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Precision Cleaning in 21st Century: New Solvent with Low Global Warming Potential

Rajat Basu, Ryan Hulse, Kane Cook and Diana Mercier
Honeywell International
20 Peabody St, Buffalo, NY 14210

Abstract

As we progress in the 21st century, electronics manufacturing will need more and more precision. Parts will get more complex since more components have to be assembled in smaller spaces. Circuit boards and other electronic assemblies will become more densely populated; spacings between components will be shorter. This will require precision manufacturing and efficient cleaning during and post manufacturing. In addition, with population and technology progressing, larger amount of greenhouse gases will be emitted resulting in higher global warming. Intense research effort is going on to develop new generation of chemicals to address both cleaning and global warming issues. Low global warming solutions in refrigeration and as insulating agents are already in the marketplace. This paper will detail the development of a new very low global warming potential environmentally friendly non-flammable solvent with excellent cleaning abilities. Environmental properties, cleaning efficacies, stability in various conditions, and compatibility with plastics, elastomers, and metals of the solvent will also be described in this paper.

Introduction

In 1970 Professors Rowland and Molina[1] discovered earth's stratospheric ozone depletion by chlorofluorocarbons (CFCs) and various halogenated compounds which brought about a big change in the use of CFCs for use as cleaning solvents, as refrigerants, 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 used to be the workhorses in industrial cleaning. The printed circuit board industry primarily used CFC-113 in cleaning solder flux post-soldering. These solvents were also used in metal degreasing, precision cleaning of aerospace components, cleaning of medical devices and in many other applications. Since the phase-out of these solvents in 1996, industrial solvent users have been using many different solvents but with a different solvent or group of solvents for each specific application. No one solvent has been found that can be used effectively for many applications in the same way that CFC-113 and 1,1,1-trichloroethane were. In this article we are going to discuss the discovery of a new solvent in cleaning. This chemical that will be described has the chemical name of trans-1-chloro-3,3,3-trifluoro-1-propene. Using the numbering system of halogenated compounds it can also be referred to as 1233zd(E) as will be described below. It has been found to be as good as CFC-113 but with superior environmental properties. In this paper we are going to describe the advantages 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.

Background

After CFC-113 was phased out in 1996 following the phase-out schedule of substances that deplete earth's stratospheric ozone following Montreal Protocol ratified by UNEP (United Nations Environmental Program), many alternate solvents and technologies have been introduced in the marketplace for cleaning printed circuit boards. This industry has gone through a tremendous change in the manufacturing and cleaning of printed circuit boards since then. A detailed description of many of these alternates may be found in "Handbook for Critical Cleaning[2]".

These cleaning technologies can be divided into a few major categories such as solvent, aqueous, semi-aqueous and not-in-kind which includes so-called "no-clean" fluxes. Solvent cleaning has included various hydrocarbons, halogenated hydrocarbons, hydrofloroethers and several others, and blends of these materials with alcohols and other compounds. Aqueous cleaning generally involves the use of water with various detergents. Semi-aqueous generally involves the removal of soils with terpene or citrus based solvents and then washing these materials with water. None of these cleaning alternatives became the workhorse of the industry as CFC-113 used to be many years back. All of them have some disadvantages.

One new problem has arisen with cleaning of printed circuit boards. As technology in printed circuit board design is advancing, the 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 to clean, resulting for an increasing 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 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. However, these compounds have low but non-zero ozone depletion potential. As a result, 141b was phased-out several years back, and HCFC-225 isomers will be phased out in a few years. So companies have realized a need to adapt new technologies in using these materials as solvents. Certain azeotropic mixtures of HFCs and HFEs have replaced some of these in defluxing. However, these materials have not had sufficient solvency to be used alone, the chlorinated hydrocarbon tr-1,2-dichloroethylene has frequently been 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. As a result, it is common that even “no-clean” fluxes are 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 often used in defluxing applications.

As a result, Honeywell has recognized the need in the industry for better solvents and technology in cleaning and defluxing. A new generation of compounds, hydrochlorofluoroolefins and hydrofluoroolefins have been identified and developed for various applications including refrigeration and air conditioning, foam expansion agents and some solvent applications. In the rest of the paper we are going to describe properties, performance and other characteristics of a new solvent that was invented in our laboratories for use in defluxing and other applications.

New Solvent Structure and Properties

The new solvent that will be described here is a hydrochlorofluoroolefin. The molecular structure is shown in Fig 1 below, chemical formula, IUPAC name, refrigerant number etc. are also listed below.

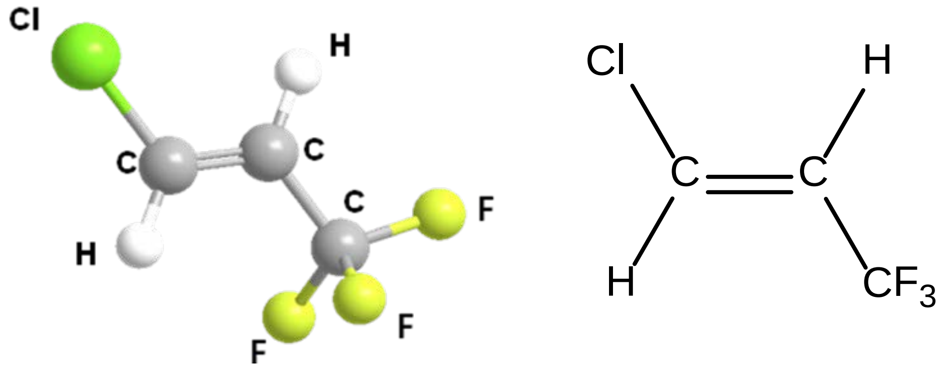

Fig 1 – Chemical Structure of Solvent 1233zd(E)

- **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 next generation solvent must satisfy a complex mosaic of properties. One of the first considerations in the identification of such a solvent 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 Table 1 Perc is used as an abbreviation for perchloroethylene.

After extensive study, testing and analysis, we have found that the performance of 1233zd(E) compares quite favorably with CFC-113, making it an excellent CFC-113 alternate, while providing dramatically superior environmental properties. Moreover, the fact that 1233zd has a slightly lower boiling point point than CFC-113 could be an advantage in certain applications. One of the advantages of 1233zd(E) is its high heat of vaporization. Because of the high heat of vaporization it vaporizes slowly even when used at temperatures above the boiling point of the material. 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°C the solvent takes quite a while to evaporate. However, because of higher vapor pressure it has to be packaged and handled differently. The lower boiling point can also be an advantage in many applications where faster evaporation will be required.

Because of its higher vapor pressure, 1233zd(E) will require shipping and handling that is different than many of the existing materials. It will be shipped in a pressure rated drum or cylinder.

Table 1 - Selected Physical Properties of Solvents

	1233zd	HFC 43-10mee	HFE-7100	HCFC-225	CFC-113	n-Propyl Bromide	Perc
Molecular Weight	130.5	252	250	203	187.4	122	165.8
Boiling Point (°C)	19.52	54	61	54	47.6	71	121.3
Vapor Pressure, psi @20C	15.23	4.4	3.2	5.6	5.27	2.1	0.27
Heat of Vaporization (kJ/kg) at bp	193.9	129.7	112.4	145 @25° C	144.7	246	207
Flash Point (° C)	None	None	None	None	None	None	None

Besides being completely non-flammable, 1233zd(E) also has a very low surface tension.1233zd(E) has a surface tension of 12.7 dynes/cm and a Kauri-Butanol value of 25, providing it with a balance of penetration ability (low surface tension – compare to water at 72.1 dynes/cm) and solvent power (Kauri-Butanol (KB) value – compare to CFC-113 at 31) that makes it an excellent candidate to become the new environmentally friendly workhorse of solvents. Because of the low surface tension it will be 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(1)	~0(1)	~0(1)	0.03	0.002-0.03	~0(1)
GWP_{100}	7	1700	320	180/620	N/A	10
VOC	No (2)	No	No	No	Yes(3)	Yes

(1) No impact on ozone layer depletion and is commonly referred to as statistically zero (Wuebbles[3])

(2) A measured MIR 0.04, expected to be non-VOC

(3) Applied for but not granted

Table 2 shows that 1233zd(E) has low Global Warming Potential (GWP) compared to other solvents. It is also not photochemically reactive to produce smog in the lower atmosphere. 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[4]) is well below that value, therefore, it is expected to be ruled as a non-VOC. Lower lifetime compounds have lower GWP since they do not stay in the atmosphere longer which results in lower greenhouse warming of the earth. The lifetime of the compound and GWP and ozone depletion potentials for 1233zd(E) is determined by world renowned scientists[5].

1233zd(E) cleaning performance

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 3. This is an initial mode of testing to check how well the solvent performs in dissolving the soils.

Table 3 - Soil Dissolution in Solvents

Soil	1233zd(E)	n-propyl bromide
Mineral Oil	Miscible	Miscible
Solder Flux	Miscible	Miscible
Refrigerant oil	Miscible	Miscible
Silicone Lubricant	Miscible	Miscible

The table showed that 1233zd(E) has miscibility properties similar to n-propyl bromide which is a very good solvent. This comparison is not shown with all the other solvents. All of these oils were found insoluble in HFCs and HFEs. However, HFCs and HFEs are not used by themselves as solvents so a comparison with neat HFCs and HFEs is not meaningful.

In addition a few other soils were also tested for solubility in 1233zd(E). Soils, such as, perfluorinated lubricants, polyalkylene glycols all showed solublity in the 1233zd(E) at greater than 10 percent.
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 4 - 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

We also conducted a defluxing study with 1233zd(E) and alcohol blend. Small pieces of metal coupons with baked solder fluxes were immersed in solvent for 2 minutes and dried in the vapor. The laboratory experimental set-up is same as mentioned before with 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 by visual observations and gravimetric analysis. It showed equal or better performance compared to another commercial solvent/alcohol blends as shown in the Table 5 below. Ionic contamination tests were not performed.

Table 5 - Solder Flux removal from coupons

Solvent	Wt% flux removed
1233zd/alcohol blend	96.9
HFC-43-10/alcohol blend	95.3

1233zd(E) and alcohol blend has also shown promising result in tests as a cleaner in defluxing with aerosol spray cleaning applications. 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.

1233zd(E) Stability Studies

The chemical stability of the compound 1233zd(E) by itself and also in the presence of water, metals, flux 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 and aluminum. 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. After the test 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 solvents. Tests showed that there was no increase of chlorides and fluorides in the solvent over the baseline and no other degradation products 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. The important thing to note is that the solvent does not turn acidic which has been a problem with some solvent blends which use 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 also 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 HFEs. The detailed results will be presented in future.

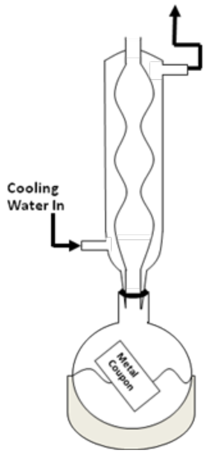

Fig 2 - Reflux test study set-up

Compatibility of 1233zd(E) with plastics and elastomers

Compatibility of common plastics and elastomers were studied in 1233zd(E). Here also 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 and at the end of 2 weeks they 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. Again 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 of plastics and elastomers. So we would advise testing compatibility prior to using any solvent.

Conclusions

In this paper we have demonstrated that a new solvent 1233zd(E) or trans-1-chloro-3,3,3-trifluro-1-propene 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. 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. This solvent will be sold in the solvent marketplace under the tradename Solstice® Performance Fluid.

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