MONTREAL PROTOCOL

ON SUBSTANCES THAT DEPLETE

THE OZONE LAYER

REPORT OF THE
TECHNOLOGY AND ECONOMIC ASSESSMENT PANEL

SEPTEMBER 2022

DECISION XXVIII/2 TEAP WORKING GROUP REPORT
INFORMATION ON ALTERNATIVES TO HFCS

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Report of the Technology and Economic Assessment Panel

September 2022

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Foreword

The 2022 TEAP Report

The 2022 TEAP Report consists of five volumes:

Volume 1*: TEAP 2022 Progress Report*

Volume 2*: Evaluation of 2022 critical use nominations for methyl bromide and related issues – Interim Report – May 2022*

Volume 3*: Decision XXXIII/5 task force report on energy-efficient and low-global-warming-potential technologies*

Volume 4*: Evaluation of 2022 critical use nominations for methyl bromide and related issues – Final Report – September 2022*

Volume 5*: TEAP Decision XXVIII/2 working group report: Information on alternatives to HFCs*

This is Volume 5

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TECHNOLOGY AND ECONOMIC ASSESSMENT PANEL

VOLUME 5

DECISION XXVIII/2 WORKING GROUP REPORT

INFORMATION ON ALTERNATIVES TO HFCS

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Overview

Decision XXVIII/2, "Decision related to the amendment to phasedown hydrofluorocarbons", included a request to the Technology and Economic Assessment Panel (TEAP) under paragraph 4 "to conduct periodic reviews of alternatives, using the criteria set out in paragraph 1 (a) of decision XXVI/9, in 2022 and every five years thereafter, and to provide technological and economic assessments of the latest available and emerging alternatives to hydrofluorocarbons."

To respond to paragraph 4 of Decision XXVIII/2, TEAP considered that the first year of the requested review of alternatives to hydrofluorocarbons in 2022 coincided with the preparation of 2022 quadrennial assessment report of the TEAP, based on the assessment reports prepared by its Technical Options Committees (TOCs). Decision XXXI/2, "Potential areas of focus for the 2022 quadrennial reports of the Scientific Assessment Panel, the Environmental Effects Assessment Panel and the Technology and Economic Assessment Panel", included a request for the TEAP "to assess and evaluate…technical advancements in developing alternatives to HFCs." Information on alternatives to HFCs for this report is based on the current understanding and information available to the relevant TOCs (the Flexible and Rigid Foams TOC (FTOC), the Halons TOC (HTOC), the Medical and Chemicals TOC (MCTOC), and the Refrigeration, Air Conditioning, and Heat Pumps TOC (RTOC)) at the time of preparation of this report. Information contained in this report, which was requested ahead of the 34th Meeting of the Parties (MOP-34), may be further updated in the TOCs 2022 assessments, to be completed by the end of 2022, as part of the TEAP quadrennial assessment report.

Foams

HFC alternatives are already in use today with most providing necessary technical benefits to the foams end-product. Some characteristics are specific to the foam blowing agent (FBA), including commercial availability; environmental soundness, or economic viability and cost effectiveness, and safe for use in areas with high urban densities (considering flammability and toxicity issues, including risk evaluation). However, the technical performance of FBAs is specific to the end-use. Some specific concerns are identified with safety of FBAs in certain situations with specific foam types.

In flexible and rigid foam applications, for an alternative to be available, it must have passed all Decision XXVI/9 criteria, i.e., it is commercially available, technically proven, environmentally sound, economically viable and cost effective, and safe to use, according to the FTOC's evaluation of the requirements. It should be noted that foams are not generally maintained, and the category "easy to service" was considered not generally relevant for foams.

Manufacturers of a number of foam types had transitioned away from ozone-depleting chlorofluorocarbon (CFC) and hydrochlorofluorocarbon (HCFC). However, it is possible that some manufacturers may choose to incorporate fluorocarbon (FCs) into foams to meet performance requirements (e.g., energy efficiency or structural requirements). Most flexible foams manufacturers no longer use FCs and are unlikely to be impacted by the hydrofluorocarbon (HFC) transition.

Historically, the transition from CFCs led to a significant fragmentation of the FBA market because no substitutes have the same technical properties and low cost of CFCs. Each sub-segment required a different FBA for optimal performance, with regional and national variations.

The heterogeneous nature of the FBA market has increased with each transition. No single FBA will likely be optimal for all sub-segments in the future. The divisions are more plentiful now than ever. For example, an overwhelming majority of the foam in appliances utilises hydrocarbon (HC) FBAs, but some companies are using HFCs or hydrofluoroolefins (HFOs) or hydrochlorofluoroolefins (HCFOs)[1] to meet mandated energy efficiency levels. A few companies are also considering blends of

[1] HFCs or hydrofluoroolefins (HFOs) or hydrochlorofluoroolefins (HCFOs) are chemically unsaturated HFCs and HCFCs respectively

HFOs/HCFOs with HCs or methyl formate (MF) to optimise performance characteristics with cost. Finally, water[2] content in FBA blends has increased in many circumstances to reduce costs and enhance performance and is being used with at least one HFO/HCFO.

The transition away from ODS foam blowing agents in some regions and market segments (e.g., spray foam and extruded polystyrene [XPS]) may be delayed because of cost, especially where local codes require higher thermal performance[3]. However, the price of HFC blowing agents has risen substantively during the pandemic and are now becoming comparable to HFO/HCFO blowing agent prices prior to the pandemic in some A5 parties. In locations where HFCs are used HFO/HCFO costs will be higher but more comparable than when replacing HCFCs.

Small- and Medium-Sized Enterprises
It should be noted that small- and medium-sized enterprises (SMEs) and spray foam manufacturers may still be facing challenges related to the adoption of HFOs/HCFOs, due to their operating cost, and hydrocarbons, due to potentially cost-prohibitive capital investment or impractical safety requirements for field application. This continues to be an unresolved challenge for smaller companies and field applications for all parties.

Information provided for this report is based on information currently being developed for the "FTOC 2022 Assessment Report" and may be further updated as part of that report to be completed by the end of 2022.

Fire protection

The fire protection industry has worked on developing alternatives to halons, HCFCs and now HFCs for over four decades as environmental concerns have evolved. Extensive research was conducted initially to identify alternatives to halons, while simultaneously implementing improvements to maintenance, servicing and storage of halons, user awareness and training, replacement of halon systems where practical, as well as highly improved risk management. The evolution of alternatives has proceeded along the path of selection of chemicals with the most similar characteristics followed by research and development including testing, certification, toxicity and safety analyses, standards development, and commercialization. In that process, several HFCs were developed through to commercialization (note: both the agent and hardware must successfully pass all testing and certifications). Following the commercialisation of HFCs, development of further alternatives continues, and other chemicals were developed including FK-5-1-12, 2-BTP, CF3I, and some combinations with inert gases, water mist, or solid particulates. This evolution has been fairly linear, as makes sense, in that the most likely candidates would be the most commercially viable due to the extensive cost of research and development.

For fire protection applications, information where alternatives to HFCs are available are provided for applications in the following sectors of use: civil aviation; military ground vehicles, naval, and aviation applications; oil and gas; general industrial fire protection, and merchant shipping. For an alternative to be available, it must have passed all six Decision XXVI/9 criteria, i.e., it is commercially available, technically proven, environmentally sound, economically viable and cost effective, safe to use, and easy to service, according to HTOC's interpretation of these criteria. HTOC notes that some alternatives are actually halon alternatives rather than HFC alternatives. Furthermore, in some sectors or applications, HFCs were not used and there are no alternatives to the halons

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[2] Water reacts with other chemicals allowing carbon dioxide to be released as a foam blowing agent. When FTOC refers to water, it is referring to this reaction and the carbon dioxide released. This is done to differentiate from the use of transcritical carbon dioxide which is a very high-pressure physical foam blowing agents still heavily studied but rarely used commercially.

[3] Although the cost of hydrochlorofluorocarbons (HCFCs) was approximately 20-30% of the cost of high-GWP HFCs, HCFC price is increasing as they are phased out globally. The low price of some high-GWP HFCs, particularly HFC-365mfc which is banned in some non-A5 parties, is leading to an increase in market share, which is slowing the conversion to low-GWP blowing agents

available, e.g., in aircraft cargo compartments. In these cases, it seems appropriate to state that, currently, alternatives to HFCs are not applicable (N/A). Information provided for this report is based on information currently being developed for the "HTOC 2022 Assessment Report" and may be further updated as part of that report to be completed by the end of 2022.

Medical and chemical uses

For medical and chemical uses, information on alternatives for HFCs are provided for the following: aerosols (consumer, technical, and medical), metered dose inhalers, solvents, semiconductor and other electronics manufacturing, and magnesium production. Information on the status of alternatives for HFCs in these uses is summarised in tables that address the relevant Decision XXVI/9, paragraph 1(a) criteria. Information provided in this report is based on information currently being developed for the "MCTOC 2022 Assessment Report" and may be further updated as part of that report to be completed by the end of 2022.

Aerosols incorporate propellants and solvents with the appropriate technical properties and characteristics in formulations designed to deliver a product for its intended purpose. Propellants include compressed gases (nitrogen, nitrous oxide, carbon dioxide) or liquefied gases, which are liquid inside the pressurized container. Liquefied gas propellants include HCFCs (e.g., HCFC-22), HFCs (e.g., HFC-134a, HFC-152a), HFOs (e.g., HFO-1234ze(E)), HCs, and DME. Some aerosol products contain solvents, including HCFCs, HFCs, hydrofluoroethers (HFEs), aliphatic and aromatic solvents, chlorinated solvents, esters, ethers, alcohols, ketones, and HCFOs (e.g., HCFO-1233zd(E)). HCFCs, including HCFC-141b, are still currently used and are being replaced by HFCs, HFEs and HCFOs. Aerosol production has developed differently in each country due to regulations for flammability and occupational safety, VOC controls, and the availability from suppliers of HCFCs, HFCs, or their alternatives for aerosol production. The availability and number of different aerosol products varies within parties and regions and is closely related to the development of the local aerosol industries. Hence, alternatives are not necessarily interchangeable because of regional or local differences. The aerosol product type can also determine the propellant used, which could be related to performance requirements for the end use or the higher market value of the product, e.g., allowing a more expensive propellant.

The more common types of inhalers for the delivery of respiratory drugs are the pressurised metered dose inhaler (pMDI) and the dry powder inhaler (DPI). Other methods of delivering drugs to the airways include soft mist inhalers (SMIs) and nebulisers. DPIs and SMIs are propellant-free inhalers. The choice of the most suitable treatment method is a complex decision taken between the health care provider and the patient. It is not uncommon for patients to be prescribed a mix of medications in a range of devices. There are HFC pMDIs available to cover all key classes of drugs in the treatment of asthma and COPD. Emerging in-kind propellant alternatives are in earlier stages of development or commercialization in pMDIs, such as isobutane, HFC-152a, and HFO-1234ze(E) propellants.

For solvents, many alternative solvents and technologies developed as alternatives to ODS are also the candidates for alternatives to HFCs. These include not-in-kind technologies, such as aqueous cleaning, semi-aqueous cleaning, hydrocarbon and oxygenated solvents, and in-kind solvents, such as chlorinated solvents and fluorinated solvents, including high GWP HFCs not listed in Annex F and low GWP HFOs, HCFOs, and HFEs, with various levels of acceptance. Alternatives to Annex F HFCs are being used for electronics defluxing/cleaning and precision cleaning in several industries, including automotive, aerospace, medical device, and optical components where high levels of cleanliness are required.

Semiconductors are fabricated by forming circuit patterns on silicon-based wafers by using chemicals to form the circuit pattern. More recently dry etching processes using reactive ion etching (RIE) are used for this process. Chemical vapour deposition chamber walls are also cleaned using fluorinated chemicals to remove the build-up of silicon materials. RIE and chamber cleaning use fluorinated gaseous chemicals, including perfluorocarbons (PFCs), HFCs, sulfur hexafluoride (SF_6) and nitrogen trifluoride (NF_3). The most commonly used HFCs are HFC-23 (CHF_3), HFC-41 (CH_3F) and HFC-32 (CH_2F_2). The usage of cyclic C_4F_8, HFC-41, HFC-32 and perfluoro butadiene is expected to increase due to their use in high aspect hole etching. HFCs are only minimally used for chamber cleaning. Heat transfer fluids control the wafer temperature during etching, which is an important factor for high aspect ratio hole etching. The most commonly used fluorinated chemicals used as heat transfer fluids are a saturated PFC (PFC and perfluoroalkyl amine), hydrofluoroethers, and perfluoropolyethers. HFCs (HFC-134a and HFC-23) are not commonly used as heat transfer fluids. Like semiconductor manufacturing, other electronics manufacturing, including flat panel display (FPD), photovoltaics (PV) and microelectromechanical systems (MEMS), use fluorinated chemicals for etching and chamber cleaning. These manufacturing processes primarily use PFCs, HFC-23, SF_6, and NF_3. In photovoltaic manufacturing, HFCs are not commonly used. Alternatives to HFC use in semiconductor and other electronics manufacturing are other fluorinated gases, such as PFCs, SF_6 and NF_3, many of which have higher GWPs and lower utilization rates than HFCs, such as HFC-32 and HFC-41.

Cover gases are used in magnesium production, casting processes and recycling to prevent oxidation and combustion of molten magnesium. The majority (80-90%) of primary magnesium production occurs in China, followed by the US, Israel, and Brazil. Without protection, molten magnesium will oxidize and ignite in the presence of air and form magnesium oxide (MgO) deposits that greatly reduce the quality and strength of the final product. An effective cover gas will modify and stabilise the MgO surface film to form a protective layer that prevents further oxidation. Sulfur hexafluoride (SF_6) is the most widely used cover gas. However, SF_6 has a GWP of 22,800. Several gases with lower GWPs have been identified as alternatives to SF_6, including HFC-134a (GWP of 1,430) and a fluoroketone (GWP of 0.1), both of which are being used by the industry as a cover gas. HFC-134a has been shown to have adequate melt protection but careful selection of the diluent gas and concentration is required to prevent damaging corrosion. More recently, researchers have begun exploring the addition of small amounts of unique alloying elements (e.g., Be, Al, Ca) to enhance the oxidation resistance of the alloy and possible reduce the need for a cover gas.

Refrigeration and air conditioning

For the Refrigeration and Air Conditioning sectors, information on alternatives for HFCs are disaggregated into the different application sectors as per the RTOC 2022 Assessment Report, currently under development. Applications include: factory-sealed domestic and commercial appliances, food retail and service refrigeration, transport refrigeration, air-to-air conditioners and heat pumps, applied building cooling systems, mobile air conditioning/heat pumps, industrial refrigeration, and heating only heat pumps. Information on the status of alternatives to HFCs for these applications has been extracted from the forthcoming “RTOC 2022 Assessment Report” and is summarised in tables that address the relevant Decision XXVI/9, paragraph 1(a) criteria. Information may be further updated as part of the “RTOC 2022 Assessment Report” to be completed by the end of 2022.

Currently, the entire global production of domestic refrigeration appliances is based on non-ODS refrigerants, predominantly HC-600a (isobutane) and to some extent HFC-134a. Migration from HFC-134a to HC-600a is expected to continue, driven by the Kigali Amendment schedule or local regulations on HFCs. In the EU the transition to R-600a in new domestic refrigeration appliances was completed by 2015. In the USA, substantial progress has been made to convert from HFC-134a to HC-600a and is expected to be complete by 2023. Many A5 parties, including China, India and others are rapidly phasing out HFC-134a in domestic refrigerators using HC-600a. Energy efficiencies of refrigerators are constantly increasing, including in many A5 parties, mainly due to Minimum Energy Performance Standards (MEPS) and increasing awareness of consumers.

Stand-alone commercial refrigeration appliances, which are globally used, include a wide variety of appliances, including ice-cream freezers, ice machines, beverage vending machines, and display cases. Typical refrigerants used include HFC-134a, R-404A, and HCs. With the revision of safety standards, in low charge systems, migration is taking place to HC-290 with better energy efficiencies.

This trend is spreading to some of the A5 parties. Multinational companies that supply food and drink retailers with refrigeration appliances usually have their own environmental policies that favour lower-GWP refrigerants and improved energy efficiency.

Domestic heat pump tumble dryers (HPTD) are significantly more efficient than conventional electrically heated dryers, using only about 40–50% of the electricity of conventional dryers. HPTDs continue to gain market share and concurrently costs have also reduced substantially. The most commonly used refrigerants in HPTDs are HFC-134a, R-407C, and R-410A. Some transition to HC-290 (propane) has happened, e.g., in EU parties.

For transport refrigeration, the majority of trucks and trailers today use R-404A. New equipment in Europe typically uses lower GWP A1 alternative, R-452A. Light commercial vehicles use mainly HFC-134a, while some new platforms will use HFO-1234yf. The majority of marine ISO-container refrigeration units operate on HFC-134a. The latest of these units are being offered as being retrofittable to R-513A. A marine container operating on R-744 is available with limited market penetration. The GWP of the refrigerants used is expected to come down consistently with present and future regulations; the pace at which the transition will occur is unclear as transport regulations make it hard to introduce flammable refrigerants (e.g., Agreement on the International Carriage of Perishable Foodstuffs and on the Special Equipment to be used for such Carriage (ATP) Regulation). Some experts predict that the long-term solution will be based on R-290 or R-744. However, challenges need to be overcome. The trend towards higher efficiency (lower fuel consumption) continues in all industry segments in parallel. Various refrigerants are used on board different types of ships; HFCs are today being replaced by alternative system which are finding their way from other market segments, such as R-744 for chilling water and for food storage systems, or HFO-1234ze(E) for chillers in cruise lines. R-717 today is experiencing revival in many ships and in particular fishing vessels.

Air-to-air conditioners, including reversible air heating heat pumps (generally defined as reversible air conditioners), sold within non-A5 parties use non-ODS refrigerants and around 90% of new systems in A5 parties do not use HCFCs, although a significant proportion of the installed population still use HCFC-22. In addition to the widespread use of R-410A, the extensive introduction of lower GWP HFC-32 in small split air conditioners continues in many parties around the world, accounting for nearly half of the total production of split room air conditioners in 2021. Enterprises within all regions continue to evaluate and develop products with various HFC/HFO blends, such as those comprising HFC-32, HFC-125, HFC-134a, HFC-1234yf and HFC-1234ze. Products are being introduced with lower GWP alternatives, R-454A, R- 454B, R-452B and R-463A. Further conversion of production lines to HC-290 in China, Southeast Asia and South America is underway but there is limited market introduction (except for small and portable units). Some enterprises within the Middle East still see R-407C and HFC-134a and in some applications R410A as favourable alternatives to HCFC-22.

Applied Building Cooling systems are used in medium and large sized buildings. They require engineering services to design and install air conditioning in larger buildings of all types. The dominant products used in these systems are water chillers although packaged commercial unitary product can also be used. There are now complete lines of all chiller types in all major markets that use refrigerants having lower GWP than their predecessors. Additionally non-fluorinated refrigerants, e.g., ammonia and HCs, are available in some chiller types, albeit in select sizes not complete product lines. Products using the existing refrigerants will continue to be sold and the installed base of these products will remain in service for years to come. Despite the new refrigerant choices that are now available for new and existing equipment, they may not be the final choices. There is continued pressure from regulators to move to yet another generation of zero ODP and near zero GWP, if technically possible and economically reasonable. New refrigerant choices, notably replacements for R-134a (medium pressure) and R-410A (high pressure), include flammable refrigerants, safety class A2L. Safety regulations that allow use of A2L refrigerants, supported by recent research, are being written, but are not uniform nor adopted in all regions. This is not a trivial matter, since health, safety and property issues are involved. Adoption and enforcement of revised codes and standards may slow the adoption new flammable refrigerants.

Currently, more than one refrigerant is used for car and light truck air conditioning: HFC-134a will remain largely adopted worldwide, while HFO-1234yf is currently the main option in Europe and North America. The deployment of highly electrified vehicles (plug-in hybrid electric vehicles (PHEV) and battery electric vehicles (BEV)) in Europe, China and North America will lead to the implementation of heat pump function and of a new generation of thermal systems. Manufacturers are working on the improvement of this feature by using cycle variations such as economiser coupled with vapor injected compressors. R-744 is increasingly applied in fully electrified vehicles due to its good performance when operating as a reversible heat pump. However, R-744 is less suitable in hot and humid climates where energy efficiency is somewhat lower than that of HFC-134a and HFO-1234yf systems. So, some European OEMs introduced reversible R-744 heat pumps for their high-volume BEV models, which they currently sell in the EU, North America (Canada), and China. It cannot be foreseen whether all these refrigerants will all remain in the market for a longer period of time (in parallel). It is also unclear whether the bus sector (where currently HCFC-22, HFC-134a, R407C, R-744, and R-449A are used and HFO-1234yf has been introduced) and the heavy-duty truck sector will follow these trends.

In industrial refrigeration applications, R-717 (ammonia) has been widely used for many years in large industrial systems. In small industrial systems there has historically been significant use of HCFC-22 and, more recently, HFCs such as R404A and HFC-134a. Looking forward, R-717 and R-744 are the dominant options for large industrial systems (e.g., in food and drink manufacturing and bulk cold storage), with HCs used in some large specialised applications (e.g., in the petrochemical industry). In smaller systems A2L blends such as R-454C and R-455A are starting to be used. In heat pumps above 100°C HCs will be dominating, partly because of their stability at high temperatures, partly due to the price of the fluids and finally due to their higher efficiency.

Heat pumps commercialised today make use of non-ODS refrigerants, including R-410A, HFC-32, HFC-134a, R-407C, HC-290, HC-600a, R-717 and R-744. The majority of new equipment currently uses R-410A. Safety constraints restrict the use of R-290 to monobloc units located outdoors. Recently HFC-32 and R-454B introduced as lower GWP alternatives for R-410A. The issue of high ambient temperature conditions is of importance for heating-only heat pumps. The main parameters to select the refrigerant are efficiency, cost effectiveness, economic impact, safe use and easiness of use. Replacements using lower GWP HFC blends have been developed and are under way to become commercially available. The temperature ranges in which HC-290 and HFC-32 can be operated are better than those for R-410A, moreover, their efficiencies are generally better. The application of R-410A, HFC-32 or HC-290 is most cost effective when used in small- to medium-sized systems.

2 Introduction

2.1 Decision XXVIII/2 paragraph 4

At their Twenty-eighth Meeting in 2016, the parties took Decision XXVIII/2, "Decision related to the amendment to phasedown hydrofluorocarbons", which included a request to the Technology and Economic Assessment Panel (TEAP) under paragraph 4 "to conduct periodic reviews of alternatives, using the criteria set out in paragraph 1 (a) of decision XXVI/9, in 2022 and every five years thereafter, and to provide technological and economic assessments of the latest available and emerging alternatives to hydrofluorocarbons [(HFCs)]."

The text of Decision XXVI/9, "Response to the report by the Technology and Economic Assessment Panel on alternatives to ozone-depleting substances", and specifically the above referenced paragraph 1(a) criteria is as follows:

1. To request the TEAP, if necessary, in consultation with external experts, to prepare a report identifying the full range of alternatives, including not-in-kind technologies, and identifying applications where alternatives fulfilling the criteria identified in paragraph 1(a) of the present decision are not available, and to make that report available for consideration by the [Open-ended Working Group (OEWG)] at its 36th meeting and an updated report to be submitted to the 27th [Meeting of the Parties (MOP)] that would:

   a) Update information on alternatives to [ozone-depleting substances (ODS)] in various sectors and subsectors and differentiating between parties operating under paragraph 1 of [Article 5 (A5)] and parties not so operating, considering energy efficiency, regional differences and high ambient temperature conditions in particular, and assessing whether they are:

      I. Commercially available;
      II. Technically proven;
      III. Environmentally sound;
      IV. Economically viable and cost effective;
      V. Safe to use in areas with high urban densities considering flammability and toxicity issues, including, where possible, risk characterization;
      VI. Easy to service and maintain;

      and describe the potential limitations of their use and their implications for the different sectors, in terms of, but not limited to, servicing and maintenance requirements, and international design and safety standards;

2.2 Approach

To respond to paragraph 4 of Decision XXVIII/2, TEAP considered that the first year of the requested review of alternatives to hydrofluorocarbons in 2022 coincided with the preparation of 2022 quadrennial assessment report of the TEAP, based on the assessment reports prepared by its Technical Options Committees (TOCs). Decision XXXI/2, "Potential areas of focus for the 2022 quadrennial reports of the Scientific Assessment Panel, the Environmental Effects Assessment Panel and the Technology and Economic Assessment Panel", included a request for the TEAP "to assess and evaluate…technical advancements in developing alternatives to HFCs." Information on alternatives to HFCs for this report is based on information developed by the relevant TOCs for the TEAP quadrennial assessment report. Information contained in this report, which was requested ahead of MOP-34, may be further updated in the TOCs 2022 Assessment Reports to be completed by the end of 2022.

Decision XXVIII/2 requests review of alternatives to HFCs in 2022 and every five years thereafter. These future reviews would no longer align with the TEAP quadrennial assessment report timelines.

Since the review of alternatives are typically conducted as part of the TEAP quadrennial assessment reports, parties may wish to consider streamlining the schedule for a report to either a continuation of the quadrennial schedule or shifting to a quintennial schedule that would provide an assessment, including a review of alternatives to HFCs to the extent new information is available, just ahead of phasedown milestones for HFCs under the Kigali Amendment. This would take into consideration the workload of the TEAP to avoid duplicative work and be able to respond to other decisions of parties that may request other information from the TEAP during the same periods.]

To address the initial review requested under Decision XXVIII/2, paragraph 4, TEAP established a working group from within its membership, including the co-chairs of relevant TOCs (the Flexible and Rigid Foams TOC (FTOC), the Halons TOC (HTOC), the Medical and Chemicals TOC (MCTOC), and the Refrigeration, Air Conditioning, and Heat Pumps TOC (RTOC)), as follows:

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Paulo Altoe	FTOC	Brazil	A5
Adam Chattaway	HTOC	UK	NA5
Ray Gluckman	TEAP	UK	NA5
Bella Maranion	TEAP	USA	NA5
Keiichi Ohnishi	MCTOC	Japan	NA5
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Helen Tope	MCTOC	Australia	NA5
Dan Verdonik	HTOC	USA	NA5
Helen Walter-Terrinoni	FTOC	USA	NA5
Jianjun Zhang	MCTOC	China	A5

The working group conducted its work electronically and through virtual meetings.

3 Information on alternatives for HFCs in the foams sectors

3.1 Introduction

Much of the information requested by Decision XXVIII/2 is based on information currently being developed for the "FTOC 2022 Assessment Report". Hopefully, this concise summary will provide a straightforward reference that may be helpful for parties. Information contained in this report, which was requested ahead of MOP-34, may be further updated in the "FTOC 2022 Assessment Report" to be completed by the end of 2022.

3.2 Approach

3.2.1 Evolution of Foam Blowing Agents

There are a number of important criteria considered when foam manufacturers select a new suitable foam blowing agent (FBA), and not all FBA characteristics are equally important in the manufacturing of each type of foam. Since no one single low GWP, zero ODP FBA embodies all the criteria, foam manufacturers must prioritize these traits and select the most suitable option for their application. Various perspectives on key characteristics in the manufacture of certain types of foam has led to a proliferation of the number of FBAs with more variation in the development of FBAs as noted in the Executive Summary.

One key challenge has been the increasing cost of FCs with each generation, which has created some preference in minimizing the use of FCs in foam systems and seeking lower cost alternative to use alone or in blends with FCs. Despite best efforts by chemical manufacturers to find alternatives that closely emulate the performance of the previous generation, newer FCs generally bring specific challenges that do not necessarily meet the needs of the entire industry. In addition, the demand for FCs for foam is significantly smaller than the demand for refrigerants, and the research and commercialization priority at fluorocarbon chemical companies is more focused on the larger refrigerant markets with an effort to use refrigerants as FC FBAs for foams rather than to develop and commercialise FC FBAs specifically for foam use alone, in some companies.

Cost and robust fitness of FCs for foams have led to the growth in the use of other FBAs, such as hydrocarbons, water, and methyl formate.

Figure 3.1 illustrates how the foam market has changed over the lifetime of the Montreal Protocol. Note that the height of the bars in the histogram are normalized. It should not be interpreted that the total market size is the same for each decade.

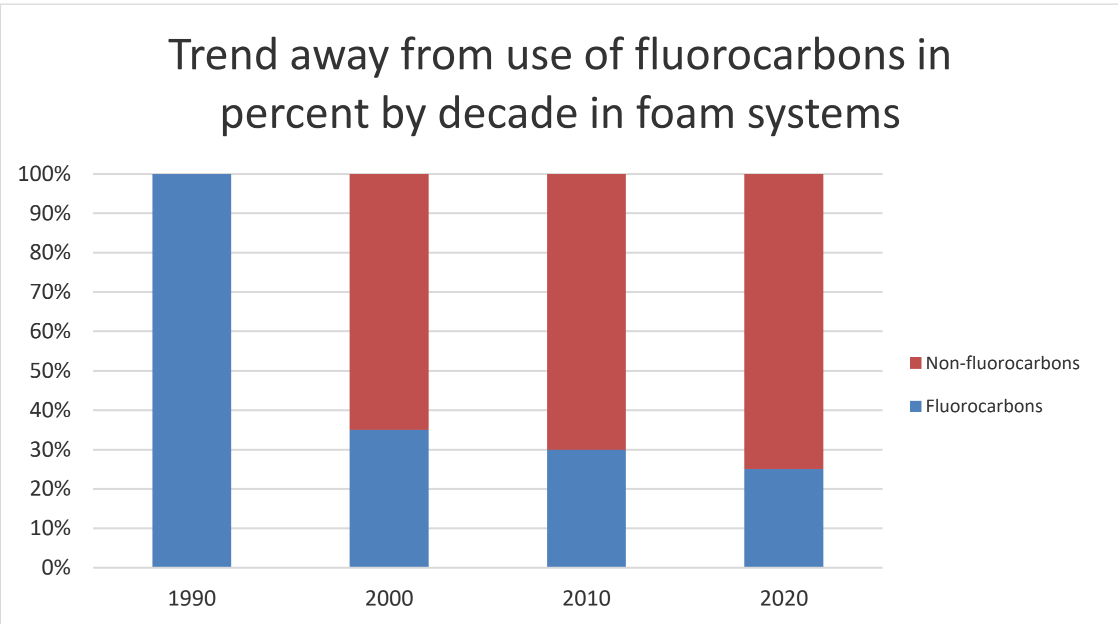


Figure 3.1: Estimated trend in foam systems

3.2.2 FTOC interpretation of criteria listed in Decision XXVI/9 paragraph 1(a)

The criteria outlined in Decision XXVI/9 paragraph 1 (a) can be subject to interpretation depending on the context of their use. The FTOC interprets the criteria as:

i. **“Commercially available**”

Foam blowing agents are generally researched, developed, and tested in the laboratory first in very small quantities (less than a tonne). Small quantities (less than 10 tonnes per annum) may then be manufactured in a pilot plant sufficient only to further prove fitness for purpose, optimise manufacturing processes, market development, and for toxicity, safety, and other testing. Once potential market adoption is proven, required testing is passed, and production facilities are designed, larger scale commercial facilities may be built to serve the foam, and in many cases, refrigerant market. Full-scale chemical plants tend to be costly to build, which leads to a limited number of chemical plants with product shipped around the world, using a generally efficient, well-proven supply chain.

FTOC considers FBAs to be commercially available once commercial facilities are operational supplying a minimum of 2,000 tonnes per year of product. However, it should be noted that the FBA FC market is much greater, and this quantity would be insufficient to supply all of the demand globally. However, the product has met critical testing and certification criteria, government approvals and is generally accepted in some significant part of the market. Finally, the alternative is in use in significant volumes in commercial foam systems. The product must be available for sale with some certainty of future supply and allowed to be used in multiple regions or parties.

However, this does not necessarily mean that the foam blowing agent or foam systems are accessible in all parties (for example A5s versus non-A5s). In this context “accessible” follows the concept explained in section 6.1.2 of this report but in the context of FBAs. It is also important to note that there can be insufficient capacity of “commercially available” alternatives to meet global demand and that there may be interruptions to global supply chains of “commercially available” alternatives. FTOC discusses capacity, alignment of supply and demand, and supply chain interruptions in more detail in its 2022 Assessment Report.

ii. **“Technically proven”**

FTOC considers an FBA to be “technically proven” when the foam blowing agent is accepted by regulators and industry because the FBA and the foam systems meet all necessary performance, safety, and environmental requirements for the intended application. Safety and efficacy properties for each foam type must be met including, but not limited to, compatibility testing with metals and elastomers for reactivity and corrosiveness, density, fire testing of foams, initial and long-term thermal performance, structural integrity, compressive strength and other mechanical properties, foam cell size, stability of foam systems, loss of blowing agent over time and others to demonstrate that the alternative agent provides acceptable results. High ambient temperature testing is also required especially for stability of foam systems.

It should be noted that some of this testing is mandated in certain jurisdictions by building codes or regulators, while other testing is voluntary or may be required by foam end-users. For example, fire and smoke testing are required in some building codes with conformity needed to International Organization for Standardization (ISO) and American National Standards Institute (ANSI) recognized Underwriters Laboratories (UL™) standards. In addition, testing is done with a variety of additives, such as catalysts and surfactants to further optimise performance.

Different companies apply different performance standards, which differ again in the various foam sectors. FTOC concludes that alternatives are “technically proven” once there is some commercial uptake of the alternative in a sector. Alternatives that are still in testing but not yet used commercially have been designated by FTOC as "show technical promise".

"Environmentally sound"

New chemicals must be approved by regulators in a number of parties including, but not limited to, China, Japan, The Republic of Korea, Australia, Switzerland, Europe, and the United States through new chemical registries such as the European Chemicals Agency (ECHA) registration process, the U.S. Environmental Protection Agency (EPA) Toxic Substances Control Act, and Inventory of Existing Chemical Substances in China (IECSC). Chemical approvals for specific uses, along with the U.S. EPA Significant New Alternatives Policy (SNAP) program create a clearinghouse of approved alternatives that foam manufacturers and some parties rely on to ensure that alternatives are, at least comparatively similar to existing FBAs overall in safe use and improved environmental impact relative to incumbent FBAs.

FTOC considers that alternatives must have minimal environmental impact (e.g., short atmospheric lifetime) compared to ODS or HFC FBAs. They have zero or very low ODP (which could be subject to individual party determination), have very low GWP and are not foreseen to be subject to future production phasedowns.

iii. **"Economically viable and cost effective"**

FBA price sensitivity is different for various foam segments and even for different manufacturers and end-users. It should be noted that price of the alternative is not the only consideration impacting cost to foam manufacturers and end-users. Capital investment to use flammable alternatives, the cost of new additives to address stability performance, foam density, and thermal performance all impact economic viability and cost effectiveness.

FTOC concludes that alternatives are economically viable and cost effective once there is some commercial uptake of the alternative because of the variability of the optimization process for different foam types and different end-users that must balance performance with cost. No assessment has been made for alternatives that are not yet commercial, because there is likely significant information to be learned regarding FBA price, cost of foams and foam systems and in addition to performance in foams.

iv. **"Safe to use in areas with high urban densities considering flammability and toxicity issues, including, where possible, risk characterization**"

HFO/HCFO foam blowing agents have similar toxicity exposure limits and routes to currently used HFCs and other FCs, with key exposure concerns for workers being frostbite and oxygen deprivation in the case of large releases in enclosed spaces. A significant body of work has been completed by the Center for Polyurethane Institute (CPI) to assess safe re-entry times after spray foam is applied in buildings and homes for other workers and families. To date, there has been no difference shown between residual off-gassing of hydrofluorooelfin or hydrochlorofluoroolefin (HFO or HCFO) FBAs compared to the FBAs in current use. It should be noted that personal protective equipment should be worn to prevent exposure from all chemicals in foam systems, including non-FBA chemicals.

Flammability of hydrocarbons (HCs) and oxygenated alternatives is mitigated to reduce the risk of reaching flammable mixtures and to remove potential for introduction of ignition sources[4]. References have been added below to provide some examples of the methodologies

[4] Hydrocarbon solvents handling and safety: ESIG Flammability Guide and resource videos Facility storage

used to mitigate flammability. Please note that local safety requirements may vary. Mitigation is costly. The use of flammable alternatives may not be cost effective for small and medium enterprises because of this significant capital investment requirement. There are also shipping and transportation requirements regarding flammable foam blowing agents.

It should be noted that some testing has been done to examine whether the addition of foam blowing agents to foam systems might reduce flammability sufficiently to avoid mitigation requirements. However, to date, no blends have been found to sufficiently reduce concentrations such that flammable transportation regulations could be eliminated. Additional details will be found in the upcoming 2022 FTOC Assessment Report.

Handling and transportation of flammable fluids and blends, including the addition to foam systems, must comply with international shipping requirements, such as those in the Global Harmonized System (GHS). Safety Data Sheets (SDSs) must include flash points and safety information. Local building codes, fire safety requirements, and laws may limit the use of flammable FBAs and even systems containing flammable FBAs. The flash point of blends may not be a sufficient indication of risk while applying spray foam (or other foam manufacturing processes) where there may be localized concentrations greater than the lower explosivity limit (LEL). FTOC is not aware of any testing confirming that LEL concentrations are not reached while spraying foam systems containing flammable FBAs.

Finally, foam blowing agents can be categorized as "volatile organic compounds" (VOCs) further requiring mitigation to reduce smog-forming off-gassing and releases into communities, forming ground-level ozone or smog. HFOs/HCFOs and other chemicals are often compared an index chemical, such as ethane, using a parameter such as Maximum Incremental Reactivity[5] (MIR) to determine whether chemicals will be considered VOCs, perhaps requiring mitigation. HFOs/HCFOs known to have been evaluated have been determined to be lower than this index and have been exempted from mitigation requirements in some jurisdictions[6]. It should be noted that use of FCs in VOC abatement systems would require significant upgrades to raise temperatures to avoid production of dioxins and other chemicals. FCs by-products are also corrosive to standard carbon-steel equipment.

FTOC notes that safety precautions must be taken in all foam manufacturing. Many of the chemicals used to manufacture foams are hazardous and require the use of personal protective equipment and mitigation to reduce exposure and flammability during blending, foaming and even off-gassing of finished foams. FTOC also notes that several of the replacements of HFCs have been in use for some time and the hazards associated with them are well understood. The one exception is HFOs/HCFOs which have similar safety and toxicity properties to HFCs, as noted above.

Due to the general hazards related to foam manufacturing, the precautions that must be taken regardless of the FBA used, the current use of many alternatives, and the similarities between HFCs and HFOs/HCFOs, FTOC has highlighted specific precautions needed for alternatives when used in densely populated areas. FTOC has concluded that HC foam manufacture in densely populated areas could be challenging to mitigate but finished products containing HC

and handling modifications required by some building codes. Flammable liquid tank storage requirements

[5] Maximum Incremental Reactivity (MIR) is one measure of photochemical reactivity, which estimates the weight of ozone produced from a weight of a chemical (e.g. lbs ozone per lb of chemical) under worst case conditions.

[6] An example of a jurisdiction determining exemption to requirements for HFO/HCFO foam blowing agent based on MIR.

are likely safe in use.

v. **"Easy to service and maintain"**.

Foam blowing agents are used to manufacture foams, as a finished product or part. As such, they are not serviced like refrigeration systems for example.

FTOC notes that the HFC alternatives are already in use today with most providing necessary technical benefits to the end-product. However, mitigation may be needed for some specific uses highlighted below.

FTOC also notes that some characteristics are specific to the FBA, including commercial availability; environmental soundness, or economical viability and cost effectiveness, and safe for use in areas with high urban densities (considering flammability and toxicity issues, including risk evaluation). However, the technical performance of FBAs is specific to the end-use. FTOC has identified some specific concerns with safety of FBAs in certain situations with specific foam types.

The following table describes the required characteristics that are specific to FBAs for the most commonly used alternatives to HFCs. This excludes a discussion of technical suitability which is specific to the type of foam being manufactured. Please note that additional details regarding selection for commercialization by sector are included later in the report. FTOC has assumed that only solutions that are economically feasible and cost effective have been selected for use by foam manufacturers. This table refers to the manufacture of foam and not the safe use of finished products in areas of high urban density.

Considerations Related to Hydrocarbons (HCs)

HCs are frequently used in a number of foam types as non-ODS with low GWP and are not controlled by the Montreal Protocol. It should be noted that hydrocarbons are considered VOCs which produce smog at ground level and may require investment for abatement in some populated communities. FCs in VOC abatement systems would require significant upgrades to raise temperatures to avoid production of dioxins and other chemicals. FCs by-products are also corrosive to standard carbon-steel equipment.

HCs integrated into foam systems provide good energy efficiency performance. HCs can be blended with fluorocarbons to further enhance thermal efficiency. However, blended foam blowing agents containing hydrocarbons create flammable mixtures and require similar safety precautions to HC alone.

Necessary safety precautions include explosion proofing of facilities and use of non-sparking tools. Capital costs have been reported to range between US$ 250,000 to US$ 1,000,000 per operating facility. HCs have lower operating costs, but the significant capital investment has made them unattractive SMEs.

Table 3.1 Attributes specific to most commonly used alternative FBAs to HFCs

Foam Blowing Agent	Commercially Available	Environmentally Sound	Safe for use in high urban densities	Cost
HFOs/HCFOs	Yes	Low GWP, very low or no ODP, generally exempted from VOC requirements	HFC handling precautions	Higher operating cost than HFCs
Hydrocarbons (HC)	Yes	Low GWP, no ODP, VOC mitigation may be needed	May be limitations due to flammability / explosivity properties	Lower operating cost, but capital investment for safety needed
Methyl formate (MF)	Yes	Low GWP, no ODP, Generally exempted from VOC mitigation requirements	May be limitations due to flammability properties and local requirements. Methyl formate in a foam system can be provided to foam manufacturers which may reduce limitations of use.	Lower operating cost, but capital investment for safety needed
Methylal	Yes	Low GWP, no ODP, VOC mitigation - unknown	May be limitations due to flammability properties	Lower operating cost, but capital investment for safety needed
CO_2 (Water)	Yes	Yes	Yes	Low cost

As a reminder, FTOC has assumed that only HFC alternatives that are economically feasible and cost effective *and* technically proven have been selected for widespread commercialisation.

3.3 Refrigeration foam insulation

Refrigeration foam insulation systems require specific thermal and structural performance. Flammable blowing agents (HC or HC blends) require major capital investment for safety during manufacturing and this makes large plants more cost-effective because of the economies of scale. Necessary safety precautions include explosion proofing of facilities and use of non-sparking tools. Capital costs have been reported to range between US$ 250,000 to US$ 1,000,000 per operating facility, which makes HC/blends unattractive for SMEs. However, most medium and large manufacturers of transport and domestic refrigeration equipment have converted away from HCFC-141b and HFC-245fa to HC or HC/FC blends.

Small- and medium-sized enterprises (SMEs) worldwide, continue to face difficult choices with the choice of FBA, between the higher operating costs of HFOs/HCFOs versus the higher capital costs of HCs.

3.3.1 Domestic refrigeration

As noted in previous reports, the major emerging technologies in the appliance sector are based mostly around HFO/HCFOs. These are all similar in their properties with a stepwise improvement in thermal performance over other lower-GWP alternatives. Although HCFO-1233zd (E) and HFO-1336mzz(Z) are successfully in use, they are limited by supply chain issues and manufacturing capacity. However, their high cost compared to non-fluorinated alternatives has led to some market preference to use lower operating cost options or blending with HCs.

There are other considerations besides relative costs which must be balanced by manufacturers, especially energy efficiency, which is often mandated by regulation. To achieve a good balance of thermal insulation performance and cost, various co-blowing technologies are being adopted. Many manufacturers use HFCs or HFO/HCFOs to co-blow with pentane. A company in China uses HC-600/HC-600a to co-blow with pentane and HFCs – achieving more than 7% injection weight reduction in appliances. It should be noted that hydrocarbons are widely used in domestic refrigeration products with vacuum panels, which increase operating costs, but provide better energy efficiency.

3.3.2 Commercial refrigeration

FCs are increasing used in commercial refrigeration systems especially in parties with increasingly stringent energy efficiency requirements. HFO/HCFO FBAs improve thermal performance compared to other low-GWP alternatives. However, conversion away from HFCs to HFO/HCFO FBAs in non-A5 parties has stalled due to the limited supply.

3.3.3 Transport refrigeration

HCs are used as the FBAs in many polyurethane (PU) foam systems for transport refrigeration systems, especially those manufactured by medium and large enterprises.

The table below shows FTOC's assessment of the most used HFC alternatives for refrigeration applications against the six Decision XXVI/9, paragraph 1(a) criteria.

Table 3.2 Summary of most commonly used HFC alternatives for refrigeration foam insulation

Decision XXVI/9 Criterion		Alternatives			
		HFOs/ HCFOs	**HCs**	**Methyl formate: commercial refrigeration only**	**Water**
I	Commercially available	Yes	Yes	Yes	Yes
II	Technically proven	Yes	Yes	Yes	No
III	Environmentally sound	Yes	Yes	Yes	Yes
IV	Economically viable and cost effective	Widely adopted in commercial refrigeration, and can be used to improve energy efficiency is required	Yes	Adopted in commercial refrigeration Can be blended with FCs to optimise cost and thermal performance	NA
V	Safe to use in densely populated areas	Yes	May be limitations due to flammability properties and local safety codes and requirements	May be limitations due to flammability properties and local requirements Methyl formate in a foam system can be provided to foam manufacturers which may reduce limitations of use.	NA
VI	Easy to service	NA	NA	NA	NA

3.4 Polyurethane boardstock

HCs are generally the FBA in commercial use in PU boardstock. Most medium and large manufacturers with larger facilities use HCs, with the higher initial capital cost balanced by the lower operating costs for pentanes. However, it is likely that HFO/HCFO blends with HCs may be required in future to meet the demand for increased thermal performance in buildings.

The table below shows FTOC's assessment of the most used HFC alternatives for PU boardstock against the six Decision XXVI/9, paragraph 1(a), criteria.

Table 3.3 Summary of most commonly used HFC alternatives for PU Boardstock

Decision XXVI/9 Criterion		Alternatives			
		HFOs/ HCFOs	**HCs**	**Methyl formate**	**Water**
I	Commercially available	Yes	Yes	Yes	Yes
II	Technically proven	Yes	Yes	No	No
III	Environmentally sound	Yes	Yes	Yes	Yes
IV	Economically viable and cost effective	No	Yes	NA	NA
V	Safe to use in densely populated areas	Yes	May be limitations due to flammability properties and local safety codes and requirements	NA	NA
VI	Easy to service	NA	NA	NA	NA

3.5 Polyurethane panels

HCs are generally the FBA in commercial use in PU panels. Most medium and large manufacturers with larger facilities use HCs, with the higher initial capital cost balanced by the lower operating costs for pentanes. However, it is likely that HFO/HCFO blends with HCs may be required in future to meet the demand for increased thermal performance in buildings.

The table below shows FTOC's assessment of the most used HFC alternatives for PU panels against the six Decision XXVI/9, paragraph 1(a), criteria.

Table 3.4 Summary of most commonly used HFC alternatives for PU Panels

Decision XXVI/9 Criterion		Alternatives			
		HFOs/ HCFOs	**HCs**	**Methyl formate**	**Water**
I	Commercially available	Yes	Yes	Yes	Yes
II	Technically proven	Yes	Yes	No	No
III	Environmentally sound	Yes	Yes	Yes	Yes
IV	Economically viable and cost effective	Some use when thermal performance needs to be enhanced	Yes	NA	NA
V	Safe to use in densely populated areas	Yes	May be limitations due to flammability properties and local safety codes and requirements	May be limitations due to flammability / properties and local requirements. Methyl formate in a foam system can be provided to foam manufacturers which may reduce limitations of use.	NA
VI	Easy to service	NA	NA	NA	NA

3.6 Polyurethane spray foam

Safety is primary importance in the application of spray foams. Historically, non-flammable FBAs have been used because of concerns about flammable mixtures especially in enclosed spaces. In the past 10 years, there has also been research to confirm the appropriate timing to allow entry of other trades or occupants without protective equipment after chemicals have dissipated. These studies have focused on several emissive chemicals including FBAs. Spray foam requires focused solutions because the foaming process essentially requires that small portable chemical application equipment be brought into residential and commercial settings during renovation or construction of new buildings. Recently there have been trials using flammable foam blowing agents/components in spray foam including the inclusion of the flammable foam agent in the polyol or isocyanate or both. Concentrations above the lower flammability level (LFL) have been detected in some testing. FTOC does not have data related to further safety testing.

There has been a major focus on reducing heating and cooling loads in buildings. This has increased the use of spray foam to "seal" the building envelope and minimise air infiltration. HFOs/HCFOs improve thermal performance over other low-GWP alternatives but HCFO-1233zd (E) and HFO-

1336mzz (Z) which are in use, are limited by supply chain issues and manufacturing capacity.

The cost of FC alternatives remains a concern, which can be reduced by the addition of water. Water used alone as a FBA for spray foam as a lower cost alternative to HFOs/HCFOs. Water reacts with isocyanate to form carbon dioxide (CO_2) and is frequently used in residential construction in North America. The reaction with water results in very high temperatures and can result in charring or burning of foams if layers are applied with insufficient time between applications to allow for cooling and for the reaction to be complete.

With the advent of the pandemic there is increasing focus on ventilation and air exchange in buildings which might cause some modifications to building design, including the procedures to apply foams.

The table below shows FTOC's assessment of the most commonly used HFC alternatives for PU spray foam against the six Decision XXVI/9, paragraph 1(a), criteria.

Table 3.5 Summary of most commonly used HFC alternatives for PU Spray Foam

Decision XXVI/9 Criterion		**Alternatives**			
		HFOs/ HCFOs	**HCs**	**Methyl formate**	**Water**
I	Commercially available	Yes	Yes	Yes	Yes
II	Technically proven	Yes	No (flammability concerns)	Yes	Yes
III	Environmentally sound	Yes	Yes	Yes	Yes
IV	Economically viable and cost effective	Some use when thermal performance needs to be enhanced	NA	Yes	Yes
V	Safe to use in densely populated areas	Yes	No	May be limitations due to flammability / properties and local requirements. Methyl formate in a foam system can be provided to foam manufacturers which may reduce limitations of use.	Yes
VI	Easy to service	NA	NA	NA	NA

3.7 Polyurethane in-situ and block foams

HCs are generally the FBA in commercial use in PU in situ and block foams. Most medium and large manufacturers with larger facilities use HCs, with the higher initial capital cost balanced by the lower operating costs for pentanes. However, it is likely that HFO/HCFO blends with HCs may be required in future to meet the demand for increased thermal performance in buildings.

The table below shows FTOC's assessment of the most commonly used HFC alternatives for PU in-situ and block foams against the six Decision XXVI/9, paragraph 1(a), criteria.

Table 3.6 Summary of most commonly used HFC alternatives for PU In-situ and Block Foams

Decision XXVI/9 Criterion		Alternatives			
		HFOs/ HCFOs	**HCs**	**Methyl formate**	**Water**
I	Commercially available	Yes	Yes	Yes	Yes
II	Technically proven	Yes	Yes	No	No
III	Environmentally sound	Yes	Yes	Yes	Yes
IV	Economically viable and cost effective	Could be used if thermal performance needs to be enhanced	Yes	NA	NA
V	Safe to use in densely populated areas	Yes	May be limitations due to flammability properties and local safety codes and requirements	NA	NA
VI	Easy to service	NA	NA	NA	NA

3.8 Polyurethane integral skin

Cost and structural performance have been the most important considerations in selecting next generation FBAs for PU integral skin foams. As such, water and some HCs are generally used for these products. HFOs/HCFOs are coming into use and have better thermal performance compared to other lower-GWP alternatives but are more expensive. HCFO-1233zd (E) and HFO-1336mzz(Z) are successfully in use, limited by supply chain issues and available capacities. Water has been increasingly used as a FBA as a lower cost alternative/blend with HFOs/HCFOs.

The table below shows FTOC's assessment of the most used HFC alternatives for PU integral skin against the six Decision XXVI/9, paragraph 1(a), criteria.

Table 3.7 Summary of most commonly used HFC alternatives for PU Integral Skin

Decision XXVI/9 Criterion		Alternatives			
		HFOs/ HCFOs	HCs	Methyl formate	Water
I	Commercially available	Yes	Yes	Yes	Yes
II	Technically proven	Yes	Yes	Yes	No
III	Environmentally sound	Yes	Yes	Yes	Yes
IV	Economically viable and cost effective	Could be used if structural performance needs to be enhanced	Yes	Yes	Yes
V	Safe to use in densely populated areas	Yes	May be limitations due to flammability properties and local safety codes and requirements	May be limitations due to flammability properties and local requirements. Methyl formate in a foam system can be provided to foam manufacturers which may reduce limitations of use.	Yes
VI	Easy to service	NA	NA	NA	NA

3.9 Extruded polystyrene (XPS)

CO_2 is the primary blowing agent in commercial use in non-HFC/HCFC extruded polystyrene (XPS). It is typically used with smaller quantities of co-blowing agents, including, but not limited to Ethanol, dimethyl ether (DME), water, and HCs (iso-butane). HFOs are also used for increased thermal performance of XPS in building construction where increasing thickness is not an option. HFC-152a with its lower GWP can be used either as a co-blowing agent to enhance the process/product or alone as an alternative to CO_2 in SMEs.

The table below shows FTOC's assessment of the most used HFC alternatives for XPS against the six Decision XXVI/9, paragraph 1(a), criteria.

Table 3.8 Summary of most commonly used HFC alternatives for XPS

Decision XXVI/9 Criterion		Alternatives			
		HFOs/ HCFOs	HCs	Methyl formate	Water
I	Commercially available	Yes	Yes	Yes	Yes
II	Technically proven	Yes	Yes - usually as co blowing agents except in some specific regions where codes allow)	Yes	Yes -e in blends
III	Environmentally sound	Yes	Yes	Yes	Yes
IV	Economically viable and cost effective	Could be used to achieve desired thermal performance	Yes (may require significant capital investment)	Yes	Yes
V	Safe to use in densely populated areas	Yes	Mitigation required, building codes may not allow use of hydrocarbons May be limitations due to flammability properties and local safety codes and requirements	May be limitations due to flammability properties and local requirements .	Yes
VI	Easy to service	NA	NA	NA	NA

3.10 Phenolic foam

HCs are generally the FBA in commercial use in phenolic foams. Most medium and large manufacturers with larger facilities use HCs, with the higher initial capital cost balanced by the lower operating costs for pentanes. However, it is likely that HFO/HCFO blends with HCs may be required in future to meet the demand for increased thermal performance in buildings. Chloropropane is also used as a FBA for phenolic foam co-blown with HCs. This is a non-ODS with low GWP and are not controlled by the Montreal Protocol.

Table 3.9 Summary of most commonly used HFC alternatives for Phenolic Foam

Decision XXVI/9 Criterion		Alternatives			
		HFOs/ HCFOs	HCs	Methyl formate	Water
I	Commercially available	Yes	Yes	Yes	Yes
II	Technically proven	Yes	Yes	No	No
III	Environmentally sound	Yes	Yes	Yes	Yes
IV	Economically viable and cost effective	Some use when thermal performance needs to be enhanced	Yes	NA	NA
V	Safe to use in densely populated areas	Yes	May be limitations due to flammability properties and local safety codes and requirements	NA	NA
VI	Easy to service	NA	NA	NA	NA

3.11 Other alternatives under development or used in small quantities

DME, ethanol and butanes are used in XPS. DME is also used in some one-component PU foams that are dispensed from an aerosol can.

Methylene chloride is still used as a blowing agent in the production of flexible foams in A5 parties. Japan no longer allows the use of methylene chloride in foams and the US SNAP program changed the status of methylene chloride to “unacceptable” for use in foams. However, foam produced with methylene chloride in A5 parties can be exported to the United States provided the foam is open-celled.

Methylal (Dimethoxymethane), is used as a co-blowing agent in low-resistance, high-density (“memory”) foams and in very low concentrations in combination with water in rigid foams. Flammability of the polyol blend is a limiting factor when used as a sole blowing agent.

Trans-1,2 dichloroethylene (1,2-DCE) is also used as a co-blowing agent, primarily in spray foam, with HFCs and is approved for use in the US and Europe. Flammability of the polyol blend is a limiting factor when used as a sole blowing agent.

In the PU HC-blown sector, FTOC had previously become aware of two perfluorocarbon foam additives (FA-188 and PF-5056), both from the same manufacturer, which are being used to optimise cell formation in order to gain maximum thermal performance. FA-188 is a perfluorinated olefin, which is used in very small quantities and has a GWP of around 100, but there are concerns about its potential breakdown products, which currently remain uncertain. PF-5056 has a high GWP.

3.12 Summary

The table below summarises where alternatives to HFCs in foams are available on a sector-by-sector basis. For an alternative to be available, it must have passed all Decision XXVI/9, paragraph 1(a), criteria, i.e., it is commercially available, technically proven, environmentally sound, economically viable and cost effective, and safe to use, according to FTOC’s interpretation of these criteria.

Table 3.10 Summary of alternatives for HFCs in foams applications

Sector	Comment	HFCs being used?	Alternatives Available?
Domestic Refrigeration	Some use to improve thermal performance	Some	Yes
Commercial Refrigeration	Frequently used to improve thermal performance	Yes	Yes
Transport Refrigeration	Frequently used to improve thermal performance but cost sensitivity prevents some use	Yes	Yes
Polyurethane boardstock (PU)	Used to improve thermal performance	Some	Yes
PU Panels	Rarely used in continuous panels but could be used to improve thermal performance	Yes, in discontinuous panels) but rarely used in continuous panels	Yes
PU Spray Foam	Commonly used (safety and to improve thermal performance)	Yes	Yes
PU i*n-situ* and Block Foams	Rarely used (could be used to improve thermal performance	Yes	Yes
PU Integral Skin	Some use for unique structural properties	Yes	Yes
Extruded polystyrene (XPS)	Some use for higher thermal or structural performance	Yes	Yes
Phenolic Foam	Some use for higher thermal or structural performance	Yes	Yes

Continuing Challenges Especially for Small- and Medium-Sized Enterprises and Spray Foam

The transition away from HCFC FBAs in some regions and market segments (e.g., spray foam) may be delayed because of cost, especially where local codes require higher thermal performance[7]. The price of HFC blowing agents has risen substantively during the pandemic and is almost as high as HFO/HCFO prices were prior to the pandemic in some A5 parties. In

[7] Although the cost of HCFCs was approximately 20-30% of the cost of high-GWP HFCs, HCFC price is increasing as they are phased out globally. The low price of some high-GWP HFCs, particularly HFC-365mfc which is banned in some non-A5 parties, is leading to an increase in market share, which is slowing the conversion to low-GWP blowing agents

locations where HFCs are used HFO/HCFO costs will be higher but more comparable than when replacing HCFCs.

Finally, SMEs and spray foam manufacturers may still be facing challenges related to the adoption of HFOs/HCFOs, due to their operating cost, and hydrocarbons, due to potentially cost-prohibitive, capital investment or impractical safety requirements for field application. This continues to be an unresolved challenge for SMEs and in field applications for all foams for all parties

4 Information on alternatives to HFCs in the fire protection sector

4.1 Introduction

Much of the information requested by Decision XXVIII/2 is contained in the HTOC 2022 Assessment Report and the recently updated Technical Note A. However, as is explained below, owing to the evolution of fire protection agents, the information is not easy to extract, and the HTOC is responding to this Decision by providing the information below and updating its technical note. This confers several advantages: the information will be presented in a clear and systematic manner; it should be easy for the parties to find; and it should be easy for the HTOC to update in five years' time, as required by the decision. Information contained in this report, which was requested ahead of MOP-34, may be further updated as part of the HTOC 2022 Assessment Report to be completed by the end of 2022.

4.1.1 Evolution of fire protection approaches

The fire protection industry was an early and strong supporter of the Montreal Protocol. Extensive research was conducted to identify alternatives, while simultaneously implementing improvements to maintenance, servicing and storage of halons, user awareness and training, replacement of halon systems where practical, as well as highly improved risk management. All these actions have reduced dependence upon halons. The evolution of halon alternatives has proceeded along the path of selection of chemicals with the most similar characteristics followed by research and development including testing, certification, toxicity and safety analyses, standards development, and commercialization. During this period several HCFCs were developed for fire suppression applications.

As many of the early candidates were eliminated due to failure in one or more of the aforementioned steps, more challenging chemicals, many with less favorable characteristics, were added to the research and development process. Several HFCs were developed through to commercialization (note: both the agent and hardware must successfully pass all testing and certifications). Following the commercialisation of HFCs, other chemicals were developed including FK-5-1-12, 2-BTP, CF_3I, and some combinations with inert gases, water mist, or solid particulates. This evolution has been fairly linear, as makes sense, in that the most likely candidates would be the most commercially viable due to the extensive cost of research and development. The fire protection industry has worked on developing alternatives to halons, HCFCs and now HFCs for over four decades as environmental concerns have evolved. Figure 4.1 illustrates how the fire protection market has changed over the lifetime of the Montreal Protocol. Note that the height of the bars in the histogram are normalized. It should not be interpreted that the total market size is the same for each of the years included.

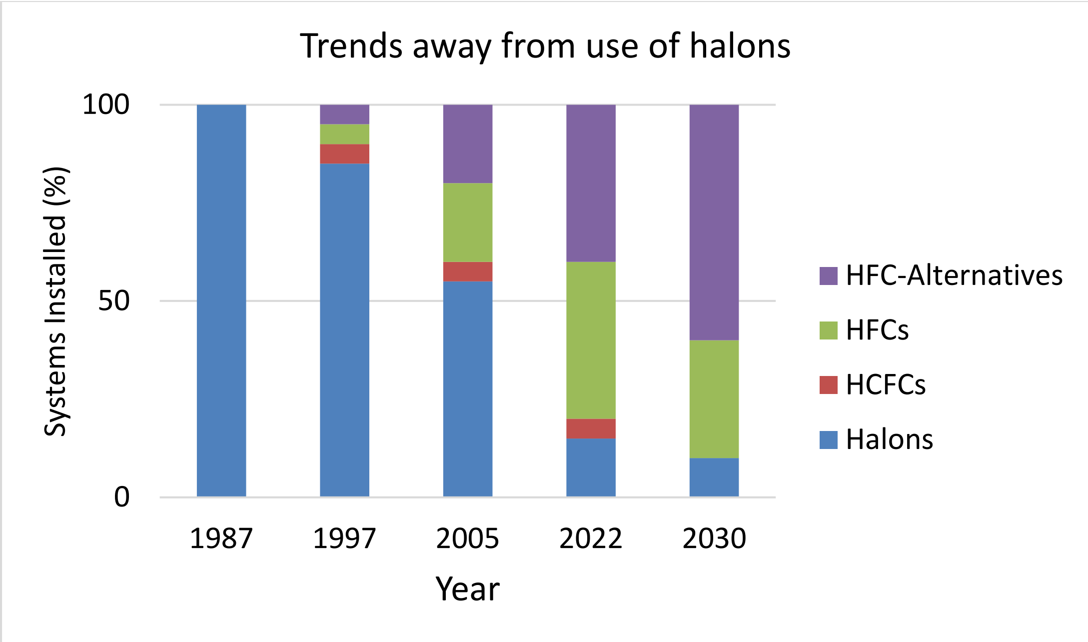


Figure 4.1: Estimated trend in fire protection systems installed

4.1.2 HTOC interpretation of criteria listed in Decision XXVI/9 paragraph 1(a)

The criteria outlined in Decision XXVI/9 paragraph 1 (a) can be subject to interpretation depending on the context of their use. From a fire protection perspective, the HTOC interprets the criteria as:

ii. **"Commercially available"**
The fire suppression agent for use in portable or mobile fire extinguishers and fixed fire protection systems which are offered for commercial sale is available on the open market and there is future certainty in the supply, i.e., the agent is not included in any future production phase-down legislation. Commercial availability may also be influenced by national or local governmental requirements affecting the import of one agent over another into the region or country. This does not necessarily mean that the extinguishers, systems, or extinguishing agents are accessible in all parties (for example A5s versus non-A5s). In this context "accessible" follows the concept explained in section 6.1.2 of this report but in the context of fire extinguishing agents/systems.

iii. **"Technically proven"**
The fire protection system design for the fire suppression agent is accepted by regulators and industry because the fire extinguishers and fire protection systems have passed all necessary performance tests for the intended application. The tests, which may include extreme ambient temperatures, full-scale, small-scale, test vessel or test enclosure performance, demonstrate that the alternative agent provides acceptable fire extinguishment/suppression effectiveness and safety. The system design does not require further development and have acceptable space and weight characteristics. The agent is appropriately rated by a notified body or a body accredited by the American National Standards Institute (ANSI) to assess conformity to recognized standards, for example, Underwriters Laboratories (UL™), or all reviews under the U.S EPA Toxic Substances Control Act and the Significant New Alternatives Policy (SNAP) program are completed. Other technical considerations for HFC replacements include that the agent has long-term stability in storage, is non-corrosive to metals, and is chemically compatible with materials it will contact. In some cases, the agent must also be "clean," that is, it leaves no residues during use, and/or be electrically non-conductive.

iv. **“Environmentally sound”**
The alternative fire suppression agent has minimal environmental impact (e.g., short atmospheric lifetime) compared to ODS or HFC extinguishing agents. They have zero or very low ozone depleting potential (which could be subject to individual party determination), have very low global warming potential and are not foreseen to be subject to future production phasedowns.

v. **“Economically viable and cost effective”**
The cost to manufacture the alternative fire suppression agent is reasonable and therefore the cost of obtaining the alternative is not prohibitive, the alternative is competitively priced and available on the market; and there is little or no reluctance by owners to adopt the new agent. In the context of fire protection, cost-effectiveness can be a subjective issue and needs to be viewed in the context of the value of the asset being protected, and the cost-effectiveness to replace or modify existing fire suppression systems and components with an alternative agent. For example, in the case of system fire protection, where the asset may be a multi-million dollar building or military platform, cost-effectiveness would be viewed differently compared to a portable fire extinguisher in a domestic situation.

vi. **“Safe to use in areas with high urban densities considering flammability and toxicity issues, including, where possible, risk characterization**”
For fire extinguishing agents, the flammability criterion is not relevant in the case of high urban density. In terms of toxicity, fire extinguishing agents are used in two different ways; total flooding and local application (also referred to as streaming). For total flooding agents, especially when used in “normally occupied areas,” the toxicology considerations are more stringent than for local applications. For normally occupied areas, the agent must have no observable adverse effects on biological tissue when used at the design concentration. Although for portable extinguishers in enclosed spaces, consideration must also be given to minimum room volume to ensure that the concentration of the agent does not present a hazard to occupants.

vii. **“Easy to service and maintain”**
Recognized and approved standards exist for the servicing and maintenance of the portable and mobile fire extinguisher and fixed fire protection system. Training on service and maintenance the system is available and accessible. In the United States and Canada, for example, portable fire extinguishers are intended to be selected, installed, inspected, maintained, and tested in accordance with National Fire Protection Association (NFPA) 10, Standard for Portable Fire Extinguishers. In general, servicing of fire extinguishing systems and portable extinguishers is a highly technical task. However, the differences between servicing an HFC system and its alternative are relatively small, as is the amount of additional training that would be required.

In carrying out the assessment below, the HTOC considers that a single “No” for any criterion means that the alternative is not currently acceptable for the application being considered. However, as the alternative agent undergoes further development, it could meet all six criteria in the future.

4.2 Sectors and applications where HFCs are used

As HFCs are only used as halon replacements, the following table provides a summary of which fire protection sub-sectors do or do not use HFCs that originally used halons.

Table 4.1 Summary of alternatives for HFCs in fire protection

Sector	Application	HFCs being used?
Civil Aviation	Normally unoccupied cargo compartments	No
	Aircraft cabins, cockpits and crew rest compartments	Yes (1)
	Engine nacelles and auxiliary power units	Yes (1)
	Lavatory waste receptacles	Yes
	Fuel tank inerting	No
	Crash rescue vehicles	No
Military Ground Vehicles	Crew compartment	Yes
	Non-occupied compartments	Yes
Military Naval	Normally occupied spaces	Yes
	Normally unoccupied spaces (engine, machinery, electrical etc.)	Yes
Military Aviation	Engine and APU	Yes
	Occupied spaces	Yes (1)
	Dry bays	Yes
	Fuel tank inerting	No
	Cargos compartments	No
Oil & Gas	Computer and control rooms	Yes (1)
	Hydrocarbon production (liquids)	Yes
General Industrial Fire Protection	Normally occupied spaces including data centres and telecommunications facilities	Yes
	Non-occupied spaces	Yes
Merchant shipping	Main engine rooms	No
	Other normally occupied spaces	Yes
	Other normally unoccupied spaces	Yes

Notes:

1. In some specific instances only.

4.3 Where can alternatives to HFCs be used?

4.3.1 Civil Aviation

4.3.1.1 Cargo compartments

Halon 1301 continues to be used in all cargo compartment applications; HFCs have never been used for the protection of cargo compartments in civil aircraft and are unlikely to be so in the future. HFC-125 (amongst other agents) failed a key element of the US Federal Aviation Administration (FAA) Cargo Compartment Minimum Performance Standard (MPS), FAA (2004). This effectively ruled out HFCs for this application.

4.3.1.2 Aircraft cabins, cockpits, and crew rest compartments

These areas on aircraft are protected using portable (handheld) fire extinguishers. Although portable fire extinguishers have been developed using HFCs (e.g., HFC-236fa and HFC-227ea) and some were approved for civil aviation use, it is the HTOC's understanding that they were only sold commercially for some business jets and in general aviation. HFCs were never adopted in main fleet passenger aircraft. One alternative is available, 3,3,3-trifluoro, 2-bromo-prop(-1)ene (2-BTP) that is being installed on most newly produced aircraft. It has a "negligible" GWP (WMO(2018)) and can therefore be considered to be commercially available, technically proven, environmentally-sound, economically viable, safe to use and easy to service and maintain for this application. It is worth noting, however that 2-BTP does have a larger minimum room volume requirement than the HFC agents for an equivalent fire rating which can restrict its use in smaller aircraft cabins and cockpits.

4.3.1.3 Engine nacelles and auxiliary power units

Of the agents evaluated for the protection of engine nacelles, only one (HFC-125) has been approved and is in use for some military applications. Potential alternatives to HFC-125 include (a) CF_3I, (b) a finely-ground sodium bicarbonate-based dry chemical (referred to as Powdered Aerosol F in the US EPA SNAP Regulations, (EPA(2022)), (c) the fluoroketone FK-5-1-12, and (d) possibly carbon dioxide (CO_2). The table below shows HTOC's assessment of these four agents against the six Decision XXVI/9 criteria.

Table 4.2 Summary of alternatives for HFCs in Engine Nacelle and APU

Decision XXVI/9 Criterion		Alternatives			
		CF_3I(1)	Powdered Aerosol F (1)	FK-5-1-12	CO_2
I	Commercially available	Yes	No	Yes	Yes
II	Technically proven	No	No	No (2)	No (3)
III	Environmentally sound	Yes (4)	Yes	Yes	Yes
IV	Economically viable and cost effective	Yes	Yes	Yes	No
V	Safe to use	No (5)	Yes	Yes	No (5)
VI	Easy to service	Yes	Yes	Yes	Yes

Notes:

1. Both CF_3I and Powdered Aerosol F are currently being tested against the FAA Minimum Performance Standard (MPS) for aircraft engine nacelles. This will define the certification criteria for these agents and once a certification program has been completed the agent could be considered to be technically proven.
2. FK-5-1-12 failed a low temperature fire test and is effectively excluded from this application.
3. Although CO_2 has passed the FAA MPS test, its weight and volume characteristics make it very unattractive in this application.
4. CF_3I has a "negligible" GWP (WMO(2018)).
5. Concern has been expressed by some stakeholders regarding the toxicity of CF_3I. Although engine nacelles are unoccupied, an agent of higher toxicity may present issues during installation, service, and maintenance operations. The same is true of CO_2.

4.3.1.4 Lavatory waste receptacles

Two HFCs (HFC-227ea and HFC-236fa) are used in this application. No alternatives have been evaluated to date; the civil aviation industry is focussing on halon replacement in engine nacelle and cargo compartment applications. The table below lists some possible alternatives and their assessment against the six Decision XXVI/9 criteria. The alternatives have been divided into two categories: "in-kind" (vaporizing liquids that would operate in a similar fashion to the current HFC agents) and "not-in-kind" (agents with different physical characteristics)

Table 4.3 Summary of "in-kind" alternatives for HFCs in Lavatory Waste Receptacles

Decision XXVI/9 Criterion		"In-kind" Alternatives		
		2-BTP	CF_3I	FK-5-1-12
I	Commercially available	Yes	Yes	Yes
II	Technically proven	No	No	No
III	Environmentally sound	Yes	Yes	Yes
IV	Economically viable and cost effective	Yes	Yes	Yes
V	Safe to use	Yes (1)	Yes (1)	Yes
VI	Easy to service	Yes	Yes	Yes

Notes

1. Calculations suggest that the quantity of agent required may be close to, or exceed, the allowed concentration in small lavatory areas.

Table 4.4 Summary of "not-in-kind" alternatives for HFCs in Lavatory Waste Receptables

Decision XXVI/9 Criterion		"Not-in-kind" Alternatives (1)		
		CO_2	Inert Gas	Water Mist
I	Commercially available	Yes	Yes	Yes
II	Technically proven	No	No	No
III	Environmentally sound	Yes	Yes	Yes
IV	Economically viable and cost effective	Not Known (NK)	NK	NK
V	Safe to use	Yes	Yes	Yes
VI	Easy to service	Yes	Yes	Yes

NK: not known to HTOC at this time.

Notes:

1. These agents are no more than concepts at this stage. Moving to a "not-in-kind" solution would require more research and development and may also give rise to additional technical challenges.

4.3.1.5 Fuel Tank Inerting

Flammable hydrocarbon vapour can accumulate in the headspace or ullage of fuel tanks on commercial aircraft. If an ignition source is present a fuel-air explosion can occur, which can destroy the aircraft. To prevent this from occurring, fuel tank atmospheres are inerted using on-board inert gas generating systems (OBIGGS). These systems are based on an air separation technology, which generates a flow of oxygen-depleted air which is used to inert the fuel tanks. These are commercially available and have passed all the Decision XXVI/9 criteria. HFCs have never been used in this application and are unlikely to be used in the future.

4.3.1.6 Crash Rescue Vehicles

Historically this application used halon 1211. Halon alternatives employed include HCFC Blend B, FK-5-1-12, and dry powder. HFCs were not used in this application, so although halon alternatives are available, they are not HFC alternatives in the strictest sense.

4.3.2 Military ground vehicles

4.3.2.1 Crew Compartments

In recent years, many parties have replaced halon 1301 with HFC-227ea/dry chemical blend or HFC-236fa for vehicle fire protection in occupied compartments. For these specialized military applications, only these high-GWP HFCs have been technically proven to meet the stringent performance and safety criteria. Research is ongoing to evaluate alternatives to HFCs, however no low-GWP alternative has been identified to meet stringent design requirements. Therefore, these high-GWP HFCs will be required for the foreseeable future in occupied compartments.

Table 4.5 Summary of "in-kind" alternatives for HFCs in Crew Compartments

Decision XXVI/9 Criterion		"In-kind" Alternatives		
		2-BTP	CF_3I	FK-5-1-12
I	Commercially available	Yes	Yes	Yes
II	Technically proven	No	No	No
III	Environmentally sound	Yes	Yes	Yes
IV	Economically viable and cost effective	No (1)	No (1)	No (1)
V	Safe to use	No	No	No
VI	Easy to service	Yes	Yes	Yes

Notes:

1. System cost and integration impacts are unknown.

Table 4.6 Summary of "not-in-kind" alternatives for HFCs in Crew Compartments

Decision XXVI/9 Criterion		"Not-in-kind" Alternatives		
		CO2	Inert Gas	Water Mist
I	Commercially available	Yes	Yes	Yes
II	Technically proven	No	No	No
III	Environmentally sound	Yes	Yes	Yes
IV	Economically viable and cost effective	No (1)	No (1)	No (1)
V	Safe to use	No	No	No
VI	Easy to service	Yes	Yes	Yes

Notes:

1. System cost and integration impacts are unknown.

4.3.2.2 Non-occupied Compartments

In non-occupied compartments of military ground vehicles such as engine compartments, most halon applications have been replaced with HFCs or other chemicals. The HFC alternatives in the two tables below have been/are being considered for implementation where feasible, however technical challenges in comparison to gaseous HFC agents need to be considered (e.g., additional distribution, nozzles, etc).

Table 4.7 Summary of "in-kind" alternatives for HFCs in Non-occupied Compartments

Decision XXVI/9 Criterion		"In-kind" Alternatives		
		2-BTP	CF_3I	FK-5-1-12
I	Commercially available	Yes	Yes	Yes
II	Technically proven	No	No	No
III	Environmentally sound	Yes	Yes	Yes
IV	Economically viable and cost effective	NK	NK	NK
V	Safe to use	No	No	Yes
VI	Easy to service	Yes	Yes	Yes

Table 4.8 Summary of "not-in-kind" alternatives for HFCs in Non-occupied Compartments

Decision XXVI/9 Criterion		"Not-in-kind" Alternatives		
		CO_2	Inert Gas	Dry Chemical
I	Commercially available	Yes	Yes	Yes
II	Technically proven	Yes (1)	Yes	Yes
III	Environmentally sound	Yes	Yes	Yes
IV	Economically viable and cost effective	Yes	No (2)	Yes
V	Safe to use	Yes	Yes	Yes
VI	Easy to service	Yes	Yes	Yes (3)

Notes:

1. More research and development would be required and may also give rise to additional technical challenges.
2. Weight and volume characteristics make this a very unattractive option for this application
3. The requirements for post-discharge clean-up may make dry chemical systems unattractive, e.g., if removal of the vehicle powerpack is a time-consuming and costly process.

4.3.3 Military naval applications

4.3.3.1 Occupied Spaces

Some parties use alternatives to HFCs, including FK-5-1-12, in some applications on-board naval vessels. However due to technical and economic challenges associated with retrofits, halons continue to be used in many critical legacy applications. For example, if the enclosure must stay manned during a fire event, then a limited number of agents are available for consideration due to toxicity concerns. It should be noted that agent selection and approval criteria can vary from one party to another. For example one party might consider gaseous agents to be the only alternative for a specific application, but another would accept other agents such as dry chemicals. Issues such as post-discharge clean-up may affect how cost-effectiveness is viewed.

4.3.3.2 Machinery and Other Unoccupied Spaces

A wide range of agents that include both high-GWP and low/zero-GWP fire suppressants is used for the main machinery and other spaces of new vessels. These include HFC-227ea, fine water spray, hybrid HFC-227ea/water spray, FK-5-1-12, foam, and carbon dioxide systems. However, carbon dioxide systems are prohibited in all spaces on new U.S. naval vessels due to crew safety considerations. In some applications, such as electrical compartments or where HFCs are not acceptable because of national legislation, inert gas systems such as IG-541 are used.

Table 4.9 Summary of alternatives for HFCs in Machinery and Other Unoccupied Spaces

Decision XXVI/9 Criterion		Alternatives				
		Water Spray	FK-5-1-12	AFFF	CO_2	Inert Gas
I	Commercially available	Yes	Yes	Yes	Yes	Yes
II	Technically proven	Yes	Yes	Yes	Yes	Yes
III	Environmentally sound	Yes	Yes	Yes (1)	Yes	Yes
IV	Economically viable and cost effective	Yes	Yes	Yes	Yes	Yes
V	Safe to use	Yes	Yes	Yes	No (2)	Yes
VI	Easy to service	Yes	Yes	Yes	Yes	Yes

Notes:

1. PFAS-containing foams are being eliminated, however PFAS-free foams are commercially available.
2. An agent of higher toxicity may present issues during installation, service, and maintenance operations.

4.3.4 Military aviation applications

4.3.4.1 Engine and APU Spaces

Some parties have successfully implemented HFC-125 as an alternative to halons for engine and APU fire protection. It is unlikely that any HFC alternative will be implemented in the foreseeable future.

4.3.4.2 Occupied Spaces

Military aviation applications are similar to civilian aviation, where these spaces are mainly protected by portable extinguishers.

4.3.4.3 Dry bays

Dry bays are the compartments in military aircraft immediately adjacent to fuel tanks or other flammable fluids. They frequently contain fluid lines, control lines, electrical equipment, etc. Ballistic damage to these bays may allow fuel to enter the bay causing fire after contact with electrical components or other ignition sources which could result in loss of the aircraft. Accordingly, key dry bays are protected with fast response fire detection and suppression systems. Some of these systems use HFCs, notably HFC-236fa. Other systems use dry chemical fire extinguishant, which can be considered to be commercially available, technically proven, environmentally-sound, economically viable, safe to use and easy to service and maintain. However, the impacts of replacing HFCs with dry chemical would have to be evaluated on a case-by-case basis, including the effects of post-discharge clean-up.

4.3.4.4 Fuel Tank Inerting

HFCs have never been used to inert fuel tanks in military aircraft and are unlikely to be so in the future.

4.3.4.5 Cargo Spaces

HFCs have never been used for cargo spaces in military aircraft and are unlikely to be so in the future.

4.3.5 Oil and gas

4.3.5.1 Computer and Control Rooms

Halons were the agent of choice for mitigating the threat of fire and explosion events in enclosed oil and gas production and transportation facilities due to the harsh climatic conditions. Because of the effectiveness and availability of halons 1301 and 2402 at the time of initial development of the facilities, it was also commonly provided in the enclosures housing various support infrastructure (communication/data rooms, facility control rooms, primary/standby power generation, and electrical equipment rooms). HFCs have been used in this application for the protection of support areas such as battery or electrical rooms, or pipeline maintenance buildings.

Table 4.10 Summary of alternatives for HFCs in Computer and Control Rooms

Decision XXVI/9 Criterion		Alternatives			
		Inert Gas	Water Mist	FK-5-1-12	CO_2
I	Commercially available	Yes	Yes	Yes	Yes
II	Technically proven	Yes	Yes (1)	Yes (1)	Yes
III	Environmentally sound	Yes	Yes	Yes	Yes
IV	Economically viable and cost effective	No	Yes (2)	Yes	No
V	Safe to use	Yes (3)	Yes (2)	Yes (3)	No (4)
VI	Easy to service	Yes	Yes	Yes	Yes

Notes:

1. In cold climates, water mist and FK-5-1-12 may require additional infrastructure (i.e., additional heat loads) to work in conjunction with the facility safety systems to provide adequate protection.
2. Electrical safety measures need to be evaluated.
3. Specific to computer rooms co-located in low temperature hydrocarbon production facilities, concern has been expressed by some stakeholders regarding the possibility that protection for some of these hazards may necessitate a design concentration near or above the NOAEL for some alternatives. As these types of rooms may or may not be normally occupied this may present issues during installation, service, and maintenance operations which need to be more carefully evaluated.
4. Many authorities will not allow CO_2 in normally occupied areas. When allowable, CO_2 systems need to be set to a manual mode when people are present in the space being protected.

4.3.5.2 Hydrocarbon Production

Oil and gas production and transportation facilities face many different hazards, with the most significant being fires and explosions involving flammable liquids or gases. Halons were the agent of choice to mitigate the threat of both fires and explosions in facilities that are enclosed due to harsh climatic conditions. Because of the effectiveness of halon for both inerting the enclosure (i.e., creating a non-explosive environment) and flame extinguishment, and availability of halons at the time of development of the facilities, it was also commonly provided in the enclosures housing oil and gas production areas. In enclosed areas with gas production, the vapour cloud explosion potential eliminates a number of fire suppression mediums from consideration as they are generally effective at either flame extinguishment or inerting the atmosphere, but not both. The decision to use halons as the primary fire protection tool was arrived at after carefully evaluating the agents available at the time. Originally, only halons and CO_2 were assessed to have the ability to both inert hydrocarbon atmospheres and extinguish fires very low temperature applications. With the introduction of HFCs, HFC-23 was added to this list (under those climatic conditions). However, CO_2 was rejected because it is too slow acting to accomplish inerting or extinguishment in the desired time periods and because it presents a hazard to life at extinguishing concentrations, thus leaving halons and HFC-23. Depending upon the ability to handle the vapour cloud through other means such as high-rate ventilation, some HFC alternatives exist.

Table 4.11 Summary of alternatives for HFCs in Hydrocarbon Production

Decision XXVI/9 Criterion		Alternatives		
		Dry Powder	Water Mist	FK-5-1-12
I	Commercially available	Yes	Yes	Yes
II	Technically proven	No (1)	Yes (1,2)	Yes (1,2)
III	Environmentally sound	Yes	Yes	Yes
IV	Economically viable and cost effective	No	No	Yes
V	Safe to use	Yes	Yes	Yes (3)
VI	Easy to service	Yes	Yes	Yes

Notes:

1. Depending upon the ability to handle the vapour cloud through other means such as high-rate ventilation, this alternative is technically proven.
2. In cold climates, water mist and FK-5-1-12 may require additional infrastructure (i.e., additional heat loads) or modifications away from accepted industry practice to work in conjunction with the facility safety systems. However, the fire protection scheme may not allow additional heat load systems to operate during specific events or the cost to provide explosion proof heating affects economic viability.
3. Concern has been expressed by some stakeholders regarding the possibility that protection for some of these hazards may necessitate a design concentration near or above the No Observed Adverse Effects Level (NOAEL) for some halocarbon agents. As these types of rooms may or may not be normally occupied this may present issues during installation, service, and maintenance operations which need to be more carefully evaluated.

4.3.6 General industrial fire protection

4.3.6.1 Normally Occupied Spaces including Data Centres and Telecommunications Facilities

A number of alternatives to HFCs for the protection of normally occupied spaces are available for the protection of these hazards. The table below shows the HTOC assessment against the Decision XXVI/9 criteria.

Table 4.12 Summary of alternatives for HFCs in Normally Occupied Spaces

Decision XXVI/9 Criterion		Alternatives				
		Inert Gas	Water Mist	FK-5-1-12	Halocarbon Blend 55	CO_2
I	Commercially available	Yes	Yes	Yes	No (1)	Yes
II	Technically proven	Yes	Yes	Yes	No	Yes
III	Environmentally sound	Yes	Yes	Yes	Yes	Yes
IV	Economically viable and cost effective	Yes	Yes	Yes	NK	No
V	Safe to use	Yes	Yes	Yes	NK	No (2)
VI	Easy to service	Yes (3)	Yes	Yes	NK	Yes

Notes:

1. The blend is not commercially available but the two separate components (FK-5-1-12 and HCFO-1233zd(E)) are available commercially.
2. Carbon dioxide systems need to be set to a manual mode when people are present in the space being protected.
3. While in some areas these systems can be easy to service, in remote locations with limited transportation alternatives fire protection systems can be very expensive to recharge. Factors such as air

transport and ice roads need to be considered. This is especially true in the case of inert gas systems because of the larger amount of extinguishing agent / number of cylinders required.

4.3.6.2 Non-occupied Spaces

A number of alternatives to HFCs for the protection of non-occupied spaces have been available for the protection of these hazards for some time. The table below shows the HTOC assessment against the Decision XXVI/9 criteria.

Table 4.13 Summary of alternatives for HFCs in Non-occupied Spaces

Decision XXVI/9 Criterion		Alternatives				
		Inert Gas	Water Mist	FK-5-1-12	Halocarbon Blend 55	CO_2
I	Commercially available	Yes	Yes	Yes	No (1)	Yes
II	Technically proven	Yes	Yes	Yes	No	Yes
III	Environmentally sound	Yes	Yes	Yes	Yes	Yes
IV	Economically viable and cost effective	Yes	Yes	Yes	NK	Yes
V	Safe to use	Yes	Yes	Yes	NK	Yes (2)
VI	Easy to service	Yes	Yes	Yes	NK	Yes

Notes:

1. The blend is not commercially available but the two separate components (FK-5-1-12 and HCFO-1233zd(E)) are both available commercially
2. In the event of a discharge of a carbon dioxide system, a means to prevent people from entering the space is required until it is safe to do so.

4.3.7 Merchant shipping

4.3.7.1 Main Engine Rooms & Machinery Spaces

Historically these applications were protected with carbon dioxide. In the mid-1970s passenger ships and tankers switched from carbon dioxide to halon 1301 for fire suppression in the main engine rooms as it was more cost effective. When the International Maritime Organization (IMO) banned the use of halons in new construction in 1992 (IMO, 1992), carbon dioxide once again became the agent-of-choice for these types of ships. It is the HTOC's understanding that HFCs were never used in this application. Thus, carbon dioxide is a halon alternative, but should not be viewed as an HFC alternative. Additionally, in some smaller vessels FK-5-1-12 has been used.

4.3.7.2 Normally-occupied Spaces

The alternatives to HFCs for the protection of normally occupied spaces in the Merchant Shipping sector are considered to be comparable to those available for the General Industrial Fire Protection sector. Refer to section 4.3.6.

4.3.7.3 Non-occupied spaces

The alternatives to HFCs for the protection of non-occupied spaces in the Merchant Shipping sector are considered to be comparable to those available for the General Industrial Fire Protection sector. Refer to section 0.

4.4 Effect of proposed PFAS regulations on alternatives to HFCs in Fire Protection

4.4.1 Background

PFAS (perfluoroalkyl and polyfluoroalkyl substances) refers to a class of chemicals that contain fluorine atoms bonded to carbon atoms. Historically, PFAS was used to describe longer chain compounds that were used in products such as paper, textiles, leather, carpets, and firefighting foam. The regulation of PFAS initially focused on the eight-carbon chemicals PFOS (perfluorooctane sulfonic acid) and PFOA (perfluorooctanoic acid). More recently PFAS definitions have been broadened to include over 4,000 different fluorinated compounds ranging from gases to liquids to solids that include carbon chain lengths as short as a single carbon. PFASs are defined as fluorinated substances that contain at least one fully fluorinated methyl or methylene carbon atom (without any H/Cl/Br/I atom attached to it), i.e., with a few noted exceptions, any chemical with at least a perfluorinated methyl group (–CF3) or a perfluorinated methylene group (–CF2–) can be considered a PFAS under this broader definition. (OECD (2021)). However, it should be noted that OECD states "The term "PFASs" is a broad, general, non-specific term, which does not inform whether a compound is harmful or not, but only communicates that the compounds under this term share the same trait for having a fully fluorinated methyl or methylene carbon moiety." Regarding the PFAS definition, OECD also notes "It also does not conclude that all PFASs have the same properties, uses, exposure and risks."

4.4.2 Implications for alternatives to HFCs in Fire Protection

The recent broadened definitions of PFAS may now include both HFCs and also HFC alternatives such as HFOs, fluoroketones, and 2-BTP. This could mean that many of the alternatives to HFCs listed above might be restricted or disallowed. However, it has been argued that the definitions for PFAS need to be revised so that they no longer include substances such as HFCs and HFC alternatives that environmentally degrade to produce only trifluoroacetic acid (TFA). (Wallington (2021)). The important question is which HFC alternatives will be designated as PFAS under OECD regulations and be subject to controls. It is important to note that this is an evolving situation, and the HTOC expects to understand more fully in the future how these proposed regulations will affect both HFCs and their alternatives in fire protection. Nevertheless, concern is being expressed in the fire protection sector regarding the long-term viability of HFCs and their alternatives (including halon alternatives, such as 2-BTP). HTOC will be reviewing the potential implications in more detail in the 2022 TEAP Assessment Report.

4.5 Summary

The table below summarises where alternatives to HFCs are available on a sector-by-sector basis. For an alternative to be available, it must have passed all six Decision XXVI/9 criteria, i.e., it is commercially available, technically proven, environmentally sound, economically viable and cost effective, safe to use, and easy to service, according to HTOC's interpretation of these criteria.

Note: some alternatives listed here are actually halon alternatives rather than HFC alternatives. See footnote. Furthermore, wherein some sectors or applications HFCs were not used and there are no alternatives e.g., in aircraft cargo compartments. In these cases, it seems appropriate to state that alternatives to HFCs are not applicable (N/A).

Table 4.11 Summary of alternatives for HFCs in Fire Protection

Sector	Application	HFCs being used?	Alternatives Available?
Civil Aviation	Normally unoccupied cargo compartments	No	N/A
	Aircraft cabins, cockpits and crew rest compartments	Yes (1)	Yes
	Engine nacelles and auxiliary power units	Yes (1)	No
	Lavatory waste receptacles	Yes	No
	Fuel tank inerting	No	Yes (2)
	Crash rescue vehicles	No	Yes (2)
Military Ground Vehicles	Crew compartments	Yes	No
	Non-occupied compartments	Yes	Yes (3)
Military Naval	Normally occupied spaces	Yes	Yes
	Normally unoccupied spaces (engine, machinery, electrical etc.)	Yes	Yes
Military Aviation	Engine and APU	Yes	No
	Occupied Spaces	No	Yes (2)
	Protection of dry bays	Yes	Yes
	Fuel Tank Inerting	No	N/A
	Cargo compartments	No	N/A
Oil & Gas	Computer and control rooms	Yes (1)	Yes (3)
	Hydrocarbon production (liquids)	Yes	Yes (3)
General Industrial Fire Protection	Normally occupied spaces including data centres and telecommunications facilities	Yes	Yes (3)
	Non-occupied spaces	Yes	Yes
Merchant Shipping	Main engine rooms	No	Yes (2)
	Protection of other normally occupied spaces	Yes	Yes
	Protection of other normally unoccupied spaces	Yes	Yes

Notes:

1. In some specific instances only.
2. Alternatives to **halons** are available, but as HFCs were not used in this application, the alternatives are not HFC alternatives in the strictest sense.
3. May not be useable in all circumstances, or some additional caveats exist.

4.6 References

EPA(2022): Significant New Alternatives Policy (SNAP), Substitutes in Total Flooding Agents; https://www.epa.gov/snap/substitutes-total-flooding-agents

FAA(2004): John W. Reinhardt, "Behavior of Bromotrifluoropropene and Pentafluoroethane When Subjected to a Simulated Aerosol Can Explosion" FAA Report No. DOT/FAA/AR-TN04/4

OECD (2021): Reconciling Terminology of the Universe of Per- and Polyfluoroalkyl Substances: Recommendations and Practical Guidance, OECD Series on Risk Management, No. 61, OECD Publishing, Paris. https://www.oecd.org/chemicalsafety/portal-perfluorinated-chemicals/terminology-per-and-polyfluoroalkyl-substances.pdf

IMO(1992): "1992 Amendments to the 1974 SOLAS Convention". IMO Resolution MSC.27(61), Page 6 Para 16. https://wwwcdn.imo.org/localresources/en/KnowledgeCentre/IndexofIMOResolutions/MSCResolutions/MSC.27(61).pdf

Wallington (2021): Wallington *et al*. *The case for a more precise definition of PFAS*, Environ. Sci. Processes Impacts 2021 (23) 1834-1838.

WMO(2018): World Meteorological Organization, Global Ozone Research and Monitoring Project-Report No. 58: "Scientific Assessment of Ozone Depletion 2018, Appendix A, Table A-1.

5 Information on alternatives to HFCs in medical and chemical use

5.1 Introduction

In this section, information on alternatives for HFCs are provided for the following medical and chemical uses: aerosols (consumer, technical, and medical), metered dose inhalers, solvents, semiconductor and other electronics manufacturing, and magnesium production. Information on the status of alternatives for HFCs in these uses is summarised in tables that address the relevant Decision XXVI/9, paragraph 1(a) criteria. Information provided in this report is based on information currently being developed for the "MCTOC 2022 Assessment Report" and may be further updated as part of that report to be completed by the end of 2022.

5.2 Aerosols

Aerosols incorporate propellants and solvents with the appropriate technical properties and characteristics in formulations designed to deliver a product for its intended purpose.

Propellants include compressed gases (nitrogen, nitrous oxide, carbon dioxide) or liquefied gases, which are liquid inside the pressurized container. Liquefied gas propellants include HCFCs (e.g., HCFC-22), HFCs (e.g., HFC-134a, HFC-152a), HFOs (e.g., HFO-1234ze(E)), HCs, and DME.

Some aerosol products contain solvents, including HCFCs, HFCs, hydrofluoroethers (HFEs), aliphatic and aromatic solvents, chlorinated solvents, esters, ethers, alcohols, ketones, and HCFOs (e.g., HCFO-1233zd(E)). HCFCs, including HCFC-141b, are still currently used and are being replaced by HFCs, HFEs and HCFOs, which are further discussed in the solvents section.

Aerosols can be divided into categories:

- Consumer aerosols, including personal care products like deodorants and hair sprays, cleaning products, air fresheners, furniture and textile care, household pesticides, food, and convenience products;
- Technical aerosols, including automotive and industrial, lubricant sprays, dusters, contact cleaners, safety horns, degreasers, mould release agents, paints;
- Medical aerosols, including aerosols that deliver medical treatment through nasal and topical aerosol sprays. These medical aerosols are used to deliver topical medication mostly onto the skin, but also to the mouth, and other body cavities. Pressurised metered dose inhalers (pMDIs) are the major application for medical aerosol products, described separately in the next section.

A significant proportion of aerosol propellants have migrated to hydrocarbons and DME, which now dominate in the consumer aerosol market. Hydrocarbons and DME are highly flammable propellants. They are also used in technical aerosols where flammable propellants can be used safely. Hydrocarbons and oxygenated hydrocarbons (such as DME) are volatile organic compounds (VOCs) that contribute to photochemical smog generation. In some jurisdictions, strict VOC controls (e.g., in California) can have an impact on the choice of propellant, where hydrocarbons are avoided. The use of compressed gases (nitrogen, nitrous oxide, carbon dioxide) as propellants has increased because of these regulations and the availability of better cans.

A smaller proportion of aerosols migrated to HFC propellants where:

- Emissions of VOCs, such as hydrocarbons and DME, are controlled
- A non-flammable propellant is needed, and/or
- A propellant is necessary that is safe to inhale.

Of the HFC propellants, HFC-134a is used more commonly in technical and medical aerosols, where its non-flammable and inhalation safety properties have advantages. HFC-152a is more commonly used as a propellant in consumer aerosols.

5.2.1 Technical and economic assessment aerosol uses of controlled substances and their alternatives

An assessment follows of the technical and economic feasibility of alternatives to Annex F HFCs in aerosol uses. The assessment criteria referenced in decision XXVIII/2 have been slightly modified to remain relevant to this application, using the following criteria:

i. Commercially available
ii. Technically proven
iii. Environmentally sound
iv. Economically viable and cost effective
v. Safety in production and use, considering flammability and toxicity issues
vi. Easy to use

"Safe to use in areas with high urban densities considering flammability and toxicity issues, including, where possible, risk characterization" has been adjusted to *safety in production and use, considering flammability and toxicity issues*. "Easy to service and maintain" has been adjusted to *easy to use*. Technically proven is interpreted to mean the technology has been proven to work for that application, or an aspect of it.

Aerosol production has developed differently in each country due to regulations for flammability and occupational safety, VOC controls, and the availability from suppliers of HCFCs, HFCs, or their alternatives for aerosol production. The availability and number of different aerosol products varies within parties and regions and is closely related to the development of the local aerosol industries. Hence, alternatives are not necessarily interchangeable because of regional or local differences. The aerosol product type can also determine the propellant used, which could be related to performance requirements for the end use or the higher market value of the product, e.g., allowing a more expensive propellant.

Table 5.1: Technical and economic assessment of aerosol uses of controlled substances and their alternatives

Controlled substances and alternatives	Aerosol products	Commercially available	Technically proven	Environmentally sound	Economically viable	Safety in production and use	Easy to use
Propellants							
HCFC-22 HCFC-141b	Medical aerosols, including topical coolants to numb pain, burns treatment. HCFC-141b is a solvent in the product formulation.	◆ (green)[1]	◆ (green)	◆ (red)[1]	◆ (green)	◆ (green)	◆ (green)
HFC-134a	Technical aerosols, including dusters, electronic contact cleaners, flux removers, wasp and hornet sprays, aircraft insecticides. Medical aerosols, including metered dose corticosteroid spray, throat/mouth topical sprays (disinfectants, anti-inflammatories, anaesthetics), anaesthetic, analgesic, calamine sprays for minor blunt injuries or itches, nitroglycerin sublingual sprays.	◆ (green)[1]	◆ (green)	◆ (red)[1]	◆ (orange)[2]	◆ (green)	◆ (green)
HFC-152a	Consumer and medical aerosols, including tyre inflators, safety horns, personal care products (e.g., hairspray, cosmetics, deodorants), food, novelty aerosols, household cleaning, room fresheners, for diaper rash for babies, nitroglycerin sublingual sprays, sunscreen sprays.	◆ (green)[1]	◆ (green)	◆ (orange)[1]	◆ (green)	◆ (orange)[3]	◆ (green)

Controlled substances and alternatives	**Aerosol products**	**Commercially available**	**Technically proven**	**Environmentally sound**	**Economically viable**	**Safe to use in production and use**	**Easy to use**
			Propellant Alternatives				
HFO-1234ze(E)	Aerosols like those using HFC-134a and HFC-152a. Replacing HFC propellants in higher priced aerosol products. Electronic cleaners, dust removers, novelty, and cleaning/disinfection products used on board aircraft.	◆ (green)	◆ (green)	◆ (green)	◆ (orange)[2]	◆ (orange)[3]	◆ (green)
Blends of: Propane n-Butane iso-Butane	Consumer and medical aerosols, including personal care products (e.g., hairspray, cosmetics, deodorants), food, room fresheners, anaesthetic, analgesic, calamine sprays for minor blunt injuries or itches; cut or wound sprays; sprays to prevent bedsores; foot sprays and other anti-fungal products; vaginal hygiene sprays, rectal foams for treatment of colitis; foams for scalp hair loss; sunscreen sprays.	◆ (green)	◆ (green)	◆ (orange)[4]	◆ (green)	◆ (orange)[3]	◆ (green)
Dimethyl ether (DME)	Consumer aerosols including cosmetics, especially hairsprays and styling foams, sunscreen sprays. Medical aerosols including, anaesthetic, analgesic, calamine sprays for minor blunt injuries or itches; anti-fungal products.	◆ (green)	◆ (green)	◆ (orange)[4]	◆ (green)	◆ (orange)[3]	◆ (green)
Carbon dioxide	Technical and medical aerosols including dust cleaners, anaesthetic, analgesic, calamine sprays for minor blunt injuries or itches.	◆ (green)	◆ (green)[5]	◆ (green)	◆ (green)	◆ (green)	◆ (green)
Nitrogen	Consumer and medical aerosols including shaving cream, sunscreen sprays, food, cosmetics, air fresheners, deodorants, throat/mouth topical sprays (disinfectants, anti-inflammatories, anaesthetics), sterile saline solutions.	◆ (green)	◆ (green)[5]	◆ (green)	◆ (green)	◆ (green)	◆ (green)

Controlled substances and alternatives	Aerosol products	Commercially available	Technically proven	Environmentally sound	Economically viable	Safety in production and use	Easy to use
"Not-in-kind" Alternatives							
Pump sprays	Variety of consumer and medical applications	◆	◆	◆	◆	◆	◆[6]
Drops		◆	◆	◆	◆	◆	◆[6]
Creams		◆	◆	◆	◆	◆	◆[6]

◆ Yes or More acceptable; ◆ Not always or Less acceptable; ◆ No or Unacceptable.

1. HCFCs and high-GWP HFCs for the production of aerosols (excluding MDIs) are either phased out (HCFCs in non-Article 5 parties) or restricted by regulation or actively discouraged by suppliers in many parties. HCFCs and HFC-134a are non-flammable propellants. HFC-134a is used when flammability and/or toxicity are a consideration. HFC-152a, while another Annex F HFC, has a lower GWP and is becoming more commercially available than HFC-134a, with its higher GWP, for those regions starting their HFC phase downs.

2. HFC-134a and HFO-1234ze(E) are expensive compared with hydrocarbons and therefore only used when their safety properties are necessary for the specific product (non-flammable, low toxicity), and the benefits outweigh the increased cost.

3. Hydrocarbons and DME are highly flammable propellants. HFC-152a has low to moderate flammability and is often used alone or in blends with hydrocarbons to lower their flammability. HFC-152a can also be blended with HFC-134a propellant to produce a propellant with lower GWP and lower flammability. HFO-1234ze(E) is classified as non-flammable, with a flammable range of 8.0-8.5 volume percent in air (at one atmosphere and temperatures > 30°C). Flammable propellants require special equipment, training and handling during production, and the more flammable propellants require special precautions in use.

4. Hydrocarbons and oxygenated hydrocarbons are volatile organic compounds (VOCs) that contribute to photochemical smog generation in areas of high urban density. In some jurisdictions, strict VOC controls (e.g., in California) can have an impact on the choice of propellant, where hydrocarbons are avoided, although medical aerosols have been largely exempted from these requirements.

5. Carbon dioxide and nitrogen are gaseous propellants, not liquefied propellants, and as such are technically suitable for some but not all aerosol product applications.

6. Aqueous sprays and drops are well-established as "not-in-kind" alternatives for many consumer and medical aerosol products, including nasal sprays. Aqueous formulations in general and other "not-in-kind" alternatives, such as creams, are used in many consumer and medical aerosol applications. "Not-in-kind" alternatives can sometimes be less convenient to use. Aerosols can be favoured due to their ease of use.

Table 5.2: Characteristics of controlled substances and their alternatives used as propellants and solvents in aerosols

Controlled substances and alternatives	ODP	100-year GWP[1]	Flammability	Comments
Propellants				
HCFC-22	0.055	1810	Non-flammable at atmospheric temperature and pressure	Recommendations for workplace exposure limits.
HFC-125	0	3500	Non-flammable	-
HFC-134a	0	1430	Non-flammable	Approved for use in metered dose inhalers (pMDIs). Very low acute inhalation toxicity.
HFC-152a	0	124	Flammable, less so than HCs (LEL 3.9 % volume in air)	Low acute inhalation toxicity. Recommendations for workplace exposure limits.
HFC-227ea	0	3220	Non-flammable	Approved for use in pMDIs. Very low acute inhalation toxicity. Due to cost and high GWP, probably used exclusively in pMDIs.
Propellant Alternatives				
HFO-1234ze(E)	0	<1	Non-flammable. A flammable range of 8.0-8.5 volume percent in air (at one atmosphere and temperatures >30°C). Exhibits flame limits at elevated temperatures.	Used as replacement for aerosols previously using higher GWP HFC propellants (e.g., novelty). Recommendations for workplace exposure limits.
Hydrocarbons and blends (propane, n-butane, iso-butane)	0	≤4	High flammability (iso-butane, LEL 1.8 % volume in air)	Recommendations for workplace exposure limits.
Dimethyl ether (DME)	0	1	Highly flammable	-
Compressed gases - CO_2 - N_2 - Air - N_2O	 0 0 0 0.017	 1 0 - 298	Non-flammable	 Recommendations for workplace exposure limits. - - Recommendations for workplace exposure limits.
"Not-in-kind", e.g., - Pump sprays - Liquids - Roll-on liquids/sticks	 0 0 0	 0 0 0	Non-flammable where liquid dispensed is non-flammable	Indirect life cycle climate impacts

Controlled substances and alternatives	ODP	100-year GWP[1]	Flammability	Comments
Solvents				
HCFC-141b	0.11	725	Non-flammable	Recommendations for workplace exposure limits.
Blends of HCFC-225ca/ HCFC-225cb	0.025 0.033	122 595	Non-flammable	Recommendations for workplace exposure limits.
HFC-43-10mee	0	1640	Non-flammable	Recommendations for workplace exposure limits.
HFC-365mfc	0	794	Flammable	Recommendations for workplace exposure limits.
HFC-245fa	0	1030	Non-flammable	Recommendations for workplace exposure limits.
Solvent Alternatives				
HFO-1336mzz(Z)	0	2.08[2]	Non-flammable	Recommendations for workplace exposure limits.
HCFO-1233zd(E)	<0.000 4	3.88[2]	Non-flammable	Recommendations for workplace exposure limits.
HCFO-1233yd(Z)	0.00003	<1	Non-flammable	Recommendations for workplace exposure limits.
Hydrofluoroethers HFE-449s1 HFE-569sf2	 0 0	 297 59	 Non-flammable Non-flammable	 None. Recommendations for workplace exposure limits.
Aliphatic and aromatic solvents (e.g., Hexane, Heptane)	0	≤3	Highly flammable	Recommendations for workplace exposure limits.
Halogenated solvents e.g. Trichloroethylene Perchloroethylene Methylene chloride n-Propyl bromide	 ~0 ~0 ~0 ~0.011[3]	 140 Low 9	 Non-flammable Non-flammable Non-flammable (combustible at high temperature) Highly flammable	Recommendations for workplace exposure limits.
Oxygenated organic compounds (e.g., Esters, Ethers, Alcohols, Ketones)	0	<20	Flammable	Check recommendations for workplace exposure limits.
Water-based formulations	0	0	Non-flammable	Indirect life cycle climate impacts
"Not-in-kind" (see above)	0	0	Non-flammable where liquid dispensed is non-flammable	Indirect life cycle climate impacts

1. AR4 2. AR6 3. Latitude dependent.

Commercially available— Technically and economically feasible alternatives to ozone-depleting propellants (CFCs and HCFCs) are commercially available for all aerosols, although not all alternatives are suitable and therefore commercially available across all aerosol applications.

Aerosol products were reformulated to use CFC-free propellants, mainly hydrocarbons (butane, propane, isobutane, DME), although HCFCs and HFCs have been used in specific applications.

NIK alternatives, including hand-pumped aqueous sprays, drops and creams, are also used where CFC-containing aerosols might have been used previously.

Many external factors affect the selection of a given propellant or alternative, including regulatory approval of products, industry codes of conduct, VOC controls, supplier or regulatory controls on HCFCs and HFCs, ease of use, and propellant properties, such as flammability or safety for certain uses.

Regulatory controls for HFCs used as aerosol propellants and solvents are increasingly limiting and/or prohibiting high-GWP HFC use where other suitable alternatives are available. For example, HFC-134a is no longer used as a propellant in technical aerosols in Europe. In some instances, HFC-152a, with a GWP of 124, can be considered relatively more acceptable within these regulatory controls than HFC-125 and HFC-134a, with their significantly higher GWPs of 3500 and 1430.

Technically proven— Aerosols incorporate propellants and solvents with the appropriate technical properties and characteristics in formulations designed to deliver a product for its intended purpose. The alternatives listed in Table 5.2 are technically proven for use in aerosols, although sometimes only for certain product types depending on the properties of the alternatives and/or the intended product purpose. Some alternatives will not be technically suitable for some formulations.

Hydrocarbons and DME are highly flammable chemicals that are also VOCs that contribute to photochemical smog generation. Like CFCs before them, non-flammable and non-toxic HFC-134a is often used in aerosols when flammability or toxicity is a consideration. HFCs are also used where emissions of VOC are controlled. However, HFCs are more expensive than hydrocarbons and are therefore mostly used when their properties are necessary for the aerosol product and the advantages outweigh the costs.

HFC-134a is used more commonly as a propellant in technical aerosols where its non-flammable properties have advantages. HFC-134a is also used in medical aerosols. Extensive respiratory toxicological studies were conducted for HFC-134a (IPACT-1) and HFC-227ea (IPACT-2), which proved their safety as propellants in respiratory use (e.g., MDIs). Any propellant intended for inhaled medications requires toxicological tests.

Propane or iso-butane (and their blends) tend to cause an "oily" or slightly stinging taste, and so are not favoured for nasal or oral use. Most other pressurised medical aerosol products tend to use propane/butane mixtures or DME and compressed gases to a lesser extent. Medical aerosol products for use on or near the nose or mouth, and on babies, where flammability and safety are of importance, tend to use HFCs or nitrogen. For treatments where there is a significant risk of inhalation into the respiratory tract, HFCs are preferred, where safety has been proven for HFC-134a and HFC-227ea.

HFC-152a is used more commonly as a propellant in consumer aerosols. HFC-152a is also being used in medical aerosols. HFC-152a has low to moderate flammability, and is used alone, or in blends with hydrocarbons to lower their flammability. HFC-152a is also blended with HFC-134a to produce a propellant with lower GWP and lower flammability. It is also used in jurisdictions that have VOC emission controls.

HFO-1234ze(E) is emerging as an in-kind alternative for all HFC aerosol propellant uses, although currently mainly in high value products due to its higher cost than HFCs.

NIK alternatives are sometimes not as easy to use or achieve lower performance for some applications.

In most parties, there are no regulatory requirements for the use of *specific* propellants for medical aerosols. However, a change in propellant for products approved for a medical use (like the nasal MDIs) would necessitate a new development programme and regulatory approval. In the United States, some regulated products may not require prior approval following the over-the-counter monograph system (also known as “grandfather clause” for products with a long time of use), provided they do not change propellant. In Japan, the Japanese pharmacopoeia codex for additives, and other official compendia limit propellants for medical aerosols. If a pharmaceutical company uses a new propellant in an aerosol product, necessary toxicity data on both propellant and the aerosol product are required for registration. All aerosols in the European Union are regulated, especially relating to flammability, under the Aerosol Dispensers Directive 75/324/EEC and subsequent amendments.

Environmentally sound— Aerosols are a totally emissive use, and so the propellant and solvent can have a direct environmental impact. In some parties, HCFCs and some HFCs are prohibited for use in the manufacture of aerosol products. In some non-Article 5 parties that have phased out HCFC production, stockpiles continue to be used for some specific aerosol products. HCFCs are gradually being phased out in Article 5 parties in aerosol manufacturing. Some parties have prohibited the introduction to market of some new aerosol products containing HFCs. Other parties are implementing the Kigali Amendment phase downs into regulations that will gradually limit the supply of HFCs to end uses.

HFC-125, HFC-134a, HFC-227ea, and HFC-43-10mee, have high GWPs. In some applications, HFC-152a is used because it has a lower GWP than HFC-134a and lower flammability than hydrocarbons. HFC-152a are currently a preferred propellant choice where VOC controls limit the use of hydrocarbon propellants, although there is also increasing use of HFO-1234ze(E) as an in-kind alternative to HFC-152a. HFC-152a can also be blended with HFC-134a propellant to produce a propellant with lower GWP and lower flammability.

In Article 5 parties, HFC-134a can be preferred to HFC-152a due to aerosol manufacturing concerns about the flammability of HFC-152a. HFO-1234ze(E) is a small use in Article 5 parties, where it is generally used to manufacture aerosols (e.g., novelty aerosols) for export.

When considering direct climate impacts, the more climate-friendly alternative propellants include hydrocarbons and their blends, DME, HFO-1234ze(E), carbon dioxide and nitrogen, and NIK alternatives. The more climate-friendly alternative solvents include hydrofluoroethers, oxygenated organic compounds, aliphatic and aromatic solvents, chlorinated chemicals, low-GWP fluorinated chemicals, and NIK alternatives.

In areas with high urban densities, photochemical smog generation can be a major environmental and health problem. Hydrocarbons and oxygenated hydrocarbons, such as DME, are VOCs that contribute to photochemical smog generation. In some jurisdictions, strict VOC controls (e.g., in California) can have an impact on the choice of propellant, where hydrocarbons are avoided.

Economically viable and cost effective— Hydrocarbons and their blends are the most affordable propellant for aerosol products. HFCs and HFO-1234ze(E) are more expensive and are therefore used by manufacturers for specific applications where a propellant with low flammability and proven safety is needed, and often for high value products.

Safety in production and use— The flammability of hydrocarbons, DME, HFC-152a, and their flammable blends, makes safety a priority in the production and use of aerosols containing these ingredients. Flammable propellants and solvents require special equipment, training and handling in aerosol production, and special precautions in aerosol use.

HFO-1234ze(E) is classified as non-flammable although possesses a flammable range of 8.0-8.5 volume percent in air at one atmosphere under certain conditions, which needs to be considered in manufacturing, storage, and handling.

Easy to use— Pressurised aerosols, using propellants, are sometimes considered more convenient products to use than NIK alternatives, such as aqueous sprays, drops and creams. Flammable propellants and solvents require safety precautions in the use of aerosol products.

5.3 Pressurised Metered Dose Inhalers

Inhaled therapy remains the mainstay of treatment for established asthma and COPD. Inhalers offer effective symptomatic benefit and/or control of disease, by delivering drugs directly to the airways, whilst minimising systemic side effects, e.g., as may occur with oral treatments.

The more common types of inhalers for the delivery of respiratory drugs are the pressurised metered dose inhaler (pMDI) and the dry powder inhaler (DPI). Other methods of delivering drugs to the airways include soft mist inhalers (SMIs) and nebulisers. The choice of the most suitable treatment method is a complex decision taken between the health care provider and the patient. It is not uncommon for patients to be prescribed a mix of medications in a range of devices.

The available delivery options for inhaled therapy are summarised as follows:

- ***HFC pMDIs***—HFCs (HFC-134a, and to a lesser extent HFC-227ea) are used as propellants in pMDIs, which are aerosol products with a metering valve that delivers a precise dose of medication to the airways. There are HFC pMDIs available to cover all key classes of drugs in the treatment of asthma and COPD.
- ***Dry powder inhalers***— DPIs are not-in-kind alternatives to HFC pMDIs because they do not require a propellant, instead using a micronized dry powder that is inhaled and deposited in the airways of patients. DPIs fall into two categories: single-dose DPIs and multi-dose DPIs. There are two main types of multi-dose DPI: reservoir and multi-unit dose devices. Commonly used respiratory drugs have been formulated successfully for DPIs and are widely available.
- ***Soft mist inhalers***— SMIs are propellant-free aqueous mist inhalers. They are small portable devices that produce aerosols of respirable diameter from aqueous formulations that are commercially available from one global pharmaceutical company. They are different from nebulisers in that they deliver a complete dose in a few breaths.
- ***Nebulisers***— Nebulisers are devices used to inhale aqueous drug solutions, which are converted to inhalable droplets using compressed air, ultrasonic waves, or vibrating mesh. Despite recent innovations that have led to more patient-friendly options (e.g., handheld nebulisers), nebulisers are generally not considered as direct replacements for pMDIs. Nebulisers are mainly recommended for the treatment of infants and severely ill patients. Nebulisers take 3-10 minutes to deliver a dose and are relatively inconvenient to maintain.
- ***Emerging in-kind propellant alternatives*** are in earlier stages of development or commercialization in pMDIs, such as isobutane, HFC-152a, and HFO-1234ze(E) propellants.

Metered dose inhalers remain the dominant option for the delivery of inhaled therapy in most markets. In different markets, the proportion of pMDIs to DPIs and SMIs use differs. For example, single dose DPIs are used extensively in India. These variations are for many reasons, including prescribing practices, availability or accessibility, cost, patient preference, and national government guidance for asthma and COPD treatments.

In some markets, there are available HFC-based pMDIs intended for nasal administration of corticosteroids. It must be noted that there are widely available metered, aqueous pump sprays with a large variety of active moieties, all that can be considered acceptable and affordable alternatives to these pMDIs. There seems to be very little rationale for HFC-based nasal pMDIs from the standpoint of public health.

5.3.1 Technical and economic assessment of pMDIs containing controlled substances and their alternatives

An assessment follows of the technical and economic feasibility of alternatives to Annex F HFCs in aerosol uses. The assessment criteria referenced in decision XXVIII/2 have been slightly modified to remain relevant to this application, using the following criteria:

i. Commercially available and accessible
ii. Technically proven
iii. Environmentally sound
iv. Economically viable and affordable
v. Suitable for high humidity regions
vi. Safety in production and use, considering flammability and toxicity issues
vii. Easy to use

“Commercially available” has been interpreted to include *commercially accessible*, which has a specific relevance and importance for pMDIs and their alternatives. “Safe to use in areas with high urban densities considering flammability and toxicity issues, including, where possible, risk characterization” has been adjusted to *safety in production and use considering flammability and toxicity issues*. “Economically viable and cost effective” has been adjusted to *economically viable and affordable*. “Easy to service and maintain” has been adjusted to *easy to use*. An additional criterion has been added, *suitable for high humidity regions*. Technically proven is interpreted to mean the technology has been proven to work for that application, or an aspect of it.

The assessment below includes only those alternatives considered as direct alternatives to pMDIs, i.e., it excludes oral tablets and nebulisers.

Table 5.3: Technical and economic assessment of use of controlled substances for pMDIs and alternatives

Controlled substances and alternatives	Party	Commercially available and accessible	Technically proven	Environmentally sound	Economically viable and affordable	Suitable for high humidity regions	Safety in production and use	Easy to use
HFC pMDI (HFC-134a, HFC-227ea)	Article 5 parties	orange ◆[1]	green ◆	red ◆[2]	orange ◆[3]	orange ◆[4]	green ◆	orange ◆[5]
	Non-Article 5 parties	green ◆[1]	green ◆	red ◆[2]	green ◆[3]	orange ◆[4]	green ◆	orange ◆[5]
				Alternatives				
Dry powder inhalers	Article 5 parties	orange ◆[1]	green ◆	green ◆[2]	orange ◆[3]	orange ◆[4]	green ◆	orange ◆[5]
	Non-Article 5 parties	green ◆[1]	green ◆	green ◆[2]	green ◆[3]	orange ◆[4]	green ◆	orange ◆[5]
Soft-mist inhalers	Article 5 parties	orange ◆[1]	green ◆	green ◆[2]	orange ◆[6]	green ◆	green ◆	orange ◆[5]
	Non-Article 5 parties	orange ◆[1]	green ◆	green ◆[2]	orange ◆[6]	green ◆	green ◆	orange ◆[5]

green ◆ Yes or More acceptable; orange ◆ Not always or Less acceptable; red ◆ No or Unacceptable.

1. Although classed by the World Health Organisation as essential medicines, commercial availability and accessibility of inhaled therapy for airways disease is not universal across all products/drugs and regions. This can be due to many reasons, including regulatory drug product approvals, health policy, presence of companies in pharmaceutical markets, as well as patient and prescriber preferences. pMDIs and DPIs can be less accessible in some Article 5 parties/regions than in non-Article 5 parties (more information will be provided in the MCTOC 2022 Assessment Report). The range of commercially available medications in SMIs is limited to short or long-acting bronchodilators, either as single drugs or combinations; these are primarily treatments for COPD. SMIs are also likely to be far less commercially available and accessible in Article 5 parties than in non-Article 5 parties, as is the case for pMDIs and DPIs.
2. This assessment of environmentally sound considers relative climate impact only. HFC-134a and HFC-227ea are controlled substances with high GWPs that are subject to the phase down control measures for Annex F HFC of the Montreal Protocol. Currently available pMDIs have a large carbon footprint, though newer pMDIs with lower GWP propellants are in development, with the first commercially available products planned to be available from 2025, though full availability of lower GWP propellant alternatives to the current pMDIs across regions may take many years beyond. One of those candidate propellants is HFC-152a, which has a relatively low GWP and is also a controlled substance, subject to the Article 2J phase down control measures for Annex F HFCs. The most widely used pMDI globally is the salbutamol pMDI, which utilises HFC-134a, constitutes about 60% of all pMDI use, and contributes most to the environmental impact of pMDIs. Further detail is provided in the discussion below about broader environmental impacts, which are less studied than relative climate impacts.

3. Multi-dose DPIs can be less affordable than single-dose DPIs and pMDIs; single-dose DPIs can be more affordable than pMDIs. In Article 5 parties, locally made pMDIs are more affordable than some imported brands. In all parties, the cost of any treatment can be unaffordable for a portion of patients.
4. Older reservoir DPIs and some HFC pMDIs can be affected by high humidity. Newer multi-dose DPIs function equally well in areas of high humidity.
5. While most patients can be taught to use any of these devices, some patients may struggle with any particular device and ideally a range of options should be available so as to assure individual patient needs can be met.
6. SMIs are usually more expensive than pMDIs for short-acting reliever medication, but they can be equally cost-effective as DPIs or pMDIs for some drugs, particularly long-acting bronchodilators. SMIs are generally likely to be unaffordable in Article 5 parties for most patients. The range of commercially available medications in SMIs is limited to short or long-acting bronchodilators, either as single drugs or combinations; these are primarily treatments for COPD. SMIs are increasingly available as refillable devices, making them even more environmentally sound and potentially more affordable.

Commercial availability and accessibility— There are a wide variety of pMDIs, DPIs (both multidose (MDPIs) and the technically simpler single-dose DPIs), and SMIs available globally, albeit with great regional variation in specific availability and accessibility and use patterns. In aggregate, these medications provide a broad array of pharmacologic mechanisms and choice for patients with asthma or COPD. While this is true in general, local regulatory requirements, economic considerations, as well as practice of medicine/patient preference, lead to considerable regional differences in specific availability and choice of inhaler type. In many cases, the delivery device selected has been chosen because of individual discussion between patient and physician to suit their individual needs and economic circumstances such that it provides the best possible opportunity to stabilise their disease.

Pressurised MDIs remain a mainstay of treating respiratory disease in much of the world, a situation further solidified by the COVID-19 pandemic.[8] Of the pMDIs use globally, the largest single molecular entity delivered by pMDI is salbutamol (albuterol). This is a short- acting bronchodilator (SABA), which is used as rescue medicine for asthma patients who are undergoing an acute shortage of breath. Some estimates put the total global use of salbutamol pMDIs at greater than 60% of total pMDI use. While there is projected to be a slow reduction of salbutamol use in the coming years, salbutamol is still expected to be a significant portion of overall pMDI use. While the transition from CFCs to HFCs in pMDIs has been successfully completed, there are currently no pMDIs marketed utilising lower GWP propellants, though active research and development is ongoing.

Dry powder inhalers, both MDPIs and single-dose DPIs are widely available containing a full array of therapeutic classes of treatment, although they are variably used. In addition, not all combinations of medication are available, and approval of DPI devices varies between regions. In many Article 5 parties, single dose DPIs providing short-acting relievers (which provide rapid temporary symptom relief by opening up the airways) can be more affordable because MDPIs (and pMDIs) require the purchase of a relatively large number of doses at once.

Soft mist inhaler technology, providing an aqueous aerosol without the use of pressurised propellant, are commercially available from one company, although availability is limited in many regions.

Technically proven— HFC pMDIs and DPIs are recommended options in national and international guidelines for the treatment of asthma and COPD. DPI alternatives are available for all key classes of drugs, although not all combinations. For SMIs, only bronchodilators (short- and long-acting) are available; these are primary treatments in COPD but play a smaller role in the treatment of asthma compared with inhaled corticosteroids administered by pMDI or DPI.

In recent years, once-daily (i.e., long-acting) DPI, and triple combination DPI and pMDI have become available. These inhalers have the potential to reduce the number of devices needed, simplify therapy, and improve outcomes. They are supported by clinical studies and included in national and international guidelines.

At the time of the introduction of the Montreal Protocol, extensive research had already identified the two currently used hydrofluorocarbons as alternative propellants – HFC-134a and HFC-227ea. Two international consortia (IPACT-I and IPACT-II) conducted toxicological testing to ensure that these propellants were safe for inhalation by humans.

Lower GWP chemicals, HFC-152a and HFO-1234ze(E), are under development as potential propellants for pMDIs. Studies on these new lower GWP propellants are well underway, but none are yet technically proven (or commercially available for use). Any new inhalation propellant must be safe for human use and meet criteria relating to toxicity, safety, and efficacy. The first products are

[8] Bloom, C.I., Wong, E., Hickman, K. *et al,*. Influence of the first wave of COVID-19 on asthma inhaler prescriptions, *npj Prim. Care Respir. Med.,* 2021, **31,** 45. https://doi.org/10.1038/s41533-021-00260-w.

projected to come to market in 2025, with some pharmaceutical companies aiming for 2030 to complete the transition away from current HFC propellants to lower GWP propellants. More information will be provided in the MCTOC 2022 Assessment Report.

Environmentally sound— All currently available HFC pMDIs have a far greater carbon footprint than DPIs or SMIs. Despite efforts to mitigate propellant release during manufacture, life cycle assessments consistently demonstrate that the large majority (88-98%) of the carbon footprint of pMDIs is due to propellant release during use or at end-of-life. There are therefore large differences in the carbon footprint depending on the amount and type of propellant used, varying from 50 to 300gCO_2e per actuation or 9,900 to 36,500gCO_2e per device.

DPIs and SMIs are propellant-free inhalers and consequently have far smaller carbon footprint. The largest contributions to their carbon footprint are made by the production of the active pharmaceutical ingredient (API) and the device manufacturing stage. Published life cycle assessments show their carbon footprint to range from 6 to 27g per dose, or 359 to 917gCO_2e per device.

The smallest carbon footprints are seen in reusable soft-mist inhalers or single-dose DPIs. Re-usable single-dose devices are the most popular devices in some regions due to their affordability. A once-daily single dose DPI could represent a suitable alternative to pMDI for many patients, but with a 200-fold smaller carbon footprint than an HFC-227ea pMDI and 100-fold smaller than an HFC-134a pMDI per day of maintenance treatment. Multi-dose DPIs, which are the most popular type of device amongst patients in some studies, have a carbon footprint of 588-917g CO_2e per device, though they are not available for use in all parties.[9,10]

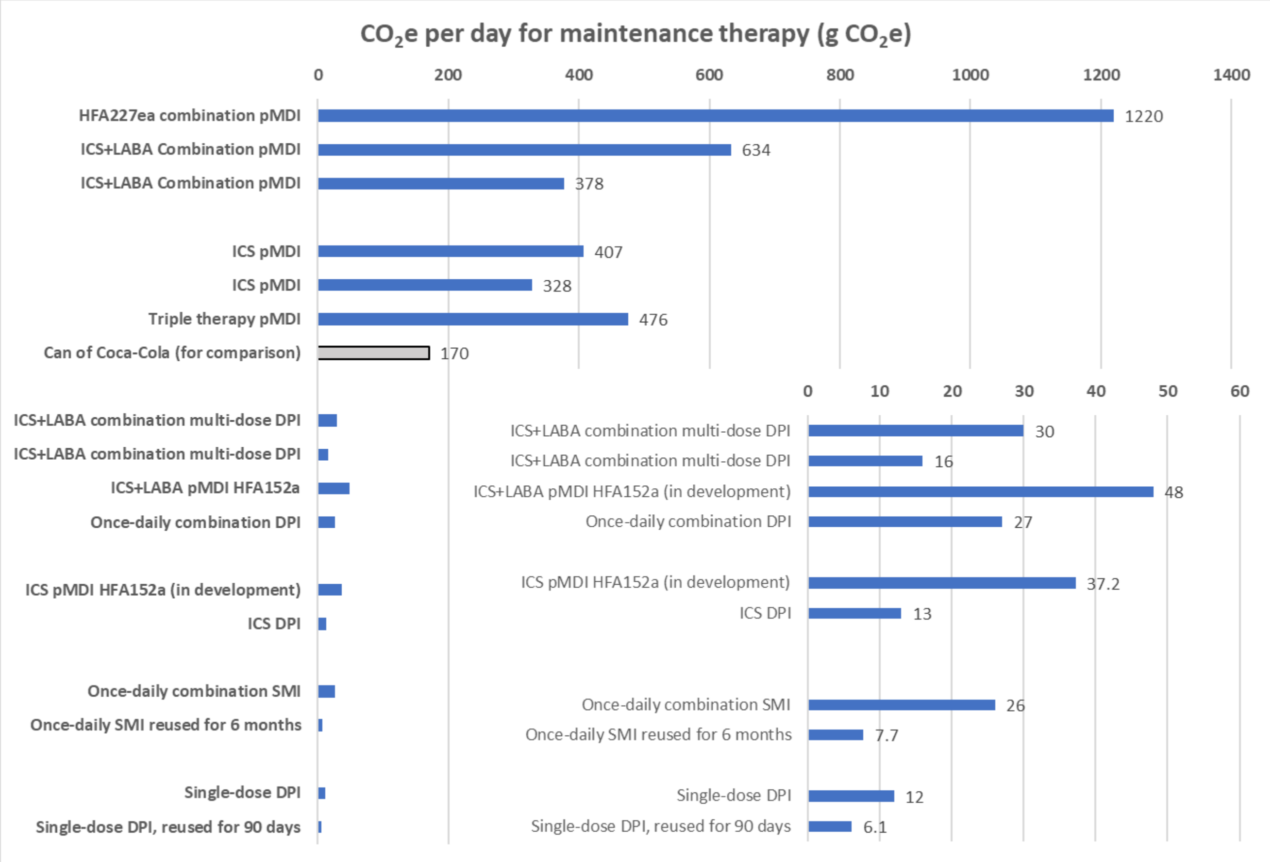
Limited information is available on potential new pMDIs in development using lower GWP propellants, though it is clear they will have far smaller carbon footprints. One life-cycle assessment has been performed using HFC-152a as a propellant. The volume of the propellant required in the final product was estimated. The carbon footprint per actuation was estimated to be 9-14g CO_2e per actuation for a range of steroid or combination pMDIs.[11]

[9] Schreiber J, Sonnenburg T, Luecke E., Inhaler devices in asthma and COPD patients – a prospective cross-sectional study on inhaler preferences and error rates, *BMC Pulm. Med.,* 2020, **20**, 222. doi:10.1186/s12890-020-01246-z.

[10] Fulford B, Mezzi K, Aumônier S, *et al*., Carbon Footprints and Life Cycle Assessments of Inhalers: A Review of Published Evidence, *Sustainability,* 2022, **14**, 7106. doi:10.3390/su14127106

[11] Panigone S, Sandri F, Ferri R, *et al.,* Environmental impact of inhalers for respiratory diseases: decreasing the carbon footprint while preserving patient-tailored treatment, *BMJ Open Respir. Res.,* 2020, **7**, e000571. doi:10.1136/bmjresp-2020-000571.

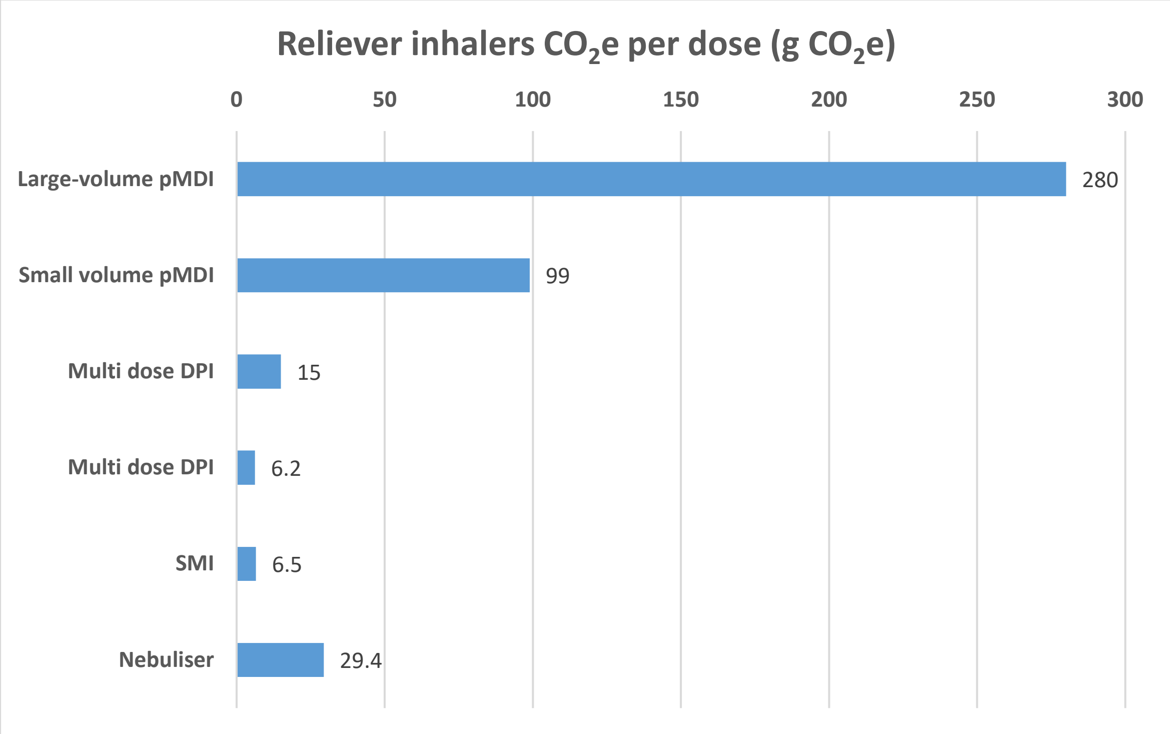
Figure 5.2 Carbon footprint of maintenance inhalers based on published life cycle assessments (gCO_2e)*



*Footnote: For all inhalers containing corticosteroids, it is assumed that 2 inhalations twice daily are used, apart from once-daily devices. Where 2 results are given for the same inhaler, different brands are represented.[12] Different lifecycle analyses may use different GWP values for HFCs, which can significantly impact the estimated carbon footprint of an inhaler.

[12] Fulford B, Mezzi K, Aumônier S, *et al,*. Carbon Footprints and Life Cycle Assessments of Inhalers: A Review of Published Evidence, *Sustainability,* 2022, **14**, 7106. doi:10.3390/su14127106.

Figure 5.2 Carbon footprint of reliever inhalers based on published life cycle assessments (gCO_2e)* (Fulford *et al.*, 2022)



*Footnote: The dose of albuterol (salbutamol) is 200mcg for inhalers and 3g for nebuliser. Where 2 results are given for the same inhaler, these represent different brands.[13,14] Different lifecycle analyses may use different GWP values for HFCs, which can significantly impact the estimated carbon footprint of an inhaler.

The greatest uncertainty about the carbon footprint of pMDIs relates to uncertainty about the carbon footprint of the HFC propellants. In the 2021 IPCC Assessment Report 6, the 100-year GWP value of HFC-134a was reported as 1,530, up from 1,300 in the previous assessment, with a total uncertainty of 38%. Similarly, HFC-227ea increased from 3,350 to 3,600 and HFC-152a from 138 to 164. Using these updated values would significantly increase the estimated carbon footprint of pMDIs as most previous analyses use figures from the fifth Assessment Report. For instance, applying these updated values and uncertainties to a large volume salbutamol pMDI (the most used pMDI globally) would increase its estimated carbon footprint from 28,000 to 31,500 (20,000-43,500) gCO_2e per device.

To avoid shifting the burden of impact from one category of environmental impacts to another, life cycle impact assessments (LCIA) explore additional impact categories to provide a more comprehensive understanding of environmental impacts.[15] Understanding the relative significance of impacts other than carbon footprint is an evolving area of research, and data on inhalers is limited to two studies; the first examined the relative impacts of one DPI product versus pMDIs using a range of

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[13] Fulford B, Mezzi K, Aumônier S, *et al.* Carbon Footprints and Life Cycle Assessments of Inhalers: A Review of Published Evidence. *Sustainability* 2022, **14**, 7106. doi:10.3390/su14127106.

[14] Goulet, B.; Olson, L.; Mayer, B.K., A Comparative Life Cycle Assessment between a Metered Dose Inhaler and Electric Nebulizer, *Sustainability*, 2017, **9**, 1725. https://doi.org/10.3390/su9101725.

[15] Huijbregts, M.A.J., Steinmann, Z.J.N., Elshout, P.M.F. *et al.*, ReCiPe2016: A Harmonised Life Cycle Impact Assessment Method at Midpoint and Endpoint Level, *Int. J. Life Cycle Assess.,* 2017, **22**, 138–147. https://doi.org/10.1007/s11367-016-1246-y.

propellants – HFC-134a, HFC-227ea and HFC-152a.[16] This study found the DPI product to have the greatest environmental impacts across most categories (such as fine particulate matter formation, terrestrial acidification, human and animal toxicity and others[17]) but did not consider the relative overall importance of these impacts on the environment or whether they may be specific to the specific DPI product assessed.

Fulford *et al.* found quite different impacts in their LCIA of a single-dose DPI, indicating that these environmental impacts are not generalisable to all DPIs, although they also used different assumptions and databases.[18] "Person equivalents" were used to assess the relative importance of different environmental impact categories. The carbon footprint was found to be the most significant impact, and the only impact in which the difference between devices exceeded an order of magnitude.

At present there is no public comparable data regarding impacts other than carbon footprint of HFO-1234ze(E). However, HFC-152a pMDIs are likely to have a carbon footprint similar to DPIs with the lowest carbon footprints.

Attempts have been made to minimise HFC propellant emissions at the end-of-life of pMDIs because pMDIs still contain a significant residual amount of remaining propellant at the end of dose completion. A national inhaler recycling scheme ran for 9 years in the United Kingdom (UK), which recovered and recycled more than 2 million inhalers, representing less than 1% of all inhalers used in that period.[19] Smaller recycling schemes are running, though achieving significant returns of inhalers is challenging. In addition to the end-of-life residual propellant, surprisingly large amounts of propellant were found in returned pMDIs, with 48% of doses remaining in discarded pMDIs; 27% of doses were also found remaining in discarded DPIs. While these results might reflect the large number of pMDIs in the UK that lack dose counters, it also highlights the potential to reduce HFC emissions through proper disposal of pMDIs. Incineration of used pMDIs along with hazardous medicines waste has been proposed as a method to reduce HFC emissions. Incineration in medical waste incinerators can degrade HFC-134a into less potent greenhouse gases. The impact of incineration in municipal solid waste incinerators is less certain as the temperatures involved are typically lower, which may not result in efficient destruction.[20]

Patients care about the environmental impact of their treatment. By far the biggest survey on this topic was performed in the UK where 12,145 people with asthma were surveyed. The most important factor was that their inhaler worked; however, among pMDI-users the majority (60%) said they would change device for environmental reasons, while a further 21% indicated they might.[21]

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[16] Jeswani HK, Azapagic A., Life cycle environmental impacts of inhalers, *J Clean Prod.,* 2019, **237**, 117733. doi:https://doi.org/10.1016/j.jclepro.2019.117733.

[17] Global warming potential; fossil depletion; metal depletion; terrestrial acidification; freshwater eutrophication; marine eutrophication; carcinogenic human toxicity; non-carcinogenic human toxicity; freshwater ecotoxicity; marine ecotoxicity; terrestrial ecotoxicity; ozone depletion; photochemical oxidant formation for human health; and photochemical oxidant formation for ecosystems.

[18] Fulford B, Mezzi K, Aumônier S, *et al.,* Carbon Footprints and Life Cycle Assessments of Inhalers: A Review of Published Evidence, *Sustainability,* 2022, **14**, 7106. doi:10.3390/su14127106.

[19] Inhaler recycling scheme that cut carbon emissions equivalent to more than 8,500 cars is scrapped. Pharmaceutical Journal Published Online First: 3 July 2020. doi:10.1211/pj.2020.20208144.

[20] Mi T, Han J, He X, *et al.,* Investigation of HFC-134a decomposition by combustion and its kinetic characteristics in a laboratory scale reactor, *Environment Protection Engineering,* 2015,143--150. doi:10.5277/epe150411.

[21] D'Ancona G, Cumella A, Renwick L, *et al.* The sustainability agenda and inhaled therapy: what do patients

Economically viable and cost-effective— Multi-dose DPIs (MDPIs) can be less affordable than single-dose DPIs and pMDIs; single-dose DPIs can be more affordable[22] than pMDIs. In Article 5 parties, locally made pMDIs are more affordable than some imported brands. SMIs are usually more expensive than pMDIs for short-acting reliever medication, but they can be as equally cost-effective as DPIs or pMDIs for some drugs, particularly long-acting bronchodilators. SMIs are generally likely to be unaffordable in Article 5 parties for most patients. In all parties, the cost of some or any treatments can be unaffordable for a portion of patients.

Non-pMDI alternatives (MDPIs, soft-mist inhalers) to HFC-based pMDIs are available for many products in many regions. Despite this, there are gaps in the availability of therapeutically equivalent alternatives. Consideration of these products replacing a significant proportion of pMDIs is complex, as there are complicated economic considerations, as well as differences in patient-preference or even effectiveness.[23,24] Further, in many parties, even if available, differences in costs may be prohibitive to use over generic pMDIs or single-dose dry powder inhalers.

In 2022, there are no pMDIs containing low-GWP propellants available as alternatives to the current pMDIs containing high GWP HFCs. It is projected that the first of these lower GWP alternative pMDI products will be launched in 2025, a full array of inhaled products widely available globally will more likely continue into 2030 or beyond. The speed of introduction will depend on manufacturer development efforts and regulatory expectations across parties for the switching to pMDIs with lower GWP propellants, which would benefit from a rationalised, coordinated regulatory approach. Parties may wish to consider their regulatory frameworks for the approvals of these lower GWP pMDIs, to provide for efficient, timely development and approval while assuring the safety and effectiveness of the new pMDIs.

Unlike the CFC phase-out, with an HFC phase down, the lack of imperative for the uptake of the newer alternative pMDI products may present a barrier to large-scale, rapid transition in the marketplace without parties providing incentives or policy frameworks that might stimulate the uptake of the new lower GWP products while the high-GWP HFC pMDIs remain in parallel on the market.

It would be expected that these products will be price competitive with current HFC pMDIs, but costs of development and meeting local regulatory considerations may impact price. It is also possible that the cost of high GWP HFCs and their pMDI products increase as the phase down progresses and pharmaceutical-grade HFC supply dwindles, which might lead to a market driven transition. Initial safety evaluations have been promising with no significant safety issues reported.[25,26]

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want? In: *ERS international conference*. 2021.

[22] This is due to the small amount of medication being purchased at any one time, making the single-dose DPI more affordable for the patient; multi-dose DPIs are cheaper overall on a cost per dose basis.

[23] Kemp L, Haughney J, Barnes N, Sims E, von Ziegenweidt J, Hillyer EV, Lee AJ, Chisholm A, Price D., Cost-effectiveness analysis of corticosteroid inhaler devices in primary care asthma management: A real world observational study, *Clinicoecon Outcomes Res.,* 2010, **2**, 75-85. doi: 10.2147/ceor.s10835. Epub 2010 Jul 1. PMID: 21935316; PMCID: PMC3169968.

[24] Wilkinson, Alexander & Braggins, Rory & Steinbach, Ingeborg. Costs of switching to low global warming potential inhalers. An economic and carbon footprint analysis of NHS prescription data in England, *BMJ Open*, 2019, 9. e028763. 10.1136/bmjopen-2018-028763.

[25] Kuehl, P. *et al*., Safety, tolerance and pharmacokinetics of HFA-152a in healthy volunteers. In Respiratory Drug Delivery 2022, eds Dalby, R. et al, 87-95, Virginia Commonwealth University.

[26] Hulse R, Boldt E, Decaire B, Smith G, *A Journey to Net Zero Using Solstice Air*, Respiratory Drug Delivery

Safety in use— HFC-152a and HFO-1234ze(E) have some flammability characteristics requiring special considerations in manufacturing. However, it is not anticipated that these considerations would impact pMDIs in relation to their means of use (i.e., generally not proximate to ignition sources). However, as with the transition to high GWP HFC propellants, toxicology and tolerability testing will be important not only for any novel propellant, but also for any new formulations (surfactants, co-solvents) and leachable/extractable components of the valves and canisters. This testing is anticipated to be conducted and completed successfully in accordance with the usual toxicologic testing for novel inhaled products, and initial safety evaluations of the alternative propellants are encouraging. Clinical testing will explore any potential issues of safety, including impact on airway function in patients (both efficacy as well as any untoward airway tolerability issues).

Ease of use— Incorrect inhaler technique is extremely common in clinical practice and is linked to worsened health outcomes. Moreover, adherence to inhaled maintenance therapy is poor, so finding the right choice of inhaler that a particular patient can and will use is important for effective treatment.

Different patients find different inhaler devices easier to use, depending on their abilities and preferences, and a range of options can help match the correct device to the patient. There are advantages and disadvantages with the ease of use of pMDIs and DPIs. pMDIs with spacers provide an option for patients with low inspiratory flow, as they may not be able to use DPIs optimally, e.g., patients with severe lung disease and very young children, and for severe asthma attacks (where nebulisers are another alternative). Nevertheless, inability to coordinate actuation and inhalation is one of the most common errors with traditional pMDI use and is associated with worsening disease outcomes. Some patients, particularly older patients or those with arthritis, struggle to effectively actuate pMDIs. With information and training, poor pMDI technique can be improved, although this requires reinforcement, which is rarely provided on a regular basis. Breath-actuated pMDIs are now available for many drug combinations. pMDIs and SMIs can be effectively used with very little inspiratory effort, whereas insufficient inspiratory flow through DPIs can result in diminished drug delivery. Drug delivery is breath-actuated with DPIs, which does not require the patient to actuate the inhaler at the same time as inhalation. Most patients with asthma and COPD have sufficient inspiratory flow to use DPIs, but patients at the extremes of age may struggle. Given these overall considerations and various limitations, a range of devices is needed to effectively meet the needs of all patients.[27,28]

Systematic reviews have found that DPIs are no less effective in managing exacerbations compared with pMDIs, though GINA (Global Initiative for Asthma) guidelines recommend short-acting bronchodilator via pMDI with spacer as the most cost-effective option.[29,30] However, this may not be

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2022. Volume 1, 2022: 97-102.

[27] Haughney J, Lee AJ, McKnight E, *et al.,* Peak Inspiratory Flow Measured at Different Inhaler Resistances in Patients with Asthma, *Journal of Allergy and Clinical Immunology: In Practice,* 2021, **9**, 890–6. doi:10.1016/j.jaip.2020.09.026.

[28] Clark AR, Weers JG, Dhand R., The Confusing World of Dry Powder Inhalers: It Is All about Inspiratory Pressures, Not Inspiratory Flow Rates, *J Aerosol Med Pulm Drug Deliv*. 2020, **33**, 1–11. doi:10.1089/jamp.2019.1556.

[29] Selroos O, Borgström L, Ingelf J., Use of dry powder inhalers in acute exacerbations of asthma and COPD, *Ther Adv Respir Di,s* 2009, **3**, 81–91. doi:10.1177/1753465809103737.

[30] Rodrigo GJ, Neffen H, Colodenco FD, *et al.,* Formoterol for acute asthma in the emergency department: a systematic review with meta-analysis, *Annals of Allergy, Asthma and Immunology,* 2010, **104**, 247–52.

the recommendation in all regions. The evidence is less clear for life-threatening asthma or hospitalised COPD patients, where nebulised treatment is recommended.[31,32]

Many additional factors influence the overall ease of use and acceptability of an inhaler. Many pMDIs require priming sprays or shaking before use. Further, many pMDIs need washing regularly with warm water to keep them from clogging or providing suboptimal delivery. Similarly, spacers should be regularly cleaned and drip-dried. Many pMDIs globally have no dose counter making it harder to know when to replace them, since pMDIs will expel propellant beyond end-of-use. This can result in patients unknowingly using empty or near-empty inhalers with ineffective drug dosing or discarding part-used inhalers.[33,34]

A range of aids are available to assess technique and aid with inhaler technique training. Some of these include whistles when inspiratory flow is correct, which are available for DPI placebo and as add-ons to pMDIs. Most pMDI placebos use HFC propellants and so have a large carbon footprint without direct benefit, although an HFC-free device has also been developed.[35]

To effectively use single-dose DPIs requires sufficient manual dexterity to load the capsule, and numerous steps are required to effectively prepare the inhaler. Multi-dose DPIs generally have the fewest steps involved in preparing the medication, take the least time to use, and in one study were found to be the most popular class of device when a wide range of options are offered.[36,37] However, different DPI products require different techniques and patients require training for each different device, which can be confusing as many patients use more than one inhaler at any given time to maintain stable disease.

5.4 Solvents

Controlled substances (CFC-113, 1,1,1-trichloroethane, CTC, CFC-11, HCFC-141b, HCFC-225ca/cb, HFC-43-10mee, HFC-365mfc, and to a limited extent HFC-245fa) were chosen due to their favourable chemical and physical properties in various solvent applications, including metal,

doi:10.1016/j.anai.2009.11.064.

[31] 2022 GINA Main Report - Global Initiative for Asthma - GINA. https://ginasthma.org/gina-reports/ (accessed 31 Jul 2022).

[32] 2022 GOLD Reports - Global Initiative for Chronic Obstructive Lung Disease - GOLD. https://goldcopd.org/2022-gold-reports-2/ (accessed 31 Jul 2022).

[33] Conner JB, Buck PO., Improving Asthma Management: The Case for Mandatory Inclusion of Dose Counters on All Rescue Bronchodilators, *The Journal of Asthma*, 2013, **50**, 658–63. doi:10.3109/02770903.2013.789056.

[34] Price DB, Román-Rodríguez M, McQueen RB, *et al*., Inhaler Errors in the CRITIKAL Study: Type, Frequency, and Association with Asthma Outcomes, *Journal of Allergy and Clinical Immunology: In Practice*, 2017, **5**,1071-1081.e9. doi:10.1016/j.jaip.2017.01.004.

[35] Clement Clarke International. Trainhaler pMDI training system. https://www.haag-streit.com/clement-clarke/products/inhaler-technique/trainhaler/ (accessed 5 Mar 2020).

[36] Schreiber J, Sonnenburg T, Luecke E., Inhaler devices in asthma and COPD patients – a prospective cross-sectional study on inhaler preferences and error rates, *BMC Pulm. Med.,* 2020, **20**, 222. doi:10.1186/s12890-020-01246-z.

[37] Sanchis J, Gich I, Pedersen S., Systematic review of errors in inhaler use: Has patient technique improved over time?, *Chest,* 2016, **150**, 394–406.http://dx.doi.org/10.1016/j.chest.2016.03.041.

electronics, and precision cleaning, and in formulations for adhesives[38], coatings, and inks. HCFCs and HFCs have been used to a much lesser extent than the high ODP ODS solvents that were phased out, with other alternatives substituting many of those previous solvent uses of ODS.

HFCs are commonly used as azeotropic mixtures, which are mixtures of two or more liquids that have the same mixture concentration in liquid and vapour phases. Fluorinated solvents have poorer solvency than chlorinated solvents. As a result, HFCs are often mixed with chlorinated chemicals to boost the solvency.

Many alternative solvents and technologies developed as ODS alternatives are also the candidates for HFC alternatives. These include not-in-kind technologies, such as aqueous cleaning, semi-aqueous cleaning, hydrocarbon and oxygenated solvents, and in-kind solvents, such as chlorinated solvents and fluorinated solvents, including high GWP HFCs not listed in Annex F and low GWP HFOs, HCFOs, and HFEs, with various levels of acceptance.

Alternatives to HFCs that are controlled substances are being used for electronics defluxing/cleaning and precision cleaning in several industries, including automotive, aerospace, medical device, and optical components where high levels of cleanliness are required.

5.4.1 Technical and economic assessment of solvent uses of controlled substances and their alternatives

An assessment follows of the technical and economic feasibility of HFC alternatives in solvent uses. The assessment criteria referenced in decision XXVIII/2 have been slightly modified to remain relevant to this application, using the following criteria:

i. Commercially available
ii. Technically proven
iii. Environmentally sound
iv. Economically viable and cost effective
v. Safe to use in industrial applications considering flammability and toxicity issues
vi. Easy to use and maintain

"Safe to use in areas with high urban densities considering flammability and toxicity issues, including, where possible, risk characterization" has been adjusted to *safe to use in industrial applications considering flammability and toxicity issues*. "Easy to service and maintain" has been adjusted to *easy to use and maintain*. Technically proven is interpreted to mean the technology has been proven to work for that application, or an aspect of it; not necessarily commercialised for that application.

[38] Adhesive uses no longer use controlled substances, which were phased out with 1,1,1-trichloroethane.

Table 5.4: Technical and economic assessment of solvent uses of controlled substances and their alternatives

Controlled Substances and Alternatives	Characteristics	Commercially available	Technically proven	Environmentally sound	Economically viable	Safe to use	Easy to use
HCFCs (-141b, -225ca/cb)	HCFCs were implemented as in-kind alternatives to CFCs and 1,1,1-trichloroethane. The compounds are non-flammable, effective cleaning agents with defined ODPs.	◆ yellow	◆ green	◆ red	◆ green	◆ green	◆ green
HFCs (43-10-mee, 365mfc)	HFCs have limited utility in cleaning applications due to their mild solvent strength. They are most often used in blends and azeotropic mixtures with compounds such as *trans*-1,2-dichloroethylene and/or alcohols. These formulations are effective cleaning agents but can often be more expensive than other in-kind alternatives.	◆ yellow	◆ green	◆ red	◆ yellow	◆ green	◆ green
	Alternatives						
Aqueous and semi-aqueous cleaning	Water-based cleaning processes often use surfactants and saponifiers and in the case of semi-aqueous high boiling hydrocarbon solvents followed by several water rinses. These processes can present challenges to maintain water purity and typically consume more energy to dry water.	◆ green	◆ green	◆ green	◆ green	◆ green	◆ yellow
Organic solvents	Organic solvents, such as alcohols, ethers, ketones, esters, aromatics, can be low cost, effective solvents but users must address flammability and/or toxicity concerns and the fact that most are precursors to smog formation which are regulated as volatile organic compounds (VOCs).	◆ green	◆ green	◆ yellow [1]	◆ green	◆ yellow	◆ yellow
n-Propyl bromide	n-Propyl bromide has been used in several solvent applications but has a non-zero ODP and occupational exposure limits as low as 0.1 ppmv in some parties. n-Propyl bromide is considered a suspected carcinogen and mutagen. This compound is listed as a hazardous air pollutant in some parties, e.g., the USA.	◆ green	◆ green	◆ yellow	◆ green	◆ yellow	◆ yellow
Trichloroethylene, perchloroethylene, dichloromethane, chloroform	Chlorinated solvents are non-flammable, low cost, effective cleaning agents with relatively low occupational exposure limits (≤50 ppmv) and classified as confirmed or suspected carcinogens in many parties. These compounds are listed as hazardous air pollutants in some parties, e.g., the USA.	◆ green	◆ green	◆ yellow	◆ green	◆ yellow	◆ yellow
HFCs	Saturated HFCs not listed as controlled substances in Annex F are used in low volume quantities in solvent applications, including HFC-c447ef (5-carbon cyclic HFC, $(-CHFCH_2(CF_2)_3-)$), HFC-52-13p ($CF_3(CF_2)_4CHF_2$) and HFC-76-13sf ($CF_3(CF_2)_5CH_2CH_3$).	◆ green	◆ green	◆ yellow [2]	◆ green	◆ green	◆ green

Controlled Substances and Alternatives	Characteristics	Commercially available	Technically proven	Environmentally sound	Economically viable	Safe to use	Easy to use
	Alternatives						
HFEs	Hydrofluoroethers have limited utility in cleaning applications due to their mild solvent strength. They are most often used in blends and azeotropic mixtures with *trans*-1,2-dichloroethylene and/or alcohols. These formulations are effective cleaning agents but can often be more expensive than other in-kind alternatives.	◆ (green)	◆ (green)	◆ (green)[3]	◆ (yellow)	◆ (green)	◆ (green)
HCFOs	HCFO-1233zd(E), -1233zd(Z), and -1233yd(Z) are emerging as effective cleaning agents with negligible ODPs and GWPs. HCFO-1233zd(E) alone can present technical challenges in some solvent applications due to its 19°C boiling point. HCFO-1233zd(Z) (bp 39 ºC), and HCFO-1233yd(Z) (bp 54 ºC) have more suitable boiling points and do not present these same challenges.	◆ (green)	◆ (green)	◆ (green)	◆ (green)	◆ (green)	◆ (yellow)
HFOs	Like HFEs, hydrofluoroolefins have limited utility in cleaning applications due to their mild solvent strength. They are most often used in blends and azeotropic mixtures with *trans*-1,2-dichloroethylene. These formulations are effective cleaning agents but can often be more expensive than other in-kind alternatives.	◆ (green)	◆ (green)	◆ (green)	◆ (yellow)	◆ (green)	◆ (green)

◆ (green) Yes or More acceptable; ◆ (yellow) Not always or Less acceptable; ◆ (red) No or Unacceptable.

1. Most organic solvents are VOCs, which are regulated in some regions due to their potential for photochemical smog generation.
2. HFC-c447ef is reported to have a 100-year GWP of 231 (IPCC AR6). HFC-52-13p is calculated to have a 100-year GWP of 2000. HFC-76-13sf is calculated to have a 100-year GWP of 136. HFC-52-13p has a GWP higher than those for HFC-43-10-mee and HFC-365mfc and would be rated as red. When used as solvents, these HFCs can be used neat or with a co-solvent, which would lower the overall GWP.
3. HFEs, including HFE-449s1, HFE-569sf2, HFE-64-13s1, and HFE-347pc-f2 have 100-year GWPs ranging from around 300-600. However, being most often used in mixtures with lower GWP chemicals, HFE solvents can be rated as being environmentally sound.

Commercial availability and accessibility— In-kind and not-in-kind alternatives are commercially available and accessible for solvent applications. By comparison, HCFCs and HFCs have decreasing commercial availability and accessibility due to Montreal Protocol control measures to phase out or phase down these controlled substances.

Technically proven— All alternatives have been technically proven in specific solvent applications.

HFC (and HCFC) solvents using have been used in several different industries, for example, in aerospace, micro-mechanical part manufacturing, plating, aerosol cleaners, circuit flushing, electronics defluxing/cleaning, oxygen service cleaning, and the medical industry in coating deposition. Each of these industries has its own set of specific solvent requirements and associated test procedures, e.g., to ensure cleaned parts are acceptable for use. The consequences of incomplete cleaning can be anything from poor performance in the next step, which can be seen in applications like plating, decreased product lifetime, performance in electronics cleaning, or even large potential safety concerns, such as when parts are cleaned for use in oxygen services. It is important for manufacturers to match their cleaning requirements with the new solvent or cleaning system. Typically, when seeking an alternative, manufacturers will evaluate alternative solvents, aqueous cleaners, no clean solutions, or complete system changes. Each of these alternatives will be evaluated to assess how they meet the specific cleaning or coating deposition requirements, as well as cost and health and safety requirements.

Aqueous and semi-aqueous cleaning can present challenges in maintaining water purity and consume more energy to dry water.

Environmentally sound— Trichloroethylene, perchloroethylene, dichloromethane, chloroform, and n-propyl bromide have been listed as hazardous air pollutants in some parties, e.g., the USA. These halogenated solvents have low ODPs; they are not controlled substances.

HFC-52-13p is calculated to have a 100-year GWP of 2000, which is higher than the GWPs for HFC-43-10-mee (1640) and HFC-365mfc (794). HFC-c447ef is reported to have a 100-year GWP of 231. HFC-76-13sf is calculated to have a 100-year GWP of 136. When used as solvents, these HFCs can be used neat or with a co-solvent that lowers the overall GWP.

HFEs, including HFE-449s1, HFE-569sf2, HFE-64-13s1, and HFE-347pc-f2 have 100-year GWPs ranging from around 300-600. HFEs are most often used as azeotropic mixtures with lower GWP chemicals, meaning HFE solvents are considered environmentally sound.

HCFO-1233zd(E), 1233zd(Z), and 1233yd(Z) are emerging as effective cleaning agents with negligible ODPs and GWPs.

Economically viable and cost effective— HFEs and HFOs are more expensive than other in-kind solvent options. For this reason, they can often find their way into high value and/or specialist applications.

Safe to use in industrial applications considering flammability and toxicity issues— Organic solvents require consideration of flammability concerns. Most organic solvents are photochemical smog precursors that are regulated as volatile organic compounds (VOCs)

Trichloroethylene, perchloroethylene, dichloromethane, chloroform, and n-propyl bromide are confirmed or suspected carcinogens in many parties. They have been listed as hazardous air pollutants in some parties, e.g., the USA. They have relatively low (≤50 ppmv) or very low (n-propyl bromide, 0.1ppmv) occupational exposure limits in some parties.

Easy to use and maintain—Due to their different technical or chemical/physical properties, or safety profiles, aqueous and semi-aqueous cleaning, organic solvents, trichloroethylene, perchloroethlylene, dichloromethane, chloroform, n-propyl bromide can be options that are more difficult to use. HCFO-1233zd(E) alone can present technical challenges in some solvent applications due to its low boiling point. HFEs, HFOs, and HCFO-1233zd(Z), and HCFO-1233yd(Z) are easier to use than the other alternatives.

5.5 Semiconductor and Other Electronics manufacturing

Semiconductors are fabricated by forming circuit patterns on silicon-based wafers by using chemicals to form the circuit pattern. More recently dry etching processes using reactive ion etching (RIE) are used for this process. RIE uses plasma-generated fluorine radicals and other reactive fluorine-containing ions that react with the substrate or thin-film to be etched. Chemical vapour deposition chamber walls are also cleaned using fluorinated chemicals to remove the build-up of silicon materials.

RIE and chamber cleaning use fluorinated gaseous chemicals, including perfluorocarbons (PFCs), such as carbon tetrafluoride (CF_4), perfluoro butadiene (C_4F_6) and cyclic C_4F_8, HFCs, sulfur hexafluoride (SF_6) and nitrogen trifluoride (NF_3). The most commonly used HFCs are HFC-23 (CHF_3), HFC-41 (CH_3F) and HFC-32 (CH_2F_2). The usage of cyclic C_4F_8, HFC-41, HFC-32 and perfluoro butadiene is expected to increase due to their use in high aspect hole etching (e.g., used in manufacturing DRAM, NAND[39]).[40,41] HFCs are only minimally used for chamber cleaning.

Fluorinated heat transfer fluids are used for thermal management, much like a refrigerant in other applications. Heat transfer fluids control the wafer temperature during etching, which is an important factor for high aspect ratio hole etching. The most commonly used fluorinated chemicals used as heat transfer fluids are a saturated PFC (PFC and perfluoroalkyl amine), hydrofluoroethers, and perfluoropolyethers.[42] HFCs (HFC-134a and HFC-23) are not commonly used as heat transfer fluids.

Like semiconductor manufacturing, other electronics manufacturing, including flat panel display (FPD), photovoltaics (PV) and microelectromechanical systems (MEMS), use fluorinated chemicals for etching and chamber cleaning. These manufacturing processes primarily use PFCs, HFC-23, SF_6, and NF_3. In photovoltaic manufacturing, HFCs are not commonly used.

Alternatives to HFC use in semiconductor and other electronics manufacturing are other fluorinated gases, such as PFCs, SF_6 and NF_3, many of which have higher GWPs and lower utilization rates than HFCs, such as HFC-32 and HFC-41.

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[39] In digital electronics, a NAND gate (NOT-AND) is a logic gate in semiconductor circuitry.

[40] Current status and future prospects of the semiconductor materials market in 2020 (Fuji Keizai Corporation).

[41] Kondo, Y., Ishikawa, K., Hayashi, T., Miyawaki, Y., Takeda, K., Kondo, H., Sekine, M., Hori, M. Silicon nitride etching performance of CH_2F_2 plasma diluted with argon or krypton, *Jpn. J. Appl. Phys.*, 2015, **54**, 040303.

[42] https://eetimes.itmedia.co.jp/ee/articles/2205/18/news053.html (in Japanese).

5.5.1 Technical and economic assessment of semiconductor and other electronics manufacturing uses of controlled substances and their alternatives

An assessment follows of the technical and economic feasibility of the alternatives to HFC use in semiconductor and electronics manufacturing. The assessment criteria referenced in decision XXVIII/2 have been slightly modified to remain relevant to this application, using the following criteria:

i. Commercially available
ii. Technically proven
iii. Environmentally sound
iv. Economically viable and cost effective
v. Safe to use in industrial applications considering flammability and toxicity issues
vi. Easy to use and maintain

"Safe to use in areas with high urban densities considering flammability and toxicity issues, including, where possible, risk characterization" has been adjusted to *safe to use in industrial applications considering flammability and toxicity issues*. "Easy to service and maintain" has been adjusted to *easy to use and maintain*. Technically proven is interpreted to mean the technology has been proven to work for that application, or an aspect of it; not necessarily commercialised for that application

Table 5.5 Technical and economic assessment of controlled substances and alternatives for etching, chamber cleaning, and heat transfer fluids

Controlled Substances and Alternatives	Gas Category	100-year GWP	Alternative characteristics	Commercially available	Technically proven	Environmentally sound	Economically viable	Safe to use	Easy to use
Semiconductor Manufacturing									
Plasma Etching and Chamber Cleaning									
HFC-23 (CHF_3)	Saturated HFC with 2 or fewer C-H bonds	14,800	Used for etching. HFCs are minimally used for chamber cleaning. Etch SiO_2 and SiNx, sidewall passivation.	◆ green	◆ green	◆ red	◆ green	◆ green	◆ green
HFC-32 (CH_2F_2)	Saturated HFC with 2 or fewer C-H bonds	675	Used for etching. HFCs are minimally used for chamber cleaning. Etch SiO_2 and SiNx, sidewall passivation; good for high-aspect hole etching.	◆ green	◆ green	◆ red	◆ green	◆ green	◆ green
HFC-41 (CH_3F)	Saturated HFC with 3 or more C-H bonds	92	Used for etching, not known to be used for chamber cleaning. Good for high-aspect hole etching.	◆ green	◆ green	◆ amber	◆ green	◆ green	◆ green
Alternatives									
SF_6	Fully fluorinated GHG	22,800	Used for etching and chamber cleaning. Etch Si, SiO_2, SiNx, Bosch process.	◆ green	◆ green	◆ red	◆ green	◆ green	◆ green
NF_3	Fully fluorinated GHG	17,200	Used for etching and chamber cleaning, including remote plasma. Etch Si, Si_3N_4.	◆ green	◆ green	◆ red	◆ green	◆ green	◆ green
Saturated PFCs (CF_4, C_2F_6, c-C_4F_8)	Fully fluorinated GHGs	7,390-12,200	Used for etching and chamber cleaning. Etch Si, TiN, SiO_2, SiNx, Organics, Sidewall passivation. c-C_4F_8 is good for high-aspect hole etching. More difficult to abate, esp. CF_4.	◆ green	◆ green	◆ red	◆ green	◆ green	◆ green
Unsaturated PFCs (C_4F_6, C_5F_8)	Unsaturated PFCs	<2	Used for etching. Good for high-aspect hole etching. Not known to be used for chamber cleaning.	◆ green	◆ green	◆ green	◆ green	◆ green	◆ green
F_2	Molecular Fluorine	N/A	Very aggressive, therefore more suitable for chamber cleaning. Not known to be used for etching (not technically proven).	◆ green	◆ amber	◆ amber	◆ green	◆ amber	◆ amber

Controlled Substances and Alternatives	Gas Category	100-year GWP	Alternative characteristics	Commercially available	Technically proven	Environmentally sound	Economically viable	Safe to use	Easy to use
Semiconductor Manufacturing									
Heat Transfer Fluids									
HFC-134a	Saturated HFC	1,430	Small temperature range.	◆ green	◆ yellow	◆ red	◆ green	◆ green	◆ green
Alternatives									
Saturated PFCs	Saturated perfluoroalkanes and perfluorotrialkylamines $(C_nF_{2n+1})_3N$	9,300	Wide temperature range, high dielectric strength, high GWP.	◆ green	◆ green	◆ red	◆ green	◆ green	◆ green
Perfluoropolyethers (PFPE)	Saturated perfluoropolyethers $CF_3[O\text{-}CF(CF_3)CF_2]_m(OCF_2)_nOCF_3$	10,300	Wide temperature range, high dielectric strength, high GWP.	◆ green	◆ green	◆ red	◆ green	◆ green	◆ green
HFE	Saturated hydrofluoroethers $C_nF_{2n+1}OC_mH_{2m+1}$	59-297	Wide temperature range, dielectric strength not as high as PFC or PFPE.	◆ green	◆ green	◆ green	◆ green	◆ green	◆ green
Flat Panel Display									
HFC-23 (CHF_3)	Saturated HFC with 2 or fewer C-H bonds	14,800	HFC-23 can be used in plasma etching.	◆ green	◆ green	◆ red	◆ green	◆ green	◆ green
Alternatives									
Saturated PFCs (CF_4, C_2F_6, c-C_4F_8)	Fully fluorinated GHG	7,390-12,200	Saturated PFCs are used for etching and chamber cleaning.	◆ green	◆ green	◆ red	◆ green	◆ green	◆ green
SF_6	Fully fluorinated GHG	22,800	SF_6 is used for etching and chamber cleaning.	◆ green	◆ green	◆ red	◆ green	◆ green	◆ green
NF_3	Fully fluorinated GHG	17,200	NF_3 is used for etching and chamber cleaning.	◆ green	◆ green	◆ red	◆ green	◆ green	◆ green
F_2	Molecular Fluorine	N/A	Used for chamber cleaning, not known to be used for etching.	◆ green	◆ yellow	◆ yellow	◆ green	◆ yellow	◆ yellow

Controlled Substances and Alternatives	Gas Category	100-year GWP	Characteristics	Commercially available	Technically proven	Environmentally sound	Economically viable	Safe to use	Easy to use
Photovoltaics									
HFC-23 (CHF_3)	Saturated HFC with 2 or fewer C-H bonds	14,800	HFC-23 is used in plasma etching, although is not commonly used.	◆ (green)	◆ (green)	◆ (red)	◆ (green)	◆ (green)	◆ (green)
Alternatives									
Saturated PFCs (CF_4, C_2F_6, c-C_4F_8)	Fully fluorinated GHG	7,390-12,200	Saturated PFCs are used for etching and chamber cleaning.	◆ (green)	◆ (green)	◆ (red)	◆ (green)	◆ (green)	◆ (green)
SF_6	Fully fluorinated GHG	22,800	SF_6 is used for etching and chamber cleaning.	◆ (green)	◆ (green)	◆ (red)	◆ (green)	◆ (green)	◆ (green)
NF_3	Fully fluorinated GHG	17,200	NF_3 is used for etching and chamber cleaning.	◆ (green)	◆ (green)	◆ (red)	◆ (green)	◆ (green)	◆ (green)
F_2	Molecular Fluorine	N/A	Used for chamber cleaning, not known to be used for etching.	◆ (green)	◆ (orange)	◆ (orange)	◆ (green)	◆ (orange)	◆ (orange)

◆ (green) Yes or More acceptable; ◆ (orange) Not always or Less acceptable; ◆ (red) No or Unacceptable.

Commercial availability and accessibility— All alternatives are commercially available and accessible for their specific uses.

Technically proven— F_2 is a suitable replacement for CVD chamber cleaning in semiconductor manufacturing; although it is very aggressive and not known to be used for etching. Some flat panel display manufacturers have piloted the use of F_2 to replace NF_3 in remote plasma chamber cleaning processes.[43] F_2 has also been explored as an alternative to SF_6 in photovoltaic manufacturing.[44]

HFC-134a has a smaller temperature range as a heat transfer fluid compared with alternatives. Most semiconductor heat transfer processes require the material to operate over a relatively large temperature range, which is better accomplished with a liquid.

Environmentally sound— Alternatives to HFC use in semiconductor manufacturing include other fluorinated gases, such as saturated PFCs, SF_6 and NF_3, many of which have higher GWPs and lower utilization rates than HFCs, such as HFC-32 and HFC-41. Emissions from electronics manufacturing include the unutilised portion of the process gas and gases formed as a by-product during the process from other process gases. Abatement and scrubbing of process emissions is considered best practice. Pollutant emissions would be required to meet local regulatory standards.

For heat transfer fluids, the HFE is relatively the best available option environmentally compared with HFC-134a and the higher GWP alternatives; however, the HFE may not always be suitable due to its dielectric properties.

Economically viable and cost effective—All alternatives are economically viable and cost effective.

Safe to use in industrial applications considering flammability and toxicity issues—Whether HFCs or their alternatives, all chemicals require appropriate storage and handling. Abatement and scrubbing of process emissions is considered best practice. Pollutant emissions would be required to meet local regulatory standards.

Molecular fluorine (F_2) has challenges associated with transport, storage and use due to extremely high reactivity and oxidizing capability, which require the use of special safety precautions. Safe installation and operation procedures are required due to corrosivity and toxicity. For example, special mass flow controllers and valves are required in addition to special passivation process of the process gas lines.[45] F_2 can be supplied in cylinders mixed with nitrogen (Wild-Scholten 2007) or produced on-site, which would eliminate any transportation challenges.

Easy to use and maintain— Molecular fluorine (F_2) has challenges associated with transport, storage and use. Safe installation and operation procedures are required due to corrosivity and toxicity. F_2 can be supplied in cylinders mixed with nitrogen or produced on-site, which would eliminate any transportation challenges.[46]

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[43] U.S. Environmental Protection Agency, *F-GHG Emissions Reduction Efforts: Flat Panel Display Supplier Profiles*, May 2013, https://www.epa.gov/sites/default/files/2015-07/documents/supplier_profiles_2013.pdf. Accessed September 2022.

[44] M.J. de Wild-Scholten, *et al.*, *Fluorinated Greenhouse Gases in Photovoltaic Module Manufacturing: Potential Emissions and Abatement Strategies*, 22nd European Photovoltaic Solar Energy Conference, Fiera Milano, Italy, 3-7 September 2007, Version: 30 August 2007.

[45] Ibid., de Wild-Scholten, *et al.*, 2007.

[46] Ibid., de Wild-Scholten, *et al.*, 2007.

5.6 Magnesium Production

Cover gases are used in magnesium production, casting processes and recycling to prevent oxidation and combustion of molten magnesium. Without protection, molten magnesium will oxidize and ignite in the presence of air and form magnesium oxide (MgO) deposits that greatly reduce the quality and strength of the final product. An effective cover gas will modify and stabilise the MgO surface film to form a protective layer that prevents further oxidation.

Sulfur hexafluoride (SF_6) is the most widely used cover gas. SF_6 widely replaced SO_2 and salt fluxes in the 1970s and improved operator health and safety and equipment life.[47] However, SF_6 has a GWP of 22,800. A cover gas of dilute SF_6 in dry air and/or carbon dioxide protects the melt from oxidation and potential fires.

Several gases with lower GWPs have been identified as alternatives to SF_6, including HFC-134a (GWP of 1,430) and a fluoroketone (GWP of 0.1). HFC-134a has been shown to have adequate melt protection but careful selection of the diluent gas and concentration is required to prevent damaging corrosion.[48,49] Both HFC-134a and the fluoroketone are reported as being used by the industry as a cover gas.[50] More recently, researchers have begun exploring the addition of small amounts of unique alloying elements (e.g., Be, Al, Ca) to enhance the oxidation resistance of the alloy and possible reduce the need for a cover gas.[51]

The majority (80-90%) of primary magnesium production occurs in China, followed by the US, Israel, and Brazil.

5.6.1 Technical and economic assessment of magnesium production uses of controlled substances and their alternatives

An assessment follows of the technical and economic feasibility of the alternatives to HFC use in magnesium production. The assessment criteria referenced in decision XXVIII/2 have been slightly modified to remain relevant to this application, using the following criteria:

i. Commercially available
ii. Technically proven
iii. Environmentally sound
iv. Economically viable and cost effective
v. Safe to use in industrial applications considering flammability and toxicity issues
vi. Easy to use and maintain

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[47] N. J. Ricketts, R. Esdaile, S. Ramakrishnan, *Environmental Implications of using HFC-134a as a replacement for sulphur hexafluoride in the magnesium industry*, International Conference on SF_6 and the Environment, 2002.

[48] Won Ha, Young-Jig Kim, Effects of cover gases on melt protection of Mg alloys, *Journal of Alloys and Compounds,* 2006, **422**, 208–213.

[49] N. J. Ricketts, R. Esdaile, S. Ramakrishnan, *Environmental Implications of using HFC-134a as a replacement for sulphur hexafluoride in the magnesium industry*, International Conference on SF_6 and the Environment (2002).

[50] U.S. Environmental Protection Agency. PA Greenhouse Gas Reporting Program (GHGRP) Envirofacts. Subpart I: Electronics Manufacture. Available online at: http://www.epa.gov/enviro/facts/ghg/search.html.

[51] Fabrizio D'Errico, Martin Tauber and Michael Just, *Magnesium Alloys for Sustainable Weight-Saving Approach: A Brief Market Overview, New Trends, and Perspectives*, April 5th, 2022, DOI: 10.5772/intechopen.102777. https://www.intechopen.com/chapters/81125.

“Safe to use in areas with high urban densities considering flammability and toxicity issues, including, where possible, risk characterization” has been adjusted to *safe to use in industrial applications considering flammability and toxicity issues*. “Easy to service and maintain” has been adjusted to *easy to use and maintain*. Technically proven is interpreted to mean the technology has been proven to work for that application, or an aspect of it; not necessarily commercialised for that application.

Table 5.6 Technical and economic assessment of uses of controlled substances and their alternatives for magnesium production

Controlled Substances and Alternatives	Gas Category	100-year GWP	Characteristics	Commercially available	Technically proven	Environmentally sound	Economically viable	Safe to use	Easy to use
HFC-134a	HFC	1,430	May not be suitable for all products. Cost may be a factor for using HFC-134a instead of higher priced fluoroketone. HFC-134a is less expensive than SF_6.	◆ (green)	◆ (green)	◆ (red)	◆ (green)	◆ (green)	◆ (green)
			Alternatives						
Dodecafluoro-2-methyl-3-pentanone ($(CF_3CF_2C(O)CF(CF_3)_2)$)	Fluoroketone	~1	100% Dry air carrier not recommended due to formation of HF. Suitable with N_2 or CO_2 or with dry-air/N_2 carrier or CO_2 with dry-air. Emits trace C_3F_8. Even distribution of gas is required, which sometimes requires adjustments to equipment with the use of this fluoroketone, as it is more reactive than SF_6.	◆ (green)	◆ (green)	◆ (green)	◆ (green)	◆ (green)	◆ (green)
SF_6	Fully fluorinated GHG	22,800	Less reactive gas. Suitable for the majority of applications. SF_6 is relatively expensive compared to alternatives.	◆ (green)	◆ (green)	◆ (red)	◆ (amber)	◆ (green)	◆ (green)
SO_2 (gas)	Non-GHG	0	Requires SO_2 scrubber to be environmentally sound. Corrosion issues.	◆ (green)	◆ (green)	◆ (red)	◆ (green)	◆ (red)	◆ (green)
CO_2	CO_2	1	May not be suitable for all products.	◆ (green)	◆ (green)	◆ (green)	◆ (green)	◆ (green)	◆ (green)
Salt Flux	N/A (Granular cover material)	N/A	Mixture of chlorides (KCl, NaCl, $MgCl_2$), fluorides (CaF_2) and/or oxides (MgO). Negatives: flux entrapment, release of corrosive gases, melt loss; may still need trace HFC-134a to purge molds.	◆ (green)	◆ (green)	◆ (amber)	◆ (green)	◆ (green)	◆ (green)
Vacuum	N/A	N/A	Not technically proven. Technically challenging and requiring significant equipment and process adjustments.	◆ (amber)	◆ (amber)	◆ (green)	◆ (green)	◆ (green)	◆ (amber)
S (powder)	N/A	N/A	Older technology, with technical issues associated with potential contamination of Mg.	◆ (green)	◆ (green)	◆ (red)	◆ (green)	◆ (red)	◆ (green)

◆ (green) Yes or More acceptable; ◆ (amber) Not always or Less acceptable; ◆ (red) No or Unacceptable.

Commercial availability and accessibility— Most alternatives are commercially available and accessible. Vacuum technology has not been technically proven and would require significant equipment and process adjustments.

Technically proven— The HFE has been identified as technically suitable but has not been used commercially for this application. Vacuum technology has not been technically proven and would require significant equipment and process adjustments.

Environmentally sound— SF_6 has a much higher GWPs than HFC-134 and other alternatives (HFE, fluoroketone, CO_2). Sulfur dioxide is a toxic air pollutant and contributor to acid rain. HFE has a higher GWP than the fluoroketone. Salt flux is less environmentally sound due to the release of corrosive gases and may still require trace HFC-134a to purge molds.[52] The use of sulfur produces emissions of sulfur dioxide, which is a toxic air pollutant.

Economically viable and cost effective— SF_6 is relatively expensive compared with alternatives. The operating costs for other alternatives are likely to be lower than SF_6. Technologies, such as vacuum, or using sulfur dioxide or sulfur, would likely require significant capital investment to upgrade equipment and process for safe use.

Safe to use in industrial applications considering flammability and toxicity issues—Sulfur dioxide requires scrubbing to be considered environmentally sound. Sulfur powder is flammable and strongly reactive with magnesium, leading to potential contamination of magnesium.

Easy to use and maintain—Dodecafluoro-2-methyl-3-pentanone may require equipment adjustments for use in some magnesium production processes for more even distribution of the cover gas.[53] Implementation of vacuum technology would require significant modification of current processes to prevent exposure of molten magnesium to air and may not be applicable to all stages of production.

[52] California Air Resources Board, *Magnesium casters successfully retool for a cleaner future: Two firms develop climate-friendly process in response to regulation*, Release Number 15-07, February 2, 2015, https://ww2.arb.ca.gov/news/magnesium-casters-successfully-retool-cleaner-future. Accessed September 2022.

[53] Milbrath, D. S., *3M™ Novec™ 612 Magnesium Protection Fluid*, 3M Industrial Chemicals, International Conference of SF_6 and the Environment, December 1-3, 2004.

6 Information on alternatives to HFCs in the refrigeration, air conditioning and heat pump sectors

6.1 Introduction

6.1.1 Approach

In this section, the information requested by Decision XXVIII/2 for the Refrigeration, Air Conditioning and Heat Pump (RACHP) sectors are disaggregated into the different application sectors as per the forthcoming "RTOC 2022 Assessment Report". Each Table reports the alternatives to HFCs for the applications of the relevant sector/Chapter. All the information contained in this report, which was requested ahead of MOP-34, has been extracted from the draft "RTOC 2022 Assessment Report" and may be further updated based on the latest revisions by the end of 2022.

6.1.2 RTOC interpretation of criteria listed in Decision XXVI/9 paragraph 1(a)

The criteria outlined in Decision XXVI/9 paragraph 1(a) can be subject to interpretation depending on the context of their use. From a RACHP perspective, the RTOC interprets the criteria as:

i. **"Commercially available"**
The topic has been extensively discussed in the May 2021 report of the Energy Efficiency Task Force (available at: [TEAP-EETF-report-may2021.pdf (unep.org)]). For the RACHP sector it is considered necessary to distinguish between "availability" and "accessibility" of technologies. The definitions of "availability" and "accessibility" given in the above-mentioned report are listed below for convenience:

"**Availability**" is the ability of the industry to manufacture products with new technologies using lower-GWP refrigerants and higher efficiency. Availability is controlled by the manufacturers and is related to technology. The factors affecting availability of products that are manufactured locally are described in the abovementioned Energy Efficiency report and are summarized as:

- The ability of the industry in a country to absorb new technologies;
- Technical capabilities needed to implement the technology;
- Scalability of operations; and
- Technology barriers such as Intellectual Property Rights (IPR) and patents.

"**Accessibility**" on the other hand is focussed on the consumer and varies with location within a region, country, or even with district within a country. Some of the factors which affect accessibility include:

- Supply chain; Importers/Suppliers for complete systems or parts, including refrigerants;
- Presence of local manufacturing and/or assembly;
- Regulations affecting energy efficiency and safety; collaboration with Energy Departments on integrated MEPS
- Service sector capacity and quality;
- Electricity quality, reliability, and price;
- Affordability;
- Acceptability and preferences; and
- Presence or absence of laboratories and certification/verification bodies.

Where appropriate, the information is given separately for A5 and non-A5 parties.

ii. **"Technically proven"**

The refrigerants listed in the following have been divided into two classes:

- Technically proven
- Currently under test

For the RACHP sector, being "technically proven" means:

- The technology has thermodynamic properties that makes it able to perform the required cooling or heating application, while maintaining:
    i. good energy efficiency (and high performance);
    ii. pressure range compatible with components availability;
    iii. component materials compatibility;
    iv. lubricating oil compatibility;
- The technology has been extensively tested in actual RACHP operations.

On the other hand, currently under test technologies are being tested to evaluate their potential for a given application.

iii. **"Environmentally sound"**

The environmental soundness of the alternatives is measured by their ODP and GWP. On "Environmentally Sound Technologies", please we referred to the UNEP page: https://www.unep.org/regions/asia-and-pacific/regional-initiatives/supporting-resource-efficiency/environmentally-sound. In this report, we list ODP and GWP as per RTOC 2018 Assessment Report which lists the IPCC AR4 data.

"Economically viable and cost effective"

In typical RACHP application, the cost of the refrigerant itself marginally affects the life-cycle cost of the equipment operation – except for applications that involves significant refrigerant leakage. It is important to note that the current best-practice is to limit direct refrigerant emissions through reduced refrigerant leakage. As such, in RACHP applications the life-cycle operation is mostly impacted by the system energy efficiency and the associated energy costs. The life cycle cost is also greatly affected by the components cost and safety requirements.

In this section, "Economical" refers to a technology that result in a life-cycle cost that is not higher than the baseline technology and "Not known" refers to a technology where the economic impact of the refrigerant selection is either not fully studied or greatly impacted by other factors.

iv. **"Safe to use in areas with high urban densities considering flammability and toxicity issues, including, where possible, risk characterization"**

The safety of alternatives for RACHP applications considers:

- availability of risk classification (such as the two digits code of ASHRAE Std. 34 or ISO 817);
- availability of Safety Standards able to dictate the maximum allowable charge admissible for different types of:
    i. equipment,
    ii. application sector,
    iii. final use of equipment;
- availability of Safety Standards with rules and regulations for safe and effective servicing and maintenance.
- In the table below we list the equipment safety standard relevant to the application (e.g., IEC 60335-2-24, IEC 60335-2-40, and IEC 60335-2-89), and when relevant, used the EN 378 as a proxy for the need to consider application safety standard and building

code; other relevant application standards include ISO 5149 and ASHRAE standard 15.

v. **"Easy to service and maintain"**
- availability on site of skilled personnel able to adequately service and maintain equipment charged with the alternative fluid and with new energy efficient technologies;
- availability on site of educational programs and institutions that can be used for the training of skilled personnel.

6.2 Factory sealed domestic and commercial refrigeration appliances

Currently, the entire global production of domestic refrigeration appliances is based on non-ODS refrigerants, predominantly HC-600a (isobutane) and to some extent HFC-134a. Migration from HFC-134a to HC-600a is expected to continue, driven by the Kigali Amendment schedule or local regulations on HFCs. In the EU the transition to R-600a in new domestic refrigeration appliances was completed by 2015. In the USA, substantial progress has been made to convert from HFC-134a to HC-600a and is expected to be complete by 2023. Many A5 parties, including China, India and others are rapidly phasing out HFC-134a in domestic refrigerators using HC-600a. Energy efficiencies of refrigerators are constantly increasing, including in many A5 parties, mainly due to Minimum Energy Performance Standards (MEPS) and increasing awareness of consumers.

Stand-alone commercial refrigeration appliances, which are globally used, include a wide variety of appliances: ice-cream freezers, ice machines, beverage vending machines, and display cases. Typical refrigerants used include HFC-134a, R-404A, and HCs. With the revision of safety standards, in low charge systems, migration is taking place to HC-290 with better energy efficiencies. This trend is spreading to some of the A5 parties. Multinational companies have their own environmental policies that favour lower-GWP refrigerants and energy efficiency.

Domestic heat pump tumble dryers (HPTD) are significantly more efficient than conventional electrically heated dryers. HPTDs only use about 40–50% of the electricity of conventional dryers. Some EU manufacturers have even ceased their development of conventional electrical dryers. HPTDs continue to gain market share and concurrently costs have also reduced substantially. The most commonly used refrigerants in HPTDs are HFC-134a, R-407C, and R-410A. Some transition to HC-290 (propane) has happened in EU parties.

Table 6.1 FACTORY SEALED DOMESTIC AND COMMERCIAL REFRIGERATION APPLIANCES (Chapter 4 of RTOC 2022 AR)

Refrigerant	Availability & Accessibiity	Technically proven	Environmentally sound	Economics	Safety	Servicing	Other (applications)
HC-290 (propane)	Available Accessible in some A5	Yes	ODP=0 $GWP_{100}\leq 1$	Economical	A3 (higher flammability) See Std IEC 60335-2-89	Skilled personnel (on flammable refrigerants)	Commercial plug-in appliances Heat Pump tumble dryers
HC-600a (isobutane)	Available Accessible in some A5	Yes	ODP=0 $GWP_{100}\leq 1$	Economical	A3 (higher flammability) See Std IEC 60335-2-24	Skilled personnel (on flammable refrigerants)	Domestic refrigeration and small Commercial plug-in appliances
R-450A (HFO-HFC blend)	Available Not yet accessible in *most A5*	Yes	ODP=0 GWP_{100}=570	Economical	A1	Skilled personnel	Heat Pump tumble dryers
R-454C	Available Little accessibility in A5	Yes	ODP=0 GWP_{100}=150	Economical	A2L (lower flammability) See Std IEC 60335-2-24	Skilled personnel (on lower flammability refrigerants)	Commercial plug-in appliances
R-455A	Available	Yes	ODP=0 GWP_{100}=150	Economical	A2L (lower flammability)	Skilled personnel	Commercial plug-in appliances

	Little accessibility in A5				See Std IEC 60335-2-24	(on lower flammability refrigerants)	
R-744 (carbon dioxide)	Not available	Under test	ODP=0 GWP_{100}=1	Not known	A1	Skilled personnel	Commercial plug-in appliances Heat Pump tumble dryers
HFO-1234yf	Not yet available	Under test	ODP=0 $GWP_{100} \leq 1$	Not known	A2L (lower flammability) See Std IEC 60335-2-24	Skilled personnel (on lower flammability refrigerants)	Domestic refrigeration
HFO-1234ze(E)	Not yet available	Under test	ODP=0 $GWP_{100} \leq 1$	Not known	A2L (lower flammability) See Std IEC 60335-2-24	Skilled personnel (on lower flammability refrigerants)	Domestic refrigeration

6.3 Food retail and food service refrigeration (larger systems)

This section only refers to larger food retail and food service systems such as condensing units and central systems. Small stand-alone equipment were discussed in Section 6.2. The commonly used HFCs in existing food retail and food service are R-404A and HFC-134a and in many A5 parties, HCFC-22 is also currently used.

Non-halocarbon refrigerants such as R-744 (CO_2) are increasingly being used in food retail systems worldwide – both in cascaded systems (R-744 for low temperature cascaded with a second refrigerant like HFC-134a, R-450A, R-513A, HFO-1234ze(E) or similar and R-717 or R-290 in limited cases) and in transcritical, all-R744 systems. Transcritical systems are being modified extensively to reduce their energy penalty at high ambient conditions with improved component and system technologies. R-744 is also beginning to see its use in food service applications with condensing units.

Various HFC/HFO blends (both A1 and A2L) are also being approved for use worldwide in various equipment types with A2L refrigerants being used in smaller charge systems like distributed systems and condensing units. Low GWP A3 refrigerant R-290 (propane) is also increasingly used in food retail and food service, but mainly in small charge factory built stand-alone systems. There is some use of R-290 in small condensing units. The newer A1 blends such as R-448A, R-449A, R-450A and R-513A are important for retrofitting existing R404A and HFC-134a equipment to lower GWP A1 alternatives; retrofits are a growing trend in Europe and North America, where the recovered and recycled or reclaimed R-404A and HFC-134a is used for service. Managing the refrigerant in the existing fleet of equipment as an asset is a positive trend. Leak sensors and leak mitigation methods used for flammable refrigerants are also beginning to be used with lower GWP A1 refrigerants in existing systems.

Table 6.2 FOOD RETAIL AND FOOD SERVICE REFRIGERATION (Chapter 5 of RTOC 2022 AR)

Refrigerant	Availability & Accessibility	Technically proven	Environmentally sound	Economics	Safety	Servicing	Other (applications)
HC-290 (propane)	Available Accessible in some A5	Yes	ODP=0 $GWP_{100}\leq 1$	Economical	A3 (higher flammability) See Std IEC 60335-2-89	Skilled personnel (on flammable refrigerants)	Small (charge limited) remote condensing units
R-744 (carbon dioxide)	Available Accessible in some A5	Yes	ODP=0 $GWP_{100}=1$	Economical	A1	Skilled personnel	Remote condensing units Centralized and distributed systems
R-407A (HFC blend)	Available Not accessible in most A5	Yes	ODP=0 $GWP_{100}=2100$	Economical	A1	Skilled personnel	Remote condensing units Centralized and distributed systems Retrofit alternative to R-404A. Becoming less used as lower GWP options are now available.
R-407F (HFC blend)	Available Not accessible in most A5	Yes	ODP=0 $GWP_{100}=1800$	Economical	A1	Skilled personnel	Remote condensing units Centralized and distributed systems Retrofit alternative to R-404A. Becoming less used as lower GWP options are now available.

R-407H (HFC blend)	Available Not accessible in most A5	Yes	ODP=0 GWP_{100}=1500	Economical	A1	Skilled personnel	Remote condensing units Centralized and distributed systems
R-448A (HFO-HFC blend)	Available Accessible in some A5	Yes	ODP=0 GWP_{100}=1400	Economical	A1	Skilled personnel	Remote condensing units Centralized and distributed systems Retrofit alternative to R-404A.
R-449A (HFO-HFC blend)	Available Accessible in some A5	Yes	ODP=0 GWP_{100}=1400	Economical	A1	Skilled personnel	Remote condensing units Centralized and distributed systems Retrofit alternative to R-404A.
R-449B (HFO-HFC blend)	Not available	Under test	ODP=0 GWP_{100}=1400	Not known	A1	Skilled personnel	Remote condensing units Centralized and distributed systems Retrofit alternative to R-404A.
R-450A (HFO-HFC blend)	Available Accessible in some A5	Yes	ODP=0 GWP_{100}=570	Economical	A1	Skilled personnel	Remote condensing units Centralized and distributed systems Retrofit alternative to HFC-134a.
R-452A	Available	Yes	ODP=0 GWP_{100}=2100	Economical	A1	Skilled personnel	Remote condensing units

(HFO-HFC blend)	Accessible in some A5						Centralized and distributed systems Retrofit alternative to R-404A. Becoming less used as lower GWP options are now available.
R-454A (HFO-HFC blend)	Not available	Under test	ODP=0 GWP_{100}=250	Not known	A2L (lower flammability) See Std IEC 60335-2-89	Skilled personnel (on lower flammability refrigerants)	Remote condensing units Small Distributed systems
R-454C (HFO-HFC blend)	Available Not accessible in most A5	Yes	ODP=0 GWP_{100}=150	Economical	A2L (lower flammability) See Std IEC 60335-2-89	Skilled personnel (on lower flammability refrigerants)	Remote condensing units Small Distributed systems
R-455A (HFO-HFC blend)	Available Not accessible in most A5	Yes	ODP=0 GWP_{100}=150	Economical	A2L (lower flammability) See Std IEC 60335-2-89	Skilled personnel (on lower flammability refrigerants)	Remote condensing units Small Distributed systems
R-457A (HFO-HFC blend)	Not available	Under test	ODP=0 GWP_{100}=150	Not known	A2L (lower flammability) See Std IEC 60335-2-89	Skilled personnel (on lower flammability refrigerants)	Remote condensing units Small Distributed systems

R-513A (HFO-HFC blend)	Available Accessible in some A5	Yes	ODP=0 GWP_{100}=600	Economical	A1	Skilled personnel	Remote condensing units Centralized and distributed systems . Retrofit alternative to HFC-134a
HFO-1234yf	Not available	Under test	ODP=0 $GWP_{100} \leq 1$	Not known	A2L (lower flammability) See Std IEC 60335-2-89	Skilled personnel (on lower flammability refrigerants)	Remote condensing units Distributed systems
HFO-1234ze(E)	Not available	Under test	ODP=0 $GWP_{100} \leq 1$	Not known	A2L (lower flammability) See Std IEC 60335-2-89	Skilled personnel (on lower flammability refrigerants)	Remote condensing units Distributed systems
R-717 (ammonia)	Available Accessible in some A5	Yes	ODP=0 GWP_{100}=0	Generally, more expensive as equipment costs are high. Difficult to get good energy efficiency.	B2L (lower flammability & higher toxicity) See Std EN378	Skilled personnel (on flammable and toxic refrigerants)	Only used in secondary systems.

6.4 Transport refrigeration

The majority of trucks and trailers today use R-404A. New equipment in Europe typically uses lower GWP A1 alternative, R-452A. Light commercial vehicles use mainly HFC-134a, while some new platforms will use HFO-1234yf. The majority of marine ISO-container refrigeration units operate on HFC-134a. The latest of these units are being offered as being retrofittable to R-513A. A marine container operating on R-744 is available with limited market penetration.

The GWP of the refrigerants used is expected to come down consistently with present and future regulations; the pace at which the transition will occur is unclear as transport regulations make it hard to introduce flammable refrigerants (e.g., Agreement on the International Carriage of Perishable Foodstuffs and on the Special Equipment to be used for such Carriage (ATP) Regulation). Some experts predict that the long-term solution will be based on R-290 or R-744. However, challenges need to be overcome. Because of this, some expect a transition step: possibly to A2L or A1 blends, with GWP levels below 500.

There is an additional trend to reduce the direct CO_2 emissions, through the elimination of possible leak points, and alternative ways of powering the refrigeration system, eliminating the diesel engine emissions (hybrid or fully electric). The trend towards higher efficiency (lower fuel consumption) continues in all industry segments in parallel.

Various refrigerants are used on board different types of ships. HCFC-22 was previously often used in the period from about 1970 to 2000. HFCs, the most common since then, are today being replaced by alternative system which are finding their way from other market segments, such as R-744 for chilling water and for food storage systems, or HFO-1234ze(E) for chillers in cruise lines.
R-717 was common before 1970 and today experiences revival in many ships and in particular fishing vessels.

Table 6.3 TRANSPORT REFRIGERATION (Chapter 6 of RTOC 2022 AR)

Refrigerant	Availability & Accessibility	Technically proven	Environmentally sound	Economics	Safety	Servicing	Other (applications)
HFO-1234yf	Available Not accessible in most A5	Yes, for light commercial vehicles	ODP=0 $GWP_{100} \leq 1$	Economical	A2L (lower flammability) See Std EN378	Skilled personnel (on lower flammability refrigerants)	Truck, trailers, light commercial vehicles (vans)
R-452A (HFO-HFC blend)	Available Accessible in some A5	Yes	ODP=0 GWP_{100}=2100	Economical	A1	Skilled personnel	Truck, trailers, light commercial vehicles (vans) Marine containers
R-717 (ammonia)	Available in A5 & nA5 Accessible in some A5	Yes	ODP=0 GWP_{100}=0	Economical	B2L (lower flammability & higher toxicity) See Std EN378	Skilled personnel (on flammable and toxic refrigerants)	Ships (refrigeration and comfort cooling)
R-744 (carbon dioxide)	Available for certain applications Accessible In some A5	Yes Marine containers Ships (refrigeration and comfort) Under test Other sub-sectors	ODP=0 GWP_{100}=1	Economical	A1	Skilled personnel	Truck, trailers, light commercial vehicles (vans) Marine containers Ships (refrigeration and comfort cooling) Rail air conditioning

HC-170 (ethane)	Not available	Under test	ODP=0 GWP_{100}=1,4	Not known	A3 (higher flammability) See Std EN378	Skilled personnel (on flammable refrigerants)	Marine containers for ultra-low temperature
HC-290 (propane)	Not available	Under test	ODP=0 $GWP_{100} \leq 1$	Not known	A3 (flammability) See Std EN378	Skilled personnel (on flammable refrigerants)	Truck, trailers, light commercial vehicles (vans)
R-473A (HFO-HFC blend)	Not available	Under test	ODP=0 GWP_{100}=1830	Not known	A1	Skilled personnel	Marine containers for ultra-low temperature Ships (refrigeration and comfort cooling)
R-513A (HFO-HFC blend)	Available Accessible in some A5	Yes	ODP=0 GWP_{100}=600	Economical	A1	Skilled personnel	Marine containers Ships (refrigeration and comfort cooling Rail air conditioning

6.5 Air-to-air air conditioners and heat pumps

Air-to-air conditioners, including reversible air heating heat pumps (generally defined as reversible air conditioners), range in size from 1 kW to 750 kW although the majority are less than 70 kW. The most populous are non-ducted single splits, which are produced in excess of 80 million units per year. All products sold within non-A5 parties use non-ODS refrigerants and around 90% of new systems in A5 parties do not use HCFCs, although a significant proportion of the installed population still use HCFC-22. In addition to the widespread use of R-410A, the extensive introduction of lower GWP HFC-32 in small split air conditioners continues in many parties around the world, accounting for nearly half of the total production of split room air conditioners in 2021.

Enterprises within all regions continue to evaluate and develop products with various HFC/HFO blends, such as those comprising HFC-32, HFC-125, HFC-134a, HFC-1234yf and HFC-1234ze. Products are being introduced with lower GWP alternatives, R-454A, R- 454B, R-452B and R-463A. Further conversion of production lines to HC-290 in China, Southeast Asia and South America is underway but there is limited market introduction (except for small and portable units). Some enterprises within the Middle East still see R-407C and HFC-134a and in some applications R410A as favourable alternatives to HCFC-22.

Table 6.4 AIR-TO-AIR AIR CONDITIONERS AND HEAT PUMS (Chapter 7 of RTOC 2022 AR)

Refrigerant	Availability & Accessibility	Technically proven	Environmentally sound	Economics	Safety	Servicing	Other (applications)
HC-290 (propane)	Available Accessible in some A5	Yes	ODP=0 $GWP_{100} \leq 1$	Economical	A3 (higher flammability) See Std IEC 60335-2-40	Skilled personnel (on flammable refrigerants)	Small Self-Contained AC Non ducted split (charge restricted) Ducted split (charge restricted) Charge restricted Packaged ducted
HFC-32	Available Accessible in many A5	Yes	ODP=0 GWP_{100}=675	Economical	A2L (lower flammability) See Std IEC 60335-2-40	Skilled personnel (on lower flammability refrigerants)	Small Self-Contained AC Non ducted split Ducted split Multi split Packaged ducted
HFC-152a	Not available	Under test	ODP=0 GWP_{100}=148	Not known	A2 (flammable) See Std IEC 60335-2-40	Skilled personnel (on flammable refrigerants)	Small Self-Contained AC Non ducted split Ducted split Multi split Packaged ducted
HFC-161	Not available	Under test	ODP=0 GWP_{100}=12**	Not known	Flammable – not listed in ASHRAE std. 34/ISO 817	Skilled personnel (on flammable refrigerants)	Small Self-Contained AC Non ducted split Ducted split

							Multi split Packaged ducted
HFO-1234yf	Not available	Under test	ODP=0 $GWP_{100}\leq 1$	Not known	A2L (lower flammability) See Std IEC 60335-2-40	Skilled personnel (on lower flammability refrigerants)	Small Self-Contained AC Non ducted split Ducted split Multi split Packaged ducted
R-454A (HFO-HFC blend)	Not available	Under test	ODP=0 $GWP_{100}=250$	Not known	A2L (lower flammability) See Std IEC 60335-2-40	Skilled personnel (on lower flammability refrigerants)	Small Self-Contained AC Non ducted split Ducted split Multi split Packaged ducted
R-454B (HFO-HFC blend)	Available Accessible in some A5	Yes	ODP=0 $GWP_{100}=490$	Economical	A2L (lower flammability) See Std IEC 60335-2-40	Skilled personnel (on lower flammability refrigerants)	Small Self-Contained AC Non ducted split Ducted split Multi split Packaged ducted
R-455A (HFO-HFC blend)	Not available	Under test	ODP=0 $GWP_{100}=150$	Not known	A2L (lower flammability) See Std IEC 60335-2-40	Skilled personnel (on lower flammability refrigerants)	Small Self-Contained AC Non ducted split Ducted split Multi split Packaged ducted

R-457A (HFO-HFC blend)	Not available	Under test	ODP=0 GWP_{100}=150	Not known	A1	Skilled personnel	Remote condensing units
R-459A (HFO-HFC blend)	Not available	Under test	ODP=0 GWP_{100}=480	Not known	A2L (lower flammability) See Std IEC 60335-2-40	Skilled personnel (on lower flammability refrigerants)	Small Self-Contained AC Non ducted split Ducted split Multi split Packaged ducted
R-463A (HFO-HFC blend)	Not available	Under test	ODP=0 GWP_{100}=1377	Not known	A1	Skilled personnel	Small Self-Contained AC Non ducted split Ducted split Multi split Packaged ducted
R-466A (HFC-FIC blend)	Not available	Under test	ODS≤0.04 GWP_{100}=733	Not known	A1	Skilled personnel	Small Self-Contained AC Non ducted split Multi split Packaged ducted
R-511A (HC/HFC blend)	Not available	Under test	ODP=0 GWP_{100}=1	Not known	A3 (higher flammability) See Std IEC 60335-2-40	Skilled personnel (on flammable refrigerants)	Small Self-Contained AC Non ducted split Ducted split Multi split Packaged ducted

6.6 Applied building cooling systems

Applied Building Cooling systems are used in medium and large sized buildings. They require engineering services to design and install air conditioning in larger buildings of all types. The dominant products used in these systems are chillers although packaged commercial unitary product can also be used. There are now complete lines of all chiller types in all major markets that use refrigerants having lower GWP than their predecessors. Additionally non-fluorinated refrigerants, e.g., ammonia, are available in some chiller types, albeit in select sizes not complete product lines. Existing products using HFC refrigerants have zero-ODP but relatively high GWP refrigerants. These products have not been discontinued, but remain the dominant products being sold in most markets. Normal market forces will cause this to slowly change. The Kigali Amendment to the Montreal Protocol is providing some regulation to cause a more rapid change. Products using the existing refrigerants will continue to be sold and the installed base of these products will remain in service for years to come. Despite the new refrigerant choices that are now available for new and existing equipment, they may not be the final choices. There is continued pressure from regulators to move to yet another generation of zero ODP and near zero GWP, if technically possible and economically reasonable.

New refrigerant choices, notably replacements for R-134a (medium pressure) and R-410A (high pressure), include flammable refrigerants, safety class A2L. Safety regulations that allow use of A2L refrigerants, supported by recent research, are being written, but are not uniform nor adopted in all regions. This is not a trivial matter, since health, safety and property issues are involved. Adoption and enforcement of revised codes and standards may slow the adoption new flammable refrigerants.

Table 6.4 APPLIED BUILDING COOLING SYSTEMS (Chapter 8 of RTOC 2022 AR)

Refrigerant	Availability & Accessibility	Technically proven	Environmentally sound	Economics	Safety	Servicing	Other (applications)
HCFO-1233zd(E)	Available Accessible in some A5	Yes	ODP=0.00034 GWP_{100}=1	Economical	A1	Skilled personnel	Large Centrifugal chillers
HFO-1234ze(E)	Available Accessible in some A5	Yes	ODP=0 $GWP_{100} \leq 1$	Economical	A2L (lower flammability) See Std IEC 60335-2-40 See Std EN378	Skilled personnel (on lower flammability refrigerants)	Screw and Centrifugal chillers
HFC-32	Available Accessible in some A5	Yes	ODP=0 GWP_{100}=675	Economical	A2L(lower flammability) See Std IEC 60335-2-40 See Std EN378		Small chillers
R-452B (HFO-HFC blend)	Available Accessible in some A5	Yes	ODP=0 GWP_{100}=710	Economical	A2L (lower flammability) See Std IEC 60335-2-40 See Std EN378	Skilled personnel (on lower flammability refrigerants)	Small chillers

R-717 (ammonia)	Available Accessible in some A5	Yes	ODP=0 GWP_{100}=0	Economical	B2L (lower flammability & higher toxicity) See Std EN378	Skilled personnel (on flammable and toxic refrigerants)	Large chillers
R-718 (water)	Available Accessible in some A5	Yes	ODP=0 GWP_{100}=0	Economical for certain applications	A1	Skilled personnel	Very large chillers
HFO-1224yd(Z)	Not available	Under test	ODP=0.00023 GWP_{100}<1	Not known	A1	Skilled personnel	Centrifugal chillers
R-454B (HFO-HFC blend)	Not available	Under test	ODP=0 GWP_{100}=490	Not known	A2L (lower flammability) See Std IEC 60335-2-40 See Std EN378	Skilled personnel (on lower flammability refrigerants)	Small chillers
R-466A (HFC-FIC blend)	Not available	Under test	ODP≤0.04 GWP_{100}=733	Not known	A1	Skilled personnel	Small chillers

6.7 Mobile air conditioning/heat pumps

Currently, more than one refrigerant is used for car and light truck air conditioning: HFC-134a will remain largely adopted worldwide until controlled under the Kigali Amendment to the Montreal Protocol, while HFO-1234yf is currently the main option in Europe and North America.
The deployment of highly electrified vehicles (plug-in hybrid electric vehicles (PHEV) and battery electric vehicles (BEV)) in Europe, China and North America will lead to the implementation of heat pump function and of a new generation of thermal systems. Manufacturers are working on the improvement of this feature by using cycle variations such as economiser coupled with vapor injected compressors.

R-744 is increasingly applied in fully electrified vehicles due to its good performance when operating as a reversible heat pump. However, R-744 is less suitable in hot and humid climates where energy efficiency is somewhat lower than that of HFC-134a and HFO-1234yf systems. So, some European OEMs introduced reversible R-744 heat pumps for their high-volume BEV models, which they currently sell in the EU, North America (Canada), and China.

Cost, safety, heat pump capability could limit the global use of HFO-1234yf. Recently, actions promoted by a group of European parties investigating PFAS substances are very broad and not product-specific at this time. Anyway, this could lead to some limitations of HFO leading to reconsider the current refrigerant choices to include both R-744 and HFO as viable options.
Even if the R-744 is the mainstream alternative to HFO-1234yf, class 2 and class 3 (e.g., HCs, R-152a) refrigerants represent still a backup solution favoured by the fact that the electrified vehicle thermal systems are moving toward dual-loop architectures.

It cannot be foreseen whether all these refrigerants will all remain in the market for a longer period of time (in parallel). It is also unclear whether the bus sector (where currently HCFC-22, HFC-134a, R-407C, R-744, and R-449A are used and HFO-1234yf has been introduced) and the heavy-duty truck sector will follow these trends.

Table 6.5 MOBILE AC/HP (Chapter 9 of RTOC 2022 AR)

Refrigerant	Availability & Accessibiity	Technically proven	Environmentally sound	Economics	Safety	Servicing	Other (applications)
HFO-1234yf	Available Accessible in some A5	Yes	ODP=0 $GWP_{100} \leq 1$	Economical	A2L (lower flammability)	Skilled personnel (on lower flammability refrigerants)	Light & Heavy Duty
R-744 (carbon dioxide)	Available Accessible in some A5	Yes	ODP=0 $GWP_{100}=1$	Economical when both cooling and heating needed	A1	Skilled personnel	Light & Heavy Duty
HC-290 (propane)	Not available	Under test	ODP=0 $GWP_{100} \leq 1$	Not known	A3 (higher flammability)	Skilled personnel (on flammable refrigerants)	Light & Heavy Duty
HFC-152a	Not available	Under test	ODP=0 $GWP_{100}=148$	Not known	A2 (flammable)	Skilled personnel (on flammable refrigerants)	Light & Heavy Duty
R-513A (HFO-HFC blend)	Not available	Under test	ODP=0 $GWP_{100}=600$	Not known	A1	Skilled personnel	Light & Heavy Duty

6.8 Industrial refrigeration

R-717 (ammonia) has been widely used for many years in large industrial systems. In small industrial systems there has historically been significant use of HCFC-22 and, more recently, HFCs such as R-404A and HFC-134a.

Looking forward, R-717 and R-744 are the dominant options for large industrial systems (e.g. in food and drink manufacturing and bulk cold storage), with hydrocarbons used in some large specialised applications (e.g. in the petrochemical industry). In smaller systems A2L blends such as R-454C and R-455A are starting to be used.

In heat pumps above 100°C hydrocarbons will be dominating, partly because of their stability at high temperatures, partly due to the price of the fluids and finally due to their higher efficiency.

Table 6.6 INDUSTRIAL REFRIGERATION (Chapter 10 of RTOC 2022 AR)

Refrigerant	Availability & Accessibility	Technically proven	Environmentally sound	Economics	Safety	Servicing	Other (applications)
R-717 (ammonia)	Available Accessible in many A5	Yes	ODP=0 GWP_{100}=0	Economical	B2L (lower flammability & higher toxicity) See Std EN378	Skilled personnel (on flammable and toxic refrigerants)	Many large industrial applications
R-744 (carbon dioxide)	Available Accessible In some A5	Yes	ODP=0 GWP_{100}=1	Economical	A1	Skilled personnel	Growing use in large and medium sized industrial applications
R-454C	Available Accessible in some A5	Yes	ODP=0 GWP_{100}=150	Economical	A2L	Skilled personnel (on lower flammability refrigerants)	Used in smaller industrial systems as an alternative to R-404A
R-455A	Available Accessible in some A5	Yes	ODP=0 GWP_{100}=150	Economical	A2L	Skilled personnel (on lower flammability refrigerants)	Used in smaller industrial systems as an alternative to R-404A

HFC-32	Available Accessible in some A5	Yes	ODP=0 GWP_{100}=675	Economical	A2L (lower flammability) See Std EN 378	Skilled personnel (on lower flammability refrigerants)	Various industrial applications
HFO-1234ze(E)	Available Accessible in some A5	Yes	ODP=0 $GWP_{100}\leq1$	Economical	A2L	Skilled personnel (on lower flammability refrigerants)	Industrial Chillers
HCFO-1233zd(E)	Not available	Under test	ODP=0.00034 GWP_{100}=1	Not known	A1	Skilled personnel	Industrial Heat pumps and large chillers
HFO-1336mzz(Z)	Not available	Under test	ODP=0 GWP_{100}=2	Not known	A1	Skilled personnel	Industrial Heat pumps
R-718 (water)	Available Accessible In some A5	Yes	ODP=0 GWP_{100}=0	Economical in certain applications	A1	Skilled personnel	Large industrial chillers
HC-170 (ethane)	Available Accessible in some A5	Yes	ODP=0 GWP_{100}=1.4	Economical	A3 (higher flammability) See Std EN 378	Skilled personnel (on flammable refrigerants)	Ultra-Low Temperature applications

HC-600a (isobutane)	Available Accessible in some A5	Yes	ODP=0 $GWP_{100} \leq 1$	Economical	A3 (higher flammability) See Std EN 378	Skilled personnel (on flammable refrigerants)	
HC-290 (propane)	Available Accessible in some A5	Yes	ODP=0 $GWP_{100} \leq 1$	Economical	A3 (higher flammability) See Std EN 378	Skilled personnel (on flammable refrigerants)	
HC-1150 (ethylene)	Available Accessible in some A5	Yes	ODP=0 $GWP_{100}=3.7$	Economical	A3 (higher flammability) See Std EN 378	Skilled personnel (on flammable refrigerants)	Ultra-Low Temperature applications
HC-1270 (propylene)	Available Accessible in some A5	Yes	ODP=0 $GWP_{100} \leq 1$	Economical	A3 (higher flammability) See Std EN 378	Skilled personnel (on flammable refrigerants)	Ultra-Low Temperature applications

6.9 Heating only heat pumps

Heat pumps commercialised today make use of non-ODS refrigerants, including R-410A, HFC-32, HFC-134a, R-407C, HC-290, HC-600a, R-717 and R-744. The majority of new equipment currently uses R-410A. Safety constraints restrict the use of R-290 to monobloc units located outdoors. Recently HFC-32 and R-454B introduced as lower GWP alternatives for R-410A.

The issue of high ambient temperature conditions is of importance for heating-only heat pumps. The main parameters to select the refrigerant are efficiency, cost effectiveness, economic impact, safe use and easiness of use. From the ones mentioned above HFC-134a, R-744 and the HFC blends R-410A and R-407C are the commercially available solutions that have the highest grade of safety and easiness to use. Replacements using lower GWP HFC blends have been developed and are under way to become commercially available.

Due to the HFC quota requirements the current trend is to go to move from R-410A to alternatives such as HC-290 and HFC-32 in most of Europe. The temperature ranges in which HC-290 and HFC-32 can be operated are better than those for R-410A, moreover, their efficiencies are generally better. The application of R-410A, HFC-32 or HC-290 is most cost effective when used in small to medium-sized systems.

Table 6.7 HEATING ONLY HEAT PUMPS (Chapter 11 of RTOC 2022 AR)

Refrigerant	Availability & Accessibiity	Technically proven	Environmentally sound	Economics	Safety	Servicing	Other (applications)
HC-290 (propane)	Available Accessible in some A5	Yes	ODP=0 $GWP_{100} \leq 1$	Economical	A3 (higher flammabilitye) See Std IEC 60335-2-40	Skilled personnel (on flammable refrigerants)	Monobloc heat pumps
HFC-32	Available Accessible in some A5	Yes	ODP=0 $GWP_{100}=675$	Economical	A2L (lower flammability) See Std IEC 60335-2-40	Skilled personnel (on lower flammability refrigerants)	Monobloc and split heat pumps
R-454B (HFO-HFC blend)	Available Not yet Accessible in A5	Yes	ODP=0 $GWP_{100}=490$	Economical	A2L (lower flammability) See Std IEC 60335-2-40	Skilled personnel (on lower flammability refrigerants)	Monobloc and split heat pumps
R-744 (carbon dioxide)	Available in A5 & nA5 Accessible in A5 & some nA5	Yes	ODP=0 $GWP_{100}=1$	Equipment more expensive	A1	Skilled personnel	Mainly used for domestic water heating