

09/30/1999

Products of incomplete combustion of POSF Based Fluorochemicals

This document summarizes what is known about the products of incomplete combustion and of thermal degradation of perfluorooctanesulfonylfluoride (POSF) based fluorochemical products. POSF based fluorochemicals are salts of perfluorooctane sulfonate (PFOS) and primary or substituted perfluorooctyl sulfonamides. The perfluorooctyl portion of these compounds is typically a mixture of about 70% linear and 30% branched isomers. In addition to the perfluorooctyl portion, POSF based products typically contain a small percentage of homologues with shorter and longer fluoroalkyl chains.

The perfluoroalkyl portions of POSF-based fluorochemicals, and many other perfluorocompounds, are very stable. Thus, perfluoroalkyl chains requires more time and higher temperatures to be fully destroyed than hydrocarbon chains. In order to ensure complete destruction, incineration experts at 3M suggest residence times in the combustion chamber greater than 1 second and a temperature 1,700 °F (926 °C) or greater. If combustion chamber temperatures and retention times drop below certain levels, destruction efficiency can drop off rapidly. For nonfluorinated compounds, considerable quantities of incomplete combustion products are formed as incinerator temperatures drop to 1,300°F. The temperature at which this would occur for perfluorochemicals would be somewhat higher because of their greater stability.

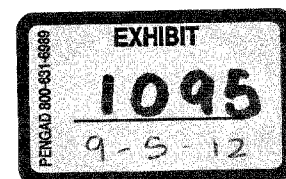
Fluorochemicals are typically incinerated in the presence of fuels or other organic wastes. Under these conditions, the primary products of fluorochemical incineration are hydrogen fluoride HF and CO₂. Incinerators that burn fluorochemicals require pollution control equipment to remove the HF. If not removed from the exhaust, HF could cause environmental effects. The most likely effects are damage to vegetation. Fluoride concentration in the 5-10 ppb range can affect sensitive vegetation exposed for greater than 2-4 hours. Effects can also occur with chronic fluoride exposures for 30 to 60 days above 0.3 - 0.6 ppb. HF formed from burning fluorochemicals also affects the incinerator. It causes more rapid deterioration of the brick lining of the combustion chamber. In parts of the incineration system where temperatures drop below the dew point, the hydrofluoric acid containing condensate can cause considerable corrosion damage. HF formed from burning waste with a higher than expected fluorochemical concentration can cause the pH of the scrubbing solution to drop precipitously. When this occurs, HF and other combustion products that are scrubbed more completely in neutral and basic solutions will escape to the atmosphere. This can also cause the formation of a visible white tail on the stack plume. Some of these problems can be minimized by slowly metering POSF based and other fluorochemicals into incineration waste streams.

Formation of Dioxin and Furans

Dioxin formation is most likely to occur during the incomplete combustion of halogenated aromatics, such as chlorinated phenols. Chlorinated, brominated and fluorinated aromatics, require very little molecular rearrangement to form dioxins, so relatively large amounts are formed from incomplete burning. For other types of halogenated compounds, such as polyvinyl chloride, researchers have found that relatively little dioxin is formed. Particularly

Made Available by 3M for Inspection and Copying as Confidential Information:
Subject to Protective Order In Palmer v. 3M, No. C2-04-6309

3MA01412209



**Exhibit
1615**

State of Minnesota v. 3M Co.,
Court File No. 27-CV-10-28862

09/30/1999

in this case, the conditions of the incinerator, not halocarbon concentration, play the predominant role in dioxin formation. The scientific literature contains vastly more information about the formation of chlorinated and brominated dioxins than about formation of fluorinated dioxins.

Tests have shown fluorinated dioxins and furans appear to be less toxic than chlorinated dioxins. For example Weber and Hagenmaier found that octafluorodibenzodioxin and 2,3,7,8-tetrafluorodibenzofuran were, respectively, 1000-fold less active or inactive in inducing CYP1A activity in the EROD test than TCDD and TCDF. Induction, in this test, has been correlated with dioxin and furan toxicity (Weber 1995). Other studies show 10-fold less CYP1A induction by 2,3,7,8-TFDD than by 2,3,7,8-TCDD. This confirmed bioassays that showed no toxicity of 2,3,7,8-TFDD to NMRI mice at 10-100 ug/kg. (How toxic would TCDD be at this concentration?) Fluorinated dioxins also have other properties that make them less hazardous. The slow phase elimination of fluorinated 2,3,7,8-TFDD has a half-life of approximately 4.5 hours, much lower than the 8.5-day elimination half-life of chlorinated 2,3,7,8-TCDD (Weber 1995). Additionally, fluorinated dioxins are highly volatile (Weber 1995). This perhaps means that they would more readily enter the atmosphere, higher percentages of that in the atmosphere would be in the gas phase. It is also likely that a higher proportion would photodegrade in the atmosphere and less would return to the surface soil or waterways.

Chlorinated dioxins and furans that are partially fluorinated also appear to be much less toxic. Weber and Hagenmaier found that a four order of magnitude increase in concentration was required to cause comparable EROD activity when fluorine atoms replaced two 2,3,7,8-TCDD chlorine atoms. They also showed that organisms can metabolize and eliminate fluorinated dioxins and furans more rapidly than their chlorinated analogs. (Reference Weber, R. and H. Hagenmaier. Synthesis and analysis of mixed chlorinated-fluorinated dibenzo-p-dioxins and dibenzofurans and assessment of formation and occurrence of the fluorinated and chlorinated-fluorinated dibenzo-p-dioxins and dibenzofurans. Chemosphere 34 (1997) 13-28.)

Weber et al. (Chemosphere, 30(4), 629-639, 1995), working with detection limits in the range of 10 ppt, detected no formation of PFDDs and PFDFs from heating copper fluoride, sodium fluoride, and fly ash in an air stream between 300°C and 500 °C. Under these conditions, comparable mixtures of fly ash and chlorine or bromine salts form dibenzodioxin and dibenzofuran. The authors propose that the reason for the absence of fluorinated dioxin and furan formation could be the lack of C-F bond formation. C-F bonds form only at temperatures above 900 °C, a temperature at which dioxins are destroyed. The same reasons possibly also explain why fluorinated dioxins and furans are not formed as by products of aluminum production even though C-F bonds are formed.

Webber found that burning polytetrafluoroethylene (PTFE) causes no detectable PFDD or PFDF formation. Additionally calculations, combustion data, and mass spectral data all suggest that the carbon-sulfur bonds of the less extensively studied PFOS based compounds are more labile and break before the carbon-carbon bonds in the perfluoroalkyl

09/30/1999

chain. These pieces of information are relevant to the likelihood of POSF based compounds forming dioxins. The fluoroalkyl radicals formed from breakage of the C-S bond in POSF based products would be on average shorter but otherwise analogous to those formed from PTFE. Since these fluoroalkyl radicals do not rearrange to form dioxins or furans when PTFE is burned, there is no reason to believe these same radicals would form dioxin during the combustion of POSF based products. For the same reason burning other compounds with perfluoroalkyl groups should not form dioxins.

Polyfluoroethylenepropylene (PFEP) is another fluoropolymer that has been studied more extensively than POSF based products. The perfluoroalkyl radicals formed from thermal degradation of this polymer would have a structures analogous to radicals formed from the burning of POSF based fluorochemicals with branched fluoroalkyl chains.

The a U.S. EPA Peer Review Draft on health risks of combustion facilities states that available data suggests that fluorinated dioxins and furans are not likely products of incomplete combustion from incineration facilities. There is some concern (EPA530-D-98-001A) that fluorine in combustion gases may increase the formation of chlorinated dioxins.

POSF based fluorochemicals, when burned in the presence of paper and presumably other hydrogen containing organic materials are destroyed by combustion and the major product of combustion is HF. HF was the only fluorine product detected when

have are by in large One of the questions about fluorochemical incineration is

Perfluoromethane CF_4 is a particularly stable molecule due to the strength of its CF bonds. Its complete destruction in incineration virtually insures the complete destruction of other organic compounds in the same stream. (Tsang, W, et al., Combust. Sci. Technol. 1998, 139(1-6), 385-402.)

** In 1992, Philip H. Taylor of the University of Dayton Environmental Sciences Group, who at the time was involved in studies of CFCs and SF_6 , told us that anything including fluorochemicals that goes directly through the flame is destroyed. For this reason, there is no point in doing flame work. It is the materials that bypass the flame that could form partial degradation products. Another important point of our conversation with him is that it is the kinetics that limit the reaction as opposed to the thermodynamics. The important thing to study is the reaction kinetics in secondary combustion.

** Another problem with the combustion of fluorochemicals is that regulations may restrict the amounts of HF that can be emitted. For example, we have had this problem with an industrial customer in Germany (15-Jan-1992 memo from Dr. Sik Toh Ting).

** 3M fluorochemicals, including POSF based products, contain no fluorinated aromatic compounds. Thus, fluorinated dioxins would have to be formed by a total rearrangement of

09/30/1999

the combustion products in the incineration exhaust. Thus, fluorinated dioxins would be found at most at trace levels.

** 3M has conducted a two part study on the combustion of FC-807. (J. W. Miller, 3M Corporate Research Laboratories, 1986.) The first part involved combustion studies on paper samples coated with the SCOTCHBAN products. In these tests, no organic fluorine containing combustion products were detected. The analyst suggested that a possible reason for this was that combustion products may have been below detectable concentration due to the very low coating weight of FC-807 on paper. Another probable reason is that very little organofluorine combustion product would be expected to survive the likely conditions as is discussed below.

In the "neat" combustion portion of the study, combustion products of SCOTCHBAN fluorochemicals were measured after heating the FC-807 fluorochemical solids to 450 °C. This produced easily detectable levels of organofluorine degradation products. Sixty percent of the initial product was collected as volatile thermal degradation products. Measured degradation products accounted for nearly 40% of the original product weight. A fluorochemical alcohol (EtFOSE) accounted for approximately half of the detected degradation products. Nearly a quarter of the degradation products consisted of C3 to C7 fluorinated alkanes containing a single hydrogen atom. Other degradation products included perfluorocarboxylic acids and perfluorosulfonamides. (Were there shorter chain Perfluorosulfonamides?) No fluoroolefinic materials were detected suggesting that olefins are less likely degradation intermediates. This was an important finding because some fluoroolefins, e.g., perfluoroisobutylene,

As these degradation products had structures related to the original SCOTCHBAN products, they were initial or early degradation intermediates. They likely accumulated because the heat capacity of the fluorine atoms and the formation of combustion products generating fluorochemical radicals prevented the temperature from rising above the temperature to which the combustion products are heated to initiate the decomposition process, in this case 450 °C.

As was observed, the concentrations of partial degradation products is expected to be much reduced during the burning of SCOTCHBAN treated paper. When SCOTCHBAN treated paper is burned, the initially formed fluorochemical thermal decomposition products would pass through the flame reaction zone of the burning paper as they are formed. This zone would have a temperature in the range of 800 to 1000 °C. Under these conditions, fluorochemicals would decompose much more rapidly than in the neat conditions, why all of the detectable fluorochemical was not detected.

** PTFE begins to degrade at 400 °C. The fluorochemical portion of the used fluorochemical begins to degrade at this temperature as is evident from the FC-807 conversion products which are C3 to C7 monohydrogenated fluorochemicals along with many other products with the still intact C8F17 chain. The hydrocarbon portion of POSF

09/30/1999

based fluorochemicals with hydrocarbon portions will begin to degrade at lower as is evidenced by the following initial decomposition temperatures.

FC-171	350 °C
FC-135	260 °C
FC-430	450 °C
FC-99	535 °C
FC-129	450 °C
FC-170C	300 °C

Carbonyl fluoride is found to be the main oxidative pyrolysis product of PTFE at higher temperatures. Carbonyl fluoride concentrations decreases significantly as temperature drop to at 550 C and disappears when temperatures drop to 500C. When water vapor is present in the carrier gas, carbonyl fluoride is converted to CO₂ and HF.

Oxygen in the air stream prevents the formation of toxic very toxic octafluoroisobutylene from PTFE pyrolysis. Oxygen would presumably also prevent its formation from 3M of POSF based fluorochemicals.

** 02/09/90, Roger G. Perkins 3M Toxicology 1. The 3M exposure guideline for perfluoroisobutylene is 0.01 parts per million as a ceiling value. It is not a time-weighted average value! (Is this still the exposure guideline?)

** This basic wash should destroy the PFIB dissolved in the liquid phase.

** We discussed how to determine the formation of degradation products during activated carbon regeneration. After our call, I talked to John Hunter. Based on that conversation, I concluded that there is not a significant need to evaluate carbon regeneration. The reason is that fluorochemical containing activated carbon from our plant site is now destroyed in cement kilns. We are not regenerating of the spent carbon, and to my knowledge, we are not advocating activated carbon treatment of fluorochemical waste streams to our customers.

The conditions of the cement kilns would certainly fully destroy the fluorochemical to inorganic products. These conditions are 2700°F (1482°C) with a several second retention time.