for the STA runs at 700D. The same results were found for SN23 also where the corresponding numbers are 88% for STA and 90% for tube furnace experiment 21, although the efficiency of the $CaCO_3$ used for this compound is much higher than that used for C3.

DISCUSSION

It has been shown often that thermoanalytical experiments can offer a good indication of the reactions during the burning of a polymeric material [13–16]. In this particular example, the STA technique has been used to understand both the order in which combustion processes occur, in a tube furnace test and in a coil test devised to measure emission of acid gases (HCl) from burning PVC wire coating compounds, and their mechanism. It is important to keep in mind, when such tests are being developed, that the ultimate objective is the modelling of hazard in a real fire situation. Therefore, the test conditions should be such that the material is not subjected to excessive stresses, because otherwise some of the safeguards introduced by the manufacturers to improve safety may be destroyed during the test, while they would remain intact during an actual fire.

The $T_{1\%}$ (temperature of 1% weight loss [17–18], representing the thermal stability of the PVC compound) is *ca* 260°C, for both C3 and SN23. Furthermore, virtually the entire organic fraction of the PVC compounds is lost at a temperature well below 700°C (Table 11), with the dehydrochlorination (first stage [19, 20]) taking place well below 400°C. There is very little difference in the total weight lost or in the distribution of weight lost in the various stages of polymer breakdown when the STA experiments are carried out isothermally at 800 or 900°C in dry air or at 700, 800 or 900°C in wet air (Tables 5–10). The main difference between these five conditions is given by the rates of weight loss at the various stages, and even these are, to a large extent, governed by the mechanical rates of heating and evaporation of the sample itself. Runs at 700°C in dry air are relatively little affected by long further heating.

The presence of an atmosphere saturated with water will lead to an increased emission of HCl, a result which can be deduced also from the presence of a smaller amount of residue, both in the STA runs and in the tube furnace experiments.

The reactions of interest are:

$$\sim H_2C\text{–}CHCl\sim \;\rightarrow\; \sim HC{=}CH\sim + HCl \qquad (1)$$

$$2HCl + CaCO_3 \rightarrow CaCl_2 + H_2O + CO_2 \qquad (2)$$

$$HCl\,(s) \rightarrow HCl\,(g) \qquad (3)$$

$$CaCO_3 \rightarrow CaO + CO_2 \qquad (4)$$

$$CaCl_2 + H_2O \rightarrow 2HCl + CaO \qquad (5)$$

Reaction (1) is normally complete at *ca* 360°C (see Table 11 and Ref. 20). A molecule of HCl formed as a result of reaction (1) can either react with $CaCO_3$ [reaction (2)], until the efficiency of the filler is reached (i.e. the filler becomes saturated) or it can be emitted [reaction (3)]. Reactions (4) and (5) will only occur at very high temperatures: reaction (4) above 650°C (Table 11) and reaction (5) above the melting point of $CaCl_2$ viz. 772°C (Fig. 3, Ref. 21).

The fact that the efficiency of $CaCO_3$ is virtually identical between isothermal STA runs and tube furnace runs at optimized conditions (70% for runs 14 and 15 and 68% average for isothermal runs, in the case of C3; 90% for run 21 and 88% average for isothermal runs, in the case of SN23) suggests that STA is in fact here too a good model for the test.

It is clear that, the higher the temperature at which the tube furnace test is carried out, the higher the HCl emission will be. This is further confirmed by the fact that the emission from the coil test is much lower than that of the STA test, while it corresponds very well with the emission at 650°C (see SN8 and SN9 in Tables 2 and 3). The results have shown that a high temperature for the test (above 700°C) has two types of effects on HCl emission from these compounds (or on the efficiency of the $CaCO_3$ filler).

On the one hand, the lower efficiency during isothermal runs (after 3 weight loss stages) than during gradual heating runs (Table 12), coupled with the fact that there is a significantly larger weight loss in the first stage of the isothermal runs, indicates that there is a much greater likelihood of HCl being emitted before it has had the opportunity of reacting with the filler. This is a consequence of the fact that it is at this first stage of weight loss when the dehydrochlorination takes place [19, 20]. This means that reaction (3) will occur, to some extent, even before the efficiency of $CaCO_3$ has been reached, i.e. if the $CaCO_3$ filter is overwhelmed by the amount of HCl formed, due to extremely rapid occurrence of reaction (1). If the temperature of the experiment exceeds 650°C, reaction (4) will also contribute to an early decrease in the efficiency of the $CaCO_3$.

On the other hand, prolonged heating in wet air at a high temperature (700°C or above) will cause thermal decomposition of the $CaCl_2$ already formed, as evidenced by the results with $CaCl_2$ itself. In other words, reaction (5) will start. In this connection it is worth pointing out that the structure of most carbonaceous combustion products (whether soot or char) is C_8H [22]. This small presence of H atoms is generally totally irrelevant from the point of view of the weight of carbonaceous residue, but it is potential source of H atoms in dry atmospheres. When $CaCl_2$ undergoes prolonged heating in dry air at high temperatures, it starts volatilizing soon after reaching its melting point (772°C) [21], which is consistent with what has been shown elsewhere [23], viz. that $CaCl_2$ will volatilize (or even sublime) at very high temperatures. It has also been shown that the oxidation of $CaCl_2$, in dry atmosphere (i.e. containing no H atoms) can yield chlorine. The reaction of $CaCl_2$ oxidation will be strongly dependent on the environmental conditions, since the reaction leading to formation of HCl is three times as fast as that leading to chlorine evolution (Fig. 3), and since various other factors can affect it. These include the heating history [24], the type and extent of surface exposed [25, 26] and the presence of catalysts (in particular alumina [25]) and the presence of radiation [27]. All this has shown that $CaCl_2$ cannot be used as a thermogravimetric standard [28] because of the potential variations in its behaviour. It is clear, however, that $CaCl_2$ will oxidize primarily, albeit rather slowly, by reaction (5), in the presence of moisture. Under dry conditions $CaCl_2$ does not generate chlorine quantitatively, as reported elsewhere [29], but the weight loss found, in the absence of H atoms at high temperatures, is partially due to chlorine formation and partially due to volatilization. In an actual fire atmosphere, moreover, no chlorine is at all likely to be formed, in view of the ubiquitous presence of H atoms in various compounds.

The values of efficiency of $CaCO_3$ calculated from STA runs and shown in Table 12 can be used to calculate the emission of HCl at the end of the three main weight loss stages or at the end of the entire (long) STA runs. Table 13 compares these calculated results with the actual observed emissions from the tests and with the maximum amount which could have been emitted, from the chlorine content of the original compound. The values of HCl emission calculated at the end of the fourth STA stage are only slightly higher than the theoretical values, which is a good indication that the assumptions used for estimating efficiencies have internal consistency.

It can be assumed that the STA runs at 10°C min^{-1} are fairly representative of the efficiency of the $CaCO_3$ in terms of a slow heating process and they show the lowest values of HCl emission. When the samples are subjected to a sudden heat stress, the efficiency of the filler may be decreased, depending on the severity of the stress. Thus, the coil test method will represent a sudden rise in temperature, which is not sustained for a long period, and only reaches a top temperature of 350°C. On the other hand, the tube furnace test represents a sudden (albeit slightly less sudden than in the coil test) rise in temperature, but where the final temperature is maintained for a considerable period. This means that, in the coil test, there may be a small effect of reaction (3) occurring before the filler has been saturated. However, the efficiencies calculated (Tables 4 and 12) show that the amount of HCl emitted under both conditions is virtually the same. It has been shown (Tables 2 and 3 and Ref. 11) that the coil test gives results equivalent to those from a tube furnace test carried out at 650°C. It is not, however, clear which stage of the thermal decomposition process represents the end of the tube furnace test at 800 or 900°C. In fact, the combined effects of test temperature and test duration will alter the exact moment in the breakdown process to which the test results refer. Thus the relatively high emissions found with the tube furnace test indicate that it is modelling a moment in the thermal decomposition between the end of the first three stages and the total destruction or volatilization of the $CaCl_2$ formed. In these high temperature tube furnace tests, the efficiency of the $CaCO_3$ is decreased by reactions (4) and (5), and by premature occurrence of reaction (3). In the coil test and in the tube furnace test at 650°C neither reaction (4) nor reaction (5) will occur.

There are several conditions required to optimize the tube furnace test and make it as representative as possible to real life hazard. The most important are:

(*a*) *Furnace temperature*

If the temperature exceeds 700°C, there will be a certain proportion of the HCl generated from the PVC compound which will be emitted before it can react with $CaCO_3$. This is counterproductive, because it means that the test will have destroyed one of the safeguards introduced by the manufacturer without there being any gain in safety. The temperature at which "flashover" occurs in a compartment fire is 500–600°C [22, 30, 31], so that there is no possibility of any survivors being present after such a condition is reached. Even after a prolonged fire, the temperatures of wire coating materials will only gradually reach very high values, and will only remain high for short periods.

(*b*) *Presence of soot*

Soot is a combustion product, generated by most polymeric materials [22], with a very sorptive surface, which will, therefore, strongly adsorb HCl [32–34] and even retain a significant proportion of the HCl

Table 13. Hydrogen chloride emission (wt %)*

	C3	SN23
Tube furnace (800°C)	2.8	3.3
Tube furnace (900°C)	3.2	4.0
Coil	1.9	2.8
STA isothermal (after stage 3)	3.9	4.5
STA 10°C min^{-1} (after stage 3)	1.7	0.0
STA isothermal (after stage 4—700D)	11.8; 15.0	16.2
STA isothermal (after stage 4—700W)	27.0	28.2; 27.7
STA isothermal (after stage 4—800W)	27.0	30.6
STA isothermal (after stage 4—900W)	27.4	28.6
STA isothermal (after stage 4—800D; 900D)	†	†

*HCl emission from STA was calculated based on the efficiencies; the total amount of HCl available is 23.4 wt % for C3 and 26.2 wt % for SN23.

†The STA runs in dry air at temperatures above 700°C emit very little HCl beyond the third weight loss stage.

generated. It is, therefore, very important to eliminate the soot generated (by burning it off) before measuring the amount of HCl emitted, to avoid errors, particularly of reproducibility. It is extremely difficult, if not impossible, to extract any HCl which has been trapped by soot particles, because it is likely to be formed in layers which grow with the growth of the carbonaceous layers themselves. The complete destruction of the soot formed will result in a measured value for HCl emission which is higher than it should be, compared to a large-scale situation, but it will nevertheless improve test performance. Of the various methods investigated to trap the soot particles, the use of a ceramic fibre downstream from the sample boat, within the heated zone of the combustion tube, was found to be the most efficient.

(c) *Size of the boat*

A long (> 15 mm) boat will result in uneven heating of the sample, as evidenced by the temperature profiles in Fig. 2, and thus in a decreased efficiency of the filler and in poor reproducibility of the procedure. This is due to the fact that the efficiency of the filler is related to the rate of temperature rise of the sample, since very high heating rates (unlikely to affect a wire coating in a fire) decrease $CaCO_3$ efficiency. The steep temperature gradients at the entrance of the furnace mean that a relatively small boat will be much more likely to have a better temperature distribution.

(d) *Rate of introduction of the boat*

If the boat is introduced into the furnace in a few rapid steps, this will again result in uneven heating and in irreproducibility of results, for analogous reasons to the use of a long boat, i.e. temperature gradients in the furnace. A continuous entry process, or one of many short steps, will result in best test performance.

(e) *Air access to sample*

If the sample is covered, the temperature distribution is improved considerably. This results, however, in a somewhat greater isolation of the sample from the air and from the combustion products (typically water), and thus in lower HCl emission. Since in a real fire the sample will not be shielded from air and combustion products and since good access of the sample to the atmosphere will result in better reproducibility, notwithstanding the inferior temperature control, the sample boat should not be covered.

(f) *Sample size*

The size of the sample is not crucial to test results, but the use of a small sample, probably no larger than 0.5 g, will improve the temperature distribution and thus reproducibility. This is particularly the case since a large sample may have cooler spots which will not emit HCl as quickly as the rest of the sample. There is an additional reason for preferring a small sample, and it involves the issue of safety: the larger the sample the greater the risk of achieving flaming combustion, rather than smouldering combustion, and thus creating potentially hazardous conditions because of the confined area and the very high temperatures.

(g) *Ambient humidity*

The amount of water present in the atmosphere will affect the efficiency of the filler and the test results. A combustion process will already liberate water as one of its products. Therefore, to maximize reproducibility of the test, the air fed into the chamber should be dry.

(h) *Condensed non-sooty material*

Brown/black material is often condensed on the walls of the combustion tube and can be burnt off, either during or after the test. This represents non-graphitic material of a very different nature from either soot or char. The presence of this condensate, to a large extent derived from plasticizer breakdown, is of little practical importance in terms of HCl production, since it is a very non-sorptive material and will not affect HCl concentration [33]. On the other hand, the presence of soot will decrease the amount of HCl measured. Thus, the elimination of soot formation during the test will lead to an exaggerated upper limit of the amount of HCl formed from the material tested, but to a more reproducible test.

CONCLUSIONS

A tube furnace test can be used to model the acid gas emission from PVC wire coating materials in a fire in such a way that it yields reproducible results and, simultaneously, avoids destroying some of the acid retention measures (typically $CaCO_3$) introduced by the manufacturers. The technique of simultaneous thermal analysis has been used successfully to investigate the mechanisms of the reactions during the combustion. This has shown that the efficiency of the $CaCO_3$ filler as a trap for HCl can be strongly affected by the conditions under which the combustion is carried out. The $CaCl_2$ formed can be decomposed slowly, by the prolonged action of heat and humidity, into HCl and CaO. In the absence of humidity, $CaCl_2$ will volatilize, partially and slowly, at temperatures above its melting point. It is thus essential to choose test conditions which represent the potential hazard of acid gas in a fire. The most important parameters which need to be controlled are the temperature, the formation of soot and the humidity.

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