Background

The U.S.EPA has information that suggests that the perfluorooctanoate anionis present at low part per billion levels in the blood of a cross section of the United States population.[1] The ammonium salt of this anion, ammonium perfluorooctanoate (APFO) is a fluorinated polymerization aid used in the manufacture of fluoropolymers.

This document is a summary of the fluoropolymer and fluorotelomer industry's efforts to understand possible sources of PFOA exposure. This document also summarizes industry's commitment to significantly reduce or eliminate the number of possible PFOA exposure routes and to better understand all potential exposure routes.

The efforts discussed herein are primarily the work of two industry groups; the Fluoropolymers Manufacturing Group (FMG), and the Telomers Research Program (TRP). Both groups have been working in cooperation with the United States Environmental Protection Agency and other global regulatory agencies (i.e. Environment & Health Canada, U.K. DEFRA, Environment Agency and Heath & Safety Executive and METI, Japan) to better understand this issue.

Introduction

The FMG and TRP have attempted to identify all the possible sources of PFOA that might lead to general population exposure, including sources not related to the fluoropolymer or telomer industries. At this time, no attempt has been made to rank or validate the possible routes. Based on the extremely low levels of PFOA in the blood data reported by 3M, all possible routes are being considered until enough information has been gathered to rule out potential routes. Each potential route is described below, as is a summary of the proactive efforts of the industry to reduce or eliminate potential sources of PFOA exposure.

Potential Exposure Route: Manufacture of Fluorinated Polymerization Aids (FPAs)

Background

APFO is the most widely used FPA of interest in the United States. For many years, 3M was the only US manufacturer of APFO, with facilities in Decatur, Alabama and Cottage Grove, Minnesota. Annual production from these facilities peaked at approximately 500,000 pounds per year(2)

3M has indicated that APFO emissions from these manufacturing facilities were approximately 50,000 pounds per year.(3) These emissions occur at specific manufacturing facilities and would be characterized as resulting in localized environmental exposure. 3M announced in May 2000 that it would no longer produce APFO in the United States and would not market APFO on a global basis. 3M has communicated that U.S. production of APFO will cease by year-end, 2002(a).
(a) 3M phase out announcement, May 16, 2000 – or what?

Industry Actions

[1] AR226-xxx reference(s) of the submission(s)

Because APFO is essential to the manufacture of fluoropolymers, DuPont announced in October 2001 its intention to manufacture APFO by the telomerization process in the US(b). The announced capacity of this facility, which started up operations in October 2002, will be about 300,000 pounds per year, or 40% less than the actual annual production at the two 3M manufacturing locations.

(b) DuPont announcement (?)

DuPont has also announced it is installing state of the art emissions control technology at their new manufacturing facility that will limit emissions to less that 500 pounds per year at capacity.

The net result of 3M closing its U.S. APFO production plants and DuPont installing new manufacturing capacity will be a minimum 40% reduction in the amount of APFO manufacturing in the US and a minimum 99% reduction in APFO manufacturing emissions.

Outside the U.S., APFO will be manufactured by Daikin in Japan and for internal use only by Dyneon (a wholly-owned subsidiary of 3M) in Germany, and by Miteni in Italy.

Potential Exposure Route: Non-Fluoropolymer Products

Background

3M has indicated that its greater than 97% of its APFO sales were to the fluoropolymer manufacturing industry. The remainder was sales to customers outside of the Fluoropolymer industry. They have not shared information on specific markets, but have indicated total annual non-fluoropolymer sales of 13,000 pounds per year(4) Without a complete understanding of the applications and the industries served, one must consider it possible that there is potential for environmental and direct consumer exposure.

Industry Actions

Both Daikin and DuPont have communicated that they will only sell APFO to responsible users within the Fluoropolymers industry. Dyneon has announced that they will only manufacture for internal use and will not market APFO. As a result, there will be no APFO sales outside of the Fluoropolymer industry from these producers when 3M stops marketing APFO at the end of 2002.

Potential Exposure Route: Fluoropolymer Manufacture

Background

FPAs, of which APFO is the most widely used, are used as a surfactant in the manufacture of fluoropolymers. FPAs are not part of the actual fluoropolymer molecule, but enable the growth of the polymer chain in the aqueous fluoropolymer polymerization process, and stabilize the resultant aqueous fluoropolymer dispersion.

A material balance conducted by the fluoropolymer manufacturers indicates that the global total FPA[2] use in 1999 was about 450,000 pounds.(5) The material balance indicated that 64% of this material was emitted to the environment (air, water, and land), 14% was captured and recycled, 7% was destroyed, and 14% remained in products that leave the fluoropolymer manufacturing site, primarily aqueous dispersion products designed for further

[2] The global total includes pounds of APFO and all other fluoropolymer processing aids utilized in the manufacture of fluoropolymers.

processing. Like emissions from FPA manufacture, emissions from fluoropolymer manufacture are localized.

Industry Actions

The FMG has communicated a voluntary commitment to emission containment that requires emissions to be reduced by a minimum of 50% by year-end 2006. To facilitate this emissions reduction commitment, Dyneon has offered to license its APFO recovery and recycle technology to fluoropolymer producers. DuPont has volunteered to share its "capture for destruction" technology with the industry group license free and has also offered to license its "capture for recycle" technology.

The FMG has recently completed a material balance forecast that reflects a 49% reduction in emissions by 2004 and a 67% reduction by 2006 (c). These reductions significantly exceed the voluntary commitment to contain emissions made by the FMG.

In the forecast material balance, the amount of material recycled increases to 50%, which results in less APFO being manufactured.

(c) SPI FMG submission to the US EPA July 2002?

Potential Exposure Route: Fluoropolymer Finished Products

Background

As mentioned previously, a small percentage of the APFO used leaves manufacturing sites in commercial aqueous fluoropolymer dispersion products. Dry fluoropolymers, which are the dominant products produced and sold, are expected to contain little or no APFO. Of the aqueous products containing APFO, about 90% receive additional heat treating that most likely destroys the residual APFO before leaving the down stream processor in a finished product.

Industry Actions

To assure that the fate of the APFO leaving the fluoropolymer manufacturing and dispersion processing facilities is understood, the FMG has volunteered to initiate and/or facilitate two activities.

First, the FMG will complete and submit an analysis to determine the residual amount of APFO that may remain in dry finished products. This analysis should help confirm the common belief that most of these products have enough heat history to destroy residual quantities of APFO, or may identify specific applications in which the APFO is truly carried on with the finished product.

Second, the FMG will facilitate the development of a material balance at aqueous fluoropolymer dispersion customers' manufacturing facilities. This material balance will provide a better understanding of the fate of the APFO at these facilities and aid in determining whether any additional containment efforts will be needed.

Potential Exposure Route: PFOA Impurities in POSF Related Products

Background

Using POSF (perfluorooctyl sulfonyl fluoride) as a building block, 3M manufactured a family of surfactants, polymers, and additive products that have been sold around the world. "POSF related products" describes this family of products. 3M has indicated in the production of POSF, PFOA was also produced as a minor by-product.(6) This PFOA by-product subsequently may have been an impurity in some of the POSF related products. The PFOA concentration has been reported by 3M to be in the neighborhood of 500 ppm.(7) The presence of PFOA in POSF related products has been confirmed independently and published.[3]

The EPA has been informed that there is a correlation between the levels of PFOS and PFOA found in the blood of the US general population.[4] This correlation may indicate that exposure to the POSF related products resulted in the PFOA in blood, or it may indicate that exposure to similar products such as fluorotelomer based protective products was the cause.

Industry Actions

3M announced in May 2000, that it will cease manufacture of POSF related products by the end of 2002. This announcement was followed by the publication of a proposed SNUR in December 2001 by the US EPA regulating the use of PFOS derivatives in the United States. These actions will ensure that any PFOA impurities formerly found in these products will no longer be released.

Potential Exposure Route: Transformation to PFOA

Background

Another possible route of exposure is the abiotic or biotic transformation of other materials into PFOA. Two potential pathways are postulated which may result in the formation of PFOA from other substances.

The first route is from sulfonate-based materials (or POSF related products). 3M has provided data to U.S. EPA that indicates that perfluorosulfonamide derivatives may transform abiotically to PFOA.[6] Ovanes Mckenyan, in his PBT modeling using CATABOL[ACWI], has also predicted that ??? of the POSF related products manufactured by the 3M Company will break down to PFOA, what proves to be a thermodynamic minimum in his modeling. [WHAT DOES THIS MEAN?]

The second potential route is from transformation of Telomer based materials.[7] This route was first theorized based on a report that 8-2 Telomer B Alcohol , when orally dosed to rats, is metabolized to form PFOA.[8] More recent TRP study results indicate that PFOA is not the only metabolic transformation product in rats, and may not be the predominant metabolite.[9] Furthermore, TRP members believe that it is unlikely this material is readily available for generalized oral ingestion.

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[3] Cite Field publication (s)
[4] AR226-xxxx reference(s)
[6] AR226-xxxx reference(s)
[7] For a definition of what a Telomer is and products therefrom see: Baker and Kissa References
[8] reference: 3M, 1981, Analytical Paper
[9] TRP reference AR226-XXXX

What about abiotic transformation to PFOA? What about residual content of low molecular weight telomer building blocks in these products?

Industry Actions

The TRP is conducting a research program with a focus on three parallel work-streams: toxicology, pharmacokinetics, and environmental fate and effects studies. Metabolic, abiotic and biotic transformation routes are being investigated. In addition, the potential for the presence of PFOA and/or creation of PFOA during the production or industrial use/application of Telomer-based products will be examined. Finally, the TRP is working to clarify potential routes for release of the Telomer-based materials into the environment as well as potential routes for human exposure.

The Telomer Research Program (TRP) industry group will be conducting a series of pharmacokinetic studies with ^{14}C-radiolabeled 8-2 Telomer B Alcohol study material to determine the metabolic pathway for this substance in a number of species.[10] In addition, the TRP will utilize the same radiolabeled substance to conduct biodegradation studies to define what this substance may become when microbial populations act upon it under environmental biodegradation conditions. Although the TRP is initially studying 8-2 Telomer B Alcohol, the majority (80% +/-) of Telomer-based products manufactured are polymeric substances. As such, the TRP is working to develop methodologies that will define whether and if so, how, these polymeric materials may transform abiotically or biotically in the environment or under production, industrial processing / application or consumer use conditions.

[RESIDUALS?]

Summary

The possible exposure routes classified as "Non-Fluoropolymer Products", "PFOA Impurities in POSF Related Materials", and "Transformation to PFOA from Sulfonate Based Materials", may have contributed to both environmental and direct consumer exposure. A conclusive determination of whether these routes have significantly contributed to general population exposure will probably never be realized,. However, future contribution via these routes will be eliminated as the existing inventory gets depleted.

Future APFO manufacture to support the ongoing Fluoropolymer industry will have a significantly reduced environmental footprint. An improved process, with state of the art containment technology, will cut emissions by more than 99% as compared with the previous technology practiced by 3M.

There is little question that Fluoropolymer manufacturing sites have been a large contributor to environmental exposure, , although that exposure is localized. Fluoropolymer manufacturers have conducted a plant site material balance and, based on that assessment, have made a voluntary commitment to reduce emissions by over 50% before 2006. Current forecasts predict meeting the commitment around 2004, with an ultimate forecast for a 67% reduction by 2006. Although a large source of emissions, fluoropolymer manufacturing is not considered to be the source of PFOA exposure for the general population, because of its localized nature.

To better understand the fate of the material going to dispersion customers, the Fluoropolymer industry will be conducting material balance at the different dispersion

[10] TRP reference AR226-xxxx

processors. Once a better understanding is developed for the fate of APFO in dispersion processing, a plan will be developed to facilitate containment, if necessary.

The industry is also committed to understand the potential for APFO to be present in finished products. Although a vast majority of fluoropolymers produced are heat-treated at a temperature believed to be high enough to either remove or destroy APFO, the industry is committed to verify fully this assumption by completing the measurement of residual APFO levels in the finished products.

The pattern of use of articles made of or containing fluoropolymers also argues against them being a source of exposure for the general US population. The vast majority (95%?) of fluoropolymers are used in industrial applications. The consumer is not in contact with these articles, such as engine and transmission seals, chemical plant equipment and wire and cable coatings. The remaining 5% of fluoropolymers are used in consumer products such as cookware and weatherproof clothing, but these products experience high temperatures during processing, and the APFO content is likely extremely low or non-detectable.

The TRP is committed to a conducting a rigorous research program and end-use analysis to understand the potential for PFOA to be present in Telomer products as a result of production, to be created during industrial or end-user processing, and to be created as a result of abiotic or biotic transformation processes. More broadly, the TRP is conducting its research program with a focus on three parallel work-streams: toxicology, pharmacokinetics, and environmental fate and effects studies. Finally, the TRP is working to clarify how the Telomer-based materials might enter the environment as well as potential routes for human exposure.