

TO D. Dobay	FIELD POINT OR ARROW DEPARTMENT & BLDG. NO. Sponge Products - Shelton	DATE THIS LETTER August 3, 1973
FROM M. M. O'Mara	FIELD POINT OR ARROW DEPARTMENT & BLDG. NO. Avon Lake Technical Center	
SUBJECT Combustion Products From Rigidcell		

Combustion Products From Rigidcell

Summary:

An analysis of the primary combustion products from Rigidcell (PVC-urethane foam from GPC) was carried out. Three different foams were exposed to radiant heat in the NBS smoke chamber (one foam exposed to flaming conditions) and the concentrations of CO, CO₂, HCL and HCN were monitored as a function of time. Concentration data were subjected to a toxicity factor calculation (I) and toxicity factors (T) were determined for each of the foams.

In general, significant contributions to T were made from HCL, HCN and CO. The yields of HCN from Rigidcell are within the yield limits already published in the literature. There is an approximate 2-10% conversion of nitrogen in the samples to hydrogen cyanide.

Under NBS flaming conditions, only a very low level of HCN was found.

Introduction

You submitted three samples of Rigidcell, the G.P.C. urethane - PVC foam, which exhibits an excellent flame spread rating, for a combustion product analysis. The main concern was the evolution of HCL, HCN and the oxides of carbon. As of this writing, we are continuing our investigation with respect to the identification of combustion/degradation products other than these primary products. A subsequent note will be published on this aspect of the analysis.

Analytical

Three materials R-650 (5/73), R-650 (1/71) and R-300 were exposed to 2.5 watts/cm² of radiant heat in the NBS smoke chamber. One of these (R-300) was exposed to flaming conditions. The combustion gases were analyzed by the following methods:

HCL - ion specific electrode
CO, CO₂ - gas chromatography
HCN - benzidine-hydrochloride method

(a) gas analysis

The carbon oxide analysis was performed by sampling a stream of combustion products from the NBS chamber. This was accomplished with the aid of a gas sampling loop (lcc volume) connected to a vacuum pump. Sample is withdrawn at a rate of 0.8 liters/minute and the batch analysis is initiated after a 15 second purge time. Dual column chromatography (Porapak Q, Molecular Sieve 5A) is used to separate the primary combustion products.

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The HCl, HCN analyses were obtained with a 50cc ground glass syringe. Previous work with an HCN gas standard indicated this was an acceptable procedure.

(b) C, H, N Analysis of Foams

The three rigid foams were submitted for a carbon, hydrogen, nitrogen analysis. The data are summarized in Table 1.

Table 1

C, H, N Analysis of Rigidcell Foams

	<u>C</u>	<u>H</u>	<u>N</u>
R-650 (5/73)	45.6±.3	4.8±.0	6.5±.1
R-650 (1/71)	47.4±.2	5.14±.03	6.8±.1
R-300	48.6±.3	5.0±.1	6.7±.1

Analysis R-650 (5/73)

Table 2 contains a summary of the combustion gas analysis for R-650 (5/73).

Table 2

Analysis of R-650 (5/73)

Sample weight: 6.48g

<u>time</u> (min.)	<u>HCl</u> (ppm)	<u>HCN</u> (ppm)	<u>CO₂</u> (ppm)	<u>CO</u> (ppm)
2.5	159	0	-	-
4.0	-	-	-	-
5.0	-	-	1006	0
8.0	-	-	-	-
10.5	439	-	-	-
12.0	-	28	-	-
15.0	-	-	4044	971
16.0	-	77	-	-
20.0	-	87	-	-
24.0	-	62	-	-
25.0	-	-	5369	1959

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Since we are still developing the chloride specific electrode it should be pointed out that the weakest link is this analysis. Theoretically this particular sample should release 2600 ppm of HCl (53.4% PVC; sample weight, 6.48g; volume of chamber, 514 liters). The fact that the actual value is less than 25% of this theoretical value is, however, not surprising due to the absorptivity of this gas.

Although there is no accepted method for assessing the toxicity of combustion products, Sumi⁽¹⁾ has suggested the use of a toxicity factor. In this application the overall toxicity of the combustion products is:

$$T = \sum Ce/Cf$$

where Ce is the concentration of the gas when one gram of material is burned and the products are diffused in a volume of one cubic meter and Cf is the concentration that is fatal (or dangerous) to man in a 30 minute exposure. With respect to Rigicell, this equation becomes:

$$T = \frac{Ce(CO_2)}{Cf(CO_2)} + \frac{Ce(CO)}{Cf(CO)} + \frac{Ce(HCl)}{Cf(HCl)} + \frac{Ce(HCN)}{Cf(HCN)}$$

The following values for Cf apply:

<u>gas</u>	<u>Cf</u>	<u>Reference</u>
HCN	135	2
CO	4000	3
CO ₂	70,000-100,000	2
HCl	1000	4

I have calculated Ce values based on the combustion of 1 gram of material diffused in a volume of one cubic meter. These values for R-650 (5/73) are based on maximum concentrations of each gas with no reference to time. Data are summarized in the next table.

Table 3

Toxicity Factor Calculation For R-650 (5/73)

<u>gas</u>	<u>Maximum Concentration in HBS Chamber</u>	<u>Ce</u>
HCl	439	34.7
CO	1959	154.7
CO ₂	5369	424.2
HCN	87	6.86

$$T = \frac{\text{HCl}}{1000} + \frac{\text{CO}}{4000} + \frac{\text{HCN}}{135} + \frac{\text{CO}_2}{70,000}$$

(cont.)

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T = .035 + .039 + .051 + .0061

T = .131

This analysis indicates significant toxicological contributions from HCl, HCN and (CO+CO₂).

Analysis of R-650 (1/21/71)

This material is similar to R-650 (5/73) except for the date of preparation. The question with respect to this sample was what effect does aging have on the subsequent release of hydrogen cyanide under combustion conditions. The C, H, N analysis of this material indicated that it was identical to R-650 (5/73).

The combustion gas data and toxicity calculation are summarized in the following tables.

Table 4

Analysis of R-650 (1/21/71)

Sample weight: 4.84g

<u>Time</u> (min.)	<u>HCl</u> (ppm)	<u>HCN</u> (ppm)	<u>CO₂</u> (ppm)	<u>CO</u> (ppm)
3.0	558	--	--	--
5.0	--	--	1326	138
8.0	--	11	--	--
12.0	--	25	--	--
13.0	634	--	--	--
15.0	--	--	4169	834
16.0	--	20	--	--
17.0	684	--	--	--
25.0	--	--	4441	894

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Table 5
Toxicity Factor Calculation For R-650 (1/21/71)

<u>gas</u>	<u>Maximum Concentration in NBS Chamber</u>	<u>Ce</u>
HCl	684	72.4
CO	894	94.6
CO ₂	4441	469.8
HCN	25	3.65

$$\begin{aligned}
 T &= \frac{\text{HCl}}{1000} + \frac{\text{CO}}{4000} + \frac{\text{HCN}}{135} + \frac{\text{CO}_2}{70,000} \\
 T &= .072 + .024 + .020 + .007 \\
 T &= .127
 \end{aligned}$$

The combustion analysis shows that aging does affect the subsequent release of hydrogen cyanide from R-650 when the material is burned. Although the nitrogen contents of the two materials are the same, the concentration of the molecular nitrogen structure which is responsible for the release of HCN is not.

In this case, the main contribution to the toxicity factor is due to the release of hydrogen chloride. One of the interesting outcomes of this analysis and the previous one is the different Ce values obtained for carbon monoxide. I have previously demonstrated⁽⁵⁾ that charring has a significant effect on the rate of carbon monoxide generation. We observed more charring under smoldering conditions with R-650 (5/73) than with R-650 (1/21/71). Thus this trend in carbon monoxide generation i.e., higher Ce value for R-650 (5/73), was expected.

The balance of carbon monoxide and carbon dioxide was constant for these samples. If a comparison of $Ce(\text{CO}_2) + Ce(\text{CO})$ is made the following results:

	<u>$\Sigma Ce(\text{CO}_2) + Ce(\text{CO})$</u>
R-650 (5/73)	578.9
R-650 (1/71)	564.4
R-300 (pg. 7, Table 7)	574.3

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It should be noted once again the C_e is the concentration of combustion product resulting from the combustion of 1.0g of product in a volume of 1000 liters. The fact that the total carbon oxide concentration for each of the three foams is constant is somewhat fortuitous. The C, H, N analysis indicates that this should not be so. The presence of other organic decomposition products would have to be accounted for to obtain a true material balance. In a previous communication⁽⁵⁾ it was shown that there is a slow gas phase oxidation of organic degradation products which occurs under NBS smoldering conditions.

Analysis of R-300 (5/73)

The combustion gas data and toxicity calculations for R-300 (5/73) are summarized in the following table.

Table 6

Analysis of R-300 (5/73)

Sample weight: 3.28g

<u>Time</u> (min.)	<u>HCl</u> (ppm)	<u>HCN</u> (ppm)	<u>CO₂</u> (ppm)	<u>CO</u> (ppm)
4.0	90	--	--	--
5.0	--	--	2047	413
7.0	120	--	--	--
8.0	--	17	--	--
10.0	730	--	--	--
12.0	--	32	--	--
13.0	--	--	--	--
15.0	120	--	2793	591
16.0	--	82	--	--
17.0	--	--	--	--
20.0	--	73	--	--
25.0	--	--	2905	774

The toxicity factor calculation from these data are summarized in Table 7.

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Table 7
Toxicity Factor Calculation For R-300 (5/73)

<u>gas</u>	<u>Maximum Concentration in NBS Chamber</u>	<u>Ce</u>
HCl	730	114.0
CO	774	120.8
CO ₂	2905	453.5
HCN	82	12.8

$$\begin{aligned}
 T &= \frac{114.0}{1000} + \frac{120.8}{4000} + \frac{12.8}{135} + \frac{453.5}{70,000} \\
 T &= .114 + .030 + .094 + .006 \\
 T &= .244
 \end{aligned}$$

This analysis shows that again the main contribution to the toxicity factor is hydrogen chloride. The contribution from HCN is also significant.

Discussion

The validity of the toxicity factor as proposed by Sumi (and as presented in this paper) is open to discussion.

Personally I feel that it is too simple. It does not take into account the rate of gas build-up nor, more importantly, the time at which the maximum concentration of gas occurs. With respect to this study, the early evolution of HCl is of concern. This study has gone beyond Sumi's study⁽⁶⁾ on PVC however, in that my Ce values for HCl take into account the decay of HCl; Sumi presented theoretical HCl concentrations. Even my approach leaves something to be desired. The decay of HCl in a large scale fire is going to be more dramatic than in the NBS smoke chamber^(7,8). Until we have more large scale fire data on PVC and have an understanding of the factors which cause the decay of HCl, this problem cannot be resolved. However, if we assume that all of the HCl will be lost during the early stages of a fire, the toxicity factors change significantly. I have recalculated these factors assuming a zero contribution from HCl. They are:

		<u>CO + CO₂</u>	<u>HCN</u>
R-650 (5/73):	T =	.045	+ .051
R-650 (1/71):	T =	.031	+ .020
R-300 (5/73):	T =	.036	+ .094
(average for 3 rooms)	=	.037	+ .055

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This approach indicates that the toxicity of the combustion products from these foams is due in part to carbon oxides (40%) and in part to hydrogen cyanide (60%). Sumi⁽¹⁾ has reported that the toxicity of the combustion products from an unmodified urethane foam was due in part to carbon monoxide (50%) and in part to hydrogen cyanide (50%). A comparison between the absolute toxicity factors of Sumi's urethane foam ($T = .10$) and Rigidcell* ($T = .092$) shows no significant difference.

It is of interest to compare the yields of HCN from the Rigidcell foams with yields reported in the literature. In this analysis, the yields are compared on a "g of HCN/g sample consumed" basis. Data as summarized in the next table.

Table 8

HCN Yields From Rigidcell and Other
Urethane Foams (Literature Values)

	<u>HCN Yield (g/g sample)</u>
Rigidcell 650 (5/73)	0.0076
Rigidcell 650 (1/21/71)	0.0029
Rigidcell 300 (5/73)	0.014
Rigid urethane foam ^(a)	0.008
Flexible urethane foams ^(b)	0.007-0.046 ^(c)
BFG's Estane 5707F1 ^(b)	0.034
BFG's Estane 5740X210 ^(b)	0.015

It can be seen from this calculation that the HCN yields from Rigidcell are within the limits already determined by others for a variety of urethane materials. One other calculation which is of interest is the per cent conversion of nitrogen in the polymer to hydrogen cyanide. Based on the C, H, N analyses of Rigidcell, the following yields of HCN would result if all of the nitrogen in the sample was converted to HCN:

	<u>HCN Yield (g/g sample)</u>
R-650 (5/73):	0.125
R-650 (1/71):	0.131
R-300 (5/73):	0.129

* ignoring the contribution from HCl.

(a) see reference 1

(b) see reference 9

(c) range of cyanide found for four flexible foams under varying combustion conditions

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Comparing these values with the actual experimental values (Table 7) indicates that there is a 2.2 - 10.9% conversion of nitrogen to HCN. The intriguing question at this point is what chemical structure or physically induced combustion condition is responsible for this range of yields.

As stated in the introduction, we carried out one experiment in which R-300 (5/73) was burned in the flaming mode. The purpose of this experiment was to determine the fate of HCN under flaming conditions. Under these conditions, the maximum amount of HCN found was less than 10ppm. Most of the HCN formed thus undergoes combustion in the NBS burner. The toxicity factor should be a function of both modes of burning. Obviously the contribution from HCN would be diminished.

It is obvious that more work needs to be done in this area. However the results should provide some guidelines with respect to the toxicity of the combustion products. Unfortunately we cannot put a "number" on the toxicity. One of the problems with respect to this is our current inability to analyze every combustion product present. Current pyrolysis-gas chromatographic-mass spectrometric studies are now underway to provide us with some guidelines along this line. Nevertheless, this study is in good agreement with other published studies and provides some information with respect to possible toxicological hazards from the burning of Rigidell.

M. M. O'Mara

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