

## **Nonflammable, Nonaqueous, Low Atmospheric Impact, High Performance Cleaning Solvents**

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### **INTRODUCTION**

For many years, chlorofluorocarbon (CFC) and chlorocarbon solvents have played an important part in aerospace operations. These solvents found extensive use as cleaning and analysis [EPA] solvents in precision and critical cleaning. However, CFCs and chlorocarbon solvents have deleterious effects on the ozone layer, are relatively strong greenhouse gases, and some are suspect or known carcinogens. Because of their ozone-depletion potential (ODP), the Montreal Protocol and its amendments, as well as other environmental regulations, have resulted in the phaseout of CFC-113 and 1,1,1-trichloroethane (TCA). Although alternatives have been recommended, they do not perform as well as the original solvents. In addition, some analyses, such as the infrared analysis of extracted hydrocarbons, cannot be performed with the substitute solvents that contain C-H bonds.

CFC-113 solvent has been used for many critical aerospace applications. CFC-113, also known as Freon<sup>®</sup> TF, has been used extensively in NASA's cleaning facilities for precision and critical cleaning, in particular the final rinsing in Class 100 areas, with gas chromatography analysis of rinse residue. While some cleaning can be accomplished by other processes, there are certain critical applications where CFC-113 or a similar solvent is highly cost-effective and ensures safety. Oxygen system components are one example where a solvent compatible with oxygen and capable of removing fluorocarbon grease is needed. Electronic components and precision mechanical components can also be damaged by aggressive cleaning solvents.

A number of alternative cleaning processes and solvents have been promoted in the last few years.

Supercritical carbon dioxide can provide excellent cleaning, but has the drawbacks that the high-pressure systems used are expensive and limited in size. The cleanliness obtained with supercritical CO<sub>2</sub> depends strongly on the pressure and temperature of the system, so these parameters must be closely controlled. In addition, the rapid temperature and pressure changes may damage structures and affect components.

Many conventional solvents (e.g., hydrocarbons) are effective cleaners but are flammable, not compatible with oxygen, and require special precautions.

Ethyl lactate has been developed as an effective, zero ODP, low GWP, biodegradable, low toxicity, solvent that can be made from renewable resources. However, its boiling point and

other physical properties are not suitable for cleaning many components and assemblies, as it evaporates too slowly and can become entrapped in small spaces. In addition, it is not compatible with oxygen.

Isopropyl alcohol (IPA) can be used in some cleaning, but engineering and safety measures are needed to minimize flammability risk. As a result, systems designed for IPA are expensive (on the order of \$100,000). In addition, large volumes of IPA are often needed as final rinse and dry, generating large volumes of solvent waste.

Hydrofluorocarbons (HFCs) are nonflammable, have zero ODP and low toxicity, but they also have poor solvency and moderately high GWP. Some blends containing HFCs are under investigation.

Hydrofluoroethers (HFEs) have recently been introduced by 3M as cleaning solvents. HFEs possess the attractive properties of some solvency for oils and greases, low toxicity, reasonable cost, no ozone depletion, and modest global warming. However, their performance for many applications has had to be augmented by addition of better solvents such as dichloroethylene, which puts them back in the chlorinated solvent category.

One alternative solvent that is being investigated heavily and used in some applications is 1-bromopropane (EnSolv<sup>®</sup> and similar products). This solvent has good cleaning ability, relatively fast evaporation, is not flammable, and can be used in some precision cleaning applications. However, it is not compatible with oxygen, and there have been some reports of toxicity from exposure to 1-bromopropane. Haloalkanes also tend to be carcinogens.

Volatile methyl siloxane (VMS) solvents have been developed by Dow Corning. These compounds show promise as nonflammable (but combustible) cleaning solvents with good environmental properties. However, they are not compatible with oxygen and have relatively high boiling points and low volatilities, thus requiring longer drying times.

Plasma cleaning is being developed as a solvent-less process, but it requires sophisticated equipment and is not suitable for all materials.

### **Iodofluorocarbon (IFC) Solvents**

Iodofluorocarbons (IFCs) were identified by Jon Nimitz and Lance Lankford as potentially attractive nonflammable, nonaqueous solvents for replacement of CFC and chlorocarbon solvents. The 3-carbon to 6-carbon IFCs containing one iodine atom have low boiling points, high volatilities, low viscosities, and low surface tension, which make them attractive candidates as alternative solvents. In addition, they have essentially zero ODP (<0.0025), extremely low global warming potential (GWP), acceptable toxicity, and good thermal stability. They are chemically similar enough to chlorofluorocarbon and chlorocarbon solvents that they also promised to have good soil removal abilities.

Although IFC solvents appeared to have much promise, there were a number of issues. There were little or no toxicity, stability, biodegradability, and compatibility data available on the compounds. For oxygen system cleaning, compatibility with liquid oxygen needed to be

determined. Atmospheric lifetime had to be calculated to obtain a good estimate of ODP and GWP. Cleaning abilities compared to CFC-113 and other solvents had to be established, as well as ability to purify and reuse the IFC solvent. Perhaps most importantly, since the IFCs are not bulk commercial products, a low cost synthetic route had to be identified.

From 1995 to 1999, in projects sponsored by the Air Force Research Laboratory and NASA, ETEC developed two new solvents, Ikon<sup>®</sup> Solvent P and Ikon<sup>®</sup> Solvent M, based on iodofluorocarbons (IFCs). The Air Force's interest in new solvents was for replacement of CFC-113 in mission-critical aircraft maintenance operations. NASA's interest in the solvents resulted from difficulties replacing CFC-113 in oxygen system cleaning.

## RESULTS AND DISCUSSION

### Cleaning Ability and Recovery for Reuse

A preliminary series of cleaning tests were performed with the three-carbon, four-carbon, and six-carbon IFCs. Testing was performed based on a procedure developed at Sandia National Laboratories. One by three inch tared coupons of substrate material were intentionally soiled with one of six representative soils: the three perfluorinated greases Braycote<sup>®</sup> 601 EF, Krytox<sup>®</sup> 240, and Tribolube<sup>®</sup> 16; Amoco Rykon<sup>®</sup> Grease No. 2EP (a hydrocarbon grease); Dow-Corning DC-55M (a silicone grease); and Royco 782 Superclean Hydraulic Fluid MIL-H-83282 (a fire-resistant hydraulic fluid containing phosphate esters). Soiling levels were from 1.0 to 5.0 g/ft<sup>2</sup>. Each coupon was weighed to measure the amount of soil, then cleaned, air dried, and reweighed to determine soil removal effectiveness. Figure 1 shows some of the results from this testing. Perfluoro-n-butyl iodide (CF<sub>3</sub>CF<sub>2</sub>CF<sub>2</sub>CF<sub>2</sub>I, 1-C<sub>4</sub>F<sub>9</sub>I, Ikon<sup>®</sup> Solvent P), specified hereafter in this paper as PFBI, was identified as the most attractive cleaning solvent from this group, and as can be seen it removes perfluorinated greases significantly faster than CFC-113.

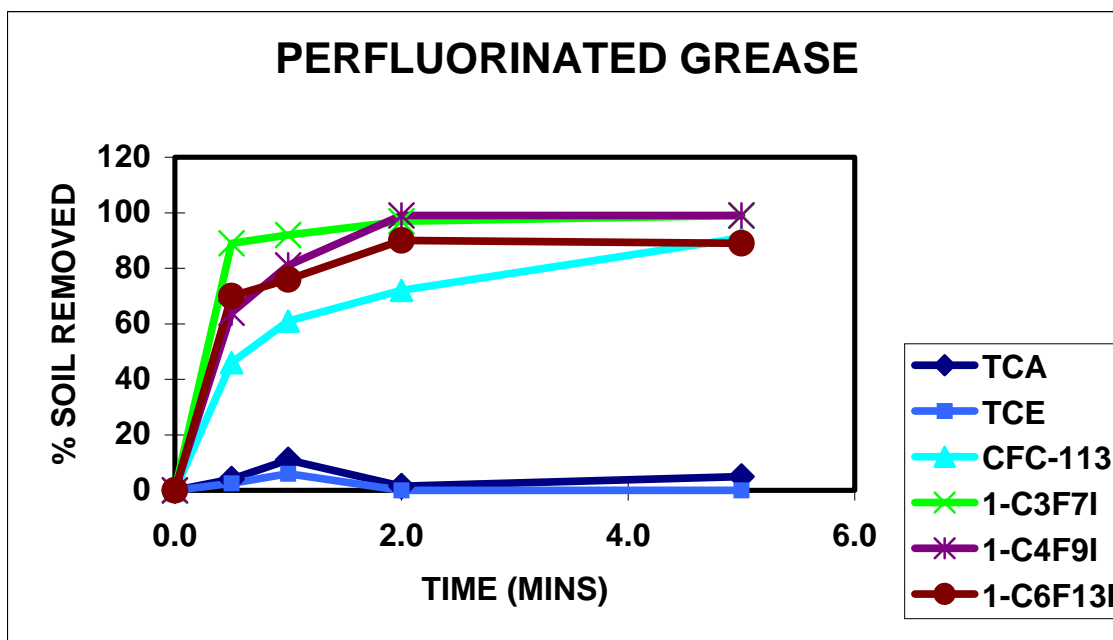
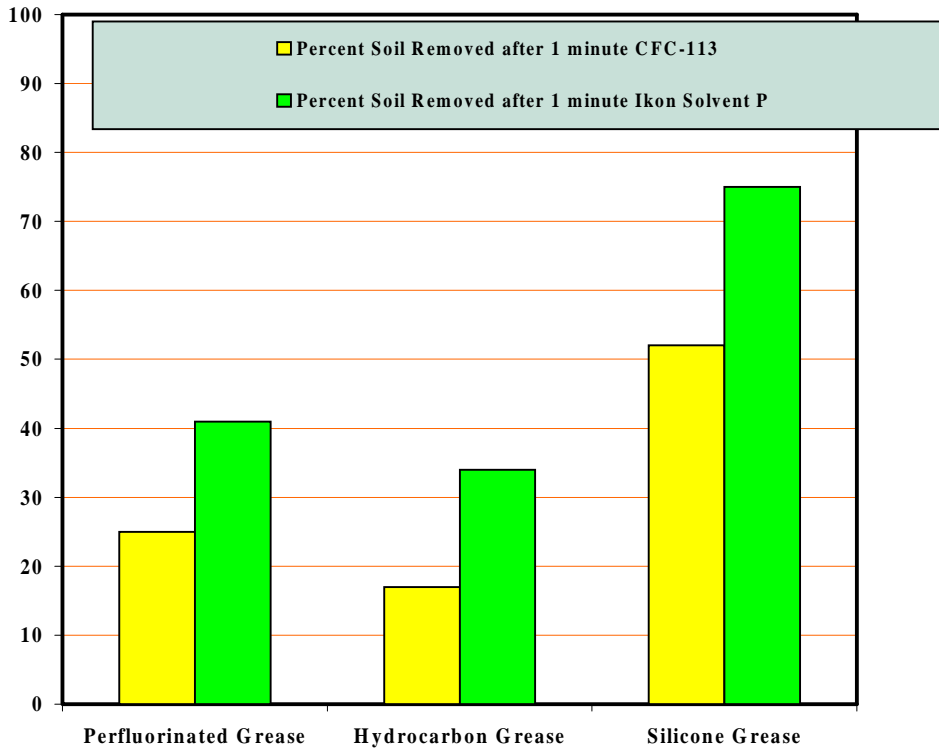


Figure 1. Removal of Perfluorinated Grease by Selected Solvents

Continued cleaning tests examined the ability of the IFC solvents and CFC-113 to remove a soil when the solvent was already saturated with that soil. Braycote<sup>®</sup> 601, Rykon<sup>®</sup> Grease No. 2, and Dow-Corning DC-55M were chosen as representative soils. The results of these tests were even more encouraging than the tests with clean solvents. As shown in Figure 2, Ikon Solvent P (PFBI) consistently removed the three soils from 316 stainless steel significantly faster than CFC-113, indicating superior cleaning ability over extended use applications.



**Figure 2. Soil Removal Ability of Soil-Saturated CFC-113 and Soil-Saturated PFBI**

Upon determination of our best replacement solvent candidate, it was considered worthwhile to explore testing ability to recover the solvent to reduce its cost of use and the amount of waste solvent generated. This study was performed at the Air Force Research Laboratory/MLBT. They found that used or “dirty” PFBI could easily be distilled to a purity equal to that of new or unused solvent. At least 85-90% of the solvent was recoverable. AFRL/MLBT concluded that PFBI could be recovered easily and economically, greatly reducing the cost of using the solvent and the amount of waste solvent generated.

### **Compatibility and Stability**

Compatibility tests consisted immersing selected materials in PFBI for 10 days at room temperature.

Of nineteen polymers and elastomers tested in this manner for compatibility, only Aflas, silicone rubber, and urethane were found to be incompatible. Compatible polymers included polyacrylic, cyanate ester, graphite/epoxy composite, nylon, phenolic, polyimide, poly (vinyl

chloride) and Teflon. Compatible elastomers included Buna-N, neoprene, EPDM, fluorosilicone, and Viton.

Compatibility tests were conducted with aluminum alloys 2024, 5052, 6061, and 7075T6; stainless steels 303 and 416; titanium; mild steel; cast iron; magnesium; copper; brass; bronze; acid-core solder; plumbing solder; and rosin core solder. PFBI was completely compatible with all metals tested except mild steel. Mild steel showed significant oxidation (rust), which was likely due to air and moisture that were not rigorously excluded, because there is no reaction between iron and PFBI alone that could have formed iron oxide. At the temperatures expected in cleaning operations, PFBI is also compatible with other common solvents, water, and adsorbents.

One indication of the relatively high stability of PFBI is its compatibility with liquid oxygen. This is a harsh test for any solvent, and almost all solvents will react with oxygen under these test conditions. In this test, a sample of the solvent is frozen in a pool of liquid oxygen and struck with a striker to attempt to initiate reaction. CFC-113 passes this test at 72 ft-lbs striking force. Only two out of seventeen samples of PFBI reacted at 72 ft-lbs, and none out of 20 samples at 65 ft-lbs. Thus, PFBI appears to be only slightly more reactive toward oxidation than CFC-113.

The autogenous ignition temperature of PFBI in 100% oxygen at 13.8 Mpa (2000 psia) was measured as 171 - 175°C. This test also reveals excellent stability for PFBI. In fact, PFBI is a known combustion suppressant.

Suppliers package, ship, and store PFBI without any special precautions. During our cleaning tests, PFBI was re-purified by distillation and reused many times without evidence of significant decomposition. PFBI often comes from the supplier with a slight pink color from free iodine in solution, and left out in the sun or under fluorescent lights for an extended period of time it will always develop a pink color from free iodine. The free iodine is a photolysis product from exposure of the solvent to UV light. The amount of iodine produced under these conditions is very small, at most several parts per million, and can easily be removed from the solvent with activated carbon.

### **Atmospheric Lifetime, ODP, and GWP**

The estimated low atmospheric impact of the IFCs is a result of their susceptibility to short wavelength ultraviolet light. The carbon-iodine bond in these compounds is weak enough that UV wavelength photons in sunlight can break it. Breaking the C-I bond begins a decomposition chain that proceeds completely to CO<sub>2</sub>, HF, and HI, as the fluorinated free radical from the C-I bond breakage reacts with water to form fluorinated alcohols that are highly unstable and quickly decompose.

Other than their susceptibility to photolysis, normal IFCs containing one iodine atom are stable because the fluorine atoms withdraw electron density from the iodine atom and make it much less reactive. The fluorines also block back-side attack on the iodinated carbon atom.

The atmospheric lifetimes, ODPs, and GWPs of the three-carbon, four-carbon, and six-carbon IFCs were determined by Dr. Don Wuebbles at the Department of Atmospheric Sciences

at the University of Illinois (Urbana-Champaign). Dr. Wuebbles is one of the world's foremost researchers on ODP and GWP. He concluded that the atmospheric lifetimes for these compounds are approximately 2 days. This is extremely short compared to most fluorinated chemicals, which have lifetimes ranging from years to centuries. He concludes that the ODPs of FICs are less than or equal to 0.0025, "much less than is of concern within the U.S. and international guidelines." The GWPs are also extremely small, less than 6 relative to CO<sub>2</sub> for the 20 year time horizon and less than 2 for the 100 and 500 year time horizons. Dr. Wuebbles concluded that "these results imply essentially a negligible effect on future climate from use of 1-C<sub>3</sub>F<sub>7</sub>I, 1-C<sub>4</sub>F<sub>9</sub>I, and 1-C<sub>6</sub>F<sub>13</sub>I."

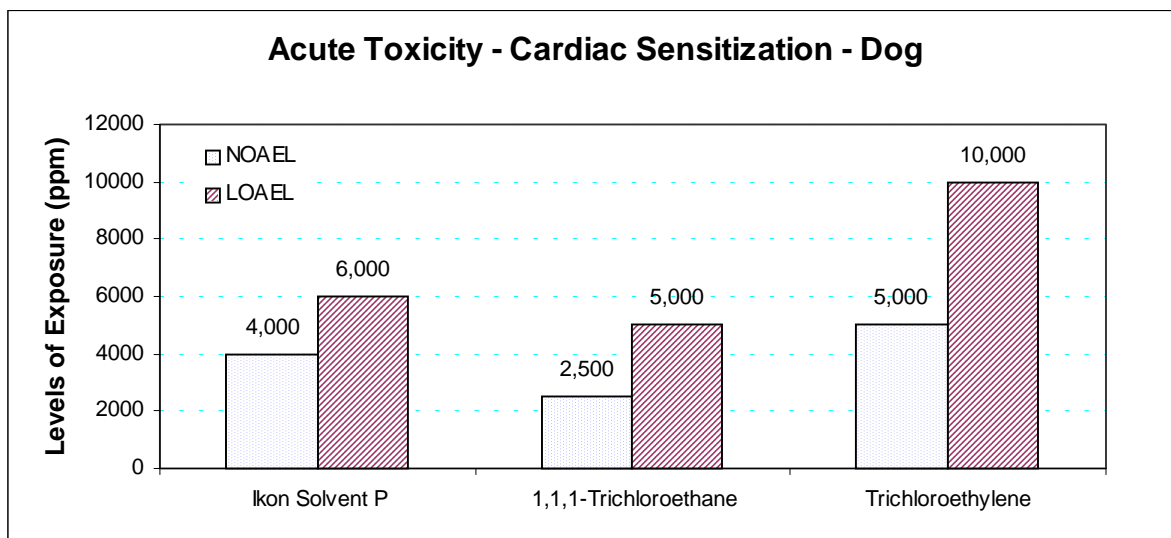
### **Toxicity and Biodegradability**

Toxicity studies on PFBI were conducted by Huntingdon Life Sciences (HLS).

PFBI was found non-mutagenic in the Ames test and non-clastogenic in the human lymphocyte chromosome aberration test.

Twenty-eight day rat subchronic inhalation (6 hrs per day) exposure tests were performed. Results showed somewhat elevated thyroid hormone levels at 100 ppm exposure; elevated thyroid hormone, triglyceride, and iodide levels in the 1,000 and 10,000 ppm test groups; and some physical effects in the males (low weight and enlarged livers) at 10,000 ppm exposure. A medical expert in thyroid chemistry who has reviewed inhalation test data for the related compound CF<sub>3</sub>I has noted that rats are much more sensitive to iodine levels than humans, and concluded that humans should suffer no effects at the recommended average 8-hour exposure level (AEL) of 150 ppmv for CF<sub>3</sub>I (Capen). It cannot be stated positively that the same reasoning can be applied to the IFC solvents, but it seems likely.

Cardiac sensitization inhalation tests were performed on PFBI. Many gaseous or volatile hydrocarbons and halocarbons sensitize animal hearts to adrenalin through the inhalation pathway. The possibility of death from heart fibrillation after exposure to a halocarbon was first realized in the 1960s. A standard test was developed at that time to measure the relative cardiac sensitization of compounds. The test uses Beagle dogs that are injected with enough ephinephrine (adrenalin) to be barely under the amount that would cause that dogs' heart to go into fibrillation (this dosage is determined for each individual dog in the test group). After injection, the dogs are exposed to concentrations of the test compound in air. The minimum amount of the compound found to induce heart irregularities is the LOAEL, or Lowest Observable Affect Exposure Limit. The NOAEL, or No Observable Affect Exposure Limit, is the maximum concentration the dog can be exposed to with no affect. This test is quite rigorous, since the dogs are already just below the point of fibrillation due to the very high ephinephrine level, and the test was not originally intended to established exposure limits. It has been estimated that the ephinephrine levels used in this test may be 100 times or more higher than would be seen in even a very frightened test subject (Vinegar). The cardiac sensitization test's relevance is being questioned, but it remains the standard at this time. PFBI had a No Observable Adverse Effects Limit (NOAEL) of 0.4% (4,000 ppm), and a Low Observable Adverse Effects Limit (LOAEL) of 0.6% (6,000 ppm) in this test. PFBI's NOAEL is significantly higher than that of TCA (i.e., it is significantly less cardiac sensitizing than TCA), and only slightly lower than that of trichloroethylene (TCE). Figure 3 shows the comparison graphically.



**Figure 3. Comparison of Cardiac Sensitization NOAELS and LOAELS for Solvents**

The aquatic toxicity of PFBI is considerably greater than for common chlorinated solvents. The 96 hour Fathead minnow  $LC_{50}$  was 2.3 ppm by weight for PFBI, compared to 40 ppm by weight for TCE and 53 ppm by weight for TCA.

Biodegradability testing was conducted by HLS in accordance with EEC Methods for Determination of Ecotoxicity Annex to Directive 92/69/EEC (O.J. No. L383A, 29.12.92) Part C, Method 4-E “Determination of Ready Biodegradability Closed Bottle Test” and the OECD Guideline for Testing of Chemicals No. 301D “Ready Biodegradability: Closed Bottle Test.” Over 28 days, a mean PFBI concentration of 59 mg/L showed maximum oxygen depletion in the test vessels equivalent to 9% biodegradation, relative to the theoretical oxygen demand. Therefore, PFBI cannot be termed readily biodegradable as the ‘pass level’ of 60% was not attained. However, PFBI was not found to be inhibitory to activated sewage sludge bacteria under the conditions of this test.

### **Regulatory Status**

PFBI is not a RCRA listed substance, but spent solvents are typically RCRA listed. The value of PFBI and its recoverability make it highly unlikely that spent liquid PFBI would be disposed of as hazardous waste.

For regulatory purposes, a chemical is classified as a volatile organic compound (VOC) if, when released into the air in the presence of sunlight and other common urban air contaminants, its breakdown results in production of higher ozone levels than an equivalent amount of ethane released (the standard). VOC testing on PFBI was conducted by the Environmental Science and Engineering Department at the University of North Carolina at Chapel Hill under the direction of Dr. Harvey Jeffries. The test is conducted on a summer day with high solar irradiance. Shortly before dawn a synthetic mixture simulating urban smog is injected into both of two large, clear plastic chambers, followed by samples of ethane into one chamber and the test substance into the other. The temperature, solar irradiance, and levels of ozone and nitrogen oxides are monitored until after sunset (about 13-hours total for the test). PFBI created more ozone than the ethane, and so would probably not be VOC-exempt, although there is an exclusion for point sources below a certain level of emissions per year.

The U.S. Environmental Protection Agency (EPA)'s Significant New Alternatives Policy (SNAP) program approves replacements for ozone-depleting substances. An application for Ikon<sup>®</sup> Solvent P has been submitted to EPA.

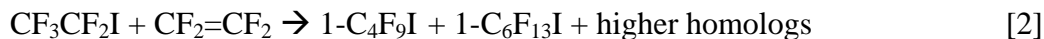
### **Occupational Exposure Assessment**

Waldemar S. Nelson and Company, Inc. (Nelson) performed an occupational exposure assessment on PFBI. PFBI was compared to trichloroethylene, 1,1,1-trichloroethane, 1,1,2-trichloroethane, and CFC-113 using existing data to assess its relative occupational exposure. Nelson concluded that worker exposure to PFBI needed to be limited to 73 ppmv or less at present to freely substitute PFBI for other solvent chemicals without a potential increased health risk. This assumed the worst case (i.e., maximum continuous exposure level at the TLV) for the solvent, and it was Nelson's opinion that this assumption exaggerated anticipated exposure levels in a modern cleaning facility. Nelson stated, "It is unlikely that the exposure levels at a modern degreasing facility would approach the TLV for the solvent in use. If the real exposure level was far below the TLV, it would be far easier to achieve a level of comfort with the anticipated exposure to IKON-P." Nelson concluded that site-specific exposure information would be needed to evaluate this properly. Personnel protection equipment Nelson recommended for PFBI was similar to that for 1,1,1-trichloroethane and trichloroethylene.

### **Synthesis, Price, and Availability of the IFC Solvent**

One of the greatest barriers to widespread use of IFC-based solvents is their current high cost. At present they are still essentially research chemicals, although PFBI's price continues to decrease and is now at about \$60/lb versus over \$200/lb several years ago. Successful introduction will require manufacturing PFBI at a sufficiently low cost that its selling price will be competitive with other alternative solvents.

The current method used for manufacturing PFBI is not disclosed in the literature, but we know from published patents and personal communications that PFBI is now made from tetrafluoroethylene. Tetrafluoroethylene ( $\text{CF}_2=\text{CF}_2$ ) is a relatively inexpensive monomer used in manufacturing Teflon (a polymer of tetrafluoroethylene). Appropriate reactions of tetrafluoroethylene yield pentafluoroethane and higher even-carbon homologs, as shown in Reactions [1] and [2].



EETEC personnel identified and evaluated a number of alternative synthetic routes, including the Hunsdiecker reaction (iodination with decarboxylation of a fluorinated carboxylic acid), and alternative gas-phase reactions of several types. It was found that a modification of the gas-phase synthesis of PFBI from tetrafluoroethylene was by far the least expensive synthetic method. The yield reported in the literature is about 90% PFBI. EETEC's chemical engineering personnel prepared a conceptual design for a facility based on this process, producing 5 million pounds of PFBI per year. Equipment costs, materials costs, and operating costs were estimated from the design. Iodine is the principal cost driver in the synthesis. At the present bulk iodine cost of about \$22/kg, the estimated cost of PFBI production is \$18/kg. Assuming a markup of 25% by the manufacturer, 30% by the distributor, and a royalty of about \$2/kg, this gives a retail selling price for PFBI of about \$31/kg. This price is competitive with other fluorinated solvents



such as HFE-7100, and PFBI is a much more effective cleaning solvent than HFE-7100. Assuming bulk iodine price drops back to near its historic level, say \$11/kg, PFBI could be produced for an estimated \$15/kg. Under the same assumptions as above, the retail price of PFBI would be about \$26/kg, significantly less than HFE-7100.

The available data indicate that iodine supply for producing PFBI and other IFCs as replacements for CFCs, HCFCs, and halons will not be a problem. Present world production of iodine is approximately 15 million kilograms per year. Currently, iodine prices are near a modern all time high due to China's decision several years ago to iodize their table salt. This decision caught iodine producers by surprise and raised iodine prices. New iodine production facilities are being built. Iodine price should return closer to its historic level of about \$11/kg. Proven worldwide reserves of iodine recoverable at less than \$15/kg are about 6.4 billion kilograms (Bureau of Mines). In addition, the oceans contain an estimated 34.5 billion kilograms of iodine, part of which can be recovered directly during extraction of chlorine, bromine, or magnesium from seawater, or indirectly by collecting and processing kelp. Seaweeds of the Laminaria family accumulate up to 0.45% iodine on a dry weight basis; before 1959 seaweed represented a major source of iodine. At least one company in China is now producing iodine extracted from seaweed at a quoted price of \$23.50/kg. The price of iodine recovered from seaweed should decrease as production volume increases. Cultivation and harvesting of seaweed for iodine and food products such as alginates can create an alternative source of income for coastal peoples, reducing economic pressure to over-fish and providing marine habitat.

## **CONCLUSIONS**

If PFBI is produced in quantity at a reasonable cost, it should be an effective substitute for CFC-113 and chlorinated solvents in a variety of critical cleaning and analytical applications.

## **ACKNOWLEDGEMENTS**

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