HYDROFLUOROCARBONS

1. Introduction

This article is limited to the applications of hydrofluorocarbons (HFCs) in refrigeration, foam blowing agents, solvent, and fire fighting agents.

1.1. Influence of the Fluorine Substituent. Substitution of fluorine for hydrogen in an organic compound has a profound influence on the compound's chemical and physical properties. Several factors that are characteristic of fluorine underlie the observed effects. Fluorine is the most electronegative of all the chemical elements while possessing a small van der Waals radius, 1.47 versus 1.2 Å for hydrogen. Hence, the C−F bond is considerably stronger, and is the main contribution to the pronounced chemical and thermal stability of HFCs. The substitution of fluorine for hydrogen also reduces the flammability and increases the heat capacity of the materials. In general, compounds that have more than one-half of the hydrogen replaced by fluorine are nonflammable. Because of these properties, fluorochemicals and chlorofluorochemicals (CFCs) have been used in applications where heat capacity, chemical and thermal stability, and/or nonflammability are important properties. These traditionally include refrigeration fluids, foam blowing agents, solvents, and fire fighting agents. However, in 1974 chlorofluorochemicals CFC were found to deplete the stratospheric ozone layer (1). Because of this, a phase-out program for production and applications of these chemicals was developed under the United Nation's Montreal Protocol in 1987. Since that time, the industry has been seeking alternative materials that provide the benefits afforded by the CFCs.

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1.2. Ideal CFC Substitute and Strategy.

The ideal substitute should have identical or better performance properties than the chlorofluorocarbon it replaces. The ideal CFC substitute must not harm the ozone layer, or contribute to other detrimental atmospheric phenomenon such as global warming. It also must be nontoxic, nonflammable, and thermally and chemically stable under normal use conditions, and be reasonably priced. The fluorocarbon producers have found substitutes that match many, but not all of these criteria.

The general strategy has been twofold. First, at least one hydrogen atom should be incorporated in the proposed CFC substitute's structure. This provides a means for the destruction of the chemical in the atmosphere via hydrogen atom abstraction by tropospheric hydroxyl radicals. Second, all of the chlorine must be removed from the chemicals, as the chlorine radicals that are produced from the CFCs are the main reason for ozone depletion. The halo alkyl radicals thus, formed are then rapidly degraded to acids and CO_2, which are both removed from the atmosphere by natural processes. Since fluorine does not participate in the ozone destruction cycle, a substitute composed of only hydrogen, fluorine, and carbon would be ideal. However, it has not been easy to find HFC substitutes for every application. Thus, the industry has been slowly transitioning through the 1980s and 1990s to lower ozone-depleting substances. In some applications, (HCFCs) and even perfluorinated carbons (PFCs) have been suggested as transient replacements to accelerate the phase-out of the much more harmful CFCs.

2. Hydrofluorocarbons as Blowing Agents

2.1. Physical Properties.

Physical properties of the new hydrofluorocarbons are listed in Table 1.

For insulation foams, the most important property is obviously the thermal conductivity. One of the advantages of fluorochemical blowing agents is that most of the material remains entrapped in the foam cells; thus, the low thermal conductivity of these blowing agents contributes to the insulating properties of

Table 1. **Physical Properties of HFC Blowing Agents**

Properties	134a	245fa	365fmc
chemical formula	CF_3CH_2F	$CF_3CH_2CHF_2$	$CF_3CH_2CF_2CH_3$
molecular weight	102.03	134	148
boiling point, °C	−25.9	15.3	40
freezing point, °C	−96.6	<−160	−35
critical temperature, °C	101.06		
critical pressure PSI	588.7		
vapor density, g/cm^3	.00526		
liquid density, g/cm^3	1.207	1.32	1.27
solubility of water, ppm	1100	1600	840
flammability limit in air, vol.%	none	none	3.5−13
flash point, °C	none	none	−27
ozone depletion potential ODP	0	0	0
global warming potential GWP	1300	950	890
atmospheric lifetime, years	13.8	7.2	9.9

Table 2. **Thermal Conductivity of CFC, HCFC, and HFC**[a]

Blowing agent	Thermal conductivity at 111°F 1 atm. BTU in/ft^{2}h°F
CFC 11 ($CFCl_3$)	0.05
HCFC-141b (CH_3CFCl_2)	0.057
HCFC-142b (CH_3CF_2Cl)	0.051
HFC-245fa ($CF_3CH_2CHF_2$)	0.097
HFC-365mfc ($CF_3CH_2CF_2CH_3$)	0.072
HFC-134a (CF_3CH_2F)[b]	0.048

[a] Measured in liquid state.
[b] Measured at 77°F.

the final product over long periods of time. Other important properties of the foam are total density; dimensional stability; and a high percentage of closed foam cells, which helps to retain the cell gases. The final thermal conductivity of the foam will be a result of a combination of the thermal conductivity of the solid polymer, the percent of closed foam cells and the thermal conductivity of the cell gas, including that of the foam-blowing agent. Table 2 provides the thermal conductivities of the various foam-blowing agents including CFCs, HCFCs, and HFCs.

Furthermore, closed foam cell structures should have good aging properties, which means that it should not allow fast exchange of the entrapped blowing agent with air that has a higher thermal conductivity. Finally, the foam should have a lower density.

Because of the higher costs of the newly developed HFCs, the foam industry has become willing to consider blowing agents of a totally different nature, such as simple hydrocarbons like cyclopentane or isopentane, even though these materials are known to be highly flammable, and usually have higher thermal conductivity than the fluorocarbons. Table 3 compares the physical properties of polyurethane foam that has been expanded using HCFC-141b, HFC-245fa, and a hydrocarbon.

2.2. Manufacture. *HFC-365mfc ($CF_3CH_2CF_2CH_3$) (**2**).* The U.S. Patent 5,917,098 describes a one-step liquid-phase fluorination of 1,1,1,3,3-pentachlorobutane (1) to 1,1,1,3,3-pentafluorobutane (2) using a $SbCl_5$ catalyst,

Table 3. **Physical Properties of Polyurethane Foam, Using Different Blowing Agents**[a]

Properties	HCFC-141b	*c*-Pentane	HFC-245fa
core density, kg/m^3	32		33
compressive strength, kPa	143	140	165
dimensional stability, −30°C/28 days Δvol%	−0.7	0.1	−0.5
dimensional stability, 70°C/7days Δvol%	2.7	−0.5	1.1
initial thermal conductivity at 10°C, Mw/Mk	18.5	20.4	19.6

[a] Ref. 2.

as shown in equation 1 (3).

$$\underset{(\mathbf{1})}{\mathrm{CCl_3CH_2CCl_2CH_3}} + 5\,\mathrm{HF} \xrightarrow{\mathrm{SbCl_5/liq.phase}} \underset{(\mathbf{2})}{\mathrm{CF_3CH_2CF_2CH_3}} + 5\,\mathrm{HCl} \qquad (1)$$

The precursor (1), was obtained by the free-radical addition of CCl_4 to 2-chloropropene, using a copper salt/amine catalyst (eq. 2) (3).

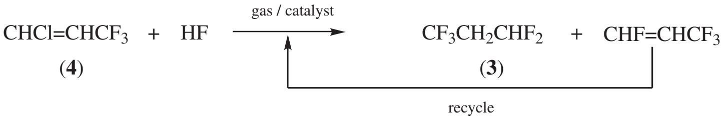
$$\mathrm{CCl_4} + \mathrm{CH_2{=}C(Cl)CH_3} \xrightarrow{\text{copper salt/amine}} \underset{(\mathbf{1})}{\mathrm{CCl_3CH_2CCl_2CH_3}} \qquad (2)$$

A similar process for the synthesis of HFC-365mfc precursor has been reported (4). The 2-chloropropene was obtained by catalyzed HCl addition to propyne gas (eq. 3) (5).

$$\mathrm{HCl} + \mathrm{H_3C{-}{\equiv}} \xrightarrow{\mathrm{PtCl_2}\ \text{catalyst}} \mathrm{CH_2{=}C(Cl)CH_3} \qquad (3)$$

However, HF and HFC-365fmc form an azeotrope, and their separation requires the use of an organic solvent such as perchloroethylene, to recover the HFC-365-mfc (6).

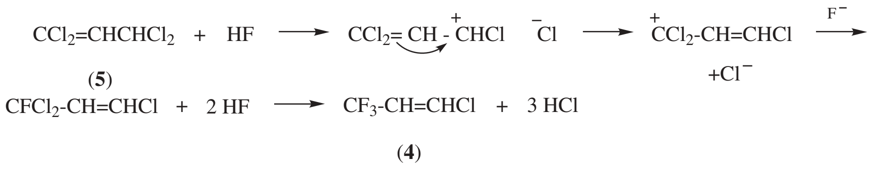
HFC 245fa, ($CF_3CH_2CHF_2$) (3). Two major producers of fluorochemicals, have independently reported the syntheses of this product in the patent literature. One process is based on the gas phase, catalytic fluorination of 1-chloro-3,3,3-trifluoropropene (4), as shown in equation 4 (7). The coproduct, 1,3,3,3-tetrafluoropropene, can be recycled back to the gas-phase reactor.



$$\underset{(\mathbf{4})}{\mathrm{CHCl{=}CHCF_3}} + \mathrm{HF} \xrightarrow{\text{gas / catalyst}} \underset{(\mathbf{3})}{\mathrm{CF_3CH_2CHF_2}} + \mathrm{CHF{=}CHCF_3} \qquad (4)$$

By changing the gas-phase catalyst in the above process from a chromium-based to a supported Lewis acid catalyst Sb/C, one can obtain exclusively the desired product HFC-245fa (3) (8).

The required precursor (4) is best prepared in one step by the liquid-phase fluorination of 1,1,3,3-tetrachloropropene (5). The process is believed to proceed by an allylic rearrangement, as shown in equation 5 (9).



$$\underset{(\mathbf{5})}{\mathrm{CCl_2{=}CHCHCl_2}} + \mathrm{HF} \longrightarrow \mathrm{CCl_2{=}CH\text{-}\overset{+}{C}HCl}\ \ \overset{-}{\mathrm{Cl}} \longrightarrow \underset{+\mathrm{Cl^-}}{\mathrm{\overset{+}{C}Cl_2\text{-}CH{=}CHCl}} \xrightarrow{\mathrm{F^-}} \qquad (5)$$

$$\mathrm{CFCl_2\text{-}CH{=}CHCl} + 2\,\mathrm{HF} \longrightarrow \underset{(\mathbf{4})}{\mathrm{CF_3\text{-}CH{=}CHCl}} + 3\,\mathrm{HCl}$$

Because HF and HFC-245fa form an azeotrope, the separation of HFC-245fa from HF poses a practical problem. To address this problem, a process has been developed that is based on the addition of a near-stoichiometric amount of HF to the intermediate alkene 1,3,3.3-tetrafluoropropene in the gas phase equation 6 (10).

$$\mathrm{CF_3CH{=}CHF} + \mathrm{HF} \xrightarrow{\text{gas / catalyst}} \underset{(\mathbf{3})}{\mathrm{CF_3CH_2CHF_2}} \qquad (6)$$

The other industrial approach to the preparation of HFC-245fa is based on a liquid-phase fluorination of 1,1,1,3,3-pentachloropropane, (6) as presented in equation 7 (11).

$$\underset{(\mathbf{6})}{\mathrm{CCl_3CH_2CHCl_2}} + 5\,\mathrm{HF} \xrightarrow{\text{liquid / catalyst}} \mathrm{CF_3CH_2CHF_2} + 5\,\mathrm{HCl} \qquad (7)$$

Since this process requires the use of a large excess of HF, the liquid-phase process does not alleviate the problems in the recovery of HFC-245fa discussed above. Furthermore, the catalyst mixture, which contains Sb(V) in HF, is highly corrosive.

The feedstock for this reaction, 1,1,1,3,3-pentachloropropane (6) can be obtained by addition of CCl_4 to chloroethylene, under photolytic conditions (12).

Thus, the industry has been slowly transitioning through the 1980s and 1990s to lower ozone-depleting substances. In some applications, hydrochlorofluorocarbons (HCFCs) and even perfluorinated carbons (PFCs) have been suggested as transient replacements to accelerate the phase out of the much more harmful CFCs.

2.3. Use as Foam-Blowing Agents. Rigid plastic foam has a cellular structure, which is created by the chemical or physical action of a blowing (foaming) agent. While many chemicals can be used to produce foams for insulating foams, it is desirable to use gases that improve the thermal resistance, and thus, add value to the product. Halocarbons have long been used in this application because they have excellent insulating properties. Halocarbons are used as blowing agents in the manufacture of polyurethane, polyisocyanurate and polystyrene foams. Chlorofluorocarbons (CFCs), such as CFC 11 ($CFCl_3$) and CFC 12 (CF_2Cl_2), were used extensively as foam-blowing agents prior to 1996.

Hydrochlorofluorocarbons, such as 141b (CH_3CFCl_2) (13) and 123 (CF_3CHCl_2), were developed as blowing agents for polyurethane foams as an interim solution under the Montreal Protocol. While HCFC 123 was later found to be a toxic substance, and therefore never used commercially to any great extent, other fluorochemicals such as HCFC-22 (CHF_2Cl), and mixtures of HCFC-22 and HCFC-142b (CH_3CF_2Cl), have also been used in urethane foams.

Because of its high solubility, HCFC- 142b has been used very extensively in polystyrene foam (XPS) since the phase out of CFC 12. However, the impending 2010 phase out of HCFC 142b in the United States is causing XPS manufactures to search for a new blowing agent.

Table 4. **Physical Properties of the New HFC Refrigerants**

Properties	HFC-134a	HFC-32	HFC-152a	HFC-125
chemical formula	CF_3CH_2F	CH_2F_2	CH_3CHF_2	CF_3CHF_2
molecular weight	102	52.02	66	120
boiling point, °C	−26.5	−51.6	−24.7	−48.5
critical T, °C	100.6	78.4	113.5	66.3
critical P, atm	40.03	57.8	44.4	34.7
liquid density at 20°C, g/cm^3	1.203	0.977	0.911	1.23
flammability range by vol / air	none	14–31	3.9–16.9	none
ODP[a]	zero	zero	zero	zero
GWP[b]	1300	650	140	2800

[a] By definition, all HFCs have zero ODP.

[b] EPA Scientific Assessment of Ozone Depletion 1998.

While these interim products were used throughout the 1990s and early into the 2000s, longer range environmental regulations, which required the development of products having zero ozone depletion potential ODP, have promoted the phase out of HCFC-141b and the development of the new hydrofluorocarbons such as 134a (CH_2FCF_3), 365mfc ($CF_3CH_2CF_2CH_3$) (14), and 245fa (14) ($CF_3CH_2CHF_2$). These products have been accepted as alternative blowing agents because of their good physical properties, which are summarized in Table 1. The fact that HCFC-365mfc is a liquid at room temperature, whereas HCF's 134a and 245fa are gases, makes handling of HFC-365mfc more manageable relative to the gaseous products.

3. Hydrofluorocarbons as Refrigerants

3.1. Physical Properties. A summary of the physical properties of these new refrigerants together with their environmental properties can be found in Table 4.

3.2. Manufacture. *HFC 134a, 1,1,1,2-Tetrafluoroethane (**7**).* Syntheses of this product can be grouped into three different types of processes. The first is a two-step process based on fluorination of trichloroethylene to 1,1,1-trifluoro-2-chloroethane, HCFC-133a, (11) followed by a second fluorination to the 1,1,1,3-tetrafluoroethane HFC-134a, (7). The first step can be carried out in the liquid phase (15) or in the gas phase (16). The catalyst used in a liquid-phase process is a Lewis acid catalyst selected from, $SbCl_5$, $SnCl_4$, $TaCl_5$, or $TiCl_4$ (15). The second step is a gas-phase fluorination of the HCFC-133a to HFC-134a. This second step requires a high temperature fluorination catalyst such as CrF_3, NiF_2, CoF_2, etc, supported or unsupported on fluorinated Al_2O_3, as shown in equation 8 (17).

$$CCl_2{=}CHCl\ \ \text{TCE} + 3\,HF \xrightarrow{\text{gas or liquid}} CF_3CH_2Cl\ \ \text{133a} + 2HCl$$

(11)

$$\underset{(\mathbf{11})}{CF_3CH_2Cl\ \ 133a} + HF \xrightarrow[\text{low level } O_2]{\text{gas / cat}} \underset{(\mathbf{7})}{CF_3CH_2F\ \ 134a} + HCl \tag{8}$$

The second process involves the catalytic hydrogenation of CFC-114a, 1,1,1,2-tetrafluoro-2,2-dichloroethane (12) (18). This feed stock is most conveniently prepared by chlorofluorination of perchloroethylene (PCE), using AlF_3 as a catalyst to produce a mixture of CFCs 114a and 114, 1,1,2,2-tetrafluoro-1, 2-dichloroethane (13) (19). It is possible to hydrogenate the CFCs 114 and 114a mixture without the need to separate CFCs 114a from 114 (19). A summary of this process is given in equation 9.

$$\begin{gathered} CCl_2{=}CCl_2 + Cl_2 + HF \xrightarrow{AlF_3} \underset{(\mathbf{12})}{CF_3CFCl_2\ \ 114a} + \underset{(\mathbf{13})}{CF_2ClCF_2Cl\ \ 114} \\ 114/114a + H_2 \xrightarrow{Pd/C} \underset{(\mathbf{7})}{CF_3CH_2F} \end{gathered} \tag{9}$$

A third process for the manufacture of HFC-134a has also been reported (20). In this process, trichloroethylene (TCE) is fluorinated in the gas phase using a chromium-based catalyst to produce HCFC-133a; (11) as the major product and HFC-134a (7) as the minor product. The desired product HFC-134a was recovered by distillation, and the 133a recycled back through the reactor.

Because addition of HF to TCE is highly exothermic, this process is difficult to control. One approach is to build an adiabatic reactor, which is an expensive engineering solution. An alternative solution is to cofeed diluents together with the TCE and HF. The most convenient diluent found is HCFC-133a. Therefore in practice, the order of the reactors is reversed in such a way that the first step of the process is the gas-phase fluorination of HCFC-133a to HFC-134a. After recovering HFC-134a by distillation, the unreacted HCFC-133a and HF are recycled to a second reactor together with some added TCE and HF (19). This novel process design is shown in equation 10 displayed in Fig. 1.

*HFC-32, Methylene Fluoride (**8**).* Industrial processes for the manufacturing of HFC-32 are based on the fluorination of methylene chloride either in

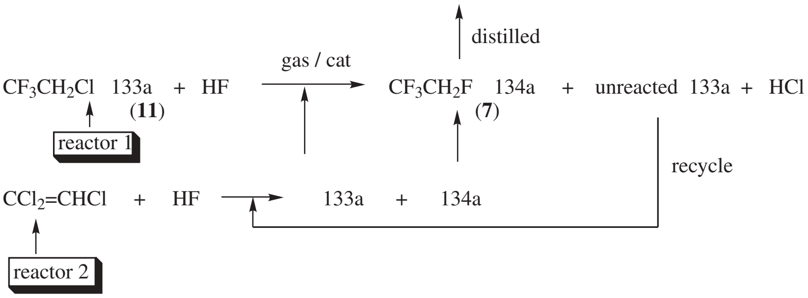


Fig. 1. Manufacturing of 134a, by fluorinating first 133a to 134a, followed by TCE fluorination to 133a.

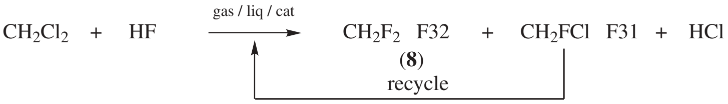


Fig. 2. Fluorination of methylene chloride to methylene fluoride.

the gas or liquid phase. For gas process, it is an advantage to cofeed low levels of chlorine gas, to maintain the catalytic activity of the supported chromium catalyst (21). If an unsupported chromium catalyst is used, the activity can be maintained using low levels of oxygen (21). The process can also be carried out in the liquid phase (22). The coproduct from either of these processes, chlorofluoromethane, HCFC-31 CH_2ClF, can be recycled back to the reactor, as shown in equation 11 displayed in Fig. 2.

Implementation of the liquid-phase fluorination technology on industrial scale has not proven to be desirable because of the corrosion problem. However, it was found that using an inert solvent such as HFC-245fa (23), or a reactor lined with fluorinated polymer (24), can substantially reduce the extent of corrosion.

HFC-125, 1,1,1,2,2-Pentafluoroethane (9). The manufacture of HFC-125 is described in the patent literature as a two-step process. The first step is aimed at preparing HCFC-123, 1,1,1-trifluoro-2, 2-dichloroethane (14). This process can be carried out in the liquid phase (25) or in the gas phase (26). In both cases, the starting material is perchloroethylene (PCE).

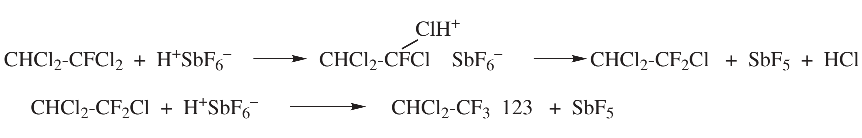
Under electrophilic conditions, the reactivity of HF addition to haloalkenes decreases with increasing number of chlorines in the olefin (27), as shown below:

$$CH_2{=}CH_2 > CH_2{=}CHCl > CH_2{=}CCl_2 > CHCl{=}CCl_2 > CCl_2{=}CCl_2$$

$$\xrightarrow{\hspace{6cm}}$$

decreasing activity of HF addition to chloroalkenes

Thus the presence of a superacid, such as hydrogen hexafluoroantimonate, $H^+SbF_6^-$, is required, to compensate for the very weak electrophilic center. The addition proceeds by electrophilic addition of H^+ to the PCE to form the carbocation, $CHCl_2{-}CCl_2^+SbF_6^-$, which rearranges to HCFC-121, $CHCl_2CFCl_2$ and releases the catalyst SbF_5. The intermediate, HCFC-121, then undergoes two consecutive elimination–addition reactions first forming HCFC-122, $CHCl_2CF_2Cl$ and finally the desired product HCFC-123, $CHCl_2CF_3$ (14), as shown in equation 12.



$$\begin{aligned}
&HF + SbF_5 \longrightarrow H^+SbF_6^- \\
&H^+SbF_6^- + CCl_2{=}CCl_2 \longrightarrow CHCl_2\text{-}CCl_2^+\,SbF_6^- \longrightarrow CHCl_2\text{-}CCl_2F + SbF_5 \\
&CHCl_2\text{-}CFCl_2 + H^+SbF_6^- \longrightarrow CHCl_2\text{-}\overset{ClH^+}{CFCl}\;\; SbF_6^- \longrightarrow CHCl_2\text{-}CF_2Cl + SbF_5 + HCl \\
&CHCl_2\text{-}CF_2Cl + H^+SbF_6^- \longrightarrow CHCl_2\text{-}CF_3\ 123 + SbF_5
\end{aligned} \tag{12}$$

(14)

Because of the corrosive nature of SbF_5 in HF in liquid-phase fluorination, a gas-phase process for high temperature fluorination of PCE has been developed, using a chromium-based catalyst (25). The major product obtained is HCFC-123 along with a minor quantity of under-fluorinated products, such as HCFC-121 and HCFC-122, and both of these compounds can be recycled.

*HFC 152a, 1,1-Difluoroethane (**10**).* Processes reported in the literature for the manufacture of 152a can be classified into three different routes, depending on the feedstock used.

The first reported process is a gas-phase fluorination of acetylene (28) using a magnesium and bismuth catalyst coadsorbed on aluminum fluoride ($Mg/Bi/AlF_3$). This method proceeds via the intermediate product, vinyl fluoride, as shown in equation 13.

$$\mathrm{HC{\equiv}CH} + \mathrm{HF} \xrightarrow{\text{catalyst}} \mathrm{CH2{=}CHF} \longrightarrow \underset{(\mathbf{13})}{\mathrm{CH_3\text{-}CHF_2}\ \ 152a} \qquad (13)$$

The second process is a nonselective reaction, which produced 57.9% of HFC-152a at 67% conversion, when 1,2-dichloroethane was fluorinated in the liquid phase using a Lewis acid catalyst (29) such as $SnCl_4$.

Perhaps the most promising industrial route for the manufacture of HFC-152a is based on the fluorination of the vinyl chloride monomer. The two-step process (30) involves initial addition of HF in a liquid-phase process to form the intermediate HCFC-151a (CH_3CHClF). This is followed by a second liquid-phase fluorination of HCFC-151a to HFC-152a (10) as shown in equation 14.

$$\begin{aligned} &\mathrm{CH_2{=}CHCl} + 2\mathrm{HF} \xrightarrow{\text{liq. SnCl}_4} \mathrm{CH_3CHClF}\ \ 151a + \mathrm{HCl} \\ &\mathrm{CH_3CHClF}\ 151a + \mathrm{HF} \xrightarrow{\text{liq. SnCl}_4} \mathrm{CH_3CHF_2}\ \ 152a + \mathrm{HCl} \end{aligned} \qquad (14)$$

Attempts to carry out this process in one step resulted in high levels of tar formation (31). However, by maintaining the vinyl chloride monomer, VCM, in the gas phase and HF in the liquid phase, less tar was observed (31). Alternatively, one can carry out the reaction in an inert solvent such as perchloroethylene or HCFC-123 (CF_3CHCl_2) (32). The addition of alkali metals, like KF or NaF to the $SnCl_4$, also encourage the fluorination of VCM to HFC-152a with minimum tar or polymer formation (33).

3.3. Use as Refrigerants. Between differences in operating conditions of the interior and exterior heat exchangers, refrigeration applications cover a wide variety of conditions. These differences often dictate the use of different fluids. While a variety of HFC substitutes have been developed for theses applications, in many cases it has not been possible to find any single material that provides all of the properties of the CFC or HCFCs that are being replaced. Thus, for many applications the industry is switching to blends of two to as many as four components.

In addition to efficient performance, the other important properties of refrigerants include: flammability, operating pressures, and compatibility with a variety of materials used in manufacturing the refrigeration equipment, such as hoses, seals, etc. In addition, the refrigerant must be chemically and thermally stable. In many of today's applications, refrigerants have been in constant use for decades. Another important issue in refrigeration is the fact that the compressor oil is carried out of the compressor with the refrigerant fluid and must be returned to the compressor.

The most efficient HFCs developed for the refrigeration market are 134a, 1,1,1,2-tetrafluoroethane, (7) and 32, methylene fluoride (8). HFC-134a is widely used in automotive air conditioning because it is more efficient at higher temperatures. While HFC-32 is an efficient material for air conditioning applications, it is flammable gas; therefore, it is blended with other nonflammable, but lower efficiency refrigerants such as HFC-125, 1,1,1,2,2-pentafluoroethane (9) to produce nonflammable blends. While a large variety of blends have been developed, a 50:50 (by weight) mixture of HFC-32 and 125, which has been designated R-410A by the ASHRAE, is becoming the most widely accepted of these materials for new equipment installations.

However, the use of HFCs in new refrigeration equipment is not required in the United States until 2010. Until then, HCFCs, such as HCFC-22 ($CHClF_2$), will continue to dominate the market. The HCFCs can also be used for maintenance of installed equipment until January 1, 2030.

Although HFC-152a, 1,1-difluoroethane (10) has a lower Global Warming Potential GWP than HFC-134a and was found to have a more efficient cooling cycle (34). The fact that it is flammable gas has limited its use as a refrigerant.

4. Hydrofluorocarbons as Solvents

4.1. Physical Properties. The physical properties of three materials are given in Table 5; however, the industrial products offered in this industry are usually complex, proprietary mixtures.

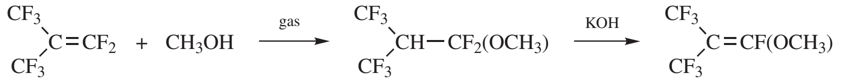
Table 5. **Physical properties of HFC-43-10 (15), HFE(16) and HFC-365mfc (2)**

Properties	HFC-43-10-mee (15)	HFE- (16)	HFC-365mfc (2)
chemical formula	$CF_3CHFCHFCF_2CF_3$	$CF_3CF_2CF_2CF_2OCH_3$	$CF_3CH_2CF_2CH_3$
chemical name	1,1,1,2,3,4,4,5,5,5-decafluoropentane	1-methoxy-nonafluorobutane	1,1,1,3,3 -pentafluorobutane
molecular weight	137	250	148
boiling point, °C	36	60	40°C
liquid density, g/cm^3	1.33	1.52	1.27
surface tension, dyn/cm	16.9	13.6	13.3
flash point	none	close cup or open cup, none	−24°C
flammability range /air	lower limit 6.5, upper limit 11.5	none	lower limit 3.5 upper limit 13
freezing point, °C	−135	−20	
dielectric breakdown voltage			22,300 V
dielectric constant			11

4.2. Manufacture. *1-Methoxy-Nonafluorobutane* ***(15).*** Preparation of compound (15) is a multistep procedure. The first step is the addition of KF to heptafluorobutyryl fluoride in diglyme. The intermediate obtained, potassium nonafluorobutoxide, was then methylated by reaction with heptafluoroisobutenyl methyl ether at −50°C. After warming to room temperature, the product was obtained by distillation to give the desired ether (15) (35), as shown in equation 15.

$$\begin{aligned} &CF_3CF_2CF_2C(O)F + KF \longrightarrow CF_3\,CF_2CF_2CF_2\bar{O}\,K^+ \\ &CF_3CF_2CF_2CF_2\bar{O}\,K^+ + (CF_3)_2C{=}CF(OCH_3) \longrightarrow \underset{\textbf{(15)}}{CF_3(CF_2)_3OCH_3} + (CF_3)_2C{=}CF\bar{O}\,K^+ \end{aligned} \qquad (15)$$

The required methylating agent, heptafluoroisobutenyl methyl ether, can be obtained from a number of commercial sources, or it can be prepared by addition of methanol to perfluoroisobutene to produce octafluoroisobutenyl methyl ether, followed by dehydrofluorination to form the desired product heptafluoroisobutenyl methyl ether, as shown in equation 16 (35).



$$(CF_3)_2C{=}CF_2 + CH_3OH \xrightarrow{\text{gas}} (CF_3)_2CH{-}CF_2(OCH_3) \xrightarrow{\text{KOH}} (CF_3)_2C{=}CF(OCH_3) \qquad (16)$$

The solid residue, potassium α-hydrohexafluoroisobutanoyl fluoride, which resulted as a coproduct in equation 15, could be protonated by addition of water to form the corresponding perfluoroenol ether (or its isomer, hexafluoropivaloyl fluoride). This was further hydrolyzed to form hexafluorobutyric acid, which could be decarboxylated to form 1,1,1,3,3,3-hexafluoropropane, as shown in equation 17 (35).

$$\begin{aligned} &(CF_3)_2C{=}CF\bar{O}\,K^+ + H_2O \longrightarrow (CF_3)_2C{=}C(F)OH \rightleftharpoons (CF_3)_2HC(O)F \xrightarrow{H_2O} \\ &(CF_3)_2CHCO_2H \xrightarrow{-CO_2} CF_3CH_2CF_3 \end{aligned} \qquad (17)$$

HFC- 43-10-mee, 1,1,1,2,3,4,4,5,5,5-Decafluoropentane ***(16).*** The preparation of HFC-43-10-mee, 1,1,1,2,3,4,4,5,5,5-decafluoropentane, is a two-step process. The first step is the addition of tetrafluoroethylene to hexafluoropropylene, catalyzed with fluorinated $AlCl_3$ (36). The product obtained, decafluoro-2-pentene, is then hydrogenated to form HFC-43-10-mee using a Pd/C catalyst, as shown in equation 18.

$$\begin{aligned} &CF_3CF{=}CF_2 + CF_2{=}CF_2 \xrightarrow{AlF_{2.8}Cl_{.2}} CF_3CF{=}CFCF_2CF_3 \\ &CF_3CF{=}CFCF_2CF_3 + H_2 \xrightarrow[Pd/C]{H_2} CF_3CFHCFHCF_2CF_3 \end{aligned} \qquad (18)$$

The industrial process for making HCFCs-225ca and 225cb involves an insertion reaction of the C−F or C−Cl bond of $CHFCl_2$ to tetrafluoroethylene, in the presence of a Lewis acid catalyst such as $SbCl_5$, $TaCl_5$, $NbCl_5$ (37), as shown in equation 19. The product distribution depends on the processing conditions and the specific catalyst used (37). For example, $ZrCl_4$ was found to favor the formation of HCFC-225ca over HCFC-225cb, whereas a catalyst such as $TiCl_2F_2$, produced more HCFC-225cb compared to HCFC-225ca, using the same processing conditions (37).

$$\mathrm{CHFCl_2} + \mathrm{CF_2{=}CF_2} \xrightarrow{\text{catalyst}} \mathrm{CF_3CF_2CHCl_2}\ \text{225ca} + \mathrm{CF_2ClCF_2CHClF}\ \text{225cb} \qquad (19)$$

4.3. Use as Solvents. Perhaps the most important application of fluorinated solvents is to remove oil, grease, and related contaminants from plastics and metals, hence its use in the electrical and electronic industries where metal–plastic combinations pose numerous cleaning problems. Another important application of HFC solvents is in the area of precision engineering, eg, in aerospace and militarily uses, where the solvents need to have high thermal and chemical stability, must be noncorrosive, and readily removed from the equipment without leaving a residue. While advances in the design of the fluxes and polishing compounds often allow the use of aqueous cleaning agents, even in these cases, final water removal and drying can be a problem. For articles that may be damaged at temperatures >100°C, drying can consume much time and still may fail to remove water from blind holes or crevices.

This application is an interesting problem for fluorochemicals. While the hydrophobicity introduced by the fluorine facilitates the evaporation of the solvents at low temperatures, it also hinders its ability to absorb and azoetrope the water. This problem can be overcome by using mixtures of hydrophilic solvents, such as alcohols, ethers or ketones, and fluorocarbons such as HFC-365 mfc 2 and HFC- 43-10-mee (15) (1,1,1,2,3,4,4,5,5,5-decafluoropentane), or by incorporating both functions into one molecule. An example of the second approach is the hydrofluoroether HFE (1-methoxy-nonafluorobutane) (16).

Blends of HFC-43-10-mee with various alcohols are claimed in many application patents to be better degreasing agents and drying solvents (38). Also, an azeotrpic mixture of HFC-43-10-mee with 1-bromopropane (39) has been used for the same application.

In the early 1990s, two hydrochlorofluorocarbons, HCFCs-225ca (CF_3CF_2-$CHCl_2$) and 225cb (CF_2ClCF_2CHClF), were introduced as interim products for this application. These two products have very low ODP and a lower GWP than CFC- 113 (CCl_3CF_3), as shown in Table 6.

Table 6. **Environmental and Physical Properties of HCFCs 225ca, 255cb, and CFC 113**

Compound	Lifetime, years	ODP (CFC11=1)	GWP, 100/yrs	Bp, °C	Flash point
HCF-C225ca $CF_3CF_2CHCl_2$	2.5	0.025	170	52	none
HCF-C225cb CF_2ClCF_2CHClF	6.5	0.033	530	56	none
CFC-113 CF_3CCl_3	8.5	0.8	6800	46.5	none

Table 7. **Physical Properties of 1,1,1,2,3,3,3-Heptafluoropropane and Nonafluoro-4-trifluoromethylpent-3-one, Fire Fighting Agents**

Properties	227ea 1,1,1,2,3,3,3-Heptafluoropropane (**17**)	Nonafluoro-4-trifluoro-methylpentane-3-one (**18**)
chemical formula	CF_3CHFCF_3	$CF_3CF_2C(0)CF(CF_3)_2$
molecular weight	170.03	316.04
boiling point, at 1 atms, °C	−16.4	49.2
freezing point, °C	−131	−108
vapor pressure, at 20°C, psia	56.71	5.87
density saturated liquid, g/cm^3	1.41 at 20°C	1.6 at 25°C
density of gas, g/cm^3	0.0072 g/cm^3 at 200°C	0.0136, g/cm^3 at 25°C
heat of vaporization, at bp	57.05 Btu/lb	37.9 Btu/lb

5. Hydrofluorocarbons as Fire Fighting Agents

5.1. Physical Properties. The physical properties of these products are given in Table 7, and their methods of preparation are summarized below (Table 7).

5.2. Manufacture. *HFC-1,1,1,2,3,3,3-Heptafluoropropane (**17**).* The method for the manufacture of HFC-1,1,1,2,3,3,3-heptafluoropropane (17) involves the addition of HF to hexafluoropropene in the gas phase (40). The best gas-phase catalyst is Cr_2O_3, derived from the pyrolysis of ammonium dichromate. This catalyst is known to have a very high surface area (>200 m^2/g) and large pore volume (0.25 cm^3/g). The process is shown in equation 20.

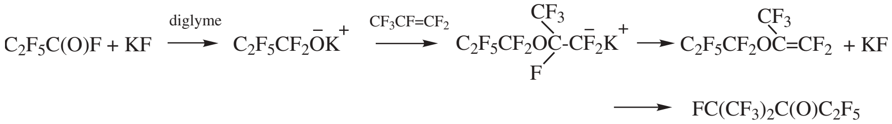
$$(NH_4)_2Cr_2O_7 \longrightarrow Cr_2O_3 + N_2 + 4\,H_2O$$

$$CF_3CF{=}CF_2 + HF \xrightarrow{Cr_2O_3} CF_3CHFCF_3 \qquad (20)$$

Under these conditions, the product obtained contains <10 ppm of the highly toxic perfluoroisobutylene. Activated carbon, which has a very high surface area (500–1500 m^2/g), was found to be very selective in adsorbing perfluoroisobutylene in the presence of heptafluoropropane (17) (41).

The fluorination of hexafluoropropylene can also be carried out in the liquid phase, using SbF_5 (42) or tributylamine (43) as the catalysts, to produce very high purity heptafluoropropane (>99.95% and 99.999%, respectively) without the formation of perfluoroisobutylene.

*HFC-Ketone Nonafluoro-4-Trifluoromethylpentan-3-One (**18**).* The preparation of HFC-ketone nonafluoro-4-trifluoromethylpentan-3-one (18) was carried out via a batch process involving the bubbling of hexafluoropropylene and pentafluoropropionyl fluoride into a mixture of spray dried KF in anhydrous diethylene glycol dimethyl ether (diglyme) (44) as shown in equation 21.



$$C_2F_5C(O)F + KF \xrightarrow{\text{diglyme}} C_2F_5CF_2\overset{-}{O}K^+ \xrightarrow{CF_3CF=CF_2} C_2F_5CF_2O\underset{F}{\overset{CF_3}{C}}\text{-}\overset{-}{C}F_2K^+ \longrightarrow C_2F_5CF_2O\overset{CF_3}{C}{=}CF_2 + KF \longrightarrow FC(CF_3)_2C(O)C_2F_5 \qquad (21)$$

Table 8. **Environmental Properties of Fire-fighting Agents**

Product	ODP	GWP	Atmospheric lifetime, years
1,1,1,2,3,3,3-heptafluoropropane (**17**) CF_3CHFCF_3	0	3500	33
nonafluoro-4-trifluoromethylpent-3-one (**18**) $CF_3CF_2C\,(O)\,CF\,(CF_3)_2$	0	1	0.014

5.3. Use as Fire-Fighting Agents.

The three Halons, 1211 (CF_2ClBr), 1301 (CF_3Br), and 2402 (CF_2BrCF_2Br) have been used as fire fighting agents to replace the highly toxic substances, methyl bromide and carbon tetrachloride. These materials were in use as fire fighting agents from 1960 until their phase out in 1994 under the Montreal protocol. The current selected replacements for these substances are HFC-227ea, 1,1,1,2,3,3,3-heptafluoropropane (**17**), and HFC-ketone nonafluoro-4-trifluoromethylpent-3-one (**18**). The ODP and GWP of these products are given in Table 8.

These two products extinguish fires by physically cooling the flame and removing heat from the flame to the extent that the combustion reaction cannot sustain itself. Both are suited for extinguishing fires in areas containing high value equipment, such as telecommunications facilities, computer rooms, electronic and data processing equipment, record storage facilities, art galleries, museums, and electrical control rooms.

6. Conclusion

The fluorochemical industry concurred with the scientific finding of Molina and Rowland in 1974, concluding that CFCs are responsible for atmospheric ozone depletion. Thus there was imposed a voluntarily ban of the use of CFC for aerosol applications. Upon the signing of the Montreal Protocol in 1987, which banned the production and use of CFCs in all applications, the fluorocarbon industry was successful in developing new products to fulfill the need created by the ban. These products include the new HFCs-134a, 32, and 125 for refrigeration applications. HFC-227ea and hydrofluoroethers, HFEs, are used as a fire-fighting agents, while HFCs 43-10-mee and HFEs are used for solvent applications. However, it is the developments of products for use in foam applications that is requiring the greatest industrial efforts. Initially, the interim product HCFC-141b was developed for use in polyurethane and polyisocyanate foams and HCFC-142b for polystyrene foam. HCFC-141b was used in developed countries throughout the 1990s and until the end of 2003. By that time, companies had learned to use the lower boiling HFCs such as 134a as foam blowing agents and were able to manufacture and introduce the two new, higher boiling HFCs-245fa and 365fmc. In addition, many urethane foam applications switched to the use of hydrocarbons, especially pentanes, even though this change usually resulted in poorer fire performance of the foam. For polystyrene foam, HCFC-142b has been replaced by blends of HFC-134a and ethanol or CO_2 in Europe and Japan, but in the United States, these alternatives have not been able to meet the more stringent requirements of this industry and HCFC-142b will probably be in use until 2010.

These changes cost the industry hundreds of million of dollars in research to develop the processes and products, to complete the toxicity and flammability testing, to carry out pilot plant operation, and finally to build new plants or retrofit existing facilities for their manufacture. This has been an enormous task, taking between 5 and 10 years of effort from hard working dedicated professionals to bring a product from the laboratory scale to the market place. It is very costly process, and the developed technology must, by necessity, be protected by written patents.

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