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# The Economic Benefits of Chlorine Chemistry in Fluorocarbons in the United States and Canada

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## Executive 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 many applications in which they are currently used, but the alternative materials and processes are not as efficient, in many cases not as effective, and substitution costs can be very high.

We estimate that almost \$1.2 billion in new investments would be required in the United States and Canada to produce alternative materials and processes that would substitute for fluorocarbons if they were not available, and that the costs of the nearly 40 million units per year of new household and commercial refrigeration and mobile and stationary air-conditioning systems that would have to use alternative refrigerants would be about \$5.4 billion per year. In addition, the total additional cost that consumers would be required to spend for all fluorocarbon uses amounts to \$1.5 billion per year to purchase or use chlorine-free alternative products and processes and to operate and maintain the new equipment since they would generally be more complex, less efficient, and have shorter service lives. These costs exclude any costs that would be borne by consumers as the HCFCs and HFCs 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 the new class of more environmentally friendly fluorocarbons known as HFOs. These products do not contribute to ozone depletion and have almost no global warming potential as compared to the fluorocarbons they replace. The HFO family of products also has versatility by being an easy replacement for the HCFC and HFC fluorocarbons formerly used in air conditioning, refrigeration, plastic foam blowing, aerosol propellants, and solvents.

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. The value of chlorine chemistry can be extremely high for many fluorocarbon applications, often exceeding 10 times the cost of the fluorocarbon contained in them.

## Introduction

Fluorocarbons are a class of chemicals widely used in consumer, industrial, and medical applications ranging from refrigeration and air-conditioning equipment, plastic foam blowing agents, fire suppression, aerosol propellants, and solvents to non-stick cookware and metered dose inhalers. Most of the chemical compounds used in these applications have a similar structure that consists 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 and regulatory status of these products:

- Fluorocarbon compounds containing bromine are known as Halons—several of the products in this group are subject to restriction or phase-out due to concerns about ozone depletion or global warming potential.
- Fluorocarbon compounds containing only chlorine and fluorine on the carbon skeleton are known as CFCs—these products are only sold as raw materials and have been replaced world-wide by other fluorocarbons or not-in-kind alternatives.
- Fluorocarbon compounds that contain hydrogen as well as chlorine and fluorine are known as HCFCs—these products are only sold as raw materials in the United States and Canada, but may still be found in air conditioning or refrigeration equipment and are being replaced by other fluorocarbons or not-in-kind alternatives.
- Fluorocarbon compounds that contain only hydrogen, fluorine, and carbon and are derived from saturated hydrocarbons (alkanes) are known as HFCs—these products have replaced both CFCs and HCFCs and do not contribute to ozone depletion, but have global warming potential. They are in the early stages of being replaced by HFOs or not-in-kind technologies in the United States and Canada.
- Fluorocarbon compounds that contain only fluorine and carbon are known as perfluorocarbons, or PFCs—these products typically have restricted uses as they have global warming potential.
- Fluorocarbon compounds with ether linkages are known as hydrofluoroethers, or HFEs—these products typically have restricted uses as they have global warming potential.
- Fluorocarbon compounds that contain only hydrogen, fluorine, and carbon and are unsaturated are known as HFOs. Fluorocarbon compounds that contain hydrogen, fluorine, chlorine, and carbon and are unsaturated are known as HCFOs. These products are replacing HCFCs and HFCs because they have either no impact on ozone depletion in the case of HFOs or nearly no impact in the case of HCFOs, and have extremely low global warming potential.

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 compounds such as ammonia or propane. Many other applications have been developed including solvents, fire suppression, blowing agents, or propellants.

In the United States, the Environmental Protection Agency (EPA) has implemented the Montreal Protocol on Substances that Deplete the Ozone Layer under the terms of the Clean Air Act and its Amendments to stipulate the permissible conditions for use of fluorocarbons and other ozone depleting substances (ODS).<sup>[1]</sup> Also stipulated are conditions involving their manufacture, controls on potentially emissive uses, recycling, labeling, disposal, and the use of alternatives. Currently, the US EPA also regulates fluorocarbons with global warming potential under the Significant New Alternatives Policy (SNAP), 40 C.F.R., Part 82, Subpart G. To prevent the release of these materials with ozone depleting potential, all ODS must be captured when removed from existing equipment. The collected material must be recycled for reuse or destroyed.

<sup>1</sup> The ozone depleting potential of a compound measures the relative power of the compound to degrade the ozone layer compared with a reference compound.

This analysis evaluates the benefits of chlorine chemistry in fluorocarbons *only for those compounds and uses that are and will be permitted under 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.

Chlorine chemistry is intrinsic to the production of fluorocarbons. 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 HFC-152a.<sup>[2]</sup> Multiple products, including 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. It should be noted that some fluoropolymers are produced using chlorocarbons as a starting material.

As mentioned above, fluorocarbons are consumed as intermediates in the production of fluoropolymers, fluoroelastomers, and HFOs. 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. Nevertheless, chlorine chemistry is integral to the production of the product.

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 estimate the economic benefits to consumers if these products and applications are no longer available to them.

<sup>2</sup> 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, HFO-1234yf, or R-1234yf, is 2,3,3,3-Tetrafluoro-1-propene. 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). The fluorocarbons will be characterized in this research as being either CFCs, HCFCs, HFCs or HFOs with the appropriate code appended when a specific compound is identified.

## 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 has generally reduced total consumption. The estimated current consumption profile for fluorocarbons in the United States and Canada is summarized below.

United States and Canadian consumption of all fluorocarbon products in 2014 amounted to about 937 million pounds with a market value of about \$3.5 billion. Consumption in refrigeration and air conditioning has slowed along with the slowdown of residential construction since the economic recession of 2008. Consumption in foam blowing, fire suppression, and solvent applications has decreased as some applications have shifted to not-in-kind alternatives or are being phased out in other applications. On the other hand, consumption of fluorocarbons as intermediates in the production of fluorinated polymers and elastomers has grown faster than GDP as these versatile and high-value products capture new applications. Consumption of fluorocarbons and alternatives in these applications are discussed in more detail below.

### Consumption of fluorocarbons in the United States, Canada, and Mexico, 2014

Application	Percent consumed
Refrigeration and air conditioning	43
Intermediates for polymer production	36
Foam blowing agents	12
Aerosol propellants	8
Solvent cleaning and degreasing	1
All other uses	1
Total	100

Note: Numbers may not add due to rounding.

Source: IHS Chemical Consulting

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### 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 non-flammable fluorocarbons result in their classification by the American Society of Heating, Refrigerating and Air Conditioning Engineers as Class 1 refrigerants, whereas alternatives such as methylene chloride or ammonia are classified as Class 2 and flammable and explosive alternatives such as propane, butane, or pentane are classified as Class 3 refrigerants and are subject to much more stringent design and operation standards.

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 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 in order to achieve the desired properties for 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 the table.

### Current market for fluorocarbons as refrigerants and potential substitutes

Type of refrigeration system	Percent of refrigerant fluorocarbon consumption	Fluorocarbons sold for use current systems <sup>1</sup>	Potential substitutes in these systems <sup>1</sup>
Stationary air conditioning (coolers, chillers and heat pumps)	43	HFC-134a HFC-125 HFC-32 HFC blends	HFC-134a HFC-32/125 HFC-125/143a/134a HFC-32/125/134a HFO-1234yf Ammonia (vapor compression and absorption) Hydrocarbons
Commercial and industrial refrigeration	31	HFC-125 HFC-143a HFC-134a HFC-152a HFC blends	HFC-134a HFC-125/ 143a/134a HFC-125/143a HFC-32/125/134a HFO-1234ze Ammonia Hydrocarbons CO <sub>2</sub>
Mobile air conditioning	24	HFC-134a HFO-1234yf	CO <sub>2</sub> HFC-134a HFO-1234yf
Household refrigerators/freezers	3	HFC-134a	Hydrocarbons Ammonia

(1) Excludes substitution by other fluoropolymers or products based on chlorine chemistry.

Source: IHS Chemical Consulting

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Ammonia-based refrigeration systems currently account for a very large share of refrigerant fluorocarbons used in cold storage facilities. These systems are also heavily utilized in industrial systems for process cooling and for chillers. They were in use in household refrigeration systems as recently as 70 years ago before being displaced by fluorocarbons. While expanded use of ammonia in industrial and commercial applications is possible, the reintroduction in household appliances does not seem likely because of safety concerns. National and local building codes may preclude this use in residential and some commercial applications unless specific, costly measures are taken to isolate the material.

Household refrigeration systems based on hydrocarbons have been broadly introduced in Europe, as well as in Japan, China, and elsewhere, and could be the most likely substitute for HFC fluorocarbons. Automakers in the US are required to charge all mobile air conditioning units with an alternative to HFC-134a as of model year 2021. In Europe, the transition away from HFC-134a is to be fully implemented by 2017. Regional regulations that restrict the use of refrigerants that have high global warming potential have led to the use of low global warming potential alternatives (HFO-1234yf) for automotive refrigeration. Other low global warming potential alternatives have been evaluated or are under evaluation, including carbon dioxide.

### 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 industrial use applications 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 (HCFC-22 and HCFC-142b) and difluoroethane (HFC-152a). While there are many resin grades with differing compositions and properties, the largest volume fluoropolymer resin is polytetrafluoroethylene (PTFE). While PTFE has been commercially available for over 60 years, it continues to find new uses due to its unique properties. Consumption of PTFE in the United States has grown at about the same rate as GDP over the last decade. Other fluoropolymers are growing slightly faster than PTFE, while fluoroelastomer growth exceeds the growth rate of US GDP. Generally, these products 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 below.

#### Applications and potential substitutes for fluorocarbon-based polymers and elastomers

Material	US consumption (thousands MT)	Major applications	Potential substitutes <sup>1</sup>
Polytetrafluoroethylene (PTFE)	26.3	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, high nickel alloys), other polymers (e.g., nylon, polyimide)
Fluorinated ethylene- propylene (FEP)	12.5	Coatings for wire and cable, release and lamination films, chemical processing equipment and fittings	Corrosion resistant metals and other polymers
Polyvinylidene fluoride (PVDF)	11.4	Architectural coatings, chemical processing equipment, cable insulation	Other polymers
Fluoroelastomers	9.0	Automotive under the hood components, seals and fittings in aerospace and chemical process equipment, specialty hoses and tubing	Other elastomers (SBRs, nitriles, TPES)
Polyvinyl fluoride (PVF)	4.3	Photovoltaics, laminates for architectural and automotive applications, protective and release films	Other polymers (polyesters, polyolefins)
Perfluoroalkoxy polymers (PFA/MFA)	2.4	Parts and piping for semi-conductor manufacturing, wire and cable insulation	Limited choices among corrosion resistant metals and other polymers
All other fluoropolymers (E-CTFE, ETFE, CTFE-VDF, THV, PCTFE, amorphous)	6.7	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) Excludes substitution by other fluoropolymers or products based on chlorine chemistry.

Source: IHS Chemical Consulting

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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 for service. For example, certain consumer and military electrical codes require the use of fluorinated ethylene-propylene (FEP) or polyvinylidene fluoride (PVDF) as jacketing for plenum cable because its properties, including flame resistance, are superior to alternatives. Components fabricated from perfluoroalkoxy polymers (PFA) are used to provide the ultrapure water required in semiconductor manufacture and are used in corrosive situations since they do not release undesirable corrosion products. Polyvinyl fluoride (PVF) has a special use in the back sheets of solar panels; this application has been growing rapidly. In many cases, the preferred substitute for a fluorocarbon polymer would be another fluorocarbon polymer.

Historically, prices for the polymers can range from less than \$10 per kilogram for commodity grades of polytetrafluoroethylene (PTFE) to more than \$100 per kilogram for smaller volume specialties. Fluoroelastomer prices are in the \$45 per kilogram range, and the market value of these materials in the United States was about \$405 million in 2014.

## Foam blowing agents

Foam blowing agents are used to impart porosity, reduce the density, and increase the thermal resistance (insulation properties) of plastics such as polyurethanes, polystyrene, and polyolefins. Foam blowing agents are commonly used to insulate refrigerators and freezers, residential and commercial buildings, marine, automotive, and many other applications. 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. Hydrocarbons (particularly cyclopentane), carbon dioxide/water systems, HFCs, and HFOS have replaced the use of fluorocarbons that had ozone depletion potential (CFCs and HCFCs). HCFCs were only a transition solution introduced in the 1990s and their use has been subject to phase down schedules. However, HFC fluorocarbon blowing agents—HFC-134a, HFC-245fa, and HFC-365mfc—will no longer be listed as acceptable substitutes under the EPA SNAP program in the next few years because low global warming potential alternatives like HFOs and non-fluorinated alternatives will be available.<sup>[3]</sup> These products will also potentially no longer be allowed in Canada based on proposed rules by Environment and Climate Change Canada.<sup>[4]</sup>

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

### Blowing agent alternatives to fluorocarbons for polymer foam systems

Polymer system	Alternative blowing agents <sup>1</sup>
Rigid polyurethane <sup>2</sup>	CO <sub>2</sub> /H <sub>2</sub> O Pentanes Butanes/pentanes with CO <sub>2</sub>
Flexible polyurethane <sup>2</sup>	Liquid CO <sub>2</sub> CO <sub>2</sub> / H <sub>2</sub> O Acetone Polyols H <sub>2</sub> O/variable pressure foaming
Polystyrene	CO <sub>2</sub> Hydrocarbons
Polyolefins	CO <sub>2</sub> Pentanes
Polyisocyanurate <sup>2</sup>	Pentanes

(1) Other than HCFCs and products based on chlorine chemistry.

(2) These products are based on chlorine chemistry.

Source: IHS Chemical Consulting

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## 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.

3 Federal Register, volume 80, No. 138, July 20, 2015 available online at <https://www.gpo.gov/fdsys/pkg/FR-2015-07-20/pdf/2015-17066.pdf>.

4 Consultation Document: Proposed Regulatory Measures on Hydrofluorocarbons available at <https://ec.gc.ca/ozone/default.asp?lang=En&n=77A94123-1>.

HFCs in aerosol applications are approved substitutes under the EPA SNAP program because they have zero ozone depleting potential. However, HFC-134a, HFC-125, and HFC-227ea are scheduled for phase out over the next few years as they have higher global warming potential than other alternatives. They will also potentially no longer be available in Canada based on proposed rules by Environment and Climate Change Canada. Despite the scheduled transition, consumers value their performance properties of inertness, vapor pressure, and nonflammability (with the exception of HFC-152a which is flammable)—advantages that can justify their higher price in certain applications. HFOs, particularly HFO-1234ze, are replacing HFCs as aerosol propellants in many applications.

The major non-fluorocarbon 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 the not-in-kind alternative, aerosol bladder (Bag-on-Valve) systems.<sup>[5]</sup> In terms of total volume, consumption of these alternative aerosol propellant technologies 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 by limitations on the allowable release of volatile organic compounds (VOCs). Not-in-kind substitution would be possible in some applications through the use of alternative delivery systems such as aerosol bladders, hand pumps for liquids, and systems analogous to the dry powder inhalers (DPIs) used to deliver medications.

## Fire extinguishants

Halons were widely used in fire suppression until alternatives which have zero ozone depleting potential became available. The fire industry has developed disciplined practices that have made fire extinguishants nearly non-emissive, except in the case of fire. Fluorocarbons are generally used in occupied spaces where very low toxicity solutions are needed and where water is not appropriate due to the potential nature of the fire or limitations in system design.

## Solvent cleaning and degreasing

Historically, fluorocarbon solvents have been used in aerospace, electronics, and precision cleaning applications where parts had to be cleaned to exacting standards. For a limited time, HFCs such as HFC-134a, HFC-4310mee, and HFC-245fa are still filling this role. HFOs, particularly HFO-1234ze, are solvent cleaning products that are taking the place of HFCs.

Alternatives to fluorocarbons as solvent cleaning agents are presented in the table.

### Alternatives to the use of fluorocarbons in solvent cleaning and degreasing applications

Alternative processes	Alternative solvents <sup>†</sup>
Plasma arc or UV/ozone cleaning	High (>55°C) flash point hydrocarbons
Supercritical CO <sub>2</sub> or CO <sub>2</sub> 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

(1) Excludes alternatives based on chlorine chemistry.

Source: IHS Chemical Consulting

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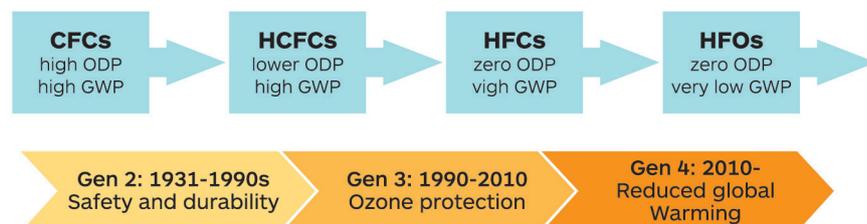
5 D. Douglas Fratz, "Aerosol Product Technology and Current Regulatory Definitions," Consumer Specialty Products Association, Washington, DC available at <http://www.nist.gov/pml/wmd/upload/Doug-Fratz-CSPA-NIST-Meeting-1-9-14.pdf>.

## The convergence of keeping cool and being green

Until other chemistries were invented, household refrigerators used ammonia as a coolant. Small leaks sometimes resulted in explosions, fires, damage to property, and even death. Refrigerators were often placed in separate rooms or outdoors to mitigate these dangers. In the 1930s, ammonia was replaced by chlorofluorocarbons (CFCs), a much safer and more

effective product. These second-generation fluorocarbon refrigerants were chemically stable, non-toxic, and non-flammable, and they experienced dramatic growth over the next four decades in a wide range of applications, including mobile air-conditioning and chillers, solvents, foam blowing agents, aerosol propellants, and fire extinguishing. Scientists determined, however, that CFCs contributed to a gradual reduction in the stratospheric ozone layer, the layer that protects life on earth from harmful ultraviolet radiation from the sun. The Montreal Protocol, an international environmental accord, called for a phased elimination of CFCs and the HCFC transition products in the developed world, ushering in the third generation of refrigerants – the HFCs (or hydrofluorocarbons). While these products do not deplete the ozone layer and they are relatively nonflammable and chemically stable, they are potent greenhouse gases. For example, the average 100-year global warming potential of HFCs was estimated to be 3,770 times that of carbon dioxide which has a global warming potential equal to 1 by definition. Thus, researchers began to look for chemistries to discover a better group of alternative refrigerants that do not contribute to global warming. The fourth generation of refrigerants are HFOs (hydrofluoroolefins). These products became commercialized within the last ten years, and they have better performance and are more energy efficient when compared to the refrigerants they are intended to replace. Furthermore, because they have short atmospheric lifetimes, they have two very important characteristics – they have no effect on the ozone layer and have an extremely low global warming potential. The step-by-step improvements – moving from ammonia, then to CFCs and HCFCs, then to HFCs, and now to HFOs – shows that technology progress and innovation is possible as society moves toward sustainable development while also advancing its standard of living and protecting the environment at the same time.

### The evolution of fluorocarbon technology



Source: IHS

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Source: Ronald Whitfield and Jeanne McNett, "A Primer on Sustainability," Business Expert Press, <http://www.britannica.com/science/hydrofluorocarbon>; <http://www.honeywell-refrigerants.com/india/?document=reducing-the-impact-on-climate-change-low-gwp-hydrofluoroolefins-hfo&download=1>

Even if revising the parts production process to eliminate the need for subsequent cleaning 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. Other non-fluorocarbon substitutes include 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

PFCs such as sulfur hexafluoride (SF<sub>6</sub>) remain in very limited use as a flooding agent for fire suppression for civilian and military aircraft, where other alternatives are not technically feasible due to safety or performance requirements. Additional niche applications of PFCs include perfluorohexane (C<sub>6</sub>F<sub>14</sub>) used as a detector fluid in leak testing for military specifications.<sup>[6]</sup>

## 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 much 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 would 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 could be found, consumers would be forced to forgo using fluorocarbons altogether and products derived from them. We do not believe that such a situation would exist since we believe that acceptable substitutes could be found, even if substitution may be imperfect in many cases.
- If cost effective chlorine-free processes could 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.
- If cost effective chlorine-free production processes could not 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 could be developed for all the HFOs, HFCs, fluoropolymers and fluoroelastomers described above, except for products that contain chlorine in the final product.<sup>[7]</sup> These materials would have to be substituted at the product level to avoid utilizing chlorine chemistry. However, the ability to develop a set of theoretical chemical reactions is no guarantee that a cost effective production process could be commercialized based on the particular materials chosen.

<sup>6</sup> See 3M, Fluorinert Electronic Liquid, FC-84 available at <http://multimedia.3m.com/mws/media/648950/fluorinert-electronic-liquid-fc-84.pdf>.

<sup>7</sup> Some examples of products that contain chlorine in the final product include: PCTFE (polychlorotrifluoroethylene), which has good water repulsion and chemical stability properties, PVF (polyvinyl fluoride) which is used in photovoltaic module backsheets, and ECTFE (poly(ethylene/chlorotrifluoroethylene)) which has excellent corrosion protection properties.

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 1) careful control of process conditions because of the reactivity of the materials and 2) 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 based on acetylene has been practiced, 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 would be very difficult to develop new, low cost chlorine-free processes for the production of the fluoropolymers presently derived from CFCs and HCFCs. 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 would 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 safety and 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 would be borne by consumers. These include costs such as the research and development costs for new product introductions and the administrative costs for revising codes and standards.

## Refrigerants

Fluorocarbon refrigerants are used in many different types and sizes of systems, with millions of units being placed into service each year in both mobile systems and residences, commercial, and industrial establishments. While some equipment has been designed in recent years to be capable of using HCFC, HFC, or HFO 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 would have to be developed in the absence of fluorocarbons, and these may cost more to produce and operate than those based on fluorocarbon refrigerants.

Initial costs would be higher for a given level of efficiency because systems designed to use either ammonia or 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 which may result in an increase in overall greenhouse gas emissions due to the additional energy consumption.

We estimate that nearly 40 million refrigeration systems per year would have to be designed and built to use alternative refrigerants for residential applications (refrigerators, freezers, and air-conditioning), transportation applications for mobile air-conditioning in transportation, and for commercial and industrial uses. The incremental initial cost of these systems is estimated to be about \$5.4 billion per year, with more than 40% of the additional costs borne 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 \$396 million per year, with 85% of the additional costs borne in residential and commercial space conditioning and mobile systems. In addition, nearly \$60 million would be required in additional capital to construct the plants required to produce the new refrigerants.

The increase in annual operating costs would result 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 would be higher than that of the fluorocarbon-based products they would be replacing. Consumers may experience reduced service lives, more frequent replacement, and reduced performance.

The incremental capital requirements to produce these substitute products would not be large, about \$110 million, because they are all currently produced in far greater volumes for applications not serviced by fluorocarbon-based materials. We estimate, however, that consumers would experience increased life cycle costs and losses in utility amounting to more than \$830 million per year because the substitutes would not provide the same level of service as the fluoropolymers and fluoroelastomers. We estimate that about half of the cost increase would be due to substitution for fluoroelastomers and products made from PTFE, with another one third due to the substitution for the relatively high volume FEP and PDVF products. Unit replacement costs for the other fluoropolymers would be about twice as high as the average because substitution would be 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 HFCs in applications where they impart better properties to the products at a lower cost or where flammable blowing agents cannot be used. These applications could be substituted by the most effective alternative blowing agent or process available, but at additional costs or worse thermal performance. 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 may not be as effective. For example, using a less effective blowing agent in insulating or cushioning applications may require more resin to achieve comparable performance. Furthermore, if insulating performance is compromised to keep initial costs low, the consumer would experience higher life cycle costs in terms of greater heating or cooling costs for products or applications containing that material and there would be a negative impact to overall greenhouse gas emissions.

HFCs comprise the vast majority of the fluorocarbons currently used as blowing agents, but they can be substituted with HFOs which are significantly more expensive than the HFCs in use today. HFO consumers in the appliance (refrigerator) insulation application can use a blend of cyclopentane and HFO. This combination emulates the insulation performance of pure HFO, but significantly reduces the overall cost since cyclopentane is about 10% of the current cost of HFO. Typically, such consumers already use cyclopentane so they have already paid for retrofits from HCFCs or HFCs; they then boost thermal insulation performance by adding HFO in the blend. We estimate that the incremental costs to convert existing blowing systems using HFCs to new processes or materials would be about \$390 million. Additionally, the increased manufacturing and life cycle costs of using less efficient products produced with the substitute blowing agents or processes would be about \$118 million per year.

### **Aerosol propellants**

Fluorocarbons hold a minor share in the overall aerosol propellant market today, being primarily used in applications where their properties provide some special advantage that justifies their higher cost, such as in metered dose inhalers (MDIs). Significant efforts would be required to develop substitute systems that could match the fluorocarbons' performance in these applications. Some alternative materials could be precluded for particular uses for safety or environmental reasons, particularly the hydrocarbons and materials such as dimethyl ether; others could be precluded for reasons of incompatibility 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.

US and Canadian consumers of chlorine-free DPI and MDI devices suffering from maladies such as COPD and asthma would incur significant additional medical costs. Furthermore, it is not clear that aerosols could be developed as effective drug delivery devices to dispense the medications required for other medical conditions like fibrosis because a minority of patients cannot use currently available alternatives to HFC-based MDIs.<sup>[8]</sup> The increased investments to replace filling lines and containers and substitute alternative propellants or delivery devices for all aerosol applications are estimated to be over \$420 million, with increased annual costs of about \$133 million per year.

### **Cleaning solvents**

Consumption of HFCs, HFEs, HFOs and PFCs as cleaning solvents is small, at about 9.7 million pounds per year, and is restricted to applications where their unique properties provide better performance than alternative solvents or not-in-kind cleaning systems. Substitution in most other applications would be far more difficult, and we estimate that new investments of the order of \$120 million and annual costs of about \$28 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 for which we attribute no costs of substitution to consumers.<sup>[9]</sup> 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 remaining applications would be difficult and we estimate that additional capital of about \$50 million and increased costs of about \$20 million per year would be required if consumers did not have access to the fluorocarbon-based products they do today.

<sup>8</sup> Dr. Helen Tope, Workshop on HFC Management, UNEP Report of the Technology and Economic Assessment Panel, April 15, 2015.

<sup>9</sup> The "all other uses" category includes many disparate uses that are too small and fragmented to be evaluated individually. This assumption is conservative because there must be some cost of substitution away from the fluorocarbon-based product, otherwise consumers would have already switched to a fluorocarbon-free alternative.

## 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.

We estimate that about \$1.2 billion 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. Additionally, the costs of the nearly 40 million new systems per year that would have to use alternative refrigerants would be about \$5.4 billion per year.<sup>[10]</sup>

The amount of new investments to produce alternative materials in the US would be \$1.1 billion and the amount in Canada would be \$39

million since production is largely centered in the US. In addition, the total additional cost that consumers would be required to spend for all fluorocarbon uses amounts to \$1.5 billion per year to purchase or use chlorine-free alternative products and processes and to operate and maintain the new equipment since they would generally be more complex, less efficient, and have shorter service lives.

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 many fluorocarbon applications, often exceeding 10 times the cost of the fluorocarbon contained in them.

### Summary of economic benefits of fluorocarbons for the United States and Canada, 2014

Application	Additional capital expenditure (\$MM)	Increased annual operating costs (\$MM per year)	Increased initial acquisition costs (\$MM per year)
Refrigeration and air conditioning	\$58	\$396	\$5,365
Fluoropolymers	\$112	\$832	
Foam blowing	\$390	\$118	
Aerosols	\$422	\$133	
Solvents and other	\$173	\$47	
<b>Total</b>	<b>\$1,155</b>	<b>\$1,526</b>	<b>\$5,365</b>

Note: Numbers may not add due to rounding.

Source: IHS

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<sup>10</sup> The capital stock of this equipment in the United States and Canada includes 195 million residential refrigerators and freezers, 74 million central air-conditioners and heat pumps, 46 million room air-conditioners, 18.4 million air conditioning systems in passenger cars and light trucks, and 10 million vending machines. See U.S. Energy Information Agency, Residential Energy Consumption Survey (RECS), 2009 and U.S. Energy Information Agency, Commercial Buildings Energy Consumption Survey (CBECS), 2012.

## 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 facility 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 for 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