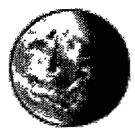


26 pgs

OPPT-2003-0071-0018



Robert J Giraud  
<Robert.J.Giraud@USA.dupont.com>

10/21/03 12:04 PM

To: Rich Leukroth/DC/USEPA/US@EPA, John Blouin/DC/USEPA/US@EPA, fritz.greg@epa.epa.gov  
cc: bill.beers@omnova.com, david.menotti@shawpittman.com, Mary A Kaiser <Mary.A.Kaiser@USA.dupont.com>  
Subject: text to review during 2 pm Oct. 22 fluoropolymer incin testing DraftingComm. call

Colleagues,

As noted in Rich's 10/17/03 e-mail, the next call of the Fluoropolymers ECA incineration testing drafting committee will be on Wednesday afternoon at 2 pm ET. The call-in details are as follows:

phone number: [REDACTED]  
code: [REDACTED]

Since, as Rich noted, many of the details for the test standards for fluoropolymers incineration testing can be applied to incineration testing for telomer-based polymeric materials (with minor changes), the October 22 call will also include representation from the Telomers ECA incineration drafting committee.

Attached is the latest draft of the fluoropolymers incineration testing program document for review by the drafting committee.

(See attached file: FP Incin Test Program draft 10-21-03.pdf)

Please note that text in brackets [ ] in italics is intended as internal comment shared among the drafting committee. Furthermore, please note that the Attachments are numbered to match the section of the Appendix that each is attached to. Hence, there is no Attachment C-2.

I plan to have a separate Appendix A for telomers ready for submission on Friday October 24 with the telomers incineration testing document.

Thank you in advance for your review and comment on this draft document as a step toward finalizing the proposal to bring to the Plenary at the end of this month. I look forward to our discussion on Wednesday.

Best Regards,  
Robert Giraud

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FP Incin Test Program draft 10-21-03.

1 **Fluoropolymers Incineration Testing Program**

2 DRAFT 10-21-03

3  
4  
5 **I. CHEMICAL SUBJECT TO THE ECA**

6 The test substances being studied in this testing program  
7 are identified in Appendix A. The basis for test substance  
8 selection and the preparation of the composites to undergo  
9 testing are also described in Appendix A.

10  
11 **II. PURPOSE OF TESTING PROGRAM**

12 The purpose of this testing program is to investigate  
13 incineration of designated test substances under  
14 laboratory-scale conditions representative of typical  
15 municipal waste combustor operations in the U.S. to  
16 quantitatively determine potential emission levels of PFOA.

17  
18 **III. SCOPE OF TESTING PROGRAM**

19 The testing program will consist of

- 20  
21 1) conducting the testing listed in Table 1 in accordance  
22 with the test standards specified in Table 1 for the  
23 test substances identified in Appendix A and  
24  
25 2) submitting the reports specified in Table 1 in  
26 accordance with the deadlines set forth in Table 1.

27  
28 **IV. DESCRIPTION OF TESTING PROGRAM**

29 The testing program has 2 phases as follows: Phase I Method  
30 Demonstration and Phase II Incineration Testing.

31  
32 **A. Phase I Method Demonstration**

33 This testing is described in Appendix B. Phase I testing  
34 provides the necessary foundation for Phase II testing.

35  
36 Following completion of Phase I and prior to initiation of  
37 Phase II, the Test Sponsor will provide a brief status  
38 report to EPA demonstrating the progress of testing. This  
39 letter report will provide the result for the overall  
40 recovery across the laboratory-scale thermal reactor system  
41 determined from transport efficiency testing.

42  
43 If this overall recovery for either PFOA or Fluorine is  
44 greater than or equal to 70%, the Test Sponsor will proceed  
45 to Phase II testing.

46  
47 If this overall recovery for neither PFOA nor Fluorine is

1 greater than or equal to 70%, then a Technical Consultation  
2 between the Agency and the Test Sponsor will be held to  
3 reach agreement on whether Phase II testing should proceed  
4 and, if so, on what (if any) revisions to the plans, test  
5 standards, and schedule for Phase II testing to adopt.  
6

7 If this consultation does not result in an agreement to  
8 proceed with Phase II testing, a more complete test report  
9 for Phase I will be submitted to EPA within 60 days of  
10 completion of the Technical Consultation.  
11

12 If Phase II testing is conducted, a more complete test  
13 report for Phase I will be included in the later Phase II  
14 Test Report rather than in a separate report.  
15

16 B. Phase II Incineration Testing

17 As described in Section IV.A, Phase II testing may be  
18 conducted depending on the result of Phase I testing or the  
19 Technical Consultation.  
20

21 Phase II testing is described in Appendix C.  
22  
23

1 **Table 1. Required Testing, Test Standards, and Reporting**

Phase I Testing	Test Standard	Deadline for Final Report <sup>1,3</sup>
Transport Efficiency	See Appendix B	TBD

2

Phase II Testing for Test Substance Composites	Test Standard	Deadline for Final Report <sup>2,4,6</sup>
Elemental Analysis <sup>5</sup>	ASTM D3176 or equivalent as described in Appendix C.1	TBD
Combustion Stoichiometry <sup>5</sup>	See Appendix C.2	TBD
Thermogravimetric Analysis <sup>5</sup>	ASTM E1868 as annotated in Appendix C.3	TBD
Laboratory-scale Combustion Testing <sup>5</sup>	See Appendix C.4 - C.6	TBD
Release Assessment	See Appendix C.6	TBD

3

4 1 Number of months after the effective date of the Order that  
5 incorporates this ECA when final report for this testing is due.  
6 Following completion of Phase I and prior to any initiation of Phase  
7 II, the Test Sponsor will provide a letter report to EPA with the  
8 result for the overall recovery across the laboratory-scale thermal  
9 reactor system determined from Phase I testing.

10 2 If the overall efficiency result from Phase I testing is less  
11 than 70% for both PFOA and Fluorine, then a Technical Consultation will  
12 be held to reach agreement on whether Phase II testing should proceed  
13 and, if so, on what (if any) revisions to adopt to the plans, test  
14 standards, and schedule for Phase II. If such agreement is not  
15 reached, Phase II testing is not required under the Order that  
16 incorporates this ECA.

17 3 A more complete test report for Phase I testing will be submitted  
18 within 60 days of the completion of the Technical Consultation if this  
19 consultation does not result in an agreement to proceed with Phase II  
20 testing. A more complete test report for this testing will be included  
21 in the Phase II test report if Phase II testing is conducted.

22 4 Number of months after initiation of Phase II testing period when  
23 final report for this testing is due. Phase II testing period will be  
24 initiated following Technical Consultation agreement to conduct Phase  
25 II testing or after completion of Phase I testing, whichever is later.

26 5 The results of this testing will be provided in the final report  
27 for Phase II.

28 6 A release assessment will be included in the final report for  
29 Phase II if quantifiable levels of PFOA are found in the exhaust gas  
30 from Phase II combustion testing.

1 **APPENDICES**

2

3 A. Test Substances

4

5 B. Method Demonstration

6

7 C. Incineration Testing

**APPENDIX A. TEST SUBSTANCES**

1. Identification

The four composite test substances for this test program will be prepared from the fluoropolymers identified in the March 14, 2003 Letter of Intent (LOI) submitted by the Society of the Plastics Industry on behalf of the four LOI signatories. The specific fluoropolymer types (with CAS numbers and associated monomers) going into each of the four composite test substances (grouped as shown) are presented in Table A-1 below.

**Table A-1. Test Substance Composites by Type and CAS Number**

Test Substance	Fluoropolymer Type	CAS Number	Associated Monomers
Composite 1 - PTFE (dry non-melt)	PTFE	9002-84-0	TFE
Composite 2 - Dry melt resins	FEP	25067-11-2	TFE, HFP
	PFA	26655-00-5	TFE, PPVE
		31784-04-0	TFE, PEVE
	THV	25190-89-0	TFE, HFP, VDF
	ETFE	68258-85-5	TFE, E
HTE	35560-16-8	TFE, HFP, E	
Composite 3 - Fluoroelastomers (dry non-melt)	Fluoroelastomer Copolymers	9011-17-0	VDF, HFP
	Fluoroelastomer Terpolymers	25190-89-0	TFE, HFP, VDF
	Base resistant elastomers	54675-89-7,	TFE, VDF, P
		27029-05-6	TFE, P
	Perfluoroelastomers	26425-79-6	TFE, PMVE
	CTFE elastomers	9010-75-7	CTFE, VDF
Low temperature elastomers	CBI	TFE, VDF	
Composite 4 - Aqueous Dispersions	PTFE	9002-84-0	TFE
	FEP	25067-11-2	TFE, HFP
	PFA	26655-00-5	TFE, PPVE
		31784-04-0	TFE, PEVE
THV	25190-89-0	TFE, HFP, VDF	

1  
2 Confidential business information (CBI) regarding the  
3 chemical identity of Low temperature elastomers has been  
4 submitted previously to EPA under separate cover.

5  
6 2. Selection

7 Review of Figure A-1 demonstrates that fluoropolymers  
8 industry products can be divided into 3 broad categories  
9 representative classes as follows:

- 10  
11 • Dry melt resins  
12 • Dry non-melt resins and gums  
13 • Aqueous dispersions  
14

15 These three broad categories can in turn be divided into  
16 four representative classes as follows:

- 17  
18 • Dry melt resins  
19     1. FEP, PFA, THV, ETFE, HTE  
20  
21 • Dry non-melt resins and gums  
22     2. PTFE  
23     3. Fluoroelastomers  
24  
25 • Aqueous dispersions  
26     4. PTFE, FEP, PFA, THV  
27

28 Composite samples of each of these four representative  
29 classes were selected as the test substance for this  
30 testing program in order to represent the entire range of  
31 fluoropolymers involved.

32  
33 3. Preparation of Composites

34  
35 3.1 Approach

36  
37 A composite mixture of representative fluoropolymers, as  
38 solids, will be prepared for each of the four test  
39 substance composites identified in Table A-1.

40  
41 The polymer samples will be unfilled first quality product  
42 polymer, substantially free of inorganic constituents.  
43 Each sample will be from a representative grade for each  
44 applicable fluoropolymer type from each applicable  
45 producer.  
46

1 For Composite 1 - PTFE, a representative sample of PTFE  
2 from each PTFE producer will be mixed together in equal  
3 proportions across applicable producers to form the  
4 Composite 1 - PTFE.

5  
6 A hypothetical example for Composite Z in Table A-2 below  
7 shows how the other composites will be assembled. In this  
8 example with 4 types across 4 producers, there are 11 x's.  
9 Hence, composite Z would be made up of 11 equal proportions  
10 of the materials indicated with an x.

11  
12 **Table A-2. Compositing Across Producers & Types**

Test Substance	Fluoropolymer Type	Producer A	Producer B	Producer C	Producer D
Composite Z	Type 1		X	X	X
	Type 2	X	X	X	X
	Type 3			X	
	Type 4	X	X	X	

13  
14 3.2 Preparation

15  
16 Representative samples of each component for each composite  
17 will be sent to the laboratory(ies) in packaging  
18 customarily used for product sample packaging or in  
19 polyethylene, polypropylene, or glass containers.

20  
21 Each composite will be prepared under laboratory conditions  
22 designed to prevent cross-contamination and designed to  
23 assure solids temperatures less than or equal to 60 °C.

24  
25 Following preparation of each composite, the composite will  
26 be placed in a polyethylene, polypropylene, or glass  
27 container.

28  
29 3.2.1 Composite 1

30  
31 PTFE is available in powder form. Equal weights of PTFE  
32 powder samples across applicable producers will be mixed  
33 together in dry form to yield Composite 1.

34  
35 3.2.2 Composite 2

36  
37 FEP, PFA, THV, ETFE, and HTE dry melt resins are available  
38 in pellet form. Each component of Composite 2 will be  
39 size-reduced (e.g., ground) to produce powder. Equal  
40 weights of the powder form of each component (following the



1 approach in the example for Composite Z in Section 3.1)  
2 will be mixed together in dry form to yield Composite 2.

3  
4 A sample of polyethylene pellets will be size-reduced using  
5 the same technique and equipment to provide a blank. The  
6 resulting polyethylene powder will be archived.

7  
8 3.2.3 Composite 3

9  
10 Fluoroelastomers are available in slab, lump, or sheet  
11 form. Composite 3 will be prepared following one of the  
12 following approaches:

13  
14 a) Equal weights of each component (following the approach  
15 in example for Composite Z in Section 3.1) will be mixed  
16 in a rubber mill to produce a homogenous slab of preset  
17 thickness to yield Composite 3.

18  
19 Or

20  
21 b) Each component of Composite 3 will be cyrogenically  
22 cooled (to make the elastomers brittle) and size-reduced  
23 (e.g., ground) to produce powder. Equal weights of the  
24 powder form of each component (following the approach in  
25 the example for Composite Z in Section 3.1) will be mixed  
26 together in dry form to yield Composite 3.

27  
28 A sample of non-fluorinated synthetic rubber will be size-  
29 reduced using the same technique and equipment to provide a  
30 blank. The resulting non-fluorinated rubber sample will be  
31 archived.

32  
33 3.2.4 Composite 4

34  
35 Aqueous dispersions of PTFE, FEP, PFA, and THV are  
36 available as dispersions containing 20 to 60% fluoropolymer  
37 solids by weight. Composite 4 will be prepared following  
38 one of the following approaches:

39  
40 a) Equal weights (on a dry solids basis) of each component  
41 in aqueous dispersion form (following the approach in  
42 example for Composite Z in Section 3.1) will be mixed  
43 together in liquid form. Solids will be separated from  
44 the resulting liquid composite to yield low water content  
45 (i.e., drip free) fine solids.

46  
47 Or

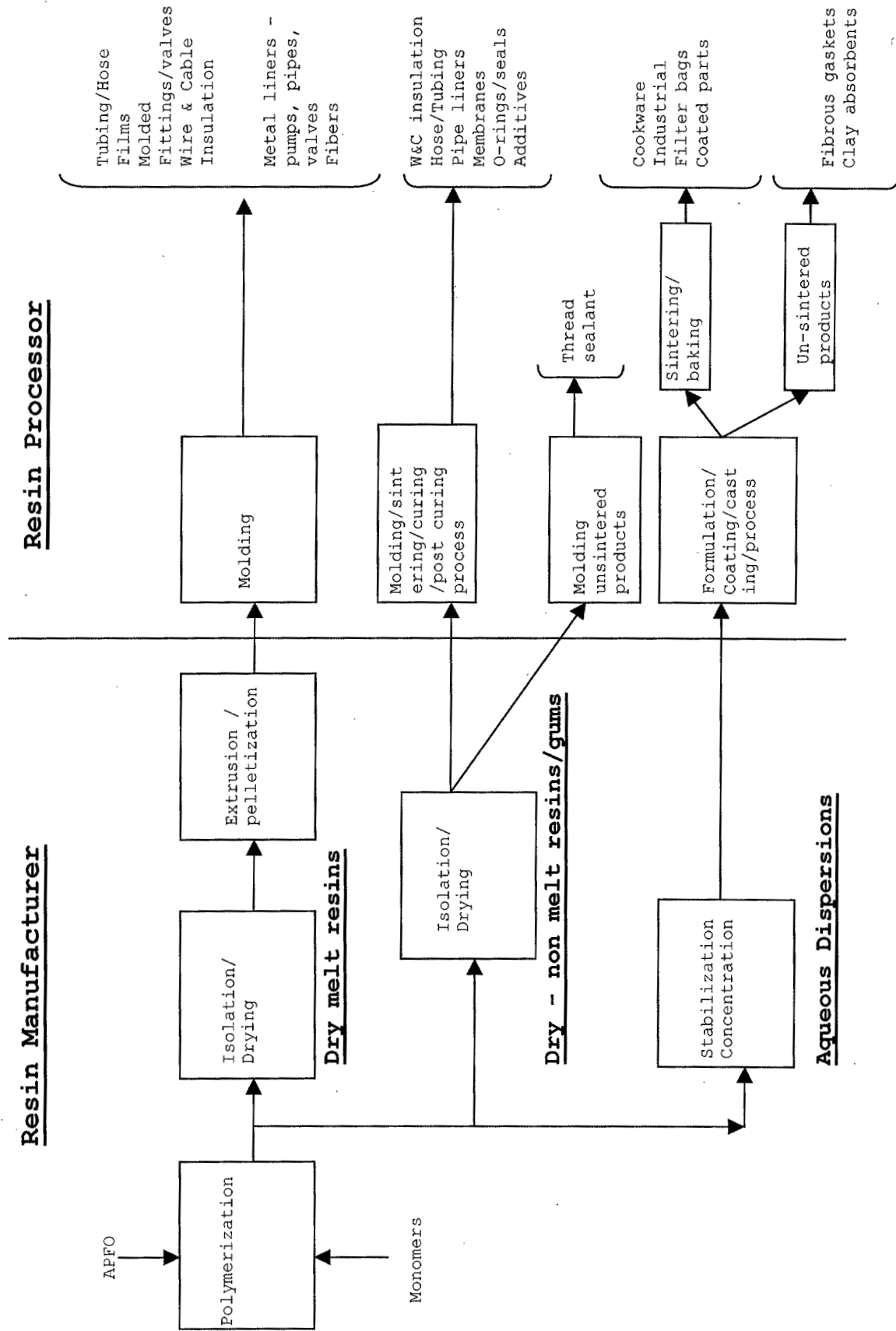
1  
2 b) Solids will be separated from liquid for each component  
3 of Composite 4 to yield low water content (i.e., drip  
4 free) fine solids for each component. Equal weights of  
5 the solids form of each component (following the approach  
6 in the example for Composite Z in Section 3.1) will be  
7 mixed together to yield Composite 4.

8  
9 3.3 Verification

10  
11 In order to assure that composite samples in this testing  
12 program have been made up of clearly identified materials,  
13 the preparation of the composites will include formal Chain  
14 of Custody procedures. A chain of custody form will be  
15 included with each component material going into the  
16 composite to show the identity of the component material  
17 and each transfer of custody from its point of origination  
18 to preparation of the composite. For documentation, the  
19 laboratory preparing a given composite will generate a  
20 report to be submitted to EPA as CBI.

21  
22 Once prepared, each composite will be accompanied by a new  
23 chain of custody until it reaches the incineration testing  
24 facility.

**Figure A-1. Fluoropolymer Industry Overview**



1 **APPENDIX B. METHOD DEMONSTRATION**

2  
3 Transport Efficiency

4 Quantitative transport of PFOA across the laboratory-scale  
5 thermal reactor system described in Appendix C will be  
6 verified. PFOA of known purity greater than or equal to  
7 97% will be used for this testing. For these transport  
8 tests, 0.5 to 5 mg of PFOA will be gasified at 150 to 250 °C  
9 (based on thermogravimetric analysis of PFOA) with transfer  
10 line and reactor temperatures 0 to 100 °C higher than the  
11 gasification temperature. Sampling and analysis will be  
12 performed to determine quantitation of PFOA and fluorine in  
13 corresponding laboratory-scale thermal reactor system  
14 exhaust gas samples.

15  
16 The amount of PFOA and fluorine determined in this exhaust  
17 gas sample will be compared to the amount of PFOA (as PFOA  
18 and as fluorine) fed to the thermal reactor system. The  
19 amount of PFOA fed to the system will be verified by  
20 weighing the pyroprobe insert cartridge before and after  
21 each experiment.

22  
23 If the resulting transport efficiency for either PFOA or  
24 fluorine is greater than or equal to 70%, then the overall  
25 recovery across the thermal reactor system is also greater  
26 than or equal to 70%.

27  
28 If the resulting transport efficiency for both PFOA and  
29 fluorine is less than 70%, then flexible tubing between the  
30 thermal reactor system and the sample collection apparatus  
31 and/or the high temperature reactor will be examined for  
32 PFOA and/or fluorine. If the flexible tubing is examined,  
33 it will either be extracted using methanol with the  
34 methanol extract being analyzed for PFOA and fluorine, or a  
35 portion of the tubing will be directly subjected to  
36 fluorine analysis. If the reactor is examined, the reactor  
37 will be removed from the system and extracted with  
38 methanol, and the solvent sample will be analyzed for PFOA  
39 and fluorine.

40  
41 In this case, the amount of the analyte (PFOA or fluorine  
42 as applicable) from examination of the tubing and/or the  
43 reactor will be added to the amount of analyte determined  
44 in the exhaust gas sample for comparison with the amount of  
45 analyte fed to the thermal reactor system to determine the  
46 overall recovery across the experimental system.

47

- 1 The thermal reactor system apparatus in this testing
- 2 program is configured such that additional extractions of
- 3 the transfer lines between the pyroprobe and the reactor
- 4 and between the reactor and the vent line (to which the
- 5 flexible tubing is connected) are not feasible.

1 **APPENDIX C. INCINERATION TESTING**

2

3 Following preliminary testing, combustion testing with  
4 associated exhaust gas sampling and analysis can be  
5 performed. The preliminary testing provides necessary  
6 background information for combustion testing.

7

8 The standards for preliminary testing are described in  
9 Sections 1, 2, and 3 below. The standard for combustion  
10 testing is presented in Section 4. Section 5 describes the  
11 standard for sampling and analysis for the combustion  
12 testing. Section 6 outlines how results of this testing  
13 program will be reported.

14

15 **1. Elemental Analysis**

16 Each test substance composite will undergo elemental  
17 analysis to provide data for stoichiometric calculations.

18

19 Ultimate analysis (ASTM D3176) is a standard practice for  
20 analysis of coal and coke. It can be used to determine  
21 carbon and hydrogen in a material via analysis of the  
22 gaseous products of its complete combustion, to determine  
23 sulfur, nitrogen, and ash in the material, and to calculate  
24 oxygen in the material by difference.

25

26 Table C-1 presents the reference standards for test methods  
27 for determination of carbon, hydrogen, nitrogen, sulfur,  
28 chlorine, ash, moisture, and oxygen for the test substance  
29 composites in this program and includes ASTM test methods  
30 referred to in ASTM D3176.

31

32 **Table C-1. Reference Standards**

Parameter	Test Method
Carbon	ASTM D3178, ASTM D5373, or equivalent
Hydrogen	ASTM D3178, ASTM D5373, or equivalent
Nitrogen	ASTM D3179, ASTM D5373, or equivalent
Sulfur	ASTM D3177, ASTM D4239, or equivalent
Chlorine	Bomb combustion (EPA 5050 or ASTM D808)/chloride ion analysis (ion chromatography or ion selective electrode), ASTM D2361, ASTM D46610B, or equivalent
Ash	ASTM D3174, ASTM D5142, ASTM D482, or equivalent
Moisture	ASTM D3173, ASTM D5142, or equivalent
Oxygen	By difference per ASTM D3176

33

34 The reference standards will be adapted, as needed, to

1 elemental analysis of the test substance composites in this  
2 testing program. Preparation steps for coal and coke noted  
3 in the ASTM standard test methods in Table C-1 are not  
4 required for application of these methods to the test  
5 substance composites. The sample sizes in the test methods  
6 in Table C-1 will be adjusted as necessary in this testing  
7 program based on available amount of sample.

8  
9 In accordance with ASTM D3176, oxygen will be determined by  
10 difference (i.e, the difference between 100% and the sum of  
11 the other measurements). If fluorine concentration is  
12 analyzed at a different laboratory from that used for the  
13 other elemental analyses, the calculated oxygen level in  
14 the material will be adjusted downward to account for  
15 fluorine.

16  
17 Fluorine (total fluorine) content will be determined via  
18 Wickbold Torch; see Attachment C-1. Based on manufacturing  
19 process knowledge, the levels of total fluorine in the  
20 components of test substance composites are orders of  
21 magnitude higher than the potential trace level of  
22 inorganic fluoride in these materials. Therefore, for this  
23 test program, the total organic fluorine value for each  
24 test substance composite will be assumed to be the same as  
25 the total fluorine value.

26  
27 Manufacturing process knowledge of the polymers will be  
28 used to review the elemental analysis results and to form  
29 the basis for interpreting non-detects. For example, if  
30 the elemental analysis result for a non-chlorinated or ash-  
31 free polymer is non-detect with a quantitation limit of  
32 0.1%, then the analytical result will be replaced with 0.

33  
34 Additionally, ASTM D3176 may be used as a reference to  
35 convert elemental analysis results to a basis (e.g., dry)  
36 other than on which the results are reported by the  
37 elemental analysis laboratory.

### 38 39 2. Combustion Stoichiometry

40 The results of the elemental analysis will form the basis  
41 for combustion stoichiometry calculations needed to help  
42 establish combustion test conditions.

43  
44 First, the weight percent values from elemental analysis  
45 (see Section 1) are converted to molar quantities.

46  
47 Second, based on Chapter 3 of Combustion Fundamentals for

1 Waste Incineration (American Society of Mechanical  
2 Engineers, 1974), the reaction products for these molar  
3 quantities are calculated assuming complete combustion with  
4 the following behavior:

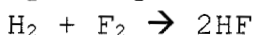
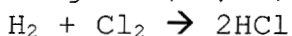
5  
6 a) All carbon (C) in feed converts to carbon dioxide (CO<sub>2</sub>)



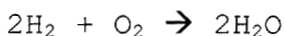
8  
9 b) All sulfur (S) in feed converts to sulfur dioxide (SO<sub>2</sub>)



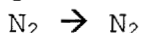
11  
12 c) The halogens (Cl, F) in feed convert to hydrogen halides



15  
16 d) Hydrogen (H) present in feed in excess of that  
17 required to yield products in item c) above will be  
18 converted to water



20  
21 e) Nitrogen (N) from feed or air is emitted as molecular  
22 nitrogen



24  
25 Third, with these rules, the balanced chemical reaction for  
26 combustion of a compound can be written.

27  
28 For a hydrocarbon like methane (CH<sub>4</sub>), the resulting reaction  
29 equation is



31  
32  
33 Note that the term feed in the preceding rules (a through  
34 e) includes both material being combusted and the fuel  
35 source of hydrogen such as methane or methanol.  
36 Additionally, stoichiometric calculations as described  
37 above presume that the compounds undergoing combustion are  
38 essentially free of inorganic constituents.

39  
40 The amount of oxygen needed for the overall combustion  
41 reaction for a feed is called the stoichiometric oxygen  
42 level. The actual oxygen level for combustion is generally  
43 set in terms of excess oxygen or excess air.

44  
45 Additional stoichiometric calculations will be performed as  
46 needed to set and adjust experimental conditions for  
47 combustion testing; see Section 4.3.



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### 3. Thermogravimetric Analysis

Thermogravimetric analysis (TGA) will be conducted to determine the temperature range required for gasification of each test substance composite. TGA will be conducted in flowing air from room temperature to 1000°C at 25°C/minute using 1 to 5 mg samples. ASTM E1868 as annotated will be used as the guideline for this analysis; see Attachment C-3.

The TGA weight-loss profile for each test substance composite will be evaluated to determine the temperature at which the weight loss reaches a final asymptote across the temperature range investigated. This temperature corresponds to the point at which no further gasification (under test conditions) occurs for the material and will be considered the temperature for complete gasification of the material.

The temperature for complete gasification for each test substance composite will be considered in establishing conditions for the gasification section (pyroprobe section) of the experimental apparatus for the combustion tests; see Section 4.3.

### 4. Combustion Testing

#### 4.1 Test Objective

The objective of this combustion testing program is to investigate incineration of the test substances under laboratory-scale conditions representative of typical municipal waste combustor operations in the U.S. to quantitatively determine potential emission levels of PFOA.

#### 4.2 Experimental Apparatus

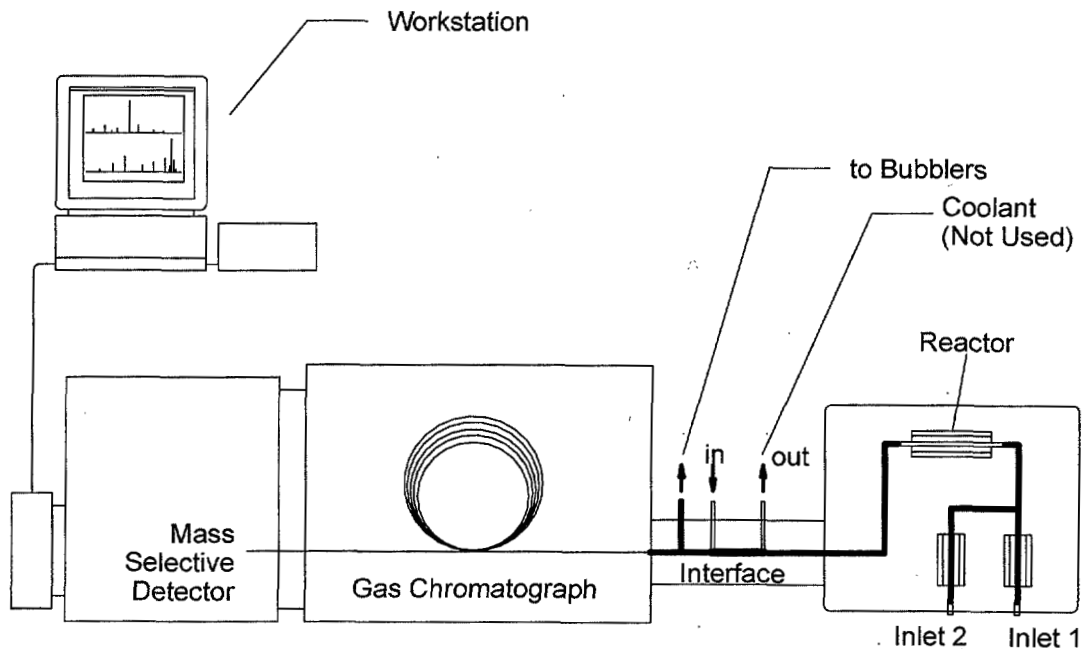
Combustion testing will make use of the Advanced Thermal Reactor System (ATRS) at the University of Dayton Research Institute (UDRI). The ATRS is a laboratory-scale, non-flame, batch-charged, continuous flow thermal reactor system. The use of a non-flame thermal reactor system gives a conservative representation of full-scale waste incineration.

In the ATRS, the test sample is gasified and transported to a high temperature fused silica reactor. In the high

1 temperature reactor, the sample vapors are subjected to  
2 controlled conditions of residence time, temperature, and  
3 excess air. Combustion products (section 5) will be  
4 collected for quantitative analysis.

5  
6 A schematic of the ATRS as configured for this test program  
7 is shown in Figure C-1.

8  
9 **Figure C-1. Schematic of ATRS for this Test Program**



10  
11  
12 The ATRS consists of a reactor assembly and in-line gas  
13 chromatograph/detector system connected via an interface.  
14 The reactor assembly consists of a thermally insulated  
15 enclosure housing the sample introduction, reactor, and  
16 transfer line systems.

17  
18 Sample introduction for solid materials (Inlet 1) employs a  
19 pyroprobe, a device designed to gasify samples by heating  
20 them at a fixed rate. The main gas flow will also be fed  
21 via Inlet 1, and Inlet 2 will be used to feed supplemental  
22 flow.

23  
24 During combustion tests, the transfer line between the  
25 pyroprobe and the reactor is heated and maintained above  
26 200 °C. The reactor is housed within its own small tube  
27 furnace and may be independently heated to as high as 1200  
28 °C. (Actual conditions for this test program are presented

1 in Section 4.3.) The transfer line from the reactor to the  
2 interface is heat traced to greater than 200 °C to prevent  
3 cool regions where reactor products could otherwise be lost  
4 through condensation.

5  
6 The interface routes the combustion exhaust gas to the in-  
7 line gas chromatograph (GC) and mass selective detector  
8 (MSD) or to sample collection for off-line analysis. For  
9 combustion testing in this test program, the interface will  
10 also be maintained above 200 °C.

11  
12 Exhaust gas sampling and analysis (including use of the in-  
13 line GC and MSD) are described in Section 5.

#### 14 15 4.3 Combustion Test Experimental Conditions

16  
17 The test substance composites will be subjected to  
18 laboratory-scale incineration using the experimental  
19 apparatus described in Section 4.2.

##### 20 21 4.3.1 Combustion Air

22  
23 Synthetic air (mixture of 21% oxygen and 79 % nitrogen)  
24 will be used in place of compressed air to prevent  
25 potential interference in the experimental system due to  
26 background levels of CO<sub>2</sub> in compressed air.

##### 27 28 4.3.2 Fuel

29  
30 Methanol will be used as needed as a supplemental fuel to  
31 ensure the presence of sufficient hydrogen to convert  
32 fluorine to hydrogen fluoride (HF) and chlorine to hydrogen  
33 chloride (HCl).

34  
35 As noted in *Municipal Solid Waste in the United States:*  
36 *2000 Facts and Figures* (EPA, 2002), paper and paper  
37 products (made from wood) make up the largest component of  
38 municipal solid waste (MSW). The sum of paper and paper  
39 products with wood in MSW makes up over 30% of MSW.

40  
41 During the 19<sup>th</sup> century, methanol was produced from wood and  
42 was known as wood alcohol. Therefore, methanol can be used  
43 in this experimental program as a surrogate for the paper  
44 and wood fraction of MSW.

1 4.3.3 Operating Conditions

2  
3 The target operating conditions for the high temperature  
4 reactor during the combustion tests are presented in Table  
5 C-2.

6  
7 **Table C-2. Combustion Test Target Operating Conditions**

Test Material	PTFE composite	Dry melt resin composite	Fluoroelastomer composite	Aqueous dispersion composite
Temperature	900 °C	900 °C	900 °C	900 °C
Residence Time	2 sec	2 sec	2 sec	2 sec
O <sub>2</sub> conc. in Exhaust Gas	10%	10%	10%	10%
H <sub>2</sub> O conc. in Exhaust Gas	14%	14%	14%	14%
No. of runs	3	3	3	3

8  
9 These conditions are representative of typical operating  
10 conditions for the high temperature zone of municipal waste  
11 combustors (MWCs) in the U.S. The temperature was selected  
12 to conservatively represent the low end of normal MWC  
13 operating temperatures and is also less than typical  
14 secondary chamber operating temperatures for medical waste  
15 incinerators in the U.S. See Attachment C-4 for supporting  
16 information.

17  
18 The expected sample size is in the range of 1 to 3 mg. The  
19 actual sample size, the gasification rate (determined from  
20 TGA), and the excess air will be adjusted to assure that  
21 the oxygen level in the exhaust will be greater than or  
22 equal to the concentration in Table C-2 to be  
23 representative of typical MWC conditions.

24  
25 Temperature and residence time values in Table C-2 will be  
26 fixed setpoints for the experiment. Fuel supply and excess  
27 air will be adjusted as needed to approach the H<sub>2</sub>O  
28 concentration target in Table C-2. Excess air will be  
29 further adjusted as needed based on fuel supply. Note that  
30 O<sub>2</sub> and H<sub>2</sub>O exhaust gas concentration values will be  
31 determined by calculation in planning the experiment.

32  
33 The temperature in the pyroprobe section will be maintained  
34 at 750 °C or as needed to assure this section is 50 to 100

1 °C above the highest temperature for complete gasification  
2 across the test materials as determined from the TGA  
3 experiments earlier in the test program; see Section 3.  
4 This is necessary to assure complete gasification of the  
5 sample of test material and a common set of experimental  
6 conditions across the test materials during combustion  
7 testing.

8  
9 4.4 Blanks

10 [under development]

11  
12  
13 4.5 Process Monitoring

14 Monitored process parameters and associated recording  
15 frequencies for each combustion test are presented in Table  
16 C-3.  
17

18  
19 **Table C-3. Combustion Test Monitoring**

Parameter	Recording Frequency
Temperature-Reactor	Before & after gasification
Temperature-Transfer line	Before & after gasification
Temperature-Inlet 1	After gasification
Temperature-Inlet 2	Before & after gasification
Gas flow rate-Inlet 1	Before & after gasification
Gas flow rate-Inlet 2	Before & after gasification
Total Gas Flow rate	Before & after combustion test
Make-up Gas (He) Flow rate	Before & after combustion test
Pressure-Reactor	Before & after gasification

20  
21 Temperature-Inlet 1 will be recorded on a log sheet at the  
22 end of the temperature ramp-up for gasification to monitor  
23 the pyroprobe final temperature.

24  
25 Recording the other values on a log sheet with the  
26 frequency noted in Table C-3 assures that each parameter is  
27 recorded at least once every 15 minutes because the  
28 expected duration of each combustion test is approximately  
29 5 to 15 minutes.

30  
31 The flow rate of the exhaust gas routed to the bubblers  
32 (described in Section 5.2) will be determined based on the  
33 flow measurements listed in Table C-3.

34  
35 The amount of material fed to the system will be verified  
36 by weighing the pyroprobe insert cartridge before and after

1 each experiment.

2  
3 Exhaust gas oxygen concentration will be calculated, based  
4 on measured total input flow rate of synthetic air and fuel  
5 assuming complete combustion.

6  
7 5. Sampling and Analysis

8  
9 5.1 Exhaust Gas Monitoring

10  
11 Combustion exhaust gas will be monitored for carbon  
12 monoxide (CO) and CO<sub>2</sub> via the in-line GC using a molecular  
13 sieve column and MSD or via off-line analysis of exhaust  
14 gas collected in Tedlar® bags.

15  
16 5.2 Exhaust Gas Sampling

17  
18 Gas samples for off-line analysis will be collected from a  
19 vent line off the interface. Flexible tubing will connect  
20 the vent line and a set of bubblers.

21  
22 Gas absorption via these bubblers will provide aqueous  
23 solution to analyze for the parameters in Section 5.3. Two  
24 to four bubblers (low pressure drop impingers) in series  
25 will be used. Each bubbler will contain a predetermined  
26 amount of aqueous solution. The temperature of the gas  
27 exiting the last bubbler will be monitored.

28  
29 An additional empty bubbler will be added to the front end  
30 of this series of bubblers to serve as a knock-out pot if  
31 stoichiometric calculations (see Sections 2 and 4.3) for  
32 the test substance or experience from earlier combustion  
33 testing with test substance indicate that greater than 10  
34 mL of water will be produced during the combustion test of  
35 a given test substance.

36  
37 Upon completion of sample collection, the amounts in each  
38 bubbler will be determined by observation or by weight, and  
39 the contents of the bubblers will be composited for  
40 subsequent analysis. Additionally, the flexible tubing  
41 will be rinsed with 5 mL of HPLC water to collect potential  
42 condensate in the tubing. This rinsate may be combined  
43 with the bubbler composite prior to analysis.

44  
45 A minimum of 60 mL of bubbler aqueous solution is expected  
46 from each combustion test. Of this, a minimum of 45 mL  
47 will be sent for PFOA analysis, a minimum of 5 mL will be

1 sent for fluoride (and chloride) ion analysis, and a  
2 minimum of 2 mL will be sent for total fluorine analysis.

3  
4 Bubbler aqueous solutions will be conveyed to analytical  
5 laboratories in a polyethylene, polypropylene, or glass  
6 containers.

### 7 8 5.3 Exhaust Gas Analysis

#### 9 10 5.3.1 Fluoride & Chloride Ion

11  
12 A portion of the composite aqueous solution sample from  
13 each combustion test collected as described in Section 5.2  
14 will be analyzed for fluoride ion and for chloride ion via  
15 ion chromatography.

#### 16 17 5.3.2 Total Fluorine

18  
19 A portion of the composite aqueous solution sample from  
20 each combustion test collected as described in Section 5.2  
21 will be analyzed for total fluorine via Wickbold Torch at a  
22 qualified laboratory; see Attachment C-1.

#### 23 24 5.3.3 PFOA

25  
26 A portion of the composite aqueous solution sample from  
27 each combustion test collected as described in Section 5.2  
28 will be analyzed for PFOA via LC/MS/MS at a qualified  
29 commercial laboratory in accordance with "Method of  
30 Analysis for the Determination of Ammonium  
31 Perfluorooctanoate (APFO) in Water Revision 1" (Docket ID  
32 OPPT-2003-0012-0040) as revised for exhaust gas bubbler  
33 sample analysis for PFOA; see Attachment C-5.

34  
35 Due to background levels of PFOA, the analytical laboratory  
36 will only report numerical values for PFOA concentration in  
37 the aqueous solution greater than or equal to the limit of  
38 quantitation (LOQ). This is required to assure that the  
39 reported concentration value is attributable to the sample  
40 rather than to background.

### 41 42 5.4 Test Substance Sampling & Analysis

43  
44 See Section 1.

## 45 46 6. Reporting of Results

1 6.1 Elemental Analysis Results

2  
3 The results of elemental analysis of the test substance  
4 composites (as noted in Section 1) will be reported.

5  
6 6.2 Combustion Stoichiometry Results

7  
8 Example combustion stoichiometry (as noted in Section 2)  
9 calculations will be included in the test report.

10  
11 6.3 TGA Results

12  
13 TGA results for test substance composites (as noted in  
14 Section 3) will be included in an appendix to the test  
15 report.

16  
17 6.4 Combustion Test Results

18  
19 6.4.1 Process Monitoring

20  
21 Process monitoring data (as noted in Section 4.5) recorded  
22 for each combustion test will be reported in tabular form.

23  
24 6.4.2 Exhaust Gas Monitoring

25  
26 Exhaust gas monitoring results will be reported as the  
27 average (integrated value) for each combustion test. CO  
28 will be reported in terms of parts per million by volume  
29 (ppmv). CO<sub>2</sub> will be reported in terms of percent by volume  
30 (%).

31  
32 6.4.3 Exhaust Gas Results

33  
34 Results of analyses noted in Section 5.3 will be reported  
35 for each combustion test.

36  
37 The analytical result for each analyte in Section 5.3 will  
38 be reported in terms of concentration (mass per volume) in  
39 the aqueous solution. For each analyte, this value will be  
40 used with the associated exhaust gas volume to compute an  
41 exhaust gas concentration.

42  
43 6.4.3.1 Fluoride and Chloride

44  
45 Fluoride ion and chloride ion in the exhaust gas will be  
46 reported in terms of concentration (mass of ion per volume  
47 of exhaust gas) in the gas and on the basis of mass of ion



1 per mass of test substance. The corresponding hydrogen  
2 halide value for each will also be computed and reported  
3 for reference.

4  
5 The fluorine ion value is also the total inorganic fluorine  
6 value.

#### 7 8 6.4.3.2 Total Fluorine and Total Organic Fluorine

9  
10 Total fluorine in the exhaust gas will each be reported in  
11 terms of concentration (mass of fluorine per volume of  
12 exhaust gas) in the gas and on the basis of mass of  
13 fluorine per mass of test substance.

14  
15 Total organic fluorine will be determined by difference  
16 between total fluorine and total inorganic fluorine.

#### 17 18 6.4.3.3 PFOA

19  
20 PFOA in the exhaust gas will be reported in terms of  
21 concentration in the gas (mass of PFOA per volume of  
22 exhaust gas) and on the basis of mass per mass of test  
23 substance.

#### 24 25 6.5 Test Substance Results

26  
27 Elemental compositions will be reported as indicated in  
28 Section 6.1 above.

#### 29 30 6.6 Release Assessment

31  
32 In the event that PFOA is found in the exhaust gas at a  
33 concentration above the LOQ (for the matrix) for the  
34 average of three runs for a given test substance composite,  
35 then the potential for release from full-scale waste  
36 incineration of the subject material will be assessed to  
37 inform the basis for possible next steps.

38  
39 This assessment will consider a number of factors such as

- 40
- 41 • test program-determined PFOA emission factor,
  - 42 • estimated amounts of subject material in feed to full-  
43 scale waste incinerators, and
  - 44 • degree of post-combustion air pollution control (e.g.,  
45 use and effectiveness of carbon adsorption).
- 46  
47

- 1 Attachments
- 2
- 3 Attachment C-1 Wickbold Torch
- 4
- 5 Attachment C-3 TGA:Annotated ASTM E1868
- 6
- 7 Attachment C-4 Waste Incineration and Operating Conditions
- 8
- 9 Attachment C-5 PFOA Analysis