



The Benefits of Chlorine Chemistry in Fluorocarbons

PREPARED FOR:

**Chlorine Chemistry Division of the
American Chemistry Council**

December 2007

Copyright © 2007 by Whitfield & Associates ALL RIGHTS RESERVED.

Reproduction or distribution of this report in whole or in part prohibited, except by permission of Whitfield & Associates or the Chlorine Chemistry Division of the American Chemistry Council.

The Benefits of Chlorine Chemistry in Fluorocarbons

Fluorocarbons are highly engineered specialty materials that often have initial costs exceeding those of the materials with which they compete. They are used in a wide variety of difficult applications because their unique chemical and physical properties provide consumers with attributes such as efficiency, safety, long life and low life-cycle cost that cannot be obtained with other materials. Substitutes for these materials are available in all applications in which they are currently used, but the alternative materials and processes are not as efficient and substitution costs are high.

We estimate that almost \$400 million in new investments would be required in the United States and Canada to produce the alternative materials and processes that would substitute for fluorocarbons if they were not available, and that the costs of the 54 million new systems per year that would have to use alternative refrigerants would be about \$8 billion per year. In addition, consumers would be required to spend an additional \$3.2 billion per year to operate and maintain them since they would generally be more complex, less efficient and have shorter service lives. These costs exclude any costs that will be born by consumers as the CFCs and HCFCs that are currently in use are phased down by regulatory action. The value of chlorine chemistry can be extremely high in certain instances, as is the case with fluorocarbon-containing metered dose inhalers, for which substitution costs are estimated at \$1.2 billion per year, more than 50 times the cost of the fluorocarbon contained in them.

These increased costs, which consumers would bear in the absence of access to fluorocarbons represent the value of chlorine chemistry to them. For the most part these products do not contain chlorine in the substances themselves, but chlorine chemistry is essential to their production.

Introduction

Fluorocarbons are a class of chemicals widely used in consumer, industrial, and medical applications ranging from refrigeration and air-conditioning equipment to non-stick cookware, and metered dose inhalers. Most of these chemical compounds have a similar structure consisting of the elements fluorine and carbon in combination with other elements that may include hydrogen, chlorine and bromine. Here is a quick summary of the nomenclature of these products:

- Fluorocarbon compounds containing bromine are known as Halons,
- Fluorocarbon compounds containing only chlorine and fluorine on the carbon skeleton are known as CFCs,

- Fluorocarbon compounds that contain hydrogen as well as chlorine and fluorine are known as HCFCs,
- Fluorocarbon compounds that contain only hydrogen, fluorine and carbon are known as HFCs,
- Fluorocarbon compounds that contain only fluorine and carbon are known as perfluorocarbons, or PFCs, and
- Fluorocarbon compounds with ether linkages are known as hydrofluoroethers, or HFEs.

The physical and chemical properties of these compounds depend on the number of each kind of element present and their locations on the molecule. Because they are non-corrosive, inert under normal conditions and have useful thermodynamic properties, they came into widespread use as refrigerants, displacing toxic or hazardous compounds such as ammonia or propane. Many other applications have been developed including those in which the materials are transformed into other fluorinated compounds or are used as solvents, blowing agents or propellants.

In the mid 1970s a number of atmospheric scientists became convinced that some fluorocarbons, as well as other compounds, could migrate through the troposphere and decompose in the stratosphere, setting off a chain of chemical reactions that would result in the destruction of ozone molecules that shield the earth from the sun's harmful UV radiation. Confirmation of their predictions by various measurements resulted in regulatory actions in the United States, Canada and around the world. The Montreal Protocol on Substances that Deplete the Ozone Layer was developed under the sponsorship of the United Nations Environmental Program and became effective in 1989. The original agreement has been amended several times, most recently in 2007, to strengthen its provisions and accelerate the phase-out schedules for some compounds.¹

In the United States the Environmental Protection Agency is required under the terms of the Clean Air Act and its Amendments to stipulate the permissible conditions of use for fluorocarbons and other ozone depleting substances, including their manufacture, controls on potentially emissive uses, recycling, labeling, disposal, and the use of alternatives. The Montreal Protocol established different phase-down schedules for ozone depleting compounds in developed and developing nations. As a result of these agreements and regulations the following actions have been taken in the United States and Canada with respect to fluorocarbons:

- The production and domestic use of CFCs in new equipment has been banned, except for "essential uses" such as reagents, in metered dose inhalers, and in uses where they are chemically transformed into other materials.
- The production of Halons for domestic use in new equipment has been banned.
- Production and domestic use of some HCFCs has been banned in new equipment and the remainder will be gradually phased down according to an agreed upon schedule. Use as intermediates in the production of other

¹ Nations Speed Up HCFC Elimination," *Chemical & Engineering News*, pg. 11, October 1, 2007.

materials is permitted, as is limited use in the production of certain types of foams.

- All refrigerants must be captured and recycled when removed from existing equipment. The recycled material is available for reuse.

At this time there are no regulations yet in force in the United States or Canada dealing with gases that may influence global climate change, often called greenhouse gases. These gases contribute to a slow warming of the earth. However, it is probable that this situation will change and greenhouse gas emissions will be come under some form of regulatory regime.² The major source of these emissions is carbon dioxide; however, fluorocarbons also have global warming potential. Given the large band of regulatory uncertainty on this issue, we have not considered this factor in the analysis.

The HFCs are not regulated under the terms of the Montreal Protocol since they have no ozone depletion potential, although they could be regulated under a global warming regime. This analysis evaluates the benefits of chlorine chemistry in fluorocarbons *only for those compounds and uses that are and will be permitted under the terms of the Montreal Protocol and other existing governmental regulations.*

Chlorine Chemistry in the Production of Fluorocarbons

Fluorocarbons are manufactured by the controlled fluorination of an organic starting material that is selected to produce the desired product. The fluorination reactions may be carried out in either the liquid or gaseous phase at carefully controlled conditions and in the presence of an appropriate catalyst. The fluorination reactions may produce significant amounts of co-products and some by-products in addition to the desired product. Yields of desired products can exceed 90% of the theoretical yields.

Since CFCs and HCFCs contain chlorine on the molecule, chlorine chemistry is intrinsic to their production. Control of the fluorination process and of the distribution of co-products and by-products, however, may be facilitated by utilizing starting materials that contain more chlorine than is required on the final products. In these cases the extra chlorine is converted into hydrogen chloride and separated from the products. This approach was quite common in the production of CFCs and HCFCs, and typical starting materials include methylene chloride, chloroform, carbon tetrachloride, trichloroethylene, perchloroethylene and trichloroethane. The presence of chlorine on the molecule promotes favorable reaction rates and improved commercial operations.

This approach is also used in the production of HFCs that do not contain chlorine on the molecule. Methylene chloride, chloroform, vinyl chloride, trichloroethylene, perchloroethylene, and trichloroethane can be used to produce HFC-23, HFC-32, HFC-125, HFC-134a, HFC-143a and HFC152a, for example.³ Multiple products, including

² Proposals to regulate greenhouse gases include cap-and-trade systems, carbon taxes, mandates, efficiency standards, and combinations of these methods. In January 2005 the European Union commenced operation of a cap-and-trade emissions trading system.

³ An identification scheme has been developed for refrigerant materials that characterize fluorocarbons in terms of the number of fluorine, hydrogen and carbon atoms on the molecule and their isomeric structure. Thus, for example, CFC-12, or R-12, is dichlorodifluoromethane.

HCFCs and HFCs, may be made from a common starting material by controlling the extent of fluorine in the reaction or its location on the molecule. It is also possible to conceive of chemistries that can produce HFCs from chlorine-free starting materials. For example, HFC-152a has been produced by the selective fluorination of acetylene, although that process is no longer operated commercially in North America.

As mentioned above, fluorocarbons are consumed as intermediates in the production of fluoropolymers and fluoroelastomers. When CFCs or HCFCs are used as the starting material, chlorine may be removed during the production of the monomer and would not appear on the polymer, unless a chlorinated fluoropolymer were being produced, but chlorine chemistry is implicated in the production of the product nevertheless. Conversion of HFCs into fluorinated polymers would also involve chlorine chemistry if the HFC starting material were based on a chlorinated precursor.

In summary, except for HFCs that are derived from chlorine-free starting materials, consumers benefit from chlorine chemistry in the production of fluorocarbons and the products derived from them because chlorine chemistry is integral to their production. In the remaining sections of this paper, we discuss the uses and possible substitutes for fluorocarbon products and the economic benefits to consumers estimated on the basis of a scenario in which these products and applications are no longer available to them.

Uses and Substitutes for Fluorocarbons

The impact of production bans, phase-outs and emission reduction requirements has changed fluorocarbon consumption patterns for individual materials and generally reduced total consumption. The estimated current consumption profile for fluorocarbons in the United States and Canada is summarized in Table 1.

Table 1
Consumption of Fluorocarbons in the United States and Canada, 2005

Application	Percent Consumed
Refrigeration and air conditioning	49
Intermediates for polymer production	33
Foam blowing agents	10
Aerosol propellants	5
Solvent cleaning and degreasing	1
All other uses	2
Total	100

Source: Whitfield & Associates estimates.

Mixtures of fluorocarbons and other inorganic and organic refrigerant compounds are also assigned specific identifying codes. The codes are listed in various references, e.g. American Society of Heating, Refrigerating and Air-Conditioning Engineers (ASHRAE) publication 34-1992. The fluorocarbons will be characterized in this research as being either CFCs, HCFCs or HFCs with the appropriate code appended when a specific compound is identified.

Consumption of all fluorocarbon products in 2005 amounted to about 350,000 metric tons with a market value of about \$3.5 billion. Consumption levels in 1988 (pre-Montreal Protocol) were 25% higher than volumes produced today. New capacity is being installed as required to produce new fluorocarbon products. Consumption in refrigeration and air conditioning has grown less rapidly than the growth rate of Gross Domestic Product (GDP) over the last decade due to the requirement to capture and recycle the refrigerants, thereby reducing the need for virgin material. Consumption in foam blowing and solvent applications has decreased as these uses are being phased out in many applications. On the other hand, consumption of fluorocarbons as intermediates in the production of fluorinated polymers and elastomers has grown faster than the growth rate of GDP as these highly-valued products capture new applications. Consumption of fluorocarbons and alternatives in these applications are discussed in more detail below.

Refrigeration and Air Conditioning. Fluorocarbons have been used widely as refrigerants for many decades because they are chemically stable, have excellent thermodynamic properties, and they are relatively nontoxic, nonflammable, and noncorrosive. Consumers are most familiar with their use in household refrigeration and space conditioning systems and in automotive air conditioners. The favorable attributes of fluorocarbons result in their classification as Group 1 refrigerants, whereas toxic alternatives such as methylene chloride or ammonia are classified as Group 2 and flammable and explosive alternatives such as propane, butane or pentane are classified as Group 3 refrigerants and are subject to much more stringent design and operation standards. CFC-type refrigerants, particularly R-12⁴, were used historically in many refrigeration applications; however, production of these CFCs has virtually ceased for emissive uses. Consumers who need to service existing refrigeration equipment may purchase recycled CFCs as long as supplies are available or until the old equipment is replaced.

Fluorocarbon refrigerants function by removing heat at low temperatures and pressures by evaporation, and then being compressed and condensed to reject that heat at higher temperatures and pressures. Selection of the optimum refrigerant in a particular application depends on many factors, including the temperatures at which the heat will be removed and rejected, the amount of heat that will be removed per unit time, the nature of the service (i.e. continuous and steady or variable), and any size or other mechanical design constraints on the refrigeration system. These factors influence the physical size of the components, the type of compressor and lubricants used, the inventory of refrigerants required, and the service and maintenance requirements of the system. In some cases, blends of different fluorocarbons, or blends of fluorocarbons and other compounds, are used as refrigerants for the properties required to optimize particular applications. This interplay of factors constrains designers' abilities to substitute one refrigerant for another without total redesign of the refrigeration system. The types of fluorocarbons for major types of refrigeration systems currently in use and possible substitutes are summarized in Table 2.

⁴ Consumers may be familiar with this product when sold under various brand names such as Freon, Genetron or Forane.

Table 2
Current Use of Fluorocarbons as Refrigerants and Possible Substitutes

Type of Refrigeration System	Percent of Refrigerant Fluorocarbon Consumption	Fluorocarbons Used in Current Systems ¹	Potential Substitutes in These Systems ²
Residential and commercial space conditioning (coolers, chillers and heat pumps)	33	HCFC-22, HFC-134a, HFC-125, and HFC-32 as blends	HFC-134a, HFC-245fa, HFC-236, HFC-32/125, HFC-125/143a/134a, HFC-32/125/134a, ammonia (vapor compression and absorption), hydrocarbons
Commercial and industrial systems ³	30	HCFC-22, HCFC-124, HFC-125, HFC-143a, HFC-134a, HFC-152a	HFC-134a, HFC-125/143a/134a, HFC-125/143a, HFC-32/125/134a, ammonia, hydrocarbons, CO ₂
Mobile systems	23	HFC-134a	HFC-152a, CO ₂ , HFC-134a
Warehouses and Cold Storage	7	HCFC-22, HFC-125, HFC-143a	Ammonia, HFC-125/143a/134a, HFC-125/143a, hydrocarbons, CO ₂
Industrial Processes	6	HCFC-22, HFC-125, HFC-134a, HFC-143a	Hydrocarbons, ammonia, CO ₂ , HFC-125/143a/134a, HFC-125/143a, HFC-32/125, various PFCs
Household refrigerators/freezers	1	HFC-134a	Hydrocarbons, ammonia

(1) Accounting for at least 95% of current consumption, excluding continued use of CFCs in existing equipment.

(2) Substances not under phase-down (e.g. HCFCs or HCFC blends), not currently used in specific applications, and in-kind and not-in-kind substitutes for fluorocarbons. Blends are shown as composed of constituents.

(3) Includes refrigerators and freezers in retail establishments and refrigerated transport.

Source: Whitfield & Associates estimates.

This summary shows that fluorocarbons without ozone depletion potential such as HFC-134a and fluorocarbon blends are available and being used for many but not all applications. Ammonia-based refrigeration systems currently account for a very large share of those currently used in cold storage facilities and a significant share in industrial systems for process cooling and for chillers, for example. They were in use in household refrigeration systems as recently as 60 years ago when they were displaced by fluorocarbons. While expanded use of ammonia and hydrocarbons in industrial and commercial applications is possible, their reintroduction in household appliances does not seem likely because of safety concerns. National and local building codes may preclude their use in residential and some commercial applications unless specific, costly measures are taken to isolate the hazardous materials.

Household refrigeration systems based on hydrocarbons have been introduced in Europe, and could be the most likely substitute for fluorocarbons despite the safety issues. Typically refrigerator sizes and refrigerant charges in Europe, however, are smaller than

in the United States and Canada, so that safe operation is easier to insure. Either ammonia or hydrocarbon-based systems could be used in all other applications, although design requirements for safety, e.g. to contain releases during accidents, could make them much more complex. The safety concern of automakers has led them to evaluate the use of alternative types of refrigeration solutions, including the use of carbon dioxide as a refrigerant.

Intermediates for Polymer Production. Consumption of fluorocarbons as intermediates for the production of fluorine-containing polymers and elastomers represents the second most important use of these compounds, a consumptive use that is exempted from the regulations directed at ozone-depleting materials. Consumers are perhaps most familiar with the fluoropolymers that impart “non-stick” properties to cookware. However, these materials find widespread use in industrial, commercial, and consumer applications in which their durability, chemical resistance, lubricity and dielectric properties are superior to less costly alternatives. Fluoroelastomers are valued for their resistance to a variety of solvents and chemicals as well as their excellent mechanical properties and heat resistance. They are specified in demanding applications in industrial uses where their superior performance justifies their higher cost vis-à-vis alternatives, and in difficult automotive under-the-hood applications such as hoses, seals and gaskets that are exposed to high temperatures, fuels and lubricants.

The primary raw materials used to produce fluoropolymers and fluoroelastomers are the HCFCs chlorodifluoromethane and chlorodifluoroethane (R-22 and R-142b) and HFC-152a, difluoroethane. While there are many resin grades with differing compositions and properties, the largest volume fluoropolymer resin is polytetrafluoroethylene, familiar to consumers under the brand name Teflon®. Consumption of fluorinated polymers and elastomers in the United States and Canada has grown at rates of more than 5% per year over the last decade, well above the growth rates of other commodity polymers and elastomers. Generally, they compete with a variety of other materials based on performance in service and life cycle cost, not on price. Some applications and potential substitutes for fluorine-containing polymers and elastomers are listed in Table 3.

Table 3
Applications and Potential Substitutes for
Fluorocarbon-Based Polymers and Elastomers

Material	Consumption ('000 MT)	Major applications	Potential Substitutes¹
Polytetrafluoroethylene (PTFE)	24.4	Chemical process equipment and fittings, mechanical parts (e.g. seals, bushings) wire and cable insulation, cookware coating, lubricants, textile fibers and laminates, automotive components	Corrosion resistant metals (e.g. stainless steel, Hasteloy, zirconium, titanium, high nickel alloys), other polymers (e.g., PVC, nylon, polyimide, silicones, epoxy)
Fluorinated Ethylene-Propylene (FEP)	12.3	Coatings for wire and cable, release and lamination films, chemical processing equipment and fittings	Corrosion resistant metals and other polymers
Polyvinylidene Fluoride (PVDF)	11.6	Architectural coatings, chemical processing equipment, cable insulation	Epoxies and other polymers
Fluoroelastomers	7.6	Automotive under the hood components, seals and fittings in aerospace and chemical process equipment, specialty hoses and tubing	Other elastomers (SBRs, nitriles, silicones, TPEs, chloroprene)
Perfluoroalkoxy polymers (PFA)	2.4	Parts and piping for semiconductor manufacturing, wire and cable insulation	Limited choices among corrosion resistant metals and other polymers
Polyvinyl Fluoride (PVF)	2.1	Laminates for architectural and automotive applications, protective and release films	Other polymers (vinyls, polyesters, polyolefins)
All other fluoropolymers (E-CTFE, ETFE, CTFE-VDF, THV, PCTFE, amorphous)	4.4	Specialty uses as chemical process equipment, wire and cable coatings, specialty packaging, military and aerospace components, automotive components	Corrosion resistant metals and other polymers in specific applications, with limited choices in many cases

(1) Excluding substitution by other fluoropolymers
Source: Whitfield and Associates

Fluoropolymers and fluoroelastomers are specialty materials that find use in applications where service conditions and requirements are so severe that alternative, lower priced materials do not provide adequate performance. While substitutes can be found for these materials in all of their applications, the range of choices in any particular use may be quite limited because of the specific requirements of the service. Certain consumer and military electrical codes require the use of FEP or PVDF as jacketing for plenum cable, for example, because its properties, including flame resistance, are superior to alternatives. Components fabricated from PFA are used to provide the ultra pure water required in semiconductor manufacture and are used in corrosive situations since they do not release undesirable corrosion products. In many cases the preferred substitute for a fluorocarbon polymer would be another fluorocarbon polymer.

Prices for the polymers can range from less than \$10 per kilogram for commodity grades to more than \$100 per kilogram for smaller volume specialties. Fluoroelastomer prices

are in the \$50 per kilogram range, and the market value of these materials in the United States and Canada was about \$1.6 billion in 2005.

Foam Blowing Agents. Foam blowing agents are used to impart porosity, reduce the density and increase thermal resistance of bulk polymer materials such as polyurethanes, polystyrene, and polyolefins. Control of blowing conditions can result in the formation of closed cells that help retain the blowing agent within the foamed matrix. If the blowing agent has low thermal conductivity, the foamed products will have good insulating properties. CFCs were the main blowing agents in the United States and Canada until their use was banned. They were replaced by hydrocarbons (particularly pentane), carbon dioxide and carbon dioxide/water systems, and HCFCs but HCFCs were only a transition solution and their use has been subject to phase down schedules. Newer fluorocarbon blowing agents – HFC-134a, HFC-245fa, and HFC-365mfc – were developed for applications where their performance advantages and properties justify their higher prices.

The type and amount of blowing agent that give optimum insulating or cushioning performance to foams depend both on the polymer material and the circumstances of its use. For example, where thicker foams can be used for insulation in architectural applications, hydrocarbons such as pentane may be the blowing agent of choice for rigid polyurethane foams. Where thin, high-performance blown-in-place polyurethane foams are used in household refrigerators, however, HFCs would be preferred because they have lower thermal conductivity and produce better insulating foams. In other polyurethane applications, and for other polymers, carbon dioxide or carbon dioxide/water blowing agents might be preferred given the cost-performance trade offs. Depending on the type of polymer system, the major alternative blowing agents to HCFCs are listed in Table 4.

Table 4
Blowing Agents for Polymer Foam Systems

Polymer System	Possible Blowing Agents ¹
Rigid Polyurethane	HFCs, CO ₂ /H ₂ O, pentanes, butanes/pentanes with CO ₂
Flexible Polyurethane	HFCs, liquid CO ₂ , CO ₂ /H ₂ O, acetone, methylene chloride, polyols, H ₂ O/variable pressure foaming
Polystyrene	HFCs, CO ₂ , hydrocarbons
Polyolefins	CO ₂ , pentanes
Polyisocyanurate	Pentanes

(1) Other than HCFCs.

Source: Whitfield & Associates estimates.

The hydrofluorocarbon blowing agents compete with alternatives in all systems except polyolefins and polyisocyanurate foams based on the performance required of the final product. HFC-134a and HFC-245fa have thermal conductivities that are essentially the same as pentane, are non-flammable, less soluble in the polymer systems, are retained more completely within the foam matrix, and are easy to apply. They provide improved insulating value and longer life in applications where these attributes are required. Other

blowing agents have lower cost per unit weight but do not provide equivalent insulating or structural support. In some cases their use may be constrained by safety or environmental concerns, either at the manufacturing stage or in use. Hydrocarbon emissions are constrained because of limits on volatile organic compounds (VOC) emissions and some hydrocarbon blown foams may not meet the requirements of fire safety codes.

Aerosol Propellants. The functions of fluorocarbon and other aerosol propellants are to expel and disperse the contents of a container in a controlled manner. This is done through selection of the proper container pressure, dispersing system design, and compatibility between the aerosol material and the compound being dispersed. CFCs formerly were used as aerosol propellants in a wide variety of consumer products like hairspray, deodorant, and paint. Consumption in this application exceeded consumption as refrigerants until this use was banned in 1978 in the U.S. and several other countries. They had been selected because they were relatively low cost, nontoxic, nonflammable, and were compatible with the materials being dispersed.

Compatibility with the container contents and FDA approvals are particularly important considerations in propellant selection for medical applications such as metered dose inhalers (MDIs). CFCs have largely been replaced in metered dose inhalers by HFCs (particularly HFC-134a and HFC-227ea) for use by patients suffering from asthma or chronic obstructive pulmonary disease (COPD) who require periodic doses of salbutamol. MDIs command a 90% share of the market in North America for such applications, the remainder being served by dry powder inhalers (DPIs). Substitution by other, non-fluorocarbon propellants is very difficult in medical applications, and the most likely alternative would be substitution by DPIs where this is technically feasible and medically possible.

The use of HFC-134a, HFC-227ea, and HFC-152a is permitted in aerosol applications because they have zero ozone depleting potential. Consumers value their performance properties of inertness, vapor pressure, and nonflammability, advantages that can justify their higher price in certain applications. The major alternatives are lower cost hydrocarbons – propane and butane – as well as a variety of other aerosol propellants such as dimethyl ether, carbon dioxide, nitrogen and water-based systems. Consumption of these alternatives as aerosol propellants is much greater than that of fluorocarbons. However, use of the lower cost hydrocarbon alternatives may be constrained by both safety considerations due to their flammability and to limitations on the allowable release of VOCs. Not-in-kind substitution would be possible in some applications through the use of alternative delivery systems such as hand pumps for liquids and systems analogous to the DPIs used as medical devices.

Solvent Cleaning and Degreasing. Prior to 1988, fluorocarbons (particularly CFC-113) had been used in a variety of solvent cleaning and degreasing applications because of their convenient boiling points, low surface tension, purity and stability, low toxicity, nonflammability and high solvency for greases and contaminants. Fluorocarbon solvents were used mainly in aerospace, electronics and precision cleaning applications where parts had to be cleaned to exacting standards, and to a much lesser extent in other metal and parts cleaning applications where they competed with other, lower cost chlorocarbon

solvents. Except for government sanctioned consumption in specialty military and aerospace applications, CFCs are no longer used in these applications and HCFCs are subject to phase-down schedules.

Users of the banned fluorocarbons have switched to alternative cleaning methods. Two sometimes complimentary approaches have been taken: (a) modification of the parts production processes to allow alternative cleaning techniques and (b) use of other solvents. Examples of these approaches are presented in Table 5.

Table 5
Alternatives to the Use of CFCs and HCFCs in Solvent Cleaning and Degreasing Applications

Alternative Processes	Alternative Solvents
Inert gas or no or low-flux soldering	PFC-14, PFC-51-14, PFC-116, HFC-356mfc, HFC-43-10mme, HFE-449s1, HFE-569sf2
Plasma arc or UV/ozone cleaning	Methylene chloride, trichloroethylene, perchlorethylene, n-propyl bromide, high (>55°C) flash point hydrocarbons
Supercritical CO2 or CO2 snow cleaning	Isopropyl alcohol, propylene glycol ethers, n-butoxyethanol, methyl ethyl ketone, various other oxygenates N-methyl pyrrolidone, d-limonene water-based solvents and detergents

Source: Whitfield & Associates estimates.

Even if revising the parts production process to eliminate the need for subsequent cleaning generally is not possible, it may decrease the severity of the cleaning operation, facilitate the use of alternative techniques and solvents, or simply reduce the consumption of solvent. Alternative fluorine-containing solvents in these applications include fully fluorinated compounds (PFCs), hydrofluoroethers (HFEs) and HFCs. Other substitutes include chlorinated and oxygenated compounds, water-based systems and other organic solvents with specific, desired properties. The cost of these alternative solvents and the requirement to limit emissions of VOCs has forced consumers to “tighten up” their solvent cleaning and degreasing processes to reclaim and recycle as much solvent as possible. This has resulted in significantly reduced consumption of all solvents in these applications. It has also resulted in significantly more complex solvent cleaning systems and operations.

All Other Uses. This category includes a variety of uses that formerly represented significant volumes of Halons, CFCs, and HCFCs. Halons have been replaced as fire suppressing agents with other chemicals including the fluorocarbons HFC-23, HFC-125, and HFC-227ea, and other PFCs or iodinated compounds. Substitution in this application is imperfect because Halons were used to control and extinguish difficult-to-contain fires where water-based systems could not be used effectively, such as aircraft, ships, computer centers, and telephone switching centers.

Previously CFCs and HCFCs were used in combination with ethylene oxide to sterilize medical equipment at ambient temperatures. In most of these applications, CFCs and HCFCs have been replaced with HFC-125/ethylene oxide mixtures or mixtures of ethylene oxide with other inert gases or with other sterilization techniques based on gamma radiation. Various fluorocarbons also have been used as process solvents in the manufacture of pharmaceutical and fine chemical compounds and as sterilants and solvents in the food industry. The CFCs and HFCs formerly consumed in these applications largely have been displaced by HFC-134a and other non-fluorocarbon solvents or by process alterations. While substitute solvents or not-in-kind substitution to alternative techniques are possible in all cases, substitution may be imperfect or more costly.

The Benefits of Chlorine Chemistry in Fluorocarbons

We know that consumers benefit from the use of fluorocarbons because they select them in preference to available alternatives, even in applications where the alternatives have lower initial costs. Except in cases where HFCs are manufactured from chlorine-free starting materials, these benefits are derived from the chlorine chemistry that is used in their production. The magnitude of these benefits can be determined by estimating the additional costs that consumers would have to bear if the chlorine-based fluorocarbon products were not available. The benefits would be product and application-specific, and their magnitude will depend on the amounts of chlorine-based fluorocarbons that would have to be substituted.

We approach the benefits estimation task from three possible perspectives:

- If no cost effective chlorine-free products or processes can be found, consumers would be forced to forgo altogether using fluorocarbons and products derived from them. We do not believe that such a situation would exist since we believe the necessary substitutes can be found, even if substitution may be imperfect in many cases.
- If cost effective chlorine-free processes can be developed for the production of all HFCs and for all fluoropolymers and fluoroelastomers currently made from CFC and HCFC intermediates, consumers would have to bear the increased costs of the new processes to the extent that they exceed current costs. Direct consumption of CFCs and HCFCs would be forgone but, with few exceptions, these materials have already been displaced or are subject to phase-down schedules.
- If cost effective chlorine-free production processes cannot be developed for fluorocarbons, substitution would occur at the product level using alternative materials that are not derived from chlorine. Consumers would have to bear any increased life cycle costs and potential losses in utility since the alternatives do not generally have the same high level of performance properties.

Chlorine-Free Processes. It may be possible that new chlorine-free chemical processes can be developed for all the HFCs, fluoropolymers and fluoroelastomers described above, except for products that contain chlorine in the final product, such as

poly(chlorotrifluoroethylene/vinyl fluoride), poly(ethylene/chlorotrifluoroethylene) and polychlorotrifluoroethylene. These materials would have to be substituted at the product level to avoid implication with chlorine chemistry. However, the ability to develop a set of theoretical chemical reactions is no guarantee that a cost effective production process can be commercialized based on the particular materials chosen.

Direct fluorination of organic compounds is notoriously difficult to control and often results in the violent breaking of carbon-carbon bonds rather than the desired addition of fluorine. While addition of fluorine to triple bonds is favored thermodynamically, addition to double bonds is not favored unless chlorine is present on the molecule as well. Hydrogen fluoride (HF) gas, which is polymeric, is a more controllable fluorinating agent in the presence of suitable catalysts, but the hydrogen balance of the process may be unmanageable in the absence of an acceptor for it such as chlorine. Obtaining “clean” reactions without the formation of undesired materials is often quite difficult. Electrochemical fluorination processes carried out in liquid HF are theoretically possible but extremely difficult to control, tending to form only fully fluorinated products (PFCs).

Processes based on fluorine or hydrogen fluoride require both careful control of process conditions because of the reactivity of the materials and careful selection of materials because of the corrosive nature of the reactants. Chemical plants to make these materials are, therefore, capital intensive and process economics require a high level of efficiency with few undesired co-products or by-products. Process selection may be strongly influenced by the cost of the starting materials as well as the selectivity of the reactions to the desired products. While commercial production of HFC-152a has been practiced based on acetylene, production based on the more widely available, lower cost ethylene has not. Instead, the ethylene is converted first to vinyl chloride that is, in turn, fluorinated to produce HFC-152a commercially.

In summary, it will be very difficult to develop new, low cost chlorine-free processes for the production of HFCs and the polymers derived from them. The only fluorocarbon that can be produced today without the use of chlorine chemistry is HFC-152a, which is consumed directly in a number of applications and serves as a feedstock in the production of polyvinyl fluoride polymers.

Product Level Substitution. Consumers will bear three different types of costs when substituting other materials for fluorocarbon-based products:

- Increased capital requirements and operating costs for the equipment necessary to produce or use the substitute materials;
- Increased life cycle costs for the use of materials that are less efficient or have shorter service lives; and
- Losses in utility where the substitutes do not perform as well as the fluorocarbon-based materials displaced.

These costs are product and application specific as discussed below. In developing these estimates we have excluded any transition or switching costs that will be born by consumers, such as the research and development costs for new product introductions and the administrative costs for revising codes and standards. *Furthermore, we exclude any*

costs to consumers to develop and use substitutes for CFCs or HCFCs currently in use since they already are subject to being replaced due to regulatory actions.

Refrigerants. Fluorocarbon refrigerants are used in many different types and sizes of systems, with millions of units being placed into service each year in mobile systems and in residences and commercial and industrial establishments. While some equipment has been designed in recent years to be capable of using either HCFC or HFC refrigerants, most cannot be converted from one refrigerant to another nor can they be converted from fluorocarbons to other fluids such as ammonia, carbon dioxide or hydrocarbons. Therefore, new system designs will have to be developed in the absence of fluorocarbons, and these may be more costly to produce and operate than those based on fluorocarbon refrigerants.

Initial costs will be higher for a given level of efficiency because systems designed to use either toxic ammonia or hazardous hydrocarbons must be designed to meet more stringent safety standards. In mobile and residential applications and in some commercial establishments, this may require the use of cascade or secondary loops, which complicate designs and increase costs. This means that the equipment must be larger and more energy may be required to operate it to provide the same level of service.

We estimate that approximately 54 million refrigeration systems per year will have to be designed and built to use alternative refrigerants, about one third each in household refrigeration, mobile refrigeration and residential and commercial stationary space conditioning systems. The incremental initial cost of these systems is estimated to be about \$8 billion per year, with more than half of the additional costs born in the residential and commercial space conditioning sector, 20% in domestic refrigeration and most of the balance in mobile and commercial and industrial systems. The incremental cost to operate them is estimated to be about \$ 1.4 billion per year, with over 80% of the additional costs born in residential and commercial space conditioning and mobile systems. In addition, over \$100 million will be required in additional capital to construct the plants required to produce the new refrigerants.

The increase in annual operating costs results from the operation of more complex, less efficient systems, particularly in the residential and commercial space conditioning and mobile air conditioning sectors. Manufacturers could design more efficient systems for all applications, but doing so could significantly increase initial acquisition costs and consumers might not wish to pay for them at current energy prices.

Intermediates for Polymers. With the exception of polyvinyl fluoride, which can be produced by a technically viable chlorine-free manufacturing process based on acetylene, substitution for fluoropolymers and fluoroelastomers would take place at the product level. Most of the substitution would occur with resins, elastomers, and metals that do not have the properties that consumers value today. While they may have lower initial costs, their life cycle costs are higher than for fluorocarbon-based products they are replacing. Consumers may experience reduced service lives, more frequent replacement and reduced performance.

The incremental capital requirements to produce these substitute products are not large, about \$80 million, because they are all produced currently in far greater volumes for applications not serviced by fluorocarbon-based materials. We estimate, however, that consumers would experience increased life cycle cost and losses in utility amounting to more than \$500 million per year because the substitutes will not provide the same level of service as the fluoropolymers and fluoroelastomers. We estimate that about half of the cost increase is due to substitution for fluoroelastomers and products made from PTFE, with another one third in substitution for the relatively high volume FEP and PDVF products. Unit replacement costs for the other fluoropolymers are about twice as high as the average because substitution is more difficult in the specialty applications they serve.

Foam Blowing Agents. A variety of non-fluorocarbon blowing agents have been in use for some time, but producers of foamed products have continued to use HCFCs and HFCs in applications where they impart better properties to the products at lower cost. These applications could be substituted by the most effective alternative blowing agent or process available, but at additional cost. Incremental capital would be required to convert the blowing process to non-fluorocarbons, and costs would be significant where flammable hydrocarbons were the substitute. While the unit costs of alternative blowing agents such as carbon dioxide or hydrocarbons are much lower than those of fluorocarbons, product performance is not as effective when they are used so that more resin must be blown to obtain a product with equivalent insulating or cushioning value. If insulating performance is compromised to keep initial costs low, the consumer will experience higher life cycle costs in terms of greater heating or cooling costs for products or applications containing that material.

The vast majority of the fluorocarbons currently used as blowing agents are HCFCs to which we attribute no substitution costs. We estimate that the incremental costs to convert existing blowing systems using HFCs to new processes or materials would be about \$50 million. We estimate that the increased manufacturing and life cycle costs of using less efficient products produced with the substitute blowing agents or processes would be about \$25 million per year. This relatively low cost is a result of the relatively small volume of HFCs in these applications; however, the cost represents almost \$9 per kilogram of blowing agent, which is comparable to the materials' price.

Aerosol Propellants. Fluorocarbons hold a minor share in the overall aerosol propellant market today, being used in applications where their properties provide some special advantage that justifies their higher cost, such as in metered dose inhalers (MDIs). Significant development efforts would be required to develop substitute systems that could match the fluorocarbons' performance in these applications. Certain substitute materials could be precluded for some uses for safety or environmental reasons, particularly the hydrocarbons and toxic materials such as dimethyl ether, for example, or where they were incompatible with the materials being delivered. Substitution with compressed gases such as carbon dioxide or nitrogen would require the use of more expensive pressurized containers, and substitution of non-pressurized hand pump dispersing systems would increase container costs and be less effective or technically difficult in many applications, such as the dry powder inhalers (DPIs) used to dispense medications to asthmatics.

Estimates of the costs of substitution of DPIs for MDIs in the treatment of asthma and COPD exceed \$3 billion per year worldwide, which is of the order of 50 times the cost of the HFCs used in the devices.⁵ For the United States and Canada this would mean consumers would incur additional medical costs of \$1.2 billion per year in this use alone, and it is not clear that DPIs could be developed as effective drug delivery devices to dispense the medications required for other conditions. The increased investments to replace filling lines and containers and substitute alternative propellants or delivery devices for all other applications are estimated to be less than \$50 million, with increased annual costs of about \$25 million per year.

Cleaning Solvents. Consumption of HFCs and PFCs as cleaning solvents is small, at about 2,000 metric tons per year, and is restricted to applications where their unique properties provide better performance than alternative solvents or not-in-kind cleaning systems. HFC-152a is not widely used in this application because of its vapor pressure and flash point, but would be a chlorine-free substitute in applications where it could be used. Substitution in most other applications would be far more difficult, and we estimate that new investments of the order of \$35 million and annual costs of about \$10 million per year would be required, mainly because of the increased complexity and reduced performance of the alternative systems.

All Other Uses. This category includes a wide variety of niche applications for fluorocarbons, of which about half are HCFCs for which we attribute no costs of substitution to consumers. Substitution in other cases may be by use of alternative processes or solvents, including chlorine-free HFC-152a, depending on the application. While consumption in this category has decreased significantly in response to regulatory requirements, substitution in the applications remaining is difficult and we estimate that additional capital of about \$70 million and increased costs of about \$30 million per year would be required if consumers did not have access to the fluorocarbon-based products they do today.

Summary. Fluorocarbons are highly engineered specialty materials that often have initial costs exceeding those of the materials with which they compete. They are used in a wide variety of difficult applications because their unique chemical and physical properties provide consumers with attributes such as efficiency, safety, long life and low life-cycle cost that cannot be obtained with other materials. Substitutes for these materials are available in all applications in which they are currently used, but the alternative materials and processes are not as efficient and substitution costs are high.

As shown in Table 6, we estimate that almost \$400 million in new investments would be required in the United States and Canada to produce the alternative materials and processes that would substitute for fluorocarbons if they were not available, and that the costs of the 54 million new systems per year⁶ that would have to use alternative refrigerants would be about \$8 billion per year. In addition, consumers would be

⁵ See the Intergovernmental Panel on Climate Change, *Special Report: Safeguarding the Ozone Layer and the Global Climate System*, Chapter 8, Medical Aerosols, 2006.

⁶ Includes 18.5 million residential refrigerators and freezers, 8.6 million unitary air-conditioners and heat pumps, 8.1 million room air-conditioners, 18.5 million air conditioning systems in passenger cars and light trucks, and 645 thousand vending machines.

required to spend an additional \$3.2 billion per year to operate and maintain them since they would generally be more complex, less efficient and have shorter service lives. These costs exclude any costs that will be born by consumers as the CFCs and HCFCs that are currently in use are phased down by regulatory action.

**Table 6
Summary of Economic Benefits of Fluorocarbons**

Application	Additional Capital Expenditure (\$ MM)	Increased Annual Operating Costs (\$ MM per year)	Increased Initial Acquisition Costs (\$ MM per year)
Refrigeration and Air Conditioning	110	1,410	8,000
Fluoropolymers	80	520	
Foam Blowing	50	25	
Aerosols	40	1,200	
Solvents and Other	100	40	
Total	\$380	\$3,200	\$8,000

Note: Numbers may not add due to rounding.

These increased costs, which consumers would bear in the absence of access to fluorocarbons, fluoropolymers and fluoroelastomers, represent the value of chlorine chemistry to them. For the most part these products do not contain chlorine in the substances themselves, but chlorine chemistry is essential to their production. The value of chlorine chemistry can be extremely high in certain instances, as is the case with fluorocarbon-containing metered dose inhalers, for which substitution costs are estimated at \$1.2 billion per year, more than 50 times the cost of the fluorocarbon contained in them.

Asthma Treatment Has Come a Long Way

French author Marcel Proust was born to bourgeois parents living in Paris. He was a sickly child who suffered chronic asthma attacks. His father, a doctor, could not extricate himself from the widespread notion that asthma and hay fever were often nervous afflictions closely tied to a craving for tenderness. A prominent Parisian specialist of pulmonary disease asserted that asthma was a nervous habit and that it could be cured in a sanitarium, so Proust was sent to a sanitarium in Berne that specialized in treating such "nervous afflictions." Not surprising, his asthma got worse and without fresh air and almost no exercise, he also became prone to repeated bouts of bronchitis, pneumonia and other respiratory infections. Proust ingested caffeine, injected adrenaline, inhaled Jimson Weed, tobacco, and marijuana, and used narcotics in vain attempts to alleviate his asthma. His frustrations can be summed up in his description of an asthma patient as a "poor suffocating patient who, through eyes filled with tears, smiles at the people who are sympathizing without being able to help him."

Treatments for asthma and other pulmonary disease have come a long way since then. The early prototype of an inhaler was introduced in 1860. Made by S. Maw and Son, the ceramic, two-valve device could be used to inhale plain steam or other medicinal ingredients such as Friar's Balsam, an herbal remedy. Pressurized metered dose inhalers (pMDIs) as we know them today, have been available for nearly 50 years and have come to be regarded as the most popular and preferred form of delivery for treatment of asthma and chronic obstructive pulmonary disease (COPD). Nearly 500 million of these devices are manufactured worldwide each year. pMDIs offer a unique combination of reliability, accurate dosing, convenience, and low cost for delivering drugs to the lungs. The phase-out of CFC propellants prompted by the Montreal Protocol has challenged manufacturers to reformulate their pMDIs using more environment-friendly alternative propellants (HFC-134a and HFC-227) which are also based on chlorine chemistry.

Administering drugs to the lungs is highly desirable for a range of drug compounds because the lungs provide a large surface area for deposition and drug absorption as well as a rapid onset of action. Moreover, pulmonary delivery allows the dispensation of small, clinically effective drug doses, causing less systemic side effects. It is also considered a non-invasive treatment when compared to injectable drugs, and it is well tolerated and accepted by most patients. As such, it is not surprising to see the development of pulmonary insulin for the treatment of diabetes. This should drive the market growth for inhaled pharmaceutical aerosols even further.

According to the American Lung Association, approximately twenty million Americans suffer from asthma and about nine million are afflicted by COPD. COPD was the fourth-leading cause of death in the United States in 2002, with annual costs estimated to be \$37.2 billion, which is double that for asthma. The US market asthma and COPD drugs exceeded \$10 billion and \$3 billion in 2005, respectively.

Source: Museum of Royal Pharmaceutical Society; American Lung Association; National Institute of Health; Sharma, O.P. "Marcel Proust (1871-1922): reassessment of his asthma and other maladies" European Respiratory Journal 15 (2000): 958-960; Barnes, Kirsty "Skyepharma finds long-awaited partner for asthma device", Decision News Media, May 23, 2006; Pulmonary Delivery: Innovative technologies breathing new life into inhalable therapeutics, ONDrugDelivery, 2006