

Montreal Protocol



Process Agents Task Force

Case Study #9

Use of CFC 113 for manufacturing a family of fluoropolymer resins

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CS-9 Use of CFC 113 for manufacturing a family of fluoropolymer resins

CS-9.1 Introduction

Fluoropolymer resins that have traditionally used an ODS processing agent are manufactured by a small number of multinationals in Europe, North America, and Japan. One North American-based multinational chemical, plastics, and fiber company manufactures three basic product lines of fluoropolymers that have traditionally used CFC-113 as a process agent. Its manufacturing facilities are located only in non-Article 5(1) countries. The generic types of fluoroproducts are typically:

- Ethylene-tetrafluoroethylene or ETFE
- Ethylene-chlorotrifluoroethylene or ECTFE
- Perfluoroalkoxy, fully fluorinated resins or PFA
- Perfluorovinylethers

CS-9.1.1 Process description

These products are typically produced in batch operations where resins, process agents (solvents), and other reactants are batch charged into reaction vessels followed by product isolation, product purification, and solvent recovery.

The operations described in this case study are unique to the industry due to their much higher volume and use of some continuous instead of batch technology for much of the production.

CS-9.2 Unique product properties

The products are all high value resins used primarily in industrial applications where lower cost resins are unable to meet demanding performance criteria typically characterized by:

- Ultra-high purity and chemical inertness for chemical processing operations.
- Mechanical toughness and chemical inertness for containers dedicated to handling hazardous or toxic materials in a safe, environmentally sound manner.
- Predetermined electrical conductivity for extended use high temperature components.

Specific uses for these fluoropolymer resins include:

- Electrical and control wiring for commercial and military aircraft because of excellent electrical insulation properties, inertness to atmospheric pollutants, and retention of properties over very extreme temperatures.
- Non-stick coatings on high value cookware.
- Computer wiring.

CS-9.3 Why and how is CFC-113 used as a process agent?

	Purpose
Quality of final product	XX
Safety	X
Necessary for reaction	
Yield	X
Cost	X
Other	

Notes to Table: X signifies the main purpose, XX signifies a secondary purpose

CFC-113 was originally selected as a process agent for this family of fluorinated resins because it exhibited several key properties:

- Low toxicity.
- Provides excellent dispersions.
- Suitable solvency for several polymer structures that are insoluble and a wide range of solvents.
- Inhibits explosion of tetrafluoroethylene (TFE) (backbone of these products).
- Chemical stability to temperatures and pressure.
- Non-flammable.

Since four world scale manufacturing facilities exist and represent a combined investment of several tens of millions of dollars, it is economically impractical to convert to a flammable solvent without complete redesign of all process equipment and building to a flammable hazard classification.

The unique properties for several critical customer applications are very dependent upon the specific solvent and process conditions. Hence, finding a suitable solvent replacement requires not only that it provides similar process operability, safety, and cost, but also its specific products must be rigorously proven in every unique customer application.

Another process safety concern is to suppress the explosion tendency of the main feedstock, TFE. Experience has demonstrated that hydrocarbon solvents that may exhibit suitable solvent properties will not suppress TFE explosions. The only practical solvents

have proven to be fully halogenated materials like CFCs, perfluorocarbons (PFCs), hydrofluorocarbons (HFCs), and marginal hydrofluorocarbons (HCFCs).

Documented CFC-113 use for the global fluoropolymer plants are not accurate prior to the late 1980s since CFCs were not recognized as harmful to the environment and their use and emissions were not under any special control. Undocumented memory indicates that just one of four sites used about 400/tonnes/yr. of CFC-113. Documented use by 1988 was in the range of 250 metric tonnes per year for the four plants. By taking steps described in the following text, emissions have been cut to 15% of the 1988 documented experience, while product output has risen.

CS-9.3.1 Efficiency of ODS recovery

Emphasis has been placed on developing technology to displace CFC-113 as opposed to expenditure of large R&D plus capital to achieve 99.9+% recovery. The short-term process improvements and handling practices have generally resulted in greater than 90% efficiency in CFC-113 use. See Section C-9.4 for details.

CS-9.4 ODS abatement and containment

Overall process agent emissions are 15% of what they were in the late 1980s due to several capital and procedure steps taken at all four plant sites globally. It is important to note that one plant anticipated shutting down rather than spend the large amount of capital to convert to a non-ODS process agent; however sharply increased global demand necessitated continued operation of this facility. It is now planned to convert this facility to a non-ODS process agent if global market conditions support this activity.

All sites use similar technology to minimize ODS loss or to abate emissions. Vent collection and recovery systems capture and recycle 99% of CFC-113 in the primary vents. Product dryer modifications reduce CFC-113 emission by greater than 90% of prior experience during dryer regeneration. A fugitive emission program aimed at leak detection and repair has been instituted. Special emphasis has been devoted to mechanical seal designs and maintenance techniques and procedures that have reduced emissions. Finally, a rigorous solvent record keeping and emission tracking program pinpoints sources for future CFC-113 reductions as well as focusing attention on current emissions.

CS-9.4.1 Regulatory requirements

All four plant sites are in countries where chemical production facilities are permitted by national, state, or local authorities. CFC-113 is regulated in some states as a ground water pollutant, so any non-volatile waste is disposed of in environmentally secure landfills.

CS-9.5 Non-ODS technology options

Efforts to identify potential alternate process agents that would work in the four different global plants and for the full range of fluoropolymer products got underway in 1987, following U.S. CFC industry recognition and support for an international regime to stabilize or reduce CFC emissions globally.

Any suitable replacement solvent(s) (process agent(s)) would have to deal with a host of process and product issues that were all cost effectively managed with a single solvent, CFC-113. Safety was of foremost concern since tetrafluoroethylene (TFE), the backbone of much of the product line has a tendency towards severe deflagration (explosion). A key property of the process agent of choice suppresses the deflagration tendency of TFE. Hydrocarbons will not suppress TFE deflagration but fully halogenated solvents will. With CFCs, carbon tetrachloride, and halons already set for phase-out, and HCFCs scheduled for near term phase-out, the options were significantly limited; primarily PFCs and HFCs.

Close to fifty potential process agents have been explored over the past eight years as part of a multimillion dollar research and development program. However, there are still specific critical customer applications that have not yet been able to accept the non-ODS products. Effort is continuing to find an acceptable process agent or suitable processing conditions for these products.

After many years of extensive research and development, there are still unresolved challenges to a 100% ODS use phase-out. A Japanese manufacturer of fluoropolymer resins has converted to a non-ODS process utilizing a proprietary technology, however, the facility does not produce the full range of fluoropolymer products.