

**THE U.S. SOLVENT CLEANING INDUSTRY AND THE TRANSITION TO  
NON OZONE DEPLETING SUBSTANCES**

Prepared for

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Throughout the report, trade or manufacturer's names appear because they are considered essential to the objective of this report. The Agency does not endorse products or manufacturers. Mention of a product does not constitute endorsement or rejection of the product.

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## Executive Summary

Industrial cleaning in the United States has changed dramatically over the past 15 to 20 years. Following the discovery that chlorofluorocarbons (CFCs) and other substances such as methyl chloroform were depleting the stratospheric ozone layer that shields the Earth from the Sun's harmful ultraviolet light, a global effort to eliminate the use of such substances was launched. The U.S. ratification of the Montreal Protocol on Substances that Deplete the Ozone Layer in 1988 and the subsequent Clean Air Act Amendments of 1990 (CAAA) had major repercussions on how end-users cleaned metal parts, defluxed wiring assemblies on printed circuit boards, and removed contaminants from high value precision mechanical parts and assemblies. This report serves as an objective assessment of progress toward using alternatives to ozone depleting substances (ODS).

For the purpose of this report, the solvent cleaning industry is divided into four end-uses 1) Electronics Cleaning; 2) Metal Cleaning; 3) Precision Cleaning; and 4) Aerosol Solvent Cleaning. ODS that are used by these end-uses and controlled by the Montreal Protocol are summarized in Table ES-1. These substances are classified according to their ozone depletion potential (ODP), a relative index of the ability of a substance to cause ozone depletion.

**Table ES-1. Ozone-Depleting Substances Used as Solvents**

Class I Substances	ODP <sup>a</sup>	Class II Substances	ODP <sup>a</sup>
CFC-113	0.8	HCFC-225ca	0.025
Methyl Chloroform	0.1	HCFC-225cb	0.033
Carbon tetrachloride	1.1	HCFC-141b	0.11
CFC-11	1.0	HCFC-123	0.02-0.06

<sup>a</sup>ODP values are taken from the Montreal Protocol (UNEP 2003a).

Class I ODS were phased out beginning January 1, 1996; while Class II substances (i.e., hydrochlorofluorocarbons, or HCFCs) follow a different phaseout schedule, which began with the phaseout of HCFC-141b on January 1, 2003.<sup>1</sup>

### ES.1 Class I ODS Used as Solvents

Because of their powerful cleaning properties, methyl chloroform and CFC-113 became the two major Class I ODS used as solvents in the cleaning of industrial applications in the 1980s. Methyl chloroform was used predominantly in metal cleaning (accounting for 60 percent of use), while CFC-113 was most commonly used in electronics cleaning (accounting for 70 percent of total use). Prior to the Class I ODS phaseout, the solvent cleaning industry used as much as 543 million pounds of Class I ODS in 1986 (see Table ES-2). Of this amount, metal cleaning was responsible for 48 percent while the electronics and precision cleaning end-uses accounted for 24 and 28 percent of solvent usage, respectively. Less than one percent of total Class I ODS usage was attributed to aerosol solvent cleaning as of 1986.

**Table ES-2. U.S. Solvent Cleaning Industry Pre-Phaseout Class I ODS Usage, Million Pounds 1986-1995**

	1986	1987	1988	1989	1990	1991	1992	1993	1994	1995
CFC-113	134	127	119	112	94.3	83.8	46.8	9.42	7.81	3.26
Methyl Chloroform	407	359	311	262	251	239	228	133	22.8	20.4
Carbon Tetrachloride	0.95	0.50	0.19	0.01	0.01	0.01	0.01	0.04	0.00	0.00
CFC-11	1.01	1.00	0.98	0.97	0.67	0.58	0.56	0.32	0.08	0.02

As Table ES-2 indicates, usage declined steadily as the 1996 phaseout approached and end-users began developing and implementing alternative cleaning agents and methods. In addition, in preparation for the phaseout, end-users began to stockpile additional quantities of Class I ODS as a transitional

<sup>1</sup> Phaseout signifies the elimination of U.S. production and importation of these chemicals.

solution. It is estimated that as of the 1996 phaseout date, stockpiled quantities amounted to 53.0 million pounds of CFC-113, 47.7 million pounds of methyl chloroform, and 1.0 million pounds of CFC-11.

### ***ES.1.1 Reducing and Eliminating the Use of Class I ODS Solvent Cleaners***

In response to regulations to protect the ozone layer, the solvent cleaning industry initially developed emission reduction strategies. End-users found that such strategies offered not only health and environmental benefits, but economic benefits as well. Equipment retrofits, improvements in the design of vapor degreasers, and the practice of recycling and recovery enabled industry to reduce the demand for Class I ODS and consequently experience a reduction in solvent costs per operating hour.

These emission reduction methods did not actually replace the Class I ODS being used; non-ODS cleaning agents were also required. The research and development for new alternative solvents required tackling various issues such as poor solvency and substrate compatibility, cost, and worker safety. Many times, these difficulties were overcome through formulating blends and azeotropes of effective solvents. Industry end-users soon began adopting alternative solvents as a result of such advancements.

Another popular trend was the complete replacement of methods such as vapor degreasing with substitute technologies. Many metal and precision cleaning end-users turned to aqueous cleaning, while the electronics industry discovered that both semi-aqueous cleaning and no-clean technology were effective. The current characterization of the solvent cleaning industry that previously used Class I ODS can be summarized as follows:

- Electronics Cleaning. No-clean technology has turned out to be the most successful transition strategy and is the first preferred alternative in electronics cleaning as long as the application is able to meet acceptable performance standards.
- Metal Cleaning. Aqueous cleaning and alternative solvent cleaning have primarily replaced Class I ODS usage in metal cleaning. Chlorinated solvents are considered the most common solvent because of affordability and demonstrated performance.
- Precision Cleaning. Because precision cleaning requires a high level of cleanliness and users perceived solvents as having better cleaning performance, Class I ODS were primarily replaced with new alternative solvents instead of alternative technologies. Specifically, fluorinated solvent alternatives (i.e., hydrofluorocarbons (HFCs), HCFCs, and hydrofluoroethers (HFEs)) and to a lesser extent, n-propyl bromide (nPB), have become successful replacements because of the solvency range and substrate compatibility.
- Aerosol Solvent Cleaning. Class I ODS were first replaced by hydrocarbon cleaning agents after the ban on CFC propellants in 1977. Although considered a transitional substitute, HCFC-141b replaced any remaining CFC-based cleaners as well as much of the hydrocarbon substitute cleaners.

### **ES.2 Class II ODS Used as Solvents**

Considered interim solutions, Class II ODS were adopted by the solvent cleaning industry as replacements for Class I ODS. Class II ODS historical usage by the solvent industry is presented in Table ES-3.

**Table ES-3. U.S. Solvent Cleaning Industry Pre-Phaseout Class II ODS Usage, Million Pounds 1992-2003**

	1992	1993	1994	1995	1996	1997	1998	1999	2000	2001	2002	2003
HCFC-225 ca/cb	0.00	0.00	0.12	0.37	0.52	0.53	0.54	0.55	0.56	0.57	0.58	0.59
HCFC-141b	6.79	7.24	20.3	33.3	24.9	24.6	13.1	12.9	12.4	11.1	14.2	12.6

As shown in Table ES-3, Class II ODS historical usage patterns vary by substance. The growing demand for HCFC-141b in the early 1990s was in large part because of its excellent solvency power and near-

drop-in replacement potential for methyl chloroform and CFC-113. The aerosol solvent market adopted HCFC-141b and it was also used in vapor degreasers for the cleaning of high performance electronics components in aerospace, military, and medical applications. Usage began to decline after EPA's Significant New Alternatives Policy (SNAP) Program banned HCFC-141b use in vapor degreasing as of 1997. Nonetheless, HCFC-141b was still permitted in manual cleaning methods (e.g., hand wiping and flushing) and as the prime aerosol solvent for the spot cleaning of various electronics components.

While use of HCFC-141b continued to decline as the 2003 phaseout approached, the use of HCFC-225 ca/cb gradually increased from 1996 to 2003. Introduced to the United States in 1994, HCFC-225 ca/cb began to develop as an alternative for CFC-113, methyl chloroform, and HCFC-141b in the cleaning of electronic and precision components because of its low viscosity, high density, and low surface tension. In general, the use of this Class II ODS as a solvent has shown a minimal annual increase. HCFC-225 ca/cb is the only Class II ODS based solvent still permitted for production and importation in the United States. Continued growth for this solvent is expected until its phaseout on January 1, 2015.

As with Class I ODS, the solvent cleaning industry turned to stockpiling as a transitional solution to the phaseout of HCFC-141b. An estimated 18 million pounds of HCFC-141b was stockpiled by the solvent industry as of the 2003 phaseout. Of this amount, approximately 12.6 million pounds of HCFC-141b was extracted for use in 2003, 10 million pounds of which was used as an aerosol solvent cleaner. Industry expert opinion suggests that uncommitted quantities of HCFC-141b are readily available to industry and are still economically competitive with alternatives (Techspray 2004a; AGA Chemicals 2004).

Overall, it is expected that the majority of HCFC-141b stockpiles will last through 2005. While industry experts assume that HCFC-141b use will continue to decline, no definitive end-date for usage can be identified (Honeywell 2004a). Ultimately, all HCFC-141b end-users in the solvent cleaning industry will transition to alternatives.

### ***ES.2.1 Reducing and Eliminating the Use of Class II ODS Solvent Cleaners***

Many products are available as effective replacements for HCFC-141b. Currently, HCFC-225 ca/cb is being marketed as an interim replacement option. Other alternatives include formulations of HFCs or HFEs and trans-1,2-dichloroethylene (trans), and blends of nPB for aerosol and manual solvent cleaning. As HCFC-141b stockpiles are reduced, it is expected that the demand for these candidates will increase, manufacturers of HCFC-141b alternatives will experience economies of scale as a result of increased production, and prices will fall.

### **ES.3 The Current State and Future Outlook of ODS in the Solvent Cleaning Industry**

Through research and development efforts, viable substitutes have been qualified for most applications. However, in some cases, ODS are still used in some applications, such as the cleaning of oxygen systems, either because extensive testing and validation procedures slow the conversion process or because stockpile volumes are still large enough that users have not fully committed to finding an alternative.

While the phaseout of Class I ODS is almost complete, the use of these ODS as cleaning solvents continues minimally in specific aerospace applications that have been granted an essential use exemption (EUE) for methyl chloroform. These applications are nonetheless advancing towards the elimination of ODS. The solid rocket motor manufacturing in the Space Shuttle program has made excellent progress in lessening reliance on their EUE, and although usage of methyl chloroform is estimated to continue, the quantity used annually is very minimal. Furthermore, 2004 marks the first year that the Titan program has chosen to eliminate the need for an EUE.

The replacement of Class II ODS with alternatives is currently underway for HCFC-141b, and conversion for end-users of HCFC-225 ca/cb will begin as 2015 nears. With the numerous solvent and technology replacements available today and the demonstrated success in transition away from Class I ODS, the solvent cleaning industry is prepared to successfully phase out and complete elimination of Class II ODS based solvents.

# 1 Background

This report presents an overall market characterization of the solvent sector in the United States and in particular, the impacts that the phaseout of ozone-depleting substances (ODS) have had on solvent selection by traditional users of ODS. In 1987, the United States signed the Montreal Protocol on Substances that Deplete the Ozone Layer (later ratified in 1988), committing to the elimination of the production and importation of substances that deplete stratospheric ozone. The Clean Air Act Amendments of 1990 (CAAA) were subsequently enacted providing the legal framework for the ban on these substances in the United States. The substances first addressed by the CAAA were the Class I ODS, including chlorofluorocarbons (CFCs), halons, methyl chloroform, and carbon tetrachloride. As consumers of methyl chloroform and CFC-113, end-users in the solvent industry were directly affected by a market transformation from the use of traditional Class I ODS solvents and solvent cleaning methods to the adoption of various alternative solvents, adjustments to technology, conservation and recovery practices, and changes in solvent cleaning techniques.

This report focuses on the major end-uses that have employed ODS solvents, the historical usage of ODS across these solvent end-uses, and the transition trends that have occurred over time. The report is organized as follows:

- [Section 1](#) provides an overview of the solvent cleaning industry and describes each solvent end-use, including the types of businesses associated with each;
- [Section 2](#) presents the overall historical usage of Class I ODS by the solvent cleaning industry, the estimated usage patterns by each end-use, and the estimated quantities set aside for stockpiling before the phaseout of these substances;
- [Section 3](#) discusses the use of Class II ODS used as short-term alternatives to Class I ODS and the status of industry's transition away from these substances;
- [Section 4](#) introduces the alternative solvents and substitution technologies available to the solvent industry to replace all ODS used as solvents, and provides an overview of the substitution trends experienced by each solvent end-use; and
- [Section 5](#) presents the current state of Class I ODS use in the solvent industry and the future outlook for applications where adequate alternatives have not yet been found and/or end-uses still tend to use ODS.

## 1.1 Overview of U.S. Solvent Cleaning End-Uses

Solvents are required in a variety of different industrial end-use applications. Their primary function is to dissolve contaminants through a physical cleaning process removing soil, oils, wax, grease, or other contaminants from a number of substrate materials. Solvent cleaning is required for a range of products, from printed wiring assemblies in the electronics industry to gyroscopes in the aerospace industry, and various metal parts used in machinery and other applications. Solvents are also dispensed in an aerosol form to clean, for example, electronic components.

Solvent cleaning can be required at any point throughout the production, maintenance, repair and servicing in the electronics, precision manufacturing, and metal manufacturing industries. During these stages, there are four methods of cleaning that have been and continue to be employed: cold cleaning, vapor degreasing (open top and conveyorized), and aerosol solvent cleaning (see Box 1-1). This report focuses primarily on solvent cleaning during the original manufacture of industrial equipment, products, and assemblies.<sup>2</sup>

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<sup>2</sup> Usage and emission estimates provided in this report are assumed to characterize solvent cleaning only during original equipment manufacturing (OEM) processes for all end-uses except aerosol solvent cleaning. For the purpose of this report, aerosol solvent cleaning is characterized as maintenance, repair, and service cleaning.



Methyl chloroform and CFC-113 are considered the two primary Class I ODS that have been used as solvents across these industrial applications. (Minor quantities of CFC-11 and carbon tetrachloride have also been used as solvents.) These substances became widely used by the solvent industry because of their high solvency and powerful cleaning properties. Many end-users also turned to methyl chloroform and CFC-113 to avoid the environmental and health issues associated with trichloroethylene, and other chlorinated solvents that are volatile organic compounds (VOCs) contributing to ground-level ozone (smog), as well as suspected carcinogens. Varying ODS consumption patterns within each solvent end-use resulted as solvent end-users discovered which of these ODS were most safe and effective for their applications.

For the purpose of analyzing Class I ODS use and substitution trends, this report partitions the solvent industry into the following end-uses:

1. Electronics Cleaning;
2. Metal Cleaning;
3. Precision Cleaning; and
4. Aerosol Solvent Cleaning.

For each of the solvent end-uses identified, the North American Industry Classification System (NAICS) was used to suggest businesses that might be classified within each end-use. NAICS codes were identified and analyzed at the three-digit level and the six-digit level. Representing a broader level, some three-digit level NAICS codes may belong in more than one solvent end-use. For example, NAICS code 336, *Transportation Equipment Manufacturing*, is associated with the following three end-uses in the following manner:

- 336321, Vehicular Light Equipment Manufacturing (electronics cleaning)
- 336111, Automobile Manufacturing (metal cleaning)
- 336414, Guided Missile and Space Vehicle Manufacturing (precision cleaning)

As illustrated, the NAICS codes identified at the six-digit level provide a further specification of the industries associated with each three-digit level identified by end-use. Six digit NAICS codes are provided in Appendix A, which also contains a detailed discussion of the methodology for determining NAICS codes associated with the solvent cleaning industry.

### **1.1.1 Electronics Cleaning**

The process of electronics cleaning, including defluxing and other cleaning operations, is an integral part of the production of high reliability electronics. Defluxing involves the highest level of cleaning for printed wiring assemblies and other contamination-sensitive electronic applications. The process of defluxing

#### **Box 1-1. Solvent Cleaning Processes and Equipment**

Cold Cleaning is the process of removing contaminants from the surface of metal parts at room temperature. The parts are sprayed, brushed, flushed, or immersed and soaked into a cold cleaner (typically a spray sink or a dip tank) containing a non-boiling solvent degreaser.

Open Top Vapor Degreasing is a cleaning process using hot vapors and liquid solvent in a boiling sump to remove soils, particularly oils, greases and waxes. An open-top vapor degreaser consists of an open steel tank with a heated solvent reservoir, usually referred to as a sump, and a cooling zone near the top. The sump is heated to boil the solvent and generate a solvent vapor blanket that covers the liquid solvent in the tank. The solvent vapor condenses when it reaches the cooling zone; this clean liquid solvent condensate flows to rinse tanks which overflow back to the boil sump.

Conveyorized Vapor Degreasing is a less frequently used cleaning method involving the use of large, enclosed mechanical systems that handle a large workload capacity (UNEP 1999). Also known as in-line vapor degreasers, these units operate similarly to open top vapor degreasers with the exception that parts are continuously moved into and out of the cleaning zone (vapor or solvent liquid) and rinse zones on a conveyor belt.

Aerosol Solvent Cleaning is a specialized spot cleaning process for confined areas of machinery and parts. Contrary to the other equipment and processes where the part being cleaned is immersed into a cleaning tank, aerosol solvents are contained typically in an aerosol can and are dispensed onto the parts being cleaned. A spray tube inserted into the valve of the can or a flexible tube ending in a small brush assists in the discharge of the cleaning solvent. This process is 100 percent emissive in nature with essentially no reuse possible.

removes the flux residue and handling soils and particulates that remain after a soldering operation. Flux is a product that is used to facilitate the joining of two metallic electronic components by initially cleaning the metal surface and subsequently assisting in transferring heat from the heat source to the metal surfaces being joined (usually to a printed circuit during an assembly process). A flux is typically either an acid, rosin, or resin-based formulation. Acid fluxes have minimal use in electronics assembly since their post-soldering by-products can be highly corrosive if not removed after soldering, while rosin and resin flux residues can encapsulate harmful ionic residues (H&N Electronics 2003). After the soldering process, flux removal may be needed to ensure high reliability of the electronic assembly, facilitate conformal coating adhesion, and, in some cases, to meet essential aesthetic requirements (UNEP 2003b).

Defluxing during the assembly of electronics spans a variety of end-use applications. Table 1-1 summarizes the associated business at the three digit NAICS codes. A further breakdown of industries for each three digit NAICS level is provided in Appendix A. A total of 22 NAICS codes at the six digit level belonging to the electronics cleaning industry have been identified.

**Table 1-1. NAICS Codes for Businesses in the Electronics Cleaning End-Use**

NAICS CODE	NAICS Code Title
334	Computer and Electronic Product Manufacturing
335	Equipment Appliance, and Component Manufacturing
336	Transportation Equipment Manufacturing

### **1.1.2 Metal Cleaning**

Metal cleaning involves the removal of contamination, such as particulate matter, oils, greases, and inorganic soils from the surfaces of metal parts. Cleaning is typically followed with further processes such as electroplating, painting, coating, assembly, and inspection. All applications in the metal cleaning end-use are characterized as consisting of metal and some synthetic parts that are cleaned during manufacturing (UNEP 2003b). The one exception is those parts that are considered precision cleaning applications, which are discussed in Section 1.1.3, below.

The metal cleaning industry encompasses a broad spectrum of metal and machinery industries. Table 1-2 identifies the industries associated with this end-use at the three digit NAICS code level. Appendix A provides a further breakdown of industries within each NAICS level provided in the table. A total of 139 metal cleaning industries at the six-digit NAICS code level have been identified.

**Table 1-2. NAICS Codes for Businesses in the Metal Cleaning End-Use**

NAICS CODE	NAICS Code Title
322	Paper Manufacturing <sup>1</sup>
331	Primary Metal Manufacturing
332	Fabricated Metal Product Manufacturing
333	Machinery Manufacturing
335	Equipment Appliance, and Component Manufacturing
336	Transportation Equipment Manufacturing
337	Furniture & Related Product Manufacturing
339	Miscellaneous Manufacturing

<sup>1</sup>One NAICS code, 32225, Laminated Aluminum Foil Manufacturing for Flexible Packaging Uses, falls under NAICS code 322, which is considered applicable to metal cleaning.

### **1.1.3 Precision Cleaning**

Precision cleaning may apply to electronic components, medical devices or metal, plastic, or glass surfaces and is characterized by applications that require a high level of cleanliness to ensure the satisfactory performance of the product being cleaned (U.S. EPA 2001a). Precision cleaning occurs in

the final assembly stage where a part is repeatedly cleaned. Parts generally include a wide range of materials, small clearances, blind holes with capillary gaps, and complex shapes (UNEP 1999). Examples of products and applications that might require precision cleaning include:

- Computer disk drives;
- Gyroscopes (navigational systems in missiles, satellite controls, commercial aircraft, and underwater systems);
- Hydraulic and pneumatic control systems (control valves of these systems use gas controls that require extreme cleanliness);
- Oxygen line flushing in submarines and other life dependent applications;
- Optical components;
- Electrical contacts;
- Medical equipment applications;
- Plastic assemblies;
- Auto-riveting; and
- Application of special lubricants.

A variety of businesses require precision cleaning including those in the aerospace, microelectronics, automotive, optical, and medical manufacturing industries (UNEP 1999). NAICS codes are provided only at the three digit level in Table 1-3. Appendix A provides a further list of industries that fall within each of these three digit NAICS codes. A total of 18 NAICS codes at the six digit level that belong in the precision cleaning industry have been identified.

**Table 1-3. NAICS Codes for Businesses in the Precision Cleaning End-Use**

NAICS CODE	NAICS Code Title
333	Machinery Manufacturing
334	Computer and Electronic Product Manufacturing
336	Transportation Equipment Manufacturing
339	Miscellaneous Manufacturing
541	Professional, Scientific, and Technical Services

### **1.1.4 Aerosol Solvent Cleaning**

Aerosol solvents are contained in an aerosol package and are used by industries involved in the electronics, metal, and precision cleaning end-uses.<sup>3</sup> These specialized cleaners are used in the spot cleaning of electrical controls in confined areas of machinery within larger running systems, an example of which is telephone network switching equipment. Historically, CFC-113 was the favored aerosol cleaning solvent particularly for end-use applications where flammability issues were a concern. Smaller quantities of CFC-11 were also employed. These ODS were effective at cleaning the residual particles deposited during the assembly of electrical contacts (i.e., micro-switches used to assist in the flow of electrical current) and were commonly used for routine maintenance of electrical equipment and aircraft (UNEP 1999).

NAICS codes associated with this industry include those identified for the electronics and precision cleaning end-uses (see Appendix A). Additionally, businesses belonging to *326, Plastics and Rubber Manufacturing*, use aerosol solvent products as mold release agents. The aerosol solvent cleans the resin and excess release agent remaining from the molding process after the product is released from the mold in which it was created.

<sup>3</sup> Solvents are also used in traditional aerosol applications where they play a role in product delivery. For example, solvents are used in automobile/industrial aerosol products, paint, insecticide spray, and some household applications such as spray-on carpet/fabric stain protectors. The primary ODS solvent used in these aerosols products was methyl chloroform. The solvent in these products acted solely as a carrier, assisting in uniformly dispensing the aerosol product (UNEP 1999). Because these solvents function as carrier solvents and not cleaning solvents, these end-uses are not analyzed in this report.

## 2 History of Class I ODS Used as Solvents

ODS that are used as solvents and controlled by the Montreal Protocol include four Class I controlled substances. These substances are classified as Class I because of their relatively high ozone depletion potential (ODP). Prior to their control under the Montreal Protocol, these substances were important solvents in the U.S. cleaning market because of their excellent cleaning agent properties. For example, with no flashpoint, a boiling point within the preferred boiling temperature range, low toxicity, and low surface tension, methyl chloroform was an ideal vapor degreasing agent for metal cleaning. The non-flammability, low toxicity, moderate boiling point, high density, low viscosity, low surface tension, and low odor of CFC-113 also made it safe and effective in solvent cleaning applications. Table 2-1 lists these four ODS solvents with their atmospheric lifetime, ODP, global warming potential (GWP), and Chemical Abstract Service (CAS) registry number.

**Table 2-1. Class I Ozone-Depleting Substances Used as Solvents**

Chemical Name	CAS Number	Atmospheric Lifetime, in years	ODP <sup>a</sup>	GWP(100y) <sup>b</sup>
CFC-113	76-13-1	85	0.8	6,000
Methyl Chloroform	71-55-6	5	0.1	140
Carbon tetrachloride	56-23-5	26	1.1	1,800
CFC-11	75-69-4	45	1.0	4,600

<sup>a</sup> A chemical is designated an ODP as a relative index of the ability of a substance to cause ozone depletion. A reference level of 1.0 is assigned to CFC-11 and CFC-12. ODP values are taken from the Montreal Protocol (UNEP 2003a).

<sup>b</sup> The 100-year GWP values relative to CO<sub>2</sub> are taken from the *IPCC Third Assessment Report* (IPCC 2001).

To assess how the solvent cleaning industry adjusted as a result of ODS regulation, it is first necessary to characterize the extent to which these solvents penetrated the markets of each solvent end-use. The remainder of Section 2 discusses the varying historical usage of Class I ODS used as solvents and presents both overall and disaggregated usage estimates for the four identified solvent end-uses.

### 2.1 Size of the Class I ODS Solvent Industry before the Phaseout

Historical ODS usage, prior to the 1996 phaseout in most solvent end-use applications, was derived by researching a variety of sources documenting methyl chloroform, carbon tetrachloride, CFC-113, and CFC-11 use. A detailed description of this methodology is described in Appendix B.

Table 2-2 presents estimates of the four Class I substances used in the solvent cleaning industry from 1986 through 1995. Sections 2.1.1 through 2.1.4 illustrate how these overall usage estimates are distributed among each solvent end-use (i.e., electronics, metal, precision, and aerosol cleaning) for each solvent.<sup>4</sup>

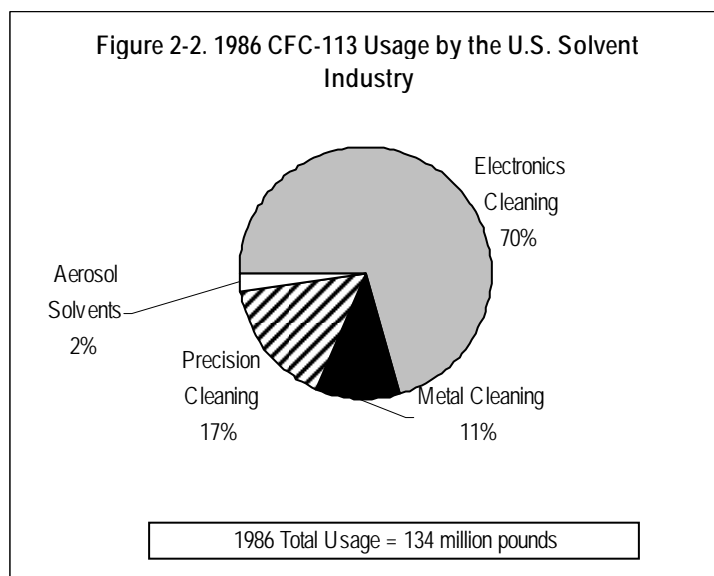
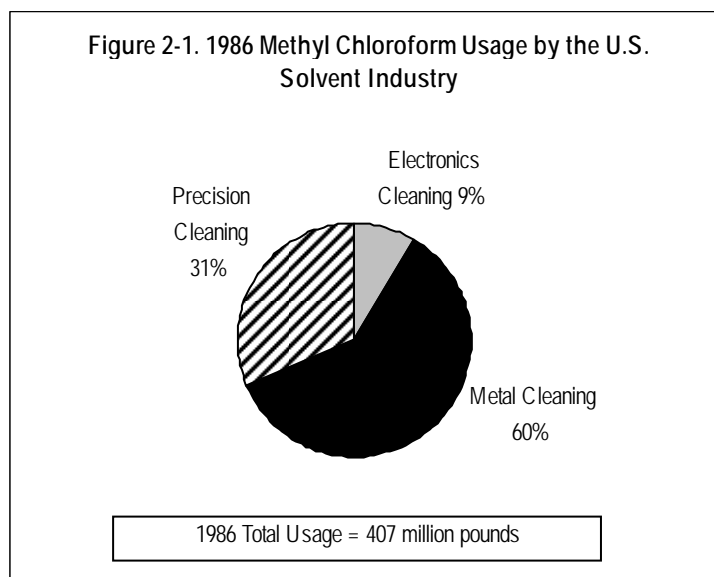
**Table 2-2. Class I ODS Usage by the U.S. Solvent Cleaning Industry, Million Pounds, 1986-1995**

	1986	1987	1988	1989	1990	1991	1992	1993	1994	1995
CFC-113	134	127	119	112	94.3	83.8	46.8	9.42	7.81	3.26
Methyl Chloroform	407	359	311	262	251	239	228	133	22.8	20.4 <sup>a</sup>
Carbon Tetrachloride	0.95	0.50	0.19	0.01	0.01	0.01	0.01	0.04	0.00	0.00
CFC-11	1.01	1.00	0.98	0.97	0.67	0.58	0.56	0.32	0.08	0.02

<sup>a</sup>Of the 20.4 million pounds of methyl chloroform estimated for usage by the solvent cleaning industry in 1995, an estimated 8.6 million pounds were drawn from stockpiles. See Section 2.2 for a discussion on stockpiled Class I ODS.

<sup>4</sup> Usage estimates for carbon tetrachloride are provided only at this aggregated level since information was unavailable with respect to use within the various end-uses.

Figures 2-1 and 2-2 illustrate the historical proportions of solvent use across these industries for methyl chloroform and CFC-113. (CFC-11, used in aerosol solvent cleaning, and carbon tetrachloride, used as a solvent degreaser, were used to such a small degree that disaggregation is not provided.)



Overall, it is estimated that in the 1980s, usage of Class I ODS in solvent cleaning end-uses was as high as 543 million pounds. The largest ODS market for the solvent industry was methyl chloroform, with the metal cleaning end-use responsible for the largest usage.

Based on Class I ODS usage in the solvent industry, ODS emissions from that industry can be estimated. Emissions were determined using a fixed percentage of the new chemical used in equipment that is assumed to be emitted in a given year. This percentage, or annual release rate, is assumed to be 90 percent based on the expert opinion that, during the cleaning process, the solvent is recycled or is continuously reused through a distilling and cleaning process until it is eventually almost entirely emitted

(U.S. EPA 2001a).<sup>5</sup> Table 2-3 presents U.S. emissions of Class I ODS used as solvents (ODP-weighted emissions also are presented).

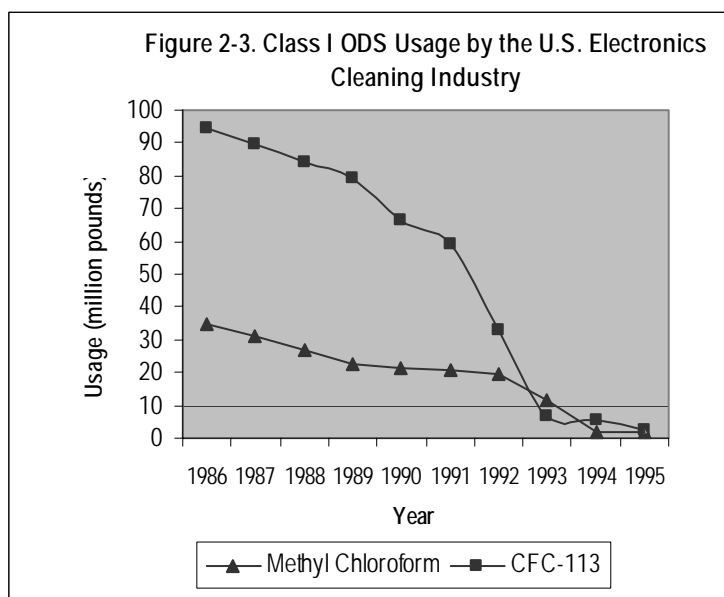
**Table 2-3. Class I ODS Emissions from the U.S. Solvent Cleaning Industry, 1986-1995**

	1986	1987	1988	1989	1990	1991	1992	1993	1994	1995
<i>Un-Weighted Emissions (Million Pounds)</i>										
CFC-113	121	114	108	101	84.9	75.4	42.1	8.48	7.03	2.93
Methyl Chloroform	366	323	280	236	226	215	205	120	20.5	18.3
Carbon Tetrachloride	0.87	0.58	0.30	0.01	0.01	0.01	0.01	0.04	0.00	0.00
CFC-11	0.91	0.90	0.88	0.87	0.60	0.52	0.51	0.29	0.08	0.02
<i>ODP Weighted Emissions (ODP- Weighted Million Pounds)</i>										
CFC-113	96.7	91.4	86.0	80.7	67.9	60.3	33.7	6.78	5.63	2.34
Methyl Chloroform	36.6	32.3	28.0	23.6	22.6	21.5	20.5	12.0	2.05	1.83
Carbon Tetrachloride	0.96	0.64	0.33	0.01	0.01	0.01	0.01	0.04	0.00	0.00
CFC-11	0.91	0.90	0.88	0.87	0.60	0.52	0.51	0.29	0.08	0.02

As Table 2-3 indicates, emissions from CFC-113 are more significant when ODP values are considered. Although methyl chloroform usage was higher than CFC-113 usage in 1986, the impact of CFC-113 on the ozone layer was larger than methyl chloroform because of its higher ODP.

### 2.1.1 Class I ODS Usage by the Electronics Cleaning End-Use

CFC-113 and, to a lesser extent, methyl chloroform have traditionally been used as solvents in electronics cleaning to remove handling solids and flux residues left behind after post-soldering assembly processes. In 1986, an estimated 130 million pounds of Class I ODS were used as solvents in this end-use. As Figure 2-3 illustrates, CFC-113 initially represented approximately 75 percent of the total ODS market. By 1993, the use of both methyl chloroform and CFC-113 diminished significantly to levels below 12 million pounds. The methodology used to calculate these estimates can be found in Appendix B.



<sup>5</sup> The remaining 10 percent of solvent is assumed to be entrained in sludge or wastes and disposed of by incineration or other destruction technologies.

Table 2-4 and Table 2-5 present electronics cleaning usage estimates for methyl chloroform and CFC-113 at the three digit NAICS code level for the period 1986-1995, respectively. As the tables illustrate, NAICS 334 (computer and electronic product manufacturing) represents the largest ODS solvent consumer within the electronics cleaning end-use. Establishments in this NAICS code include those that manufacture computers and similar electronic products, as well as components for such products (U.S. Bureau of the Census 2003).

**Table 2-4. Methyl Chloroform Usage by the U.S. Electronic Cleaning Industry, Million Pounds, 1986-1995**

NAICS <sup>a</sup>	1986	1987	1988	1989	1990	1991	1992	1993	1994	1995
334	23.5	20.7	17.9	15.1	14.5	13.8	13.1	7.66	1.31	1.17
335	9.89	8.72	7.55	6.38	6.10	5.82	5.53	3.23	0.55	0.50
336	1.66	1.46	1.27	1.07	1.02	0.97	0.93	0.54	0.09	0.08
<b>Total:</b>	<b>35.0</b>	<b>30.9</b>	<b>26.7</b>	<b>22.6</b>	<b>21.6</b>	<b>20.6</b>	<b>19.6</b>	<b>11.4</b>	<b>1.96</b>	<b>1.75</b>

<sup>a</sup>NAICS code titles are provided in Appendix A.

Note: Totals may not sum due to rounding.

**Table 2-5. CFC-113 Usage by the U.S. Electronic Cleaning Industry, Million Pounds, 1986-1995**

NAICS <sup>a</sup>	1986	1987	1988	1989	1990	1991	1992	1993	1994	1995
334	63.5	59.9	56.4	52.9	44.6	39.6	22.1	4.45	3.69	1.54
335	27.7	26.2	24.7	23.1	19.5	17.3	9.67	1.94	1.61	0.67
336	3.49	3.30	3.11	2.91	2.45	2.18	1.22	0.24	0.20	0.08
<b>Total:</b>	<b>94.7</b>	<b>89.4</b>	<b>84.2</b>	<b>79.0</b>	<b>66.5</b>	<b>59.1</b>	<b>33.0</b>	<b>6.64</b>	<b>5.51</b>	<b>2.30</b>

<sup>a</sup>NAICS code titles are provided in Appendix A.

Note: Totals may not sum due to rounding.

### **2.1.2 Class I ODS Usage by the Metal Cleaning End-Use**

During the 1980s, methyl chloroform and, to a lesser extent, CFC-113 were the primary metal cleaning solvents used in the United States. Methyl chloroform was the primary vapor degreaser and solvent used for cold cleaning of metals because of its availability and affordability. In 1986, an estimated 244 million pounds of methyl chloroform were used in the United States by the metal cleaning industry (Table 2-6) compared to only 14.5 million pounds of CFC-113 (Table 2-7). Figure 2-4 presents ODS usage estimates in the metal cleaning industry from 1986 through 1995. Appendix B provides a detailed discussion on the methodology used to calculate these estimates.

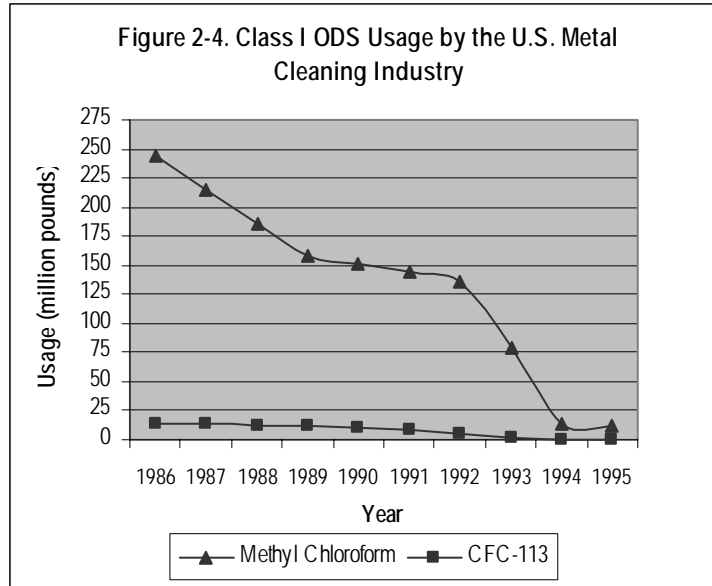


Table 2-6 presents estimates of methyl chloroform usage from 1986 to 1995 at the three digit NAICS code level. Fabricated Metal Product Manufacturing (NAICS 332) is estimated to be the largest sector represented by the metal cleaning industry. Establishments in this group engage in fabricated metal processes that shape individual pieces of metal, including forging, stamping, bending, forming, and machining. Other processes, such as welding and assembling, are also conducted to join separate parts together (U.S. Bureau of the Census 2003). These processes use solvent cleaning to remove contaminants from the surface of metal parts. Table 2-7 presents metal cleaning usage estimates for CFC-113 in 1986 through 1995 at the three digit NAICS code level. As with methyl chloroform, businesses within NAICS 332, Fabricated Metal Product Manufacturing, represent the greatest share of CFC-113 throughout the time series.

**Table 2-6. Methyl Chloroform Usage by the U.S. Metal Cleaning Industry, Million Pounds, 1986-1995**

NAICS Code	1986	1987	1988	1989	1990	1991	1992	1993	1994	1995
322	0.17	0.15	0.13	0.11	0.10	0.10	0.09	0.05	0.01	0.01
331	11.4	10.0	8.67	7.32	7.00	6.68	6.35	3.71	0.64	0.57
332	109	96.1	83.2	70.3	67.2	64.1	61.0	35.6	6.10	5.46
333	72.4	63.9	55.3	46.7	44.6	42.6	40.5	23.7	4.05	3.63
335	7.19	6.34	5.49	4.64	4.43	4.23	4.02	2.35	0.40	0.36
336	22.4	19.8	17.1	14.5	13.8	13.2	12.6	7.33	1.26	1.12
337	8.38	7.38	6.39	5.40	5.16	4.92	4.68	2.74	0.47	0.42
339	13.3	11.7	10.1	8.54	8.17	7.79	7.41	4.33	0.74	0.66
<b>Total:</b>	<b>244</b>	<b>215</b>	<b>186</b>	<b>157</b>	<b>151</b>	<b>144</b>	<b>137</b>	<b>79.8</b>	<b>13.7</b>	<b>12.2</b>

<sup>a</sup>NAICS code titles are provided in Appendix A.  
 Note: Totals may not sum due to rounding.



**Table 2-7. CFC-113 Usage by the U.S. Metal Cleaning Industry, Million Pounds, 1986-1995**

NAICS <sup>a</sup>	1986	1987	1988	1989	1990	1991	1992	1993	1994	1995
322	0.01	0.01	0.01	0.01	0.01	0.01	0.00	0.00	0.00	0.00
331	0.85	0.80	0.75	0.70	0.59	0.53	0.29	0.06	0.05	0.02
332	6.43	6.08	5.72	5.36	4.52	4.01	2.24	0.45	0.37	0.16
333	3.96	3.74	3.52	3.30	2.78	2.47	1.38	0.28	0.23	0.10
335	0.60	0.57	0.54	0.50	0.42	0.38	0.21	0.04	0.04	0.01
336	1.27	1.20	1.13	1.06	0.89	0.79	0.44	0.09	0.07	0.03
337	0.55	0.52	0.49	0.46	0.39	0.34	0.19	0.04	0.03	0.01
339	0.79	0.75	0.71	0.66	0.56	0.50	0.28	0.06	0.05	0.02
<b>Total:</b>	<b>14.5</b>	<b>13.7</b>	<b>12.9</b>	<b>12.1</b>	<b>10.2</b>	<b>9.02</b>	<b>5.04</b>	<b>1.01</b>	<b>0.84</b>	<b>0.35</b>

<sup>a</sup>NAICS code titles are provided in Appendix A.

Note: Totals may not sum due to rounding.

### 2.1.3 Class I ODS Usage by the Precision Cleaning End-Use

Methyl chloroform was used predominantly in precision cleaning, particularly for applications with heavier soils consisting of oils, greases, waxes, cutting fluids, and optical blocking materials, as a result of its higher solvency and boiling point and moderate evaporation rate (UNEP 1999). Methyl chloroform and CFC-113 use in the precision cleaning industry was estimated at 150 million pounds in 1986. Figure 2-5 illustrates the declining trend in usage, which reached less than 10 million pounds in 1995. During these years, CFC-113 represented less than 20 percent of the total Class I ODS market within this end-use. Appendix B provides a detailed discussion of the methodology used for calculating these estimates.

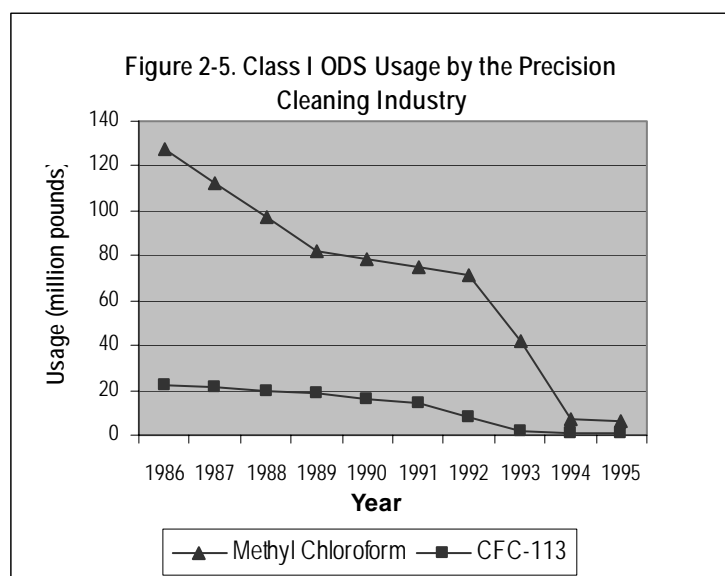


Table 2-8 and Table 2-9 provide the estimated uses of methyl chloroform and CFC-113 for precision cleaning end-uses at the three digit NAICS code level from 1986 to 1995. As Tables 2-8 and 2-9 illustrate, the largest market for methyl chloroform and CFC-113 in precision cleaning historically has been NAICS 334 (Computer and Electronic Product Manufacturing), which includes businesses associated with the manufacturing of navigational, measuring, electromedical, and control instruments. Examples of such instruments include aeronautical instruments, laboratory analytical instruments, and navigation and guidance systems (e.g., gyroscopes) (U.S. Bureau of the Census 2003). Another large ODS market in the precision cleaning industry was NAICS 336 (Transportation Equipment Manufacturing), which includes businesses that manufacture aircraft, guided Missile and Space Vehicle, and other similar products (U.S. Bureau of the Census 2003).

**Table 2-8. Methyl Chloroform Usage by the U.S. Precision Cleaning Industry, Million Pounds, 1986-1995**

NAICS <sup>a</sup>	1986	1987	1988	1989	1990					
333	0.13	0.11	0.10	0.08	0.08	0.07	0.07	0.04	0.01	0.01
334	83.8	73.9	63.9	54.0	51.6	49.3	46.9	27.4	4.69	4.20
336	37.3	32.9	28.5	24.1	23.0	21.9	20.9	12.20	2.09	1.87
339	0.92	0.81	0.70	0.59	0.57	0.54	0.51	0.30	0.05	0.05
541	5.64	4.97	4.30	3.63	3.47	3.31	3.15	1.84	0.32	0.28
<b>Total:</b>	<b>128</b>	<b>113</b>	<b>97.5</b>	<b>82.4</b>	<b>78.8</b>	<b>75.1</b>	<b>71.5</b>	<b>41.8</b>	<b>7.15</b>	<b>6.40</b>

<sup>a</sup>NAICS code titles are provided in Appendix A.

Note: Totals may not sum due to rounding.

**Table 2-9. CFC-113 Usage by the U.S. Precision Cleaning Industry, Million Pounds, 1986-1995**

333	0.01	0.01	0.01	0.01	0.01	0.01	0.00	0.00	0.00	0.00
334	14.3	13.5	12.7	11.9	10.0	8.92	4.99	1.00	0.83	0.35
336	6.83	6.45	6.08	5.70	4.80	4.26	2.38	0.48	0.40	0.17
339	0.16	0.15	0.14	0.13	0.11	0.10	0.06	0.01	0.01	0.00
541	1.05	0.99	0.94	0.88	0.74	0.66	0.37	0.07	0.06	0.03
<b>Total:</b>	<b>22.4</b>	<b>21.1</b>	<b>19.9</b>	<b>18.6</b>	<b>15.7</b>	<b>13.9</b>	<b>7.79</b>	<b>1.57</b>	<b>1.30</b>	<b>0.54</b>

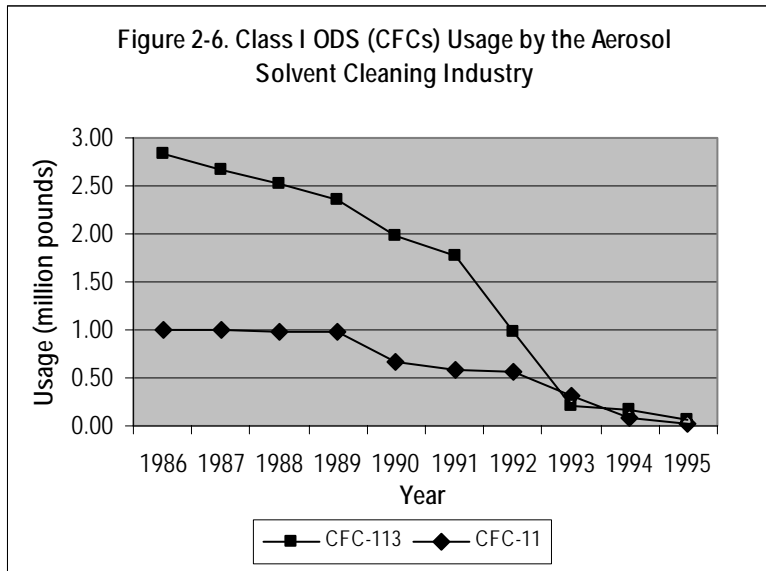
<sup>a</sup>NAICS code titles are provided in Appendix A.

Note: Totals may not sum due to rounding.

#### **2.1.4 Class I ODS Usage by the Aerosol Solvent End-Use**

Aerosol-based solvent applications tended to rely on CFC-113 and to a lesser extent on CFC-11 for use in many applications in the electronic cleaning industry, such as cleaning circuit boards and electrical contacts. These ODS were used for many years for aircraft maintenance (e.g., performing spot cleaning on pressurized oxygen systems) and as mold release agents in the production of plastic and elastomeric materials. From the standpoint of worker safety, these solvents were preferred because of their low toxicity and non-flammability. The limited use of CFC-11 in aerosol solvent applications, however, is in part because of its low boiling point, which prevented its use in situations of high heat.

Figure 2-6 and Table 2-10 present historical market size estimates of Class I ODS aerosol solvents. Because of limited data, an analysis has not been conducted to allocate these estimates by their identified three digit NAICS codes.



**Table 2-10. Class I ODS Usage by the U.S. Aerosol Solvent Cleaning Industry, Million Pounds, 1986-1995**

CFC-113	2.83	2.67	2.52	2.36	1.99	1.76	0.99	0.20	0.16	0.07
CFC-11	1.01	1.00	0.98	0.97	0.67	0.58	0.56	0.32	0.08	0.02

## 2.2 Stockpiled Class I ODS

Theoretically, in years in which a phaseout is not imminent, companies hold a certain stockpile of solvent to ensure a sufficient quantity is available in the event that new shipments are delayed. When new shipments arrive, the end-user uses the existing stockpile plus a portion of the new shipment and withholds from the shipment the amount of new material required to replace the stockpile. However, after the accelerated phaseout of Class I ODS was announced in 1992, end-users began to stockpile ODS used as solvents in preparation for the 1996 phaseout.

Total estimated stockpiles, held by the U.S. solvent industry for methyl chloroform, CFC-113, and CFC-11 as of the beginning of 1996, are presented in Table 2-11. It is important to note that, of the stockpile quantities estimated below, a portion of the material could have potentially been used prior to 1995, possibly as a result of rising Class I ODS prices. Because of data sensitivity, stockpile estimates are not based on information reported by stockpile holders, but rather were developed by comparison of data from the *Chemical Marketing Reporter* (various issues) and U.S. EPA's ODS Tracking System. The detailed methodology used to estimate stockpiled quantities is presented in Appendix B.

**Table 2-11. Class I ODS Stockpiling by the U.S. Solvent Cleaning Industry as of 1996, Million Pounds**

CFC-113	3.26	53.0
Methyl chloroform <sup>a</sup>	20.4	47.7
CFC-11	0.02	1.0

<sup>a</sup>The usage and stockpile estimates for methyl chloroform in Table 2-11 reflect that end-users used an estimated 8.6 million pounds from stockpiles in 1995.

As shown in Table 2-11, the quantity of methyl chloroform stockpiled as of 1996 was only slightly more than two times greater than 1995 estimated usage, while CFC-113 stockpiles as of 1996 were more than 16 times greater than CFC-113 usage in 1995. Given the short shelf life of methyl chloroform and the indefinite shelf life of CFC-113, this difference appears to reflect end-users' expectations regarding how long after the phaseout they would be able to employ stockpiled materials (UNEP 2003b). Although the amount of CFC-11 stockpiled as of 1996 was minimal, it was 50 times greater than CFC-11 usage in 1995.

In years following the 1996 phaseout of Class I ODS, it is likely that stockpiles of methyl chloroform and CFC-11 were depleted more quickly than those of CFC-113 to minimize the amount of wasted material as a result of deterioration over time. The short shelf life of methyl chloroform is also a likely explanation for the estimated 8.6 million pounds of methyl chloroform taken from stockpiles in 1995, which increased usage to an estimated 20.4 million pounds in 1995 and decreased stockpiles to 47.7 million pounds at the beginning of 1996 (See Table 2-11). Use of the CFC-113 stockpile has likely been more prolonged as a result of its indefinite shelf life. A discussion on the post-phaseout use of Class I ODS in the solvent industry can be found in Section 5, including a discussion on the current use of Class I ODS in limited and unique applications, especially in aerospace essential use exemptions (EUEs), as well as in applications with insufficient alternatives.

### 3 Class II Controlled Substances - An Interim Solution

For some end-use applications, hydrochlorofluorocarbons (HCFCs) have been developed as short-term substitutes for Class I ODS. The HCFCs used in the solvent industry are:

- HCFC-225 ca/cb;
- HCFC-141b; and
- HCFC-123.<sup>6</sup>

These solvents, referred to as Class II ODS, also deplete the ozone layer, but to a lesser degree than CFCs and other Class I ODS. Consequently, the use of these substances as solvents (and as substitutes for other ODS) is regulated by the Montreal Protocol and only considered an interim phaseout solution. Table 3-1 lists Class II ODS used as solvent substitutes for Class I ODS, as well as their atmospheric lifetimes, ODPs, GWPs, and CAS registry numbers.

**Table 3-1. Class II Ozone-Depleting Substances Used as Solvents**

HCFC-225ca	422-56-0	2.1	0.025	170
HCFC-225cb	507-55-1	6.2	0.033	530
HCFC-141b	1717-00-6	9.2	0.11	630
HCFC-123	306-83-2	1.3	0.02-0.06	93

<sup>a</sup>A chemical is designated an ODP as a relative index of the ability of a substance to cause ozone depletion. A reference level of 1.0 is assigned to CFC-11. ODP values are taken from the Montreal Protocol (UNEP 2003a).

<sup>b</sup>The 100-year GWP values relative to CO<sub>2</sub> are taken from the *IPCC Third Assessment Report* (IPCC 2001).

EPA's Significant New Alternatives Policy (SNAP) Program has identified these Class II controlled substances as acceptable substitutes for Class I ODS for certain applications within the solvent industry (see Box 3-1).<sup>7</sup>

**Box 3-1. Summary of HCFCs Acceptable in Solvent Applications under U.S. EPA's SNAP Program**

- HCFC-225 ca/cb is considered an acceptable solvent substitute for:
  - CFC-113 and methyl chloroform in electronics, metal, and precision cleaning.
  - CFC-113, methyl chloroform, and HCFC-141b in aerosol solvents cleaning.
- HCFC-141b is an acceptable substitute for:
  - CFC-11 and CFC-113 in aerosol solvents cleaning.
- HCFC-123 is only considered an acceptable substitute for:
  - CFC-113 and methyl chloroform in precision cleaning.

#### 3.1 Class II ODS Use in the Solvent Industry

HCFCs used as solvents are regulated by two different phaseout schedules. As authorized under Section 606 of the Clean Air Act Amendments (CAAA), the United States accelerated the phaseout date

<sup>6</sup> HCFC-123 sales have been discontinued in the United States.

<sup>7</sup> The SNAP Program, developed by the U.S. EPA to meet the requirements under Section 612 of the CAAA, identifies alternatives to Class I and Class II ODS that reduce the overall risks to human health and the environment. The SNAP Program publishes lists of acceptable and unacceptable substitutes, which is reviewed and updated several times each year.

for HCFC-141b, eliminating its production and importation on January 1, 2003. HCFC-225 ca/cb and HCFC-123 fall under the phaseout schedule mandated by Section 605 of the federal Clean Air Act, which prohibits U.S. production and importation of all HCFCs for solvent uses by 2015.

Although the SNAP Program has listed HCFC-123 as a substitute for methyl chloroform and CFC-113 in precision cleaning with an acceptable exposure limit (AEL) of 30 ppm, solvent manufacturers discontinued product lines with HCFC-123 solvent formulations because of the risks associated with worker exposure for long periods of time and concerns over product liability. HCFC-123 was originally introduced to reconcile flammability concerns in azeotropic cleaners designed for the electronics industry; however, the toxicity of the solvent prohibited its acceptance into the mainstream solvent market. It is no longer being sold as a solvent in the United States. Therefore, this analysis considers HCFC-123 consumption and emissions from the solvent industry to be negligible.

Usage estimates for HCFC-225 ca/cb and HCFC-141b were developed using EPA's ODS Tracking System and research collected from telephone interviews and questionnaires with various industry contacts knowledgeable in the area of HCFC-141b and the transition to alternatives. Table 3-2 presents estimates, expressed in million pounds, of HCFC-225 ca/cb and HCFC-141b used in the solvent industry from 1994 through 2003. The methodology used to calculate usage estimates can be found in Appendix B.

**Table 3-2. Class II ODS Usage by the U.S. Solvent Cleaning Industry, Million Pounds, 1992-2003**

	1992	1993	1994	1995	1996	1997	1998	1999	2000	2001	2002	2003
HCFC-225 ca/cb	0.00	0.00	0.12	0.37	0.52	0.53	0.54	0.55	0.56	0.57	0.58	0.59
HCFC-141b	6.79	7.24	20.3	33.3	24.9	24.6	13.1	12.9	12.4	11.1	14.2	12.6 <sup>a</sup>

<sup>a</sup>12.6 million pounds was consumed from HCFC-141b stockpiles in 2003. See Section 3.3.1 for a discussion on stockpiling. Estimate for 2003 derived using a different methodology. See Appendix B.

In Table 3-3, U.S. emissions of Class II ODS used as solvents are presented. Also presented in this table are the emissions, weighted according to the chemicals' ODPs, as provided in Table 3-1. Emissions were estimated using a fixed percentage of the new chemical used in equipment that is assumed to be released in a given year. This annual release rate is assumed to be 90 percent based on the expert opinion that during the cleaning process, the solvent is continuously reused through a distilling and cleaning process until it is eventually almost entirely emitted (U.S. EPA 2001a).<sup>8</sup>

**Table 3-3. Class II ODS Emissions from the U.S. Solvent Cleaning Industry, 1992-2003**

	1992	1993	1994	1995	1996	1997	1998	1999	2000	2001	2002	2003
<i>Un-Weighted Emissions (Million Pounds)</i>												
HCFC-225 ca/cb	0.00	0.00	0.10	0.33	0.46	0.47	0.48	0.49	0.50	0.51	0.52	0.53
HCFC-141b	6.12	6.52	18.2	30.0	22.4	22.1	11.8	11.6	11.1	9.95	12.8	11.3
<i>ODP Weighted Emissions (ODP- Weighted, Million Pounds)</i>												
HCFC-225 ca/cb	0.00	0.00	0.00	0.01	0.01	0.01	0.01	0.01	0.01	0.02	0.02	0.02
HCFC-141b	0.75	0.80	2.01	3.30	2.47	2.44	1.29	1.28	1.23	1.09	1.40	1.25

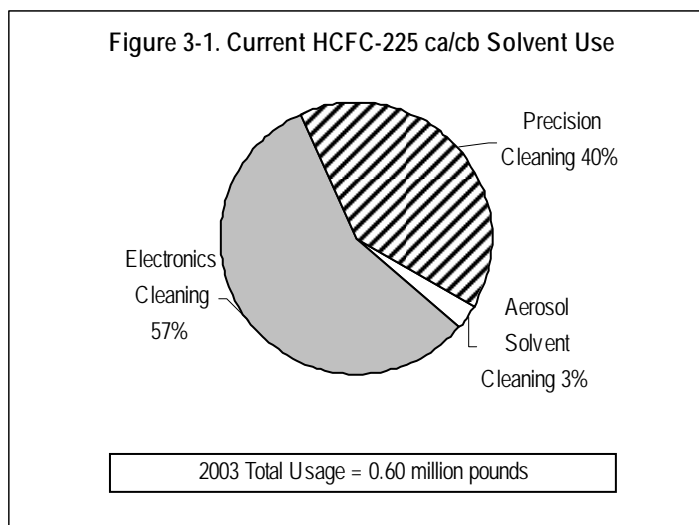
### 3.2 HCFC-225 ca/cb

Having similar physical properties and cleaning performance to CFC-113, HCFC-225 ca/cb has been established as a replacement for CFC-113 in all solvent end-uses and as a replacement for HCFC-141b in aerosol solvent cleaning. HCFC-225 ca/cb is a mixture of the two isomers HCFC-225ca and HCFC-225cb. The HCFC-225 ca/cb formulation is nonflammable, VOC exempt, and considered to have low

<sup>8</sup> The remaining ten percent of solvent is entrained in sludge or wastes and disposed of by incineration or other destruction technologies.

acute toxicity. Because of its low viscosity, high density, and low surface tension, HCFC-225 ca/cb has excellent wetting and penetration properties favorable to the cleaning of electronic and precision components.

Developed by Asahi Glass Company, Ltd., in Japan, HCFC-225 ca/cb was sold under the product name "ASAHIKLIN AK-225" and became available in the United States in 1994 (AGA Chemicals 2003a). HCFC-225 ca/cb is acceptable and being used as a solvent in each of the solvent end-uses; however, it is not used by metal cleaning end-users primarily because of its high cost. One exception is in California, where strict VOC regulations are in place; since HCFC-225 ca/cb is VOC exempt, this solvent is starting to be considered as an option for some metal cleaning end-users. As Figure 3-1 illustrates, HCFC-225 ca/cb is currently used widely as a defluxing agent and a precision cleaning solvent (AGA Chemicals 2003b).



Demand for HCFC-225 ca/cb is increasing steadily. AGA Chemicals, Inc., the U.S. distributor of AK-225, and Asahi Glass Fluoropolymers USA, Inc., plan to form a new company in early 2004, AGC Chemicals, Inc., to domestically produce AK-225 at their Bayonne, New Jersey plant. Domestic production of AK-225 is expected to accommodate the increasing demand of this product in particular by the aerospace and defense industries, which have selected it as a replacement for CFC-113 and HCFC-141b in the cleaning of liquid oxygen storage and delivery systems (AGA Chemicals Inc. 2003a, 2003c). Furthermore, many delicate medical applications (e.g., plastic catheter line cleaning) that depended on the rapid volatilization of CFC-113 are experiencing success with HCFC-225 ca/cb (Kitamura et al. 1999). As indicated by the usage estimates and the anticipated start-up of a U.S. production plant, it can be expected that HCFC-225 ca/cb will continue to evolve as a leading solvent in the industrial cleaning market despite its scheduled phaseout date in 2015. With a lower ODP than CFC-113, HCFC-225 ca/cb is considered an important transitional alternative for precision cleaning and electronics cleaning; however, efforts to identify and switch to viable zero ODP alternatives should continue over the next decade.

### 3.3 HCFC-141b

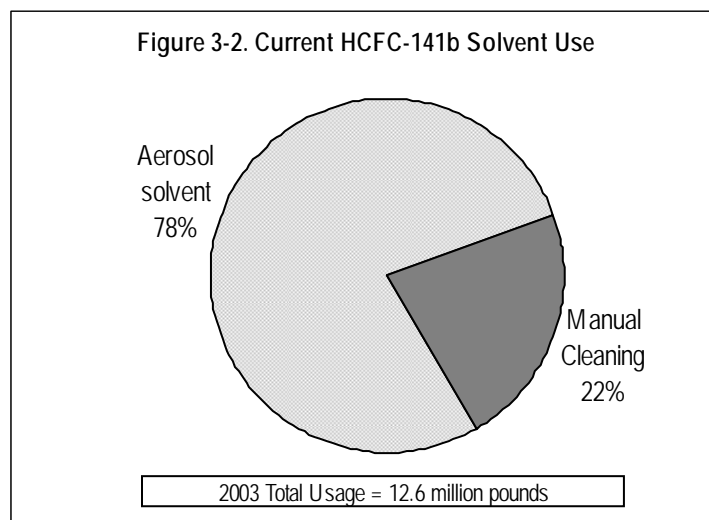
HCFC-141b has been considered an ideal solvent candidate for ODS replacement in some applications because of its rapid evaporation rate, satisfactory compatibility with plastics and effective cleaning capabilities. In addition, because of its non-flammability HCFC-141b is regarded by some as a good choice in terms of worker safety.

HCFC-141b was used in vapor degreasers especially for high performance electronics components for aerospace, military, and medical applications until 1997, when EPA's SNAP Program no longer allowed HCFC-141b for use in solvent cleaning equipment. Consequently, current HCFC-141b solvent users

either adopted alternatives to HCFC-141b or continued to use HCFC-141b by converting to other cleaning processes that do not use degreasing equipment, but instead use manual immersion, flushing, hand wiping, dipping, and agitation cleaning methods, all of which typically have higher vapor emission rates and less reuse than vapor degreasing technology.

Nonetheless, HCFC-141b remains acceptable for use in aerosol solvent cleaning and has become the prime aerosol solvent for cleaning various electronic equipment previously cleaned with CFC-113. Most U.S. aerosol markets sell into the repair industry, while manufacturing of electronics (which involves bench-top aerosol solvent cleaning) is predominately taking place in China. The current U.S. aerosol solvent industry is primarily in-situ cleaning (approximately 75 percent) for repairs and maintenance of electronic applications and the remaining 25 percent of aerosol solvent cleaning is for bench-top cleaning applications (Techspray 2004a).

While the large majority of HCFC-141b usage in the solvents industry is currently attributed to the aerosol solvent cleaning end-use, which is essential 100 percent emissive in nature with little or no reuse potential, there still remains a smaller quantity of HCFC-141b use in manual cleaning applications. One example of a manual cleaning application is the use of HCFC-141b as a flushing agent to clean air conditioning and refrigeration system units. Figure 3-2 illustrates an estimated percent distribution of HCFC-141b use by end-use (AGA Chemicals 2004; Micro Care 2004; Techspray 2004a).



On January 1, 2003, the production and importation of HCFC-141b in the United States was halted. However, consumption of existing stockpiles is considered legal. Consequently, the solvent cleaning industry pursued stockpiling as a transitional solution in response to the phaseout of HCFC-141b.

### **3.3.1 Stockpiled Class II ODS – HCFC-141b**

In 2002, with the anticipation of a supply shortage and a cost increase by manufacturers, the solvent cleaning industry began to accumulate a sufficient inventory of the stable HCFC-141b in preparation for the January 1, 2003 ban on production and importation. As of the 2003 phaseout date, it was estimated that approximately 18 million pounds of HCFC-141b was stockpiled by the solvent cleaning industry. Of this amount, 70 percent, or 12.6 million pounds of HCFC-141b was used in 2003, of which roughly 10 million pounds was used as an aerosol solvent cleaner (Techspray 2004a; AGA Chemicals 2004).

Although some replenishing of stockpiles occurred in 2003, the general notion is that additional stockpiling by chemical distributors was relatively minimal due to a weak economy and an increase in the price of HCFC-141b available from manufacturers. Furthermore, the majority of stockpiling occurred before the phaseout, when most end-users had stockpiled at least one year's worth of HCFC-141b for



post-phaseout usage (Techspray 2004a; AGA Chemicals 2004; Micro Care 2004). According to industry experts, manufacturers could readily satisfy any additional needs distributors had in 2003 for additional uncommitted stockpiled quantities of HCFC-141b (AGA Chemicals 2004).

Table 2-11 presents total estimated stockpiles, held by the U.S. solvent industry for HCFC-141b as of the beginning of 2003, along with usage estimates for the years before and after the phaseout.

**Table 3-4. HCFC-141b Stockpiling Activities by the U.S. Solvent Cleaning Industry, Million Pounds**

Aerosol Solvent Cleaning	11.0	14.0	9.80
Manual Cold Cleaning	3.15	4.00	2.80
Total Solvent Cleaning	14.2	18.0	12.6
<i>Total Stockpile Remaining (2004)</i>		<i>5.40</i>	

As shown in Table 3-4, the quantity of HCFC-141b stockpiled remaining after 2003 usage totals 5.4 million pounds. This remainder combined with the purchase of additional uncommitted stockpiles in 2003 and 2004 will cover the needs of end-users for the next couple years. However, it is difficult to ascertain when the entire solvent cleaning industry will be completely transitioned out of HCFC-141b for the following three reasons:

1. HCFC-141b's long shelf life means that use may continue until stockpiles are depleted because there are no material degradation concerns.
2. Uncommitted quantities of HCFC-141b were still available in early 2004 and experts believe that supplies will last through 2005. It is understood that one formulator is guaranteeing HCFC-141b based products until 2006 (Micro Care 2004).
3. The progress in transitioning to an alternative varies among end-users, in part because alternatives are still more expensive than HCFC-141b (Techspray 2004a; AGA Chemicals 2004).

As a result, while industry experts assume that HCFC-141b use will continue to decline in 2004 and 2005, no definitive end-date for usage can be identified (Honeywell 2004a).

Ultimately, all HCFC-141b end-users in the solvent cleaning industry will transition to alternatives. Several examples of available alternative products are described in Box 3-2 (Cook 2003; 3M Specialty Materials 2000). These products are all fluorinated solvents (with the exception of Solvon®, which is based on nPB), and are commonly formulated with alcohols, HFC-365mfc, and Versa Trans™ to make co-solvents or azeotropic blends. A more detailed discussion about these and other alternatives to ODS follows in Section 4.

**Box 3-2. Common Product Lines Available as Alternatives to HCFC-141b**

- AK-225 manufactured by AGA Chemicals Inc., AK-225 is being marketed as an HCFC-141b alternative. Also offered are AK-225A, an isomer of AK-225 that is blended into formulations and AK-225 ATE, an azeotropic blend of AK-225, Versa-Trans and ethanol.
- Vertrel® manufactured by Mitsui – DuPont Fluorochemical (MDF) and distributed by Microcare Marketing Services is a product line based on HFC-4310mee that is blended with trans, and HFC-365mfc.
- Genesolv manufactured by Honeywell is a product line with Genesolv® SF (HFC-245fa) as the primary product and two azeotropes, Genesolv® ST-Z, Genesolv® ST, that both contain HFC-245fa and varying amounts of Versa-Trans.
- Techspray® G3™ is a product line offered by Techspray with alternatives to HCFC-141b that are azeotropic blends of trans and Genesol SF (HFC-245fa).
- 3M's Novec Engineered Fluids the product line offered by 3M, includes various HFEs and azeotropic blends of HFEs, trans, and alcohols (HFE-72DE, HFE-72DA, HFE-7200, HFE-7100).
- Solvon® manufactured by Poly Systems USA Inc. is a product line that offers three blends of n-propyl bromide and HFC-365mfc for aerosol and manual solvent cleaning Solvon® FB2, Solvon® FB5, and Solvon® FB7.

The general viewpoint held by industry is that although there are products commercialized to replace HCFC-141b, these products will not become qualified and gain a considerable market share until stockpiles of HCFC-141b are virtually depleted and their production costs decrease as a result of economies of scale associated with increased production.

The first major issue delaying transition is cost. Some end-users are waiting until the price of alternatives decreases before considering a transition. Although current market prices of HCFC-141b are four times more expensive than the price of HCFC-141b at the beginning of 2003, HCFC-141b is still preferred when compared to alternatives, which are still significantly more expensive than the original pricing of pure HCFC-141b in the beginning of 2003 (Techspray 2004a).

The second major issue is the current abundance of HCFC-141b. There still remains a strong reliance on this solvent while it is still readily available. The expected shift to alternatives will greatly depend on when HCFC-141b stockpiles are completely depleted. Some experts believe that it will also depend on when larger companies will convert; many smaller companies choose to wait until competitors evaluate the alternatives in order to keep the level of customer disturbance and common risks associated with R&D ventures at a minimum (AGA Chemicals 2004).

The third major issue is qualification of alternatives for HCFC-141b replacement in various applications and the acceptance of the alternatives by the users' customers. Many times the qualification process will involve detailed short and long term exposure compatibility studies, which can take a minimum of a month to complete. In short, there is no drop-in replacement for HCFC-141b and end-users must judiciously choose an alternative that is safe and compatible for their needs.

## **4 Reducing and Eliminating the Use of ODS Cleaning Solvents**

A variety of approaches are available to replace Class I and Class II ODS thereby eliminating emissions of ODS entirely; such options include converting to non-ODS cleaning agents and alternative technologies, such as aqueous cleaning processes. In choosing an alternative solvent or technology, the end-user is faced with a variety of considerations, such as one-time conversion costs, changes in operating costs, regulations associated with the use of a new substitute, worker safety, and effectiveness and compatibility with the substrate.

Although not considered an actual replacement option for ODS, equipment upgrades, new equipment, and recovery and recycling techniques have also been developed to aid in emissions reduction. These techniques were first implemented to reduce emissions of Class I ODS and continue to be used in conjunction with non-ODS solvent cleaning agents.

This section provides an overview of the methods available to the solvent cleaning end-user to transition away from the use of ODS. Section 4 is structured as follows:

- Section 4.1 discusses emission reduction strategies;
- Section 4.2 provides an overview of the alternative solvents;
- Section 4.3 highlights substitute cleaning technologies; and
- Section 4.4 concludes with some observed substitution trends experienced by the industry.

### **4.1 Emission Reduction Strategies**

As it became increasingly clear that solvent emissions were detrimental to the ozone layer and also a concern for the health and safety of workers, the solvent cleaning industry investigated, developed, and promoted strategies to control the escape of solvent emissions. Similar to the replacement solvents and technologies available to ODS consumers in the solvent cleaning industry, these strategies aim to reduce emissions. These emission reduction techniques were successful with CFC-based solvent cleaning (although they did not serve as an actual replacement for the solvent) and have become a mainstay in the U.S. solvent cleaning market because of various regulatory, environmental, and economic reasons. Such techniques are now used in conjunction with non-ODS solvents. The two main emission reduction strategies discussed in this section are:

- Equipment retrofits and new equipment; and
- Recycling or recovery processes.

#### **4.1.1 Equipment Retrofits and New Equipment**

Emission reduction retrofit technologies can be implemented on solvent cleaning machines used in electronics, metal, and precision cleaning end-uses and include engineered improvements such as higher freeboard ratios (75 percent or higher) to minimize diffusion losses that occur with drafts, as well as low-temperature secondary cooling coils to condense solvent vapors keeping emissions at a minimum.

Technology associated with equipment retrofits primarily made headway into the solvent market as a result of Section 112 of the 1990 CAAA, or the National Emissions Standards for Hazardous Air Pollutants (NESHAP). The Halogenated Solvent Cleaning NESHAP regulates emissions from vapor degreasers using traditional chlorinated solvents (perchloroethylene, trichloroethylene, and methylene chloride). These NESHAP regulations provide work practice standards and equipment design requirements in an effort to control emissions from halogenated solvents.

The environmental features associated with NESHAP compliant equipment have been effectively marketed as cost-effective and safer for the solvent user because of their ability to conserve solvent resources and reduce workplace exposure. A number of companies using non-chlorinated solvents, witnessing the success of these upgrades, have subsequently chosen to adopt NESHAP-compliant

solvent cleaning machines. In keeping with this trend, new equipment currently on the market is configured to comply with NESHAP requirements; for instance, Ultronix, Incorporated sells only new and retrofitted vapor degreasers that meet the NESHAP regulations (Ultronix 2004). Additionally, many manufacturers of alternative solvents including, for example, DuPont, the developer and original manufacturer of Vertrel®, recommend that their customers use modern vapor degreasing equipment that has retrofit features such as higher freeboard and a secondary set of condenser coils (DuPont 2001).

Since enhancement features help to contain the solvent thereby reducing emissions, the end-user experiences a reduction in solvent costs per operating hour. After retrofitting existing equipment, one study conducted by DuPont Fluoroproducts found that the average solvent emission rate dropped by 79 percent (Ramsey and Merchant Undated). In this scenario, CFC-113 was replaced with a more expensive solvent, HFC-4310mee; nonetheless, a cost savings of \$4.65 per hour was realized, translating into an annual savings of \$9,300 on the basis of one shift and up to \$27,900 on the basis of three shifts. The scenario assumed that installing primary features cost \$15,000;<sup>9</sup> however, as a result of the reduction in solvent emissions, by the second year, the cost savings exceeded the cost of retrofitting the degreaser (Ramsey and Merchant Undated).

Some new degreasing equipment, commonly referred to as “emissionless” degreasers, have no air/vapor interface and consist of a sealed chamber where the solvent is introduced as the final rinse of the cleaning operation (Dow 2003). Such units also include a solvent recovery system where the vapors are exhausted, recovered, and condensed and then reclaimed and recycled.

#### 4.1.2 Recycling or Recovery Processes

Solvent recovery systems remove clean solvent from solvent waste in order to return some of the solvent to productive use. Larger users typically have an in-house collection and recycling system whereas smaller users generally collect used solvent and transport it to an off-site recycler (UNEP 2002). Waste solvent reclamation involves three major processes:

1. Initial treatment requires solvent vapor recovery that can be accomplished using a combination of various methods (see Table 4-1);
2. Distillation occurs after initial treatment. Vapors of solvent are continuously removed and condensed as the resulting sludge is drawn off. Distillation can include the use of steam that enters the evaporation vessel and vaporizes the solvent, facilitating the separation process; and
3. Purification of the reclaimed solvent occurs as a last step of solvent reclamation where water is removed through decanting, passage through molecular sieves, or salting (NPI 1999).

**Table 4-1. Solvent Vapor Recovery Methods Employed During Initial Treatment of the Solvent Reclamation Process**

Vapor Recovery Method	Technologies Used	Description
Condensation	<ul style="list-style-type: none"> <li>• Water-cooled Condensers</li> <li>• Refrigeration Units</li> </ul>	Solvent vapors condense using chillers. Any vapors that escape are recycled through adsorption or absorption.
Adsorption	<ul style="list-style-type: none"> <li>• Activated Carbon Adsorption Solvent Recovery System</li> </ul>	Contaminated air flows through an activated carbon bed, which captures the solvent. Steam is then used to recover solvent vapors into a liquid followed by decanting and distilling methods to separate the solvent from the water.
Absorption	<ul style="list-style-type: none"> <li>• Scrubbing Towers</li> <li>• Spray Chambers</li> </ul>	Mechanical operations that remove un-dissolved solids by filtering and draining methods. Water is removed through decanting.

Source: NPI 1999.

<sup>9</sup> The cost of retrofitting a typical size vapor degreaser (i.e., an open top area less than 13 square feet) ranges from \$10,000 to \$20,000. This cost covers basic features such as, installing a cover, a freeboard ratio greater than 0.75, a main condenser operating at 40-45° F using chilled water, refrigeration devices, and facilities for work handling that minimize solvent entrapment (Durkee 1997 and Ramsey and Merchant Undated).

Solvent reclamation is an effective means for solvent conservation with the ability to recover as much as 95 percent of the waste solvent (NPI 1999). However, the use of the resulting recycled solvents and the use of recovery and recycling systems vary within the solvent sector. For instance, although there are economic reasons for preferring recycled solvent, which typically cost between 75 and 95 percent less than pure solvents, only certain solvent cleaning operations can use recycled solvents. Although recycled solvents are feasible for use in electronics and metal cleaning, recycled solvents are not feasible for high performance applications that require a high level of cleanliness (i.e., precision cleaning). Furthermore, recycling and recovery of solvents used in aerosol spraying of solvents (which accounted for 1% of Class I ODS emissions from solvent cleaning in 1986 and 77% of Class II ODS emissions from solvent cleaning in 1994) is not feasible because the solvent is usually totally emitted in these applications (UNEP 2002).

## **4.2 Alternative Organic Solvents**

There are several alternative solvents available to solvent end-users, each of which has advantages and disadvantages. Some drawbacks include poor solvency and compatibility issues, regulatory concerns related to hazardous air pollutants, flammability, cost, and worker safety. However, manufacturers have been able to overcome some of these hurdles through formulating blends and azeotropes of effective solvents that are gaining a significant market share in the U.S. solvent industry. The base alternative solvents covered in this section include:

- Hydrofluorocarbons (HFCs);
- Hydrofluoroethers (HFEs);
- Perfluorocarbons (PFCs) and perfluoropolyethers (PFPEs);
- Chlorinated solvents (i.e., trichloroethylene, perchlorethylene, and methylene chloride);
- trans-1,2-dichloroethylene (trans);
- Brominated solvents (i.e., n-propyl bromide); and
- Hydrocarbons and oxygenated solvents (e.g., volatile methyl siloxanes, alcohols, esters).

### **4.2.1 Fluorinated Solvents**

Many solvent end-users have found success in using products formulated with hydrofluorocarbons (HFCs), hydrofluoroethers (HFEs), perfluorocarbons (PFCs), and perfluoropolyethers (PFPEs). These partially and fully fluorinated compounds were introduced as solvent replacements for Class I and Class II ODS because they exhibit zero ozone depletion potential. However, these substances are considered greenhouse gases with 100-year GWPs ranging from 250 to over 10,000 times the warming potential of carbon dioxide. A summary of each fluorinated solvent follows.

#### *Hydrofluorocarbons (HFCs)*

HFC solvents approved by SNAP include HFC-4310mee, HFC-365mfc, HFC-245fa, and heptafluorocyclopentane (HFCPA). HFC-4310mee is the most common solvent alternative; while HFC-365mfc is used as an additive to form solvent blends with HFC-4310mee, helping to reduce the cost of these products (Salerno 2001). HFC-245fa is approved for use only as an aerosol solvent to replace HCFC-141b and CFC-113 (EPA SNAP Program 2003). Table 4-2 summarizes advantages and disadvantages of HFC solvents available to solvent end-uses including some of the major trade names under which they are sold.

**Table 4-2. Summary of HFCs Used as Solvent Alternatives to ODS**

Acceptable HFC	Common Available Product Line(s)	Advantages	Disadvantages
HFC-4310mee (pure form solvent offered as Vertrel® XF)	Vertrel® Specialty Solvents – Broad product line from DuPont and Micro Care (Blends of XF with trans, alcohols, etc.)	<ul style="list-style-type: none"> <li>• Zero ODP</li> <li>• Acceptable for use in electronics, metal, precision, and aerosol solvent cleaning</li> <li>• Favorable for use with high value applications (Arthur D. Little 2002)</li> <li>• Usually blended as azeotropes to increase solvency and lower cost</li> </ul>	<ul style="list-style-type: none"> <li>• A mild solvent with limited solubility when used alone</li> <li>• Expensive base solvent (approximately \$18.00 per pound) (Mouser 2003)<sup>1</sup></li> <li>• GWP = 1,500<sup>2</sup></li> </ul>
HFC-365mfc	Offered by Solvay Fluorides, LLC  Offered by DuPont/Micro Care: Vertrel® C Series (Blends with trans, HFC-4310mee, and other solvents)	<ul style="list-style-type: none"> <li>• Zero ODP</li> <li>• Acceptable for use in electronics, metal, precision, and aerosol solvent cleaning</li> <li>• Used to form non-flammable azeotropic blends when formulated with HFC-4310mee</li> <li>• Usually blended to increase solvency</li> <li>• Lower cost</li> </ul>	<ul style="list-style-type: none"> <li>• Flammable if used alone</li> <li>• A mild solvent with limited solubility when used alone</li> <li>• GWP = 890<sup>2</sup></li> </ul>
HFC-245fa	Techspray® G3™ Genesolv® S Series (Azeotropic blends of trans and HFC-245fa)	<ul style="list-style-type: none"> <li>• Zero ODP</li> <li>• Acceptable for use as an aerosol solvent cleaner</li> <li>• Non-flammable</li> <li>• Moderately priced (approximately \$5 to \$7 per pound for Genesolv® S Series; \$10 to \$16 per pound for Techspray® G3™ Series)<sup>3</sup></li> <li>• Good compatibility properties</li> </ul>	<ul style="list-style-type: none"> <li>• GWP = 950<sup>2</sup></li> </ul>
HFCPA	Zeorara-H	<ul style="list-style-type: none"> <li>• Zero ODP</li> <li>• Acceptable for use in Electronics, Metal, and Precision Cleaning</li> <li>• Non-flammable with a relatively high boiling point</li> <li>• High solvency</li> </ul>	<ul style="list-style-type: none"> <li>• Expensive (approximately \$23.00 per pound) (Achema Daily 2003)<sup>1</sup></li> <li>• GWP = 250<sup>4</sup></li> </ul>

<sup>1</sup> Compared to Class I ODS solvents, which historically ranged from approximately \$0.60 to \$1.20 per pound.

<sup>2</sup> GWP value (over a 100-year time horizon) taken from the *IPCC Third Assessment Report* (IPCC 2001).

<sup>3</sup> Price range for Genesolv® S Series provided by Honeywell (2004b). Price range for Techspray® G3™ series provided by Techspray (2004b). Cook (2003) cites both products as slightly higher in cost relative to HCFC-141b.

<sup>4</sup> GWP value (over a 100-year time horizon) taken from the U.S. Federal Register (2000).

HFC-4310mee became commercially available in the mid-1990s under the trade name Vertrel® and can be used in vapor degreasing equipment. Originally developed by DuPont and now with support from Micro Care, the Vertrel® product line consists of a series of azeotropic formulations of HFC-4310mee with trans, various alcohols, and HFC-365mfc. Examples are Vertrel® SMT and XMS Plus for electronics cleaning and Vertrel® MCA and MCA Plus for metal and precision cleaning.

For the aerosol solvent cleaning end-use, formulations of HFC-245fa and trans are considered effective solvent replacements for HCFC-141b. Different formulations with varying levels of HFC-245fa have been developed by Honeywell and Techspray, specifically Techspray® G3™ and Genesolv® S Series. As HCFC-141b stockpiles are reduced, it is expected that the demand for these candidates will increase and prices will fall.

HFCPA is marketed under the product name Zeorara-H and is acceptable for use in electronics, metal, and precision cleaning. Although it has been considered a replacement option (Zeon Corporation 1998); this alternative has not infiltrated the U.S. solvent market, in large part because of the demonstrated success experienced by the other fluorinated solvent alternatives.

Although HFC solvents are used in many applications and have established a strong position in the solvent market in the United States, total global use in solvent is very small and estimated to be less than 2.2 to 4.4 million pounds, less than one percent of global CFC-113 uses in 1989 (UNEP 1999).

**Box 4-1. NAICS codes likely to have adopted HFC solvents: \***

- 334 - Computer and Electronic Product Manufacturing
- 335 - Electrical Equipment, Appliance, and Component Manufacturing
- 336 - Transportation Equipment Manufacturing
- 339 - Miscellaneous Manufacturing

\*See Appendix A for six digit NAICS beneath each three digit code listed here.

*Hydrofluoroethers (HFEs)*

In 1996, HFEs were first manufactured as replacements for chlorinated and/or fluorinated solvents. The three HFEs considered by SNAP as acceptable without restrictions are HFE 7000, 7100, and 7200. 3M manufactures HFEs and various azeotropic blends using solvents such as isopropanol and trans-1,2-dichloroethylene (trans), which increase solvency for more difficult cleaning applications, under the product name Novec™.

These products have successfully replaced methyl chloroform, CFC-113, and HCFCs within the U.S. solvent industry (U.S. EPA 2001a). 3M™ Novec™ Engineered Fluids are viable substitutes for various precision cleaning applications including hard disk media, disk drive assemblies, optical components, and gyroscopes. These HFEs and their azeotropic blends are also able to remove solder fluxes on printed circuit boards and contaminants from difficult to clean electronic components (3M Specialty Materials 2000) Table 4-3 provides a summary of these solvents.

**Box 4-2. NAICS codes likely to have adopted HFE solvents: \***

- 334 - Computer and Electronic Product Manufacturing
- 335 - Electrical Equipment, Appliance, and Component Manufacturing
- 336 - Transportation Equipment Manufacturing
- 339 - Miscellaneous Manufacturing

\*See Appendix A for six digit NAICS beneath each three digit code listed here.

**Table 4-3. Summary of HFEs Used as Solvent Alternatives to ODS**

<ul style="list-style-type: none"> <li>• HFE 7000 3M™ Novec™ Engineered Fluid<sup>3</sup></li> </ul>	<ul style="list-style-type: none"> <li>• Zero ODP</li> </ul>	<ul style="list-style-type: none"> <li>• Limited solubility, limiting use for specific cleaning specifications that might require a more aggressive solvent</li> </ul>
<ul style="list-style-type: none"> <li>• HFE 7100 3M™ Novec™ Engineered Fluid</li> <li>• HFE 7100-DL 3M™ Novec™ Engineered Fluid</li> <li>• HFE-711PA 3M™ Novec™ Engineered Fluid (<i>azeotropic mixture of HFE-7100 and isopropanol</i>)</li> <li>• HFE-711DE 3M™ Novec™ Engineered Fluid (<i>azeotropic mixture of HFE-7100 and trans</i>)</li> <li>• HFE-711DA 3M™ Novec™ Engineered Fluid (<i>azeotropic mixture of HFE-7100, trans, and ethanol</i>)</li> <li>• HFE-711D90 3M™ Novec™ Engineered Fluid (<i>HFE-7100 and trans blend</i>)</li> </ul>	<ul style="list-style-type: none"> <li>• Acceptable for use in electronics, metal, and precision cleaning, and for some products aerosol solvent cleaning</li> <li>• VOC exempt</li> <li>• Low toxicity</li> <li>• Selective solvency for cleaning light to medium weight oils and flux residues</li> <li>• Varying azeotropes available for compatibility</li> <li>• Low viscosity (i.e., optimum evaporation rates)</li> <li>• Non-flammable allowing for their use as an alternative for in-situ aerosol solvent cleaning applications of live electrical equipment (UNEP 2003b)</li> </ul>	<ul style="list-style-type: none"> <li>• Still considered greenhouse gases with a High Global Warming Potential of 390 for HFE-7100 and 55 for HFE-7200<sup>1</sup></li> <li>• Relatively expensive (ranging from \$16 to \$17 per pound) (Mouser 2003)<sup>2</sup></li> </ul>
<ul style="list-style-type: none"> <li>• HFE-7200 3M™ Novec™ Engineered Fluid<sup>3</sup></li> <li>• HFE-7200DL 3M™ Novec™ Engineered Fluid<sup>3</sup></li> </ul>	<ul style="list-style-type: none"> <li>• Relatively lower Global Warming Potentials (ranging from 55 for HFE-7100 to 400 for HFE-7000) when compared to HFCs, PFCs, and PFPEs</li> </ul>	

<sup>1</sup>GWP value (over a 100-year time horizon) taken from the *IPCC Third Assessment Report* (IPCC 2001).

<sup>2</sup>Compared to Class I ODS solvents, which historically ranged from approximately \$0.60 to \$1.20 per pound.

<sup>3</sup>These products are also capable of being used as aerosol solvent cleaners.

***Perfluorocarbons (PFCs) and Perfluoropolyethers (PFPEs)***

PFCs (e.g., C<sub>5</sub>F<sub>12</sub>, C<sub>6</sub>F<sub>14</sub>, C<sub>7</sub>F<sub>16</sub>, and C<sub>8</sub>F<sub>18</sub>) and PFPEs have been severely restricted by the SNAP Program to certain specialized uses for high-performance, precision-engineered applications (e.g., gyroscopes, electro-mechanical assemblies, direct access storage devices) because of these substances' long atmospheric lifetime and high GWPs. The GWPs for PFCs used in solvent cleaning are 8,900 or greater over a 100-year horizon, compared to 1,500 for the solvent with the next highest GWP and a GWP of 1 for carbon dioxide (IPCC 2001). The atmospheric lifetimes of PFCs used in solvent cleaning are 3,200 years or longer, two orders of magnitude longer than for other solvents. Because SNAP regulations restricted the use of PFCs and PFPEs, industry has moved away from their use, replacing them with other substances (predominantly lower GWP HFEs and HFC-4310mee) in many of the processes for which they have historically been used (UNEP 1999).

**4.2.2 Chlorinated Solvents**

For many years, perchloroethylene (PCE), trichloroethylene (TCE), and methylene chloride (MC) have been used by the U.S. solvent industry for a diverse number of cleaning applications. These three substances are approved as replacements for ozone-

**Box 4-3. NAICS codes likely to return to chlorinated solvents:\***

- 331 - Primary Metal Manufacturing
- 332 - Fabricated Metal Product Manufacturing
- 333 - Machinery Manufacturing
- 335 - Electrical Equipment, Appliance, and Component Manufacturing
- 336 - Transportation Equipment Manufacturing
- 339 - Miscellaneous Manufacturing

\*See Appendix A for six digit NAICS beneath each three digit code listed here.



depleting solvents. However, a recent market trend indicates a focus away from chlorinated solvents because of their health, safety, air pollution, and hazardous waste concerns (Landau 1999). The U.S. demand for chlorinated solvents has dropped by approximately 70 percent from 1987 to 2001, led by the complete phaseout of methyl chloroform. In 2001, chlorinated solvent demand was estimated at 505 million pounds (Landau 1999).<sup>10</sup> The primary drawback associated with these chlorinated solvents is their classification as hazardous air pollutants (HAPs) under Title III of the 1990 Clean Air Act Amendments. Some companies in the solvent industry have decided not to return to the use of chlorinated solvents because of regulatory hurdles, while other end-users have found these solvents to be the most effective replacements for Class I ODS because of their chlorine atoms, which provide excellent solvency. Table 4-4, summarizes the advantages and disadvantages of these solvents.

**Table 4-4. Summary of Chlorinated Solvents Used as Solvent Alternatives to ODS**

Solvent Cleaning End-Use(s)	Advantages	Disadvantages
Electronics Metal Precision Aerosol Solvent	<ul style="list-style-type: none"> <li>• Excellent Solvency</li> <li>• Low flammability</li> <li>• Moderate to extremely rapid evaporation rates</li> <li>• Very affordable (approximately no more than \$2.00 per pound) (Mouser 2003)</li> </ul>	<ul style="list-style-type: none"> <li>• Regulated OSHA and workplace standards</li> <li>• Regulated RCRA hazardous waste</li> <li>• Regulated pesticide formulation and handling standards</li> <li>• Regulated waste management standards</li> <li>• Regulated VOC standards</li> <li>• Regulated Maximum Achievable Control Technology requirements under the Clean Air Act for vapor degreasing (NESHAP)</li> <li>• Health risks and toxicity concerns related to exposure to workers and to the general public</li> </ul>

#### *Perchloroethylene*

Due to its high boiling point, perchloroethylene is used to remove difficult soils and waxes and is the favored solvent for use in cleaning aerospace (NAICS 336), appliance, and automotive metal parts (NAICS 332, 336). The solvent is also effective as a cold metal cleaner because of its low vapor pressure and non-flammability. Perchloroethylene is a preferred solvent within automotive aerosols used particularly for brake cleaning (HSIA 1999).

According to the Halogenated Solvent Industry Alliance (HSIA), in 1998, the metal cleaning and automotive aerosols industries consumed roughly 10 percent of the total U.S. perchloroethylene demand, or 34.4 million pounds (HSIA 1999). However, this estimate does not distinguish between the quantity used by those end-users who have always used perchlorethylene versus the quantity being used as an ODS replacement.

#### *Trichloroethylene*

Trichloroethylene (TCE) is an aggressive solvent cleaner with excellent solvency as well as a low flammability and boiling point, and is generally compatible with substrates. Since the introduction of vapor degreasing in the 1930s, TCE has served as a solvent in metal cleaning (HSIA 2001) (see Table A-2 in Appendix A for NAICS codes). It has also been listed by EPA as an acceptable substitute for methyl chloroform and CFC-113.

In 1998, approximately 72 million pounds of trichloroethylene were used in metal degreasing applications (HSIA 2001). Because of its low price, this quantity may represent some end-users previously using methyl chloroform that have reverted back to this chlorinated solvent option. However, not only has TCE been considered too aggressive a cleaner for more delicate parts, but TCE has also been classified as a

<sup>10</sup> This demand estimate includes chlorinated solvents for the U.S. paints and coatings industries.

potential human cancer risk and investigations into such risks associated with long-term exposures are still ongoing (Goodwin Proctor 2003).

### *Methylene Chloride*

Methylene chloride's advantageous properties include its lack of flash point, ability to reduce flammability of other substances, and excellent solvency. It is primarily used in other solvent industries, specifically as a paint remover, a carrier solvent in industrial adhesive formulations, and in specialized spray paints and lubricants.

Methylene chloride is also used in cold cleaning and vapor degreasing to remove grease and oil; about 4 percent (8 million pounds) of the 2000 demand was used within the NAICS codes associated with metal cleaning (HSIA 2003). It is assumed, however, that very little of this quantity can be attributed to solvent end-users transitioning out of ODS. Methylene chloride has an aggressive solvency that can be detrimental to various substrates.

### **4.2.3 trans-1,2-Dichloroethylene**

In addition to the traditional chlorinated solvents well known to the industry, another chlorinated solvent alternative has entered the market. trans-1,2-dichloroethylene, commonly referred to as "trans," is an aggressive solvent which because of its flammability, is most always combined with other solvents, such as HFCs and HFEs to form effective azeotropes. The powerful solvency of trans makes for a more aggressive solvent product, which can be used to enhance cleaning performance in cases where compatibility with the substrate to be cleaned is met (PPG 2002). trans is sold under the trade name VersaTRANS™ by PPG Industries, Inc. It is used in vapor degreasing by the electronics, metal, and precision cleaning end-uses, and is also used as an aerosol solvent cleaner. EPA considers trans an acceptable alternative for CFC-113, methyl chloroform, and HCFC-141b. Some suggest that worker health and safety may be a concern; trans has an OSHA PEL of 200 ppm. Examples of products that use trans include:

- Du Pont Vertrel® Specialty Fluids
- Techspray® G3™
- Genesolv® S-TZ
- 3M™ Novec™ Engineered Fluids

### **4.2.4 Brominated Solvents**

Commercially introduced about ten years ago, n-propyl bromide (nPB) has been marketed as a substitute for non-ozone-depleting chlorinated solvents (trichloroethylene and perchloroethylene) and ozone-depleting solvents (HCFCs, methyl chloroform, and CFC-113).

However, nPB is a controversial substitute because of its ozone-depleting potential value and possible health and safety concerns. nPB has a very short atmospheric lifetime of only 19 days, and its ODP depends on where it is emitted and the time of the year. In latitudes near the equator, the ODP can range from 0.071 to 0.10, yet in more temperate latitude zones, where the United States is situated, the ODP ranges from 0.013 to 0.018 (U.S. EPA 2003a).

Additionally, a number of studies have been and are currently being conducted to determine workplace exposure limits because of reproductive toxicity concerns associated with nPB exposure in

#### **Box 4-4 NAICS codes likely to have adopted nPB Products:\***

331 - Primary Metal Manufacturing  
332 - Fabricated Metal Product Manufacturing  
333 - Machinery Manufacturing  
334 - Computer and Electronic Product Manufacturing  
335 - Electrical Equipment, Appliance, and Component Manufacturing  
336 - Transportation Equipment Manufacturing  
339 - Miscellaneous Manufacturing

\*See Appendix A for six digit NAICS beneath each three digit code listed here.

the workplace. EPA, under the SNAP Program, has not yet completed the approval process for nPB as a substitute for ODS in various applications, including aerosol solvent and solvent cleaning uses.

In 2003, EPA published a proposed rule governing the use of nPB, proposing to list nPB as an acceptable substitute for methyl chloroform, CFC-113, and HCFC-141b in solvent cleaning (including aerosol solvents) as well as in adhesives (U.S. EPA 2003a). The proposed rule also addresses concerns regarding reproductive hazards in humans, and is proposing a recommended workplace Acceptable Exposure Level (AEL).

The advantages of nPB are that it can be easily recycled and is moderately priced (U.S. EPA 2001a). Because it closely mimics the banned methyl chloroform in its physical and chemical properties, nPB is compatible with most metals, has a low tendency to cause corrosion, and can be used in most modern vapor degreasing equipment. It also has been commercialized as an inexpensive replacement for HCFC-141b in aerosol solvent cleaners, although its acceptance is confronted by the emissive nature of these applications and its low occupational exposure limit. Manufacturers associated with NAICS code 334 (Computer and Electronic Product Manufacturing) have adopted nPB; however, in some instances compatibility issues may prevent this substitution trend. NAICS codes associated with metal cleaning that have had previous success with methyl chloroform are likely to have similar success with nPB; however pricing relative to the very low price of methyl chloroform and workplace exposure have played a role in moderating this substitution trend. NAICS codes likely to have adopted nPB products are provided in Box 4-4.

Due to concerns with corrosion and the range of flammability, a problem also previously encountered with methyl chloroform, nPB is not considered a technically feasible option for some precision cleaning end-use applications such as gyroscope cleaning and oxygen line flushing. Furthermore, many medical applications (e.g., plastic catheter line cleaning) that depend on the rapid and complete volatilization of CFC-113 are unable to be cleaned by nPB because of the delicate nature of some parts associated with such applications.

**Table 4-5. Summary of nPB Used as a Solvent Alternative to ODS**

Common Available nPB Product Lines	Advantages	Disadvantages
<ul style="list-style-type: none"> <li>• Solvon® FB Solvents from Poly Systems USA</li> <li>• ABZOL® Cleaners from Albemarle Corp.</li> <li>• Ensolv® from Enviro Tech International</li> <li>• Lenium® from Petroferm</li> </ul>	<ul style="list-style-type: none"> <li>• Excellent Solvency, comparable to the cleaning power of chlorinated solvents</li> <li>• Effective solvent for electronics, metal, precision, and aerosol solvent cleaning</li> <li>• Compatible with many materials including metals and plastics</li> <li>• Relatively affordable (approximately \$4.00 per lb) (Mouser 2003)</li> <li>• Ability to be recycled</li> </ul>	<ul style="list-style-type: none"> <li>• Final Ruling on SNAP approval still pending</li> <li>• Health and reproductive risks and toxicity concerns related to workplace exposure</li> <li>• ODP (although it is low when used at latitudes of the Continental U.S.)</li> <li>• Like methyl chloroform, must be highly stabilized and monitored in use</li> </ul>

#### **4.2.5 Hydrocarbons and Oxygenated Solvents**

Hydrocarbon and oxygenated solvents have high polarity, moderate to powerful solvency, and varying toxicity. Although these solvents are flammable and often inadequate for removing difficult contaminants such as waxes and grease, they have proven to be effective for final, touch up cleaning of various electronics applications and certain precision components in the aerospace industry. They are mostly used at the workbench via aerosol dispensing systems or through manual methods such as wiping. Generally, use of these solvents is required on a more irregular basis and in smaller quantities for these applications.

Solvents that are considered oxygenated or hydrocarbons (or both) include alcohols such as isopropyl alcohol (IPA), glycol ethers, esters, and ketones such as methyl isobutyl ketone and acetone. Several of these solvents originate from bio-based sources; for example d-limonene is a hydrocarbon found in oil

extracted from citrus rinds and soy methyl ester is an oxygenated solvent formed using soybean oil and methanol (Marshall and Wilcox 2003).

Many solvents in this category are very affordable; for example, isopropyl alcohol and acetone are no more than a \$1 per pound and d-limonene is within a \$2 to \$3 per pound range (Mouser 2003). However, if the intended use is in a vapor degreaser, the price of the solvent itself is offset by the costs associated with expensive explosion-proof equipment, which is necessary because of the low flash points associated with these solvents. The use of these solvents in vapor degreasing is consequently relatively minimal. Furthermore, volatilization and reactivity concerns have also resulted in the listing of several of these solvents as hazardous air pollutants (HAPs) and VOCs. These issues are drawbacks commonly considered with their use in manual or aerosol cleaning, the latter of which is usually carried out using an aerosol can with a tube ending in a brush to minimize the amount used. The overall use of hydrocarbon and oxygenated solvents in the cleaning industry is considered relatively low given these limitations and that the primary role these solvents play is in touch-up cleaning for end-use applications belonging to niche markets (e.g., the aerospace industry) with lower production levels.

#### **4.2.6 Volatile Methyl Siloxane (VMS) Solvents**

Another development in alternative solvents is a class of compounds called volatile methyl siloxanes (VMS). VMS are used as mild solvents suited primarily for cleaning silicones and other light, nonpolar residues (U.S. EPA 2001a). Although these solvents evaporate quickly leaving no residues and are safe to use on plastics, they range from flammable to combustible with low to moderate flash points and, therefore, require specialized equipment (UNEP 1999). VMS can be used in electronic and precision cleaning end-use applications for defluxing and/or degreasing high value parts. However, the extremely low volume in the U.S. market suggests that these solvents are only used in highly specialized niche applications. VMS are therefore likely to be more expensive than other solvent cleaning agents available to industry today.

**Box 4-5. NAICS codes likely to have adopted VMS solvents: \***

334 - Computer and Electronic Product Manufacturing  
335 - Electrical Equipment, Appliance, and Component Manufacturing  
336 - Transportation Equipment Manufacturing

\*See Appendix A for six digit NAICS beneath each three digit code listed here.

An example of a VMS solvent, commercialized for use as defluxers and degreasers, is the Dow Corning<sup>®</sup> OS-120 Fluid, a VMS azeotrope that has been designed for the manual cleaning through brushing or wiping of printed circuit boards and other electronic devices. VMS solvents have also shown some success for cleaning of aerospace guidance components and liquid crystal displays used in watches and digital clocks (see Box 4-5) (Dow Corning 2003).

### **4.3 Available Technology Substitutes**

In addition to the use of alternative cleaning solvents, a variety of technological practices are available that entirely replace the practice of using solvents as traditionally employed. The technological approaches discussed in Section 4.2 are:

- Aqueous cleaning;
- Semi-aqueous cleaning; and
- No-clean technologies.

#### **4.3.1 Aqueous Cleaning**

Aqueous cleaning is a multi-staged process of washing with mild detergents requiring specialty designed equipment. The equipment includes stations for washing, water rinsing, and drying and in many cases adds an increased complexity to the cleaning process with the addition of sophisticated spray systems and evaporative systems such as blowers and/or air knives. Aqueous cleaning may rely upon mechanical action and increased temperature to help remove contaminants (PPRC 1999a).

Since the early 1990s, companies have installed aqueous cleaning systems in place of ODS vapor degreasers and in doing so have experienced cost savings. Aqueous processes have lower material costs than traditional solvent processes due to the low cost of water, but there are energy costs and costs associated with wastewater treatment, depending on the level of contamination and local discharge regulations. However, despite these introduced costs, there are many examples and case studies available in industry literature discussing the operational cost savings realized when using aqueous cleaning. For example, one company replaced their cold tanks and vapor degreasers with aqueous systems and eliminated the annual purchase of 17,000 gallons of methyl chloroform, experiencing an annual cost savings of close to \$100,000 (Chaneski 1997). The findings from another study in which eight projects were evaluated, showed that after switching to aqueous cleaning, operational costs were reduced by 75 percent in three cases and more than 95 percent in the other five (PPRC 1999a). Furthermore, some companies have minimized wastewater discharge and the cost associated with wastewater discharge processes using “closed-loop” systems in which the water is separated out of the cleaning solution, treated, and reused (U.S. EPA 2001a). Table 4-6 summarizes the advantages and disadvantages associated with aqueous cleaning.

**Table 4-6. Advantages and Disadvantages of Aqueous Cleaning as an Alternative to ODS**

Advantages	Disadvantages
<ul style="list-style-type: none"> <li>• Cost savings through the elimination of the use of an ODS solvent</li> <li>• Elimination of air emissions</li> <li>• Environmentally safe and affordable detergents able to clean oils, greases, soils and salt contaminants</li> <li>• Continuous upgrades and advances in technology</li> <li>• Recovery of initial cost to the equipment through recycling products over the lifetime of the equipment</li> </ul>	<ul style="list-style-type: none"> <li>• High water consumption and resulting wastewater treatment capacity and specific discharge requirements</li> <li>• Increased difficulty to remove certain contaminants requiring increased mechanical agitation</li> <li>• Additional processes of thorough rinsing and drying with increased energy costs</li> <li>• Increased reliance on equipment, which requires more floor space compared to vapor degreasers</li> <li>• Potential for substrate corrosion (rusting), and insufficient performance for applications with complex parts</li> </ul>

Sources: Arthur D. Little 2002; UNEP 2003b; U.S. EPA 2001.

### **4.3.2 Semi-Aqueous Cleaning**

Semi-aqueous cleaning processes, also referred to as hydrocarbon-surfactant cleaning, use a cleaning solution, often a hydrocarbon/surfactant combination, to remove contaminants such as metal particulates, oil, and grease followed by a water wash and rinse. The semi-aqueous process was critical in the phaseout of ODS especially in the electronics industry, as it demonstrated that surface mount assemblies could be successfully cleaned without ODS. Semi-aqueous processes are expensive and, although initially popular in developed countries, have not maintained as strong a presence in the United States as aqueous cleaning and no-clean technologies continued to develop.

**Table 4-7. Advantages and Disadvantages of Semi-Aqueous Cleaning as an Alternative to ODS**

Advantages	Disadvantages
<ul style="list-style-type: none"> <li>• Cost savings through the elimination of the use of an ODS solvent</li> <li>• Less solvent consumption of hydrocarbon/surfactant required than compared to an ODS solvent used in a vapor degreasing process</li> <li>• Less water consumption compared to aqueous cleaning</li> <li>• Effective for cleaning heavy oils, metal particulates, greases, and tars</li> <li>• Compatibility with most metals and plastics</li> </ul>	<ul style="list-style-type: none"> <li>• Wastewater treatment and specific discharge requirements depending on level of contamination and local regulations</li> <li>• Equipment more complex than typical aqueous equipment</li> <li>• Some hydrocarbon/surfactant cleaners considered VOCs</li> <li>• Increased energy consumption resulting from required heated rinse and drying stages</li> </ul>

Sources: Arthur D. Little 2002; UNEP 1999; U.S. EPA 2001.

### 4.3.3 No-Clean Technologies

The use of low-solids solder fluxes or pastes and controlled inert atmospheres can in some circumstances negate the need for cleaning of electronic assemblies. No-clean pastes, containing two to five percent solids flux as compared to 10 to 40 percent solids flux in traditional pastes, serve the same purpose as their traditional counterparts, but leave significantly less residue on the printed circuit board after soldering. Many companies have tested low-solid fluxes in their production facilities and have determined that the small amount of residual flux remaining from the use of these formulations, depending on the active nature of the residues, does not damage the quality of the printed circuit board interconnects (U.S. EPA 2001a). Using no-clean fluxes is more effective when the soldering is conducted in an inert atmosphere, which reduces the oxidation of the metal substrates at elevated temperatures, a lower level of residue, less solder balling, and better fluxing performance resulting in cleaner parts (PPRC 1999b).

Within the electronics sector, removing the cleaning step following the solder process has been a popular alternative for many manufacturers previously using Class I ODS because of the cost savings associated with the no-clean flux technology. One study found that despite a cost of \$25,000 to convert to a no-clean process, \$100,000 to \$200,000 was saved annually. IBM has reported their assembly costs were reduced by 10 percent after switching to a no-clean flux (PPRC 1999b). Although converting to a no-clean process requires time and resources to test and investigate the alternative and cover associated conversion costs, operational savings can be significant because the post-solder cleaning process can be eliminated (PPRC 1999b).

**Table 4-8. Advantages and Disadvantages of No-Clean Technology as an Alternative to ODS**

Advantages	Disadvantages
<ul style="list-style-type: none"> <li>• Elimination of a cleaning step negating the need for a full-service cleaning process</li> <li>• Cost savings and increased efficiency in the assembly operation</li> <li>• Effective and viable option for basic electronic assemblies</li> </ul>	<ul style="list-style-type: none"> <li>• Increased need for training for use of no-clean materials and ensuring product quality</li> <li>• Additional material costs for maintaining a nitrogen atmosphere to assist in the soldering process</li> <li>• Additional resources to ensure high quality solderability</li> <li>• Remainder of visible residues, although not considered detrimental to the electronic assembly's performance</li> <li>• Back-up cleaning and the need for cleaning in the soldering process often required.</li> </ul>

Source: Salerno and Reynolds 1999.

#### 4.4 Observed Substitution Trends

The solvent cleaning industry has come a long way since the advent of the Montreal Protocol and the subsequent phaseout of ozone depleting substances. The early to mid 1980s marked an era of skepticism by many in the industry that viable substitutes existed for ODS used as solvents. However, as the phaseout date drew nearer, research developments and demonstrated success of alternatives supported the feasibility in successfully transitioning away from ODS. Box 4-6 highlights one such development.

In Figures 4-1 through 4-3, the current market share of the alternatives, discussed in Section 4, are illustrated by end-use. The percentages should be treated as general approximations and are only representative of that portion of the solvent cleaning end-use that previously cleaned with a Class I ODS.

##### *Electronics Cleaning*

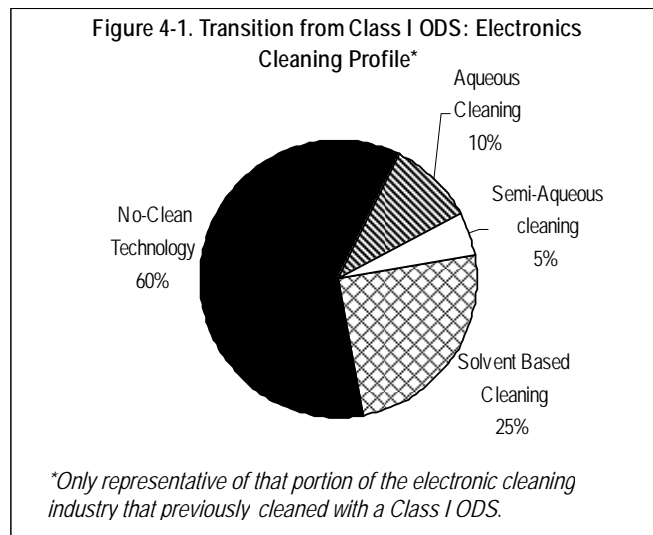
Figure 4-1 presents the current use of ODS alternatives in the electronics cleaning end-use. Characterization of the electronics market in the United States today is quite different when compared to the electronics market before the phaseout. The primary trend that took place for this end-use was the adoption of no-clean technology. Concurrent with this trend, companies overseas began dominating the home entertainment, telecommunications, computers, computer products, and office equipment markets. The domestic electronics market subsequently diminished and the remaining demand was mostly for high reliability electronics such as military, medical, avionics, aerospace, and certain automotive applications (e.g. anti-lock brake systems). These electronics applications require a higher standard of cleaning performance; therefore, as Figure 4-1 indicates, there is still a significant portion, approximately 25 percent, of the U.S. electronics cleaning end-use relying on solvents. More specifically, HFCs, HFEs, and HCFCs are the most commonly used solvents. nPB has also taken a minimal market share. No-clean technology is still the first preferred alternative in electronics cleaning and will be employed if the application being cleaned can meet achievable and acceptable performance standards.

#### Box 4-6. Advances in Solvent Cleaning Processes and Technology

Starting in the late 1980s through the mid-1990s, one observed trend experienced particularly by the metal and precision cleaning end-uses was a shift from vapor degreasing to aqueous cleaning (Reynolds 1999). The appeal of these alternative technologies was the elimination of emission problems associated with vapor degreasing. Many cleaning end-users, searching for an ODS alternative, implemented aqueous cleaning technology and established it as a "permanent" and "effective" option (Salerno and Reynolds 1998).

However, as some end-users discovered, aqueous cleaning can have drawbacks. Problems arose with more difficult contaminants, such as waxes, complex parts, rusting, drying, and elongated cycle times. Furthermore, tightening regulations surrounding water usage, waste generation, and disposal have created obstacles. In the late 90s, it was apparent that a portion of the industry was turning back to vapor degreasing with cleaning performance the primary driver for the resurgence of solvent-based cleaning. The SNAP approval of several solvents and further regulation of vapor degreasing supported the acceptance of responsible solvent based cleaning.

Vapor degreasing returned with vital improvements. Retrofitting has afforded the opportunity for end-users to use higher priced solvents since upgrades to equipment have resulted in better engineered, enclosed systems that can contain solvent vapor thereby reducing solvent usage. A survey conducted by *Precision Cleaning Magazine* indicates a rise in the use of solvent-based cleaning processes during the mid to late 90s (Salerno and Reynolds 1998). The results also show that some companies are employing both aqueous cleaning and vapor degreasers with non-ODS solvents to support the specific applications being cleaned.

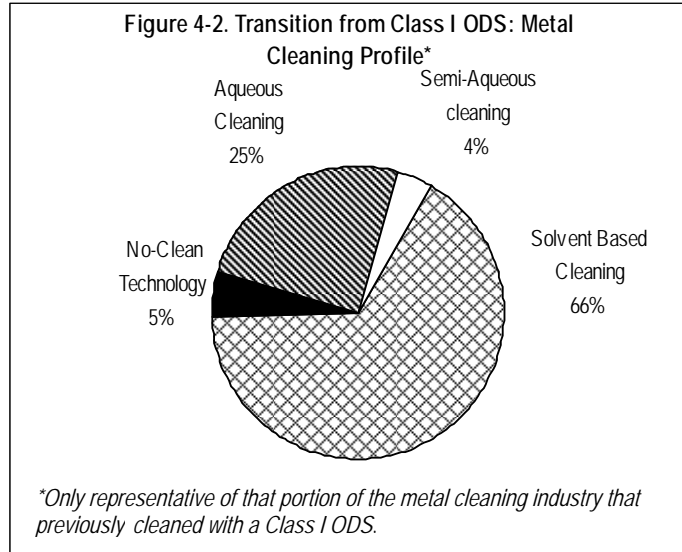


### *Metal Cleaning*

Metal cleaning relies on the same technologies as electronics cleaning, but in very different proportions. Figure 4-2 presents the proportions of each technology employed in metals cleaning. These percentages reflect the portion of the end-use that converted from an ODS solvent to aqueous cleaning, found it unsatisfactory, and then returned to a non-ODS solvent (see Box 4-6).<sup>11</sup> As shown in Figure 4-2, end-users in metal cleaning primarily use aqueous cleaning and solvent based cleaning. Of the solvents used, chlorinated solvents, particularly trichloroethylene, are considered the most common solvents chosen by the metal cleaning industry because of their cleaning properties (e.g., high stability, low flammability, high solvency for the removal of a range of soils) and affordability. Because this end-use cleans a large quantity of parts, lower priced, aggressive solvents are first choice and therefore, milder solvents formulated with HFCs, HFES, and HCFCs are not usually considered for this end use because of their associated material costs and performance, especially in high production volume applications.

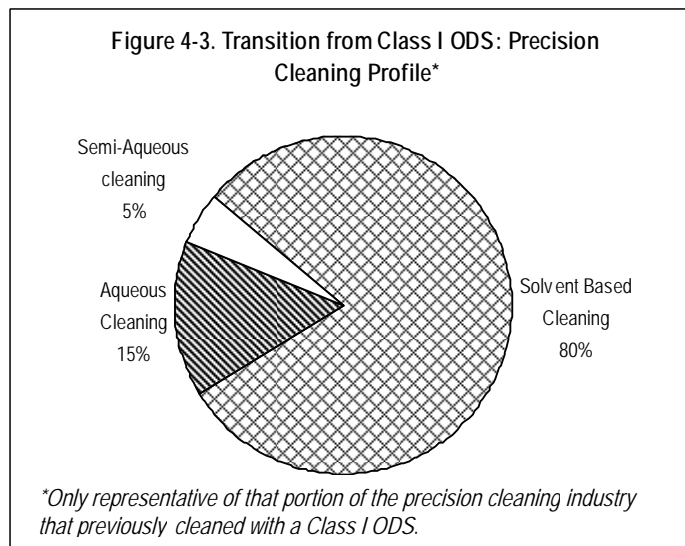
<sup>11</sup> Figure 4-2 does not distinguish between those end-users that have always used solvents such as trichloroethylene versus the quantity being used as an ODS replacement. Additionally, Figure 4-2 does not represent the portion of the metal cleaning end-use that had always used aqueous cleaning rather than the use of an ODS solvent such as methyl chloroform.





### Precision Cleaning

As with electronics and metal cleaning, precision cleaning transitioned to similar cleaning methods but with much less reliance on aqueous and semi-aqueous technologies. Figure 4-3 characterizes the current cleaning methods adopted by previous ODS users in the precision cleaning end-use. This sector faced the most difficult challenges in converting from ODS to alternatives because of application specific criteria and stricter cleaning standards. Once new alternatives and alternative processes were approved, the cost to qualify to another substitution presented a significant barrier to any further changes. Therefore, the trend experienced by other end-users from aqueous cleaning back to vapor degreasing with a non-ODS solvent occurred to a much lesser degree in precision cleaning. The solvents dominating this end-use include fluorinated based solvent alternatives (i.e., HFCs, HCFCs, HFEs) and their azeotropes and blends because of the range in solvency and compatibility these products offer to meet the specific criteria of the substrate being cleaned. As with electronics cleaning, nPB has also gained a portion of this market.



## *Aerosol Solvent Cleaning*

Unlike the other cleaning end-uses, aerosol solvent cleaning is conducted by dispensing the cleaning agent from an aerosol can onto the parts being cleaned, typically confined areas of machinery and intricate parts. This specialized spot cleaning process historically used CFC-113 (and smaller quantities of CFC-11) until the 1977 ban on the use of CFC propellants in aerosols for non-essential uses greatly affected the ability to continue to use Class I ODS cleaning agents. Without the CFC-11 and CFC-12 propellants, CFC-113 could not effectively be propelled out of the can for cleaning. New alternative propellants as well as new alternative aerosol solvents were required.

HFC-134a was the first major non-flammable propellant candidate. Eventually, aerosol solvent alternatives became available with HFC-134a as the propellant, despite competition with the refrigeration and air conditioning market that had a huge demand for HFC-134a. Interim cleaning substitutes began to develop to replace CFC-113, while only minimal quantities (i.e., in 1986 an estimated 3 million pounds of CFC-113 was used by this end-use) of this Class I ODS remained. These interim cleaning substitutes were oxygenated, aliphatic hydrocarbons such as isopropanol, which because of flammability had limited applicability.

In the late 1980s, HCFC-141b was introduced as a possible replacement, and by the early 1990s HCFC-141b recaptured the applications cleaned by the post CFC-113 transition intermediates.<sup>12</sup> The estimated use of HCFC-141b in aerosol solvent cleaning grew from approximately 5.3 million pounds in 1992 to 5.7 million pounds in 1993. By 1994, an estimated 16 million pounds of HCFC-141b was being used in the aerosol cleaning industry. This quantity not only replaced the interim hydrocarbon cleaning agents but also replaced remaining CFC-113 uses, of which approximately 160,000 pounds and 7,000 pounds was used in 1994 and 1995, respectively.

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<sup>12</sup> Section 610 of the CAA banned the use of Class II ODS in aerosol products and pressurized dispenser products after January 1, 1994. However, as authorized by Section 610(d)(2), EPA exempted certain products from this ban which were considered essential as a result of flammability and worker safety concerns. These include, for example, the use of aerosol solvent cleaners for electrical or electronic equipment, and for use in aircraft maintenance.

## 5 Current State of ODS Based Solvent Use in the U.S. Market

Despite the official phaseout of Class I ODS in 1995, a minimal use of these ODS as cleaning solvents continues in specific aerospace applications that have been granted an essential use exemption (EUE) for new production, as well as in some traditional cleaning applications sourced from existing stockpiles. In a few cases of continued use, suitable alternatives have not yet been identified for unique applications, necessitating the prolonged use of Class I ODS. However, in most cases, viable substitutes exist, but ODS may still be used either because extensive testing and validation procedures slow down the conversion process or because stockpile volumes are still large enough that users have not fully committed to developing an alternative.

Section 5 discusses current aggregated ODS usage by end-use, where appropriate, and is organized as follows:

- Section 5.1 discusses the use of Class I ODS after the phaseout.
- Section 5.2 outlines the current use of Class I ODS in limited and unique applications, especially their use in aerospace essential use exemptions (EUEs).
- Section 5.3 briefly discusses the global *de minimus* EUE for laboratory and analytical uses.
- Section 5.4 provides an overview of the sustained solvent uses of Class I and Class II ODS in electronics, metal, and precision cleaning, and aerosol applications, as well as in miscellaneous applications.

### 5.1 Size of the Class I ODS Solvent Industry after the Phaseout

ODS usage fell dramatically after the 1996 phaseout. In fact, for CFC-113, CFC-11, and carbon tetrachloride, current usage is negligible because no EUEs were authorized for solvent cleaning applications. Some usage of methyl chloroform in solvent cleaning applications is authorized under EUEs for Space Shuttle and Titan solid rocket motor manufacturing. See Box 5-1 for details regarding usage and stockpiling of ODS solvents with no EUEs.

#### Box 5-1. Non-EUE Solvent Usage and Stockpiling

Carbon Tetrachloride – As carbon tetrachloride usage was negligible even before the 1996 phaseout, current usage by the U.S. solvent industry is effectively zero.

CFC-11 – As alternatives have been identified in almost all aerosol solvent applications, current usage by the U.S. solvent industry is essentially zero. However, CFC-11 usage between 1996 and 2003 may total, but does not exceed, 1 million pounds (the estimate for stockpiling of CFC-11 as of January 1, 1996).

CFC-113 - Minimal usage of this ODS continues in select applications, in part because the shelf life of CFC-113 appears indefinite if properly stored. Industry experts have indicated that CFC-113 was still readily available in 2001, and end-users, in particular the U.S. military, have significant stockpiles of the material (AGA Chemicals 2004). However, because alternatives have been qualified for practically all applications in most end-uses, current usage is assumed to be minimal. Current usage of CFC-113 from stockpiles is assumed to be less than or equal to the level of usage in 1995, or approximately 3 million pounds a year, reflecting that users are finding and transitioning to alternatives. If consumption continued at about the same level as in 1995, only around half the amount of CFC-113 stockpiled in 1995 would remain today, or approximately 27 million pounds.

Methyl Chloroform – Methyl chloroform's short shelf life means that any methyl chloroform stockpiled from 1996 is likely decomposed sufficiently as to make its use hazardous and/or less efficient (UNEP 2003b). Thus, while some usage from stockpiles in the immediate years following the 1996 phaseout most likely occurred, current non-EUE use of methyl chloroform from existing stockpiles is assumed to be negligible. Non-EUE methyl chloroform usage between 1996 and 2003 may total, but does not exceed, 47.7 million pounds (the estimate for stockpiling of methyl chloroform as of January 1, 1996).

Assuming that Class I ODS stockpiles were used uniformly between 1996 and 2003, emissions resulting from non-EUE usage from stockpiles could be as much as 12 million pounds of material per year (not weighted by ODP). However, it is likely that annual non-EUE emissions have been lower than this estimate based on the assumed annual level of CFC-113 use (i.e., 3 million pounds) from stockpiles since 1996 and because use of stockpiled methyl chloroform was expected to cease 2 to 3 years after the phaseout date.

## 5.2 Methyl Chloroform Essential Use Exemptions

The United States has been granted EUEs for methyl chloroform for use in specific cleaning, bonding, and surface applications in solid rocket motor manufacturing.<sup>13</sup> Specifically, EUEs have been granted for the following:

1. The Reusable Solid Rocket Motor (RSRM) used in the Space Shuttle; and
2. The Solid Rocket Motor Upgraded (SRMU) used in the Titan rocket.

In the United States, solid rocket motors are used to launch communication, navigational, and scientific satellites, as well as manned Space Shuttles, into space. Because of the immediate danger to human life in many of these missions, the complexity of the science involved in manufacturing solid rocket motors, and the high cost of a failed mission, both the Space Shuttle and Titan programs have adopted conservative approaches toward process and material changes.

Since the science of solid rocket motor propellant interactions with assembly materials and storage is only partially understood, manufacturers are required to undergo long-term testing and extensive evaluation to change current methods of production. In addition, the manufacturing of solid rocket motors is unique in that the only existing method to test the performance of an individual motor before use is full-scale, ground-level static firing of a solid rocket motor. This method consumes the propellant so that it cannot be used again (although other components may be refurbished and reused) (UNEP 1999). Consequently, detailed material specifications and meticulous quality control are required to assure the success of solid rocket motors.

The remainder of this section discusses methyl chloroform usage by each of the EUE holders and the two solid rocket motors in more detail.

### 5.2.1 Space Shuttle Reusable Solid Rocket Motor (RSRM)

The 1996 Class I ODS phaseout of methyl chloroform significantly impacted future manufacturing of Reusable Solid Rocket Motors (RSRMs), produced exclusively by ATK Thiokol Propulsion. In 1989, Thiokol used more than 1.4 million pounds of methyl chloroform in the production of RSRM. In response to the phaseout, Thiokol, in partnership with NASA's Marshall Space Flight Center, enacted a three-phase Ozone Depleting Compounds (ODC) Elimination Program to eliminate the usage of methyl chloroform in all RSRM manufacturing processes. The first two phases of the program eliminated 90 percent of Thiokol's 1989 methyl chloroform usage (Evans and Golde 2001). For more information regarding the ODC Elimination Effort, see Box 5-2.

To complete the final phase of the program, Thiokol and NASA requested an essential use exemption (EUE) to allow continued usage of

#### Box 5-2. Thiokol's ODC Elimination Program

Phase 0 was completed in 1992 and involved the conversion to greaseless shipping of metal components.

Phase I was completed in 1997 and involved the elimination of vapor degreasing using methyl chloroform and the usage of methyl chloroform in propellant cleaning operations.

*Total Methyl Chloroform Abated by Phases 0 and I: 1.26 million pounds (Evans and Golde 2001).*

<sup>13</sup> The use of methyl chloroform in solvent cleaning applications in the manufacturing of solid rocket motors is classified by this report as a precision cleaning end-use under NAICS 336415, Guided Missile and Space Vehicle Propulsion Unit Parts Manufacturing.

the remaining 10 percent of methyl chloroform after the 1996 phaseout. The last phase, Phase II, involves the elimination of methyl chloroform in hand-wipe cleaning operations and rubber activation (Evans and Golde 2001).

In response to Thiokol/NASA's request, the United States has been granted essential use allowances for methyl chloroform for use in specific cleaning, bonding, and surface applications in rocket motor manufacturing for the Space Shuttle and Titan Rockets. In 1998, the Parties ruled that the remaining amount of methyl chloroform authorized for the United States at previous meetings of the Parties would be made available for use in manufacturing solid rocket motors (for both the Space Shuttle and Titan programs). Thus, EPA is authorized to allocate methyl chloroform until the allowance is depleted or until safe alternatives are implemented. Since the exemption period for methyl chloroform ends on January 1, 2005 (Section 604(d)(1) of the CAA), between 1999 and 2004 EPA allowed the production or import of the 1999-2001 allowance quantity of 0.39 million pounds (U.S. EPA 2002a). Table 5-1 shows the EUE allocations granted to the Space Shuttle program from 1996 to 2004.

**Table 5-1. Essential Use Allocation for Methyl Chloroform for ATK Thiokol/NASA RSRM Manufacturing, Million Pounds, 1996-2004**

Methyl Chloroform	1996	1997	1998	1999	2000	2001	2002	2003	2004
Essential Use Allocation	<0.01	<0.01	0.13	0.13	0.13	0.13	0.10	0.02	0.31

Sources: UNEP 1996; U.S. EPA 1998a; U.S. EPA 1998b; U.S. EPA 2000; U.S. EPA 2001b; U.S. EPA 2002a; U.S. EPA 2002b; U.S. EPA 2004

Since 1996, however, the actual production and import of methyl chloroform for these exempted applications has been lower than the allocation granted by the Parties. Despite the difference between allocation and usage, ATK Thiokol/NASA has stated that prior to the January 1, 2005 importation and production deadline, they plan to manufacture RSRMs such that they deplete the full quantity of essential use exemption authorization remaining (UNEP 2003c). Accordingly, the EUE allowance for 2004 is 0.31 million pounds, the remainder of the allocation (U.S. EPA 2004). While usage is minimal, use of methyl chloroform will likely continue until ATK Thiokol/NASA's EUE allocations run out. NASA uses, however, a leak-tight storage system for methyl chloroform stockpiles that ensures near-zero emissions of methyl chloroform (UNEP 2003c).

### 5.2.2 Titan Solid Rocket Motor Upgrade (SRMU)

At the same time that amendments to the Montreal Protocol accelerated ODS phaseout requirements, the production rate of the U.S. Air Force's Titan SRMUs was slowed, causing the expected completion date for the SRMUs to be extended from 1995 to 1999. As a result, the Titan program was unable to qualify alternatives for all uses of methyl chloroform by the 1996 phaseout date. Consequently, the program was granted an essential use exemption to allow minimal use for various applications. In following years, it was determined that small additional quantities of methyl chloroform were still necessary in the manufacturing of Titan SRMUs, especially in light of the fact that the Titan SRMU has launched such valuable payloads as the Gemini manned space program, Helios solar observers, Viking Mars Landers, and Cassini deep space probes (UNEP 1997). In 2003, the U.S. Air Force Titan program informed EPA that it had no need for a methyl chloroform EUE in 2004 (Foote 2002). Consequently, the entire quantity was allotted to the Space Shuttle program (U.S. EPA 2003b). Table 5-2 shows the EUE allocations granted to the Titan program between 1996 and 2003; a discussion on the methodology used to calculate these estimates is provided in Appendix B.

**Table 5-2. Essential Use Allocation for Methyl Chloroform for Titan SRMU Manufacturing, Million Pounds, 1996-2003**

Methyl Chloroform	1996	1997	1998	1999	2000	2001	2002	2003
Essential Use Allocation	<0.01	<0.01	0.01	0.01	0.01	0.01	0.01	0.01

Sources: UNEP 1996, U.S. EPA 1998a, U.S. EPA 1998b, U.S. EPA 2000, U.S. EPA 2001b, U.S. EPA 2002a, U.S. EPA 2002b.

### 5.3 Laboratory and Analytical Uses

In addition to the essential use exemption for methyl chloroform for use in the Space Shuttle and Titan Rockets, a global *de minimis* exemption has been granted for laboratory and analytical essential uses. Under this exemption, the following laboratory purposes qualify:

- Equipment calibration;
- Use as extraction solvents, diluents, or carriers for chemical analysis;
- Biochemical research;
- Inert solvents for chemical reactions, as a carrier or laboratory chemical; and
- Other critical analytical and laboratory purposes.

While methyl chloroform, CFC-113, CFC-11, and carbon tetrachloride are used in these applications as carrier and extraction solvents, their use as cleaning solvents in laboratory procedures is negligible. Although there is no cap on the amount of Class I ODS that can be used for laboratory and analytical purposes under this *de minimus* exemption, Table 5-3 presents the minimal amount of Class I ODS supplied to U.S. laboratories for all purposes.

**Table 5-3. Amount of Class I ODS Supplied to U.S. Laboratories, 1996-2002, Million Pounds**

	1996	1997	1998	1999	2000	2001	2002
CFC-113	0.01	0.03	0.02	0.01	0.00	0.00	0.00
Methyl Chloroform	0.01	0.01	0.01	0.01	0.00	0.00	0.02
Carbon Tetrachloride	0.02	0.02	0.01	0.02	0.02	0.01	0.01
CFC-11	0.00	0.00	0.00	0.00	NAV	NAV	0.00

Note: Due to rounding, 0.00 million pounds indicates that less than 0.005 million pounds was supplied to U.S. laboratories.

Sources: U.S. EPA 2001c was referenced for years 1996 to 1999, and U.S. EPA 2003c was referenced for years 2000 to 2002.

### 5.4 Applications with Continued ODS Use and Stockpiled ODS

Minimal use of Class I ODS remains in the U.S. solvent cleaning industry. Alternatives to Class I ODS have been identified, qualified, and implemented for practically all solvent cleaning applications in all end-uses. Moreover, applications which continue to use Class I ODS are generally specific, niche applications, such as oxygen systems cleaning. For applications for which the substitute process has not been completed, stockpiles of Class I ODS produced prior to the 1996 phaseout continue to be used, as permitted by the Clean Air Act Amendments (CAAA), for purposes that are not expressly named non-essential. It is likely that the industry extracted stockpiled Class I ODS for use in years directly following the phaseout; however, because of the commercial sensitivity of these data, it is difficult to estimate the volume of methyl chloroform, CFC-113, CFC-11, and carbon tetrachloride consumed from stockpiles in the United States in years following the phaseout. Additionally, while the use of Class I ODS from existing stockpiled and recycled material is still permitted, the usage of some of these substances is limited by shelf life (UNEP 2003b). For estimates of Class I ODS stockpiles as of January 1, 1996, see Section 2.2.

Currently, most Class I ODS stockpiled since 1996 will likely have decomposed sufficiently as to make their use hazardous and/or less efficient, as well as endangering the quality of the equipment in which they are used (UNEP 2003b). Thus, even if significant portions of the stockpiles estimated to exist as of 1996 (see Section 2.2) still remain, it is unlikely that they will be used today because of concerns about the quality of the material. With regard to CFC-113, industry expert opinion suggests that while CFC-113 was still readily available in 2001, and both aircraft companies and the U.S. military maintain stockpiles of the material, CFC-113 is currently not used in significant quantity (AGA Chemicals 2004; ICF Consulting 2004).

Class II ODS used as solvents follow a different course. As substitutes to Class I ODS, HCFCs entered the market as short term alternatives. However, the use of HCFC-141b was banned in vapor degreasers as of 1997, and as of January 1, 2003, its manufacture and use as a solvent were banned completely. Conversely, the use of HCFC-225 ca/cb is growing and is being marketed as a replacement for HCFC-141b.

The progress of each end-use in transitioning away from solvents containing Class I or Class II ODS is discussed below in Sections 5.4.1 and 5.4.2 respectively.

#### **5.4.1 Continued Use of Class I ODS**

Electronics Cleaning. The transition away from the use of methyl chloroform and CFC-113 has been almost complete for several years. Because technologies exist to achieve a complete phaseout of Class I ODS, the major obstacle was the process of choosing the most suitable substitute for a given application, as no drop-in replacement could be identified.

Metal Cleaning. Essentially all uses of CFC-113 and methyl chloroform in metal cleaning applications have viable alternatives, and, in general, the phaseout of CFC-113 and methyl chloroform in metal cleaning applications has been achieved.

Precision Cleaning. Although no drop-in replacement solvent has been found for CFC-113 and methyl chloroform in precision cleaning applications, alternatives exist for these ODS in virtually all applications (UNEP 2003b). The U.S. Air Force has recently validated alternatives to CFC-113 and methyl chloroform used for precision cleaning of electronic and oxygen system components in space and missile systems. The transition to these alternatives is expected to occur in 2004 and will eliminate around 24,000 pounds of Class I ODS use by the Air Force (The Monitor 2003).

CFC-113 and methyl chloroform have also been used to inspect for cleanliness of oxygen systems by flushing the solvent through the clean part and analyzing the solvent for extracted non-volatile material. Because it is crucial that the solvent used be able to remove all suspected contaminants and not remain on the cleaned parts, ODS are still being used in some cases. Viable alternatives exist, however, and include HCFC-225 ca/cb, trichloroethylene, and multi-step processes including initial flush with alcohol, followed by ultra-pure water, HFE, or HFC (UNEP 2003b). Choosing an alternative for oxygen line flushing must be done with care, including a careful assessment of the behavior of any flushing material in a pure oxygen environment.

In addition, methyl chloroform and CFC-113 are still being used as cleaning solvents for critical bonded joints of aerospace assemblies (UNEP 2003b). Because the Space Shuttle program has experienced difficulty in identifying qualified alternatives for similar applications, methyl chloroform and CFC-113 are most likely still used in these applications because alternatives have not been identified. However, as the Space Shuttle program plans to implement alternatives for hand-wipe cleaning of critical bonded joints in solid rocket motors in 2004, it is possible that this action may prompt end-users that are hand-wiping using stockpiled ODS without an EUE to follow the lead of ATK Thiokol/NASA in qualifying and implementing alternatives.

Aerosol Solvent Cleaning. Essentially all uses of CFC-113 and CFC-11 in aerosol cleaning applications have suitable alternatives, and, in general, the transition away from these ODS in aerosol cleaning has been achieved.

Other Cleaning Applications.<sup>14</sup> The U.S. Air Force stockpiled CFC-113 for use as a hand-wipe solvent in base aircraft maintenance, although as of 2001 the Air Force indicated that these stockpiled resources were being used up (Schroll 2001). Because the U.S. Air Force stockpiled sufficient CFC-113 prior to the 1996 phaseout, research to identify and qualify non-ODS alternatives was a lower priority, and consequently, funding was difficult to obtain (Schroll 2001). Thus, while aeronautics companies initially looked to the military for guidance, because of the Air Force's timing of investigations into alternatives, many companies converted to non-ODS alternatives before the Air Force.

While the Air Force continues to use CFC-113 in many cleaning processes, this seems to be in large part because of the convenience in using remaining stockpiles rather than because there are technical difficulties in switching to alternatives.

#### **5.4.2 Continued Use of Class II ODS**

Electronics Cleaning. HCFC-141b and HCFC-225 ca/cb based blends and azeotropes have replaced CFC-113 in removing the flux residue that remains after a soldering operation. Although the use of HCFC-141b in electronics vapor degreasing ceased in the late 1990s, demand for HCFC-225ca/cb is increasing. Any progress in finding an alternative for this Class II ODS defluxer will probably not commence until the 2015 phaseout date approaches. Some end-users previously using Class I ODS have chosen to avoid a conversion to Class II ODS entirely; in fact, an estimated 60 percent of Class I ODS end-users transitioned directly to no-clean technology.

Metal Cleaning. Currently, HCFC-141b is not being used by the metal cleaning industry. Although HCFC-141b may have been used historically in vapor degreasers to clean metal parts, the use of HCFC-141b for this practice was banned in 1997. HCFC-225 ca/cb is acceptable in metal cleaning but because it is considered a relatively expensive solvent, it has not gained any significant market share. However, since HCFC-225 ca/cb is VOC exempt, this solvent is starting to be considered as an option for some metal cleaning end-users in California where strict VOC regulations are in place, limiting the use of more common metal cleaning solvents such as trichloroethylene (AGA Chemicals 2003a).

Precision Cleaning. Although small quantities of HCFC-141b are still being used for the manual cleaning of some precision parts, its presence in the market is dwindling as stockpile supplies diminish and alternatives are qualified. The Air Force is currently conducting a project to identify and qualify alternatives to HCFC-141b in cleaning aerospace systems components. The conversion to successfully qualified alternatives is expected in 2004 and when implemented will eliminate 27,000 pounds of HCFC-141b used in the Air Force annually (The Monitor 2003). In general, the aerospace and defense industries recently approved HCFC-225 ca/cb as a replacement for CFC-113 and HCFC-141b in the cleaning of liquid oxygen storage and delivery systems (AGA Chemicals Inc. 2003a, 2003c). Furthermore, small quantities of stockpiled HCFC-141b remain for use as a flushing agent to clean air conditioning and refrigeration systems. As with aerosol solvent cleaning, viable non-ODS alternatives have been identified for such applications and will gain a larger share of the market once HCFC-141b stockpiles are eliminated.

HCFC-225 ca/cb is also being used for degreasing of precision parts and it has been considered a replacement of CFC-113 for cleaning of plastic medical equipment (e.g., plastic catheter line cleaning) (Kitamura et al. 1999).

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<sup>14</sup> 'Other Cleaning' refers to applications, such as the maintenance of aircraft requiring manual hand wiping of large surfaces, that do not fit traditionally into the end-uses described in this report. Although hand wiping can be classified as a critical method for precision cleaning applications, with respect to the application above, the cleaning operation usually is performed on or near the flight line, rather than in a clean room, limiting the level of cleanliness because airborne contaminants may settle on the surface being cleaned (Schroll 2001).



Aerosol Solvent Cleaning. The aerosol solvent cleaning end-use is currently relying on stockpiles of HCFC-141b. Industry expert opinion suggests that this ODS is continuing to be used after the 2003 phaseout because it is relatively inexpensive with respect to alternatives, and not because technically feasible alternatives cannot be identified (Techspray 2004a; AGA Chemicals 2004; Micro Care 2004). Nonetheless, some end-users have converted. For example, a mass-transit system has successfully transitioned to an HCFC-141b alternative for the in-situ cleaning for maintenance and repair of applications such as turnstiles, automatic ticket machines, gears, and switches, even though such applications are essentially 100 percent emissive in nature (Techspray 2004a).

HCFC-225 ca/cb is one of the alternatives that exist for HCFC-141b in aerosol cleaning and currently holds a small portion of the aerosol solvent market. It is expected that the demand for HCFC-225 ca/cb as well as other available non-ODS alternatives will increase as HCFC-141b stockpiles run out and the pricing of these alternatives fall (Micro Care 2004; AGA Chemicals 2004; Techspray 2004a).

### 5.4.3 Summary of Continued Use and Overall Progress

Class I and Class II ODS based solvents that are still used as of 2004 in each solvent cleaning end-use are summarized in Table 5-4.

**Table 5-4. Summary of ODS Still Used as Solvents**

End-Use	Class I	
Electronics Cleaning	None	HCFC-225 ca/cb
Metal Cleaning	None	None
Precision Cleaning	CFC-113, Methyl Chloroform	HCFC-141b, HCFC-225 ca/cb
Aerosol Solvent Cleaning	None	HCFC-141b, HCFC-225 ca/cb
Other Cleaning <sup>a</sup>	CFC-113, Methyl Chloroform	N/A

N/A – Not applicable.

Overall, the replacement of Class I ODS used as solvents with alternatives has proceeded smoothly, with only a small fraction of Class I ODS use as solvents remaining. In addition, the usage of methyl chloroform under the EUEs has been less than the allowed allocation, indicating good progress. As the replacement of Class II ODS with alternatives is currently underway for HCFC-141b, and will begin for HCFC-225 ca/cb as 2015 nears, it remains to be seen when the elimination of Class II ODS used as solvents will ultimately take place. Currently, there is no clear “drop-in” replacement for HCFC-225 ca/cb and the work to identify and switch to viable zero ODP alternatives needs to continue over the next decade. Nonetheless, with the numerous solvent and technology replacements available today and the demonstrated success in transition away from Class I ODS, the solvent cleaning industry is well equipped to successfully handle the phaseout and complete the elimination of Class II ODS based solvents.

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## **Appendix A: NAICS Codes Associated with the Electronics, Metal, and Precision Solvent Cleaning End-Uses**

The North American Industry Classification System (NAICS) was adopted by the United States in 1997 for the purpose of classifying business establishments and facilitating the ability to compare and measure economic statistics. The North American Industry Classification System (NAICS) has replaced the U.S. Standard Industrial Classification (SIC) system. In a previous analysis, conducted in 1986 on the solvent industry, SIC codes associated with the solvent industry were identified and subsequently assigned consumption estimates (ICF Incorporated 1986).<sup>15</sup>

### **A.1 Methodology**

To identify businesses associated within the three primary solvent end-uses: electronics, metal, and precision cleaning for this report, the NAICS in conjunction with the SIC code solvent analysis were used. The U.S. Census Bureau provides correspondence tables between SIC and NAICS codes (see <<http://www.census.gov/epcd/www/naics.html>>). The following steps were taken to identify NAICS codes at the three digit and six digit code levels for each end-use.

- Each SIC code identified in the 1986 analysis was matched to its corresponding North American Industry Classification System (NAICS) code using the U.S. Census Bureau's website.
- NAICS codes were then categorized into metals, electronic, and precision cleaning sub-sectors based on industry descriptions.

### **A.2 Results**

Tables A-1 through A-3 display the resulting NAICS codes for the electronics, metal, and precision cleaning end-uses. The NAICS code titles provided in the tables were taken directly from the U.S. Census Bureau's website (U.S. Bureau of the Census 2003). In some instances, the symbol, (pt), appears after the code's title. This symbol indicates that the NAICS code was derived from more than one SIC code. For codes where the (pt) is not shown, the SIC code from which the NAICS code was derived falls entirely into the newly assigned NAICS code.

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<sup>15</sup> Appendix B discusses the methodology for developing 1986 methyl chloroform and CFC-113 consumption estimates for each NAICS code identified, based on data previously provided by SIC code.

**Table A-1. NAICS Codes Associated with the Electronics Cleaning Industry**

NAICS CODE	NAICS CODE TITLE
<b>NAICS Code 334</b>	<b>Computer and Electronic Product Manufacturing</b>
334210	Telephone Apparatus Manufacturing
334220	Radio and Television Broadcasting and Wireless Communications Equipment Manufacturing (pt)
334310	Audio and Video Equipment Manufacturing (pt)
334411	Electron Tube Manufacturing
334412	Bare Printed Circuit Board Manufacturing
334413	Semiconductor and Related Device Manufacturing
334414	Electronic Capacitor Manufacturing
334415	Electronic Resistor Manufacturing
334416	Electronic Coil, Transformer, and Other Inductor Manufacturing (pt)
334417	Electronic Connector Manufacturing
334418	Printed Circuit Assembly (Electronic Assembly) Manufacturing (pt)
334419	Other Electronic Component Manufacturing
<b>NAICS Code 335</b>	<b>Electrical Equipment, Appliance, and Component Manufacturing</b>
335121	Residential Electric Lighting Fixture Manufacturing (pt)
335122	Commercial, Industrial, and Institutional Electric Lighting Fixture Manufacturing
335129	Other Lighting Equipment Manufacturing (pt)
335311	Power, Distribution, and Specialty Transformer Manufacturing (pt)
335911	Storage Battery Manufacturing
335912	Primary Battery Manufacturing
335931	Current-Carrying Wiring Device Manufacturing
335932	Noncurrent-Carrying Wiring Device Manufacturing
<b>NAICS Code 336</b>	<b>Transportation Equipment Manufacturing</b>
336321	Vehicular Lighting Equipment Manufacturing
336322	Other Motor Vehicle Electrical and Electronic Equipment Manufacturing (pt)

**Table A-2. NAICS Codes Associated with the Metal Cleaning Industry**

NAICS CODE	NAICS CODE TITLE
<b>NAICS Code 322</b>	<b>Paper Manufacturing</b>
322225	Laminated Aluminum Foil Manufacturing for Flexible Packaging Uses
<b>NAICS Code 331</b>	<b>Primary Metal Manufacturing</b>
331221	Rolled Steel Shape Manufacturing (pt)
331314	Secondary Smelting and Alloying of Aluminum (pt)
331315	Aluminum Sheet, Plate, and Foil Manufacturing
331316	Aluminum Extruded Product Manufacturing
331319	Other Aluminum Rolling and Drawing (pt)
331421	Copper Rolling, Drawing, and Extruding
331422	Copper Wire (except Mechanical) Drawing
331423	Secondary Smelting, Refining, and Alloying of Copper (pt)
331491	Nonferrous Metal (except Copper and Aluminum) Rolling, Drawing, and Extruding (pt)
331492	Secondary Smelting, Refining, and Alloying of Nonferrous Metal (except Copper and Aluminum) (pt)
331511	Iron Foundries (pt)
331512	Steel Investment Foundries
331513	Steel Foundries (except Investment)



NAICS CODE	NAICS CODE TITLE
331528	Other Nonferrous Foundries (except Die-Casting)
<b>NAICS Code 332</b>	<b>Fabricated Metal Product Manufacturing</b>
332111	Iron and Steel Forging
332112	Nonferrous Forging
332114	Custom Roll Forming
332115	Crown and Closure Manufacturing
332116	Metal Stamping
332117	Powder Metallurgy Part Manufacturing
332211	Cutlery and Flatware (except Precious) Manufacturing (pt)
332212	Hand and Edge Tool Manufacturing (pt)
332213	Saw Blade and Handsaw Manufacturing
332214	Kitchen Utensil, Pot, and Pan Manufacturing
332311	Prefabricated Metal Building and Component Manufacturing
332312	Fabricated Structural Metal Manufacturing (pt)
332313	Plate Work Manufacturing
332321	Metal Window and Door Manufacturing (pt)
332322	Sheet Metal Work Manufacturing
332323	Ornamental and Architectural Metal Work Manufacturing (pt)
332410	Power Boiler and Heat Exchanger Manufacturing (pt)
332420	Metal Tank (Heavy Gauge) Manufacturing
332439	Other Metal Container Manufacturing (pt)
332510	Hardware Manufacturing (pt)
332611	Spring (Heavy Gauge) Manufacturing
332612	Spring (Light Gauge) Manufacturing
332618	Other Fabricated Wire Product Manufacturing (pt)
332710	Machine Shops
332721	Precision Turned Product Manufacturing
332722	Bolt, Nut, Screw, Rivet, and Washer Manufacturing (pt)
332811	Metal Heat Treating
332812	Metal Coating, Engraving (except Jewelry and Silverware), and Allied Services to Manufacturers
332813	Electroplating, Plating, Polishing, Anodizing, and Coloring (pt)
332912	Fluid Power Valve and Hose Fitting Manufacturing (pt)
332913	Plumbing Fixture Fitting and Trim Manufacturing
332919	Other Metal Valve and Pipe Fitting Manufacturing (pt)
332991	Ball and Roller Bearing Manufacturing
332992	Small Arms Ammunition Manufacturing
332993	Ammunition (except Small Arms) Manufacturing
332994	Small Arms Manufacturing (pt)
332995	Other Ordnance and Accessories Manufacturing
332996	Fabricated Pipe and Pipe Fitting Manufacturing
332998	Enameled Iron and Metal Sanitary Ware Manufacturing
332999	All Other Miscellaneous Fabricated Metal Product Manufacturing (pt)
<b>NAICS Code 333</b>	<b>Machinery Manufacturing</b>
333111	Farm Machinery and Equipment Manufacturing
333112	Lawn and Garden Tractor and Home Lawn and Garden Equipment Manufacturing

NAICS CODE	NAICS CODE TITLE
333120	Construction Machinery Manufacturing
333131	Mining Machinery and Equipment Manufacturing
333132	Oil and Gas Field Machinery and Equipment Manufacturing
333210	Sawmill and Woodworking Machinery Manufacturing
333220	Plastics and Rubber Industry Machinery Manufacturing
333291	Paper Industry Machinery Manufacturing
333295	Semiconductor Machinery Manufacturing
333298	All Other Industrial Machinery Manufacturing (pt)
333311	Automatic Vending Machine Manufacturing (pt)
333312	Commercial Laundry, Drycleaning, and Pressing Machine Manufacturing
333313	Office Machinery Manufacturing (pt)
333319	Other Commercial and Service Industry Machinery Manufacturing (pt)
333411	Air Purification Equipment Manufacturing
333412	Industrial and Commercial Fan and Blower Manufacturing
333414	Heating Equipment (except Warm Air Furnaces) Manufacturing (pt)
333415	Air-Conditioning and Warm Air Heating Equipment and Commercial and Industrial Refrigeration Equipment Manufacturing
333511	Industrial Mold Manufacturing
333512	Machine Tool (Metal Cutting Types) Manufacturing
333513	Machine Tool (Metal Forming Types) Manufacturing
333514	Special Die and Tool, Die Set, Jig, and Fixture Manufacturing
333515	Cutting Tool and Machine Tool Accessory Manufacturing
333516	Rolling Mill Machinery and Equipment Manufacturing
333518	Other Metalworking Machinery Manufacturing
333611	Turbine and Turbine Generator Set Unit Manufacturing
333612	Speed Changer, Industrial High-Speed Drive, and Gear Manufacturing
333613	Mechanical Power Transmission Equipment Manufacturing
333618	Other Engine Equipment Manufacturing (pt)
333911	Pump and Pumping Equipment Manufacturing (pt)
333912	Air and Gas Compressor Manufacturing
333913	Measuring and Dispensing Pump Manufacturing
333921	Elevator and Moving Stairway Manufacturing
333922	Conveyor and Conveying Equipment Manufacturing (pt)
333923	Overhead Traveling Crane, Hoist, and Monorail System Manufacturing (pt)
333924	Industrial Truck, Tractor, Trailer, and Stacker Machinery Manufacturing
333992	Welding and Soldering Equipment Manufacturing
333999	All Other Miscellaneous General Purpose Machinery Manufacturing (pt)
<b>NAICS Code 335</b>	<b>Electrical Equipment, Appliance, and Component Manufacturing</b>
335211	Electric Housewares and Household Fan Manufacturing (pt)
335312	Motor and Generator Manufacturing (pt)
335313	Switchgear and Switchboard Apparatus Manufacturing
335921	Fiber Optic Cable Manufacturing
335929	Other Communication and Energy Wire Manufacturing
335991	Carbon and Graphite Product Manufacturing
335999	All Other Miscellaneous Electrical Equipment and Component Manufacturing (pt)

NAICS CODE	NAICS CODE TITLE
<b>NAICS Code 336</b>	<b>Transportation Equipment Manufacturing</b>
336111	Automobile Manufacturing
336112	Light Truck and Utility Vehicle Manufacturing
336120	Heavy Duty Truck Manufacturing
336211	Motor Vehicle Body Manufacturing (pt)
336212	Truck Trailer Manufacturing
336311	Carburetor, Piston, Piston Ring, and Valve Manufacturing
336312	Gasoline Engine and Engine Parts Manufacturing
336322	Other Motor Vehicle Electrical and Electronic Equipment Manufacturing (pt)
336330	Motor Vehicle Steering and Suspension Components (except Spring) Manufacturing
336340	Motor Vehicle Brake System Manufacturing (pt)
336350	Motor Vehicle Transmission and Power Train Parts Manufacturing
336370	Motor Vehicle Metal Stamping
336391	Motor Vehicle Air-Conditioning Manufacturing
336399	All Other Motor Vehicle Parts Manufacturing (pt)
336510	Railroad Rolling Stock Manufacturing (pt)
336992	Military Armored Vehicle, Tank, and Tank Component Manufacturing (pt)
<b>NAICS Code 337</b>	<b>Furniture and Related Product Manufacturing</b>
337127	Institutional Furniture Manufacturing (pt)
337215	Showcase, Partition, Shelving, and Locker Manufacturing (pt)
337920	Blind and Shade Manufacturing
<b>NAICS Code 339</b>	<b>Miscellaneous Manufacturing</b>
339111	Laboratory Apparatus and Furniture Manufacturing (pt)
339912	Silverware and Hollowware Manufacturing (pt)
339914	Costume Jewelry and Novelty Manufacturing (pt)
339942	Lead Pencil and Art Good Manufacturing (pt)
339911	Jewelry (except Costume) Manufacturing (pt)
339912	Silverware and Hollowware Manufacturing (pt)
339913	Jewelers' Material and Lapidary Work Manufacturing
339992	Musical Instrument Manufacturing
339931	Doll and Stuffed Toy Manufacturing
339932	Game, Toy, and Children's Vehicle Manufacturing
339920	Sporting and Athletic Goods Manufacturing
339941	Pen and Mechanical Pencil Manufacturing
339942	Lead Pencil and Art Good Manufacturing (pt)
339943	Marking Device Manufacturing
339944	Carbon Paper and Inked Ribbon Manufacturing
339914	Costume Jewelry and Novelty Manufacturing
339994	Broom, Brush, and Mop Manufacturing (pt)
339950	Sign Manufacturing
339995	Burial Casket Manufacturing
339999	All Other Miscellaneous Manufacturing (pt)

**Table A-3. NAICS Codes Associated with the Precision Cleaning Industry**

NAICS CODE	NAICS CODE TITLE
<b>NAICS Code 333</b>	<b>Machinery Manufacturing</b>
333924	Industrial Truck, Tractor, Trailer, and Stacker Machinery Manufacturing (pt)
<b>NAICS Code 334</b>	<b>Computer and Electronic Product Manufacturing</b>
334511	Search, Detection, Navigation, Guidance, Aeronautical, and Nautical System and Instrument Manufacturing
334512	Automatic Environmental Control Manufacturing for Residential, Commercial, and Appliance Use
334513	Instruments and Related Products Manufacturing for Measuring, Displaying, and Controlling Industrial Process Variables
334514	Totalizing Fluid Meter and Counting Device Manufacturing (pt)
334515	Instrument Manufacturing for Measuring and Testing Electricity and Electrical Signals
334518	Watch, Clock, and Part Manufacturing
334519	Other Measuring and Controlling Device Manufacturing
<b>NAICS Code 336</b>	<b>Transportation Equipment Manufacturing</b>
336214	Travel Trailer and Camper Manufacturing (pt)
336411	Aircraft Manufacturing (pt)
336412	Aircraft Engine and Engine Parts Manufacturing (pt)
336413	Other Aircraft Parts and Auxiliary Equipment Manufacturing
336414	Guided Missile and Space Vehicle Manufacturing
336415	Guided Missile and Space Vehicle Propulsion Unit and Propulsion Unit Parts Manufacturing
336419	Other Guided Missile and Space Vehicle Parts and Auxiliary Equipment Manufacturing
336999	All Other Transportation Equipment Manufacturing
<b>NAICS Code 339</b>	<b>Miscellaneous Manufacturing</b>
339112	Surgical and Medical Instrument Manufacturing (pt)
<b>NAICS Code 541</b>	<b>Professional, Scientific, and Technical Services</b>
541710	Research and Development in the Physical, Engineering, and Life Sciences (pt)

## Appendix B: Methodology to Calculate ODS Usage and Stockpiling by the Solvent Cleaning Industry

Appendix B outlines the methodology used to calculate annual usage estimates (see Section B.1) and stockpiling estimates (see Section B.2) in various end-uses within the U.S. solvent industry. Usage and stockpiling were estimated for the following ODS in the following manner:

- Methyl chloroform. Annual usage of this solvent was calculated for electronics, metal, and precision cleaning end-uses between 1986 and 1995. Stockpiling of methyl chloroform was calculated for the solvent cleaning industry as a whole as of January 1, 1996.
- CFC-113. Annual usage of this solvent was calculated for electronics, metal, precision cleaning, and aerosol solvent cleaning end-uses between 1986 and 1995. Stockpiling of CFC-113 was calculated for the solvent cleaning industry as a whole as of January 1, 1996.
- Carbon Tetrachloride. Annual usage was calculated only for the solvent industry as a whole because of data limitations. Estimates were generated for 1986 to 1995. Stockpiling was not estimated for carbon tetrachloride.
- CFC-11. Annual usage was estimated for the only end-use where usage occurred, aerosol solvents cleaning. Estimates were generated for 1986 to 1995. Stockpiling of CFC-11 was calculated for the solvent cleaning industry as a whole as of January 1, 1996.
- HCFC-225ca/cb and HCFC-141b. Annual usage was estimated for the solvents industry as a whole and was calculated between 1994 and 2003. Stockpiling of HCFC-141b was calculated for the solvent cleaning industry as a whole as of January 1, 2003.

The remainder of the Appendix is organized by ODS. Sections B.1.1 through B.1.4 discuss the methodologies employed to determine usage of Class I ODS (i.e., methyl chloroform, CFC-113, carbon tetrachloride, and CFC-11, respectively). Sections B.1.5 and B.1.6 provide the methodologies used to determine usage of Class II ODS, HCFC-225 ca/cb and HCFC-141b, respectively. Section B.2 presents the methodologies used to estimate stockpiling of Class I and Class II ODS.

For the purpose of this analysis, usage is defined as the quantity of the solvent used by the U.S. solvent cleaning industry. In general, usage estimates were derived from *demand* estimates in the Chemical Marketing Reporter and *consumption* estimates in the ODS Tracking System (see definitions in Box A-1). Usage can be based on *consumption* and *demand* estimates because in years in which stockpiles are expected to be relatively constant, it can effectively be assumed that *demand* is equal to *consumption*, and both are equal to usage.

### Box B-1. Definition of Terms

For the purpose of this analysis, the following terminology is used:

Demand – is equal to purchases of Class I ODS sold to the solvent industry. A portion of the solvents that are purchased can be held for stockpile.

Consumption – is equal to production plus imports minus exports, as defined by the Montreal Protocol.

Usage – is equal to the quantity of solvent used by the industry.

Theoretically, consumers in the solvent industry hold a certain stockpile of ODS for production assurance. When new shipments arrive, the consumer uses the existing stockpile plus a portion of the new shipment and withholds from the shipment the amount of new material required to replace the stockpile. Therefore, what is *demand*ed or *consumed* is assumed equal to what is used.

Further to this assumption, in years in which stockpiles are not expected to be constant (e.g., years preceding ODS phaseouts), it was assumed that *demand* will reflect an increase in stockpiling, while

*consumption* will remain in line with usage. Therefore, it was assumed that in the few years preceding the phaseouts, although demand is not equal to consumption, *consumption* will continue to be equal to usage.

Thus, this analysis assumes that *consumption* is always equal to usage in years before a phaseout. In years following a phaseout, *consumption*, as authorized by essential use exemptions, can only be considered equal to a portion of usage while the remaining portion is equal to the quantity extracted from stockpiles. Section B.2 elaborates on the assumptions used to calculate stockpiling estimates.

## **B.1 Usage Methodology**

Section B.1 outlines the methodology used to calculate annual usage estimates for Class I and Class II ODS used in the solvent cleaning industry.

### ***B.1.1 Methyl Chloroform***

Annual methyl chloroform usage was calculated for all solvent cleaning end-uses except for aerosol solvent cleaning. Methyl chloroform was not effective as an aerosol solvent cleaner, and therefore has not been used to any degree in this application area.

*In Year 1986:*

- All End-Uses – Because it was assumed that *demand* is equal to usage, total methyl chloroform demand in 1986 was taken from the Chemical Marketing Reporter (CMR) (CMR 1986a). While this publication did not specify the percent of demand associated with the solvent industry, it did present a breakout by end use, including electronics, cold cleaning, and vapor degreasing.
  - Electronics, Metal, and Precision Cleaning – The electronics, cold cleaning, and vapor degreasing end-uses were used as proxies for methyl chloroform solvent usage in electronics, metal, and precision cleaning, which was calculated as 69 percent of total reported demand for methyl chloroform. It was further assumed that cold cleaning and vapor degreasing end-uses represent metal and precision cleaning end-uses, and were calculated as 91 percent of the usage by the solvent industry with the remaining nine percent attributed to electronics cleaning.<sup>16</sup> The 91 percent was further broken down into 60 percent (metal) and 31 percent (precision) (U.S. EPA 1992).

*In Years 1987-1988:*

- All End-Uses – For 1987 and 1988, methyl chloroform demand within each solvent end-use (i.e., electronics, metal, and precision) was linearly interpolated using the demand calculated for 1986 from CMR data, and for 1989 from ODS Tracking System data (CMR 1989a, U.S. EPA 2003c).

*In Years 1989-1994:*

- All End-Uses – Methyl chloroform usage, for the period 1989 to 1995, was derived from EPA's ODS Tracking System data (years 1990 and 1991 were linearly interpolated due to lack of available data). Total methyl chloroform consumption was calculated by adding imports and subtracting exports from total production of methyl chloroform (U.S. EPA 2003c). Consumption estimates were assumed to equal usage for these years preceding the phaseout.

Since the EPA ODS Tracking System data did not provide the percent of methyl chloroform produced for any of the end-uses, the ratio of the demand for each end-use to total demand for methyl chloroform as cited in the CMR for each year was applied (CMR 1989a, CMR 1992, CMR

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<sup>16</sup> Other sources support this 90/10 percent split between these end-uses, including studies conducted by HSIA (1994) and U.S. EPA (1992).

1995). In years that the CMR did not provide such information, a percentage was linearly interpolated. However, since total demand for methyl chloroform in the CMR includes demand for use as a chemical intermediate, whereas total production in the ODS Tracking System does not, it was necessary to adjust the end-use breakout percentages given by CMR to reflect the absence of intermediate applications.

- Electronics, Metal, and Precision Cleaning - After arriving at an estimate for total methyl chloroform demand by the solvent industry for electronics, metal, and precision cleaning applications, demand was broken down into metal (60 percent), precision (31 percent), and electronics (9 percent) cleaning (U.S. EPA 1992).

*In Year 1995:*

- All End-Uses – Methyl chloroform usage in 1995 was calculated using the same methodology as in years 1989-1994. However, the stockpile analysis (see Section B.2) yielded a negative amount of methyl chloroform stockpiled in 1995, indicating that some methyl chloroform was used in that year from stockpiles. Thus, this estimate of usage from stockpiles in 1995 was added to the consumption estimate derived from the EPA ODS Tracking System to reflect usage for that year (U.S. EPA 2003c).

### **B.1.2 CFC-113**

Annual CFC-113 usage was calculated for all solvent cleaning end-uses.

*In Year 1986:*

- All End-Uses – Total CFC-113 demand in 1986 was taken from the Chemical Marketing Reporter (CMR) (CMR 1986b) and was assumed equal to usage,
  - Electronics, Metal, and Precision Cleaning – Expert opinion indicates that approximately 93 percent of CFC-113 was manufactured for electronics, metal, and precision solvent cleaning end-uses. End-use break-out into metal (11 percent), precision (17 percent), and electronics (72 percent) cleaning was subsequently employed to arrive at CFC-113 usage estimates by solvent end-use (U.S. EPA 1992).
  - Aerosol Solvents Cleaning – Industry expert opinion indicates that approximately 2 percent of CFC-113 was manufactured for aerosol solvent cleaning.

*In Years 1987-1988:*

- All End-Uses – For 1987 and 1988, CFC-113 demand within each solvent end-use was linearly interpolated using the demand calculated for 1986 from CMR data and 1989 from ODS Tracking System data (CMR 1989b, U.S. EPA 2003c).

*In Years 1989-1995:*

All End-Uses – CFC-113 usage, for the period 1989 to 1995, was derived from EPA's ODS Tracking System. Total CFC-113 consumption was calculated by adding imports and subtracting exports from total production of CFC-113 (U.S. EPA 2003c). Consumption estimates were assumed to equal usage for these years preceding the phaseout.

Since the EPA ODS Tracking System data did not provide the percent of CFC-113 produced for electronics, metal, and precision solvent cleaning and aerosol solvent cleaning end-uses, the 93 percent consumption estimate applied in 1986 was also used for the 1989-1995 timeframe.

- Electronics, Metal, and Precision Cleaning – End-use break-out into metal (11 percent), precision (17 percent), and electronics (72 percent) cleaning was subsequently employed to arrive at CFC-113 usage estimates by solvent end-use for each year (U.S. EPA 1992).
- Aerosol Solvents Cleaning – To arrive at a usage estimate, industry expert opinion, indicating that 2 percent of total demand for CFC-113 was for aerosol solvents cleaning, was applied.

*In Years 1996-2003:*

It is estimated that usage of CFC-113 continued at a level equal to or less than usage in 1995, or approximately 3 million pounds, annually.

### **B.1.3 Carbon Tetrachloride**

Since information on the break-out of carbon tetrachloride solvent usage by end-use was not available, usage estimates were only calculated for the solvent industry as a whole and not broken down into end-uses.

*In Year 1986:*

Because it was assumed that *demand* is equal to usage, demand for carbon tetrachloride in solvent application for 1986 was derived from the Chemical Marketing Reporter's (CMR) estimate for total demand for carbon tetrachloride in all applications. The percent breakout of end-uses from the CMR included an "Other, mainly chemical intermediate" category, and carbon tetrachloride was assumed to be 5 percent of this category (CMR 1986c).

*In Years 1987-1988:*

For the solvent cleaning industry, carbon tetrachloride demand from 1987 to 1988 was linearly interpolated using the demand calculated from 1986 CMR data (CMR 1986c) and usage calculated from EPA's ODS Tracking System data for 1989 (U.S. EPA 2003c).

*In Years 1989-1995:*

Carbon tetrachloride usage between 1989 and 1995 was derived from the EPA's ODS Tracking System (years 1990 and 1991 were linearly derived due to lack of available data). Total carbon tetrachloride consumption was calculated by adding imports and subtracting exports from total production of carbon tetrachloride (U.S. EPA 2003c). Consumption estimates were assumed to equal usage for these years preceding the phaseout.

However, since total demand for carbon tetrachloride in the CMR includes demand for use as a chemical intermediate, whereas total production in the ODS Tracking System does not, it was necessary to adjust the solvent percentage taken from the CMR to reflect the absence of intermediate applications. Chemical intermediates were assumed to be half of the "other, mainly chemical intermediates" category. After the adjustment, as for years 1986-88, carbon tetrachloride was assumed to be 5 percent of this category (CMR 1989c).

*In Years 1996-2003:*

Because there were no essential use exemptions for carbon tetrachloride as a solvent cleaner and because historical carbon tetrachloride usage was extremely minimal as a solvent cleaning agent, carbon tetrachloride usage from 1996 to 2003 was assumed to be zero.



#### **B.1.4 CFC-11**

Annual CFC-11 usage was calculated only for the aerosol solvent cleaning end-use.

*In Year 1986:*

Total CFC-11 demand for 1986 was taken from the Chemical Marketing Reporter (CMR) and was assumed equal to usage (CMR 1986b). Expert opinion indicates that approximately 0.5 percent of CFC-113 was manufactured for aerosol solvent cleaning.

*In Years 1987-1988:*

CFC-11 demand from 1987 to 1988 for the aerosol solvent cleaning end-use was linearly interpolated using the demand calculated for 1986 from CMR data and 1989 from ODS Tracking System data (CMR 1989b, U.S. EPA 2003c).

*In Years 1989-1995:*

CFC-11 usage between 1989 and 1995 was derived from EPA's ODS Tracking System. Total CFC-11 consumption was calculated by adding imports and subtracting exports from total production of CFC-11 (U.S. EPA 2003c). Consumption estimates were assumed to equal usage for these years preceding the phaseout.

Since the EPA ODS Tracking System data did not provide the percent of CFC-11 produced for aerosol solvent cleaning end-uses, expert opinion was applied as in 1986.

*In Years 1996-2003:*

Because there were no essential use exemptions for CFC-11 and because historical CFC-11 usage was extremely minimal as a solvent cleaning agent, CFC-11 usage from 1996 to 2003 was assumed to be negligible.

#### **B.1.5 HCFC-225ca/cb**

Annual HCFC-225 ca/cb usage was calculated at the aggregate level for the solvent cleaning industry.

*In Years 1992-2003:*

For estimating HCFC-225ca/cb use by the solvent cleaning industry, usage data were first derived from EPA's ODS Tracking System. A modeling approach using EPA's Vintaging Model was then applied to EPA's ODS Tracking System data. Assuming that the solvent cleaning industry is the sole consumer of HCFC-225ca/cb, the Vintaging Model generated usage of HCFC-225ca/cb through the incorporation of factors that reflect market growth and historical market transition from ODS to alternatives. Because the Vintaging Model's approach phases in a substitute, steadily increases usage estimates at the market growth rate, and decreases usage estimates when the substitute is phased out, the usage estimates do not exactly match the ODS Tracking System data and therefore maintain confidentiality of certain data. The estimates do, however, agree with the ODS Tracking System data in principle.

#### **B.1.6 HCFC-141b**

Annual HCFC-141b usage was calculated at the aggregate level for the solvent cleaning industry.

*In Years 1992-1997:*

Since it was assumed that *consumption is equal to usage*, HCFC-141b usage by the solvent cleaning industry from 1992 to 1997 was derived from EPA's ODS Tracking System. Total HCFC-141b

consumption was calculated by adding imports and subtracting exports from total production of HCFC-141b (U.S. EPA 2003c). Consumption estimates were assumed to equal usage for these years preceding the phaseout.

Since the EPA ODS Tracking System data did not provide the percent of HCFC-141b produced for solvent cleaning, industry expert opinion was applied. Industry information indicated that prior to the 1997 ban on vapor degreasing, approximately 25 percent of total HCFC-141b usage was used by the solvent cleaning industry (HCFC Aerosol Coalition 2000). This percentage was applied to raw usage data to arrive at aggregated annual HCFC-141b usage estimates for use as solvent in 1992 to 1997.

*In Years 1998-2002:*

HCFC-141b usage was also derived from EPA's ODS Tracking System for years 1998 to 2002. Total HCFC-141b consumption was calculated by adding imports and subtracting exports from total production of HCFC-141b (U.S. EPA 2003c). Consumption estimates were assumed to equal usage for these years preceding the phaseout.

Since the EPA ODS Tracking System data did not provide the percent of HCFC-141b produced for solvent cleaning, industry expert opinion was applied. Industry expert opinion indicates that after the 1997 ban on vapor degreasing, the percent of HCFC-141b usage attributed to solvent cleaning decreased to approximately 9 percent of total HCFC-141b usage (U.S. EPA 2003c; Micro Care 2003). This percentage was applied to raw usage data to arrive at aggregated annual HCFC-141b usage estimates for use as solvent in 1998 to 2003.

*In Year 2003:*

As of the phaseout of HCFC-141b, which occurred on January 1, 2003, the 2003 usage estimate was a certain percentage of stockpiled quantities for the solvent industry. The percentage and resulting estimates were all derived through conversations with various industry experts (AGA Chemicals 2004; Micro Care 2004; Techspray 2004; Honeywell 2004).

## **B.2 Stockpiling Methodology**

Section B.2 outlines the methodology used to estimate stockpiles of Class I and Class II ODS, as of their respective phaseout dates, which were held by the solvent cleaning industry.

*Methyl Chloroform, CFC-113, and CFC-11 as of January 1, 1996:*

By comparing Class I ODS *consumption* and *demand* in years directly leading up to the 1996 phaseout, the extent to which stockpiling occurred was evaluated. *Consumption* estimates were taken from EPA's ODS Tracking System and *demand* estimates were taken from the Chemical Marketing Reporter (CMR). Because the ODS Tracking System does not include data before 1989, the comparison begins in that year.

Stockpiles were estimated using the following methodology:

- 1) The average difference between the CMR demand estimates and the ODS Tracking system estimates over the period 1989-1992 was calculated. For methyl chloroform, the average difference over the period 1989-1993 was calculated because it was assumed that, given the shorter shelf life of methyl chloroform, users would not begin stockpiling methyl chloroform until 1994.
- 2) The accumulation of stockpiles was estimated by subtracting the average difference calculated in Step 1 from the difference between the CMR demand estimates and the ODS Tracking System consumption estimates during the years 1993-1995 for CFC-113 and CFC-11, and during the years 1994-1995 for methyl chloroform.

- 3) Total stockpile in 1995 was calculated by summing the totals calculated in Step 2 for each year over the period 1993-1995 for CFC-113 and CFC-11, and 1994-1995 for methyl chloroform. This analysis yielded a negative estimate for stockpiling of methyl chloroform in 1995, indicating that usage of methyl chloroform from stockpiles occurred in that year. Thus, that usage from stockpiles was added to the total usage estimate for methyl chloroform in 1995, as detailed in Section B.1.1 and the stockpile estimate for 1996 was adjusted by subtracting out the estimated usage from stockpiles.

It is also important to note that, of the stockpile quantities estimated, a portion of the material could have potentially been used between 1993 and 1995 because of rising Class I ODS prices.

*HCFC-141b as of January 1, 2003:*

Because the phaseout of HCFC-141b occurred recently, the methodology used to estimate the quantity of HCFC-141b stockpiled as of the 2003 phaseout date involved data collection from correspondences with several industry experts (AGA Chemicals 2004; Micro Care 2004; Techspray 2004; Honeywell 2004).

## Appendix C: Peer Review Comments on U.S. Solvent Cleaning Industry Report

In the preparation of this report, outside experts were asked to review and comment specifically on the technical information contained in the report, to ensure that information was both current and accurate. Mr. Joe Felty of Raytheon Systems Company and Dr. Kenneth Dishart, an independent consultant in the cleaning agent formulation/process development industry, reviewed the report. Based on their input, edits and corrections have been incorporated. Appendix C presents a brief synopsis of the more substantive reviewer comments and the responses and/or revisions that were consequently made. Minor edits and changes were also incorporated directly into the report per the reviewers' comments, but are only summarized below.

- **General**

*Comments from Kenneth Dishart:*

Overall, I find the report factual and quite consistent with my knowledge of the solvent cleaning industry, both before and during the transition away from ODS and of the alternative solvents and/or process options that replaced them.

*Comments from Joe Felty:*

The report will make a nice reference document. The report is very thorough and provides history as well as the latest incorporated solutions for many former ODS applications.

***Response:***

No changes made.

- **Question 1: Are the usage and stockpile estimates reasonable for Class I ODS and Class II ODS by solvent cleaning end-use?**

*Comments from Kenneth Dishart:*

The total U.S. cleaning usage estimates for methyl chloroform and CFC-113, products which I am most familiar with, appear reasonable. The 1986 electronics, precision and metal cleaning breakdown percents (Figures 2-1 & 2-2) fit reality at the time. Freon® TMS (CFC-113 methanol azeotrope) dominated electronics cleaning, while methyl chloroform dominated metal cleaning. Dow's Prelete® was never able to make much headway in the electronics segment. The HCFC-225ca/cb and HCFC-141b estimates are also reasonable considering the time of market availability and use interest. Consultation with an industry colleague confirmed the above opinions. Carbon Tetrachloride and CFC-11 volumes were small and your values seem reasonable. I cannot comment on stockpile usage numbers. These are, of course, best obtained from those with the stockpiles.

*Comments from Joe Felty:*

[The following comments are based on a telephone conversation with Mr. Felty.] While Mr. Felty noted he has limited visibility with regard to these estimates, he stated that to his knowledge, these estimates seem reasonable. He noted, however, that the usage estimate of 11 million pounds of methyl chloroform in 1995 versus the 52 million pounds stockpiled as of 1996 seemed quite a jump especially considering the short shelf life of methyl chloroform.

***Response:***

To clarify that the stockpile estimates were not calculated based on information reported by stockpile holders, the following language was inserted on page 12, paragraph 2: "Because of data sensitivity, stockpile estimates are not based on information reported by stockpile holders, but rather were developed by comparison of data from the *Chemical Marketing Reporter* (various issues) and U.S. EPA's ODS Tracking System."

In addition, the estimate for stockpiled methyl chloroform in 1996 and usage of methyl chloroform in 1995 were re-evaluated and the methodology (see Appendix B) subsequently revised using the assumption that stockpiling of methyl chloroform started in 1994 rather than 1993, which is considered a more realistic start given methyl chloroform's short shelf life. As a result of this review, it was determined that an additional 8.6 million pounds of methyl chloroform was used from stockpiles in 1995, bringing total usage of methyl chloroform in 1995 to 20.4 million pounds. It was also determined that approximately 47.7 million pounds of methyl chloroform was stockpiled as of 1996, which is only slightly more than twice the usage of methyl chloroform in 1995, and thus better accounts for the short shelf life of this substance.

Mr. Felty was contacted to elicit his comments on these revised figures. Mr. Felty felt that the revised methodology was reasonable and that the resulting new estimates seemed to fit better with his understanding of events that had happened in preparation for the phaseout, especially considering the short shelf life of methyl chloroform. He noted that methyl chloroform was typically stored in drums with a liner material which is intended to prevent the solvent from contacting the metal of the drum. As end-users assessed the amount of methyl chloroform they felt was necessary to stockpile in preparation for the future ban, Mr. Felty indicated that end-users probably drew from older stockpiled drums that were more susceptible to deterioration, which is likely to account for additional use from stockpiles in 1995.

- **Question 2: Is the assessment of alternatives and trends associated with the adoption of these alternatives consistent with your understanding? Do you agree with our transition patterns away from ODS to either an alternative technology or solvent as discussed in Section 4.4?**

*Comments from Kenneth Dishart:*

Yes, the sections dealing with the alternative products and events during the ODS solvent phasedown period are consistent with my understanding. In the early stages much effort went into the retrofit of old and design of new vapor degreasers to reduce emissions and usage. Also interim products were offered with lower ODS content. Examples were DuPont Freon® SMT and MCA which were CFC-113 azeotropes with about 20% trans content each. This was the first use of trans which later was also blended with and enhanced the solvency of HFC-4310. Also in the early phasedown period HCFCs 141b and 123, as is, and in blends were offered as alternatives for vapor degreasing. These low boiling HCFCs were actually the alternatives for CFC-11 primarily for foam blowing, but necessity dictated the solvent degreasing use. Containing these low boiling liquids in a vapor degreaser created the challenge that resulted in the low emission equipment designs in use today. Not till late in the transition period were the HCFC-225ca/cb, HFC-4310 and HFE alternatives with proper boiling ranges available. By this time conversions had been made to aqueous, semi-aqueous, no-clean and the other options as spelled out in your report. In 4.4 the observed substitution trends appear valid and the breakdown profiles in Figures 4-1 and 4-2 appear to be a good approximation.

*Comments from Joe Felty:*

[The following comments are based on a telephone conversation with Mr. Felty.] Mr. Felty stated that he agreed with the assessment of the alternatives and trends associated with the adoption of alternatives discussed in the report. He mentioned that he was surprised to see trans-1,2-Dichloroethylene considered an acceptable alternative because of worker safety concerns associated with it.

The pie charts in Section 4.4 also pass the "sensible test." For electronics cleaning, he agreed with the percent breakout, noting that those who can't employ no-clean technology rely on solvents or aqueous cleaning, and semi-aqueous cleaning is predominately for unique or niche cleaning applications. He noted that the common solvents used in metal cleaning are not only trichloroethylene but the other chlorinated solvents, methylene chloride and perchloroethylene as well because these solvents are stable and able to clean heavy machining oils. As for precision cleaning, Mr. Felty agreed that an estimated 80 percent of the industry previously using ODS solvents converted to alternative solvents. Mr. Felty also emphasized the need to state throughout the report that aerosol solvent cleaning processes are 100 percent emissive leaving no opportunity for re-use.

**Response:**

Inserted the following language regarding the emissive nature of aerosol solvent cleaning applications:

- In Box 1-1, under the heading Aerosol Solvent Cleaning: “This process is essentially 100% emissive in nature with essentially no reuse possible.”
- In Section 3.3: “While the large majority of HCFC-141b usage in the solvents industry is currently attributed to the aerosol solvent cleaning end-use, which is essentially 100% emissive in nature with little or no reuse potential.”

Inserted the following language about the worker safety issues relating to trans in Section 4.2.3: “Some suggest that worker health and safety may be a concern; trans has an OSHA PEL of 200 ppm.”

- **Question 3: Do you agree with the conclusions about the current use of ODS in the solvent cleaning industry?**

*Comments from Kenneth Dishart:*

I have no comment on this and assume the information was obtained from those with EUEs and known to still have ODS stockpiles.

*Comments from Joe Felty:*

[The following comments are based on a telephone conversation with Mr. Felty.] Mr. Felty has no concerns with regard to the conclusion about the current use of ODS in the solvent cleaning industry.

***Response:***

No changes made.

- **Significant Digits**

*Comments from Kenneth Dishart:*

It is suggested that a statement be included, possibly a footnote, about the ODS estimate values reported and significant figures. At best these estimates are only valid to two and at most three significant figures. Much of the CFC-113 and its blended products were sold through distributors making it difficult to track to what industries and end uses it went to. The same is true for the other ODS products as well.

***Response:***

Changed all ODS estimate values to three significant digits to reflect the fact that estimates are likely only valid to three significant digits.

- **NAICS Codes**

*Comments from Kenneth Dishart:*

The breakdown of the total usages to the numerous NAICS industry codes make the numbers further suspect. It is suggested that this breakdown data appear in Appendix A or a separate appendix. This level of detail will be of interest, in my opinion, to very few readers.

***Response:***

To clarify that the NAICS codes are used only to suggest possible business categories that may use solvents in different end-uses, the following language was inserted: “For each of the solvent end-uses identified, the North American Industry Classification System (NAICS) was used to suggest businesses that might be classified within each end-use.”

- **Product Information**

*Comments from Kenneth Dishart:*

Table 4-2, page 23: Changes were made to give balance compared to Table 4-3. More accurate HFC product information included and more named products (also included in text below).

[In the table below, Dr. Dishart inserted the underlined text and deleted the text in strike-out.]

Acceptable HFC	Common Available Product Line(s)	Advantages	Disadvantages
HFC-4310mee (Pure form solvent offered as Vertrel® XF)	Vertrel® Specialty Solvents – Broad product line from DuPont and Micro Care (Blendeds of XF with trans, alcohols, etc. HFC-4310mee, and HFC-365)	<ul style="list-style-type: none"> <li>• Zero ODP</li> <li>• Acceptable for use in electronics, metal, precision, and aerosol solvent cleaning</li> <li>• Favorable for use with high value applications (Arthur D. Little 2002)</li> <li>• Usually blended as azeotropes with other compounds to increase solvency as needed and lower cost</li> <li>• <del>Cost can be lowered when formulated into azeotropes</del></li> </ul>	<ul style="list-style-type: none"> <li>• A mild solvent with limited solubility when used alone</li> <li>• Expensive base solvent (approximately \$18.00 per pound) (Mouser 2003)<sup>1</sup></li> <li>• GWP = 1,300<sup>2</sup></li> </ul>
HFC-365mfc	Offered by Solvay Fluorides, LLC  Offered by DuPont /Micro Care: Vertrel® C Series (Blendeds with trans, HFC-4310mee, and other solvents HFC-365)	<ul style="list-style-type: none"> <li>• Zero ODP</li> <li>• Acceptable for use in electronics, metal, precision, and aerosol solvent cleaning</li> <li>• Used to form non-flammable azeotropic blends when formulated with HFC-4310mee</li> <li>• Usually blended with other compounds to increase solvency as needed</li> <li>• <del>Inexpensive-Lower Cost</del></li> </ul>	<ul style="list-style-type: none"> <li>• Flammable if used alone</li> <li>• A mild solvent with limited solubility when used alone</li> <li>• GWP = 890<sup>3</sup></li> </ul>

[Table 4-5] 4.2.4, page 28: Added “Lenium®” an nPB product line of Petroferm, Inc. Also added a major disadvantage of nPB products – needs stabilization and monitoring just like methyl chloroform. You may want to list the suppliers:

Solvon® FB Solvents – Poly Systems USA, Inc  
 Abzol® Cleaners – Albemarle Corp.  
 Ensolv® - Enviro Tech International, Inc  
 Lenium® - Petroferm , Inc

**Response:**

In Table 4-2, on page 23, Dr. Dishart’s edits were accepted as shown above.

In Table 4-5, on page, 29, inserted the following underlined text:

Common Available nPB Product Lines	Advantages	Disadvantages
<ul style="list-style-type: none"> <li>• <u>Solvon® FB Solvents from Poly Systems USA</u></li> <li>• <u>ABZOL® Cleaners from Albemarle Corp.</u></li> <li>• <u>Ensolv® from Enviro Tech International</u></li> <li>• <u>Lenium® from Petroferm</u></li> </ul>	<ul style="list-style-type: none"> <li>• Excellent Solvency, comparable to the cleaning power of chlorinated solvents</li> <li>• Effective solvent for electronics, metal, precision, and aerosol solvent cleaning</li> <li>• Compatible with many materials including metals and plastics</li> <li>• Relatively affordable (approximately \$4.00 per lb) (Mouser 2003)</li> <li>• Ability to be recycled</li> </ul>	<ul style="list-style-type: none"> <li>• Final Ruling on SNAP approval still pending</li> <li>• Health and reproductive risks and toxicity concerns related to workplace exposure</li> <li>• ODP (although it is low when used at latitudes of the Continental U.S.)</li> <li>• <u>Like methyl chloroform, must be highly stabilized and monitored in use</u></li> </ul>

- **GWP of PFCs**

*Comments from Kenneth Dishart:*

[Dr. Dishart inserted the following underlined text:] “PFCs (e.g., C<sub>5</sub>F<sub>12</sub>, C<sub>6</sub>F<sub>14</sub>, C<sub>7</sub>F<sub>16</sub>, and C<sub>8</sub>F<sub>18</sub>) and PFPEs, because of their very long atmospheric life and high GWP, have been severely restricted by the SNAP Program to certain specialized uses for high-performance, precision-engineered applications (e.g., gyroscopes, electro-mechanical assemblies, direct access storage devices).”

*Comments from Joe Felty:*

Need to state why SNAP has severely restricted their [PFCs and PFPEs] use. Is it because of their Global Warming Potential values? Would be nice to include a table here listing their GWP values similar to what was done for other solvents in the report.

**Response:**

Inserted the following text on page 25, paragraph 1: “PFCs (e.g., C<sub>5</sub>F<sub>12</sub>, C<sub>6</sub>F<sub>14</sub>, C<sub>7</sub>F<sub>16</sub>, and C<sub>8</sub>F<sub>18</sub>) and PFPEs have been severely restricted by the SNAP Program to certain specialized uses for high-performance, precision-engineered applications (e.g., gyroscopes, electro-mechanical assemblies, direct access storage devices) because of these substances’ long atmospheric lifetime and high GWPs. The GWP for PFCs used in solvent cleaning are 8,900 or greater over a 100-year horizon, compared to 1,500 for the solvent with the next highest GWP and a GWP of 1 for carbon dioxide (IPCC 2001). The atmospheric lifetimes of PFCs used in solvent cleaning are 3,200 years or longer, two orders of magnitude longer than for other solvents.”

- **Editorial and Minor Factual Corrections**

In addition to the comments provided above, Dr. Dishart and Mr. Felty also provided several editorial/grammatical comments, as well as some minor factual corrections. The types of corrections provided by each commenter are briefly listed below, and ICF incorporated these comments where appropriate. In response to comments regarding the discussion of products, ICF ensured that the language was revised to be objective. This report is to serve as an objective assessment of the solvent industry; EPA does not endorse products or manufacturers. Any mention of a product does not constitute endorsement or rejection of the product.

*Comments from Kenneth Dishart:*

- Minor factual correction of isomer classification and terms used to describe chemical properties of HCFC-225 ca/cb.
- Additional details relating to the vapor degreaser process.
- Clarification of the current sales status of HCFC-123.
- Clarification of the price ratio between HCFC-141b and pure HFC or HFE, as compared to HFC or HFE blends.
- Toning down of language that may be perceived as biased; for example, Dr. Dishart felt that by claiming that HFEs “can replace HFCs in many applications,” ICF was making a decision that should take place in the competitive marketplace rather than in this report.



- Editorial/grammatical/typographical changes.

*Comments from Joe Felty:*

- Minor factual correction on substrates cleaned during defluxing, and the properties of types of fluxes.
- Minor factual correction regarding the chemical properties of TCE (i.e., TCE is a relatively unstable material).
- Toning down of language to allow for exceptions to a rule, for example, changing “flux removal *is necessary*” to “flux removal *may be needed* to ensure high reliability of the electronic assembly.”
- Toning down of language that may be perceived as biased; for example, Mr. Felty felt that the statement that HFC-4310mee “is considered ideal for use in vapor degreasing equipment” could be construed by readers that ICF/EPA is endorsing this substance as the ideal degreasing solvent.
- Editorial/grammatical/typographical changes.