As originally published in the IPC proceedings.

An Alternative Solvent with Low Global Warming Potential

R. Basu and R. Hulse
Honeywell International, Inc
Buffalo Research Laboratory
Buffalo, NY 14210

Abstract

In the past 20 yrs the solvent industry has gone through a great deal of change. In the early 1990s, CFC-113 and 1,1,1-trichloroethane were the workhorses of the industry. The Montreal Protocol to phase-out substances that deplete the Earth's protective Ozone Layer was implemented in the mid 1990s to reduce chemicals with ozone depletion potential. After phase-out of the CFC solvents, the solvent industry fragmented to a variety of cleaning solutions. The electronics industry was a large user of CFC solvents and many of these applications changed to aqueous based cleaners. Some of the industries moved to chlorinated and brominated solvents such as trichloroethylene and n-propyl bromide. Other industries changed to no-clean fluxes. But those alternatives are now facing various problems: e.g. aqueous based cleaners use a lot of energy, require long drying times, use equipment that requires frequent maintenance, and require a large footprint; no-clean fluxes leave flux residues; and trichloroethylene and n-propyl bromide have toxicity issues. In response to these serious issues newer solvents and blends are being introduced in the marketplace.

In this pursuit the company developed a new low global warming potential fluorinated solvent for precision cleaning. This solvent has a mosaic of properties that make it a good solution in the solvent domain. It is non-flammable, has low toxicity, environmentally friendly, low surface tension, rapid drying, excellent solvency and a number of other favorable properties. In this paper we will review the properties and performance of the new solvent.

Introduction

The hunt for a new solvent to replace chlorofluorocarbons (CFCs) started in 1974 when Professor Sherry Rowland and Mario Molina, who was a post-doctoral student in Professor Sherry Rowland's lab at UC Irvine, published[1] their work on the depletion of earth's protective stratospheric ozone depletion by CFCs and various halogenated compounds. Their findings were later confirmed by scientists around the world, especially the British Antarctic Survey in 1986. The British Antarctic Survey team discovered an Ozone hole in the stratosphere over Antarctica, which ultimately led to the Montreal Protocol[2] being ratified by UNEP (United Nations Environmental Program) in 1987 that phased-out CFCs around the world. They received the Nobel Prize for Chemistry in 1995 for their discovery.

This discovery of stratospheric ozone depletion shocked the world and brought an end to CFCs for use as cleaning solvents, as working fluids in refrigeration and air conditioning, as foam expansion agents, and in various other applications. CFC-113 (1,1,2-trichloro-1,2,2-trifluoro-ethane) and 1,1,1-trichloroethane were previously used extensively in industrial cleaning. The printed circuit board industry primarily used CFC-113 in cleaning solder fluxes and pastes after soldering and set the standards of cleaning for the boards. These solvents also found applications in metal degreasing, precision cleaning of aerospace components, cleaning of medical devices and in many other cleaning applications because of their high solvency for common soils, low toxicity, non-flammability and many other desirable properties. Since the phase-out of these solvents in 1996, the solvent market has become extremely fragmented with industrial customers using many different solvents for each specific application. No one solvent has been found that can be used effectively for many applications in the same way as CFC-113 and 1,1,1-trichloroethane. In this paper we will discuss a new cleaning solvent and some of the successes it had in cleaning. The chemical name of this new solvent is *trans-1-chloro-3,3,3-trifluoro-1-propene*. Using the numbering system of halogenated compounds[3] it can also be referred to as 1233zd(E), E in parenthesis indicates it is the trans configuration of the molecule. It has been found to be as good as CFC-113 in dissolving and cleaning most common soils but with superior environmental properties.

We will describe the properties and performance of this solvent in greater detail including its cleaning efficacy, environmental properties, stability under various conditions, including its recovery by carbon adsorption and compatibility with plastics and elastomers and compare them with some of the solvents used today.

Background

Cleaning technologies used today can be divided into a few major categories such as solvent cleaning, aqueous cleaning, semi-aqueous cleaning and not-in-kind which include "no-clean" fluxes and supercritical cleaning among others. Solvent cleaning includes various hydrocarbons, halogenated hydrocarbons, hydrofloroethers and several others, and blends of these materials with alcohols and other compounds. Aqueous cleaning refers to cleaning with water with various detergents, semi-aqueous refers to the removal of soils with terpene or citrus based solvents and then washing these materials with water. None of these cleaning alternatives became a universal alternative to CFC-113 in cleaning. A large section of the printed circuit cleaning industry is using aqueous solvents and a number of water soluble fluxes have also been introduced, however, aqueous cleaning has not been able to solve all the cleaning problems especially those in the defense and aerospace industries.

As technology in printed circuit board design is advancing, line spacing is becoming narrower, components are being spaced closer to the boards, and more surface mount devices are also being used. All of these factors are making cleaning printed circuit boards more and more difficult, leaving a need for better solvents and technologies.

Now going into some issues with existing technology we can see that hydrocarbon based solvents are flammable, which makes handling and use of such materials difficult. Semi-aqueous and aqueous cleaning technologies were initially favored to replace CFCs because of their lack of flammability, low price and availability. However, with the advances in printed circuit board design mentioned above, it has become apparent that the relatively high surface tension of water makes it difficult to penetrate in narrower spacing. The corrosive nature of water can also be problematic. In addition drying is very energy intensive and waste water disposal brings in difficulty and expense in operation. In the case of semi-aqueous techniques, the same problems mentioned above occur, and in addition odor and some flammability are also issues that users have to deal with.

Azeotropic mixtures of HCFC-225 (dichloropentafluoropropane) isomers and HCFC-141b (1,1-dichloro-1-fluoroethane) with alcohols were adopted by many users at the outset for defluxing and degreasing applications. They were actually drop-in substitutes for CFC-113. However, these compounds have lower ozone depletion potential than CFCs but are still not acceptable due to their non-zero ozone depletion potential. As a result, 141b was phased-out in early 2000, and HCFC-225 isomers will be phased out starting January 1, 2015. Users have realized a need to adapt new technologies or new solvents to replace these materials. HFCs and HFEs are introduced, however, they do not have sufficient solvency to be used alone, a chlorinated hydrocarbon, tr-1,2-dichloroethylene, had to be added to these materials to boost their solvency, while alcohols have also been added to remove ionic contaminants.

Among the not-in kind technologies, the use of so-called "no-clean" fluxes to avoid post-soldering cleaning altogether is worth discussing. Such "no-clean" fluxes with lower ionics are used by many people in the industry. While the use of such material would in theory have eliminated the need for post-soldering cleaning altogether, it was found that for many applications post-soldering cleaning is still required in order to preserve long-term reliability of the electronic components and to improve visual appearance of the boards by removing residues. As a result, it is common that "no-clean" fluxes need to be cleaned after soldering. Other technologies such as supercritical cleaning with CO_2, CO_2 snow, plasma cleaning technologies are also available in cleaning but they are not generally used in defluxing applications.

With these challenges in the industry, the company recognized the need in the industry for better solvents and technology in cleaning and defluxing. A new generation of compounds, hydrochloro-fluoro olefins and hydrofluoroolefins have been identified and developed for various applications including refrigeration and air conditioning, foam expansion agents and some solvent applications. 1233zd(E) is one such compound that is particularly well suited for solvent cleaning which we shall discuss below.

New Solvent Structure and Properties

The molecular structure of this new solvent 1233zd(E) is shown in Fig 1 below, chemical formula, IUPAC name, refrigerant number etc. are also listed below.

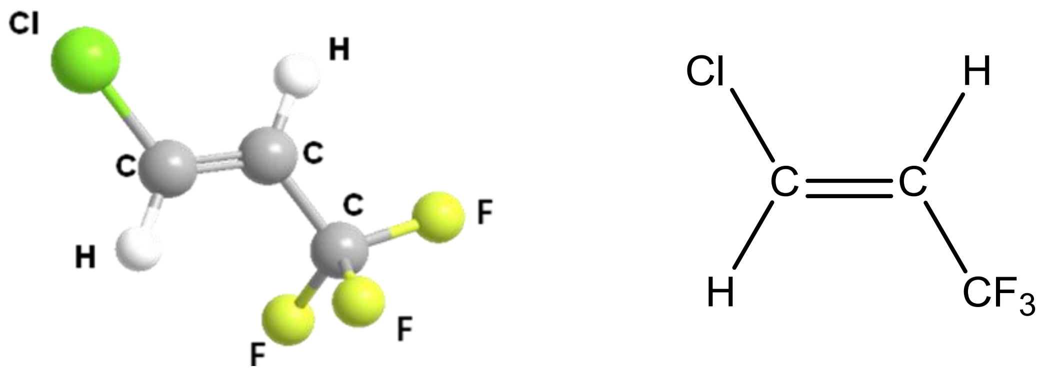

Fig 1 – Chemical Structure of Solvent 1233zd(E)

- **Molecular Formula – $CF_3CH{=}CHCl$**
- **IUPAC Name – (E) 1-chloro-3,3,3-trifluoro-1-propene**
- **Refrigerant Number – R-1233zd(E)**
  - Trans or E (*entgegen*) isomer

A versatile next generation solvent must satisfy a complex mosaic of properties. One of the first considerations is its physical properties. A comparison of some of the physical properties of 1233zd(E) with CFC-113 and a few existing solvents used today, are shown in Table 1 below. In that Table, Perc is used as an abbreviation for perchloroethylene.

One seeming disadvantage of 1233zd(E) is its slightly lower boiling point as compared to many of the current solvent used in the marketplace, however, it sometimes turns out to be an advantage in certain applications because the cleaned parts will dry faster. Another advantage of 1233zd(E) is its high heat of vaporization. Because of the high heat of vaporization it does not vaporize very rapidly despite its low boiling point. So contrary to a perception that the solvent will readily evaporate at room temperature, it has been found that if one pours the solvent in a beaker at room temperature around 25^{0}C the solvent takes quite a while to evaporate.

Because of its higher vapor pressure, 1233zd(E) requires special shipping and handling instructions that are different from many of the existing materials. It will be shipped in a pressure rated drum or cylinder. It also requires some changes to some existing cleaning equipments but it can be nearly a drop in substitute in some low emission degreaser incorporating minor modifications.

Table 1 - Selected Physical Properties of Solvents

	1233zd(E)	HFC-43-10 mee[a]	HFE-7100[a]	HCFC-225	n-Propyl Bromide	Perc
Molecular Weight	130	252	250	203	122	165.8
Boiling Point C	19	54	61	54	71	121.3
Vapor Pressure psi @20 C	15.23	4.4	3.2	5.6	2.1	0.27
Heat of Vaporization KJ/Kg at BP	194	129.7	112.4	145	144.7	207
Flash Point C	None	None	None	None	None	None

[a]HFCs and HFEs are mostly used in blends with Tr-1,2-dicholoroethylene or other substances so their values in this table are not representative of material used in practice

Besides being non-flammable, as evident by the lack of flash points, and no flame limits in air, 1233zd(E) also has a very low surface tension. 1233zd(E) has a surface tension of 12.7 dynes/cm which is the lowest among solvents shown in the above table. It has a Kauri-Butanol value of 25, providing it with a balance of penetration ability (low surface tension – compared to water at 72.1 dynes/cm) and solvent power (Kauri-Butanol (KB) value – compared to CFC-113 which has a KB value of 31) that makes it an excellent candidate to become the new environmentally friendly workhorse of solvents. The low surface tension of 1233zd(E) helps to make this compound excellent for use in applications where there is a need to penetrate narrow spacings and thus would be able to clean under surface mounts.

Environmental Properties of 1233zd(E)

In today's world of environmental awareness and preferences for environmentally safe products, it is very important to discuss environmental properties of new chemicals. A comparison of 1233zd(E) environmental properties with that of several other solvents is provided in Table 2 below.

Table 2 - Environmental Properties of Selected Solvents

Property	1233zd(E)	HFC 43-10mee	HFE-7100	HCFC-225	n-propyl bromide	Perc
Atmospheric Life	26 days	17.1 yrs	4.1 yrs	2.1/6.2 yrs	16 days	111 d
ODP	~0[a]	0	0	0.03	0.002-0.03	0
GWP_{100}	1	1700	320	180/620	N/A	10

[a] No impact on ozone layer depletion and is commonly referred to as statistically zero (Wuebbles[4])

Table 2 shows that 1233zd(E) has significantly low Global Warming Potential (GWP) compared to most other solvents used for various cleaning applications. Compounds which has lower lifetime have lower GWPs since they do not stay in the atmosphere longer to absorb infra-red radiation to make earth warmer. The lifetime of the compound, GWP and ozone depletion potentials for 1233zd(E) has been determined by world renowned scientists[5].

Volatile Organic Compound (VOC) characterization of 1233zd(E)

Certain chemical compounds are labeled as Volatile Organic Compound (VOC), depending on if they are found not to be photochemically reactive to produce smog in the lower atmosphere, hence characterized as a non-VOC chemical compound. This is measured by an experimentally determined number called maximum incremental reactivity (MIR). To be non-VOC, a chemical has to have MIR less than MIR of ethane (0.27 gms of ozone produced/gm of VOC). MIR of 1233zd(E) (measured value – 0.04, Carter[5])is well below that value. US EPA has taken final action to revise regulatory definition of volatile organic compounds (VOC) for purposes of preparing state implementation plans to attain the national air quality standards for ozone under title 1 of the Clean Air Act. This final action adds 1233zd(E) to the list of compounds excluded from the regulatory definition of VOCs on the basis that this compound makes a negligible contribution to tropospheric ozone formation. It is published in a recent Federal Register publication[7]. As a result, if someone is subject to certain federal regulations limiting emissions of VOCs their emission of this compound need not be regulated if they use this solvent for cleaning applications. This action may also affect whether 1233zd(E) is considered as a VOC for state regulatory purposes, depending on whether the state relies on the EPA regulatory definition of VOCs. 1233zd(E) is now going through review of VOC status in California.

Table 3 – Volatile Organic Compound (VOC) designation of Selected Solvents

Property	1233zd(E)	HFC 43-10 mee	HFE-7100	HCFC-225	n-propyl bromide	Tr-1,2 dichloro-ethylene	Perc
VOC	No	No	No	No	Yes[(3)]	Yes	Yes

In case of HFCs and HFEs, they are considered individually non-VOCs but most of the solvents sold today in the marketplace based on HFCs and HFEs are essentially blends with tr-1,2 dichloethylene and are therefore labeled as VOCs because of VOC designation of tr-1,2 dichloroethylene.

Safety aspects of 1233zd(E)

1233zd(E), being completely non-flammable and having no flash point or upper or lower explosion limits, requires no specific explosion proofing like some other solvents. Toxicological test data for the solvent have also been completed and the company Occupational Exposure Limit (OEL) of 800 ppm (8 hour time weighted average) has been assigned to 1233zd(E). The Table below compares the occupational exposure limits of several solvents. All values quoted below are 8-hour time-weighted-average exposure concentrations.

Table 4 – Toxicity properties of Selected Solvents

	1233zd(E)	HFC 43-10 mee	HFE-7100	HCFC-225	n-propyl bromide	Perc	Tr-1,2 DCE
Permissible Exposure Limit	800[a]	200[b]	700[c]	25[d]	10[f]	25[e]	200[e]

[a] Company OEL (Occupational exposure limit)
[b] DuPont AEL (Acceptable exposure limit)
[c] 3M Occupational AEL
[d] Asahi Glass AEL
[e] ACGIH Threshold Limit Value (TLV)
[f] Current ACGIH TLV, a significantly lower value has been proposed and is under consideration

1233zd(E) solubility with oils

We are going to describe the cleaning performance of 1233zd(E) in this section. To start with we compared the solubility of various materials which may be considered as soils to be cleaned in 1233zd(E) in Table 3 and then the cleaning test results are shown in Table 4 below. The miscibility test was done where equal parts of solvent and oils are mixed together and visual observation was made to see if the soils and the 1233zd(E) remained in a single phase, indicating that the soils were completely dissolved in the solvent. In all cases the solvent looked clear and the mixtures are reported as miscible Table 4. The purpose of the study is to test how well the solvent performs in dissolving various soils.

Table 5 - Soil Dissolution in 1233zd(E)

Soil	1233zd(E)
Mineral Oil	Miscible
RMA Solder Flux	Miscible[a]
Refrigerant oil	Miscible
Silicone Lubricant	Miscible
Lapping Compound	Miscible
Cutting Oils	Miscible

[a] In case of RMA solder flux a blend of 1233zd(E) and methanol was used

Table 5 shows that 1233zd(E) has miscibility properties similar to n-propyl bromide and AK-225 solvents which are good solvents and are currently used by a number of users in a wide variety of applications. All of these oils in Table 4 were found insoluble in pure HFCs and HFEs and require the addition of a co-solvent such as tr-1,2 dichloroethylene. So in summary 1233zd(E) has solvency characteristic as good as the current solvents for most common soils.

1233zd(E) Cleaning ability for oils

In the next step, we did an evaluation of how good the solvent is in cleaning parts soiled with oils. In these tests we soiled small 2" by 1" stainless steel coupons with various commercial oils used in the field. The coupons were immersed in boiling 1233zd(E) for 2 minutes and dried in the solvent vapors. This test was performed in small beakers with condenser coils near its lips which emulated conditions similar to a lab vapor degreaser. Coupons were visually observed for cleanliness and weight changes of the coupons were also noted. Cleaning results are given in the table below and it shows that it removed the soils from stainless steel coupons quite well for almost all the oils except for one. This demonstrates good degreasing efficacy of the solvent 1233zd(E).

Table 6 - Soil removal from Coupons Using 1233zd(E)

Test Soil	% Removed	Test Soil	% Removed
Vacuum pump oil	99.7	Mil-PRF-83282	100
Cutting oil	99.3	Mil-PRF-C-81309	98.8
Silicone oil	99.4	VV-D-1078	97.7
Mineral oil	99.8	Nye oil 438	72.4

1233zd(E) Defluxing performance

We also conducted a defluxing study with 1233zd(E) and methanol blend. The blend used is an azeotropic blend of 1233zd(E) and methanol so they would not segragate in a vapor degreaser. Small pieces of metal coupons with baked solder fluxes were immersed in solvent for 2 minutes and dried in the vapor. The experimental set-up is same as mentioned before boiling solvent in beaker with condenser coils near the lip. A commercial solder was used in this test. Test results showed that the removal was good both by visual observations and gravimetric analysis. It showed equal or better performance compared to another commercial solvent/alcohol blends.

There are a number of RMA fluxes that have been cleaned with this 1233zd(E) and methanol blend in a vapor degreaser. These fluxes were deposited on commercial parts and then removed in a vapor degreaser using immersion and vapor rinse. The fluxes cleaned are given in Table 7 below.

Table 7 – RMA Fluxes/pastes cleaned in 1233zd(E) and methanol blend

RMA Fluxes removed	
Kester 125	Kester 185
Kester 1544	Kester 48
M705-GRN 360 MZ	Kester 197

It has been found that the 1233zd(E)/methanol blend is not very effective in cleaning some of the no-clean and rosin cure fluxes. Efforts are underway to develop 1233zd(E) based solvent blends to clean these no-clean and rosin core fluxes and pastes.

1233zd(E) and alcohol blend has also shown promising results in tests as a cleaner in defluxing with aerosol spray cleaning applications[6]. Aerosol spray is generally used in a number of cases especially for rework. Here the solvent blend is used in conjunction with a propellant and sprayed onto fluxed printed circuit boards. Visual observation was made, circuit boards looked visually clean and gravimetric measurements confirmed the removal of flux from the boards.

Shipping and Handling of 1233zd(E)

Due to the higher vapor pessures and the lower boiling point of 1233zd(E) shipping and handling of solvent will be different. Solvent will be shipped in steel cylinders like refrigerant jugs with outlets fitted with liquid and vapor valves. The jugs will be under the vapor pressure of the solvent itself. Containers will be of different sizes 1 gallon, 5 gallon and higher quantities such as near 1 barrel size or bigger depending on customer needs. The conatiners are recommended to be stored under room temperature conditions.

1233zd(E) Degreaser studies

Looking at the boiling point of 1233zd(E) some users initially expressed concern if the solvent will evaporate out of a vapor degreaser. We ran several degreaser trials to better understand how 1233zd(E) behaves in a degreaser and what kind of changes in design may be needed to the degreasers if any.

Our test results showed that with a few modifications a typical degreaser can be run with very low loss rates with 1233zd(E). The major requirements for the degreaser are that it has both primary and secondary coils (free board coils). The operating condition of the coils may have to be modified. The primary coils should be operated at around 0°C and secondary coils should operate at about -20°C. Low emission vapor degreasers manufactured by most vapor degreaser manufacturer can be operated at these conditions. With these operating conditions we found the solvent loss is equivanlant to that of other solvents that are currently run in low-emission vapor degreasers.

Since the solvent will be shipped in containers like refrigerant jugs, solvent will be charged and discharged through closed loop system. It is also recommended that centrifugal pump to recirculate the solvent be located near the bottom of the rinse sump to avoid cavitation or a non-cavitating pump such as a diaphragm pump can be used.

Older degreasers with no secondary coils, have to be retrofitted with a set of secondary coils and in some cases circulation pumps may have to be changed in order to avoid cavitation. Some other retrofits have to be performed on a case-by-case basis.

1233zd(E) Stability Studies

The chemical stability of the compound 1233zd(E) with and without the presence of water, with metals and fluxes is another important factor to be considered in the identification of a next generation solvent. To test this we used a setup shown below in Fig 2. As shown in the figure, chilled water cooled condensers were connected to small flasks and the solvents were boiled in the flasks and refluxed back to the flask. This test continued for two weeks.

In the test, solvent is boiled with water alone and in presence of various metal coupons such as stainless steel 304, cold-rolled steel, galvanized steel, copper, aluminum, monel, inconel and titanium. The coupons were partially immersed in the solvent which allowed us to look at the state of the coupons at the interface of liquid and vapor. At the conclusion of the test the coupons were observed visually for rusting or pitting and the remaining solvent in the flask was examined for breakdown products including chlorides and fluorides which are good indicators of breakdown of solvent. Tests showed that there was no increase of chlorides and fluorides in the solvent over the baseline and no other degradation products were formed indicating that the solvent is quite stable under these conditions. The test coupons also showed no rusting or pitting. Similar tests also continued with addition of solder flux in the liquid and in that case also solvent showed excellent stability under these adverse conditions.

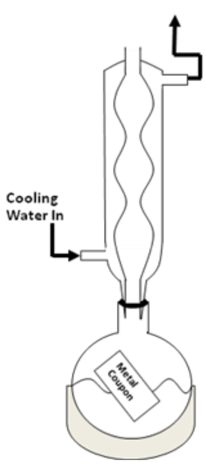

Fig 2 - Reflux test study set-up

The important thing to note is that the solvent does not turn acidic which has been a problem with some solvent such as n-propyl bromide or tr-1,2-dichloroethylene.

This test essentially simulates the condition in a vapor degreaser and as such suggests that it is unlikely that the solvent will break down in use in a vapor degreaser.

Solvent stability is also studied in recovery with carbon adsorption. The tests were done by an outside agency and showed no breakdown of solvent in adsorption and desorption with activated carbon. 1233zd(E) is found to be compatible with carbon recovery unlike some HFCs and

Compatibility of 1233zd(E) with plastics and elastomers

Compatibility of common plastics and elastomers were studied in 1233zd(E). Commonly used plastics, such as, acrylonitrile-butadiene-styrene (ABS), high-density polyethylene (HDPE), nylon, polycarbonate, polypropylene, polyethylene terephthalate, poly-vinyl chloride, high-impact polystyrene, acrylic were immersed in the solvent for 2 weeks at room temperature in enclosed cells. At the end of the 2 week exposure the coupons were taken out and weight and volume changes were recorded. Except for high-impact polystyrene and acrylic all other plastics have minimal or no effect. 1233zd(E) completely dissolved acrylic material.

Similar tests were performed with elastomers. Elastomers used in the compatibility test are fluoroelastomer (Viton®B), epichlorohydrin rubber, Buna N (nitrile butadiene rubber), butyl rubber, buna-nitrile, polyurethane 390, neoprene, silicone rubber, perfluoroelastomer (Kalrez®) and ethylene propylene diene M-class (EPDM) rubber. Here weight change and dimensional change were carried out along with visual observation for cracks or other degradation. Significant changes were observed for Buna-nitrile, EPDM and for others the changes observed are minimal.

With a vast array of plastics and elastomers in the marketplace it is not possible to test all kinds and grades of plastics and elastomers in our own labs. So users are advised to test compatibility prior to using the solvent.

Conclusions

In this paper we have described the characteristics of a new solvent 1233zd(E) or trans-1-chloro-3,3,3-trifluro-1-propene which showed excellent promise as a solvent for defluxing and other cleaning applications. It has better environmental and toxicity properties compared with many other solvents in the marketplace today and can be used in vapor degreasers. It is also a stable, non-flammable product with reasonable compatibility with materials. Presently 1233zd(E) registration for solvent and other uses is underway in many countries.

References

1. M.J. Molina and F.S. Rowland, “Stratospheric Sink for Chlofluoromethanes: Chlorine Atom Catalyzed Destruction of Ozone”, Nature, Vol. 249, 1974, pp. 810-812.

2. “The 1987 Montreal Protocol on substances that deplete the ozone layer” – United Nations Environmental Program, 1987.

3. ASHRAE Standard 34 – 2010, American Society of Refrigeration and Air Conditioning Engineers, Atlanta, GA 2010.

4. Prof. Donald Weubbles, University of Illinois at Urbana-Champaign, Private Communication 2011.

5. Prof. William P. L. Carter, University of California, Riverside, CA, Private Communications 2009.

6. Gary Knopeck, “Low GWP Solutions”, Paper presented at the National Aerosol Association, Feb 2012.

7. “Air Quality: Revision to Definition of Volatile Organic Compounds – Exclusion of trans 1-chloro-3,3,3-trifluoroprop-1-ene [Solstice^{TM} 1233zd(E)] – Federal Register. Vol 78, No 167, Aug 2013, p. 53029