FYI-0101-1378s

DuPont Haskell Laboratory
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DuPont Haskell Laboratory

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January 25, 2001

Dr. Charles M. Auer, Director
U.S. Environmental Protection Agency
Office of Pollution Prevention and Toxics
Chemical Control Division
410 M Street NW Room 403
Washington, D.C. 20460

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Dear Dr. Auer

In my June 23, 2000 letter that transmitted DuPont's Voluntary Use and Exposure Information Profile (UEIP) for Ammonium Perfluorooctanoate (APFO, CAS#3825-26-1), I noted that, as part of the ongoing surveillance of workers potentially exposed to APFO, a series of blood samples were taken in year 2000 from workers and that DuPont would voluntarily submit a summary of the results when they became available.

The results of the blood serum tests are now available. A summary of this year's results for workers with identified APFO exposure potential is below.

Year	# of Samples	Minimum Concentration (ppm)	Maximum Concentration (ppm)	Mean Concentration (ppm)
2000	72	0.02	9.0	1.53

Note the following concerning the above data:

- Five samples, all from workers in one particular job, tested greater than 5.0 ppm. Among the jobs with potential APFO exposure, this job should have the least exposure potential. We are investigating the cause of these elevated results in this group of workers. Eliminating the five data points from these workers gives a maximum concentration of 4.9 ppm and a mean concentration of 1.16 ppm.

- Some employees not routinely working with APFO provided blood samples. APFO levels in this group of people are consistently less than 0.2 ppm.

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- Blood serum APFO concentration seems to be a function of length of time in assignments with potential APFO exposure. Due to variances in length of service among workers in assignments with potential APFO exposure, average values may be influenced not only by exposure potential but also by average length of service of the volunteer group.

Additional groundwater and surface water measurements have been reported and some older data has been located. These additional data are reported on pages 5 and 6 of a revised Voluntary UEIP. Please replace the previous submission with the attached version. Note that there is a public copy and a copy containing Confidential Business Information.

If you wish to discuss the information contained in this document, please contact Robert F. Pinchot at (302)999-4074 or e-mail at Robert.F.Pinchot@usa.dupont.com or me at (302)366-5259.

Very truly yours,

Gerald L. Kennedy
Director, Applied Toxicology and Health

Attachments

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Voluntary Use and Exposure Information Profile
Ammonium Perfluorooctanoate (APFO)
(revised January 2001)

Note: The information contained in this document is submitted voluntarily and may be subject to future revision and/or modification.

CONFIDENTIAL BUSINESS INFORMATION REDACTED

I. CHEMICAL IDENTIFICATION

Chemical Name: Ammonium Perfluorooctanoate
CAS Number: 3825-26-1

II. COMPANY IDENTIFICATION

Company Name: E. I. du Pont de Nemours and Company

Site Locations:

Site where APFO is used as a reaction aid:

Washington Works
Route 892
Washington, WV 26181

Sites where APFO containing products made at Washington Works are processed:

Parlin Plant
Cheesequake Road
Parlin, NJ 08859

Spruance Plant
5401 Jefferson Davis Hwy.
Richmond, VA 23234

Site which disposes of waste containing APFO:

Chambers Works
Rte. 130
Deepwater, NJ 08023

Technical Contact: Robert F. Pinchot
(302) 999-4074
DuPont Fluoroproducts
Chestnut Run Plaza
Bldg. 711/2210
Centre Boulevard
Wilmington, DE 19805-0711

III. DUPONT AND CUSTOMER ACTIVITIES

Narrative Description of APFO Use

The block diagram on the back page titled "DuPont US APFO Balance" describes the processes discussed below and the estimated emissions associated with these activities.

DuPont uses APFO as a reaction aid in the production of polytetrafluoroethylene (PTFE) and tetrafluoroethylene (TFE) co-polymers. The process utilized at DuPont's Washington Works for making PTFE and co-polymers consists of polymerizing TFE (and other co-monomers if desired) in an aqueous media with a small amount of APFO to aid in the reaction.

Following the polymerization step, the polymer dispersion is either dried to remove water and APFO or concentrated (removing some of the APFO), stabilized and sold as an aqueous dispersion. The dried polymer contains very little, if any, APFO.

The APFO removed from the polymer is recovered for recycle, captured and destroyed off site in an incinerator, captured and sent to an offsite industrial landfill, and/or emitted to air or water at the Washington Works.

The stabilized polymer dispersions are sold by DuPont to industrial customers (both in the US and outside the US) for a variety of uses, internally transferred to the DuPont Spruance Plant for the production of Teflon® fibers and PTFE coated synthetic fibers, or internally transferred to the DuPont Parlin Plant for the production of Teflon® Finishes.

A small amount of non-hazardous waste polymer, water, APFO and other additives generated at Washington Works is treated in a wastewater treatment facility at DuPont's Chambers Works. This material is either emitted in the Chambers Works water discharge or captured on carbon and landfilled in a secure landfill.

The internal process at the DuPont Spruance Plant to produce Teflon® fibers involves, for most of the product, a "sintering" step in which the APFO contained in the product is destroyed by the following reaction:[1]

[1] P.J. Krusic, D.C. Roe, "Thermal Decomposition of C8 Fluorinated Surfactants and Related Materials Studied by High Temperature Gas-phase ^{19}F NMR. A New Alternative to Thermal Gravimetric Analysis", DuPont Internal Report.

$$CF_3(CF_2)_6COO^-NH_4^+ \rightarrow CF_3(CF_2)_5CF_2H + CO_2 + NH_3$$

This reaction goes to completion at 350°C and 0.2s residence time. A small amount of product processed at DuPont's Spruance plant does not get sintered and thus contains a small amount of residual APFO. These products are used for industrial pump, valve and compressor packing materials.

The process for making Teflon® finishes at the DuPont Parlin Plant involves a blending operation of fluoropolymer dispersions with other additives including solvents, binders, and pigments. The small amount of APFO emissions to water from this facility is due to waste generated during product changeovers. Some of the fluoropolymer dispersion is processed at contract facilities where the material is dried at temperatures >350°C thus destroying the APFO according to the reaction above. This dried material is then incorporated into finishes products.

The final product produced is then sold to applicators that apply the product to a substrate (such as cookware) via automated spraying or rollercoating. Emissions of APFO from these operations consist of overspray that is either captured on filters and landfilled or absorbed into water resulting in a water emission. Product that is applied to the substrate is then typically "sintered" at temperatures approaching 800°F resulting in the removal of the APFO from the substrate and subsequent destruction according to the reaction above.

Customers of dispersion products use the material for a variety of applications. However, most applications involve a "sintering" step where the APFO is destroyed. There are a small number of applications [ ] where the customer heats the dispersion products to temperatures that allow the APFO to sublime resulting in air emissions. There are also a small number of applications [ ] where the customer's product is not heated resulting in the APFO staying with the product. These applications include industrial packings, and industrial filter fabrics.

IV. SITE RELEASE AND TRANSFER INFORMATION FOR TRI CHEMICALS

Not applicable- APFO is not listed on the TRI

V. SITE RELEASE AND TRANSFER INFORMATION FOR NON-TRI CHEMICALS

A. On-site Air Releases

	Estimated Total Annual Releases (lbs.1999)			
	Washington Works	Parlin	Spruance	Chambers Works
Fugitive	Negligible	0	0	0
Stack (Point Source)	24000	0	0	0

Comments

Air emissions are estimated using engineering calculations and judgements and limited measurements of specific point sources conducted in the past.

B. On-site Water Releases

	Estimated Total Annual Releases (lbs.1999)			
	Washington Works	Parlin	Spruance	Chambers Works
Point Source	55000	300	150	18,500

Comments

Water emissions are estimated using engineering calculations and judgements and limited measurements of specific sources conducted in the past.

Washington Works emissions occur for approximately 350 days/yr while the other sites' emissions occur for 10-100 days/yr. Releases of APFO to the Ohio River from the DuPont Washington Works Plant were modeled using the Probabilistic Dilution Model (PDM Beta Version 4.0 Beta June 11, 1999, US EPA Office of Pollution Prevention and Toxics) and a constructed Microsoft® Excel spreadsheet model. APFO release data for 1996 were used in both modeling exercises.[2] The PDM indicated that APFO concentrations of 1.0 µAPFO/l would be exceeded about 50% of the time during the year. APFO concentrations of in the river would exceed 0.1 µg APFO/l 90% of the time during the year and 10 µg APFO/l about 2.2% of the time during the year.

Average annual APFO concentrations in the Ohio River calculated by using a Microsoft® Excel spreadsheet was 0.423 µg APFO/L. Modeled AFPO concentrations in the river ranged from a low of 0.199 µg APFO/L in March to a high of 0.965 µg APFO/l in September, which correspond to high and low river flows, respectively. Average Ohio River flows and volume data calculated from the US Geological Survey was collected at the Belleville Dam and used in the spreadsheet model. The Belleville Dam is on the Ohio River 13 miles downstream of the Washington Works Plant. This river flow data is the closest location downstream from the plant where this type of information is available.

In 1999, a drinking water sample obtained from GE plastics, Washington WV, immediately downstream on the Ohio River from DuPont Washington Works showed 0.552µg/l APFO.

[2] W.R.Berti, "Modeling Releases of Ammonium Perfluorooctanoate into the Ohio River", DuPont Internal Report EMSE-054-00.

In addition, samples obtained in January 2000 from three different wells at the Lubeck Public Service District, downstream of Washington Works on the Ohio River, showed 0.8µg/l, 0.44µg/l and 0.313 µg/l APFO. Subsequent samples in April, May, and August 2000, showed a maximum of 0.59 µg/l and a minimum of 0.07µg/l.

C. On-Site Land Releases

Chambers Works treats APFO containing waste in a wastewater treatment system. Engineering calculations and judgements and limited measurements of specific sources in the past estimate that approximately 30% of the APFO in the wastewater treated is adsorbed on to a carbon media that is landfilled on site. These land releases are estimated to be 8,000 lb in 1999.

Prior operations have resulted in measurable APFO concentrations in three landfills operated by the Washington Works in West Virginia. At Letart[3] landfill, surface water measurements in 1999 and 2000 ytd range from 2.23µg/l to 3240µg/l, with an average of 1392µg/l. Groundwater measurements taken during the same time period at Letart landfill range from 60.3µg/l to 17400µg/l, with an average of 2537µg/l. At the "local landfill", the groundwater concentrations range from 0.046µg/l to 39µg/l with an average of 8.83µg/l. Surface water samples at the "local landfill" range from 0.54µg/l to 87µg/l, with an average of 18.5µg/l. At Dry Run landfill, there are limited measurements of groundwater and surface water, with the maximum concentration in groundwater of 15µg/l and the maximum concentration in the permitted outfall of 200µg/l. In 1990, samples of surface water were taken and showed concentrations as high as 1.6mg/l[4]. In 1992, samples in the "upper" and "lower" ponds near Dry Run landfill measured 220µg/l and 230µg/l, respectively. Samples taken in these locations at Dry Run landfill have since shown lower concentrations.

In 1999, a RCRA Facility Investigation was completed for Washington Works and was submitted to EPA Region III in June 1999[5]. The report contains data on groundwater concentrations of APFO at Washington Works.

[3] Maps of the landfill locations and specific monitoring locations and results are available upon request.
[4] The validity of these 1990 analyses cannot be verified since the method used for analysis, the sample technique, the chain of custody, the sample quality control/quality assurance procedures, and therefore the accuracy of the results are not known.
[5] Report was submitted to Martin. T. Kotsch, Remedial Program Manager, EPA Region III, Philadelphia.

D. Transfers to Off-site Locations

Washington Works:

	Estimated Total Annual Releases or Transfers (lb. 1999)
Incineration	16000
Wastewater treatment	13400[6]
Underground Injection	0
Hazardous Waste Landfill	2600
Other landfill	0
Recycle or recovery	25000

VI. ON-SITE WORKPLACE EXPOSURE

A. Information on the Number of Employees Potentially Exposed

The tables below describe the number of workers that may be exposed to APFO in year 2000 during their normal work activities for each of the three sites where APFO is used or APFO containing product is processed.

Washington Works

Hours/Day	Days/yr			
	<10	10-100	100-250	>250
<0.25				
0.25-1		242		
1-8				
>8				

Routine worker activities that have potential for exposure:

- Handling raw material APFO
- Handling raw dispersions containing APFO
- Maintenance of polymerization reaction systems
- Polymer dryer operation and maintenance
- Packout of PTFE and co-polymer dispersion products
- Operation and maintenance of APFO recovery systems

[6] Transferred to Chambers Works facility (see section B and C above)

Parlin Plant

Hours/Day	Days/yr			
	<10	10-100	100-250	>250
<0.25				
0.25-1			18	
1-8				
>8				

Routine worker activities that have potential for exposure:

- Handling of PTFE and Co-polymer dispersion products
- Operation and maintenance of blending facilities
- Packout of finished product

Note that at no time is the material handled at the Parlin Plant at an elevated temperature where the APFO could sublime. Therefore, there is little potential for exposure to airborne APFO at this facility. All exposure potential is through skin contact during handling of the polymer dispersion materials, all of which contain <1% APFO with most containing <0.25% APFO.

Spruance Plant

Hours/Day	Days/yr			
	<10	10-100	100-250	>250
<0.25				
0.25-1		<10		
1-8				
>8				

Routine worker activities that have potential for exposure:

- Handling of PTFE and Co-polymer dispersion products
- Operation and maintenance of fiber coating facilities
- Operation and maintenance of sintering rolls
- Packaging of non-sintered product.

Note that the PTFE and co-polymer dispersion products used at the Spruance site contain <0.9% APFO, with most containing approximately 0.3% APFO.

B. Information on the Exposure Levels of Washington Works Employees

Since most of the processing done in the US with APFO and APFO containing intermediates and products is done at Washington Works, DuPont's airborne industrial hygiene data is concentrated at that site. The limited measurements of airborne APFO concentrations at the other sites where APFO containing products are used have shown much lower levels (mostly non-detectable) levels of APFO. The data in the table below

reflect monitoring done over the last 5 years at Washington Works. The sample results are a combination of chemical operator and maintenance worker personal samples.

Year	Sample Type	# of Samples	Minimum Concentration (mpb[7])	Maximum Concentration (mpb)	Mean (mpb)	Standard Deviation
1999	Partial Shift (mostly 6-8 hours)	100	<0.01	0.58	0.061	0.151
1998		83	.001	0.78	0.103	0.145
1997		100	<0.01	2.4	0.146	0.378
1996		73	N/D	0.29	0.055	0.069
1995		32	N/D	0.16	0.067	0.063

Partial shift air samples are taken at the rate of 200 mL/min using a Tenax collection tube that has been pretreated with sodium hydroxide/ethylene glycol/methanol. The APFO is desorbed from the tubes using methanolic hydrogen chloride, which also serves as a derivatizing reagent, converting the APFO to its methyl ester. After workup, the methyl ester is quantified using a gas chromatograph equipped with an electron capture detector. The methyl ester of perfluorodecanoic acid is used as an internal standard, and at least three calibration samples are prepared to cover the concentration range of interest. Precision is estimated to be +/- 10% relative.

The data above show averages consistently below the AGCHI TLV of 0.01mg/m^3, with only a very few samples above the TLV. Where results are above or near to the TLV, the event is investigated and corrective action (additional personal protective equipment or engineering controls) to reduce the exposure levels is undertaken. Older data from the 1980's show higher levels of exposure. In the early 1990's, Washington Works switched from receiving the APFO as a powder to receiving it as an aqueous solution. This change was done to reduce the potential for exposure during handling of the dry powder. It should be noted that in the 1997 time period, the site was starting up new APFO recovery facilities. Operating and maintenance difficulties associated with the start-up of these facilities may have contributed to the higher levels of APFO in the personal samples during that year.

Task specific monitoring data and wipe monitoring data exist. However, these data are not indicative of employee exposure and are not presented here. These samples are taken to identify areas where additional exposure controls may be necessary.

Engineering controls to reduce exposure consist of the following:

- Reaction systems are closed systems with continuous ambient monitoring for monomer concentrations
- Ventilation systems are installed where airborne concentrations are significant
- The polymer dryers operate under negative pressure to contain APFO and other materials.
- Recovery systems are in place to reduce airborne emissions.

[7] mpb= moles per billion. 0.56mpb is equivalent to the ACGIH TLV of 0.01mg/m^3

Personal protective equipment that workers regularly wear consist of the following:

- Safety shoes and side-shield safety glasses in all areas.
- Impervious gloves when handling APFO solutions or aqueous dispersion products.
- Chemical protective coveralls and goggles or face shields when the possibility of splashes of APFO containing solutions is present.
- Airline respirators or cartridge respirators where monitoring has shown to have high exposure potential.

At Washington Works, blood serum levels of APFO have been measured since 1981. Measurements of blood fluoride levels have been taken prior to 1981, but are of limited value in assessing exposure to APFO. A summary of results of employees with identified APFO exposure potential the 1995, 1989-90, 1985,and 1984 volunteer sampling events is in the table below. Due to significant job assignment movement during this period of time, analysis of trends of data are difficult. The data in the table below prior to 1995 are for employees included in the 1995 sampling data so that comparisons of relative levels of APFO in blood serum can be compared. The entire data set of blood concentrations is available upon request.

Year	# of Samples	Minimum Concentration (ppm)	Maximum Concentration (ppm)	Mean Concentration (ppm)
1995	73	0.12	4.5	1.57
1989-90	23	0.4	8.5	3.13
1985	21	0.06[8]	18[9]	2.44
1984	19	0.07[7]	24[8]	3.82

[8] This individual was working in a job that has APFO exposure potential at the time of the sample.
[9] This individual consistently has had the highest blood concentration of APFO since APFO specific samples were taken. This employee left an APFO exposure potential assignment in 1991. In 1995 this employee's blood serum level was 4.4ppm.

DuPont US APFO Balance

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