

ADVANCES IN FLUORINE CHEMISTRY

VOLUME 3

EDITORS

M. STACEY, F.R.S.

*Mason Professor and Head of Department of
Chemistry, University of Birmingham*

J. C. TATLOW, Ph.D., D.Sc.

Professor of Organic Chemistry, University of Birmingham

A. G. SHARPE, M.A., Ph.D.

University Lecturer in Chemistry, Cambridge

LONDON
BUTTERWORTHS

1963

**Exhibit
3020**

State of Minnesota v. 3M Co.,
Court File No. 27-CV-10-28862

3020.0001

NITROGEN FLUORIDES AND THEIR INORGANIC DERIVATIVES

N,N-Difluoroethylamine ($C_2H_5NF_2$)⁴⁵

<i>m/e</i>	<i>Ion</i>	<i>Pattern per cent</i>
81	$C_2H_5NF_2^+$	0.8
66	$CH_2NF_2^+$	3.8
43	$C_2H_5N^+$	7.5
33	NF^+	3.2
29	$C_2H_5^+$	100.0
28	$C_2H_4^+$	20.8
27	$C_2H_3^+$	70.6
15	CH_3^+	36.2

THE ORGANIC FLUOROCHEMICALS INDUSTRY

J. M. HAMILTON, Jr

*"Freon" Products Research and Development, Wilmington, Delaware, U.S.A.
E. I. du Pont de Nemours & Company, Inc.*

Introduction	117
Background	121
Technology	125
Nomenclature	125
Properties	126
Physical Data	127
Chemical Properties	128
Specifications	131
Technological Data	132
Handling	133
Shipping	133
Storage and Transfer	135
Hazards	137
Manufacture	146
Major Fluorochemicals	147
Minor Fluorochemicals	152
Fluorochemical Manufacturers	154
Applications	157
Refrigerants	158
Propellants	161
Intermediates	164
Blowing Agents	164
Solvents	165
Fire Extinguishing Agents	166
Anaesthetics and Biologicals	167
Special Applications	168
Coatings and Finishes	168
Lubricants	168
Dielectrics	169
Inert Liquids	169
Low Temperature Refrigeration	169
Space Technology	169
Miscellaneous	169
Appendix A	170
Appendix B	173
Appendix C	176

INTRODUCTION

Even a casual contact with the fluorochemicals industry reveals two dominant characteristics. It is, in the first place, a major enterprise, which each year manufactures and sells several hundred million pounds of relatively expensive

THE ORGANIC FLUOROCHEMICALS INDUSTRY

products. It is, furthermore, an industry built around a small group of simple, stable compounds, which are useful primarily because of their physical properties.

These points are illustrated by Table 1, which shows both the size of the industry and the dominance of the five major products. The overall market pattern is shown in *Figure 1*, from which it will be seen that two purely

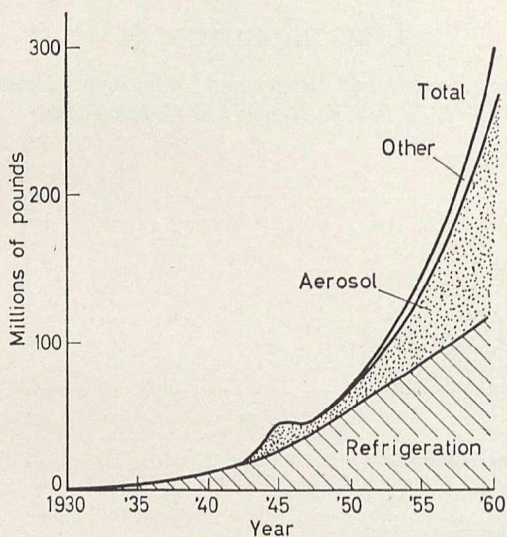


Figure 1. Total U.S. market for fluorocarbons.
(Trade announcements and reports¹⁹)

mechanical applications—as refrigerants and propellants—account for over 90 per cent of the total.

The information in Tables 2 and 3 is an elaboration of the data from Table 1, and gives a more detailed picture of the manufacturers and their products. Similarly, *Figure 2* presents the products of Table 3 in terms of boiling point, the physical property which usually governs the type of application.

Inorganic fluorochemicals and organic polymers lie beyond the scope of this paper, except insofar as the latter may be treated as end products or applications of fluorochemical monomers. In a similar manner, no attempt has been made to discuss the detailed technology of fluorochemicals containing functional groups, on the grounds that none of these products has yet established a substantial and definable commercial market. As a result, the technical portion of the paper is limited to the simple products, major and minor, listed in Table 3. The extension to include the minor products has been justified on the grounds that most of them will inevitably gain commercial stature on the impetus of their established analogues and that, in any event, their consideration does not significantly increase the complexity of the presentation.

This choice necessarily neglects future development: the many polymers

INTRODUCTION

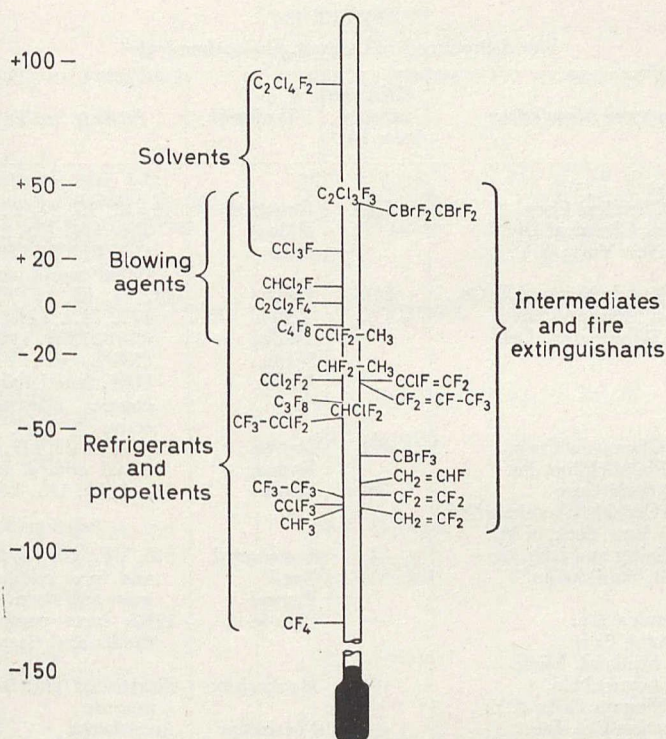


Figure 2. Boiling points of common commercial fluorochemicals (°C)

and functional compounds which may well constitute the major growth segment of the industry in the next decade. A similar lack of emphasis is accorded those manufacturers who have placed their faith largely in such developmental products, and whose present minor role in terms of production

TABLE 1
Estimated World Production of Organic Fluorochemicals, 1960

Formula	Product	Code number*	Production, lb. × 10 ⁻⁶		
			U.S.†	Other**	Total
CCl_3F	Trichloromonofluoromethane	11	72	20	92
CCl_2F_2	Dichlorodifluoromethane	12	166	50	216
$CHClF_2$	Monochlorodifluoromethane	22	40	10	50
$C_2Cl_3F_3$	Trichlorotrifluoroethane	113	6	1	7
$C_2Cl_2F_4$	Dichlorotetrafluoroethane	114	10	1	11
—	All others††	—	5	1	6
					382

* See Nomenclature.
 † U.S. Tariff Commission Report, 'Synthetic Organic Chemicals: United States Production and Sales, 1960'.
 ** European Trade Journals, plus data from U.S. Department of Commerce (Bureau of Foreign Commerce, Business and Defense Services Adm.) and International Aerosol Association reports.
 †† TFE and CTFE included in totals for $CHClF_2$ and $C_2Cl_3F_3$.

THE ORGANIC FLUORO-CHEMICALS INDUSTRY

TABLE 2
World Producers of Organic Fluorochemicals¹⁹

Country and Manufacturer	Estimated capacity lb. × 10 ⁻⁶	Trademark	Products (see Table 3)
<i>United States</i>			
Applied Chemical Corp. (General Chemical Div.) (Gen) New York, N.Y.	100	Genetron Halon Aclar	11, 12, 13, 21, 22, 23, 112, 113, 114, 115, 218, DFE, CDFE, VF ₂ , CTFE, func- tional comps. and resins
E. I. du Pont de Nemours & Co. ("Freon" Products Div.) (DuP) Wilmington, Del.	210	Freon Teflon Tedlar Viton Vydax	11, 12, 13, 14, 21, 22, 23, 112, 113, 114, 115, 116, C318, 13B1, 114B2, DFE, CDFE, VF, VF ₂ , TFE, HFP, functional and inert comps., elastomers and resins
Pennsalt Chemicals Corp. (PSa) Philadelphia, Pa.	50	Isotron	11, 12, 13, 22, 113, 114, func- tional comps. and resins
Union Carbide Corp. (Union Carbide Chemicals Div.) (UCar) New York, N.Y.	50	Kynar Ucon	11, 12, 22, 113, 114
Minn. Mining and Mfg. Co. (3M) St. Paul, Minn.	—	Scotchgard Kel-F Fluorel	218, VF ₂ , CTFE, functional and inert comps., elasto- mers and resins
Dow Chemical Co.	—	Silastic	12B2, inert comps., anaes- thetics and elastomers
Dow Corning Corp. (Dow) Midland, Mich.	—	Hookerlube	Functional and inert com- pounds
Hooker Chemical Co. (HK) Niagara Falls, N.Y.	—	Fluoromar	Anaesthetics
Air Reduction Co., Inc. (Air Reduction Chem. Div.) (AIR) New York, N.Y.	—		
<i>Argentina</i>			
Ducilo (Duc) Buenos Aires	3	Freon	11, 12, 22
Fluoder (Flu) Lanus	3	Algeon	11, 12
La Fluorhidrica (Fluor) Buenos Aires	—	Fration	12
<i>Brazil</i>			
Du Pont do Brasil (DuPB) São Paulo	3	Freon	11, 12, 22
Fongra Produtos Quimicos (Fon) São Paulo	3	Frigen	11, 12
<i>Canada</i>			
Du Pont of Canada (DuPC) Montreal	15	Freon	11, 12, 22, 113, 114
<i>England</i>			
Imperial Chemical Industries, Ltd. (ICI) Manchester	30	Arcton Fluon	11, 12, 13, 21, 22, 23, 113, 114, TFE, anaest., and resins
Imperial Smelting Co. Ltd. (IS) Avonmouth	10	Isceon	11, 12, 22, 113, 114
<i>France</i>			
Société d'Electro-Chimie . . . d'Ugine (Ug) Lyon	15	Forane	11, 12, 13, 21, 22
Pechiney (Pech) Paris	5	Flugene	11, 12, 114

BACKGROUND

Table 2—Continued

<i>Country and Manufacturer</i>	<i>Estimated capacity lb. × 10⁻⁶</i>	<i>Trademark</i>	<i>Products (see Table 3)</i>
<i>Germany (West)</i>			
Farbwerke Hoechst A.G. (Hoechst) Frankfurt am Main	30	Frigen	11, 12, 13 14, 21, 22, 23, 113, 114, CTFE and resins
Chem. Frabrik von Heyden (Heyd) Munich	2	Hostaflon Fluogen	11, 12, 22
<i>Germany (East)</i>			
V.V.B. Alcid Fluorwek Dohna (VVB) Dresden	—	Frigedohn	11, 12, 13, 21, 22, 113, 114
<i>Italy</i>			
Montecatini (Monte) Milan	12	Algofrene	11, 12, 21, 22
Societa Edison (SIC) Milan	5	Edifren	11, 12
<i>Japan</i>			
Nitto Chemicals Co., Ltd. (Nitto) Tokyo	5	Col-flon	11, 12, 22
Osaka Metal (Osaka) Tokyo	2	Daiflon	11, 12, 21, 22, 112, 113, 114
<i>Mexico</i>			
Halocarbuos (Haloc) Mexico City	3	Freon	11, 12
<i>Netherlands</i>			
Uniechemie N.V. (Unie) Apeldoorn	1	Fresane	12
<i>Russia</i>			
Unknown	—	Eskimon	Unknown
<i>Spain</i>			
Productos Quimicos Industrial Comas Ing. (Comas) Madrid	1	Flurion	12

may be dramatically changed in the near future. An attempt to offset this distortion has been made in the sections on Manufacturers and Applications, where the newer products and their producers have been discussed briefly.

It is further recognized that the paper does not do justice to research and production outside the United States. Here, however, the availability and certainty of information has been the determining factor and, as in the case of a recent British review²⁰, the discussions of technology and application are largely based on data from the industry in the United States.

BACKGROUND

The fluorochemicals industry is a relative newcomer, dating only from about 1930. This belated industrial start, however, was typical of the entire field, since fluorine chemical research had consistently lagged behind that of its companion halogens. Mineral fluorides were recognized and used in the 16th century and the acid, HF, had been characterized by Scheele as early as 1771. At this point, however, the dangers and difficulties of experimental

THE ORGANIC FLUORO-CHEMICALS INDUSTRY

work with HF slowed further progress, and another century was to pass before Moissan isolated elementary fluorine in 1886. Even after this, the difficulties of research discouraged most chemists, and for the next 35 years work in the field was essentially limited to Moissan in France, Ruff in Germany and Swarts in Belgium. During the 1920's, a number of other men became interested in such work, notably Henne in the U.S., but even so, the simplest perfluorocarbon, CF_4 , was not isolated until 1926²¹ and not fully characterized until four years later²². This then was the general state of fluorine chemistry in 1928, when it was suddenly swept into its industrial phase by the rapidly expanding field of mechanical refrigeration.

This rendezvous had been in the making since 1851, when Dr John Gorrie first obtained a patent on 'An Apparatus for the Artificial Production of Ice in Tropical Climates'. During the decades that followed, engineers and scientists worked persistently to reduce his concepts of mechanical refrigeration to successful commercial practice, and by 1928 the mechanical refrigerator

TABLE 3
Products of the Organic Fluorochemicals Industry*

Formula	Product	Code number†	Producers (see Table 2)
CCl_3F	Trichloromonofluoromethane	11	DuP, Gen, PSa, UCar, Duc, Flu, DuPB, Fon., DuPC, ICI, IS, Ug, Pech, Hoechst, Heyd, VVB, Monte, SIC, Nitto, Osaka, Haloc
CCl_2F_2	Dichlorodifluoromethane	12	DuP, Gen, PSa, UCar, Duc, Flu, Fluor, DuPB, Fon., DuPC, ICI, IS, Ug, Pech, Hoechst, Heyd, VVB, Monte, SIC, Nitto, Osaka, Haloc, Unie, Comas
$CClF_3$	Monochlorotrifluoromethane	13	DuP, Gen, PSa, ICI, Ug, Hoechst, VVB
CF_4	Tetrafluoro- or Perfluoromethane	14	DuP, Hoechst
$CHCl_2F$	Dichloromonofluoromethane	21	DuP, Gen, ICI, Ug, Hoechst, VVB, Monte, Osaka
$CHClF_2$	Monochlorodifluoromethane	22	DuP, Gen, PSa, UCar, Duc, DuPB, DuPC, ICI, IS, Ug, Hoechst, Heyd, VVB, Monte, Nitto, Osaka
CHF_3	Trifluoromethane or Fluoroform	23	DuP, Gen, ICI, Hoechst
$C_2Cl_4F_2$ **	Tetrachlorodifluoroethane	112	DuP, Gen, Osaka
$C_2Cl_3F_3$ **	Trichlorotrifluoroethane	113	DuP, Gen, PSa, UCar, DuPC, ICI, IS, Hoechst, VVB, Osaka
$C_2Cl_2F_4$ **	Dichlorotetrafluoroethane	114	DuP, Gen, PSa, UCar, DuPC, ICI, IS, Pech, Hoechst, VVB, Osaka
$CClF_2-CF_3$	Monochloropentafluoroethane	115	DuP, Gen
CF_3-CF_3	Hexafluoro- or Perfluoroethane	116	DuP
$CBrF_2$	Dibromodifluoromethane	12B2	Dow
$CBrF_3$	Monobromotrifluoromethane	13B1	DuP
$CBrF_2-CBrF_2$	1,2-Dibromotetrafluoroethane	114B2	DuP
CHF_2-CH_3	1,1-Difluoroethane (DFE)	152a	DuP, Gen
$CClF_2-CH_3$	Chlorodifluoroethane (CDFE)	142b	DuP, Gen
$CH_2=CHF$	Vinyl Fluoride (VF)	1141	DuP
$CH_2=CF_2$	Vinylidene Fluoride (VF ₂)	1132a	DuP, Gen, 3M
$CClF=CF_2$	Chlorotrifluoroethylene (CTFE)††	1113	Gen, 3M, Hoechst
$CF_2=CF_2$	Tetrafluoroethylene (TFE)††	1114	DuP, ICI
$CF_2=CF-CF_3$	Hexafluoropropylene (HFP)	1216	DuP
$CF_3-CF_2-CF_3$	Octafluoro or Perfluoropropane	218	3M, Gen
$CF_2CF_2CF_2CF_2$	Octafluoro or Perfluorocyclobutane	G-318	DuP
Compounds with Functional Groups (alcohols, ketones, ethers, acids, amines, etc.)			DuP, Gen, PSa, 3M, HK
Inert Compounds (liquids, oils, greases, waxes, and finishes)			DuP, Dow, HK, 3M
Anesthetics			AIR, Dow, ICI
Elastomers			DuP, Dow, 3M
Resins (powder, dispersion, film, tape, fibre, etc.)			DuP, Gen, PSa, 3M, ICI, Hoechst

* U.S. Tariff Commission Report plus trade announcements and reports¹⁹.

† See Nomenclature.

** Predominately the symmetrical isomer—see Chemical Properties.

†† Internal consumption only.

BACKGROUND

was essentially the machine we know today, with one exception—there was still no satisfactory refrigerant.

Many compounds had, of course, been tested as candidates and several were in extensive use, but all had serious drawbacks. Some, like ethylene, were flammable; others like SO_2 , were corrosive and toxic; and still others, like ammonia, combined all three hazards. CO_2 was, from this point of view, nearly ideal, but the necessarily high operating pressures made the resulting equipment almost prohibitively bulky and subject to leaks. The perils of the other refrigerants were so great, however, that despite the drawbacks of the CO_2 installations, the U.S. Navy of this period specified that only such systems would be permitted aboard U.S. Naval vessels.

Meanwhile, the public had become aroused by a series of fatal accidents traceable to the escape of common refrigerants into congested areas such as hospitals and theatres. It was under these circumstances that the General Motors Corporation, manufacturers of Frigidaire refrigerators, concluded in 1928 that no amount of tinkering could overcome the inherent disadvantages of the existing refrigerants. They therefore commissioned a small group of scientists, including Robert McNary, Thomas Midgley and Albert Henne, to search again for an agent that would permit a normal unhampered growth of the refrigeration industry. The group began its study on a fundamental basis, plotting trends of toxicity, flammability, and boiling point on a periodic chart of the elements. This study pointed in only one direction—fluorocarbons. The literature of that period was filled with dire reports on the corrosiveness and toxicity of such compounds but, rightly assuming that these observations were based on samples contaminated by HF and phosgene, they decided to go ahead.

Selecting as their first choice the compound CCl_2F_2 , they prepared samples by the reaction of CCl_4 and SbF_3 , a synthesis originally reported by Swarts²³. The product proved to be all they could have hoped for, and at the April 1930 meeting of the American Chemical Society, Dr Midgley was able to give a dramatic introduction of the new refrigerant, inhaling a lung-full of the gas and then extinguishing a lighted candle²⁴. In addition to being non-flammable and essentially non-toxic, the compound had a convenient boiling point of about -30°C , and acceptance was a foregone conclusion.

In the meantime, General Motors had approached E. I. du Pont de Nemours & Company with a proposal to manufacture this product, and the original work was soon supplemented by development studies designed to allow practical production on a commercial scale. In 1930, a joint corporation was formed by the two companies, named Kinetic Chemicals Inc. and physically located at Du Pont's Deepwater, New Jersey plant. By early 1931, the new product, trademarked Freon-12 or F-12*, was being produced in commercial quantities, and the refrigeration industry had begun the necessary modification of its equipment. Mention should be made of the fact that Du Pont and G.M., despite their vested interest in the new product, took immediate steps to ensure its availability to the entire refrigeration industry.

Application of the new compound was gratifyingly successful, and by the end of 1931, Kinetic had expanded its Deepwater facilities, and begun

* Freon and combinations of Freon, or F, with numerals are Du Pont's registered trademarks for fluorocarbons. See Nomenclature.

manufacture of anhydrous hydrofluoric acid, a basic raw material then unavailable in the necessary quantities. Expansion during the next few years was continuous, and the product line was extended as early as 1932 to include Freon-11 (CCl_3F) as well as Freon-113 and Freon-114, two of the completely halogenated chlorofluoroethanes (Table 1). In 1935, the fluorinated derivatives of chloroform were added, and one of these, Freon-22, soon gained wide acceptance. These five products, uniformly covering a boiling range from -41° to $+48^\circ\text{C}$ (Figure 2), satisfied the needs of the refrigeration and air-conditioning industries of that time, and have continued to serve as the backbone of the fluorochemicals industry. Even today, they constitute more than 95 per cent of the world's fluorocarbon production.

Since that time, although expansion of the industry has been continuous, certain landmarks can be identified. Chief among these was the impact of World War II, and the attendant development of aerosol insecticides, based upon Freon propellants (Figure 1). To meet the war-time demands of the armed forces, Kinetic Chemicals expanded its facilities, and, shortly after the war, was joined in the market by the General Chemical Division of the Allied Chemical Corporation (Genetron). At about this time, the Kinetic Chemicals Corporation was dissolved, and the production and distribution of Freon refrigerants and propellants passed entirely to the Freon Products Division of Du Pont. The field was further augmented by the entry of the Pennsalt Chemicals Corporation in 1957 (Isotron) and the Union Carbide Corporation in 1958 (Ucon). All four companies now offer a complete line of the basic fluorocarbons, as well as an extensive list of lesser products.

Paralleling industrial growth in the U.S., there had also been a steady development of manufacture in other countries. Beginning in the early 1940's with ICI of England, this has expanded explosively during the last decade, and today over 20 companies in 13 different countries are manufacturing at least a limited line of fluorocarbons (Table 2).

The outstanding success of the major fluorocarbons should not obscure the fact that a large number of other potentially important fluorochemicals became commercially available during this period. Allied's General Chemical Division first offered, during the 1940's, an entire line of fluorochemicals based on the reaction of acetylene and HF, and the Hooker Chemical Company similarly made available a series of fluorinated aromatic derivatives. One by one additional items were offered for sale, and by 1950 all the simple compounds of Table 3 could be manufactured in commercial quantities by some company in the U.S.

The 1950's were essentially a period of consolidation, during which the markets of the major products expanded and the uses became more clearly defined. This was also a period during which many of the minor products of Table 3 seem to have passed through their developmental stage and now stand on the threshold of large-scale commercial manufacture. It will be surprising if the number of multimillion pound/year products does not double during the next few years.

Although fluoropolymers and elastomers lie outside the scope of this paper, they are all dependent on fluorochemical intermediates and hence have played a significant part in the industry's growth. These outlets are discussed more fully under Applications, and it is sufficient to note here that, beginning

TECHNOLOGY

in the early 1940's with Du Pont's Teflon resin (polytetrafluoroethylene), the field has expanded steadily. Promoted by several different companies, the established product lines now include over a dozen plastics, films, elastomers and lubricants based on polymerization of various combinations of tetrafluoroethylene, chlorotrifluoroethylene, hexafluoropropylene, vinyl fluoride and vinylidene fluoride. Though the field is still dominated by Teflon, it collectively consumes millions of pounds of intermediates each year, and in the near future promises to become one of the major customers for fluorinated intermediates.

In summary, the fluorochemicals industry presents an attractive picture, with a small core of established large-volume products and an active growth sector, composed of several dozen small commercial products, each opening new fields of applications.

TECHNOLOGY

This paper is intended to supplement the extensive review literature on fluorine chemistry. A selection of general references has therefore been given in the bibliography¹⁻¹⁵, and this list has been extended by including several standard technological works¹⁶⁻¹⁸. In the sections which follow, reference will be made where possible to these reviews rather than to the original literature.

NOMENCLATURE

Fluorochemical nomenclature has been a favourite target for innovation, and in recent years at least nine proposals have merited review by the Nomenclature Committee of the American Chemical Society¹⁶. Little of a radical nature has come out of such suggestions, however²⁵, and the fluorochemical industry has followed the general trend of continuing to use the standard nomenclature of organic chemistry.

There is, none the less, one narrow area in which a specialized, unofficial terminology has become firmly entrenched, and it is a peculiarity of the industry that the dominating commercial products all fall within this system. The widespread acceptance of this special nomenclature reflects the historical fact that the key commercial products have all been members of a small series of simple chemicals with cumbersome names, and the importance of the system is attested by the fact that it will probably be adopted internationally for just those compounds which constitute more than 95 per cent of the present fluorochemicals market.

The system is essentially a numerical code in which the digits are related to the number of carbon, hydrogen or fluorine atoms in the molecule. It has already been employed in Tables 1 to 3, and the rules are given in Appendices A and B, together with further examples. It was originally proposed by Henne, Midgley and McNary to simplify their studies, and was extended to the refrigeration industry through its adoption by Du Pont as the basis of their trademark system. (The chemical product CCl_2F_2 , which is Compound 12 in this system, is marketed by Du Pont as Freon-12 or F-12.) Throughout the 1930's and 1940's, Du Pont was the sole manufacturer of many of the key fluorocarbon refrigerants, and during this period identification of the

THE ORGANIC FLUOROCHEMICALS INDUSTRY

compounds with the corresponding code number became firmly rooted within the refrigeration industry. As a result, later producers of these established products felt it advantageous to their customers to incorporate the number system, with Du Pont's consent, into their own individual trademark systems (Table 2).

Consumer groups were, of course, quick to recognize the advantage of this *de facto* uniformity, and through the mediation of ASHRAE (American Society of Heating, Refrigerating and Air-Conditioning Engineers) all parties interested in production and consumption agreed to adopt the number system as of June 1957. This decision was later confirmed by the American Standards Association under the title 'Numerical Designation of Refrigerants—B79.1', approved in September 1960. The system had meanwhile been generally accepted by manufacturers throughout the world, and in October 1960 a working committee of the International Organization of Standardization (IOS) recommended adoption of that portion of the code applying to halogenocarbons and hydrocarbons²⁶.

Occasional criticism is voiced concerning the complexity of the rules by which the numbers are formed, but such judgment usually results from the mistaken assumption that such a system must possess some mnemonic utility. The system is actually never employed except in the initial establishment of the proper code number, which thereafter simply becomes a useful short alternative name for the compound. Similarly the code is rarely necessary for the recognition of unfamiliar compounds, since written material employing code numbers will almost always contain an identification key.

Although the system is comprehensive and technically satisfactory, certain limiting factors should be noted. The most obvious of these is the existence of an established common name. It is, for example, highly unlikely that chloroform will ever become generally known as Compound 20. Another, more subtle, restriction arises from the fact that commercial fluorocarbons marketed by code numbers gained initial acceptance largely on the basis of non-toxicity and non-flammability. This has led to a dangerous tendency on the part of non-technical personnel to assume that any compound designated by such a code number will be similarly safe, and to proceed accordingly. To avoid this hazard, some groups restrict the use of the number code to the more stable members of the series and designate other compounds by a trivial name or acronym, e.g. DFE rather than Compound 152a for the product 1,1-difluoroethane—see Table 3.

In theory, the system provides for propane derivatives as well as the methane and ethane series. Additional rules, however, would be required for isomer designation, and the resulting code numbers would become so complex as to lose their value. Useful extensions have therefore been confined to those compounds where such problems do not occur, e.g. Compound 218 for octafluoropropane.

PROPERTIES

The section which follows is concerned only with the simple commercial fluorocarbons of Table 3. However, similar information for the remaining body of fluorochemicals is readily available in the general references, particularly Nos. 1 to 4.

PROPERTIES

PHYSICAL DATA

Because of the principal applications, the physical properties of the fluorocarbons have always been of peculiar interest. As a result, extensive tabulations have been prepared, among the most comprehensive being those of Lovelace² and Simons³. An illustrative selection appears in Appendix B.

In general, the lower fluorocarbons are clear, mobile liquids or gases, exhibiting relatively high densities, and possessing low refractive indices, surface tensions and kinematic viscosities. The boiling points are also low in relation to molecular weight, reflecting the weakness of the intermolecular attractive forces. In many cases, such simple physical data are entirely

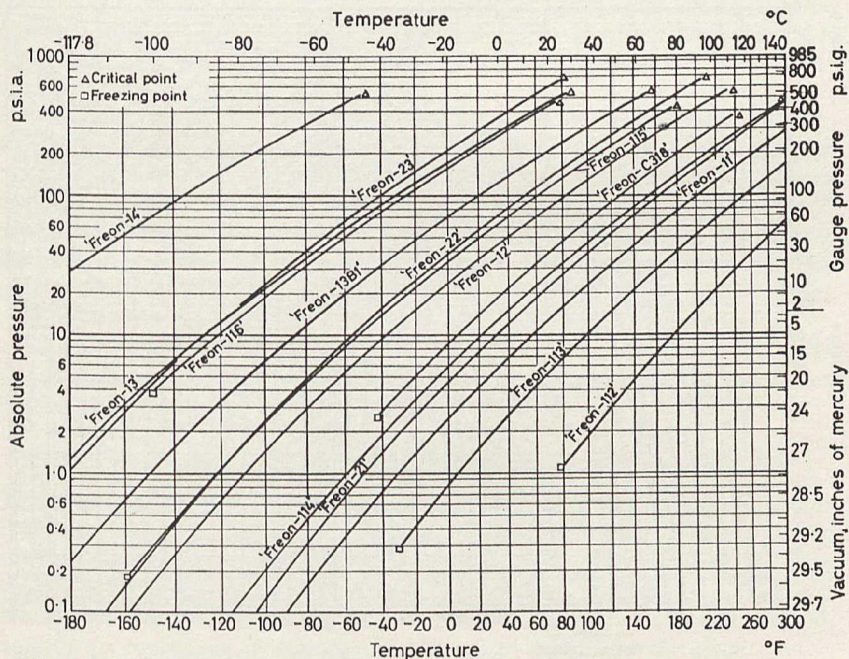


Figure 3. Pressure-temperature relationships of Freon compounds. (Copyright 1957 by E. I. du Pont de Nemours & Company, Wilmington 98, Delaware)

adequate for satisfactory application of the product, and even the aerosol industry usually needs little more additional data than the change in vapour pressure with temperature (Figure 3). Refrigeration applications, however, require a much more complete thermodynamic definition of the product, including an accurate equation of state, as well as vapour pressures, heat capacities and densities. These are usually presented in the form of detailed tables describing the refrigerant in both the saturated and superheated regions. The latter, of course, deal only with the vapour, but the saturation tables include equilibrium liquid and vapour throughout a wide temperature range, and list the corresponding pressures, densities, specific volumes, entropies, enthalpies, and specific heats.

The degree of detail will vary with the importance of the product, but for a key refrigerant such as Freon-12 may reach the proportions of a sizable

book³⁷. In this particular case all data are presented at even intervals of 1°F for the complete range -152° to +232°F, and then retabulated for the same range in terms of even pressures. A similar type of tabulation is made for the superheated vapour, extending some 300°F above saturation temperature and including a pressure range from 0.14 to 500 p.s.i. absolute.

For the convenience of refrigeration engineers, these data are also made available in the form of graphical crossplots, such as the illustrated pressure-enthalpy relation (Figure 4). In the most important cases they may also be prepared in a variety of scales, some of which are of such magnification as to permit estimation of intervals as small as 0.01 B.Th.u./lb.

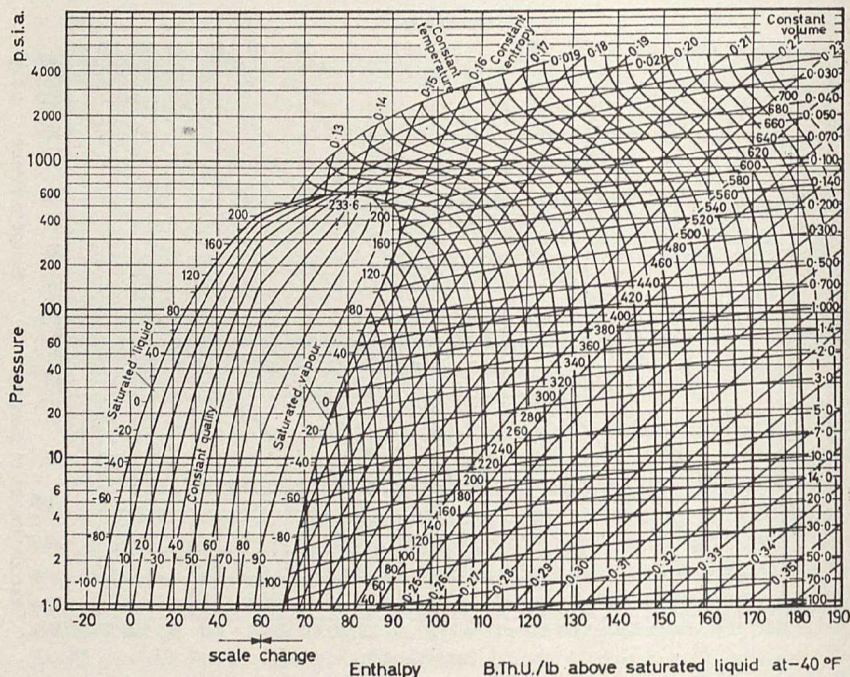


Figure 4. Pressure-enthalpy diagram. (Copyright 1955 and 1956 by E. I. du Pont de Nemours & Company, Wilmington 98, Delaware)

The fluorocarbon manufacturers have taken a lead in sponsoring such studies, and basic data have been published for Refrigerants 11²⁷, 12²⁸, 13²⁹, 14³⁰, 21²⁷, 22²⁷, 23³¹, 113²⁷, 114³², 115³³, C-318³⁴, DFE³⁵, CDFE³⁵ and VF₂³⁵. In addition, the refrigeration industry itself has shown considerable energy in disseminating such information, with the result that the best up to date summary compilations of the above data are to be found in the handbooks of ARI³⁶ (American Refrigeration Institute) and ASHRAE³⁷ (American Society of Heating, Refrigerating and Air-Conditioning Engineers).

Chemical Properties

As a corollary to their usefulness in mechanical applications, current commercial fluorochemicals exhibit a sharply limited range of chemical properties. The relatively few clean-cut reactions are identified below, and

PROPERTIES

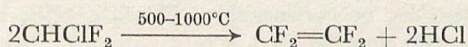
since these have been drawn almost entirely from two review sources^{2,3} they will generally be presented without individual reference. Several of the reactions are, of course, useful in synthetic work, and these discussions are amplified in the section on Manufacturing Technology, where they are referred directly to the extensive patent literature on the subject.

Major Fluorocarbons

CCl_3F and CCl_2F_2 —These compounds may obviously be further fluorinated to the tri- and tetrafluoro homologues, as discussed under the latter's manufacture. About the only other clean-cut reaction is a disproportionation over AlCl_3 to form CClF_3 and CCl_4 . A variety of other reactions have been reported, but as might be expected from the rather rigorous conditions, the yields are generally too low to consider these compounds as useful intermediates.

From the point of view of stability, both products are generally satisfactory, although CCl_2F_2 is significantly more stable to hydrolysis than CCl_3F . Under certain special conditions, of course, degradation may become a serious problem, as in the case of a free radical reaction between CCl_3F and alcohols³⁸ or the vigorous interaction of molten aluminium with CCl_2F_2 .³⁹ However, for general purposes at moderate temperatures, both compounds may be considered satisfactorily inert, and their suitability under any special condition can usually be established by contacting the manufacturer.

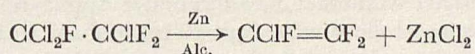
CHClF_2 —In addition to a potential for bromination or further fluorination, this compound possesses the ability to undergo a remarkably clean-cut type of dimerization at elevated temperatures:



This reaction, of course, forms the basis of a commercial synthesis of tetrafluoroethylene, discussed under Manufacturing Technology. The only other simple reaction is the expected disproportionation in the presence of AlCl_3 to yield CHF_3 and CHCl_3 . The alkaline hydrolytic stability of CHClF_2 is relatively lower than that of the dichlorodifluoro-analogue, but under normal, anhydrous conditions its stability appears to be essentially the same.

$\text{C}_2\text{Cl}_3\text{F}_3$ and $\text{C}_2\text{Cl}_2\text{F}_4$ —The normal commercial forms of these products consist predominantly of the more symmetrical isomers, $\text{CCl}_2\text{F} \cdot \text{CClF}_2$ and $\text{CClF}_2 \cdot \text{CClF}_2$, with samples of the former usually containing no more than a few tenths per cent of $\text{CCl}_3 \cdot \text{CF}_3$ and samples of the latter only 7–10 per cent $\text{CCl}_2\text{F} \cdot \text{CF}_3$. However, if the isomer ratio is of particular concern to the user, he should check his particular sample, since some synthetic routes yield far higher unsymmetrical isomer contents, and similarity of boiling points precludes further purification.

In general, both compounds show the typical low reactivity of perhalogenocarbons. A striking exception, however, is their ability to lose chlorine to zinc in the presence of polar solvents^{157,169}.



This reaction will also proceed in the presence of aluminium and magnesium, which explains the extreme care that must be taken to avoid

exposure of the common solvent mixture of $\text{CCl}_2\text{F} \cdot \text{CClF}_2$ plus ethanol to such materials as galvanized iron and aluminium. The trichloro-compound will also react with AlCl_3 , but instead of a clean-cut disproportionation, the products include predominantly the unsymmetrical isomers of the tri- and difluorochloroethanes. In hydrolytic and thermal stability, $\text{CCl}_2\text{F} \cdot \text{CClF}_2$ is intermediate between the other major products, but $\text{CClF}_2 \cdot \text{CClF}_2$ is perhaps the most stable of the five major commercial products by any test. This property recommends it for propellant and refrigeration applications where the ultimate of stability is desired.

Minor Fluorocarbons

CHCl_2F , $\text{C}_2\text{Cl}_4\text{F}_2$, CBr_2F_2 and $\text{CBrF}_2 \cdot \text{CBrF}_2$ —These compounds exhibit essentially the same chemistry as their more highly fluorinated homologues. As might be expected, their stabilities are somewhat poorer, particularly in respect to the hydrolysis of CHCl_2F . The isomer distribution of commercial $\text{C}_2\text{Br}_2\text{F}_4$ appears to be entirely symmetrical, but commercial $\text{C}_2\text{Cl}_4\text{F}_2$ is quite variable, probably reflecting the lack of standardized large-scale manufacture. Occasional samples contain as much as 50 per cent of the unsymmetrical form, but the more customary range is 10–20 per cent and recent commercial samples have shown as little as 2 per cent $\text{CCl}_3 \cdot \text{CClF}_2$. As in the case of the higher homologues, the small boiling point difference prevents further enrichment.

CBrF_3 , CClF_3 , C_2ClF_5 , CHF_3 , CF_4 , C_2F_6 , C_3F_8 , and cyclic C_4F_8 —For all practical purposes, these compounds have no chemistry, other than the ability of the first three to undergo further fluorination. In addition, CHF_3 may be pyrolysed to $\text{CF}_2=\text{CF}_2$, or converted to CBrF_3 or CF_4 by the action of elementary bromine or fluorine.

$\text{CH}_3 \cdot \text{CHF}_2$ —Commercial difluoroethane appears to consist entirely of the unsymmetrical isomer, which may be easily and smoothly chlorinated to monochlorodifluoroethane. Further substitution is also possible, but tends to result in carbon-carbon rupture, which ultimately becomes so great as to lead to the proposal of chlorinolysis as a practical synthesis for CCl_2F_2 . At elevated temperatures, difluoroethane will lose HF to form vinyl fluoride, as discussed under the manufacture of the latter compound. Apart from these two reactions the product is surprisingly stable and has found a definite market as a refrigerant in azeotropic combination with Refrigerant-12⁴⁰.

$\text{CH}_3 \cdot \text{CClF}_2$ —The purified commercial product normally consists of the single isomeric form. It may be readily dehydrochlorinated to form vinylidene fluoride, and usually forms the basic intermediate in the manufacture of that olefin. The flammability of the compound has somewhat restricted commercial development, but the excellent solvent properties have led to at least limited use as an aerosol propellant.

$\text{CH}_2=\text{CHF}$, $\text{CH}_2=\text{CF}_2$, $\text{CClF}=\text{CF}_2$, $\text{CF}_2=\text{CF}_2$ and $\text{CF}_3 \cdot \text{CF}=\text{CF}_2$ —The reactions of primary commercial significance are the polymerizations discussed below under Manufacturers and under Applications. These compounds also dimerize at elevated temperatures to form an interesting series of four-membered ring compounds, but at present these seem to have little commercial significance except perhaps for cyclic C_4F_8 , which may find use as a highly stable propellant. All undergo standard addition reactions, but

PROPERTIES

in general, such products have proved of limited commercial value, with a possible exception of $C_2Br_2F_4$. All save the last of these compounds are flammable, but in general it would appear that they have remarkably good hydrolytic and thermal stabilities.

It is beyond the scope of this article to discuss the chemical properties of the many other fluorochemicals knocking at the door of commercialization. In a great majority of cases, however, these compounds base their claim upon the possession of some functional property, and their chemistry is therefore determined largely by this active group. These compounds also tend to be the ones most thoroughly covered by the conventional chemical literature, and their properties are hence readily available to the general reader.

Specifications

In addition to information on the properties of a pure compound, it is frequently of interest to know the degree to which a commercial product approximates to this ideal. Fortunately, the rigid demands of the refrigeration industry have enforced great emphasis on quality control, and while there is some variation from product to product and between manufacturers, the following generalizations will commonly hold true for commercial quantities of the five major products. Most manufacturers are happy to discuss their specification analyses with customers⁴¹, and for this reason, the section below will not attempt to cover analytical techniques.

Moisture

The solubility of water in the perhalogeno-products is about 100 p.p.m. by weight at room temperature, and increases only to about 1000 p.p.m. for compounds such as $CHClF_2$. This in turn created one of the few problems encountered in the original application of fluorocarbons as refrigerants, namely icing of the expansion orifice. In early practice it was common to add small amounts of methanol to increase water solubility, but since this tended to offset the stability advantages of the fluorocarbon, the technique was soon abandoned, and replaced by product specifications limiting the moisture content to about 25 p.p.m. This figure has since been steadily lowered, and current moisture limits are generally *ca.* 10 p.p.m. by weight. Such low levels are achieved on a routine commercial basis only through meticulous techniques and unremitting vigilance, since it is rare that an inexperienced person can effect the transfer from a factory package to a second container without at least doubling the water content. The low moisture content, of course, enhances the stability of the fluorochemicals, but it would appear that the present trend has reached a point of diminishing returns. This arises not from the inability of the manufacturer to produce a drier product, but from the fact that the motor windings and lubricating oil of the refrigerator compressor already contribute far more moisture than is initially present in the refrigerant.

Residue, Colour, etc.

Partly because of specialized uses, and partly because of relatively high prices, product appearance has always been above reproach. Typical commercial material will almost always be water-white, and even upon

THE ORGANIC FLUORO-CHEMICALS INDUSTRY

evaporation will show only a few p.p.m. by weight of either particulate matter or soluble non-volatile residues.

Acidity

For obvious reasons acidity has been another prime concern of the industry, and commercial products will characteristically contain far less than 1 p.p.m. of acidic contamination.

'Non-condensables'

For refrigerant service, the content of 'non-condensable' gases is a major concern and, for those products which are sold as liquefied gases, the air content of the liquid phase is normally only 100–200 p.p.m. by volume. Since the major proportion of the contents is in this liquid phase, the foregoing figure is very close to the true, overall concentration of non-condensables. However, because of the greater ease of analysis, it is customary to quote specifications in terms of the gas phase concentration, where the great enrichment ratio is reflected by corresponding equilibrium values in the range of 0.5–1.0 volume per cent.

Organic Purity

Considerations of stability have likewise placed a premium upon organic purity, and the typical commercial product will commonly exceed 99.9 per cent. Since the usual organic impurities are almost as inert chemically as the parent compounds, analyses have always been made by physical methods. Historically, the primitive techniques of boiling range and molecular weight were soon superseded by infra-red and mass spectrometric analyses, and these techniques, in turn, are rapidly being replaced by gas chromatography. Indeed, the extraordinarily low concentration of the individual impurities renders many of them undetectable by any other technique. Isomer ratios are not usually covered by specifications, but typical commercial performance has already been discussed under Chemical Properties.

The above pattern of purity, though essential for refrigerants, is of course far more stringent than that required by the equally important propellant market, where the pressuring agent is customarily mixed with an active ingredient which may range from hair lacquer to flea powder. However, since dual product lines offer little if any savings, it seems likely that the requirements of the refrigerant market will continue to set the general standards of the fluorochemicals industry. Although quality control is sometimes not as uniform for developmental fluorocarbons, the standards set by the major products are clearly evident. In fact, for specialized uses such as dielectrics or polymerization intermediates, specifications may become even more stringent, and additional impurities may be limited to the p.p.m. range.

Technological Data

Standard chemical and physical properties are of common scientific interest, and are hence published promptly in the general literature. There also builds up, however, a large body of more specialized data which are published only in trade journals or manufacturers' bulletins, and hence remain unknown to the general scientific community. In the case of the

HANDLING

fluorocarbons, this information ranges from such general topics as solubility parameters and the vapour pressures of mixtures, to relatively esoteric items such as the velocity of sound in CF_4 . Data of this type become more available through periodic collection and republication, but such efforts are usually restricted to the interests of a single industrial application, as illustrated by recent comprehensive reviews of aerosol technology^{42,43}.

The best general source of such technological information is probably the manufacturer, who will usually be familiar with both the scientific and technological literature and may also have published pertinent technical sales bulletins. As the oldest producer, Du Pont has the largest file of such bulletins, comprising some eighty items of general interest and as many again dealing with specialized phases of application. However, other companies are also diligent in the field of technical service, and the industry as a whole provides a surprisingly complete fund of technical information on its products.

HANDLING

The following section is devoted to a group of related problems peculiar to the finished products of the fluorochemical industry: special techniques, regulations and hazards.

Shipping

In view of the high stability and low toxicity of the major fluorocarbons, external regulation of shipping practices might appear unnecessary. This would probably be true were not many of the largest items of commerce shipped as compressed, liquefied gases, and as such, in the United States fall within the rigorous shipping regulations of the Interstate Commerce Commission⁴⁴. The definition that covers such fluorochemicals is that portion of Clause 73.300 which establishes the applicability of Subparts A and F to 'any compressed gas', which is defined as a material exerting an absolute pressure exceeding 40 p.s.i. at 70°F, or 104 p.s.i. at 130°F, or both. These two subparts are the only portion of the Regulations applicable to any of the major fluorochemicals of Table 1, and hence will be the only ones considered below. Fluorochemicals presenting special problems of flammability or toxicity, are, of course, subject to the many other subparts dealing with these hazards, but historically such restrictions may be viewed as superimposed on the basic hazard of pressure. Potential shippers must, of course, consult the appropriate regulations directly, but the following brief discussion may give the general reader an appreciation of their underlying spirit.

A great proportion of the pertinent regulations is occupied with the safety of the containers themselves. Rigid and detailed instructions are provided in 73-A and 73-C covering the fabrication, testing, and marking of such pressure vessels. In addition, many facets of installation are regulated by 73-F, such as periodic testing, safety devices, manifolding of containers and gauging of large tanks. The overall result of these two sections is to guarantee a well-designed container which is not only safe and reliable in itself, but also in respect to the various fittings and attachments normally required.

The remainder of 73-F is concerned with the rules governing the loading of such containers. The fundamental criteria (73.304) are that (a) at 70°F

the pressure of the contents should not exceed the service pressure stamped on the cylinder, (b) at 130°F this internal pressure shall not exceed five-fourths of the service pressure, and (c) at 130°F the liquid contents, if any, shall not completely fill the cylinder. Before these criteria are accepted too literally, however, it must be appreciated that they are merely historical attempts to capture the true spirit of the regulations. In its basic form, this latter concept is simply a guarantee that the pressure within a container will never exceed the bursting limits of that container during reasonable conditions of transit or storage. Where additional experience (backed by precise data) has shown the letter of the law to be too restrictive in terms of this basic concept, modifying clauses have been promptly inserted. A number of such cases, and their justifications, are discussed below in the section on Hazards of Pressure. These modifications, however, should not obscure the fact that most of the hundreds of millions of pounds of fluorochemicals annually transported in the United States are covered explicitly by the three criteria set forth at the beginning of this paragraph.

The remainder of the regulations on compressed gases is devoted to numerous special cases involving specific products. In some instances, such as aerosols, carbonated beverages, etc., the products are exempted from all or part of the regulations under certain specified conditions of packaging and labelling. This is also true of certain small samples and of equipment such as refrigerators and fire extinguishers. In contrast to these exceptions, which recognize the decreased hazards of the product in question, there is another group in which the exceptions take the form of increasing the rigidity of the regulations. These range from additional safety precautions (acetylene or elementary fluorine) to outright prohibition (mixtures which may react in transit).

In addition to the above general types of exceptions, there is a special category (which includes many of the major fluorochemicals) in which certain compounds are listed by name (Section 73.308). For each such compound there are also listed specific permissible shipping containers and maximum filling densities (per cent ratio of the weight of product in the container to the weight of water that the container will hold). In some cases, this represents an additional restriction over and above the general requirements, but in many others (such as the original fluorocarbon refrigerants) the listing does not fundamentally affect the shipping practice set forth in the basic regulations. Historically, this listing recognized the special hazards associated with liquefied gases (see Hazards of Pressure, below) and served both to identify those materials which are shipped regularly in large quantities, and to specify the precise conditions under which, by previous agreement, all shipping operations would be conducted.

In review, it may be said that the fluorochemical industry has escaped fairly lightly in terms of regulation. The basic chemicals upon which the industry grew have presented only the single hazard of pressure, and this picture has not been greatly altered by the fact that an occasional compound (such as tetrafluoroethylene) requires chemical inhibition or that others (such as difluoroethane) present flammability hazards. What the future holds depends, of course, upon the nature of the compounds with which the industry grows. The long history of close co-operation with regulatory bodies,

HANDLING

however, seems a guarantee that these new problems will be met in a safe and effective manner.

Storage and Transfer

Although the general mechanics of storing and transferring fluorocarbons are not unusual, a considerable body of specialized procedures has been evolved over the years. Such detailed technology is properly dealt with in handbooks, but it may be helpful to indicate here some of the areas which have proved to be of unusual concern. In the case of particular problems, the reader will find that the manufacturers can give considerable technical assistance.

While the industry may have no problems which are truly unique, certain factors combine to create difficulties which are at least quantitatively outstanding. The key points usually derive from the high cost of the products and the difficulty of detecting leakage. These are compounded by the typically high densities, whereby the leakage of as little as two cubic feet of gas to the atmosphere can correspond to the loss of a full pound of material. As a result, the industry has always utilized the most advanced technology and equipment available—building originally on experience with such older compounds as SO_2 , NH_3 and Cl_2 . However, despite a continuous concern with this aspect of manufacture, the older technology has held up remarkably well, and even today the industry places primary reliance on conventional valves, welded pressure vessels, and a variety of standard connecting devices—variously welded, screwed, flared, flanged, or swaged. These have, of course, been modified with time to make use of new materials and to ensure maximum safety, but the basic evolution during the last thirty years has been primarily an ever-increasing attention to the meticulous details of fabricating, assembling, and testing such equipment.

This absence of dramatic change in techniques and procedures, however, should not obscure the steady development in these areas. As an example, many years of experimentation with pipe lutings has gone into the current choice of Teflon tape for this purpose. Similarly there has been a steady development in the design of valves and other closures, with the aim of making them more positive in action and easier to use. Paralleling this has been the increased use of direct pressure-relieving safety devices for cylinders, rather than the older fusible plugs. Another recent innovation is a quick-lock closure for the transfer lines employed by refrigerator servicemen in charging home units. These individual items may appear minor, but in the aggregate they have resulted in a major overall improvement, not only in the techniques of handling fluorochemicals, but in the concomitant advantages of lowered contamination.

The problem of detecting leakage has always been of particular concern to the industry, and has been handled in a number of different ways. The oldest technique of all, of course, is the use of a soap solution for testing small localized areas. For larger equipment, and for leaks giving a local concentration above 100 p.p.m., the Bunsen halide test has proved quite effective. Small, portable devices heated by methanol or bottled gas are available through most supply houses, and are widely used. A more sophisticated approach is furnished by various electrical devices based upon ionization of

an air sample. These instruments have sensitivities far in excess of those possible with the halide-type detector, though in field use it is seldom possible to take advantage of their full potential because of other atmospheric impurities. In the manufacture of sealed refrigerator units, however, where the necessary precautions can be taken, testing procedures can be so refined as to limit total leakage to a few grammes in the twenty-year life expectancy of the installation.

The dynamics of transferring liquefied fluorocarbons present few new problems beyond the difficulties of keeping the moving parts tight. Despite the availability of such newer devices as fully enclosed pumps, many large-scale commercial installations are still based upon the use of conventional turbine pumps with mechanical seals, installed and maintained with great care. One subsidiary consideration that must be taken into account is that stored fluorocarbons, despite their apparently high vapour pressures, are always actually at their boiling points, so that the heat of pumping may easily cause flashing and consequent vapour binding. Once recognized, this is only a minor problem, since it may be overcome by pressuring with an inert gas, use of a hydrostatic suction head, or pre-cooling the material as it enters the pump.

From the foregoing discussion it might be concluded that the industry was singularly favoured by having all its handling problems reducible to the straightforward technique of containing an inert product. The difficulty of achieving this consistently on a large industrial scale should not be underestimated, however, particularly in view of the prevailing high standards of performance. To some extent this is also true of other problems, such as contamination by moisture and air. At current specification limits, serious problems are created by minute amounts of these impurities adsorbed on

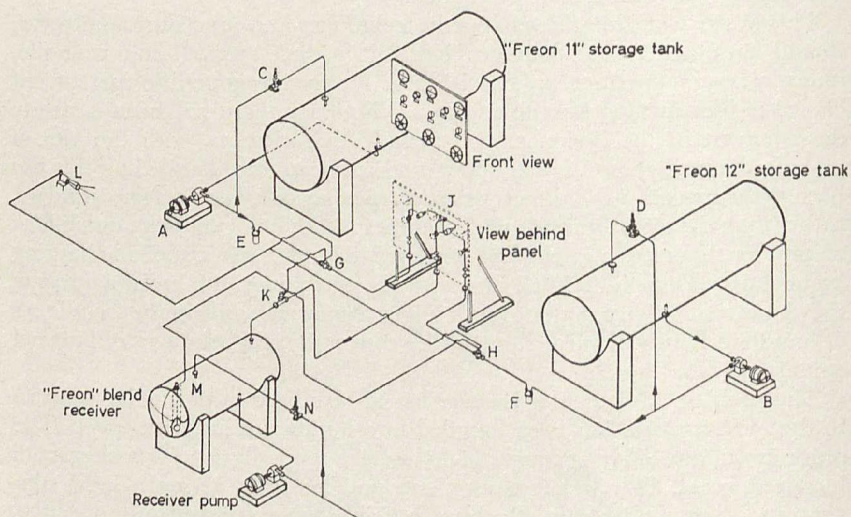


Figure 5. Blending facilities. (A, B—pumps; C, D—back-pressure regulators; E, F—filters; G, H—low-flow switches; J—blending panel; K—solenoid valve; L—alarm buzzer; M—float switch; N—back-pressure regulator)

HANDLING

container walls, and even simple metal sampling lines can desorb enough water to interfere seriously with a quality control programme.

As mentioned earlier, the manufacturers stand ready to supply considerable information and advice to customers desirous of using their products. This is particularly evident in the field of customer blending, which has become an important activity of the larger aerosol loaders in order to avoid multiple purchases of the many special mixtures required for their business. *Figure 5* is an illustration of a recommended installation and is merely one item in a 28-page booklet devoted to details of equipment specifications, installation, and operation of such a device⁴⁵.

Hazards

Pressure

Historically, pressure has been the only common source of hazard associated with the major fluorochemical products. For this reason, it is perhaps well to examine the exact nature of the danger in some detail⁴⁶.

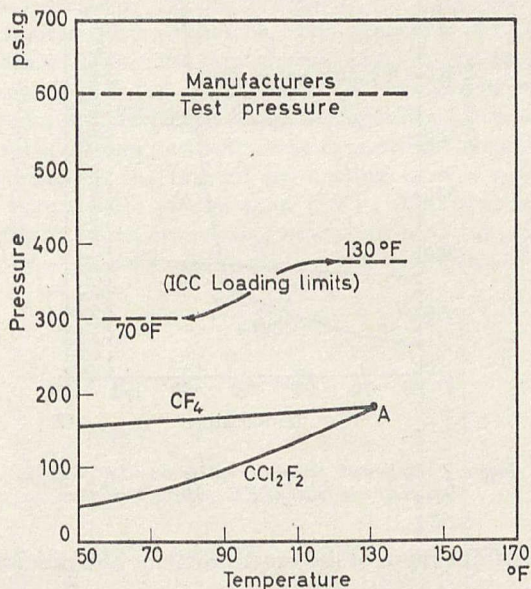


Figure 6. Pressure relations in a properly loaded ICC—4BA300 cylinder

It might be expected that this type of hazard would commonly arise through the use of substandard equipment. In actual commercial practice, however, this problem has been virtually eliminated by the competent engineering groups responsible for design and fabrication. These groups, in turn, are subject to continual monitoring by a variety of regulatory bodies, some functioning within the various companies, others under the external control of state and federal government. Only in the case of small-scale or laboratory equipment does a significant possibility exist that basically inadequate equipment will be used, and even here a few common-sense precautions will usually result in apparatus which is safe to operate.

THE ORGANIC FLUORO-CHEMICALS INDUSTRY

Experience has shown that mishaps are usually traceable to poor operating practices, particularly the overfilling or overheating of containers. In the absence of proper safety devices, these can result in rupture of the container, which will then be converted into a deadly projectile by the rapid escape of the contents. The hazard is eliminated in commercial cylinders, of course, by the many precautions taken to assure proper loading and to provide for emergency pressure relief. However, none of this will protect a purchaser, should he elect to transfer part of the contents to a second container. Since this occurrence is not infrequent, particularly in connection with sampling, it

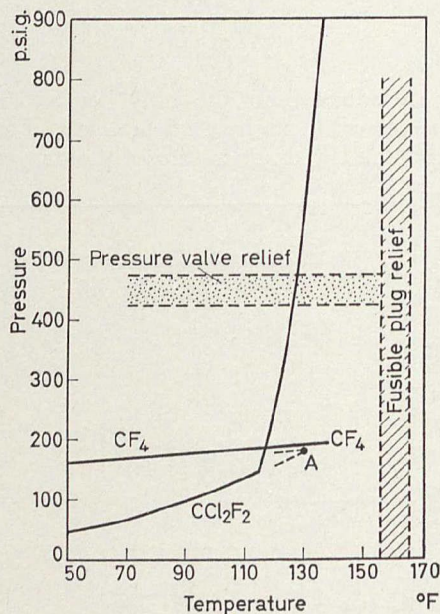


Figure 7. Hydrostatic pressure of refrigerant—12(CCl_2F_2).
Caused by over-filling of ICC—4BA300 cylinder

is felt that a brief discussion of the exact problems and necessary safeguards is worthwhile.

Ultimately, of course, safety is guaranteed by assuming that error will occur, and providing for some pressure relief device. Such safeguards, naturally, are no substitute for good operating practice, which consists essentially of choosing conditions which will guarantee acceptable pressures throughout the chosen temperature range. However, though these generalizations would be accepted by any responsible person, even the most conscientious worker is sometimes ignorant of the vast difference in the consequences of an error involving a liquefied gas, as compared to the same error made using a compressed gas. This can perhaps best be dramatized by contrasting the behaviour of the liquefied gas, CCl_2F_2 (b.p. -21.6°F , critical temperature 233.6°F) with that of the compressed gas, CF_4 (b.p. -198.4°F , critical temperature -49.9°F).

HANDLING

Figure 6 shows the behaviour of both types of material under proper conditions of loading and use. The liquefied gas is illustrated by the curve marked CCl_2F_2 , which simply reflects the vapour pressure of the liquid contents at all temperatures up to 130°F (the upper limit of concern to the Interstate Commerce Commission). If the cylinder is an ICC-4BA300, frequently used in this service, the pressure at 130°F will be well below the 360 p.s.i.g. ICC limit for this temperature, and even further below the manufacturer's minimum original test pressure of 600 p.s.i.g. The comparable behaviour of a compressed gas is shown by the curve marked CF_4 , which assumes that the cylinder was charged so as to give the same pressure at 130°F . Since CF_4 cannot be condensed above -49°F , it exists merely as a compressed gas throughout the range of immediate concern and, being only slightly associated, follows essentially a simple PT curve.

Both the above situations are equally legal and safe. However, Figure 7 shows the dramatic contrast which appears if the containers are accidentally overfilled by 5 per cent. The CF_4 cylinder will simply exhibit an approximate 5 per cent increase in pressure throughout the range (illustrated relative to Point A, transferred from Figure 6). The behaviour of CCl_2F_2 , however, will be quite different, since the legal charge (Figure 6) was originally selected so that the expanding liquid would nearly fill the cylinder at 130°F . Any significant surplus will therefore cause the cylinder to become liquid-full below 130°F , with a consequent abrupt rise in pressure. As might be expected, a similar situation can be created by heating even a properly charged cylinder to a temperature greater than 130°F . This is shown in Figure 8, which again illustrates the contrasting behaviour of CCl_2F_2 and CF_4 .

The figures also illustrate the action of the two types of safety device:

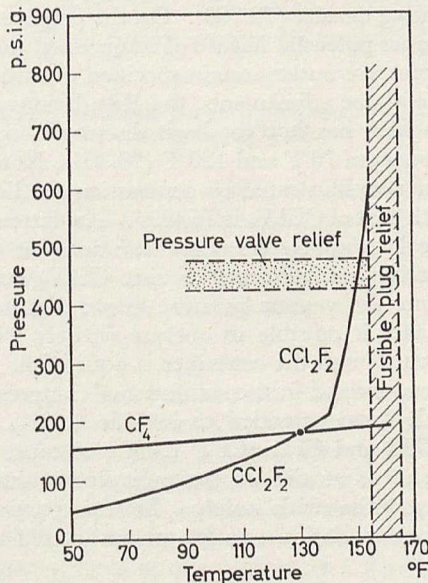


Figure 8. Hydrostatic pressure of refrigerant—12(CCl_2F_2)
Caused by overheating ICC—4BA300 cylinder

direct (frangible disc or pop valve) and indirect (fusible plug). The obvious merit of the former is that, if properly installed, it will provide safe relief under any set of circumstances. It is, therefore, generally to be preferred for applications such as sample cylinders, where loading procedures are not rigidly routinized. On the other hand, commercial loading provides just this type of rigid control, and explains the historic preference for fusible plugs. The current industrial trend seems to be in favour of the more troublesome, but more versatile, direct-acting types, although larger containers will frequently be equipped with both.

In this connection it may be noted that the performance of the fusible plug in *Figure 8* represents the extreme case of isothermal heating. In actual practice, the cylinder is always hotter than the contents, and in cases of rapid heating (as with the unwise practice of torching cylinders) the plug will melt long before the contents have reached a pressure corresponding to 130°F. A similar phenomenon may be observed in dark or rusted cylinders exposed to direct sunlight. Since the metal wall and the contiguous film of liquid are normally 30–40°F above atmospheric temperature, the effective vapour pressure of the system on a hot day may easily correspond to 130°F or even slightly higher. Test thermocouples, however, will show that the bulk of the liquid contents remains at essentially atmospheric temperature, and that the cylinder is far from liquid-full under these circumstances. It may be noted that this superheating effect is greatly reduced by coating the cylinder with aluminium paint, and that certain brands of white paint will essentially eliminate the problem.

The hazards implicit in the above illustrations are directly reflected in the ICC Shipping Regulations⁴⁴, and explain the explicit prohibition of liquid-full containers (73.304a) as well as the practice of registering, by compound, the precise legal loading density (73.308). On the positive side, the Regulations recognize the lesser potential hazard of compressed gases by authorizing a 10 per cent over-pressure under certain specified conditions (73.304d).

In addition to the above adjustments, the Regulations also recognize an area of vagueness which has not yet been discussed—compounds with a critical point lying between 70°F and 130°F (73.304a, Note 1). This special case may perhaps be best illustrated by contrasting the liquid behaviour of CClF_3 in *Figure 9* with that of CCl_2F_2 in *Figure 7*. The latter, being more than 100°F below its critical point, behaves as a substantially incompressible liquid, and gives a correspondingly abrupt pressure rise. CClF_3 , however, being near critical, departs from the vapour pressure curve along a gently sloping isometric, which makes it possible to operate entirely within the spirit of the Regulations, even though the container is liquid-full. Historically, this situation was first encountered in the shipment of compressed CO_2 , and the precedent has simply been extended to include CClF_3 , CHF_3 , $\text{CF}_3\cdot\text{CF}_3$, $\text{CF}_2=\text{CF}_2$, $\text{CH}_2=\text{CHF}$ and $\text{CH}_2=\text{CF}_2$. Each case must be decided on its own merits, to ensure that the exception is economically justified and represents no compromise with safety. In the particular instance of CClF_3 the final recommendation was for an authorized loading density of 100 per cent.

It was originally felt that these exceptions would be useful only for compounds with critical temperatures below 130°F (73.304a Note 1). Experience,

HANDLING

however, has shown that safety is influenced solely by the slope of the isometric, and that economic advantages may accrue even for materials with critical temperatures well above 130°F. It was on this basis that vinyl fluoride was authorized for shipment at supercritical densities, despite its critical temperature of 130.5°F (73.304a Note 2). The economic importance of such decisions is considerable, since the cylinders, which must be shipped both ways, frequently weigh more than the contents.

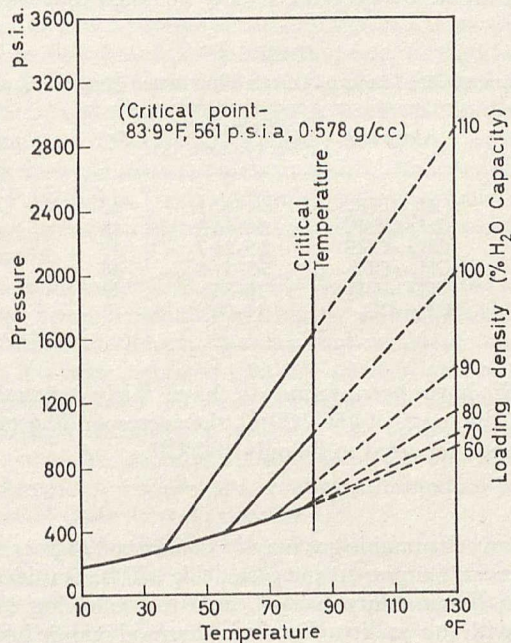


Figure 9. Hydrostatic pressure of refrigerant—13(CClF₃).
(In the critical region)

In summary, it may be seen that while a very real hazard does exist in the handling of certain compressed fluorochemicals, this hazard may be accurately forecast and eliminated by proper procedures. The only requisite for such safety is that all manipulations be carried out by alert and experienced personnel supplied with precise physical data.

Flammability

The major commercial fluorocarbons are completely non-flammable, and this property still characterizes many of the development products such as CClF₃, CF₄, C₂Cl₄F₂, and CBrF₃. To some extent, however, this safety has been counterbalanced by the dangerous assumption, particularly on the part of non-technologists, that any compound containing fluorine is correspondingly safe. Table 4 shows this to be incorrect for any fluorocarbon containing a significant amount of hydrogen or a double bond.

Since the hazards of flammable gases are recognized both in industry and in the laboratory, the subject will not be pursued, other than to point out that

THE ORGANIC FLUORO-CHEMICALS INDUSTRY

fluorocarbons present the additional hazard of by-product phosgene, HCl and HF. This possibility exists when even perhalogeno-compounds are exposed to heat, but extensive tests have shown that the rate of acid formation here is so slow that the fumes merely serve as a useful irritant warning. This is not necessarily the case for fluorocarbons which are themselves flammable, and while the fumes from any fire are necessarily toxic, it is well to bear in mind the additional hazard associated with such fluorinated materials. In connection with the tabulated data, it may be noted that while $\text{CH}_3 \cdot \text{CHF}_2$

TABLE 4
Flammability Limits of Certain Fluorinated Hydrocarbons

<i>Compound</i>	<i>Flammability limits (volume %)</i>	<i>Ref.</i>
$\text{CH}_3 \cdot \text{CHF}_2$	5.1-17.1	48
$\text{CH}_3 \cdot \text{CClF}_2$	9.0-14.8	48
$\text{CH}_2 = \text{CHF}$	2.6-21.7	49
$\text{CH}_2 = \text{CF}_2$	5.5-21.3	48
$\text{CClF} = \text{CF}_2$	16-34	48
$\text{CF}_2 = \text{CF}_2$	11-60	47

and $\text{CH}_2 = \text{CHF}$ have been found to have fairly normal autoignition temperatures in the range of 450-500°C, the corresponding temperature for $\text{CF}_2 = \text{CF}_2$ has been reported to be only 180°C⁴⁷.

Explosivity

In one sense, any flammable gas may be considered to possess an explosive potential. However, for present purposes, this will be considered merely an extension of the flammability hazard, and the following section will be concerned only with the quality of intrinsic thermodynamic instability. Such a definition will immediately exclude the saturated compounds of Table 3, but leaves all the fluoro-olefins, which, as a class, uniformly exhibit some type of instability.

The most common hazard among these olefins results from their tendency to polymerize. Often called 'spontaneous', this is more properly an unintentional polymerization, initiated during storage by some active impurity, such as oxygen¹⁶⁶⁻⁸. Although usually slow and innocuous, these reactions are exothermic, and hence present some potential hazard due to increased temperature and pressure, compounded by the possibility that the relief devices may have become plugged with polymer. The addition of an inhibitor is, of course, an effective safeguard¹⁶⁶⁻⁸ but, except in the case of clear necessity, this is strongly resisted by the purchaser. For this reason, each compound must be judged separately on the basis of its past storage history, the demonstrable polymerization rates, and the likelihood of initiation. At present, U.S. Regulations call for inhibition of three such olefins: tetrafluoroethylene, chlorotrifluoroethylene and vinyl fluoride. Increased experience, however, may dictate either the addition of further compounds, or (particularly in the case of refrigerated shipment) the relaxing of present requirements.

HANDLING

A variant of polymerization is the ability of the fluoro-olefins to form cyclic dimers⁵⁰. However, although these reactions are exothermic and not subject to inhibition, they are rapid only at rather high temperatures and pressures, and hence are believed to present little practical hazard under storage conditions.

In the usual sense of the word, neither of the above reactions is truly explosive, and the resultant pressure surges can easily be relieved by conventional protective equipment. Under extreme conditions, however, most of these olefins can also undergo decomposition reactions yielding pressure surges in the range of 1-5 p.s.i./msec. Normal relief devices are not designed to cope with such surges; but fortunately, these reactions usually require that the material be under an initial pressure of several hundred pounds, and that the ignition source be one of considerable vigour, such as a glowing wire, an arc, or in some cases a thermite squib. Because of these extreme requirements of initiation, it is generally felt that such decomposition reactions do not present a significant hazard under normal conditions of storage or transport.

One notable exception to this generally innocuous pattern is tetrafluoroethylene, whose history includes a number of explosions^{50,51}. In cases involving *uninhibited* monomer, the residual evidence usually included polymer, and it has been theorized that this unintentional reaction served as an initiating mechanism for the decomposition, with dimerization perhaps acting as a 'booster'. Experience indicates that *inhibited* monomer is completely safe at room temperature storage, but even this material must be handled with extreme care if used as a reaction intermediate, since explosions have been reported under certain conditions⁵⁰.

It may thus be concluded that only the fluoro-olefins present any true explosion hazard, and that proper handling procedures will ensure even their safety. However, particularly in the case of tetrafluoroethylene, such work should only be carried out by competent personnel who have been thoroughly instructed in the problems involved.

Toxicity

The major commercial products of Table 1 exhibit a very low order of toxicity. This is also true of their more highly fluorinated homologues, and these familiar examples have unfortunately led many persons to assume that such safety is a general characteristic of fluorocarbons. Actually, this class of compounds has been found to run a complete gamut of toxicity, ranging from the entirely innocuous to the quickly lethal.

It is the primary purpose of this section to indicate a few of the general trends that have been observed among the simpler fluorocarbons, and to point out some of the potential hazards. For more detailed information, the reader should consult the toxicological reviews by von Oettingen⁵² and Pattison⁵³ as well as standard references such as Fairhall⁵⁴ or Patty⁵⁵. In specific cases, supplementary information may be obtained from the publications of various regulatory bodies, or directly from the manufacturers of fluorochemicals.

In connection with the data which follow, it will be noted that some of the compounds have been characterized in terms of their U.S. Underwriters'

THE ORGANIC FLUOROCHEMICALS INDUSTRY

Classification. This code is discussed in Appendix C, but may be briefly described here as a numerical system in which the increasing numbers correspond to decreasing degrees of toxicity. Compounds in categories 1 to 4 will all produce death or serious injury within two hours at concentrations below 2-1/2 per cent, while those in category 6 cause no apparent injury even after two hours at 20 per cent. Materials rated between these two categories exhibit a correspondingly intermediate range of toxicities.

Another common criterion—related to toxicity but not used here—is the Maximum Allowable Concentration (MAC) for repeated eight-hour exposure. These numbers, which are assigned by various scientific and regulatory bodies, are not particularly useful for the present purpose since they take into account too many cumulative long-range effects to provide a good comparison of acute toxicities. It may, however, be noted that the MAC's of most of the standard commercial refrigerants and propellants have been set at 1000 p.p.m., the generally accepted highest allowable value.

Fluoromethanes—The relative acute toxicities of a number of chlorofluoromethanes are shown in Table 5. This tabulation has been so arranged that

TABLE 5
Underwriters' Laboratories Classification*
for Certain Halogenated Methanes

<i>Compound</i> †	<i>Underwriters' classification</i> ⁵⁶
CCl ₄	3
CCl ₃ F	5a
CCl ₂ F ₂	6
CClF ₃	6
CF ₄	6
CHCl ₃	3
CHCl ₂ F	5
CHClF ₂	5a
CHF ₃	6
(CHCl ₃)	3
(CCl ₃ F)	5a
CH ₂ Cl ₂	4-5
(CHCl ₂ F)	5
(CCl ₂ F ₂)	6

* See Appendix C for definition of categories.

† Compounds in parentheses have been repeated for comparison.

the first two groups illustrate the steady decrease in toxicity as chlorine is replaced by fluorine. The third and fourth groups illustrate an effect that is less generally appreciated: the decrease in toxicity that accompanies replacement of the hydrogen.

Table 6 shows a more limited comparison among halogenomethanes containing bromine. Here again, however, the various comparative groupings clearly show the beneficial effects of fluorine substitution, regardless of whether it is replacing a bromine, chlorine, or hydrogen.

HANDLING

While a comparison of Tables 5 and 6 shows that the bromine-containing methanes are always more toxic than their chloro analogues, the presence of enough fluorine can produce a molecule of very low toxicity, e.g. CBrF_3 is in Underwriters' Classification 6.

TABLE 6
Underwriters' Laboratories Classification*
for Certain Halogenated Methanes

Compound†	Underwriters' classification ⁵⁶
CBr_2F_2	4
CBrF_3	6
CClBrF_2	5a
CClF_3	6
(CClBrF_2)	5a
(CBrF_3)	6
CH_3Br	2
(CBrF_3)	6
CH_2ClBr	3
(CClBrF_2)	5a

* See Appendix C for definition of categories.

† Compounds in parentheses have been repeated for comparison.

Fluoroethanes, etc.—The data on halogenoethanes are too scattered to justify the detailed comparisons of the preceding section. However, many of the same generalizations seem to apply, as evidenced by the separate contributions of Greenberg, Carpenter, Henne, Robbins, and Park⁵⁷⁻⁶¹. From these data, and from the Underwriters' Ratings of such compounds as $\text{C}_2\text{Cl}_3\text{F}_3$ (category 4-5) and $\text{C}_2\text{Cl}_2\text{F}_4$ (category 6), it seems safe to conclude that highly fluorinated, saturated hydrocarbons will generally possess low toxicities. The pitfalls of detailed predictions, however, are illustrated by the data of Carpenter⁵⁸, who reports $\text{CH}_3\cdot\text{CHF}_2$ to be substantially more toxic than $\text{CH}_3\cdot\text{CH}_2\text{F}$. This observation is even more significant in view of the data of Greenberg and Lester⁵⁷ and Henne and Rennol⁵⁹ which indicate that the unsymmetrical difluoro-isomers are the less toxic.

Fluoro-olefins—These compounds present the widest range of acute toxicity values to be found in the fluorochemicals field. This is well illustrated by the data of Table 7, but in view of the relatively small number of compounds represented, the only other permissible generalization is that extreme care should be taken in any experimental work that may result in the production of fluoro-olefins. It should be stressed that the figures represent only acute toxicities. It has been found that a low acute toxicity will frequently unmask long-range damage, with the result that the MAC may be much further below the LC-50 than might have been expected.

Specific Physiological Effects of Fluorochemicals—Irritation of the respiratory system is a common condition noted in animals exposed to the more toxic organic fluorine compounds, and death is often a result of gross pulmonary damage involving oedema and hæmorrhage. For the relatively non-toxic

THE ORGANIC FLUORO-CHEMICALS INDUSTRY

compounds, evidence of irritation may be completely absent or appear in slight degree only after massive exposure.

Narcosis and anaesthesia are observed in animals exposed to certain of the fluorinated hydrocarbons, the effect generally decreasing as the number of fluorine atoms is increased. Despite these effects, most of the common fluorine compounds are not particularly suitable as anaesthetics, either failing to produce deep anaesthesia or exhibiting a dangerously small difference between anaesthetic and hazardous concentrations. Exceptions to this generalization, however, are being widely exploited at the present time in the growing field of fluorinated anaesthetics.

TABLE 7
Acute Toxicities of Halogenated Olefins

<i>Compound</i>	LC-50* p.p.m. by volume	<i>Ref.</i>
Vinyl fluoride, $\text{CH}_2=\text{CHF}$	800,000 (80 per cent)	57
Vinylidene fluoride, $\text{CH}_2=\text{CF}_2$	128,000	58
Tetrafluoroethylene, $\text{CF}_2=\text{CF}_2$	40,000	62
Vinylidene chloride, $\text{CH}_2=\text{CCl}_2$	32,000	58
Trichloroethylene, $\text{CHCl}=\text{CCl}_2$	8,000	58
Chlorotrifluoroethylene, $\text{CFCl}=\text{CF}_2$	4,000	58
Tetrachloroethylene, $\text{CCl}_2=\text{CCl}_2$	4,000	58
Hexafluoropropylene, $\text{CF}_2=\text{CF}-\text{CF}_3$	3,000	62
1,1-Dichloro-2,2-difluoroethylene, $\text{CCl}_2=\text{CF}_2$	1,000	58
Perfluoroisobutylene, $\text{CF}_2=\text{C}-\text{CF}_3$ CF_3	0.5-1.0	62

* Exposures resulting in fatality of approximately 50 per cent of rats in four hours.

Organic damage by fluorinated hydrocarbons appears to be less than that from the corresponding chlorine compounds, at least as they affect the liver, kidneys, spleen and heart. The generalization, however, cannot be extended to the unsaturated fluorine compounds, where substantial damage has been observed after chronic exposure to fluoro-olefins of low acute toxicity.

In summary it may be said that the addition of fluorine to halogenated molecules is generally beneficial and that the saturated perfluorocarbons have a very low order of toxicity. Beyond this, however, generalizations are difficult, since fluorinated chemicals cover a broad spectrum of toxicity and include compounds of extraordinary hazard. Because these latter frequently appear as impurities even during the synthesis of the most stable fluorocarbons, all experimentation should be carried out with suitable precautions.

MANUFACTURE

Little explicit information has been published on the manufacturing technology used in the fluorochemicals industry. Nonetheless, patents and the published literature usually contain one or two synthetic routes which stand out in terms of apparent practicality and economics, and these have been described below as probably illustrative of the most widely used technology. It must be remembered, however, that most fluorochemicals are made according to complex continuous processes, and that the details of application

MANUFACTURE

may differ widely even for the same basic process. It is also worth noting that present industrial technology employs only a small fraction of the many known synthetic routes to fluorocarbons. By way of compensation, however, the numerous syntheses which are not considered below are the ones most thoroughly discussed in the standard literature.

Major Fluorochemicals

All the major fluorochemicals of Table 1 may be considered as belonging to one of three families, derived respectively from CCl_4 , CHCl_3 or C_2Cl_6 . Although many syntheses have been proposed, it appears that all present manufacture is based on reaction between these basic chlorocarbons and HF. The resulting processes are relatively standard, and are reducible to a few essential and straightforward steps, illustrated in *Figure 10* and described

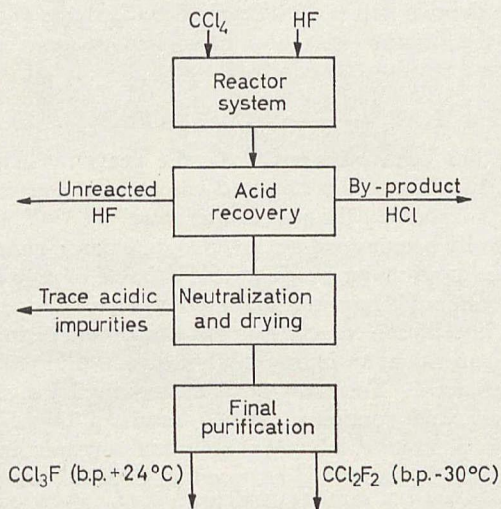
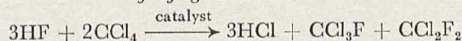


Figure 10. Typical flow diagram for the manufacture of refrigerants 11 and 12

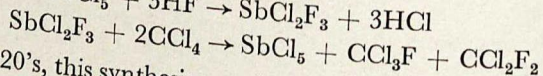
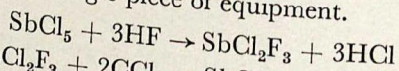


below. Actual manufacture is carried out in conventional chemical equipment, with the overall installation following the modern trend toward open-air construction (*Plate 1*). Even between the various products, the differences are almost trivial, and consist of such variations as feeding $\text{CCl}_2=\text{CCl}_2$ plus Cl_2 instead of the parent C_2Cl_6 , in order to minimize handling problems⁷⁵. Because of the simplicity of the chemistry and the stability of the products, yields are very high, and are limited almost solely by handling losses plus trace impurities in the starting materials.

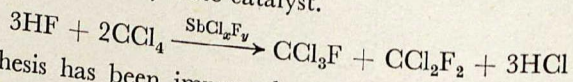
Synthesis

The non-catalytic reaction between HF and a chlorocarbon is quite sluggish, and requires extremes of both temperature and pressure to attain practical rates of production¹²⁸. In the presence of a suitable catalytic agent, however, reaction is rapid and can be carried out liquid or vapour phase over

a fairly wide range of temperatures and pressures. The original synthesis developed by Swarts²³ was a liquid phase fluorination in which SbF_3 was first contacted with chlorocarbon, and then recovered and refluorinated in a separate step. Even after the beneficial effects of added chlorine were discovered, the overall synthesis continued to be a two-step process, although now carried out in a single piece of equipment.



In the late 1920's, this synthesis was developed by Du Pont into a continuous process, the pentavalent antimony now acting more as a true catalyst, with continuous feeds of carbon tetrachloride and hydrogen fluoride⁷²⁻⁷⁷. In this embodiment the antimony salt might still be described as a fluorinating agent, but, since the two halves of the cycle described above are carried out simultaneously, the fluorine may also be looked upon as simply passing smoothly through a steady-state catalyst.



This synthesis has been improved over the years by extensive process studies, and remains one of the standard commercial routes to the major fluorocarbons. As traced by the patent literature^{72-77, 97-99}, these improvements have generally been aimed at the creation of a self-contained, flexible system, applicable to all major products and capable of producing mixtures of homologues at the ratio required to match a given sales pattern.

A commercial installation can consist most simply of a heated reaction pot charged with a pentavalent antimony catalyst dissolved in partly fluorinated organic intermediates⁷⁷. This reactor is surmounted by a conventional distillation column and condenser, which return a liquid reflux stream containing any vaporized catalyst or undesired organic intermediates⁷⁶. The ability to return the intermediate product depends upon the fact that each successive fluorination lowers the boiling point of the chlorocarbon by 40-50°C. The equipment may be constructed of steel or various stainless alloys, and steam may usually be used to heat the reactor.

Actual operation is carried out by feeding liquid HF and chlorocarbon to the reactor, and simultaneously (through proper control of the condenser temperature) withdrawing HCl and the desired organic product as vapour from the top of the reflux condenser^{76, 99}. Satisfactory operating conditions cover wide ranges^{72-77, 97-99}; pressures from 0 to 500 p.s.i.g., reactor temperatures from 45 to 200°C, catalyst concentrations from 10 to 90 wt. per cent and product take-off temperatures from -30 to +100°C. Because of the simplicity of the chemistry and the interdependence of the operating variables there is no single optimum set of conditions for any one process, but rather a series of essentially equivalent combinations. As an example, based on Reference 97, we can take a process fed with CCl_4 and HF, operating at a pressure of 100 p.s.i.g., a reactor temperature of 80°C and a catalyst concentration of 60 wt. per cent in CCl_3F . With the reflux condenser temperature set at about -5°C the product will consist primarily of HCl and refrigeration grade CCl_2F_2 (all CCl_4 and CCl_3F being returned to the pot as reflux). At a +5°C condenser temperature, however, some CCl_3F

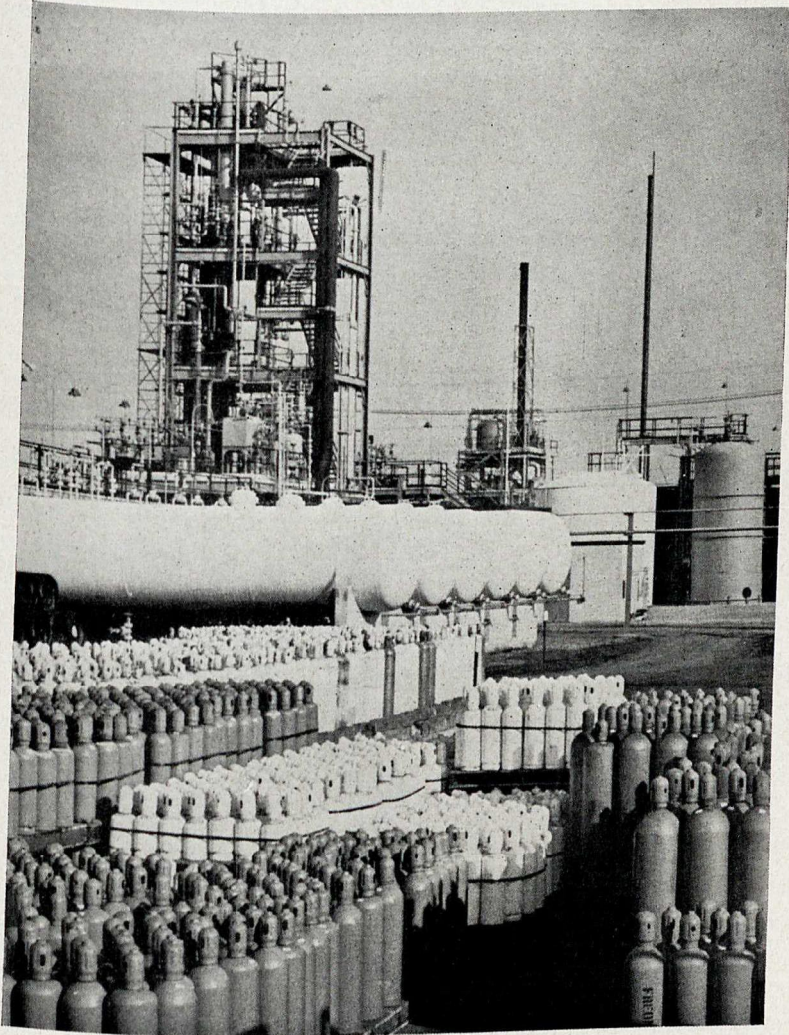


Plate 1. Modern, open-air construction is usually employed for manufacturing facilities

[*opposite page 148*]

MANUFACTURE

will escape, and the organic portion of the crude product will consist of an approximately 9:1 ratio of $\text{CCl}_2\text{F}_2/\text{CCl}_3\text{F}$; at $+15^\circ\text{C}$, the ratio will be about 4:1, etc. With an overall operating pressure of 150 p.s.i.g., however (catalyst temperature and concentration held constant), these identical product compositions can again be obtained, although this time at condenser temperatures of about $+5^\circ\text{C}$, $+15^\circ\text{C}$ and $+25^\circ\text{C}$, respectively. Satisfactory operation is thus possible throughout the range of variables cited in the references, and the choice at an individual installation is likely to be made on the basis of some relatively arbitrary factor such as equipment costs, familiarity with high pressures operation, local costs of refrigeration, etc.

This 'liquid phase' process is well adapted to the production of the major fluorocarbons: CCl_3F , CCl_2F_2 , CHClF_2 , $\text{C}_2\text{Cl}_3\text{F}_3$ and $\text{C}_2\text{Cl}_2\text{F}_4$. It is characterized by simplicity and flexibility of operation, together with easy and accurate control of reaction temperatures. In addition, the pressure-temperature relations of an operable process automatically result in a rapid and effective 'stripping' action by the gaseous HCl , which quickly removes the final organic product from the liquid reaction mass, and thus substantially eliminates overfluorination to unsaleable quantities of CClF_3 , CHF_3 or C_2ClF_5 ⁷⁶. This latter advantage is double-edged, however, and intentional production of these low boiling, highly fluorinated minor products requires operating pressures of several hundred pounds to maintain a liquid catalyst phase. For this reason, the antimony system is at its best in the manufacture of the five major fluorochemicals.

'Vapour phase' processes are also frequently used in commercial manufacture of the major fluorocarbons, and are somewhat simpler to describe. They usually consist of a heated tube (or bank of tubes) filled with a granular catalyst and fed by a vaporized mixture of HF and chlorocarbon. A variety of metallic fluorides have been reported to be effective catalysts for this reaction¹²⁹⁻⁴⁰, and may be charged either in the bulk form, or supported on some suitably inert substrate. As before, the reactor may be fabricated of steel or various stainless alloys, but the requisite higher temperatures are normally obtained by the use of flue gas or electric heaters.

The principal variables are temperature, pressure, contact time and $\text{HF}/\text{chlorocarbon}$ ratio. As in the case of the liquid phase process, wide ranges of conditions are operable¹²⁹⁻⁴⁰; 200 to 500°C , 0 to 300 p.s.i.g., 1 to 60 seconds and 0.5 to 2.0:1.0 ratios having been reported respectively for the principal variables listed above. In an illustrative example, based on the data of Reference 136, a heated tube packed with a granular basic chromium fluoride catalyst and operated at atmospheric pressure is fed with a vaporized mixture of HF/CCl_4 in a *ca.* 1.5:1.0 mol. ratio. Approximate product compositions at various temperatures and contact times are shown below:

Temp. $^\circ\text{C}$	Contact time (sec)	Composition of organic product mol. %			
		CCl_4	CCl_3F	CCl_2F_2	CClF_3
250	3	12	47	37	4
250	1	64	32	5	0.2
500	6	8	19	58	15

As mentioned earlier, the vapour phase process is quite satisfactory for commercial production of the major fluorocarbons, and at least two manufacturers, Pennsalt Chemicals Corporation and Imperial Smelting Corporation, have publicly advised that they use such a route. The only disadvantages in this type of manufacture are the relative difficulty of temperature control and the somewhat related problem of undesirable product distribution. Reactor temperature control can be improved, however, by careful design, and a recent patent¹⁴² indicates considerable progress in this direction.

A more serious drawback is the intractability of product distribution, as illustrated in the table above. The CCl_4 and excess CCl_3F are merely nuisances, which can be separated by distillation and returned through an external recycle system. More serious is the overfluorination to CClF_3 , since market outlets for this product are usually trivial compared to those for CCl_2F_2 . If the majority of the CCl_4 and CCl_3F is to be recycled, the loss to CClF_3 (based on product CCl_2F_2) is even greater than the raw figures of the table imply—amounting to 10 per cent even under the mild conditions of the first example. By way of compensation, these processes are well adapted to intentional production of the highly fluorinated minor products, since, unlike the liquid phase process, there is no gross organic phase associated with the catalyst. It is, therefore, possible to ignore the temperature-pressure interrelation which must be observed in the other process, and thus produce CClF_3 , CHF_3 or C_2ClF_5 by simply increasing the temperature or contact time at the original operating pressure. For this reason, as discussed below under Minor Fluorochemicals, a vapour phase process is frequently preferred for the synthesis of these highly fluorinated products.

A fundamentally different approach has been a route based upon HF, chlorine and acetylene as raw materials. In such a process, the HF and acetylene react to produce $\text{CH}_3 \cdot \text{CHF}_2$, and this intermediate is subsequently converted to CCl_2F_2 by energetic chlorinolysis¹²³⁻⁷. As far as is known, however, this synthesis is not in present commercial use.

Although the catalytic reaction of chlorocarbons and HF appears to be the standard industrial route for all major products, one should not overlook the many alternative syntheses which have been proposed and which may prove advantageous in the future. For the methane series, these have included a variety of reactions in which a carbon source such as CH_4 ⁷⁸⁻⁸¹, CS_2 ^{82,83}, COCl_2 ⁸⁴⁻⁸⁶, or carbon itself⁸⁷⁻⁹² reacts with a fluorine donor such as HF, SbF_5 , F_2 , NaF, CaF_2 , SF_4 or SiF_4 . In some cases chlorine is added to obtain chlorofluorocarbons; in others the process is intentionally operated to produce only CF_4 . To date, however, all such schemes appear to have foundered on the economic fact that while the standard processes employ expensive starting materials, their high yields and simplicity of operation have established them in a firm competitive position.

Acid recovery

Most fluorination processes are faced with the necessity of removing and recovering stoichiometric by-product HCl and varying amounts of unreacted HF (which, even in the liquid phase process, escapes from the reactor as an HF-organic azeotrope). These acids may of course be removed by aqueous scrubbing, and the HCl may even be subsequently recovered from this

solution as a pure gas⁹³⁻⁹⁵. Such an approach, however, usually sacrifices most of the unreacted HF to waste, despite various reported recovery schemes⁹⁶. For this reason, the concept of simply distilling pure HCl from the crude product stream has many attractions.

In a typical example of this distillation technology⁹⁷, the equipment consists of a conventional fractionating column, operating at 100 p.s.i.g. and fed by the crude effluent stream from a liquid phase fluorination reactor (e.g. $2\text{CCl}_2\text{F}_2 + \text{CCl}_3\text{F} + 5\text{HCl} + 0.5\text{HF}$). Under the fractionating influence of the column, the HCl will be concentrated at the top in a highly purified form (b.p. -38°C at 100 p.s.i.g.). In the liquid phase process, this anhydrous by-product acid is extremely pure, and may be used directly in some associated chemical synthesis, or packaged for sale. In the vapour phase process, however, the presence of over-fluorinated CClF_3 (b.p. -33°C at 100 p.s.i.g.) usually necessitates selective absorption of the acid in water and its subsequent sale as 30 per cent aqueous HCl.

Returning now to the HCl recovery still column, the primary crude stream ($2\text{CCl}_2\text{F}_2 + \text{CCl}_3\text{F} + 0.5\text{HF}$), now freed of HCl, is withdrawn as a liquid bottoms product and sent to the HF separation step. Temperatures at the bottom of the column will vary with the organic ratio, but at the composition and pressure of the illustration will be about 50°C .

Removal of the low boiling HCl component greatly simplifies the subsequent recovery of the unreacted HF. If, in the example, the liquid bottoms product from the HCl recovery column be cooled in a continuous decanter⁹⁷, the HF will immediately separate as an immiscible upper phase which can easily be withdrawn for recycle to the reactor. Mutual solubility is temperature dependent⁹⁷, and economics may justify operation as low as -30°C , where the concentration of dissolved HF in the organic phase (representing HF yield loss) has been reduced to less than 0.5 wt. per cent.

Final purification

Trace acidic impurities may be removed by neutralization, absorption or distillation, the first being by far the most common. If this is done with aqueous caustic, the product must be dried, and while sulphuric acid was used for this purpose in the early days, it is reasonable to assume that any manufacturer today would use the common desiccants of the refrigeration industry: silica gel, alumina gel or 'Molecular Sieves'. In the latter cases the product, either liquid or vapour, may be continuously passed through a tower at room temperature packed with granular drying agent, and will emerge with only a few p.p.m. residual moisture. The gel, of course, becomes progressively saturated with water, and must be periodically reactivated by heating to $100-200^\circ\text{C}$, either in vacuum or in the presence of a stream of dry, hot air.

The final step of purifying the neutralized, dried organic crude is usually accomplished by distillation. In the liquid phase process the organic components are originally withdrawn from the reactor at a ratio matching the demands of the market (see Synthesis, above), and purification consists of merely separating the two fractions at the requisite degree of purity. The vapour phase process, however, usually requires additional steps to cope with the over- and under- fluorinated components. The former (e.g. CClF_3) may,

of course, already have been removed (if the HCl was recovered by distillation); but if not, a separate distillation column must be provided for this purpose. In any event, there will always be unreacted chlorocarbon (CCl_4) and some underfluorinated product (CCl_3F) in excess of market requirements, which must be removed and recycled to the fluorination reactor.

The above distillations are all relatively straightforward, and can be successfully carried out in conventional, commercially available fractionating equipment—columns equipped with sieve plates, bubble caps, valve trays or packed with Raschig Rings, Pall Rings or Berl Saddles. As is true throughout the process, however, the simplicity of the underlying chemical and engineering principles tends to be misleading, in that it masks the high degree of sophistication actually obtaining in commercial installations. As an example, by virtue of the large scale of manufacture and the extreme requirements of purity, even the final purification step becomes an impressive example of applied chemical engineering technology. The distillation columns are frequently operated at several hundred pounds pressure, and may be several feet in diameter by 50–100 feet in height. Carefully insulated to preserve adiabaticity, they customarily develop at least 40–50 theoretical plates and are capable of reducing undesirable impurities to the p.p.m. level. This of course requires precise adjustment of operating variables such as temperature, pressure, heat flux and reflux ratio, which may be controlled through an instrument loop containing a small computer. The input information to the latter consists in turn of feed-back signals from rate meters and continuous gas chromatographic monitors on all process streams to and from the column. The outcome of this ingenuity and effort is a commercial enterprise second only to the petroleum industry in degree of automation, and probably without peer in combining product volume and quality.

Minor Fluorochemicals

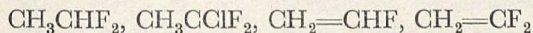
Manufacture of the remaining commercial fluorochemicals will be considered solely from the point of view of their synthesis. The subsequent processing varies in detail, but always consists essentially of the steps discussed above, with the common goal of sequentially removing acidic impurities, water, and unwanted organic components. The actual purification techniques are similarly conventional, and the greater use of methods such as selective adsorption and extractive distillation usually reflects merely the greater economic latitude inherent in small-scale production.

CHCl_2F and $\text{C}_2\text{Cl}_4\text{F}_2$; CHF_3 and CClF_3 ; C_2ClF_5 , C_2F_6 and CF_4

These compounds represent the remaining members of the CHCl_3 , C_2Cl_6 and CCl_4 series. Like their major counterparts they are commonly prepared by the reaction of HF and the parent chlorocarbon, using either the liquid or vapour phase processes discussed under Synthesis (though at either milder or more rigorous combinations of conditions). The first pair, containing only minor amounts of fluorine, are most suitably prepared by modifications of the liquid phase process (thus avoiding the overfluorination problem characteristic of the vapour phase processes). By comparison, the higher vapour pressures of CClF_3 and CHF_3 necessitate operating pressures of several

MANUFACTURE

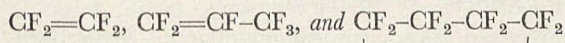
hundred pounds in the liquid phase processes, and thus increase the attractiveness of the vapour phase routes. This becomes even more marked in the case of the last three compounds of the title, where the necessarily high fluorination temperatures in combination with the extremely low boiling points make a vapour phase process mandatory.



The second important family of fluorochemicals is an interlocked series of products based upon the addition of HF to C_2H_2 . If these latter starting materials are brought together at room temperature in the presence of $\text{HSO}_3\text{F}^{100}$, BF_3^{101} , or certain metal salts¹⁰²⁻⁴, the reaction goes smoothly to $\text{CH}_3\cdot\text{CHF}_2$, which may then be isolated for sale or for further processing. In the latter case, it may be employed as an intermediate in the preparation of $\text{CH}_2=\text{CHF}$, splitting out the HF through either a simple pyrolysis^{105,122} or one catalysed by various aluminium or chromium salts^{106,107}.

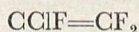
An alternative synthesis of $\text{CH}_2=\text{CHF}$ may be based upon room temperature addition of a single HF to C_2H_2 in the presence of certain mercury catalysts¹⁰⁸⁻¹⁰. As still a third possibility, HF and C_2H_2 will react at elevated temperatures in the presence of the same salts that were used to assist in the pyrolysis of CH_3CHF_2 ¹¹¹⁻¹³. In this third case a mixture of $\text{CH}_2=\text{CHF}$ and $\text{CH}_3\cdot\text{CHF}_2$ is obtained, but since these salts are also dehydrofluorination catalysts, the by-product $\text{CH}_3\cdot\text{CHF}_2$ may simply be recycled.

The comparable synthesis of $\text{CH}_2=\text{CF}_2$ is rather less complicated and usually begins with chlorination of $\text{CH}_3\cdot\text{CHF}_2$ to CH_3CClF_2 ¹¹⁴⁻¹⁷. This latter compound is then dehydrochlorinated thermally¹¹⁸, sometimes with the assistance of a catalyst¹⁴¹ or an adjuvant¹¹⁹. Alternatively, these two steps may be carried out simultaneously^{120,121}, but the reported yields are somewhat poorer.



The third important family of current commercial fluorocarbons is based upon the pyrolysis of CHClF_2 or more recently, CHF_3 . The primary pyrolytic reactions have been discussed earlier, and can be operated so as to give high yields of the product, $\text{CF}_2=\text{CF}_2$ ^{143,144,173}. This $\text{CF}_2=\text{CF}_2$ can then be readily converted to $\text{CF}_2=\text{CF}-\text{CF}_3$ or to the cyclic dimer by choosing various combinations of temperature and pressure¹⁴⁵⁻⁸. During most of these reactions there exists a strong possibility of producing the highly toxic isomer, perfluoro isobutylene, and casual preparative experimentation is to be strongly discouraged.

An even more fundamental approach to the preparation of $\text{CF}_2=\text{CF}_2$ is based upon the discovery that at temperatures above 1500°C almost any source of fluorine will combine with carbon to form CF_2 radicals. This stream may then be rapidly quenched to give a product rich in $\text{CF}_2=\text{CF}_2$, and extensive studies have been made on the ramifications of this method of fluorocarbon manufacture¹⁴⁹⁻⁵⁶.



The original synthesis of this compound was based on the dechlorination of $\text{CCl}_2\text{F}-\text{CClF}_2$ by zinc and alcohol¹⁵⁷. Judging by the several process

patents related to this basic chemistry¹⁵⁸⁻⁶¹, the synthesis is still an attractive commercial route, although alternative processes have been reported, based on the high temperature interaction of $\text{CCl}_2\text{F} \cdot \text{CClF}_2$ and H_2 ^{170,171} or the related dehydrochlorination of $\text{CHClF} \cdot \text{CClF}_2$ ¹⁷².

CBr_2F_2 , CBrF_3 and $\text{CBrF}_2 \cdot \text{CBrF}_2$

A variety of syntheses are available for the bromofluoro-compounds, based either upon fluorination of the bromocarbon or vice-versa. The former technique⁷² is merely a variation of the standard substitution process and is dependent upon the availability of a suitable starting material such as CBr_4 . The latter method is more versatile and consists of using elementary bromine to replace the hydrogen or add to the double bond of a commercially available fluorocarbon¹⁶²⁻⁴. A rather surprising variation of this latter approach has been the discovery that it is also possible to replace the chlorine of a starting chlorofluorocarbon by reaction with HBr ¹⁶⁵.

From the above, it can be seen that for all its apparent complexity the fluorochemical industry relies on rather simple, straightforward chemistry based ultimately on a few, relatively cheap raw materials: methane, acetylene, chlorine, sulphuric acid and fluorspar. Thus, even though substantial technical advances will doubtless be made in the field, it is unlikely that the basic price structure will be radically altered. At multimillion pound per year levels the similarity of technology should result in rather narrow price ranges for most of the above items, bulk value of the single-step products probably ranging from 25 to 75 cents (1s. 10d. to 5s. 4d.) a pound, while the materials derived from these might cost twice as much. Within these brackets, the price should be essentially a direct function of the fluorine content.

Fluorochemical Manufacturers

The companies currently active in fluorochemical manufacture have been listed in the following section, and each has been reviewed briefly in terms of its programme of sales and market development. These summaries have been based largely on advertisements and trade notices, together with a cursory survey of pertinent patents issued during the past five years. In this latter connection it was noted that the companies fell into three fairly distinct groups, of which the first obtained only scattered fluorine patents, the second averaged a moderate 8-10 per year, and the third pursued vigorous programmes yielding 25-50 fluorine patents annually. An indication of patent activity has therefore been included when it appeared pertinent.

U.S. Manufacturers

E. I. du Pont de Nemours & Company (Freon Products Division)—The oldest and largest of the fluorochemical manufacturers, the du Pont Company, produces and sells substantial quantities of more than a dozen fluorocarbons. In addition, it is actively developing markets for perhaps twice this many new products, and supports an extremely vigorous patent programme. Historically, as part of its Freon product line, the du Pont Company has been concerned with the halogeno-methanes and -ethanes which make up an overwhelming proportion of the market. In addition, the company also has

MANUFACTURE

substantial interests in the fluoropolymer field, which include not only Teflon TFE resin (tetrafluoroethylene) but also such newer entries as Teflon FEP resin (tetrafluoroethylene-hexafluoropropylene) and Tedlar film (vinyl fluoride) as well as fluoroelastomers such as Viton (hexafluoropropylene-vinylidene fluoride), and waxes such as Vydax. While still concerned with applications of the conventional fluorocarbons, market development in recent years has increasingly emphasized such extensions as the fluorinated alcohols and their derivatives, as well as fluorinated solvents, monomers, anesthetics and surface treating agents.

Allied Chemical Corporation (General Chemical Division)—Long established in the fluorochemicals field, this company offers almost two dozen fluorinated products, including a complete line of the simple halocarbons (Genetron). An historic interest in inorganic chemistry is also reflected in the sales offering of some 75 inorganic fluorine products, many in ton lots. Much of this company's market development effort and moderate patent activity have been concerned with the preparation and reactions of the fluoroaliphatics, particularly the group based upon hydrofluorination of acetylene. Recent work, however, has shown an increasing interest in such functional compounds as the fluorinated acids and ketones, and in plastics such as Halon (vinylidene fluoride-chlorotrifluoroethylene), also marketed as Aclar film.

Pennsalt Chemicals Corporation—Also historically engaged in inorganic fluorine chemistry, Pennsalt Chemicals Corporation has recently moved into the organic field and now also offers a complete line of fluorocarbon refrigerants and propellants (Isotron). Patent activity is moderate and still predominantly inorganic, but recent sales efforts have emphasized organic products, such as the derivatives of $\text{CF}_3\text{CH}_2\text{OH}$, and various fluoropolymers, including the vinylidene fluoride based Kynar plastic.

Union Carbide Corporation (Union Carbide Chemical Division)—Although this company is a major manufacturer of fluorinated refrigerants and propellants (Ucon), its other plans are not clear at this time, beyond an announced intention of entering the fluorochemicals field on a broad and active basis. Most of the company's past sales activity and modest patent programme have been related to polymers and derivatives of chlorotrifluoroethylene, but in recent years this sales field appears to have received diminished emphasis.

Minnesota Mining and Manufacturing Company—This company, with its acquired interest in the fluorochemicals division of M. W. Kellogg (1957), is one of the more aggressive of the newer entries in the fluorine field. It regularly offers some two dozen products, all organic, a record that is the more impressive for the fact that the line does not generally include the standard series adapted to refrigerant and propellant applications. Supporting a vigorous patent programme, this company has also given evidence of a strong commercial attitude by the recent completion of a new fluorochemicals plant in Alabama. A large part of its previous activity has been in the field of polymers and telomers of chlorotrifluoroethylene (Kel-F) and in the products of the Simons electrochemical cell such as R_fCOOH , R_fOR_f , $(\text{R}_f)_3\text{N}$ and $\square\text{R}_f\text{O}\square$. Current activity is apparently directed toward extension of these fields, as well as promotion of Scotchgard oil and water

repellent textile finishes, fluorocarbon electrical tapes, and several fluoroelastomers. Among the latter are Kel-F elastomer (vinylidene fluoride-chlorotrifluoroethylene), Fluorel (vinylidene fluoride-hexafluoropropylene) as well as experimental copolymers of trifluoronitrosomethane-tetrafluoroethylene.

Dow Chemical Company, Dow Corning Corporation—This is another element of the fluorochemicals industry whose position is difficult to assess at present. Since these companies are not engaged in the refrigerant-propellant field, the impact of their products is relatively small, but, on the other hand, they have maintained a vigorous patent programme for a number of years. Dow Corning Corporation's current sales activity seems centred around fluoro-silicon compounds, and includes a line of Silastic elastomers as well as several silicone lubricants and defoamers based on trifluoropropyl methyl polysiloxanes. Dow Chemical Company's products are restricted to a few compounds such as CBr_2F_2 and some experimental fluorinated anaesthetics, but its major position in the halogen field suggests that it could become a potent factor within the next decade.

Hooker Chemical Company—The Hooker Chemical Company offers about a dozen fluorine products for sale and has pursued a moderately active patent programme for several years. Most of its effort has been directed along the lines of aromatic derivatives, polymers of chlorotrifluoroethylene, and a variety of fluorinated butenes and pentenes.

General Electric Company, Air Reduction Company, Firestone Rubber Company, Universal Oil Products Company, Olin-Mathieson Chemical Corporation, Harshaw Chemical Company, and International Minerals and Chemical Corporation—All the above have some connection with the fluorochemicals industry, but are not considered to be major factors at this time. The first two have moderate patent programmes, but the General Electric Company's interests seem to lie mainly in the field of applications, and Air Reduction's sales efforts seem limited to the experimental fluorinated anaesthetic Fluoromar. Firestone's activities for the last several years have been similarly restricted to the Exxon copolymers, based on chlorotrifluoroethylene and used as protective coatings. Universal Oil Products and Olin-Mathieson seem concerned with fluorine chemistry mainly as an offshoot of their normal activities, such as the former's long standing and vigorous programme on catalyst development. Olin-Mathieson, however, has shown increased interest in the fluorine field *per se* in recent years. The final two companies seem primarily oriented toward inorganic fluorine chemistry.

Halocarbon Products (Fluoro-Chemical Corporation), Columbia Organic Chemicals Company, Pierce Chemical Company, Maumee Chemical Company, Peninsular Chemical Company, Nease Chemical Company—These small companies all produce fluoro organics on essentially a custom basis. They have no known patent position, but are aggressive and fully competitive in their marketing practices. Such companies frequently include among their officers men with extensive and successful prior experience in the fluorine field.

Rohm and Haas Company, Stauffer Chemical Company, Monsanto Chemical Company, American Cyanamid Company, and W. R. Grace and Company—These five relatively large companies have shown from time to time an incipient interest in fluorine research, but there is no current evidence of concrete plans.

APPLICATIONS

Manufacture outside the U.S.

European manufacturers have long played a significant part in fluorochemical developments, as witnessed by Farbwerke Hoechst's vigorous patent programme and ICI's pioneering work with the fluorinated anaesthetic Fluothane. Nonetheless, in view of the difficulty of obtaining enough information to present a balanced picture, it has been decided to limit this part of the discussion to the simple listing already given in Table 2. One may predict, however, that major companies such as ICI, Hoechst and perhaps Montecatini will not only dominate their own domestic markets, but will also play a significant role in international competition among the established products, as well as figuring prominently in the future technical development of the fluorochemicals industry. While the many smaller companies will probably concentrate on domestic production of established products, they will effectively saturate these markets, and will be in a position to extend their coverage rapidly to include any new, significant developments.

APPLICATIONS

The generally recognized commercial markets for fluorochemicals are listed below and briefly reviewed. The organization of such a list presents certain problems, since the markets for refrigerants and aerosols are so dominant as to reduce every other application to the category of a speciality. Nonetheless, several markets have been separated from the list of specialities and discussed individually, on the dual grounds that they appear to be well established and also to represent potential multimillion pound per year markets. In most cases a general reference to each field of application has been supplied, and discussion of actual application technology has been kept to a minimum.

Before proceeding, however, to a consideration of the individual applications as such, it may be helpful to identify the principal markets from the reference point of the major fluorocarbon products themselves. Accordingly there follows a brief list of the primary applications of the five major products which account for over 95% of the existing business:

- Compound-12 (CCl_2F_2 , b.p. -30°C) Most widely used product for household and commercial refrigeration and for large air-conditioners. The higher pressure component of most aerosol propellant mixtures.
- Compound-11 (CCl_3F , b.p. $+24^\circ\text{C}$) Used for certain commercial air-conditioners and water chillers. The standard low-pressure component for aerosol propellant mixtures, and the major fluorocarbon blowing agent for expanded foams.
- Compound-22 (CHClF_2 , b.p. -41°C) Employed in low temperature applications and for any use (such as window air-conditioners) where space is at a premium. Basic intermediate in the production of tetrafluoroethylene.
- Compound-113 ($\text{C}_2\text{Cl}_3\text{F}_3$, b.p. $+48^\circ\text{C}$) Occasional refrigerant, but mainly used as a solvent or as the basic intermediate for chlorotrifluoroethylene.
- Compound-114 ($\text{C}_2\text{Cl}_2\text{F}_4$, b.p. $+4^\circ\text{C}$) Occasional refrigerant, but mainly used as an inert medium, or in conjunction with Compound-12 to give

THE ORGANIC FLUOROCHEMICALS INDUSTRY

propellant mixtures of maximum stability for use in cosmetic and drug applications.

It will be noted that, except for intermediates, all these applications capitalize in some way on the reduction in chemical and physical activity that usually results from the addition of fluorine to a molecule. This is obvious in such examples as a decrease in toxicity and the elimination of flammability, but is also present as a more subtle factor in cases such as the fluorinated solvents, where reduction in solvent power has introduced a highly desirable degree of selectivity. In every case, however, since there is a cost penalty associated with the introduction of the fluorine, the economic success of an application is dependent upon the value attached to this added feature of stability.

The high electronegativity of fluorine does not, however, always result in an overall decrease in activity. It can on the contrary create a molecule which reacts more aggressively with its environment, as in the case of the acidic fluoroalcohols or the tightly hydrated fluoroketones. In addition, it can produce purely internal changes, such as in the optical properties of a dye or in the characteristics of a biologically active molecule. Thus far, only a few such examples have proved valuable enough to justify the extra cost of the fluorine, and this type of application stands as perhaps the greatest challenge to applications research.

REFRIGERANTS

As described under Background, refrigerant applications represented the first major commercial market for the fluorocarbons. For many years this was also the largest single use, but, while this market has continued to grow vigorously, it has recently been challenged and surpassed by aerosol applications. Refrigeration uses at present account for only about 40 per cent of total U.S. fluorocarbon sales, or about 120,000,000 pounds/year¹⁹.

The advantages of fluorocarbons over rival refrigerants have already been described, and are based almost entirely upon non-flammability and low toxicity combined with minimal corrosion. The technology of the field is thoroughly documented in such reference works as the ARI tables³⁶ or the ASHRAE Data Book³⁷, but readers desiring a less specialized treatment may consult any one of many excellent texts, such as MacIntire and Hutchinson³⁸.

If we discount the many ingenious cooling techniques used throughout history, the first scientific investigations, in the modern sense, date from about 1775, when William Cullen of Edinburgh first froze water by vacuum evaporation. The next 75 years of active study and experimentation revealed all the basic principles of modern refrigeration, and this period may be viewed as culminating in 1851, with Dr John Gorrie's invention of the first commercial ice-making machine. The history of commercial refrigeration since that time has been concerned largely with perfecting the technology and extending the applications of the field. Much of this early development of refrigeration technology took place in the United States, and the first large installations were all in the hot south and south-west of that country.

In tracing the subsequent development of the industry, it is useful to make a distinction between localized cooling applications, as opposed to the cooling

REFRIGERANTS

of rather large volumes of environmental air. In conformity with the conventional usage of ASHRAE (American Society of Heating, Refrigerating and Air-Conditioning Engineers) we shall use the term 'refrigeration' in the more restrictive sense of localized low temperature, and describe all environmental applications as 'air-conditioning'. In rough terms, these two types of use consume about an equal share of the 40 per cent of total fluorocarbon production allocated to the refrigeration industry in general. The individual applications of the major fluorocarbons within this general field have already been listed in the introduction to this section.

The original development of the refrigeration industry, in the restrictive sense, was closely allied with food preservation, and took the form of large central ice-plants, which served as cold-storage depots, and also supplied residential refrigeration demands by regular local deliveries. While large central installations are still common adjuncts of the food industry, the aspect of domestic refrigeration has been taken over almost entirely by the small mechanical household unit. This development became significant during the 1920's, and the resulting large-scale exposure of the general public to the hazards of earlier refrigerants played no small part in the rapid and enthusiastic acceptance of the Freon refrigerants. Today the percentage of homes equipped with refrigerators normally ranges from 97-100 per cent throughout the United States, and it is a rare rural area which will show less than 90 per cent saturation of the market. United States production of household refrigerators seems to have correspondingly levelled out between 3.5 and 4.0 million units per year⁶⁴.

Another major development of the food processing industry dates from 1921, and the discovery by Clarence Birdseye of the technique of quick freezing. On the commercial side, this has led to major expansion of the refrigeration industry in terms of facilities for freezing, transportation and retail storage. The residential market has been accommodated by including enlarged subfreezing storage compartments in home refrigerators, supplemented by larger separate home freezers. These latter are to be found in about 25 per cent of the homes throughout the United States and the market has currently stabilized at an annual sales figure of 1.0-1.5 million units⁶⁴.

This emphasis on the familiar domestic aspects of food refrigeration should not obscure the fact that the commercial side of the food processing industry is by far the more important of the two as a consumer of fluorinated refrigerants. Similarly, although the food industry is the largest user of refrigeration (in the present restricted sense), at least 30 per cent of that market is made up of industrial applications, such as the extensive demands of the chemical industry.

We turn now to air-conditioning, the other equally large segment of the overall refrigeration industry. This application has had a relatively slower development than localized refrigeration, despite the fact that Dr Gorrie's invention was largely motivated by the physician's desire to cool the rooms of feverish patients. Development during the next fifty years was slow, despite sporadic installation of air-cooling systems in a few large public buildings around the turn of the century. The first completely modern application, with its concepts of cooling, filtering, circulating and controlling the humidity of the air may be said to date from a 1902 installation engineered

THE ORGANIC FLUORO-CHEMICALS INDUSTRY

by Willis H. Carrier, in Brooklyn, New York. This unit was designed to supply constant atmospheric conditions for a difficult colour printing operation, and set the pattern for the next two decades, as more and more industries recognized the advantages of a controlled air supply. Even today, this is a major section of the air-conditioning market, and many industries such as those concerned with textiles, paper, photographic film and precision machinery are almost wholly dependent upon air-conditioning.

In the 1920's the familiar application of air-conditioning in theatres and auditoriums began to take place, and spread during the 1930's and 1940's to such similar outlets as restaurants, drug stores and the larger retail stores. The post-World War II era marked the extension of air-conditioning in office buildings and the widespread acceptance of the room air-conditioner. This latter application ranges in market penetration from about 10 per cent in northern United States homes to about 30 per cent in the south, and seems to have settled down to a relatively steady market in the neighbourhood of 1.5-2.0 million units per year⁶⁵. The fastest-growing major segment of the air-conditioning market at present appears to be the sale of central home units, whose rapid increase is shown in *Figure 11*. Another major part of growth is

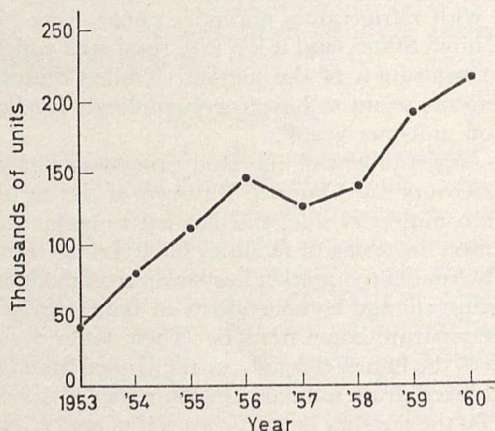


Figure 11. U.S. sales of central residential air conditioners. (Air-conditioning, Heating and Refrigeration News)

the air-conditioning of U.S. automobiles, which has risen to about 10 per cent of all cars produced in the 1961 model year⁶⁵.

Still another new and expanding application of air-conditioning is the use of the heat pump to warm houses in regions of intermediate climatic temperatures. This is a simple reverse application of normal refrigeration, whereby heat is moved from the exterior surroundings and transferred into the interior of a house. Such units depend for their success on the fact that under certain circumstances heat can be moved from one place to another more cheaply than it can be generated, but the economics of such a process are extremely involved and depend upon the costs of power, mean ambient temperatures, and the type of construction. The application, however, has

PROPELLANTS

a definite economic niche in a band of variable width between the extremes of the north, which make economics unfavourable, and the extremes of the tropics, where heating is of no importance. In much of this zone, moreover, air-conditioning is highly desirable, if not essential, and it thus becomes possible to accomplish both summer and winter comfort with a single installation.

As pointed out earlier, the total refrigerant market is about equally divided between refrigeration and air-conditioning. It is also possible to divide this total market according to the location of the application, and on this basis the divisions become approximately 20 per cent residential, 60 per cent commercial and 20 per cent industrial. The pattern of development in the United States for the immediate future seems fairly clear. Because of the saturation of the refrigeration market, any increase in this part of the business will be largely controlled by population and business growth and by necessary unit replacements. Air-conditioning, however, may be expected to grow significantly during the next decade, since, while it is frequently a luxury in the north, it becomes a near-essential to living comfort throughout large parts of the south.

Predictions with regard to other countries are more conjectural. The present European production of domestic refrigerators, which equals or surpasses that of the United States, may be taken as an indication that this type of application will grow on a world-wide scale, with nothing short of complete saturation as an eventual goal. Air-conditioning may not fare so well in the cooler climates, but this will be more than compensated for by its extension to those large areas of the world where both health and physical activity are affected by the prevailing heat. Growth in these areas should be limited only by the rate of industrial progress. Thus, though general refrigerant applications may be overshadowed by other uses, the overall picture is one of steady world-wide growth for many decades to come.

PROPELLANTS

The most spectacular application of fluorocarbons has been their use as propellants in the aerosol industry. This market had its beginning with the aerosol insecticides of World War II, and has since increased steadily, as shown in *Figure 12*, by proliferating into hundreds of specialized dispensing applications. It now accounts for 50 per cent of total sales of all fluorocarbons¹⁹ and its technology has been well documented in recent books by Herzka and Pickthall⁴² and by Shepherd⁴³. It may be noted that the original aerosol insecticides that gave the industry its name have long since become subordinate to formulations consisting merely of self-propelled liquid mixtures. A more accurate name for the industry has yet to gain general acceptance, however, and we shall follow the common practice of using the term 'aerosol' to cover all forms of pressurized packaging.

The concept of pressurized packaging goes back at least to an 1889 patent describing a self-contained spray propelled by methyl or ethyl chloride. Numerous patents were issued during the next half century, but, despite the commercial advent of the liquefied fluorocarbon gases in the early 1930's, no serious attempts were made to develop this application until the early

THE ORGANIC FLUOROCHEMICALS INDUSTRY

1940's. At that time the pioneering work of Goodhue and Sullivan first showed the extraordinary increase in insecticide efficiency that accompanied dispersing as a true aerosol, and demonstrated the use of a self-contained pack pressured with liquefied Freon-12. Quickly adopted by the United States Armed Forces, over forty million units were packaged for military use during World War II.

Post-war development was at first hampered since early formulations required the use of the relatively high-pressure Propellant-12 (70 p.s.i.g. at room temperature) and hence the use of a heavy, expensive container. This

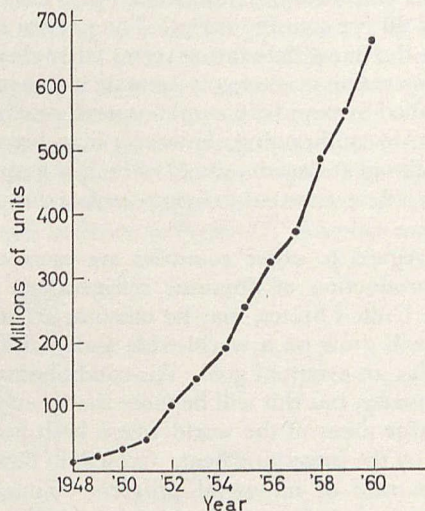


Figure 12. U.S. sales of all non-food aerosols.
(Chemical Specialties Manufacturers Association)

problem was surmounted in 1947 with the development of low-pressure valves and nozzles capable of functioning properly below 55 p.s.i.a., combined with a modification of the ICC regulations raising their applicability limit in this case to 55 p.s.i.a. This latter action freed the industry from the elaborate control and regulation required of pressure vessels, and permitted it to develop a conventional can-type package similar to that long used for beer and carbonated beverages. The required intermediate-pressure propellants were obtained by using mixtures of commercial fluorocarbons, typically Propellants 12 and 11 or 12 and 114.

Expansion and diversification has been steady since that time, and present formulations may be conveniently divided according to use. The division employed below and the market percentages assigned to each have been drawn from Shepherd⁴³.

Insecticides

This pioneer usage experienced its greatest expansion during the years 1947 to 1953, and has since levelled out at the relatively stable figure of some eighty million units per year, representing 10-15 per cent of the total pro-

PROPELLANTS

pellant market. Surveys have indicated that approximately ninety out of every hundred American homes are equipped with some form of aerosol-dispersed insecticide, and there appears to be no sign of decline in its popularity, even though the tremendous growth in other fields of propellant application have lessened its relative importance.

Personal Products

This section of the aerosol industry is the largest and fastest growing, now accounting for more than 50 per cent of the total market; about half is attributable to hair spray and another third to shaving cream, with the remainder consisting of colognes, perfumes, shampoos, body deodorants, hand lotions and miscellaneous toiletries.

Surface Coatings

These constitute another 15 per cent of the market and include a variety of surface film-forming materials such as acrylic resins, paints, etc.

Pharmaceuticals

Although sales are only 2-3 per cent of the total, it seems probable that, while it will never become a major use, it will continue to grow, and deserves to be set aside from other specialities on the basis of the elaborate precautions which will be required.

Food

By 1961, no fluorochemical had been approved for use as a food propellant, although such approval had been requested for Freon-C318. At present, penetration of this market by any propellant is limited to a few isolated cases such as the use of nitrous oxide for whipped cream. The size of the food industry, however, means that even a small penetration will lead to large sales, and on that basis this use deserves to be mentioned as a separate item.

Household and Industrial Specialities

The final 20 per cent of the aerosol market is currently in the field of specialities. Space prevents a complete cataloguing of this tribute to the ingenuity of man, but major items to date have included room deodorants, artificial snow, glass cleaners, leather dressings, waxes, fire extinguishers, ignition waterproofers and anaesthetic sprays. Lists including up to 600 additional specialized applications have been compiled, including rust preventives, cutting oils, mould release sprays, stencil inks, charcoal igniters, waterproofing formulations, spot removers, etc. It appears safe to predict that these applications will continue to be extended.

It can thus be seen that while some aerosol products may have reached their potential and are likely to increase only with the size of their parent market, most of the major applications listed above have hardly begun to be exploited. Furthermore, while much of the early development has taken place within the United States, there seems no reason to believe that general acceptance of pressurized products will be limited to that country. The 1960 European aerosol market accounted for almost 40 per cent of that area's production of fluorochemicals; and this, together with an enthusiastic

THE ORGANIC FLUORO-CHEMICALS INDUSTRY

acceptance in the more industrialized countries of Latin America, argues strongly for a world-wide repetition of the United States pattern.

INTERMEDIATES

Substantial quantities of the basic fluorochemicals are consumed in the preparation of other fluorine-containing compounds, as in the conversion of CHClF_2 to $\text{CF}_2=\text{CF}_2$. However, since these latter products are also intermediates, and since the reactions have been discussed elsewhere, they will be omitted from consideration here. A second group of intermediates is represented by the many functional compounds referred to in the section on Manufacturers, but here again discussion will be omitted, on the grounds that none of these uses has yet matured into a definable market. It may be mentioned, however, that the smaller chemical companies are playing an important role in the development of such outlets, and that some, such as Halocarbon Products Inc., offer a substantial listing of candidate compounds.

The remaining intermediates are all olefins, and are listed below in terms of their current end-products. This use has become fairly well defined and has been the subject of a review by Hanford and Sargent⁶⁶.

<i>Intermediate</i>	<i>End-products</i>
$\text{CF}_2=\text{CF}_2$	Du Pont's Teflon TFE Resins and Teflon FEP Resins, as well as fluorotelomer functional derivatives and waxes
$\text{CClF}=\text{CF}_2$	Minnesota Mining and Manufacturing's Kel-F plastics, elastomers and lubricants; Hooker Chemical's and Halocarbon Product's lubricants; General Chemical's Halon and Aclar plastics and films; Firestone Rubber Co.'s Exon coatings
$\text{CH}_2=\text{CHF}$	Du Pont's Tedlar film
$\text{CH}_2=\text{CF}_2$	Du Pont's Viton and 3M's Fluorel elastomers; Pennsalt's Kynar and General Chemical's Halon plastics, and the latter's Aclar films
$\text{CF}_2=\text{CF}-\text{CF}_3$	Du Pont's Viton and 3M's Fluorel elastomers; Du Pont's Teflon FEP Resin

The future of all these intermediates obviously depends upon the success of the corresponding polymers. However, with a variety of end-products, and a market already at the multimillion pound level, the health of this segment of the fluorochemicals business seems well assured.

BLOWING AGENTS

This application involves the gasification of various latices or plastics to produce a finished solid product in a foamed or 'expanded' state. Originally limited to foamed elastomers, this field has grown rapidly to include a major market in rigid foams, exhibiting a wide variety of tensile strengths and densities. The oldest and simplest blowing agent is compressed air, still satisfactorily used in the production of foam rubber from latex. Other techniques more common in the plastics industry have consisted of dissolved 'blowing agents' which become gasified when purposely triggered by a change in temperature or by the sudden release of a confining pressure. The

SOLVENTS

penetration of fluorochemicals into this latter field is relatively new, but has mushroomed into a multimillion pound application.

Large-scale application of fluorochemicals as blowing agents first appeared in the production of polyurethane foams, themselves relative newcomers to the building trades⁶⁷. The original technique for expanding such plastics was to include a small amount of water, which then reacted with excess isocyanate during polymerization to produce a CO₂ blowing agent *in situ*. The relatively high cost of CO₂ produced in this manner inevitably stimulated testing of other candidate blowing agents, and it was found that the simple fluorocarbons were not only cheaper but also imparted additional desirable properties to the foam. These advantages vary with application, but in general are related to better control of bubble size, superior processing characteristics, and improved insulating properties due to the high molecular weight of the fluorocarbon trapped in the cells.

This successful application to isocyanates has, in turn, stimulated further evaluations in other polymer systems. All the simple commercial fluorocarbons are currently under study for this purpose, and in many cases unexpected advantages in foam characteristics have been observed. One ironic outcome of this work has been the reevaluation of a number of previously unsuccessful plastic candidates, with the definite possibility that the newer foaming techniques will produce serious low-cost competition for isocyanates.

It is difficult to forecast the true potential of a market as new as this one. In the first place, the penetration by fluorochemical blowing agents in existing markets is far from complete, despite the extensive work that has already been done. To this must be added the fact that the competitive advantages bestowed by fluorocarbon blowing may well be reflected in an increased popularity of those products which use such agents. As a final factor there remains the proper assessment of the extent to which the relatively new field of expanded plastics will itself grow and penetrate into fields now monopolized by conventional materials of construction, and perhaps even extend the entire concept of building materials into areas previously considered impractical. In any event, the most conservative predictions would foresee that this application of fluorocarbons, already in the multimillion pound stage, will develop rapidly into a market measured in the tens of millions of pounds.

SOLVENTS

This is a promising market for the higher boiling fluorochemicals which again exploits their chemical stability, low toxicity and non-flammability. Here, however, a more positive effect of fluorination becomes evident in the 'tailoring' of the solvent molecule to the specific application. This is particularly evident in such applications as the cleaning of assembled precision equipment by C₂Cl₃F₃ (b.p. +48°C), where the solvent action of the compound is quite adequate to remove grease and dirt, and yet mild enough to avoid damage to the plastic and elastomeric components of the assembly. The literature on these newer solvents is widely scattered, but mention may be made of Mellan's *Source Book of Industrial Solvents*⁶⁸ and the discussion given on page 232 of Shepherd's review of aerosol technology⁴³.

Selective solvent cleaners will probably always remain specialities, but the solvent market as a whole is so large that even a minor penetration will result in substantial sales. Already, significant applications have been developed for the simple fluorocarbons in the cleaning of gyroscopes, teletypes, and other precision instruments, and the versatility of these products may be further increased by blending them with more polar agents, as in Du Pont's Solvent PC ($C_2Cl_3F_3$ plus ethanol). Here again the object is to achieve the desired degree of solvent action without damage to any part of the assembly, as, for instance, in the cleaning of fluxes from printed circuits. The use of such blending agents and adjuvants seems certain to increase, and may open up markets of substantial size, such as the dry cleaning of clothes without damage to plastic buttons and adornments.

Extraction is merely a variant of the solvent application in which the desirable rather than the undesirable components are usually retained in solution. Here the fluorocarbon is frequently competing against hydrocarbon solvents, and finds its main advantage in non-flammability. A variety of such extractions are already practised, among them the isolation of the edible oils of cotton seed, safflower and soy beans, as well as active ingredients of perfumes, essential oils, spices, coffee and even fish. Another example is the extraction of active virus concentrates from their original culture medium, although here the action of the solvent is more subtle and depends upon coagulation of the protein, combined with selective partial removal of the lipid components.

Experience alone will tell if the price disadvantages of the fluorocarbons can be overcome by large-scale manufacture. In the meantime they seem firmly entrenched in their special applications and may be expected at least to extend this field to similar uses.

FIRE EXTINGUISHING AGENTS

This is a minor but well established market, and although present uses are limited largely to aircraft, the leading bromofluorocarbon, $CBrF_3$, has become a standard installation on almost all U.S. commercial air transport. The technical literature is too scattered to permit easy reference, but mention may be made of the National Research Council's 'Fire Research Abstracts and Reviews'⁶⁹ and the National Fire Protection Association's 'Halogenated Extinguishing Agents'⁷⁰ as well as the latter's tabulation and review of fire extinguishing research centres⁷¹.

The development of the fluorinated fire extinguishants is a natural extension of the ability of fluorine to reduce toxicity. Carbon tetrachloride has long been used in fire extinguishing applications, and this agent was supplemented, for military uses during World War II, by two new brominated compounds, CH_3Br and CH_2ClBr (CB). The effectiveness of these materials seems to depend upon an additional mechanism of fire extinction beyond the cooling and smothering effects of conventional, non-halogenated agents. This action is believed to result from chain termination in the free radical propagating mechanism of the fire, and greatly increases the fire-fighting potential on a weight basis.

The original bromocarbon extinguishants, however, have two significant

handicaps: toxicity and corrosivity. Under these circumstances, the addition of fluorine to stabilize the molecule was obvious, and in the post-war period many combinations were prepared and tested. In general these were successful, in the sense that in most cases the fluorinated molecule had a satisfactorily low initial toxicity, yet yielded up the active bromine radical when exposed to the actual fire. From these tests several promising candidates emerged— CBrF_3 , CBr_2F_2 , CBrClF_2 and $\text{C}_2\text{Br}_2\text{F}_4$. Of these, the first seems to have become the preferred agent, primarily on the basis of its extremely low order of initial toxicity.

It may be noted here that the fire extinguisher industry has its own code nomenclature, which is used in preference to the similar system covering refrigerants. This code consists of the letters FE followed by a series of numbers corresponding successively to the number of atoms of carbon, fluorine, chlorine, bromine or iodine—omitting terminal zeros. Thus CBrF_3 , known in the one code as Refrigerant 13B1, is rewritten in the Halon code as FE-1301.

The future of this market will depend almost entirely upon some competitive combination of weight, price and safety. In congested locations where lives and valuable property are at stake, effectiveness and low toxicity put these agents in an excellent position. This is of course doubly true in vehicles and in aircraft where the factor of weight also becomes important. Beyond these specialized uses, however, future markets will depend greatly upon the price which results from large-scale manufacture.

ANÆSTHETICS AND BIOLOGICALS

This field differs from the preceding examples by being merely a loose grouping of special applications. Nonetheless, it is possible to identify certain general areas which deserve mention on the basis of their annual dollar potential alone. Reference may also be made to Pattison's monograph⁵³, which discusses current research in this general field.

The development of fluorinated inhalation anæsthetics has been the aim of extensive research efforts, spurred on by the serious fire and explosion hazards of most of the commonly used agents. A definite measure of commercial success has recently been achieved by ICI's Fluothane (CF_3CHBrCl), which has now been joined by Air Reduction's Fluoromar ($\text{CF}_3\text{CH}_2\text{OCH}=\text{CH}_2$) and Dow's Penthrane ($(\text{CH}_3\text{OCF}_2\text{CHCl}_2)$). Unexpectedly, while the original research was aimed entirely at reducing flammability, many of the candidates have shown a definite correlation between fluorine content and increased efficacy. If this effect is general, the fluoroanæsthetics may become an important link in the development of Pauling's new general theory of anæsthesia.

Another active field of research is the use of fluorine to modify the activity of drugs and other biologicals. Though the field has thus far produced more literature than business, it is possible to identify a number of commercial products, such as Vesprin, a trifluoromethyl modified phenothiazine tranquillizer, and Indoklon, a hexafluorodiethylether convulsant. In addition, there are available certain fluorine-containing steroids, which are reported to be superior to the parent compounds in regard to both efficacy and absence of detrimental side effects.

THE ORGANIC FLUORO-CHEMICALS INDUSTRY

The related fields of pesticides and agricultural chemicals contain several established markets for fluorine compounds. Chief among these are the effective pesticides, sodium fluoroacetate (usually referred to as Compound 1080) and fluoroacetamide (sold in Great Britain as Tritox). In addition to such compounds, which appear to operate by interference with the Krebs cycle, there are several other physiologically active fluorochemicals such as the substituted benzotrifluorides used in substantial quantities to kill young lamprey eels in the Great Lakes of the United States. Recent Australian studies have also shown the simple fluorocarbon $C_2Cl_4F_2$ to have a significant advantage over the toxic CCl_4 normally used in the treatment of liver flukes in sheep, and such anthelmintic applications alone represent a market of substantial proportions. In addition to these applications there is widespread research activity on the incorporation of fluorine into insecticide molecules.

In summary, it may be predicted that a number of biologically active fluorochemicals will gain commercial stature in the next few years. However, though individually lucrative, none appears to have a potential for large-volume manufacture, and it furthermore seems that each will develop as a side-line of some other enterprise.

SPECIAL APPLICATIONS

Coatings and Finishes

This is a potentially important market based upon large fluorinated molecules which have been modified to include some active functional group. The latter can serve to anchor the molecular unit to the surface of a substrate such as cloth, paper, leather, wood or metal; the resultant protective fluorocarbon layer will then impart a greatly decreased susceptibility to soiling and a significantly improved resistance to weathering. Though the Scotchgard products are the only present commercial entries, the magnitude of the potential market has long attracted the research of other companies, and it may be expected that a variety of such materials will eventually become available.

Lubricants

The fluorine-containing oils and waxes are predominantly polymeric, and hence outside the direct scope of this article. There is, however, a substantial and well-established market for them, which deserves some mention. It has been based in the past largely on fluorocarbon telomers, i.e. polymers in which the growing chain has been stopped at an intermediate length by a chain-transfer agent which simultaneously 'caps' the chain to produce a large, stable molecule⁶⁶. Historically, these telomers have been based on either $CF_2=CF_2$ or $CFCl=CF_2$, the former producing waxy materials such as Du Pont's Vydax surface coatings, and the latter yielding the oils and greases produced by Halocarbons, Inc., Hooker Chemical Co. and Minnesota Mining and Manufacturing Co. Further developments may be expected to become more complex, such as Dow Corning's fluorinated silicones and Du Pont's fluorinated esters.

SPECIAL APPLICATIONS

Dielectrics

The excellent electrical properties of Teflon have long been recognized, and added measurably to its successful commercialization. The simpler fluorocarbons also exhibit many advantageous properties, and the electrical industry is actively developing such applications. Some compounds, such as C_2F_6 and C_3F_8 , are used merely to supply a gaseous environment of high dielectric strength, but others, such as $C_2Cl_2F_4$, cyclic C_4F_8 and the fluorinated ethers may also be employed as refluxing liquids to assist in heat removal. It appears certain that a small but important market will result from this application.

Inert Liquids

This well established group of special applications takes advantage of the stability of higher boiling fluorocarbons. In most cases the liquid is used simply as an impulse transmission fluid in instruments, but in other cases, such as the bromofluoro compounds used as damping fluids in guidance gyroscopes, the medium actually 'floats' part of the instrument.

Low Temperature Refrigeration

This use has been isolated from the general section on refrigeration simply to give it individual recognition. Installations cooling to $-60^\circ C$ are commonly designed using the commercial Refrigerant-22, but below this temperature it becomes profitable to add refrigeration stages containing Refrigerants 13 or 14. There is currently a small but steady market for such refrigerants, though much of this goes to such highly specialized applications as the cooling of infra-red detectors for missile guidance or the quick freezing of bull semen. Barring significant penetration of an established market, such as the liquefaction of air, this will probably continue to be a growing, but minor, market.

Space Technology

This market could increase to substantial dimensions as intercontinental rocket flight becomes commercially important. The present direct applications are mostly related to the guidance of missiles, either through 'vector control' deflection of the primary rocket thrust, or by direct gas-jet positioning of the free flight nose cone. Factors of boiling point, molecular weight and stability all favour fluorocarbons for these applications, and this rather novel market has a definite potential. In addition to such primary applications, the general field of space technology overlaps most of the other major and minor application fields of fluorochemicals, such as the air-conditioning of vehicles, operation of low temperature direction-sensing elements, fluid stabilization of gyroscopes and even the cleaning of crucial components.

Miscellaneous

A host of odd applications for fluorocarbons have appeared over the years. Though some of these may evolve into definable markets in the future, their present status justifies little more than a listing:

THE ORGANIC FLUOROCHEMICALS INDUSTRY

Gas springs and shock absorbers

A potentially important market in which the air-spring common to inter-city buses would be improved by use of a gas with a lower specific heat ratio, and hence 'softer' compression characteristics. A modification of this principle, employing CClF_3 , is already used in the shock absorbers of certain larger U.S. automobiles.

Whistles and alarms

A variant of the aerosol field in which a fire-alarm signal or small foghorn is powered by liquefied gas.

Wind tunnels

An established but minor use exploiting the high density of the fluorocarbons to simulate the stresses of high-speed flight at low actual gas velocities.

Power fluids

The transmission of power by vaporizing stable fluorocarbons and using this energy to drive a turbine.

Particle detection

A specialized technique of atomic physics in which high-speed particles are detected by a trail of bubbles left behind in a liquid fluorocarbon medium.

Food preparation

A procedure for decreasing the cooking time of large cuts of meat by inserting a thin, commercially available tube filled with a liquid refrigerant to increase heat transfer to the centre of the joint.

APPENDIX A

CODE SYSTEM FOR NUMERICAL DESIGNATION OF FLUOROCARBONS

The following system was officially adopted June 3, 1957, as Standard 34 of the American Society of Heating, Refrigerating and Air-Conditioning Engineers (ASHRAE). It is presented below in a somewhat abridged form, which does not include certain recommendations relating to azeotropes and various non-fluorinated compounds. Examples of usage are given below, in Appendix B, and in Tables 1 to 3.

SECTION 2 DESIGNATION

2.1 Form

- 2.1.1 Each refrigerant shall have an identifying number which can either be used alone or in combination with the word 'Refrigerant' and shall be equally meaningful.
- 2.1.2 An abbreviation of the word 'Refrigerant' in any form is not permitted.

APPENDIX A

2.1.3 The identifying number of the refrigerant or the word 'Refrigerant' or both may be preceded by the manufacturer's trademark or trade name.

2.1.4 Examples

Isotron 12 or Isotron Refrigerant 12;
Genetron 12 or Genetron Refrigerant 12;
Freon-12 or Freon Refrigerant 12 or
Freon-12 Refrigerant or F-12 Refrigerant.

2.2 *Numbering System for Hydrocarbons and Halocarbons*

2.2.1 The first digit on the right is the number of fluorine (F) atoms in the compound.

2.2.2 The second digit from the right is one more than the number of hydrogen (H) atoms in the compound.

2.2.3 The third digit from the right is one less than the number of carbon (C) atoms in the compound. When this digit is zero, it is omitted from the number.

2.2.4 The number of chlorine (Cl) atoms in the compound is found by subtracting the sum of the fluorine (F) and hydrogen (H) atoms from the total number of atoms which can be connected to the carbon (C) atoms. When only one carbon atom is involved, the total number of attached atoms is four (4). When two carbon atoms are present, the total number of attached atoms is (6), unless the compound is unsaturated; in this case the total number of attached atoms is four (4).

For saturated refrigerants, the total number of attached atoms is:

$$\begin{aligned}4 & \text{ for } C = 1 \\6 & \text{ for } C = 2 \\8 & \text{ for } C = 3 \\10 & \text{ for } C = 4 \\2n + 2 & \text{ for } C = n\end{aligned}$$

For unsaturated and cyclic refrigerants, the total number of attached atoms is:

$$\begin{aligned}4 & \text{ for } C = 2 \\6 & \text{ for } C = 3 \\8 & \text{ for } C = 4 \\10 & \text{ for } C = 5 \\2n & \text{ for } C = n\end{aligned}$$

2.2.5 For cyclic derivatives, the letter C is used before the identifying refrigerant number.

2.2.6 In those instances where bromine is present in place of part or all of the chlorine, the same rules apply except that the letter B after the designation for the parent chlorofluorocompound shows the presence of bromine (Br). The number following the letter B shows the number of bromine atoms present.

THE ORGANIC FLUOROCHEMICALS INDUSTRY

- 2.2.7 In the case of isomers, each has the same number and the most symmetrical is indicated by the number without any letter following it. As the isomers become more and more unsymmetrical, the letters a, b, c, etc., are appended. Symmetry is determined by adding the atomic weights of the groups attached to each carbon atom and subtracting one sum from the other. The smaller the difference the more symmetrical the product.
- 2.2.8 In case the compound is unsaturated, the above rules apply except that number one (1) is used as the fourth digit from the right.

APPENDIX B

APPENDIX B

EXAMPLES OF NUMERICAL CODE
AND SELECTED PHYSICAL PROPERTIES

The following tables furnish a key for the application of the numerical code to the simpler fluorocarbons. The physical data have been added to assist in identifying and characterizing these compounds, and have been selected from the chemical review literature¹⁻⁸.

Code No.	Formula	mol. wt.	b.p. °C	f.p. °C	Density (g/cc)/°C	Crit. temp. °C	Code No.
<i>Chlorofluoro methanes</i>							
10	CCl ₄	153.8	76.8	-23	1.595/20	283	10
11	CCl ₃ F	137.4	23.8	-111	1.487/20	198	11
12	CCl ₂ F ₂	120.9	-29.8	-158	1.293/30	112	12
13	CClF ₃	104.5	-81.4	-181	1.298/-30	28.9	13
14	CF ₄	88.0	-128	-183.6	1.33/-80	-45.5	14
20	CHCl ₃	119.4	61.2	-63.5	1.489/20	263.4	20
21	CHCl ₂ F	102.9	8.9	-135	1.354/30	178.5	21
22	CHClF ₂	86.5	-40.8	-160	1.175/30	96	22
23	CHF ₃	70.0	-82.1	-160	1.246/-34	25.9	23
30	CH ₂ Cl ₂	84.9	40.1	-96.7	1.336/20	237	30
31	CH ₂ ClF	68.5	-9.1	-133	1.271/20	—	31
32	CH ₂ F ₂	52.0	-51.7	-136	1.100/20	—	32
40	CH ₃ Cl	50.5	-24	-97.7	0.920/18	143	40
41	CH ₃ F	34.0	-78.5	-141.8	0.8428/-60	44	41

Bromochlorofluoro methanes

10B1	CBrCl ₃	198.3	104.2	-5.8	2.012/23.5		10B1
10B2	CBr ₂ Cl ₂	242.7	135	22	2.42/25		10B2
10B3	CBrCl ₂	287.2	160	55	2.71/15		10B3
11B1	CBrCl ₂ F	181.9	52				11B1
11B2	CBr ₂ ClF	226.3	80				11B2
11B3	CBr ₃ F	270.8	106	-74.5	2.7648/20		11B3
12B1	CBrClF ₂	165.4	-4	-160.5	1.850/15	153.8	12B1
12B2	CBr ₂ F ₂	209.8	24.5	-110	2.3063/15	198.2	12B2
13B1	CBrF ₃	148.9	-57.8	-168	1.58/21	67	13B1
20B1	CHBrCl ₂	163.9	90.1	-56.9	2.006/16		20B1
20B2	CHBr ₂ Cl	208.3	125	-22	2.445/15		20B2
20B3	CHBr ₃	252.8	149.6	8.3	2.890/20		20B3
21B1	CHBrClF	147.4	38	-115	1.9058/16		21B1
21B2	CHBr ₂ F	191.9	64.5	26.5	2.4256/19		21B2
22B1	CHBrF ₂	130.9	-15				22B1
30B1	CH ₂ BrCl	129.4	67	-86.5	1.991/19	277	30B1
30B2	CH ₂ Br ₂	173.9	98.5	-52.8	2.495/20		30B2
31B1	CH ₂ BrF	113.0	17.5				31B1
40B1	CH ₃ Br	95.0	3.6	-93.7	1.732/0	191	40B1

THE ORGANIC FLUORO-CHEMICALS INDUSTRY

Code No.	Formula	mol. wt.	b.p. °C	f.p. °C	Density (g/cc)°C	Crit. temp. °C	Code No.
<i>Chlorofluoro ethanes</i>							
110	CCl ₃ CCl ₃	236.8	185	186	2.091/20	—	110
111	CCl ₃ CCl ₂ F	220.3	137	100	1.74/25	—	111
112	CCl ₂ FCCl ₂ F	203.8	92.8	23.5	1.637/30	278	112
112a	CCl ₃ CClF ₂	203.8	91.5	40.6	1.6488/20	—	112a
113	CCl ₂ FCClF ₂	187.4	47.6	-35	1.533/30	214.1	113
113a	CF ₃ CCl ₃	187.4	45.7	14	1.5790/20	—	113a
114	CClF ₂ CClF ₂	170.9	3.6	-94	1.440/30	145.7	114
114a	CCl ₂ F-CF ₃	170.9	3.0	-56.6	1.454/29	145.5	114a
115	CClF ₂ -CF ₃	154.5	-38.7	-106	1.265/30	79.9	115
116	CF ₃ CF ₃	138.0	-78.1	-100.6	1.607/-78	24.3	116
120	CHCl ₂ CCl ₃	202.3	162	-29	1.709/0	—	120
121	CHCl ₂ CCl ₂ F	185.8	116.6	-82.6	1.622/20	—	121
121a	CHClF-CCl ₃	185.8	116.5	-95.4	1.625/20	—	121a
122	CHCl ₂ CClF ₂	169.4	71.9	-140	1.5447/25	—	122
122a	CHClF-CCl ₂ F	169.4	72.5	glass	1.5587/20	—	122a
122b	CHF ₂ -CCl ₃	169.4	73	glass	1.566/20	—	122b
123	CHCl ₂ CF ₃	153	27.1	-107	1.475/15	—	123
123a	CHClF-CClF ₂	153	28.2	—	1.498/0	—	123a
123b	CHF ₂ CCl ₂ F	153	—	—	—	—	123b
124	CHClF-CF ₃	136.5	-12	—	—	—	124
124a	CHF ₂ CClF ₂	136.5	-10.2	-117	1.379/20	126.7	124a
125	CHF ₂ CF ₃	120	-48.5	-103	—	—	125
130	CHCl ₂ -CHCl ₂	167.9	146.3	-43.8	1.600/20	—	130
130a	CCl ₂ CH ₂ Cl	167.9	130.5	-68.1	1.588/20	—	130a
131	CHCl ₂ CHClF	151.4	102.5	—	1.5497/17	—	131
131a	CH ₂ ClCCl ₂ F	151.4	88	-104.7	1.4921/20	—	131a
131b	CH ₂ FCCl ₃	151.4	—	—	—	—	131b
132	CHClF-CHClF	135	59	-155	—	—	132
132a	CHF ₂ CHCl ₂	135	60	—	1.4945/17	—	132a
132b	CClF ₂ CH ₂ Cl	135	46.8	-101.2	1.4163/20	—	132b
132c	CCl ₂ FCH ₂ F	135	—	—	—	—	132c
133	CHClF-CHF ₂	118.5	17	—	1.365/10	—	133
133a	CF ₃ -CH ₂ Cl	118.5	6.1	-105.5	1.389/0	—	133a
133b	CClF ₂ -CH ₂ F	118.5	12	—	—	—	133b
134	CHF ₂ CHF ₂	102	-19.7	-89	—	—	134
134a	CF ₃ -CH ₂ F	102	-26.5	-101	—	—	134a
140	CHCl ₂ CH ₂ Cl	133.4	113.5	-36.7	1.334/20	—	140
140a	CCl ₃ -CH ₃	133.4	74.1	-30.4	1.3249/26	—	140a
141	CHClF-CH ₂ Cl	116.9	75.7	—	1.3814/20	—	141
141a	CHCl ₂ CH ₂ F	116.9	—	—	—	—	141a
141b	CCl ₂ FCH ₃	116.9	32	-103.5	1.2500/10	—	141b
142	CHF ₂ -CH ₂ Cl	100.5	35.1	—	1.312/15	—	142
142a	CHClF-CH ₂ F	100.5	—	—	—	—	142a
142b	CClF ₂ -CH ₃	100.5	-9.2	-130.8	1.096/30	137.1	142b
143	CHF ₂ CH ₂ F	84	5	-84	—	71.2	143
143a	CF ₃ -CH ₃	84	-47.6	-111	0.942/30	73.1	143a
150	CH ₂ ClCH ₂ Cl	98.9	83.5	-35.3	1.253/20	288	150
150a	CHCl ₂ CH ₃	98.9	57.3	-96.7	1.174/20	250	150a
151	CH ₂ FCH ₂ Cl	82.5	53.2	—	1.1675/25	—	151
151a	CHClF-CH ₃	82.5	16.1	—	—	—	151a
152	CH ₂ FCH ₂ F	66	30.7	—	0.913/19	107.5	152
152a	CHF ₂ -CH ₃	66	-24.7	-117	0.966/19	113.5	152a
160	CH ₂ ClCH ₃	64.5	13.1	-138.7	0.9214/0	187.2	160
161	CH ₂ F-CH ₃	48	-37.1	-143.2	0.8176/-37	102.2	161

APPENDIX B

Code No.	Formula	mol. wt.	b.p. °C	f.p. °C	Density (g/cc)/°C	Crit. temp. °C	Code No.
<i>Chlorofluoro ethylenes</i>							
1110	CCl ₂ =CCl ₂	165.8	120.8	-22.4	1.6311/15		1110
1111	CClF=CCl ₂	149.4	71.0	-108.9	1.5460/20		1111
1112 (cis)	CClF=CClF	132.9	21.1	-130.5	1.4950/0		1112 (cis)
1112 (trs)	CClF=CClF	132.9	22	-110.3	1.4936/0		1112 (trs)
1112a	CF ₂ =CCl ₂	132.9	19.0	-115	1.4385/20	186	1112a
1113	CClF=CF ₂	116.5	-27.9	-157.5	1.3048/20	106.7	1113
1114	CF ₂ =CF ₂	100	-76.3	-142.5	1.519/-76	33.3	1114
1120	CHCl=CCl ₂	131.4	88	-86.4	1.4556/25		1120
1121	CHCl=CClF	115	35.1		1.4032/16		1121
1121a	CHF=CCl ₂	115	37.3	-108.8	1.3833/20		1121a
1122	CHCl=CF ₂	98.5	-17.7	-138.5	1.230/21	127.4	1122
1122a	CHF=CClF	98.5					1122a
1123	CHF=CF ₂	82	-61	-78	1.265/27		1123
1130 (cis)	CHCl=CHCl	96.9	60.1	-80.5	1.291/15		1130 (cis)
1130 (trs)	CHCl=CHCl	96.9	48.4	-50	1.265/15		1130 (trs)
1130a	CH ₂ =CCl ₂	96.9	37		1.250/15		1130a
1131 (cis)	CHF=CHCl	80.5	16				1131 (cis)
1131 (trs)	CHF=CHCl	80.5	-4				1131 (trs)
1131a	CH ₂ =CClF	80.5	-25	-169			1131a
1132	CHF=CHF	64	-28				1132
1132a	CH ₂ =CF ₂	64	-82	-144	0.617/24	30.1	1132a
1140	CH ₂ =CHCl	62.5	-13.9	-159.7	0.9195/15		1140
1141	CH ₂ =CHF	46	-72.2	-160.5	0.615/25	54.7	1141
1150	CH ₂ =CH ₂	28.1	-103.9	-169.4	0.566/-102		1150

Cyclic compounds

C-216	CF ₂ -CF ₂ CF ₂	150	-31.5	-80			C-216
C-314	CF ₂ CF ₂ CCl ₂ CCl ₂	266	131.6	84.8			C-314
C-316	CF ₂ CF ₂ CClFCClF	233	59.9	-15.1	1.6443/17		C-316
C-317	CF ₂ CF ₂ CF ₂ CClF	216.5	25.6	-39.1	1.602/15		C-317
C-318	CF ₂ CF ₂ CF ₂ CF ₂	200	-6.06	-40.7	1.5241/20	115.3	C-318
C-324	CF ₂ CF ₂ CCl ₂ CHCl	231.5	110		1.5720/25		C-324
C-334	CF ₂ CF ₂ CH ₂ -CCl ₂	197	84.5		1.5298/25		C-334
C-344	CF ₂ -CF ₂ -CH ₂ CHCl	161.5	74		1.4251/25		C-344
C-354	CF ₂ CF ₂ CH ₂ CH ₂	128	50		1.2752/25		C-354
C-1314	CF ₂ -CF ₂ CCl=CCl	195	67.1	-43.4	1.5340/25		C-1314
C-1316	CF ₂ CF ₂ -CF=CF	162	1.1	-60.4	1.602/-20		C-1316

THE ORGANIC FLUOROCHEMICALS INDUSTRY

APPENDIX C

NATIONAL BOARD OF FIRE UNDERWRITERS'
COMPARATIVE LIFE HAZARD OF GASES AND VAPOURS⁵⁶

<i>Group</i>	<i>Definition</i>	<i>Examples</i>
1	Gases or vapours which in concentrations of the order of 0.5 to 1 per cent for durations of exposure of the order of 5 minutes are lethal or produce serious injury	Sulphur dioxide
2	Gases or vapours which in concentrations of the order of 0.5 to 1 per cent for durations of exposure of the order of one half hour are lethal or produce serious injury	Ammonia Methyl bromide
3	Gases or vapours which in concentrations of the order of 2 to 2.5 per cent for durations of exposure of the order of 1 hour are lethal or produce serious injury	Carbon tetrachloride Chloroform Methyl formate
4	Gases or vapours which in concentrations of the order of 2 to 2.5 per cent for durations of exposure of the order of 2 hours are lethal or produce serious injury	Dichloroethylene Methyl chloride Ethyl bromide
Between 4 and 5	Appear to classify as somewhat less toxic than Group 4 Much less toxic than Group 4 but somewhat more toxic than Group 5	Methylene chloride Ethyl chloride Refrigerant 113*
5a	Gases or vapours much less toxic than Group 4 but more toxic than Group 6	Refrigerant 11* Refrigerant 22* Carbon dioxide
5b	Gases or vapours which available data indicate would classify as either Group 5a or Group 6	Ethane Propane Butane
6	Gases or vapours which in concentrations up to at least about 20 per cent by volume for durations of exposure of the order of 2 hours do not appear to produce injury	Refrigerant 12* Refrigerant 114*

* See Table 1.

REFERENCES

REFERENCES

- ¹ Stacey, M., Tatlow, J. C. and Sharpe, A. G. (Ed.), *Advances in Fluorine Chemistry*, Vol. 1, 1960; Vol. 2, 1961; Butterworths, London
- ² Lovelace, A. M., Rausch, D. A. and Postelneck, W., *Aliphatic Fluorine Compounds*, Reinhold, New York, 1958
- ³ Simons, J. H. (Ed), *Fluorine Chemistry*, Vol. 1, 1950, pp. 395-397, 500-516, 536-546; Vol. 2, Academic Press, New York, 1954
- ⁴ Haszeldine, R. N. and Sharpe, A. G., *Fluorine and Its Compounds*, 1951, Methuen, London
- ⁵ Schiemann, G., *Die Organischen Fluorverbindungen*, 1951, Dietrich Steinkopff, Darmstadt
- ⁶ Slessor, C. and Schram, S. R. (Ed.), *Preparation, Properties and Technology of Fluorine and Organic Fluoro Compounds*, 1951, McGraw-Hill, New York
- ⁷ Henne, A. L., *Organic Reactions* (Ed. Adams, R.); Vol. 2, Chapter 2, 1944, Wiley, New York
- ⁸ Henne, A. L., *Organic Chemistry* (Ed. Gilman, H.); Vol. 1, 2nd Edn, Chapter 11, 1943, Wiley, New York
- ⁹ Fluorine Symposium (1947), *Ind. Engng Chem.*, 1947, **39**, 235
- ¹⁰ Bockemüller, W., *Newer Methods of Preparative Organic Chemistry*, 1948, Interscience, New York
- ¹¹ Bockemüller, W., *Organische Fluorverbindungen, Samml. chem. Vortr.*, New Series 1936, **28**
- ¹² Emcléus, H. J., *Endeavour*, 1948, **7**, 141
- ¹³ Swarts, F., *Bull. Soc. chim. Fr.*, 1924, **35**, 1533
- ¹⁴ Ruff, O., *Die Chemie des Fluors*, 1920, Springer, Berlin
- ¹⁵ Moissan, H., *Le fluor et ses composés*, 1900, Steinheil, Paris
- ¹⁶ Kirk-Othmer, *Encyclopedia of Chemical Technology*, Vol. 6, p. 738, 1951, Interscience Encyclopedia, Inc., New York
- ¹⁷ Ullmann, *Encyklopädie der technischen Chemie*, Vol. 7, 3rd Edn., p. 605, 1956, Urban & Schwarzenburg, Munich
- ¹⁸ Thorpe, *Dictionary of Applied Chemistry*, Vol. 5, 4th Edn., p. 273, 1941; Longmans Green, London
- ¹⁹ Staff Report, *Chem. Engng News*, 1960, **38**, 92
- ²⁰ Barbour, A. K., *Chem. & Ind.*, 1961, 958
- ²¹ Lebeau, P. and Damiens, A., *C.R.*, 1926, **182**, 1340
- ²² Ruff, O., and Keim, R., *Z. anorg. allgem. Chem.*, 1930, **192**, 249
- ²³ Swarts, F., *Mém. cour. Acad. R. Belg.*, 1895, **51**
- ²⁴ Midgley, T. and Henne, A. L., *Ind. Engng Chem.*, 1930, **22**, 542
- ²⁵ ACS Official Reports, *Chem. Engng News*, 1952, **30**, 4513
- ²⁶ Steinle, H., *Kältetechn.*, 1960, **12**, 392 (*Refrig. Engr.* 1957, **65**, No. 2, 49)
- ²⁷ Benning, A. F. *et al.*, *Ind. Engng Chem.*, 1939, **31**, 912; 1940, **32**, 497, 698, 814, 976
- ²⁸ McHarness, R. C., Eiseman, B. J. and Martin, J. J., *Refrig. Engr.*, 1955, **63**, No. 9, 31
- ²⁹ Albright, L. F. and Martin, J. J., *Ind. Engng Chem.*, 1952, **44**, 188
- ³⁰ Chari, N. C. S., *Dissertation*, University of Michigan, April, 1960
- ³¹ Hou, Y. C. and Martin, J. J., *J. Am. Inst. Chem. Eng.*, 1959, **5**, 125
- ³² Van Wie, N. H. and Ebel, R. A., Thermodynamic Properties of Freon-114, Report K-1430, Vol. 1 & 2, Office of Technical Services, U.S. Dept. of Comm., Washington 25, D.C.
- ³³ E. I. du Pont de Nemours & Co. (Freon Products Div.), Technical Bulletin T-115
- ³⁴ DeNevers, N. and Martin, J. J., *J. Am. Inst. Chem. Eng.*, 1960, **6**, 43
- ³⁵ Mears, W. H., *et al.*, *Ind. Engng Chem.*, 1955, **47**, 1449
- ³⁶ Air-Conditioning and Refrigeration Institute (ARI), Properties of Commonly-Used Refrigerants, 1957 Edn., 1346 Conn. Av. N. W., Washington 6, D. C.
- ³⁷ American Society of Refrigerating Engineers (ASRE, now ASHRAE), Air Conditioning Refrigerating Data Book, 10th Edn. 1957, 234 Fifth Av., New York 1, New York
- ³⁸ Sanders, P. A., *Soap Chem. Specialties*, 1960, **36**, 95
- ³⁹ Eiseman, B. J., *Chem. Engng News*, 1961, **39**, 44

THE ORGANIC FLUOROCHEMICALS INDUSTRY

- ⁴⁰ Reed, W. H. and Pennington, W. A., *U.S. Pat.* RE23,358 (2,479,259), Apr. 17, 1951 (Aug. 16, 1949)
- ⁴¹ E. I. du Pont de Nemours & Co. (Freon Products Div.), Technical Bulletins: B-8 Specification Analyses and Methods; B-21 Procedures for Sampling; B-23 Moisture Determination by Karl Fischer Tit; B-25 & 27 Moisture Determination by Model W Electrolytic Analyzer; B-28 Quantitative Analysis by Gas Chromatography
- ⁴² Herzka, A. and Pickthall, J., *Pressurized Packaging*, 1958, Butterworths, London
- ⁴³ Shepherd, H. R., *Aerosols: Science and Technology*, 1961, Interscience, New York
- ⁴⁴ Agent T. C. George's Interstate Commerce Commission Regulations, Tariff No. 13, Sept. 15, 1960
- ⁴⁵ E. I. du Pont de Nemours & Co. (Freon Products Div.), Technical Bulletins Related to Product Handling: B-3, B-11, B-11A, B-11B, B-20, B-35, FA-24.
- ⁴⁶ Safe Handling of Compressed Gases Pamphlet P-1, 1951, Compressed Gas Association, New York
- ⁴⁷ Teranishi, H., *Jap. Rev. Phys. Chem.* 1958, **28**, 9
- ⁴⁸ Allied Chem. Corp. (Gen. Chem. Div.), Genetron Aerosol Propellents, 1955; Product Data Sheets PD-6-54 and PD-9-54
- ⁴⁹ E. I. du Pont de Nemours & Co. (Freon Products Div.), Technical Bulletin D-39
- ⁵⁰ Coffman, D. D. *et al.*, *J. Amer. Chem. Soc.* 1949, **71**, 490
- ⁵¹ Duus, H. C., *Ind. Engng. Chem.* 1955, **47**, 1445
- ⁵² von Oettingen, W. F., Halogenated Hydrocarbons—Toxicity, Public Health Service Publication No. 414, 1955, U. S. Govt. Printing Office, Washington 25, D.C.
- ⁵³ Pattison, F. L. M., *Toxic Aliphatic Fluorine Compounds* 1959, Elsevier, New York
- ⁵⁴ Fairhall, L. T., *Industrial Toxicology*, 2nd Edn. 1957, Williams and Wilkins, Baltimore
- ⁵⁵ Patty, F. A., *Industrial Hygiene and Toxicology*, Vol. 1, 2nd Edn., 1958; Vol. 2, 1st Edn., 1949; *Interscience*, New York
- ⁵⁶ Underwriters' Laboratories Reports on Comparative Life, Fire and Explosion Hazards; National Board of Fire Underwriters, 109 Leonard St., New York
- ⁵⁷ Greenberg, L. A. and Lester, D., *Arch. industr. Hyg.*, 1950, **2**, 335
- ⁵⁸ Carpenter, C. P., Smyth, H. F., and Pozzani, U. C., *J. industr. Hyg.*, 1949, **31**, 343
- ⁵⁹ Henne, A. L. and Renoll, M. W., *J. Amer. Chem. Soc.*, 1936, **58**, 889
- ⁶⁰ Robbins, B. H., *J. Pharmacol.*, 1946, **86**, 197
- ⁶¹ Park, J. D. *et al.*, *Ind. Engng Chem.*, 1947, **39**, 354
- ⁶² E. I. du Pont de Nemours & Co., Haskell Laboratory of Industrial Toxicology, Unpublished Results.
- ⁶³ MacIntire, H. J. and Hutchinson, F. W., *Refrigeration Engineering*, 2nd Edn. 1954, Wiley, New York
- ⁶⁴ Electrical Merchandising Week (Annual Statistical and Marketing Issue), Jan. 1, 1961
- ⁶⁵ Air-conditioning, Heating and Refrigerating News, Jan. 2, 1961
- ⁶⁶ Hanford, W. E. and Sargent, D. E., *Organic Chemistry* (Ed. Gilman, H.), Chapter 11, Vol. 4, 1st Edn., 1953, Wiley, New York
- ⁶⁷ *Modern Packaging Encyclopedia Issue*—1959, Foamed Plastics, p. 286, Breskin Publications, Inc., Bristol, Conn.
- ⁶⁸ Mellan I., *Source Book of Industrial Solvents*, Vol. 2, 1957, Reinhold, New York
- ⁶⁹ Fire Research Abstracts and Reviews, Committee on Fire Research, National Academy of Sciences—National Research Council, Washington, D.C.
- ⁷⁰ Halogenated Extinguishing Agents, NFPA Q 48-8, National Fire Protection Association (International), 60 Batterymarch St., Boston 10, Mass.
- ⁷¹ Bond, H. (Ed.), *Research on Fire*, National Fire Protection Association (International), Boston, 1957, Lexington Press Inc., Lexington, Mass.
- ⁷² Daudt, H. W. and Youker, M. A., *U.S. Pat.* 2,005,710 (June 18, 1935)
- ⁷³ Daudt, H. W. and Youker, M. A., *U.S. Pat.* 2,005,705 (June 18, 1935)
- ⁷⁴ Daudt, H. W. and Youker, M. A., *U.S. Pat.* 2,062,743 (Dec. 1, 1936)
- ⁷⁵ Daudt, H. W. and Youker, M. A., *U.S. Pat.* 2,005,708 (June 18, 1935)
- ⁷⁶ Midgley, T., Henne, A. L., and McNary, R. R.; *U.S. Pat.* 1,930,129 (Oct. 10, 1933)
- ⁷⁷ Holt, L. C. and Mattison, E. L., *U.S. Pat.* 2,005,713 (June 18, 1935)

REFERENCES

- ⁷⁸ Benning, A. F. and Park, J. D., *U.S. Pat.* 2,407,129 (Sept. 3, 1946)
⁷⁹ McCleary, R. F., *U.S. Pat.* 2,759,026 (Aug. 14, 1956)
⁸⁰ Edwards, A. J. and Green, S. W., *Ger. Pat.* 1,026,291 (Mar. 20, 1958)
⁸¹ Henne, A. L., *U.S. Pat.* 1,973,069 (Sept. 11, 1934)
⁸² Sheppard, W. A., *U.S. Pat.* 2,972,518 (Feb. 21, 1961)
⁸³ Smith, W. C., *U.S. Pat.* 2,922,825 (Jan. 26, 1960)
⁸⁴ Haszeldine, R. N. and Iserson, H., *U.S. Pat.* 2,907,798 (Oct. 6, 1959)
⁸⁵ Coffman, D. D. and Tullock, C. W., *U.S. Pat.* 2,757,213 (July 31, 1961)
⁸⁶ Muetterties, E. L., *U.S. Pat.* 2,757,214 (July 31, 1956)
⁸⁷ Muetterties, E. L., *U.S. Pat.* 2,709,184 (May 24, 1955); *U.S. Pat.* 2,709,185 (May 24, 1955)
⁸⁸ Farlow, M. W. and Muetterties, E. L.; *U.S. Pat.* 2,709,186 (May 24, 1955); *U.S. Pat.* 2,709,190 (May 24, 1955); *U.S. Pat.* 2,709,188 (May 24, 1955); *U.S. Pat.* 2,709,187 (May 24, 1955); *U.S. Pat.* 2,722,559 (Nov. 1, 1955); *U.S. Pat.* 2,725,410 (Nov. 29, 1955)
⁸⁹ Wolfe, J. K. and Cook, N. C., *U.S. Pat.* 2,835,711 (May 20, 1958)
⁹⁰ Hager, G. F., *U.S. Pat.* 2,924,623 (Feb. 9, 1960)
⁹¹ Forshey, W. O., Jr., *U.S. Pat.* 2,924,624 (Feb. 9, 1960)
⁹² Forshey, W. O., Jr., *U.S. Pat.* 2,924,625 (Feb. 9, 1960)
⁹³ Benning, A. F., Downing, F. B. and Plunkett, R. J.; *U.S. Pat.* 2,345,696 (April 4, 1944)
⁹⁴ Laird, R. F. and Hartig, R. G.; *U.S. Pat.* 2,343,462 (Mar. 7, 1944)
⁹⁵ Société d'Electro-Chimie d'Electro-Metallurgie et des Acieries Electriques d' Ugine, *Brit. Pat.* 822,494 (Oct. 28, 1959)
⁹⁶ Sanlerville, J. and Foulletier, L., *U.S. Pat.* 2,920,941 (Jan. 12, 1960)
⁹⁷ Benning, A. F., *U.S. Pat.* 2,450,415 (Oct. 5, 1948)
⁹⁸ Benning, A. F., *U.S. Pat.* 2,450,414 (Oct. 5, 1948)
⁹⁹ Benning, A. F., *U.S. Pat.* 2,478,362 (Aug. 9, 1949)
¹⁰⁰ Calfee, J. D. and Bratton, F. H., *U.S. Pat.* 2,462,359 (Feb. 22, 1949)
¹⁰¹ Burk, R. E., Coffman, D. D. and Kalb, G. H.; *U.S. Pat.* 2,425,991 (Aug. 19, 1947)
¹⁰² Swamer, F. W., *U.S. Pat.* 2,830,099 (April 8, 1958)
¹⁰³ Swamer, F. W., *U.S. Pat.* 2,830,100 (April 8, 1958)
¹⁰⁴ Swamer, F. W., *U.S. Pat.* 2,830,101 (April 8, 1958)
¹⁰⁵ Harmon, J., *U.S. Pat.* 2,599,631 (June 10, 1952)
¹⁰⁶ Skiles, B. F., *U.S. Pat.* 2,674,632 (April 6, 1954)
¹⁰⁷ Coffman, D. D. and Cramer, R. D., *U.S. Pat.* 2,461,523 (Feb. 15, 1949)
¹⁰⁸ Whitman, G. M., *U.S. Pat.* 2,401,850 (June 11, 1946)
¹⁰⁹ Salisbury, L. F., *U.S. Pat.* 2,519,199 (Aug. 15, 1950); *U.S. Pat.* 2,426,792 (Sept. 2, 1947)
¹¹⁰ Barney, A. L., *U.S. Pat.* 2,437,148 (Mar. 2, 1948)
¹¹¹ Hillyer, J. C. and Wilson, J. F.; *U.S. Pat.* 2,471,525 (May 31, 1949); *U.S. Pat.* 2,634,300 (April 7, 1953)
¹¹² Skiles, B. F., *U.S. Pat.* 2,716,143 (Aug. 23, 1955)
¹¹³ Skiles, B. F., *U.S. Pat.* 2,892,000 (June 23, 1959)
¹¹⁴ Calfee, J. D. and Smith, L. B., *U.S. Pat.* 2,499,629 (Mar. 7, 1950)
¹¹⁵ Calfee, J. D. and Florio, P. A., *U.S. Pat.* 2,499,129 (Feb. 28, 1950)
¹¹⁶ Scherer, O. and Queck, J., *U.S. Pat.* 2,861,032 (Nov. 18, 1958)
¹¹⁷ Bower, F. A. and Heberling, J. W., *U.S. Pat.* 2,899,472 (Aug. 11, 1959)
¹¹⁸ Feasley, C. F., and Stover, W. A., *U.S. Pat.* 2,627,529 (Feb. 3, 1953)
¹¹⁹ Miller, C. B., *U.S. Pat.* 2,628,989 (Feb. 17, 1953)
¹²⁰ Johnston, H., *U.S. Pat.* 2,722,558 (Nov. 1, 1955)
¹²¹ Litant, I. and Miller, C. B., *U.S. Pat.* 2,723,296 (Nov. 8, 1955)
¹²² Downing, F. B., Benning, A. F. and McHarness, R. C., *U.S. Pat.* 2,480,560 (Aug. 30, 1949)
¹²³ Calfee, J. D. and Smith, L. B., *U.S. Pat.* 2,606,937 (Aug. 12, 1952)
¹²⁴ Calfee, J. D. and Smith, L. B., *U.S. Pat.* 2,417,059 (Mar. 11, 1947)
¹²⁵ Calfee, J. D. and Smith, L. B., *U.S. Pat.* 2,459,767 (Jan. 18, 1949)
¹²⁶ Calfee, J. D. and Miller, C. B., *U.S. Pat.* 2,674,630 (April 6, 1954)
¹²⁷ Calfee, J. D. and Smith, L. B., *U.S. Pat.* 2,572,913 (Oct. 30, 1951)
¹²⁸ McBee, E. T. and Welch, Z. D., *U.S. Pat.* 2,443,630 (June 22, 1948)

THE ORGANIC FLUORO-CHEMICALS INDUSTRY

- 129 Benning, A. F., Park, J. D. and Kraehler, S. E., *U.S. Pat.* 2,458,551 (Jan. 11, 1949)
 130 Benning, A. F., Park, J. D. and Kraehler, S. E., *U.S. Pat.* 2,576,823 (Nov. 27, 1951)
 131 Miller, C. B. and Calfee, J. D., *U.S. Pat.* 2,748,177 (May 29, 1956)
 132 Calfee, J. D., Miller, C. B. and Smith, L. B., *U.S. Pat.* 2,755,313 (July 17, 1956)
 133 Woolf, C., *U.S. Pat.* 2,860,172 (Nov. 11, 1958)
 134 Woolf, C., *U.S. Pat.* 2,714,618 (Aug. 2, 1955)
 135 Woolf, C., *U.S. Pat.* 2,850,543 (Sept. 2, 1958)
 136 Ruh, R. P. and Davis, R. A., *U.S. Pat.* 2,745,886 (May 15, 1956)
 137 Ruh, R. P. and Davis, R. A., *U.S. Pat.* 2,744,148 (May 1, 1956)
 138 Milks, W. N., *U.S. Pat.* 2,744,147 (May 1, 1956)
 139 Scherer, O., Kühn, H. and Forche, E., *Ger. Pat.* 1,000,798 (Jan. 17, 1957)
 140 Belf, L. J., *U.S. Pat.* 2,946,827 (July 26, 1960)
 141 Mantell, R. M. and Barnhart, W. S., *U.S. Pat.* 2,774,799 (Dec. 18, 1956)
 142 Foulletier, L. and Dassaud, R., *U.S. Pat.* 2,897,064 (July 28, 1959)
 143 Downing, F. B., Benning, A. F. and McHarness, R. C., *U.S. Pat.* 2,551,573 (May 8, 1951)
 144 Benning, A. F., Downing, F. B. and Park, J. D., *U.S. Pat.* 2,406,794 (Sept. 3, 1946)
 145 Downing, F. B. and Benning, A. F., *U.S. Pat.* 2,384,821 (Sept. 18, 1945)
 146 Harmon, J., *U.S. Pat.* RE23,425, (2,404,374); Oct. 30, 1951 (July 23, 1946)
 147 Nelson, D. A., *U.S. Pat.* 2,758,138 (Aug. 7, 1956)
 148 Eyck, E. H. and Larson, G. P., *U.S. Pat.* 2,970,176 (Jan. 31, 1961)
 149 Farlow, M. W. and Joyce, R. M., *U.S. Pat.* 2,709,183 (May 24, 1955)
 150 Farlow, M. W. and Muetterties, E. L., *U.S. Pat.* 2,709,189 (May 24, 1955)
 151 Farlow, M. W. and Muetterties, E. L., *U.S. Pat.* 2,709,191 (May 24, 1955)
 152 Farlow, M. W., *U.S. Pat.* 2,709,192 (May 24, 1955)
 153 Farlow, M. W. and Muetterties, E. L., *U.S. Pat.* 2,732,410 (Jan. 24, 1956)
 154 Farlow, M. W. and Muetterties, E. L., *U.S. Pat.* 2,732,411 (Jan. 24, 1956)
 155 Denison, J. T., Edlin, F. E. and Whipple, G. H., *U.S. Pat.* 2,852,574 (Sept. 16, 1958)
 156 Forshey, W. O., *U.S. Pat.* 2,941,012 (June 14, 1960)
 157 Booth, H. S., Burchfield, P. E., et al., *J. Amer. Chem. Soc.* 1933, **55**, 2231
 158 Blum, O. A., *U.S. Pat.* 2,590,433 (Mar. 25, 1952)
 159 Chernosky, A. J. and Umber, J. D., *U.S. Pat.* 2,754,336 (July 10, 1956)
 160 Abramo, J. G. and Reinhard, R. H., *U.S. Pat.* 2,903,489 (Sept. 8, 1959)
 161 Miller, W. T., *U.S. Pat.* 2,848,505 (Aug. 19, 1958)
 162 Simons, J. H., Brice, T. J. and Pearson, W. H., *U.S. Pat.* 2,658,928 (Nov. 10, 1953)
 163 Ruh, R. P. and Davis, R. A., *U.S. Pat.* 2,908,724 (Oct. 13, 1959)
 164 Pedrotti, R. L., Swamer, F. W. and Dewey, D. C., *U.S. Pat.* 2,937,210 (May 17, 1960)
 165 Sterling, J. D., *U.S. Pat.* 2,729,687 (Jan. 3, 1956)
 166 Hanford, W. E., *U.S. Pat.* 2,407,419 (Sept. 10, 1946)
 167 Dietrich, M. A., *U.S. Pat.* 2,407,405 (Sept. 10, 1946)
 168 Brubaker, M. M., *U.S. Pat.* 2,407,396 (Sept. 10, 1946)
 169 Benning, A. F., Downing, F. B. and Plunkett, R. J., *U.S. Pat.* 2,401,897 (June 11, 1946)
 170 Clark, J. W., *U.S. Pat.* 2,685,606 (Aug. 3, 1954); *U.S. Pat.* 2,704,775 (Mar. 22, 1955); *U.S. Pat.* 2,704,777 (Mar. 22, 1955)
 171 Mantell, R. M., *U.S. Pat.* 2,697,124 (Dec. 14, 1954)
 172 Dittman A. L., *U.S. Pat.* 2,667,518 (Jan. 26, 1954)
 173 Hauptschein, M. and Fainberg, A. H., *U.S. Pat.* 3,009,966 (Nov. 21, 1961)

THE PREPARATION OF ORGANIC FLUORINE COMPOUNDS BY HALOGEN EXCHANGE

A. K. BARBOUR, L. J. BELF and M. W. BUXTON

Imperial Smelting Corporation Limited, Avonmouth

Introduction	182
Reagents for Fluorination by Halogen Exchange	183
Anhydrous hydrogen fluoride	183
Antimony trifluoride	185
Antimony chlorofluoride (or bromofluoride)	185
Antimony pentafluoride	186
Alkali metal fluorides	186
Argentous fluoride	187
Mercurous fluoride	187
Mercuric fluoride	187
Other reagents	188
Preparation of Fluoroalkanes	188
Fluoromethanes	188
Perhalogenomethanes containing chlorine and fluorine	188
Perhalogenomethanes containing fluorine and bromine or iodine	192
Fluorohalogenomethanes containing one hydrogen atom	193
Fluorohalogenomethanes containing two or three hydrogen atoms	194
Fluoroethanes	194
Preparation of compounds of formula CX_3-R	194
Preparation of compounds of formula CHX_2-R	199
Preparation of compounds of formula CH_2X-R	200
Fluoropropanes	201
Orientation rules	201
Preparation of compounds of formula $R-CX_2-R'$	202
Preparation of compounds of formula $R-CHX-R'$	206
Preparation of compounds of formula $R-CH_2-R'$	207
Fluorobutanes	209
Preparation of fluoroperhalogenobutanes	209
Preparation of compounds of formula $R-CX_2-CH_2-R'$	211
Preparation of compounds of formula $R-CHX-CH_2-R'$	212
Preparation of compounds of formula $R-CX_2-CHX-R'$	213
Preparation of compounds of formula $R-CX_2-CX_2-R'$	213
Preparation of compounds of formula $R-CH_2-CH_2-R'$	214
Branched-chain fluorobutanes	215
Fluoropentanes	215
Straight-chain	215
Branched-chain	216
Cyclic	217
Fluorohexanes	217
Straight-chain	217
Cyclic	218
Fluoroheptanes	220
Fluoro-octanes	221
Higher Fluoroalkanes	222