CHAPTER 4

Industrial and Utilitarian Aspects of Fluorine Chemistry

BY H. G. BRYCE

Minnesota Mining and Manufacturing Company, St. Paul, Minnesota

Exhibit
3022
State of Minnesota v. 3M Co.,
Court File No. 27-CV-10-28862

I. Introduction

As a raw material for industrial use, fluorine is relatively abundant in nature. It comprises approximately 0.065% of the earth's crust(1) compared to 0.055% for chlorine. Most of this fluorine, however, is combined in rather complex inorganic compounds at relatively low levels and in consequence would be difficult to recover. The most important mineral is fluorspar (fluorite, CaF_2) which occurs quite widely. This is the principal source of fluorine at present. Other simple fluorides occurring as minerals are villiaumite (NaF), sellarite (MgF_2), yttrocerite $(Ca_3Ce_2Y_2)F_6$, all of which are rare.

The most important of the complex fluorides occurring naturally is cryolite (Na_3AlF_6). Other minerals in which fluorine is also present in minor amounts are fluorocarbonates, fluorosulfates, fluoroarsenates, and fluorophosphates. In the case of the natural phosphates, the amounts present are sufficient to make them an important future source of fluorine, particularly as a by-product of the manufacture of super phosphates.

Besides the naturally occurring mineral, CaF_2, the most important fluorine compound on an industrial scale is hydrogen fluoride (HF). As will be shown later in this chapter, this compound has a number of very significant uses itself directly. In addition, it is the starting point in the production of most of the commercially available compounds of carbon and fluorine including gases used as refrigerants and aerosol propellants, lubricating and heat transfer fluids, fluorocarbon-type plastics and elastomers, surface active agents, as well as stain resistant finishes for textiles, oil resistant paper sizes, and special treatments for leather.

It is not the objective of this chapter to review the method used to produce the various commercial products. As the chapter title implies, emphasis will be placed primarily on a review of industrial applications and, where important, on some of the specific technology associated with these uses. An attempt will also be made to point out the unique performance characteristics and also to emphasize the ultimate economic advantages in the particular end use. The various topics which will be covered are not necessarily handled on the basis of relative commercial merit or usage. There have been a number of areas where the commercial development has only occurred in the past five to ten years. Some of these areas will be treated in a much more complete fashion. One of the important areas of usage, namely, glass and ceramics, has already been reviewed in Volume I of this same series(2).

II. Historical and Economic Factors

The word, fluorine, is derived from the Latin word, *fluere*, to flow. From early history, man has used the mineral, fluorspar, to accelerate the melting process of many silicate minerals, thereby permitting the more complete separation of the "slags" from the metal. Following the introduction of the open-hearth process for steel manufacture, United States consumption of fluorspar increased rapidly, starting at about 5000 tons per year in 1888 and reaching a maximum of approximately 645,000 tons in 1953 (3, p. 14).

For more than 60 years the steel industry accounted for approximately 80% of the total fluorspar consumed. It is interesting to note that the use of fluorspar in the open-hearth process has decreased from 7.4 lb per ton of steel in 1927 to less than 4.0 lb per ton in 1957.

As Finger *et al.* point out (3, p. 15), the lag in consumption of fluorspar in steel manufacture, coupled with a tremendous increase in hydrofluoric acid production in recent years, has brought about the changes shown in Fig. 1, covering the span from 1941 to 1959.

While steel consumption of fluorspar has remained relatively constant, except for a certain amount of year to year cycling, the hydrofluoric acid industry has used increasing quantities of fluorspar from 100,000 tons in 1949 to 300,000 tons in 1959. There are several reasons for this growth, among which are the increasing production of aluminum, the production of fluorocarbon derivatives, and the production of uranium. Consumption figures for 1957 are shown in Table I(4). The rapid rise in the use of fluorocarbon type gases as aerosol propellants and refrigerants is shown by the data in Table II for the period from 1951 to 1961 (5, p. 91).

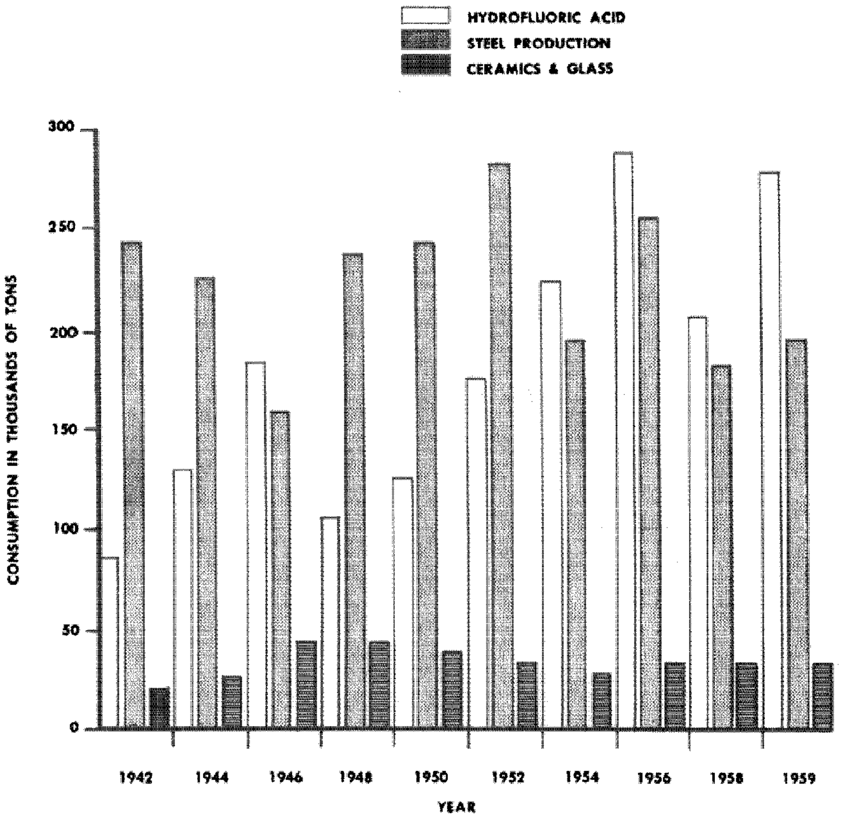


FIG. 1. Consumption of fluorspar in the United States.

The growth in this area is largely due to the usage as aerosol propellants for specialty packaging; the increase in the number of unit packages per year is shown in Fig. 2 (5, p. 96).

While the commercial usage of fluorine chemicals at this time is largely accounted for on the basis of uses listed in Table I, it may be anticipated that there will be significant increases in some of the newer products which have been introduced in the past five to ten years.

No analysis of the industrial situation would be complete without some reference to costs associated with the manufacture and use of these products. As has been pointed out earlier, fluorine is not a rare element in nature. Present production of hydrogen fluoride from fluorspar results

TABLE I

HYDROFLUORIC ACID USAGE IN THE UNITED STATES(4)

	Amount used (Short tons)	% used
Aluminum Production	53,000	39.2
Fluorocarbon Derivatives	38,500	28.5
Uranium Production	16,000	11.8
Conversion of Salts	7500	5.6
Stainless Steel Pickling	7000	5.2
Petroleum Alkylation	6000	4.5
Etching and Frosting Glass	2000	1.5
Others	2000	1.5
TOTAL	135,000	100.0

TABLE II

PRODUCTION OF FLUOROCARBON GASES FOR PROPELLANT AND REFRIGERATION USAGE—UNITED STATES

Year	Millions of pounds
1955	140
1956	170
1957	200
1958	220
1959	240
1960	300
1961	320

TABLE III

VOLUME VS SELLING PRICE FOR COMMERCIAL FLUORINE CHEMICALS FOR 1960 IN THE UNITED STATES

Commodity	Volume usage estimated (Millions of lb per yr)	Selling price ($ per lb)
Fluorospar	1200(6)	0.025
Hydrogen fluoride	300	0.17
Fluorocarbon refrigerants and propellants	300	0.20–0.70
Polytetrafluoroethylene	10	3.25–6.00

in the product being offered commercially from several sources in the range of 15 to 18 cents per pound. It has been estimated that recovery processes associated with the preparation of superphosphate fertilizers from apatite rocks could increase many-fold the volume of hydrogen fluoride at even lower costs than those at present.

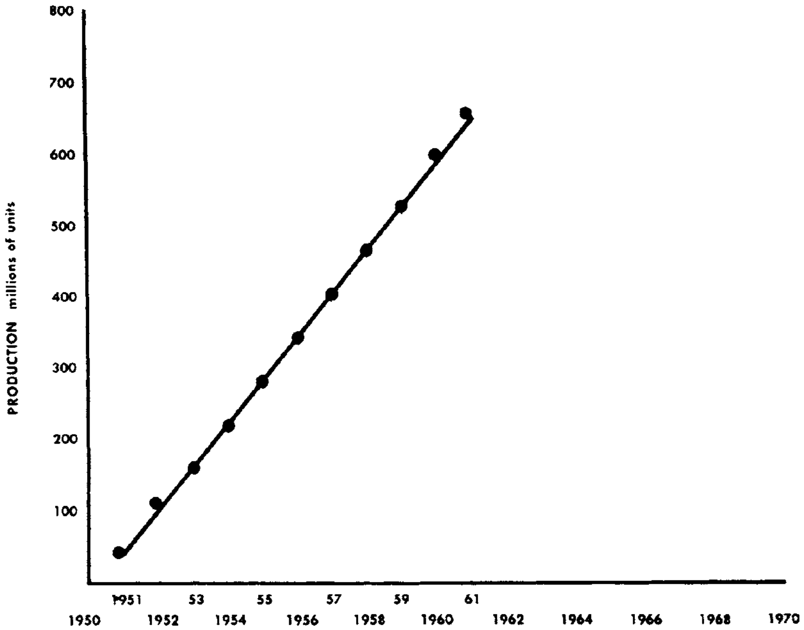


FIG. 2. Growth in production of aerosol propellants in the United States.

In Table III the relationship is shown between present selling prices and estimated sales volume for fluorine chemicals which exceed 2,000,000 lb per year for the year 1960.

Besides the above large volume items, there is an ever increasing list of new products based on fluorine, some of which are showing rapidly growing sales. As might be expected, the selling prices generally range upwards from those listed in the table. However, as the volume of these newer products increases, it would appear that the selling prices and manufacturing costs of most fluorine chemicals should fall in the general range indicated in Table III.

Compared to the general fields of inorganic and organic chemistry, there is relatively speaking a very meager amount of basic knowledge on fluorine and its compounds. Much of this knowledge has been acquired since World War II, where the need for lubricants and sealants which would be stable to uranium hexafluoride was the impetus. It is necessary, therefore, to make rather large investments in research and development in order to develop new products with new applications. Generally, entirely new types of chemical processes are involved in their manufacture, and often the uses are so unique that special marketing and selling effort are required to establish the need for these unique products before a profitable commercial market can be realized.

III. Characteristic Properties of Fluorocarbons

Fluorine is one of the most remarkable elements. This is due in large part to the unique position it occupies in the periodic table, being the first member of the halogen family. It is the most electronegative element known, exceeding in this respect its nearest competitors, chlorine and oxygen. Quantitatively the potential of the normal fluorine electrode is given as 2.85 v(7). Those of chlorine and oxygen are respectively 1.36 and 1.22. These large differences in electrode potentials between fluorine and its neighboring elements emphasize the unusual nature of this element and most of its compounds. In consequence of this, it is the most reactive element known, combining energetically with most of the other elements to form extremely stable compounds. Recent research has shown that fluorine also forms compounds with the rare gases such as xenon(190). As will be discussed later, the energetic nature of elemental fluorine is the basis for its use in rocket fuels, while the exceptional stability and non-reactivity of many compounds of fluorine have resulted in many other uses.

A. Bond Energies and Bond Distances

In Table IV the energies and interatomic distances are given for a number of specific bonds(8,9).

For comparison, one notes that the C—H bond distance is 1.09 Å, while the C—F is 1.36 Å, and C—Cl is 1.76 Å. It is also seen that the C—C bond distance is 1.54 Å. It is obvious that fluorine is unique in that it is the only halogen which has a bond radius less than that of the C—C distance, hence it can replace hydrogen in essentially all hydrocarbon structures without distorting or straining normal carbon to carbon bonds. In addition, of course, these bonds are extremely stable as evidenced by the very high heat of formation. Again, the unique position of fluorine is illustrated by the fact that the heat of formation of C—F is about 20

TABLE IV

BOND DISTANCES AND BOND ENERGIES(8)

Bond	Compound	Distance (Å)	Energy (kcal per mole)
C—H	CH_4	1.09	98.8
C—F	CF_4	1.36	116.0
C—Cl	CCl_4	1.76	78.5
S—F	SF_6	1.58	68.0
H—F	HF	0.92	147.5
H—Cl	HCl	1.28	103.2
H—O	H_2O	0.96	110.6
C—C	C_2H_6	1.54	83.1
C—C	C_2F_6	1.52	83.0

kcal greater than that of C—H, whereas that for C—Cl is about 20 kcal less than that of C—H.

Besides possessing extreme stability and inertness, fluorine compounds have other unique properties due to their low energy state. From an electronic structure point of view, most fluorine compounds exhibit a very neutral or nonpolar character which shows itself in the form of very low intermolecular forces.

B. BOILING POINTS AND MELTING POINTS

Figure 3 shows a striking similarity between the inert or noble gases and saturated fluorocarbons, when comparing boiling points and atomic or molecular weights. For example, krypton has an atomic weight of 83.7 and a boiling point of 120°K; whereas carbon tetrafluoride with a molecular weight of 88 has a boiling point of 145°K. By contrast, hexane, C_6H_{14}, which has a molecular weight of 86, has a boiling point of 342°K. It is obvious, therefore, that the molecular polarity of a fluorocarbon is very close to that of the inert gases; a saturated hydrocarbon, on the other hand, has a much more polarizable structure. Another striking example is that of uranium hexafluoride. This compound has a boiling point of 56°C, even though it has a very high molecular weight, namely 352. This low energy characteristic also shows up in the low melting points of many inorganic fluorine compounds and hence accounts for perhaps the oldest commercial usage of fluorine compounds as fluxing agents in metallurgical processing.

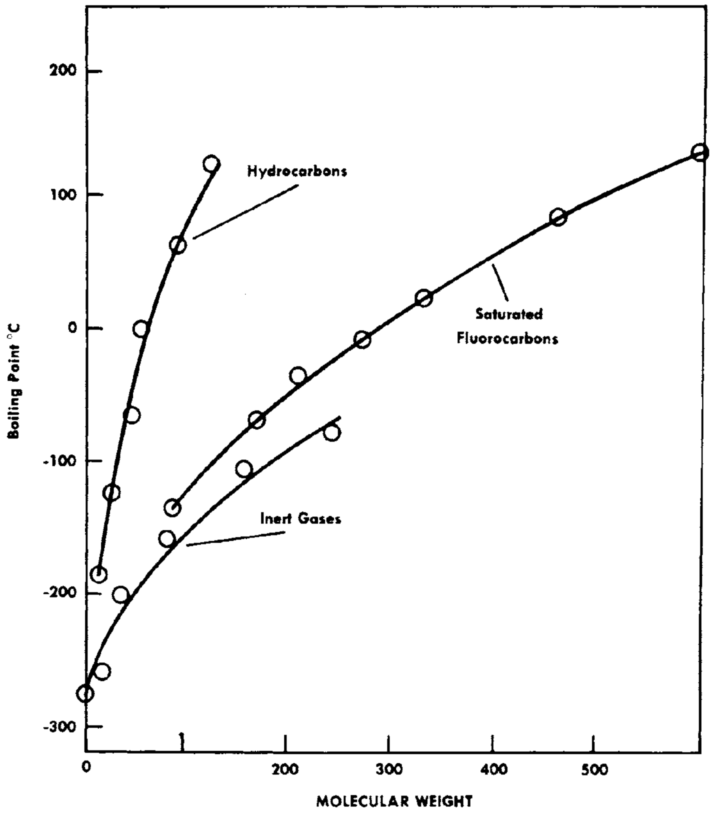


FIG. 3. Comparison of inert gases with fluorocarbon on a molecular weight vs boiling point basis.

C. SURFACE ENERGY

Another consequence of these low intermolecular forces is the very low surface energies of the fluorocarbons. While hydrocarbons have surface tensions of 20 to 35 dynes per cm, fluorocarbons have surface tensions of 9 to 18 dynes/cm. Typical values are given in Table V. As can be seen in the table, the compound *n*-C_8F_{18} has a surface tension of 13.7 dynes per cm; whereas the value for the hydrocarbon analog, *n*-C_8H_{18} is 21.8 dynes per cm.

Figure 4 shows surface tension vs concentration for a homologous series of fluorocarbon carboxylic acids(13). Of particular note are the minimum

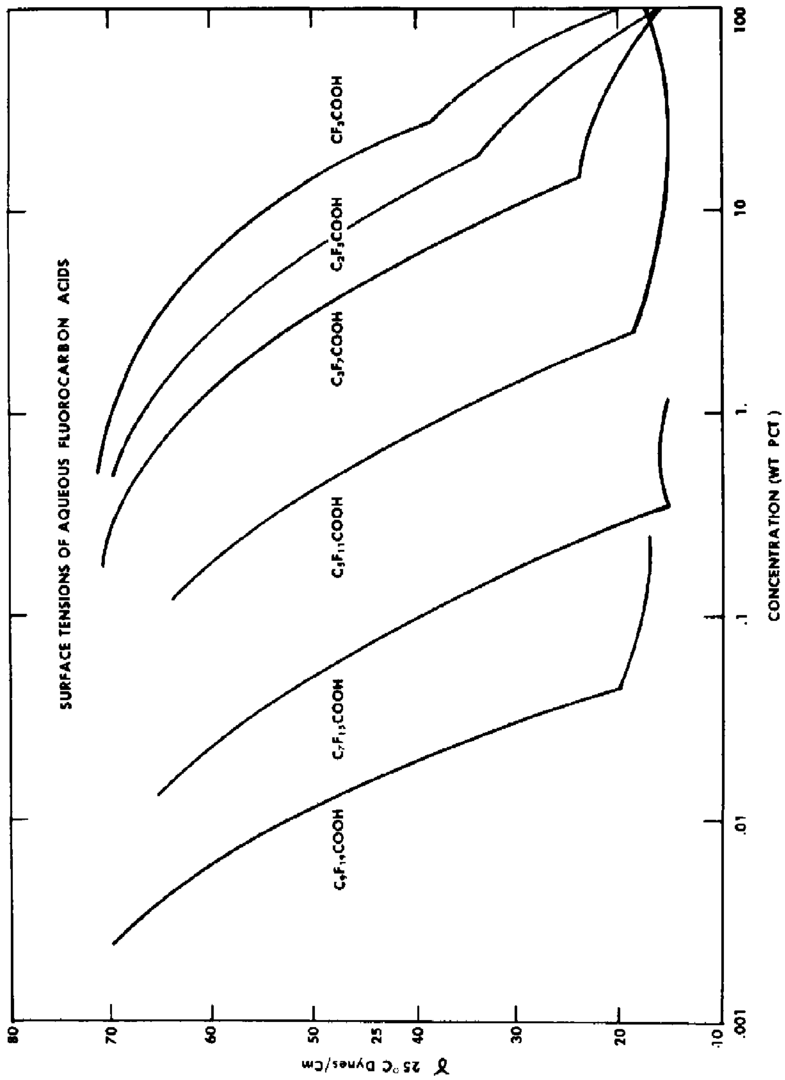


FIG. 4. Surface tensions for aqueous solution of a homologous series of fluorocarbon carboxylic acids.

TABLE V

Surface Tension for Typical Fluorocarbon Compounds

Compound	Surface tension γ (dynes per cm)	Reference
n-C_5F_{12}	9.87 (20°C)	(10)
n-C_7F_{16}	12.69 (20°C)	(10)
n-C_8F_{18}	13.7 (25°C)	(11)
cyclo-$C_8F_{16}O$	15.1 (25°C)	(12)
$(C_4F_9)_3N$	16.1 (25°C)	(45)

surface tensions between 15 and 18 dynes per cm. For comparison, typical surface active hydrocarbon compounds are capable of reducing the surface tension of water to only 28–32 dynes per cm.

W. A. Zisman and co-workers have pioneered in the study of low energy surfaces. Their work has emphasized the unique surface properties of fluorocarbon derivatives. Zisman has studied the spreading or wetting characteristics of liquid materials on a variety of low energy surfaces(14,17). In preparing the low energy surfaces he used clean, smooth glass or platinum, on which he adsorbed close-packed condensed films of various long-chain hydrocarbon and fluorocarbon type surface active compounds. In such a case the condensed films have the terminal group of the molecule oriented so as to form the new surface covering the glass or platinum.

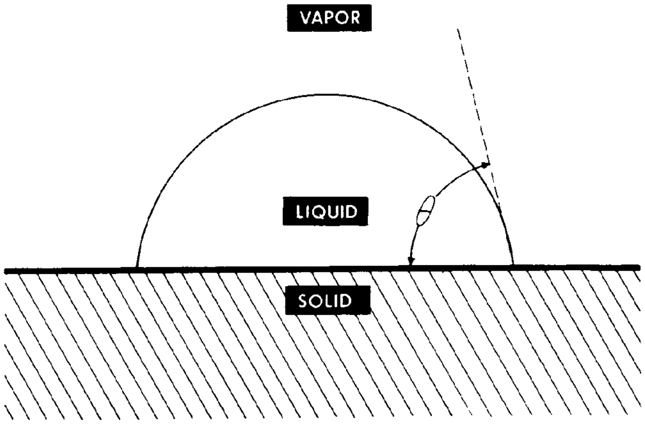


Fig. 5. Definition of contact angle for a drop of liquid on a solid surface.

Zisman and co-workers(15,16,18) have measured the contact angles for a homologous series of normal alkane liquids, whose surface tensions are known, when these liquids are placed on the "treated" surface. Figure 5 illustrates a liquid drop on such a solid surface and the contact angle, θ. Without going into theoretical details, the condition for equilibrium of a drop of liquid on a surface is:

$$\gamma_{SV^\circ} - \gamma_{SL} = \gamma_{LV} \cos\theta \tag{1}$$

where

γ_{SV° = interfacial energy for solid and saturated vapor
γ_{SL} = interfacial energy for solid and liquid
γ_{LV° = surface tension for liquid and saturated vapor.

The condition for spreading of the liquid on the surface, namely $\theta = 0$ degrees, is such that $\cos\theta = 1$.

Figure 6 shows the relationship between the known surface tensions for a series of *n*-alkane liquids and the cosine of the measured contact angle, when the liquids are placed on that surface. Three typical adsorbed surfaces are shown, namely, that formed from octadecylamine with a terminal —CH_3 group, that from polytetrafluoroethylene with —CF_2— groups, and the surface resulting from $C_{12}F_{26}COOH$ with a terminal —CF_3 group. Extrapolation of the straight lines to the value of $\cos\theta = 1$, the condition for spreading, gives what Zisman has defined as the critical surface tension value of that surface. Values for these critical surface

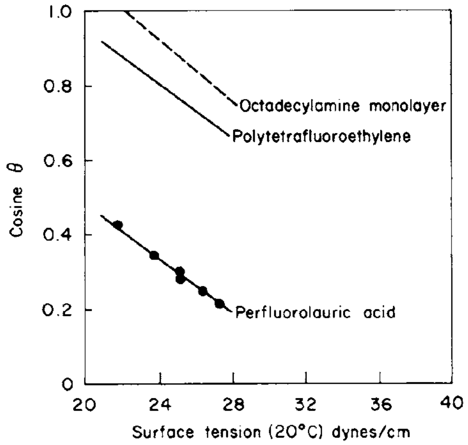


FIG. 6. Contact angles for a series of liquid normal alkanes on various types of solid surfaces. The critical surface tension γ_c, is defined as the intercept of the extrapolation of straight line with the horizontal line corresponding to $\cos\theta = 1$.

tensions, γ_c, are included in Table VI. The significance of these critical surface tension values is readily understood. For a liquid to wet a surface consisting of close-packed hydrocarbon groups with a terminal —CH_3, the liquid must have a surface tension of less than 22 dynes per cm. To wet a surface such as polytetrafluoroethylene with —CF_2— groups, the surface tension must be less than 18 dynes per cm. On the other hand, to wet a surface composed of close-packed fluorocarbon groups with terminal —CF_3 groups, the liquid must have surface tension values of less than 6 dynes per cm. This emphasizes very strongly the exceptionally low surface energy of the —CF_3 terminated fluorocarbon groups. If the surface is such that the —CF_2H terminal group is on the surface, the critical surface tension value is 15 dynes per cm, which is two and one-half times as large as that for the —CF_3 surface. The high energy of a surface containing chlorine atoms is illustrated by the data for polyvinylidene chloride in which the very high γ_c value of 43 dynes per cm has been measured. The uniqueness of the —CF_3 surface is clearly shown, and 6 dynes per cm is the most nonwettable surface ever reported.

TABLE VI

CRITICAL SURFACE TENSIONS (γ_c) OF LOW-ENERGY SURFACES

Surface constitution	γ_c(dynes per cm at 20°C)
—CF_3	6
—CF_2H	15
—CF_2—	18
—CH_3	22
—CH_2—	31
—CH— (benzene ring edge)	35
=CCl_2	43

Although the terminal groups dominate the effect on the surface energy of a surface, the data in Figure 7 shows that for a homologous series of fluorocarbon carboxylic acids, there is a significant decrease in the critical surface tension, γ_c, values as the chain length of the fluorocarbon group increases; C_3F_7COOH has γ_c value of approximately 10, C_{10}—$F_{21}COOH$ a value of 8, while $C_{12}F_{21}COOH$ has $\gamma_c = 6$. That this effect exists even in close-packed structures is important; for as will be obvious from later studies with very rough and irregular surfaces such as cotton, paper, or leather fibers, the effect of chain length is very pronounced. In the close-packed or condensed film state, the molecules are firmly held in the proper alignment for maximum orientation. On such surfaces as the fibers mentioned above, there is no real opportunity for close packing, and the proper orientation of the fluorocarbon group is entirely dependent on its ability to move freely. This free movement is, of course, much more readily achieved if the terminal —CF_3 group is attached to the surface through a —$(CF_2)_n$— group where n is at least 6.

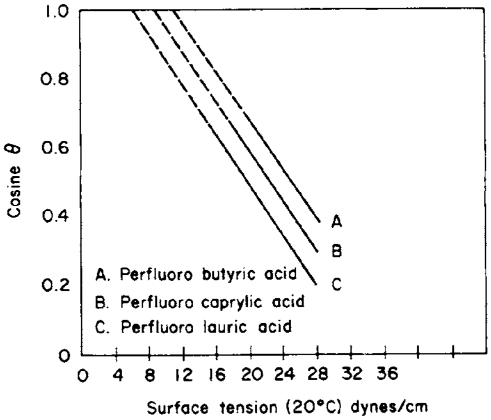


FIG. 7. The dependence of γ_c, critical surface tension, on chain length for a homologous series of fluorocarbon carboxylic acids absorbed on a solid surface.

Some idea of the degree of packing obtained on fiber surfaces may be gathered from the fact that a textile fabric treated with a —C_8F_{17} group will usually be wet by hydrocarbon liquids, whose surface tensions are less than 22 dynes per cm. It would appear that where close packing is not achieved, then the nature of the absorbing substrate will affect the critical surface tension of the surface.

As we shall see from later considerations, these characteristics are the basis for some unusual surface behavior of fluorocarbon type materials, including surface active effects in various liquid media and as surface treatments on solid surfaces including fibers such as paper, textiles, and leather.

D. STABILITY

It has already been pointed out that fluorine combines with many elements, and that in most cases, the combinations are very stable. The various compounds of carbon and fluorine illustrate this stability effect very well. With hydrocarbon compounds many of the reactions are due to reactions involving the carbon to hydrogen bond, examples being their ready oxidation in the presence of air or oxygen, substitution reactions involving halogens, etc. Two factors, at least, make the carbon to fluoride bond behave in an entirely different fashion. In the first place, the C—F bond is already in an oxidized state, whereas the C—H bond represents a reduced state. The second factor is the very high heat of formation of the C—F bond as compared to the C—H bond. These bond energies have already been referred to in Table IV. It is not at all surprising, therefore, to find the C—F bond inert to essentially all types of chemical action. Under ordinary conditions the only significant reactions involve those with molten alkali metals or with such metals as aluminum and magnesium at reasonably elevated temperatures. In these cases the reaction which occurs involves the formation of the metal fluorides, which have even higher energies of formation than the —C—F compounds.

This chemical stability also extends itself to all types of biological processes; there are no known biological organisms that are able to attack the carbon-fluorine bond in a fluorocarbon.

The principal reaction which fluorocarbons undergo at elevated temperatures in the presence of a wall is that of carbon to carbon bond cleavage. These cracking reactions are very similar to those occurring with hydrocarbons and, depending on chain length, may take place at temperatures from 600 to 1000°C. A compound such as C_8F_{18} will show some carbon to carbon bond breaking at 600°C, whereas C_2F_6 required temperatures approaching 1000°C before C—C bond cleavage occurs. It should be borne in mind that only pure fluorocarbons will exhibit stability such as given above. Many commercial fluorocarbon products are less stable due to the presence of less stable impurities. The compound, CF_4, is reported to be completely stable at temperatures in excess of 1200°C.

In the absence of a reactive environment, the thermal cracking reactions of fluorocarbon compounds produce primarily other fluorocarbons of greater or lesser molecular weight but of equal or greater thermal stability. These, of course, are formed by recombination of the various fragments such as $—CF_3$, $—C_2F_5$, $—C_nF_{2n+1}$, $—CF_2—$, $—(CF_2)_n—$, etc. If the thermal degradation is carried out in an environment which contains reactive species such as —C—H, —C—Cl, or in reaction vessels composed of silica, i.e., glass or ceramics, then a variety of reactions will occur between these reactive species and the highly energetic fluorocarbon radicals leading to products such as HF and SiF_4. On the other hand, metals—except the alkali or alkaline earths—are essentially inert to fluorocarbon radicals under cracking conditions. This is due to the protective action of very thin films of the metal fluorides, which, besides being completely stable in the presence of fluorocarbon radicals, are also impermeable; but some of them are known to be catalysts for fluorocarbon reactions. The unusual reactivity of glass or ceramic surfaces, of course is due to the fact that the fluorides of silicon and hydrogen, SiF_4 and HF respectively, are gaseous and therefore offer no protective action.

Fluorocarbons are quite stable to radiation. For example, a commercially available product known as FC-75, and consisting of a mixture of C_8F_{18} and c-$C_8F_{16}O$, has been subjected to various dosages of gamma radiation using both a spent fuel element source and also high energy electrons(19). The FC-75 was sealed in specially prepared aluminum cans. As shown in Table VII, the results are essentially the same with either the gamma rays or the high energy electrons. With increasing

TABLE VII

EXPOSURE OF FC-75 TO GAMMA AND ELECTRON RADIATION

Dosage represents	Viscosity (cs at 25°C)	Density (25°C)	Hydrolyzable fluoride (% of total fluoride)
Starting materials	0.800	1.770	0.00
1 × 10^8 (gamma)	0.974	1.783	0.07
5 × 10^8 (gamma)	2.115	1.979	0.35
0.75 × 10^8 (electron)	0.855	1.804	0.07
3 × 10^8 (electron)	1.420	—	0.23
5 × 10^8 (electron)	2.850	—	0.53

TABLE VIII

COMPARATIVE STABILITY OF FLUOROCARBONS AND HYDROCARBONS TO RADIATION

Compound	$-G_M$	G (Gas)	G (Poly)
n-butyl benzene	—	0.33	—
isopropyl benzene	—	0.18	—
n-C_6H_{14}	9.9	3.8	—
n-C_8H_{18}	—	4.48	—
$C_2F_5C_6F_{11}$	>2.2	0.75	—
C_8F_{18}	2.75	0.5	—
$C_8F_{16}O$	3.25	1.0	—
C_7F_{16}	2–3		
C_6H_6		0.088	0.93
C_6F_6		0.045	2.01

dosage there is a significant increase in both viscosity and density, presumably due to the formation of higher molecular weight products, by carbon to carbon bond cleavage and subsequent recombination of resulting fragments or fluorocarbon radicals.

In Table VIII data is given comparing the radiation stability of a number of hydrocarbon and fluorocarbon compounds(20,21,22). The results are expressed in terms of the *G* factor, *G* being defined as the number of molecules of the substance in question produced by 100 ev of energy absorbed by the material. The subscript is used to indicate the type of material produced. For instance, $G_{gas} = 3$ indicates 3 molecules of gaseous products are produced per 100 ev of energy absorbed in a sample. Similarly $-G_M$ indicates the number of molecules of the original compound destroyed per 100 ev of energy absorbed by a compound.

The data included in Table VIII is rather sketchy, but does show that the *G* values for fluorocarbons are significantly lower than the normal aliphatic hydrocarbons, and in fact are at least approaching the stability of the aromatic hydrocarbons. A survey of the literature on radiation resistance of fluorocarbon materials leads to confusing conclusions, since many workers were not careful to define purity of the starting material or to avoid use of reactive surfaces such as glass. In the case of fluorocarbons, it must be emphasized again that the presence of less stable impurities will give very erroneous results.

E. Electrical Properties

Other properties which are indicative of the low polarizability of fluorocarbon compounds are their refractive indices and their dielectric constants.

Table IX gives values of those properties which are associated with the nonpolar nature of a variety of liquid fluorocarbon compounds. Of particular note are the very low dielectric constants and the low dissipation factors which—as we shall see later—play an important role in some of the electrical applications. The extremely low values for refraction index are also shown in the table.

F. Polarity of Oxides or Nitrides and Effect of Structure

The data given in Table IX emphasize again the ability of an environment of fluorine atoms to neutralize the polar nature of a molecule. Compounds such as the $(C_3F_7)_3N$ or $(C_4F_9)_2O$, by analogy with hydrocarbon tertiary amines or ethers might be assumed to possess a definite polar character. This assumption is entirely wrong, as may be seen from a survey of not only the electrical properties but also the boiling points.

TABLE IX

ELECTRICAL PROPERTIES—FLUOROCARBON LIQUIDS (25°C)[23]

Material	Boiling point (°C)	Refractive index n_D	Density (gm per cm^2)	Dielectric constant (100c)	Dissipation factor (100c)	Resistivity (ohm-cm, 5 kv per in.)	Dielectric strength ASTM(D-877)
$(C_2F_5)_3N$	69	1.261	1.73	1.89	<0.0005	10^{15}—10^{17}	39 kv
$(C_3F_7)_3N$	129	1.279	1.82	1.85	<0.0005	10^{15}—10^{17}	44
$(C_4F_9)_3N$	178	1.290	1.87	1.86	<0.0005	10^{14}—10^{16}	45
$(C_4F_9)_2O$	101	1.261	1.71	1.77	<0.0005	10^{15}—10^{17}	43
$(C_6F_{13})_2O$	172	1.278	1.81	1.85	<0.0005	10^{15}—10^{17}	45
cyclo-$C_6F_{12}O$	56	1.263	1.69	1.85	<0.0005	10^{15}—10^{17}	41
cyclo-$C_8F_{16}O$	103	1.278	1.77	1.85	<0.0005	10^{15}—10^{17}	43
C_8F_{18}	103	1.2705	1.83	1.82	<0.0005	>10^{15}	>35

For all intents and purposes the presence of the nitrogen or the oxygen atom in the above structures does not contribute any polar character to the molecules. Hence, it is more proper to refer to such fluorocarbon compounds as fluorocarbon nitride or oxides, rather than to associate them with typical properties of hydrocarbon amines or ethers.

TABLE X

PROPERTIES OF CERTAIN 12-CARBON FLUOROCARBON COMPOUNDS

Compound	$(C_6F_{13})_2O$	$C_{12}F_{26}$	$(C_4F_9)_3N$
Boiling point, °C	172	175	177
Pour point, °C (ASTM D-97)	−90	42	−50
Viscosity, cs (25°C)	2.11	—	2.96

In Table X the effect of structure is shown for a series of twelve carbon fluorocarbon compounds(24). It will be observed that all compounds boil at about the same temperature. On the other hand, a marked difference shows up in the freezing points. $C_{12}F_{26}$ is a solid at room temperature; whereas the other two compounds are liquids, with freezing points of −50 and −90°C., respectively. The presence of the oxygen and nitrogen atoms plays an important role in contributing internal flexibility to the molecule, hence overcoming the normal stiffening effect of a fluorocarbon chain.

G. SOLUBILITY

The solubility relationships of fluorocarbon compounds are also quite unique. Hildebrand and Scott(25) have shown that the thermodynamic properties of solutions involving two components depend upon the square of the difference between the values of a quantity δ for each of the two components. These δ values have been termed "solubility parameters" and have been identified with the square roots of the internal pressure or cohesive energy densities of the pure substances. The solubility parameter for a specific substance may be defined:

$$\delta = \left(\frac{\Delta E^V}{V}\right)^{\frac{1}{2}} \tag{2}$$

where E = energy of vaporization of the pure component and V its molal volume all at the same temperature T. The term, $\Delta E^V/V$ is the "internal pressure" or "cohesive energy density."

Where the solubility parameters for two liquids, δ_1 and δ_2 are equal, there is no heat of mixing and hence the two liquids are miscible in all proportions. When the difference between δ_1 and δ_2 becomes sufficiently great, complete miscibility is no longer possible; and two phases may coexist. As the absolute value of δ_1—δ_2 increases, the mutual solubilities of the two liquids decreases, until for large differences they have become almost infinitesimal and almost "complete" insolubility is reached.

While the solubility depends primarily on the difference in δ values, it is also a function of the molal volumes, V, and the temperatures. When $V_1 = V_2 = V$, then the condition for complete miscibility is

$$V(\delta_1 - \delta_2)^2 < 2RT \qquad (3)$$

Calculation of the solubility parameter, δ_T, requires knowledge of the molal volume, V_T, and the heat of vaporization, ΔH_T^V, at the desired temperature. Table XI includes data on the thermodynamic properties of a number of fluorocarbons. As can be seen from this data, the fluorocarbons in general have values of "solubility parameter" between 5 and 6.

TABLE XI

THERMODYNAMIC PROPERTIES OF A SERIES OF CYCLIC AND NORMAL ALKFORANES

Formula	Name	Boiling point (°C)	$V_{298°K}$ (cm³ per mole)	$\Delta H_{298°K}$ (kcal per mole, estimated)	$\delta_{298°K}$ (cal per cm³)$^{\frac{1}{2}}$
C_4F_{10}	*n*-Butforane	—2	163	5.0	5.2
C_5F_{12}	*n*-Pentforane	29.5	183	6.0	5.5
C_6F_{14}	*n*-Hexforane	58	205	7.1	5.6
C_7F_{16}	*n*-Heptforane	82.4	227	8.1	5.7
C_8F_{18}	*n*-Octforane	104	253	8.9	5.7
C_9F_{20}	*n*-Nonforane	123	279	9.7	5.7
C_6F_{12}	cyclohexforane	sublimes	170	6.8	6.0
C_7F_{14}	methforyl cyclohexforane	77.5	195	7.7	6.0

Table XII gives solubility parameter values for a number of selected substances. As would be predicted from the solubility relationships discussed above, there is reasonably good correlation between the actual solubilities of the materials in Table XII with the fluorocarbons and those values predicted on the differences in "solubility parameters". The fluorocarbons have a unique position in that they have extremely low "solubility parameter" values.

TABLE XII

SOLUBILITY PARAMETERS FOR SELECTED SUBSTANCES

	$V_{298°K}$	$\delta_{298°K}$
Phosphorus	70	14.6
Iodine	59	14.1
Sulfur	136	11.7
Pyridine	81	10.7
Carbon disulfide	61	10.1
Chlorobenzene	102	9.5
Chloroform	81	9.3
Benzene	89	9.2
Ethyl acetate	99	9.1
Carbon tetrachloride	97	8.6
Cyclohexane	109	8.2
Methyl cyclohexane	128	7.8
n-Octane	164	7.6
Ethyl ether	105	7.5
n-Heptane	147	7.5
n-Hexane	132	7.3
n-Pentane	116	7.0

Having reviewed some of the characteristic properties of fluorine, and many of its compounds, it will be of interest to consider the industrial applications for this relatively new class of chemicals, bearing in mind the unique properties which they possess.

IV. Refrigerants and Propellants

In 1930 Midgley and Henne(28) discovered that various derivatives of methane and ethane, in which all—or almost all—of the hydrogen atoms were replaced by fluorine and chlorine atoms, had the desired properties for practically ideal refrigerants. They were nontoxic and

TABLE XIII

FLUOROCARBON TYPE REFRIGERANT AND PROPELLANTS OF MAJOR COMMERCIAL IMPORTANCE

Methane series		Ethane series	
Code	Compound	Code	Compound
F-11	CCl_3F	F-112	CCl_2FCCl_2F
F-12	CCl_2F_2	F-113	CCl_2FCClF_2
F-13	$CClF_3$	F-114	$CClF_2CClF_2$
F-14	CF_4	F-115	$CClF_2CF_3$
F-21	$CHCl_2F$		
F-22	$CHClF_2$		

nonflammable. They were first offered for sale in 1931 under the trademark, "Freon" halogenated hydrocarbons by the Kinetics Chemical Division of the E. I. duPont de Nemours and Company. Other companies in the United States have since introduced the same products using their own trade-names, i.e., "Genetron" (General Chemical Company), "Isotron" (Pennsalt Manufacturing Company), and "Ucon" (Union Carbide Company). All the above companies have adopted the same code numbers for the same compounds. Those having the greatest commercial usage are listed in Table XIII.

A. PROPERTIES

There are many factors that must be taken into account when selecting a chemical for use as a refrigerant or an aerosol propellant. Besides boiling point, pressure, stability, toxicity, and flammability, such factors as molecular weight, density, compression ratio, heat value, temperature of

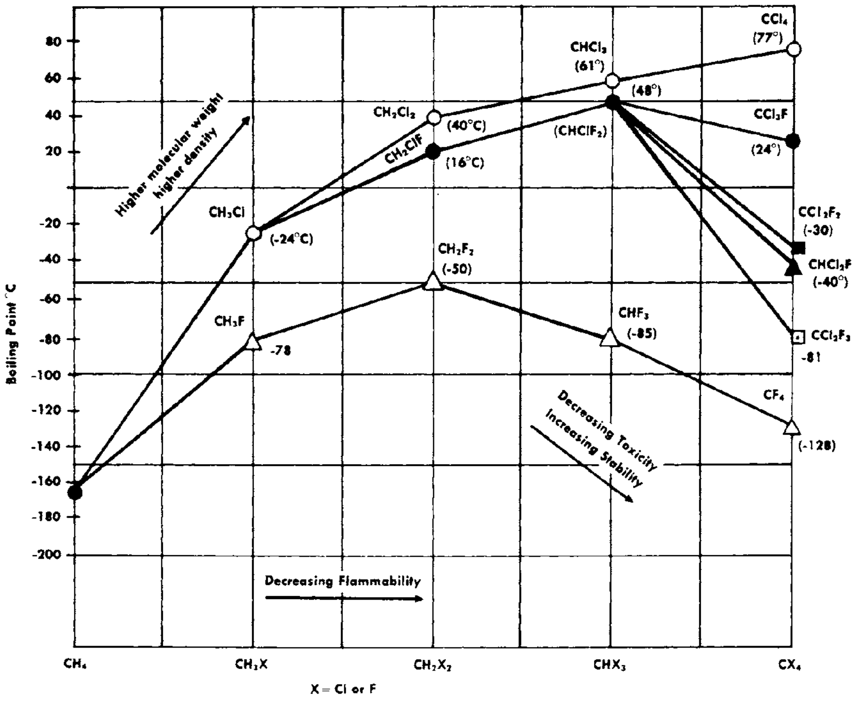


FIG. 8. Properties of chlorofluoro derivatives of methane.

compression, compressor displacement, design or type of compressor, etc., must also be considered.

A graphic presentation which was developed by Midgley and Henne(28,29) is quite useful in giving a better understanding of the properties of a number of these fluorine-containing compounds, especially those which have been so widely accepted for use as refrigerants and also as "aerosol" propellants.

In the graph shown in Fig. 8 the rules of susbtitution will apply to typical groups having one carbon atom per molecule, or the methane series. It will be noted that when the fluorine content increases from that of CH_2F_2 (F-32) to CHF_3 (F-23), the boiling point decreases, stability increases, flammability decreases, and toxicity decreases as indicated in the graph. Likewise, when the fluorine content increases still further to CF_4 (F-14), the properties change to even lower boiling point, greater stability, and less toxic nature.

However, if the fluorine content remains constant and substitution is made for hydrogen by another halogen such as chlorine, the boiling point increases, stability and toxicity increase slightly, but flammability decreases. By again referring to Fig. 8, a similar change in properties will occur when the chlorine content is increased from CH_2F_2 (F-32) to $CHClF_2$ (F-22) and still further to CCl_2F_2 (F-12).

In Table XIV are shown some of the important members of fully saturated fluorine-containing compounds in the methane series and ethane series. The general rules of substitution as reviewed for the methane derivatives will apply also to members of the ethane series; curves showing the changes in properties with halogen content have also been drawn(28). In the case of fluorine-containing compounds having two or more carbon atoms per molecule, fluorine substitutions can be made for hydrogen or chlorine on either of the two carbon atoms producing symmetrical or asymmetrical arrangement.

From a commercial viewpoint, primary interest is concerned with compounds in the methane and ethane series. In the United States F-12 accounts for almost half the production, with F-11, F-22, F-114, and F-113 making up the bulk of the remaining production.

These compounds as refrigerants are adaptable for use in all compression types of refrigeration systems. The physical, chemical, and thermodynamic properties of quite a number of the fluorine-containing methane and ethane compounds have been carefully and fully studied and data published(188). However, a few of their outstanding properties will be reviewed.

The fluorine-containing chlorohydrocarbons are colorless, almost odorless, with boiling points varying over a wide temperature range.

TABLE XIV

Chlorine and Fluorine Derivatives of Methane and Ethane

Code	Formula	Molecular weight	Boiling point	Code	Formula	Molecular weight	Boiling point
Methane derivatives							
F-11	CCl_3F	137.4	24°C	F-21	$CHCl_2F$	102.9	9°C
F-12	CCl_2F_2	120.9	−30°C	F-22	$CHClF_2$	86.5	−41°C
F-13	$CClF_3$	104.5	−81°C	F-23	CHF_3	70.0	−84°C
F-14	CF_4	88	−128°C	F-31	CH_2ClF	68.5	−11°C
				F-32	CH_2F_2	52.0	−52°C
				F-41	CH_3F	34.0	−78°C
Ethane derivatives							
F-111	CCl_3CCl_2F	220.3	137°C	F-131c	$CHCl_2CHClF$	151.4	103°C
F-112	CCl_2FCCl_2F	203.8	93°C	F-132c	$CHCl_2CHF_2$	135.0	60°C
F-113	CCl_2FCClF_2	187.4	48°C	F-133c	$CHClFCHF_2$	118.5	17°C
F-114	$CClF_2CClF_2$	170.9	4.7°C	F-134c	CHF_2CHF_2	102.0	−23°C
F-115	$CClF_2CF_3$	154.5	−38°C	F-141a	$CH_2ClCHClF$	116.9	74°C
F-116	CF_3CF_3	134.0	−78.4°C	F-142a	CH_2ClCHF_2	100.5	35°C
F-121	$CHCl_2CCl_2F$	185.8	117°C	F-143a	CH_2FCHF_2	84.0	5°C
F-122	$CHCl_2CClF_2$	169.5	71.7°C	F-151a	CH_2ClCH_2F	82.5	35°C
F-122b	$CHClFCClF_2$	152.5	28°C	F-152	CH_3CHF_2	66.0	−25°C
F-124a	CHF_2CClF_2	136.5	−10°C	F-161	CH_3CH_2F	48.0	−37°C
F-125	CHF_2CF_3	120.0	−48°C				

Those that are of primary importance in the field of refrigeration as well as propellants are essentially nontoxic, noncorrosive, nonirritating, and nonflammable under normal conditions of usage. They are generally prepared by replacing chlorine or hydrogen with fluorine. Chemically they are inert and thermally stable up to temperatures far beyond conditions found in actual use as refrigerants or propellants.

B. Refrigeration Characteristics

Pressures required to liquefy the refrigerant vapor affect the design of the system; refrigerating effect and specific volume of the refrigerant vapor determine the compressor displacement; and the heat of vaporization and specific volume of liquid refrigerant affect the quantity of refrigerant to be circulated through the pressure regulating valve or other device. Table XV covers boiling point at one atmosphere, freezing point, critical temperature, and critical pressures of not only the fluorine-containing methane and ethane derivatives, but other commonly used refrigerants.

TABLE XV

Comparison of Various Refrigerants[30]

Refrigerant	Boiling point (°C)	Freezing point (°C)	Critical temperature (°C)	Critical pressure (psi, absolute)
CF_4 (F-14)	−128	−191	−45	542
$CClF_3$ (F-13)	−81	−182	29	579
CO_2	−78	−54.7 (triple)	31	1071
$CHClF_2$ (F-22)	−41	−160	96	716
NH_3	−33	−77	132.7	1651
CCl_2F_2 (F-12)	−30	−157	111.5	582
SO_2	−10.5	−73	157	1142
$CClF_2CClF_2$ (F-114)	4.7	−94	146	474
$CHCl_2F$ (F-21)	9	−135	167.5	750
CCl_3F (F-11)	24	−111	198	635
CCl_2FCClF_2 (F-113)	48	−35	214	495

The chlorofluoro derivatives of methane and ethane have relatively low heat values. This should not be considered a disadvantage since this merely means that a greater volume of liquid must be pumped through the system per unit time to produce the required amount of refrigeration.

From an engineering point of view, this turns out to be a decided advantage, especially for small tonnage units, since more accurate and reliable control of liquid flow is possible when larger flows of liquid are involved. The heat values for both liquid and vapor, as well as relative refrigerating effect of a number of common refrigerants, is shown in Table XVI.

TABLE XVI

HEAT VALUES FOR LIQUID AND VAPOR STATES FOR VARIOUS REFRIGERANTS

Refrigerant	Heat value (BTU per lb)		Refrigerating effect
	Vapor (−15°C)	Liquid (30°C)	
CO_2	102	45	56.7
$CHClF_2$ (F-22)	106	36	69.3
NH_3	613	139	474.5
CCl_2F_2 (F-12)	79	28	51.1
SO_2	183	42	141.4
$CClF_2$—$CClF_2$ (F-114)	72	29	43.1
CCl_3F (F-11)	93	25	67.5

TABLE XVII

OPERATING PRESSURES FOR VARIOUS REFRIGERANTS(30)

Refrigerant	*Pressure (psi gauge)* At 30°C	At −15°C
CO_2	1024.3	319.7
$CHClF_2$ (F-22)	159.8	28.3
NH_3	154.5	19.6
CCl_2F_2 (F-12)	93.2	11.8
SO_2	51.8	5.9[a]
$CClF_2CClF_2$ (F-114)	22.0	16.1[a]
CCl_3F (F-11)	3.6	24.0[a]

[a] Units are inches of mercury below one atmosphere.

In Table XVII are given the operating pressures for a series of standard refrigerants based on standard ton conditions. Carbon dioxide has a much higher pressure than the others, with a consequent much higher horsepower requirement.

In Table XVIII data is given on the explosive properties of refrigerants as established by the Underwriters Laboratories(31). All the flourine-containing refrigerants are nonflammable.

Table XIX contains data on the comparative toxic properties of various refrigerants(31).

These fluorine-containing halocarbons have characteristic physical and thermodynamic properties which make them readily adaptable for use in reciprocating, rotary, and centrifugal compressors, which vary in size from fractional refrigeration tonnage to several thousand tons capacity. They produce wide ranges of temperatures from room temperatures to low subzero temperatures. The particular choice depends upon size and type of installation and also the desired cooling capacity.

TABLE XVIII

FLAMMABILITY AND EXPLOSIVE PROPERTIES OF VARIOUS REFRIGERANTS(30)

Refrigerant	Explosive range (Concentration in air % by volume)
NH_3	16—25
CH_3Cl	8.1—17.2
SO_2	nonflammable
CO_2	nonflammable
F-11	nonflammable
F-22	nonflammable
F-114	nonflammable
F-12	nonflammable

TABLE XIX

TOXICITY OF VARIOUS REFRIGERANTS(30)

Refrigerant	Duration of exposure	Concentration in air to kill or injure seriously (% by volume)
SO_2	5 min	0.7
NH_3	30 min	0.5–0.6
CCl_2FCClF_2 (F-113)	30 min	4.8–5.2
CO_2	30-60 min	29.0–30.0
CCl_3F (F-11)	2 hr	10
$CHClF_2$ (F-22)	2 hr	9.5–11.7
$CClF_2CClF_2$ (F-114)	2 hr	20.1–21.5
CCl_2F_2 (F-12)	2 hr	28.5–30.5

C. APPLICATIONS FOR SPECIFIC COMPOUNDS

F-12 (CCl_2F_2), having a boiling point of −21.6°F and a pressure of 93.2 psig at 86°F, is used extensively as an aerosol propellant for such items as insecticides, insect repellants, deodorizers, hair dressings, and a host of other products. F-22 ($CHClF_2$), besides being used as a low temperature refrigerant, is also used as an intermediate in the production of polytetrafluoroethylene. F-113 (CCl_2-$FCClF_2$) is used in heavy duty air conditioning units and is also useful as a specialty solvent and as an intermediate in the production of polychlorotrifluoroethylene.

Recently the compound, c-C_4F_8, octafluorocyclobutane(32), has been introduced as a nontoxic material for use as an aerosol propellant in food applications such as whipped cream, salad dressings, pancake mixes, etc. This material boils at −6°C and has a vapor pressure of 40 psi absolute at 21°C. Although the chlorine-containing compounds are relatively nontoxic, their use has not been permitted in food applications since, as the data in Table XIX shows, they do have some toxic effects at relatively high levels. This use emphasizes again the fact that a compound containing only carbon and fluorine is essentially nontoxic; whereas the presence of chlorine or hydrogen atoms in the molecule introduces some degree of solubility in body fluids which are both aqueous or organic in nature.

V. Heat Transfer Media

In the preceding section the advantages in using fluorochloro derivatives of methane and ethane in refrigeration systems were emphasized where the process is one of removing heat from a lower temperature to a condition of higher temperature. In this section, attention will be given to the process of removing heat from an elevated temperature and discharging it at a lower temperature. This is a process which affects the efficiency and practicality of many of the scientific and engineering developments of the world today. The average internal combustion engine used to power an automobile must be cooled, generally by circulating liquid water through chambers in the cylinder block. Of course, in many operations, such as electric motors, aircraft engines, the cooling is accomplished by circulating air. In a number of electrical components, such as transformers, a nonvolatile hydrocarbon-type oil is used, not only as a coolant, but also to provide the required dielectric properties.

A. HEAT TRANSFER PROCESSES

The process by which heat is removed from a body by the circulation of a fluid over the surface, be it a gas such as air or hydrogen or a liquid such as water, oils, etc., is referred to as *convective* cooling. The efficiency of this process is primarily a function of the heat capacity of the fluid and other factors such as rate of flow and viscosity. The most efficient means of removing heat from a hot surface involves the evaporation of a fluid, the so-called *evaporative* cooling. In this case, a relatively low boiling fluid is put in contact with the hot surface at temperatures in excess of the boiling point. The evaporation process, of course, absorbs heat, namely, the heat of vaporization, which is liberated again upon condensation on another surface where the temperature is maintained below the boiling point of the fluid.

B. MINIATURIZATION

Since World War II, the engineer has been faced with the operation of many pieces of equipment where the facilities for cooling are extremely limited. Especially is this true of man's efforts to conquer space, whether it be in the form of high speed aircraft, long range missiles, or vehicles for outer space travel. In the operation of equipment at ground level, factors such as size and weight are not nearly as important as they are when the same type of equipment is to be operated in an aircraft, missile, or space ship. For example, a piece of electrical equipment such as a radar tube requires rather sizeable auxiliary gear to provide the electrical power. All of this gear, including the tube, generate considerable heat which must be removed below some critical temperature in order that the unit will continue to operate for prolonged periods of time without failure. In ground level installations, this cooling can usually be accomplished quite readily by spacing the various components far apart and also by providing auxiliary cooling through the circulation of air or even more efficiently by use of a coolant liquid and an appropriate heat exchanger. In airborne equipment, weight and space are extremely limited; and, in addition, every extra pound carried not only required added fuel, but actually replaces fuel that might be badly needed for propulsion. Such considerations as these have led the engineer to look for radically new techniques for cooling the heat generating components which are necessary for the satisfactory operation of modern airborne or space directed aircraft, missiles, and outer space craft.

Besides the space and weight limitations, there is also the wide extremes of temperature under which the various pieces of equipment must be operable, generally from −80°F to several hundred degrees Fahrenheit. Any coolant, therefore, must not become solid or even so viscous that at a low temperature such as −80°F it cannot be pumped with relatively low horsepower. If the fluid viscosity at low temperatures is high, then any gain in weight or volume by the use of such a coolant would immediately be lost by having to provide very large start-up horsepower.

Many other requirements must also be met by such coolants besides the above. They must be good lubricants, must be nonflammable, nonexplosive, nontoxic, and noncorrosive, and especially if used around electrical equipment, should have good electrical properties.

C. APPLICATION OF FLUOROCARBON FLUIDS TO HEAT TRANSFER PROBLEMS

The heat transfer properties of inert fluorocarbons have been of interest in the past few years. In 1954, Olyphant and Brice(33) recognized that for natural convection liquid cooling, a fluorocarbon liquid had only modest heat transfer advantage over transformer oil. On the other hand, these workers found by using an electrically heated choke coil immersed in a boiling fluorocarbon liquid, that ten times as much heat was transferred for a given temperature rise as when the same coil was immersed in transformer oil where only natural convection could occur.

1. *Transformers*

Prompted at least initially by military needs, Kilham, Ursch, and Ahearn of the Raytheon Corporation(34) were the first to study the use of fluorine-containing compounds as dielectric coolants in transformers. Their work initially was directed at the problem of miniaturizing a transformer. They initially screened a wide variety of liquids including telomers of $CF_2=CFCl$, dichlorooctafluorobutane, products resulting from the direct fluorination of kerosene, conventional silicone and hydrocarbon dielectric fluids, and fluorocarbon liquids containing an oxygen or nitrogen atom, since designated commercially as FC-75 and FC-43. They also examined gaseous products, such as SF_6 and C_3F_8, as permanent dielectrics to be used in conjunction with the liquids. Kilham *et al.* found that the only fluids which satisfied all the essential requirements were the liquids, FC-75 and FC-43, and the gases, SF_6 and C_3F_8(35).

Before these fluids or gases were proven satisfactory, however, it was necessary to purify them to an extremely high degree to free them of even trace amounts of compounds containing hydrogen or chlorine. This point cannot be stressed too strongly. It is indeed unfortunate that much of the early work on so-called fluorocarbon materials is strongly suspect—due to failures to remove impurities such as trace amounts of —C—H or —C—Cl. From a process standpoint, purification procedures are often not too difficult to carry out. Generally, they involve subjection of the fluorocarbon material to action of very strong chemicals such as fused sodium hydroxide or concentrated potassium permanganate solutions, exposure to elevated temperatures, generally in the presence of metals such as copper, steel, nickel, etc. Under such conditions, any hydrogen or chlorine-containing products will be destroyed with no significant effect on the saturated fluorocarbons.

Using two commercially available fluorocarbon fluids, FC-75 and

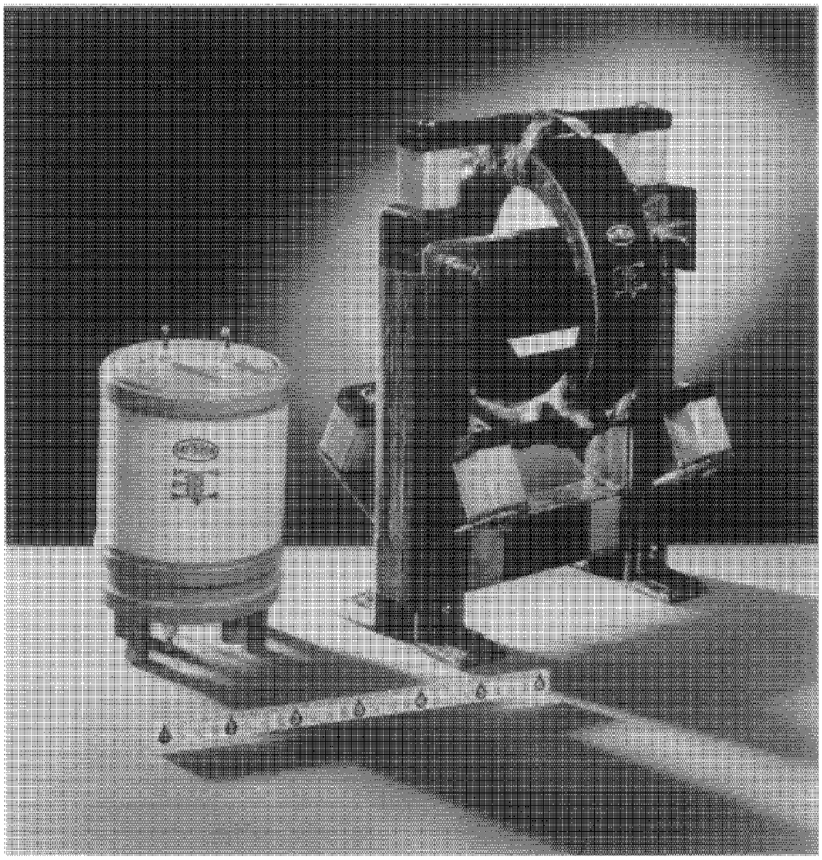


FIG. 9. (Courtesy of Raytheon Corporation.) Comparison between standard transformer and specially designed transformer of same power rating but cooled with fluorocarbon coolant.

FC-43, and SF_6, Kilham *et al.* designed transformers which had a reduction of four to one by volume and two to one by weight. The cooling was accomplished using these fluids by boiling without forced circulation and was 1.5 to 3 times more effective than natural convection using either transformer oil or a silicone oil. To give a desired operating pressure, a mixture of FC-75 (b.p. 99–107°C) and FC-43 (b.p. 170–180°C) was used.

An example of this is shown in Fig. 9 involving a magnetron filament transformer. The core on the right is from a standard transformer cooled with air; while the unit on the left of the picture is the completely assembled transformer which has been designed so as to use the evaporative cooling effect of the fluorocarbon liquids.

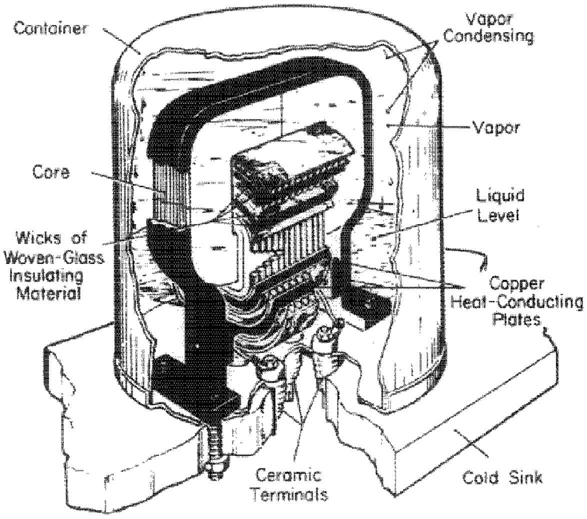


Fig. 10. (Courtesy of Raytheon Corporation.) Cutaway view of fluorocarbon cooled transformer.

Tests of this design show that the unit is capable of operating in dead-air ambients of 140°C with a hot spot rise of 35°C. Repeated dielectric breakdowns of over 50% above rated test voltages do not lower the breakdown strength of the liquid. Electrical performance is excellent, including considerable reduction in corona. The maximum operating internal pressure at full load, 125°C ambient , is less than 12 psig.

Figure 10 shows a cut-away view of a typical fluorocarbon-filled transformer. Of particular note is the level of the liquid in the unit and the wicks of woven glass insulation between the copper wire in the coil.

It will be noted that only the lower portion of the coil is immersed in the liquid and that the rest of the container is filled with vapor excepting that which is drawn up into the coil by the wicking action of the glass fabric. The fact that the fluorocarbon vapors at one atmosphere have dielectric strengths essentially equal to that of the liquid allows this partial fill technique to be used without danger of electric breakdown. At temperatures below their boiling points, the vapor pressures are too low to give enough dielectric strength for initial start-up; hence, the space above the liquid was filled to about one-half atmosphere pressure with SF_6.

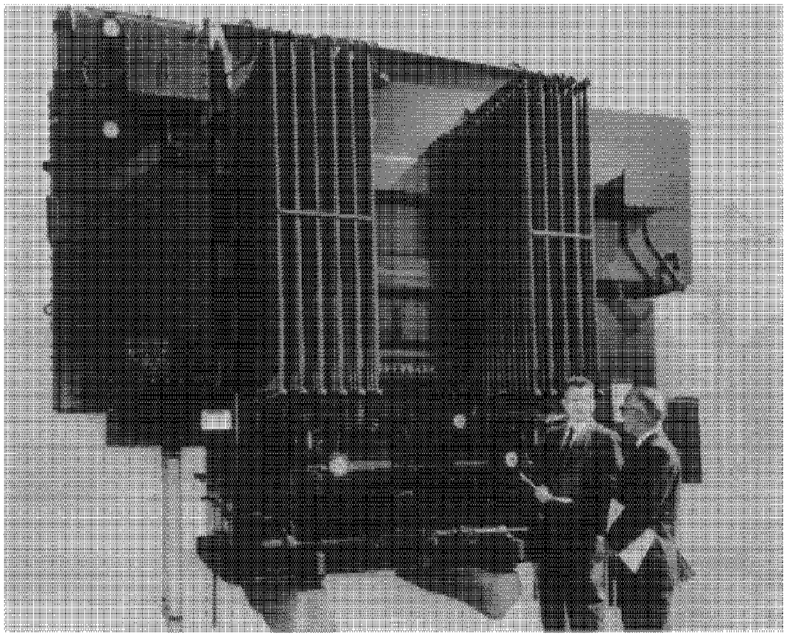


FIG. 11. (Courtesy of Westinghouse Electric Corporation.) Large-sized power transformer using fluorocarbon dielectric coolant.

The Westinghouse Electric Corporation has manufactured large power transformers in which the dielectric strength and the cooling are provided by a combination of a fluorocarbon liquid, FC-75, and gases (such as SF_6). These transformers have ratings of 7500 kva and 34.5 kv and up. Figure 11 shows a typical unit, the size being indicated by the man alongside. In these units, the transformer coils and windings are continuously sprayed with the fluorocarbon liquid, which by evaporation from the hot surfaces carries away the heat and delivers it to the case where the liquid condenses and returns to a reservoir. The liquid is then pumped again through the spray heads and repeats the cycle. In this case, a relatively few gallons of fluorocarbon fluid is able to cool the transformer and provide an excellent dielectric medium. Unlike equivalent units filled with conventional oils, all fire hazards are eliminated. These fluorocarbon-filled vapor-gas transformers can, therefore, be safely installed in downtown or residential areas, indoors or outdoors, without need for fire-fighting equipment, fire walls, or drainage pits. Besides the greater safety factor, installation and maintenance costs are reduced; and since the unit is self-cooling, operation is quieter with no exterior fans required.

2. *Power Tubes*

Etter of the R.C.A. Laboratories(37) has studied forced circulation cooling for a high power transmitting tube. The fluorocarbon fluid, FC-75, was selected as the coolant for this system on the basis of heat

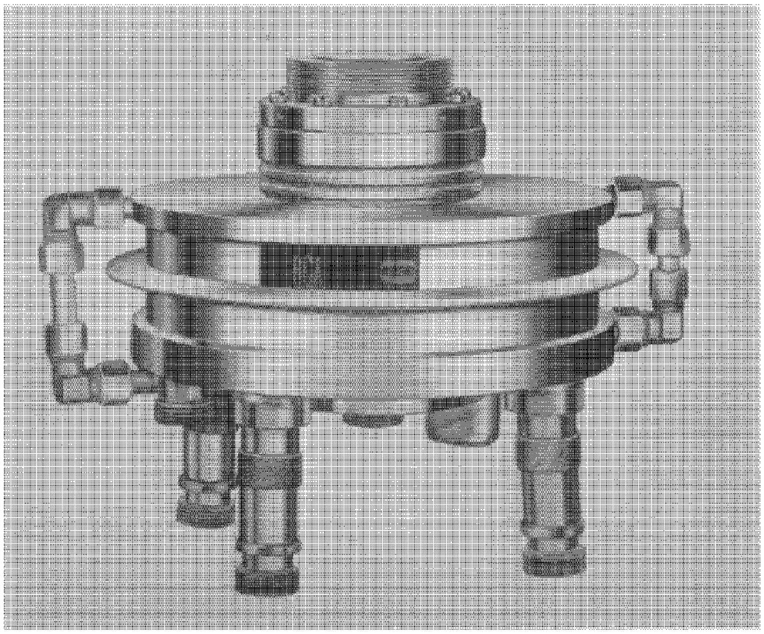


FIG. 12. (Courtesy of Radio Corporation of America.) High power radar tube cooled with fluorocarbon coolant.

transfer coefficients which were calculated by the Dittus-Boelter equation. This calculation indicated a twofold advantage over the next best liquids; namely, transformer oil and silicone oil. Experimentally, Etter utilized boiling FC-75 with forced circulation of the liquid at 3.5 ft per sec over a heated wire. In this case, the maximum heat flux obtained was 350 w per sq in. (171,000 BTU/hr/sq ft). Other factors which were important in this application, as far as the choice of fluid is concerned, included extreme thermal and chemical stability in contact with surfaces which were maintained at 300°C, self-healing under electrical discharge, and also the good resistance to X-rays resulting from the operation of this high-voltage tube. Figure 12 shows the tube designed to operate with FC-75 cooling.

3. *Electronic Assemblies*

Renaud describes a number of assemblies in which a considerable size and weight reduction was effected in high voltage power supplies(38). Techniques are described in which a kystron tube plus its auxiliary power supply were placed in a collapsible dielectric container of polytetrafluoroethylene which was then filled with FC-75. In this example, the unit was able to dissipate about 2200 w of power through ebullient cooling provided by the FC-75, with relatively low temperature differentials between the component surface and the bulk liquid temperature. An actual comparison of power units of equal KVA rating showed that whereas a gas-filled SF_6 unit weighed 12 lb and had a volume of 102 in^3, the FC-75 liquid-filled unit weighed 5 lb and had a volume of 54 in^3.

Renaud also pointed out that standard 1-w carbon resistors could be safely operated at 5 w in boiling FC-75 at 100°C with excellent life and reliability.

Drexel reviews the problem of cooling electronic equipment where tight packaging and high heat dissipation per unit volume are essential(39). He shows that a fluorocarbon fluid, such as FC-75, has many advantages over conventional fluids and in fact possesses most of the essential properties to meet such requirements as:

(1) Boiling point of about 100°C to permit ram-air cooling.

(2) Freezing point below $-50°C$ to permit low temperature operation.

(3) Low viscosity, high density, and high volumetric expansion to provide good fluid convection.

(4) Low surface tension so vapor bubbles boil off the hot surface readily producing smaller bubbles and thus promoting nucleate boiling.

(5) High thermal conductivity and high specific heat for good heat absorption.

(6) Self-healing properties; both liquid and gas will produce minimum amounts of decomposition products as a result of an electric arc.

(7) Noncorrosive, nontoxic, and nonflammable properties for the liquid and gas within the temperature range of the equipment.

TABLE XX

PROPERTIES OF SOME DIELECTRIC COOLANTS

Compound	Boiling point (°C)	Freezing point (°C)	Dielectric strength (at 25°C relative to air)
SF_6	−64 (sublimes)	−51	2.2
C_3F_8	−38	−160	2.2
CCl_3F	24	−111	3.1
CCl_2FCClF_2	47	−35	2.6
CCl_2FCCl_2F	93	26	—
FC-75	101	<−75	7.5
FC-43	178	−66	8.0
Silicate ester	>315	<−65	5.4

Comparative properties are listed in Table XX.

From the examples cited above, it was apparent that the principal advantage of the fluorocarbon liquid as a heat-transfer fluid was its ability to transfer heat by boiling. This advantage can be obtained by natural circulation pool boiling, as in Raytheon's transformer or by the forced circulation local boiling as with R.C.A.'s transmitting tube.

At this point, it would be well to review the properties of fluorocarbon liquids which are the basis for their outstanding performance as heat transfer media, especially in the electrical applications reviewed above.

D. PROPERTIES OF FLUOROCARBON FLUIDS

In Table XXI are given a number of properties of a typical fluorocarbon heat transfer fluid, FC-75, a typical silicone fluid, and a typical hydrocarbon transformer oil. Of particular note is the low pour point of the FC-75. It is also the only fluid which is actually useful at its boiling point as a heat transfer fluid, since the silicone and hydrocarbon oils are essentially nonvolatile. Low boiling hydrocarbon or silicone fluids could not be used safely due to their extreme flammability and the explosion hazard in case of a leak. The extremely small change in viscosity from 7.8 cs at −65°C to a value of 0.65 at room temperature means that the fluorocarbon fluid can be easily pumped over a wide temperature range without excessive horsepower requirements.

The extremely low surface tension of the fluorocarbon fluid is also an important factor in wetting surfaces, hence, increasing the transfer of heat. In case of boiling heat transfer, the low surface tension results in the formation of extremely small and discrete bubbles, which improves heat transfer from the hot surface.

TABLE XXI

TYPICAL PROPERTIES OF HEAT TRANSFER LIQUIDS USED IN ELECTRICAL APPLICATIONS

	FC-75	Silicone oil	Hydrocarbon oil transil
Specific gravity (25°C)	1.77	0.97	
Pour point (°C)	−130°	−62°	−56°
Boiling range (°C)	99–107	Decomposes	Decomposes
Maximum operating temperature (°C)	400°	200°	148°
Viscosity (cs)			
−65°C	7.84		
25°C	0.65	100	
37.5°C			56 sec (Saybolt)
100°C	0.33	60	
Refractive index	1.277	1.403	
Surface tension (25°C)	15.1	20.9	
Specific heat (25°C, cal per cm per °C)			
Liquid	0.248	0.33	
Saturated vapor	0.236	—	
Electrical strength (kv, ASTM D-877)	35	35	25
Dielectric constant at 1 kc	1.86	2.74	2.2
Dissipation factor at 1 kc	0.0005	<0.0005	<0.0005
Resistivity (ohm per ml)	6×10^{14}	1×10^{14}	1.25×10^{14}
Thermal conductivity (BTU per °F hr ft)			
Liquid	0.081	0.090	
Saturated vapor at 1 atm	0.008	—	

Perhaps one of the most unusual characteristics of the fluorocarbon fluid are the essentially equal values for the specific heat of the liquid, and the saturated vapor at one atmosphere of pressure. This is understandable when one considers the very high molecular weight of the fluorocarbon. For example, water with a molecular weight of 18 has the same boiling point as FC-75 with a molecular weight of about 425.

The chemical inertness and the low solvent power for most organic and inorganic materials is also a very important factor in the use of these fluids. In Table XXII are listed the solubility relationships for two commercially available fluorocarbon fluids, FC-75 and FC-43, with boiling points of 101°C and 177°C, respectively. The solubilities are in general quite low; those of the higher boiling, FC-43, being lower than those of the FC-75.

TABLE XXII

SOLUBILITIES RELATIONSHIPS FOR FLUOROCARBON FLUIDS, FC-75 and FC-43(40)

	Solubility (gm per 100 ml at 20°C)			
	FC-43 in Solvent	Solvent in FC-43	FC-75 in Solvent	Solvent in FC-75
Acetone	0.9	0.6	4.8	1.2
Benzene	0.3	0.2	2.6	3.8
Benzotrifluoride	miscible	miscible	miscible	miscible
Benzyl alcohol	insoluble	insoluble	0.2	0.4
Carbon tetrachloride	2.4	15.0	20.2	36.5
Chlorobenzene	—	0.4	1.8	3.2
Chloroform	1.2	5.4	7.7	4.5
Cyclohexane	1.8	2.2	7.7	8.4
Dioxane	0.1	insoluble	0.9	2.4
Ethyl ether	4.9	5.0	miscible	miscible
Ethyl acetate	2.2	2.4	7.5	6.5
Heptane	6.4	3.4	25.5	11.6
Isopropyl alcohol	insoluble	insoluble	4.1	1.3
Methyl alcohol	insoluble	insoluble	1.0	0.1
Oleum spirits	0.8	insoluble	5.4	2.3
Petroleum ether (low boiling)	33.2	7.0	miscible	miscible
Stoddard solvent	1.4	—	5.9	3.0
Toluene	0.4	—	2.9	4.1
Turpentine	0.9	insoluble	5.3	1.0
Xylene	—	1.0	3.0	3.0
Water	insoluble	insoluble	insoluble	insoluble

In Table XXIII the solubilities for various gases in the fluorocarbon liquid FC-75 are shown. Except for chlorine, most gases appear to follow the expected solubility according to boiling point and molecular weight.

Even under breakdown conditions where high temperature arcs occur, any changes in the fluids are of such a nature that the amount of ionic material produced is extremely small; and hence, there is essentially

TABLE XXIII

SOLUBILITY OF VARIOUS GASES IN FC-75

Gas	Temperature (°C)	Solubility Mol %[a]
Ammonia	25	0.44
Chlorine	25	ca. 10
Nitrogen	25	0.39
Air	0	0.48
	25	0.46
	80	0.42
Fluorine	25	0.14
Argon[b]	4.5	0.532
	11.6	0.521
	19.4	0.508
	25.0	0.500
	31.8	0.491
Nitrogen[b]	10.6	0.354
	14.0	0.352
	20.4	0.350
	25.0	0.349
	30.4	0.347
Oxygen[b]	5.6	0.554
	14.3	0.540
	25.0	0.520
	31.5	0.510
Carbon dioxide[b]	4.0	2.606
	9.5	2.363
	18.0	2.179
	24.9	2.000
	25.0	1.996
	31.2	1.850
Sulfur hexafluoride[c]	−35	15.5
	+25	7.3

[a] Corrected to 1 atm partial pressure of the gas.
[b] (41)
[c] (34)

no change in the electrical properties of the fluid. This point has been covered in a previous section on characteristic properties. The high energies available during an electric arc result primarily in the cleavage of carbon to carbon bonds forming fluorocarbon radicals, which readily undergo recombination to form new fluorocarbon molecules which, though differing in structure or molecular weight, possess essentially the same chemical inertness or electrical properties. This will be true, however, only in the absence of impurities containing hydrogen, silica, or other halogens.

Even under conditions of elevated temperatures in excess of 300°C for prolonged periods of time, the fluids have no corrosive action on such metals as steel, stainless steel, copper, brass, etc. In the case of FC-75, less than one per cent degradation has been noted after 240 hr at 400°C in either copper or stainless steel containers. Even exposure for 60 hr at 475°C in a stainless steel vessel results in less than 15% decomposition.

In a rather graphical demonstration, a platinum wire heated electrically to 600–650°C while immersed in FC-75 shows no noticeable breakdown or decomposition of the fluid. The photographs in Figs. 13 and 14 show

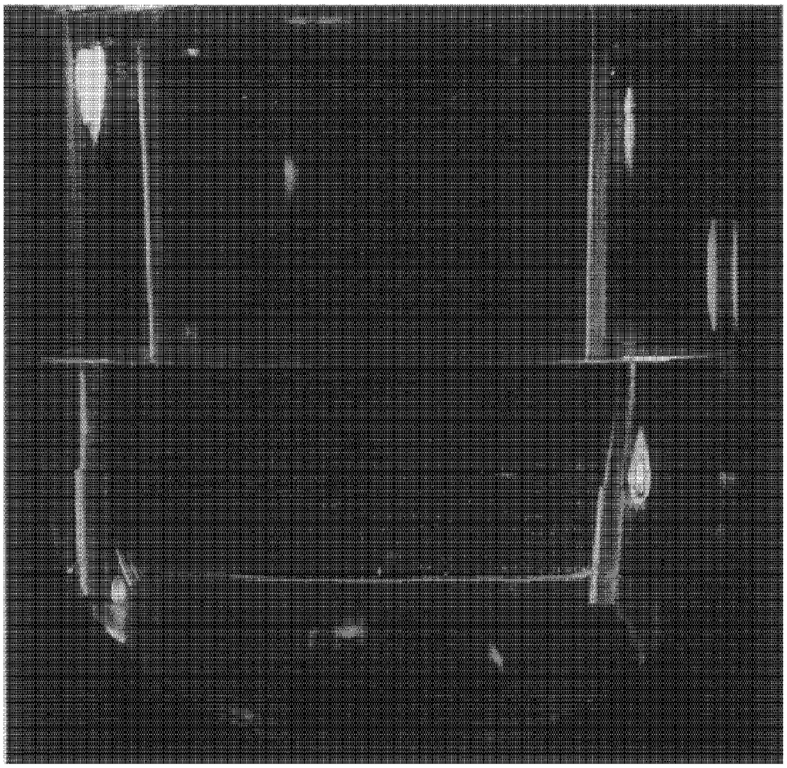


Fig. 13. Heat transfer from hot wire immersed in FC-75 showing condition for nucleate boiling. Wire temperature is approximately 105°C.

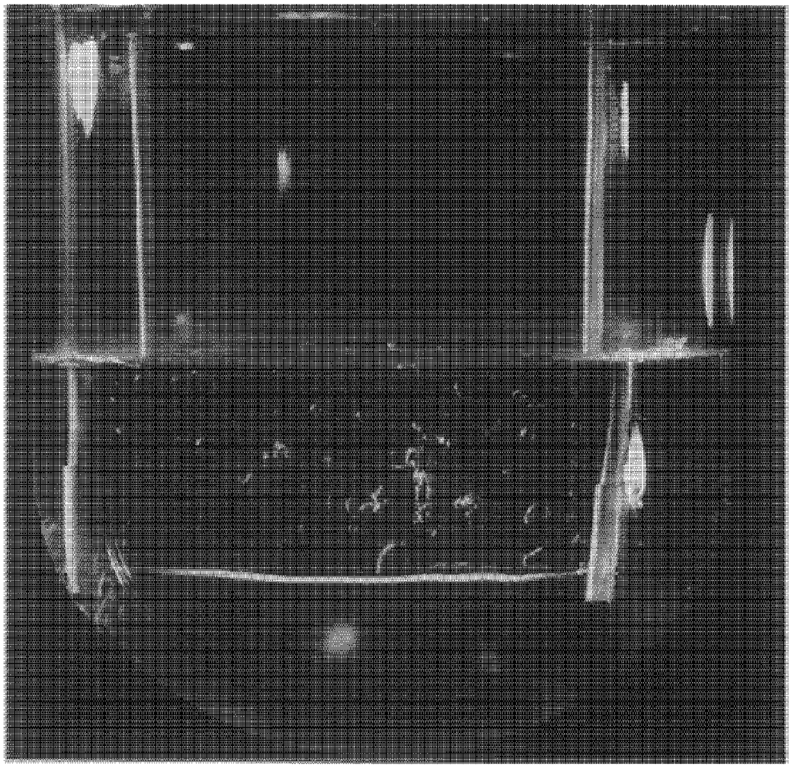


FIG. 14. Heat transfer from hot wire immersed in FC-75, showing condition for film boiling. Wire temperature is approximately 550°C.

such an experimental arrangement. Besides illustrating the thermal stability of the fluid, such an experiment also shows the exceptional heat transfer properties of the fluorocarbon liquid.

As the temperature of the wire is gradually increased from room temperature to the boiling point of the liquid, approximately 101°C, the heat is removed from the wire by convection. As the boiling point is reached, the FC-75 begins to boil, and the condition of nucleate boiling begins. This is illustrated in Fig. 13 by the appearance of a cloud of very fine, but discrete bubbles of vapor rising from the wire surface. Figure 15 shows this change in wire temperature for increasing heat flux in this nucleate boiling condition. It will be noted that even though the heat flux is increased many times, there is a relatively minor change in wire temperature. Above a certain critical heat flux, however, which—as can be seen—depends upon the degree of forced convection, there will be a sudden rapid rise in wire temperature. This transition is due to the change from the condition of nucleate boiling to one of film boiling. This condition is shown in Fig. 15. When film boiling occurs, the wire surface is no longer in direct contact with the liquid phase, but is surrounded by a film of vapor. The heat must be removed from the wire by convective forces in this vapor film and transferred to the surrounding liquid. Even when the wire temperature exceeds 870°C, there is no noticeable change in appearance of either the liquid or the surface of the platinum wire, at least for several hours. Furthermore, it is relatively easy to maintain a constant wire temperature and hence, a steady state of heat transfer without "burn out" of the platinum filament.

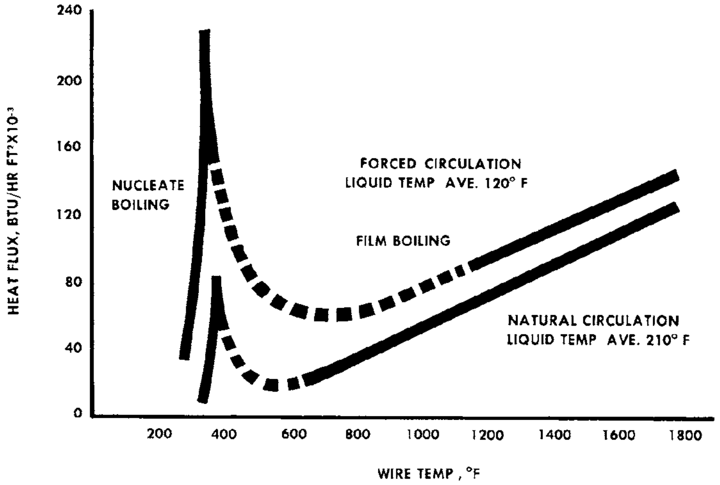


FIG. 15. Typical boiling heat transfer curves for a fluorocarbon liquid.

The results of the "hot wire" experiment described above illustrate some of the unusual characteristics of fluorocarbons as heat transfer fluids. The thermal stability of the fluorocarbon molecule is illustrated by the fact that the platinum wire can maintain a relatively constant temperature in the presence of the liquid and or vapors even at temperatures above 800°C. Decomposition to form carbon or other nonvolatile products would result in deposits forming on the wire with poorer heat transfer and hence "burn out" of the wire. The fact that the film boiling condition can be maintained so readily is also due to the high specific heat of the FC-75 vapors, which has a value at 25°C and 1 atm of 0.23 cal per gm, compared to the value for liquid of 0.26 cal per gm (see Table XX).

In many of the commercial uses described earlier, this ability of the fluorocarbon liquids to conduct heat from surfaces at these very high

TABLE XXIV

EFFECT OF FC-75 ON METALS, PLASTICS, AND ELASTOMERS

	Time (days)	Temperature (°F)	Result
A. Metals			
Stainless Steel 18-8	10	230	No change
Cold rolled steel	10	230	No change
Aluminum 52S	10	230	No change
Magnesium extrusion	10	230	No change
Silver solder on cold rolled steel	10	230	No change
High temperature solder (95%Sn-5%Sb)	10	230	No change
Copper	10	230	No change
B. Plastics			
"KEL-F" brand plastics	10	230	No change
"Formvar"	10	230	No change
"Teflon" coated wire	10	230	No change
"Teflon" sheet	10	230	No change
"Melamine" laminate (GAF)	10	230	No change
Nylon plastic sheet	10	230	No change
C. Elastomers			
Silicone DC 997 coated on copper (25° cure, 16 hr)	30	356	Slight curled edge
Silicone cured GE76	30	356	No change
Silicone DC 80	30	356	No change
Silicone DC 7181	30	356	No change
Silicone rubber-type HTC	10	230	No change
			%Volume swell
Cured "Viton" brand elastomer	3	194	7
Cured "FLUOREL" brand elastomer	3	194	7
Cured neoprene W (unplasticized)	3	194	No change
Cured thiokol FA (unplasticized)	3	194	No change
Cured butyl 150 (unplasticized)	3	194	No change
Cured hycar 1001 (unplasticized)	3	194	No change
Cured hypalon (unplasticized)	3	194	No change
LS-53 (a fluorosilicone)	3	77	3

temperatures gives the design engineer a built-in safety factor. The failure of many pieces of equipment, whether an electrical, a nuclear, or a simple thermal device, is due to the appearance of a local "hot spot" which leads to destruction of a critical element of the system.

Due to their lack of solvent power, these fluorocarbon fluids do not swell or decompose any type of organic material that might be used as seals in insulation coating, etc., at least up to the maximum usable temperature to which such materials are stable. This lack of solvent power also extends to the typical fluorocarbon plastics such as polytetrafluoroethylene and polychlorotrifluoroethylene. Typical data are included in Table XXIV.

1. *Heat Transfer Characteristics*

Marcellus, Sphilhaus, and Troeltzsch have made measurements on the heat transfer performance of FC-75 and made comparisons with a silicate ester and a silicone oil(42). Results are included in Table XXV where the heated surface temperature is 205°C.

TABLE XXV

MAXIMUM HEAT FLUX VALUES FOR DIELECTRIC FLUIDS

Liquid at 120°F	Maximum heat flux (watts/in^2) 250 rpm	450 rpm	Remarks
Fluorocarbon FC-75	338	420	Boils
Silicate oil	212	277	Nonvolatile
Silicone oil	118	232	Nonvolatile

Marcellus *et al.* have also determined experimentally the variation of heat flux with surface temperature for FC-75 in convective and nucleate boiling heat transfer with the peak heat flux at various liquid velocities and also at various pressures and temperatures. They were able to obtain a maximum heat flux with FC-75 of 518 w per sq in. (255,000 BTU per hr per sq ft) at a fluid temperature of 5°F, velocity of 7 ft per sec, and 2 atm pressure. Their data are represented graphically in Figs. 16, 17, 18, and 19 for fluid temperatures of 5°, 45°F, 120°F, and 170°F. The effect on the wire temperature resulting from increases in the heat flux, from changes in the fluid velocity, and from the changes in the pressure applied are shown in these figures.

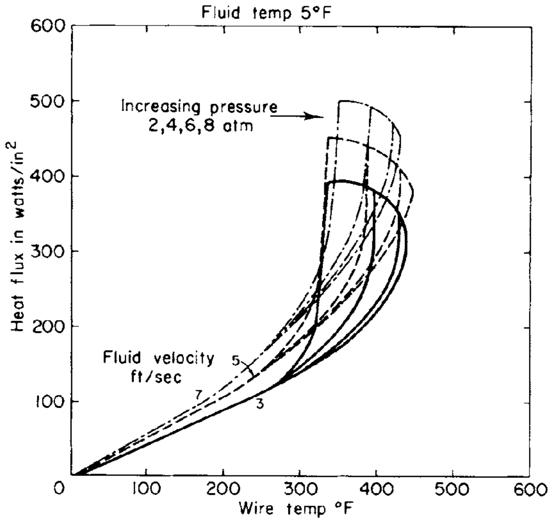


FIG. 16. Heat flux vs wire temperature at varying fluid velocities and pressures. Fluorocarbon fluid (FC-75) at 5°F.

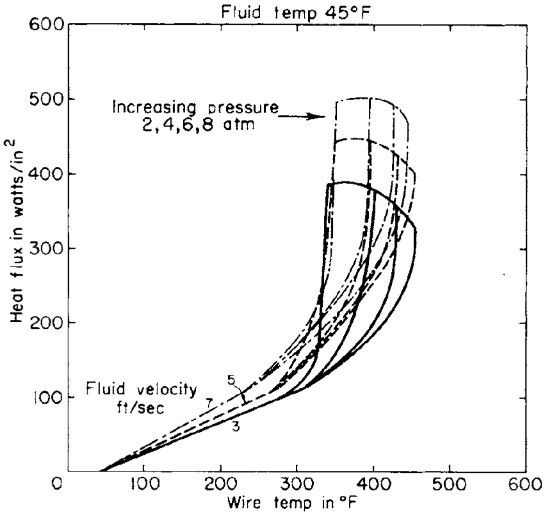


FIG. 17. Heat flux vs wire temperature at varying fluid velocities and pressures. Fluorocarbon fluid (FC-75) at 45°F.

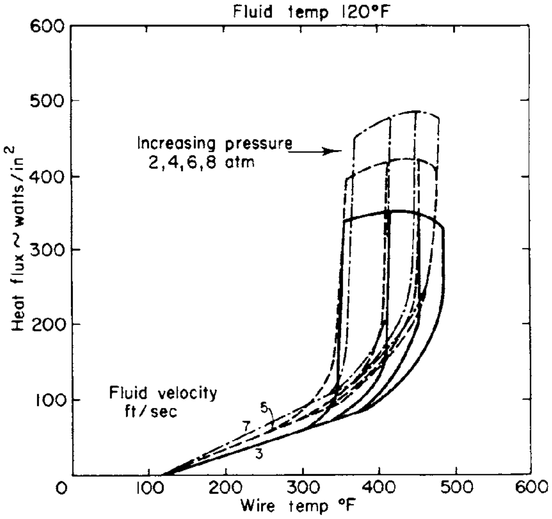


FIG. 18. Heat flux vs wire temperature at varying fluid velocities and pressures. Fluorocarbon fluid (FC-75) at 120°F.

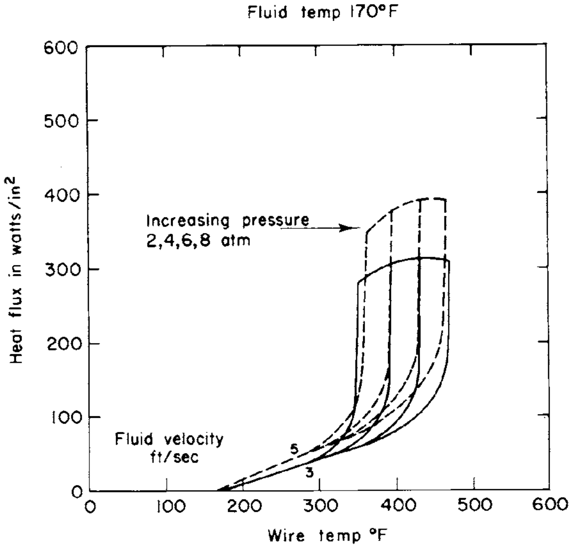


FIG. 19. Heat flux vs wire temperature at varying fluid velocities and pressures. Fluorocarbon fluid (FC-75) at 170°F.

Marcellus *et al.* have studied the heat transfer from a wire of diameter 0.028 in., which, of course, is only a fine rod. Nevertheless, it is felt that the relationships will in general apply to any geometric shape. The correlation with other geometric shapes, such as horizontal or vertical planes, should be similar to those established for fluids such as water or organic liquids.

TABLE XXVI

THERMAL CONDUCTIVITY OF FC-75 AND FC-43 IN LIQUID AND VAPOR STATES

Fluid	State	Temperature	Thermal conductivity BTU per hr ft°F
FC-75	liquid	−70°F	0.0890
		−62.5°F	0.0876
		−35.5°F	0.0836
		+76.75°F	0.0813
		212°F	0.0705
	vapor (1 atm)	214°F	0.0080
		250°F	0.0112
		300°F	0.0251
FC-43	liquid	−65°F	0.0520
		−50°F	0.0515
		+77°F	0.0490
		250°F	0.0435
	vapor (1 atm)	348°F	0.01350
		380°F	0.01300

The thermal conductivity of the fluorocarbon liquids, FC-75 and FC-43, has been measured by Hsu(43). The data are given in Table XXVI for both the liquid and vapor at various temperatures.

2. *Thermodynamic Properties*

Yarrington and Kay have determined the thermodynamic properties of c-$C_8F_{16}O$(44). The values were calculated by applying the rigorous thermodynamic equations to the data on heat capacities and *P-V-T* relations of this compound. The data is presented in Fig. 20 in the form of a log *P* vs enthalpy diagram with curves of constant temperature, constant entropy, and constant volume.

Figures 21 and 22 show the heat capacity data of Yarrington and Kay for the narrow boiling range cut of FC-75 (100.5–101.5°C). Figure 21

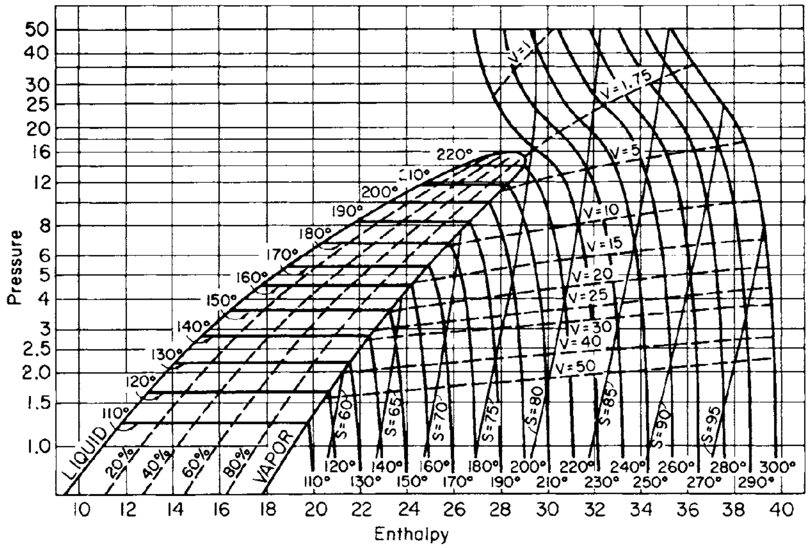


FIG. 20. Pressure–Enthalpy chart for FC-75 fraction boiling 213–215°F. Pressure—atm; enthalpy—kcal per mole; temperature—°C; entropy—kcal per mole, °K; volume—ml per gm. Source: private communication with R. M. Yarrington and W. B. Kay, Chemical Engineering Dept., Ohio State University.

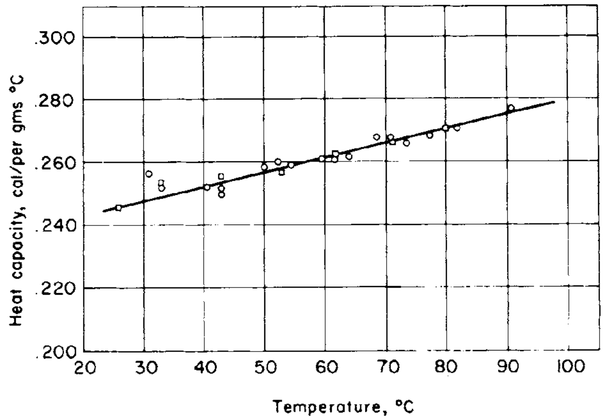


FIG. 21. Heat capacity of fluorocarbon FC-75 in liquid state.

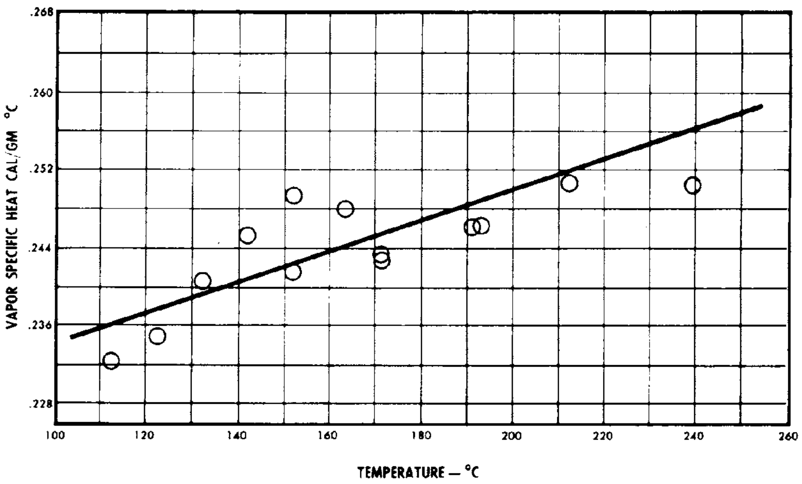


FIG. 22. Heat capacity of fluorocarbon FC-75 in vapor state.

is the heat capacity of the liquid, whereas Fig. 22 is the heat capacity of the vapor, both over their normal useful temperature ranges.

The vapor pressures of the two commercially available fluorocarbon fluids, FC-75 and FC-43, as a function of temperature are shown in Figs. 23 and 24(40,46).

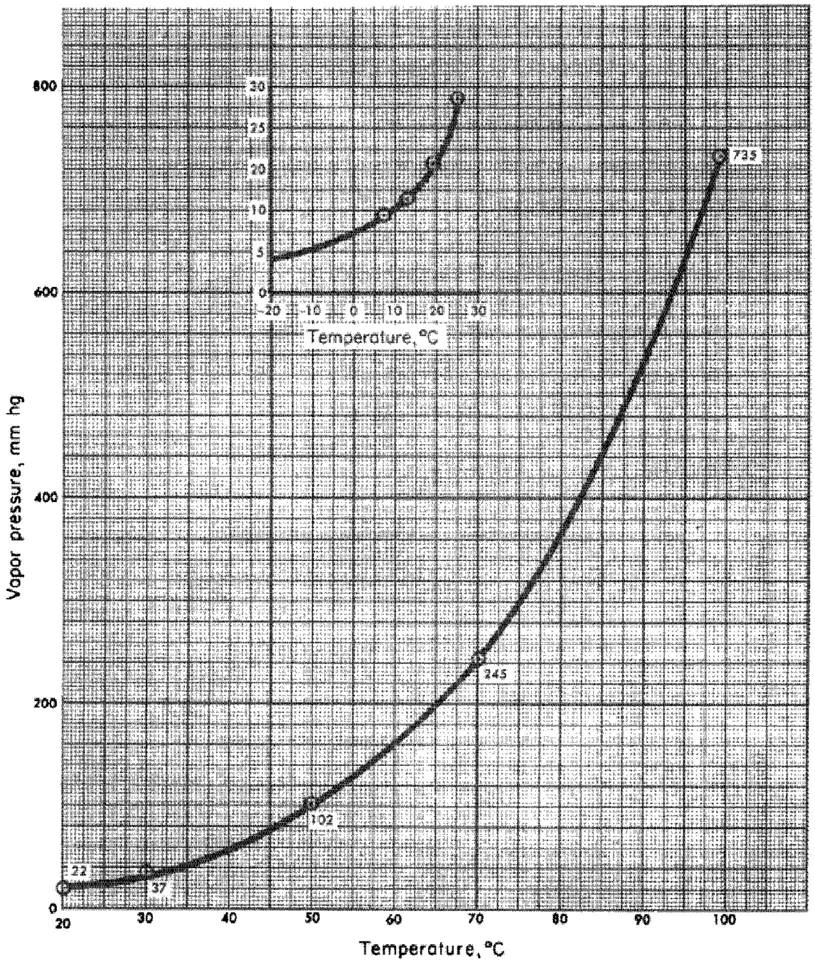


FIG. 23. Vapor pressure as a function of temperature for fluorocarbon liquid FC-75.

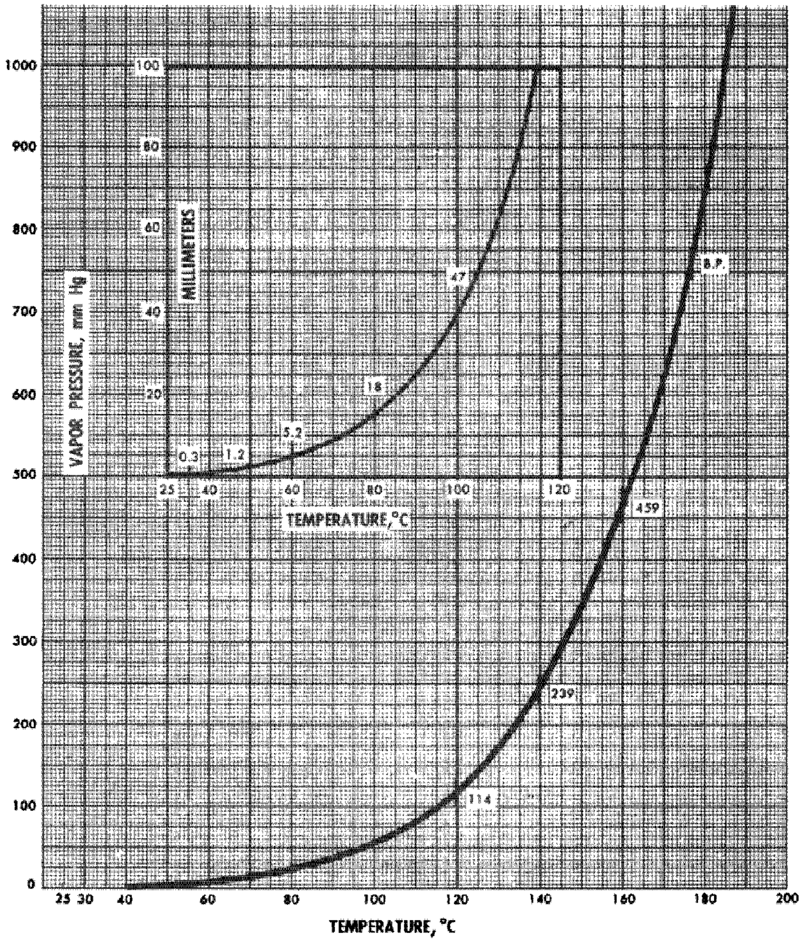


FIG. 24. Vapor pressure as a function of temperature for fluorocarbon liquid FC-43.

VI. Gaseous Dielectrics

Gaseous fluorocarbons are specifically of interest in high voltage applications because of their generally inert character and high dielectric strength.

In Table XXVII are listed a number of fluorocarbon compounds and also sulfur hexafluoride, all of which are gases at room temperature and possess useful properties as gaseous dielectrics.

TABLE XXVII

Physical Properties of Fluorocarbon Gases and Sulfur Hexafluoride

Compound	Molecular weight	Boiling point (°C)	Freezing point (°C)	Relative dielectric strength
CF_4	88	−128°C	−198	1.1
C_2F_6	138	−78.3	−101	1.8
C_3F_8	188	−37.0	−160	2.2
C_4F_{10}	238	−2.5	< −80	2.8
cyclo-C_4F_8	200	−6.0	−41	2.8
cyclo-C_4F_8O	216	+1	< −130	2.8
$C_2F_5OC_2F_5$	254	0	−125	2.8
SF_6	146	−63.(subl.)	−50.8	2.2

Factors of importance in choosing an insulating gas for electrical use are:

(1) High dielectric strength
(2) Low temperature of condensation
(3) Chemical inertness, nontoxity, and nonflammability
(4) Good heat conductivity
(5) Availability and cost.

A. Factors Affecting Dielectric Strength

Camilli and Plump(46) have reviewed a number of factors which influence the dielectric strength of a gas. They point out the importance of electrode shape and spacing with particular emphasis on whether the electrical field is uniform or nonuniform. Table XXVIII illustrates the variation to be observed with two sets of electrodes, one set being 3-in, plane disk electrodes, the other a 0.5 in. sphere to a plane disk. In both cases the spacing was 0.5 in.; the former gives a uniform field, whereas the latter gives a nonuniform field. The data is given for air and sulfur hexafluoride.

The dielectric strength of a gas is generally raised by increasing pressure; this is most true in the case of uniform fields. Special cases exist in nonuniform fields, particularly when a positively charged point electrode is used, in which case the dielectric strength may decrease with pressure.

In general, there is no effect of temperature on the dielectric strength of a gaseous dielectric provided the density of the gas is kept constant.

Cotton lint and dust have been shown to lower the breakdown strength of gaseous dielectrics.

TABLE XXVIII

Comparison of Dielectric Strengths of Air and Sulfur Hexafluoride with Different Electrode Configurations

Condition	Pressure (atm)	IV. Sparkover 60 cycle	Ratio SF_6/air
3 in. plane discs			
Air	1	23	
SF_6	1	52	2.25
0.5 in. sphere to plane			
Air	1	16	
SF_6	1	42	2.6
Air	30 lb per in^2 absolute	24	
SF_6	30 lb per in^2 absolute	60	2.5
Air	45 lb per in^2 absolute	45	
SF_6	45 lb per in^2 absolute	90	2.0

Although for any given homologous series of compounds, there is a general increase in dielectric strength with molecular weight, it does not necessarily hold that two different gases with the same molecular weight will have the same dielectric strength.

As the data in Table XXIX shows, the halogen atoms have high electronegative values, also possess high electron affinities and high ionization potentials, with the values for fluorine being particularly high.

Electronegativity is a term which refers to the ability of an atom to attract electrons from other atoms with which it has formed a molecule.

TABLE XXIX

Electronic Character of Selected Elements

Electronic characteristics	H	He	F	Cl	C	N	O	S
Relative electronegativity(8)	2.1	—	4.0	3.0	2.5	3.0	3.5	2.5
Electron affinity(47) (electron volts) $X + e^- \rightarrow X^-$	0.74	−0.53	3.65(8)	3.8	1.5	−0.6	2.3	1.5
Ionization potential(8) (electron volts) $X \rightarrow X^+ + e^-$	13.6	24.6	17.5	13.0	11.3	14.6	13.6	10.4

Thus, in a series of halides, HI, HBr, HCl, and HF the electronegativity of the halogen atom increases from that of iodine, which by its general chemical properties is recognized to be only a little more electronegative than hydrogen, to fluorine, the most electronegative of all elements.

Gases with high dielectric strength can produce negative ions on electrical breakdown; in fact, any gas which does not form negative ions is unlikely to have exceptional dielectric strength.

The electron affinity is the energy change involved when an atom or molecule forms a negative ion by electron attachment; the process may be represented:

$$X + e^- \rightarrow X^- \tag{4}$$

It may be concluded that gases with high dielectric strength will contain atoms with high electron affinities.

The ionization potential, another property of a gas, should also be an index of its dielectric strength. It is designated as the energy change in the process:

$$\mathrm{X} \rightarrow \mathrm{X}^+ + e^- \tag{5}$$

Practically all matter can produce positive ions and electrons, the ionization potential varying from substance to substance. However, the fact that helium which has the highest ionization potential has the lowest dielectric strength of any gas, would indicate strongly that ionization potential alone is not an index of dielectric strength.

From the above discussion, it would appear that no single factor can be entirely responsible for dielectric strength, the combination of physical and electrical properties in any substance undoubtedly influences the actual value.

Besides dielectric strength, there are other factors which are important in considering a gaseous dielectric, most significant of which are boiling point, melting point, vapor pressure, toxicity, chemical inertness, thermal stability, and price.

Camilli has postulated that the molecule CF_4, on adding an electron, would produce a CF_4^-. Then, if sufficient energy is present, other reactions such as the following would occur:

$$\mathrm{CF_4^-} \rightarrow \mathrm{CF_3^\circ} + \mathrm{F^-} \tag{6}$$

$$\mathrm{CF_4^-} \rightarrow \mathrm{CF_3^+} + \mathrm{F^-} + e^- \tag{7}$$

$$\mathrm{CF_4^-} \rightarrow \mathrm{CF_3^\circ} + \mathrm{F^\circ} + e^- \tag{8}$$

of these, the first two are much more likely to occur since the last one is a much higher energy reaction. These products likewise can in turn enter into further electron reactions; and by continuing to attack electrons, the effect can be one of continuing energy absorption.

The use of a gaseous dielectric as an electrical insulation and heat transfer medium is often dictated by uses involving limited space. For some applications, solids cannot be used because they block the necessary dissipation of heat generated by the equipment. In many cases organic liquids or oils are a real fire and explosion hazard as well as producing large pressure surges on voltage breakdown.

Air was the original gas used for electrical insulation, and is still used where its properties are sufficient. The early work of Charlton and Cooper(48) and Pollock and Cooper(49) demonstrated that certain chlorofluorocarbon gases and sulfur hexafluoride were distinctly superior to air. The chlorofluorocarbons have not achieved a great deal of commercial usage due primarily to the fact that upon voltage breakdown, they liberate chloride ion which has very serious effects on electrical systems.

B. Applications for Sulfur Hexafluoride

As reviewed earlier, SF_6 can form relatively stable negative ions by absorption of electrons, thus:

$$SF_6 + e^- \rightarrow SF_6^- \tag{9}$$

These electronegative gases have been likened to a sponge which soaks up free electrons which come into contact with them.

Sulfur hexafluoride is physiologically inert, is nonflammable, has a dielectric strength of 2.2 relative to nitrogen (for 60 cycle current and uniform field), has good heat conducting properties under conditions where convection or pumping circulates the gas. It is stable in the presence of most materials of construction up to temperatures of about 150°C, and it also remains a gas under most use conditions down to its boiling point of −63.8°C.

1. *Transformers*

SF_6 has been used as a gaseous dielectric in a series of power transformers with rating at 2000 kvA, 69 kv(50).

Kilham, Ursch, and Ahearn have pointed to the use of SF_6 as a padder gas above fluorocarbon liquids such as FC-75 and FC-43 in smaller "electronic" transformers(34).

2. *Interrupter Switches*

Henry, Friedrich, and Reese have described circuit breakers of a 115 kv, 1,000,000 kvA rating, which have been filled with SF_6(51).

3. *Radar and Microwave Frequency Power Transmission*

Sulfur hexafluoride has been used extensively in "long line" coaxial cables. It is reported that at 9375 mc, the power carrying capacity of SF_6 was 7.5 times that for air(52). Another worker reports that at 3000 mc, the power carrying capacity of SF_6 was 10.5 times that for air(53).

Sulfur hexafluoride has also found use in a wide variety of electrical equipment including X-ray machines, cathode ray accelerators, Van de Graaff machines, and television filterplexers.

C. Fluorocarbon Gases and Their Application

Several 3 and 4 carbon fluorocarbon gases have shown considerable promise as gaseous dielectrics. In the past two years one of these, C_3F_8, has been introduced commercially in a 1000 kvA, 15 kv transformer normally used for industrial plant or office building use(54). This unit is free from dangers of fire or explosion, and in case of a leak does not present any toxicity hazard. Other compounds which have received some attention are decafluorobutane (C_4F_{10}) and octafluorocyclobutane (c-C_4F_6).

As seen from the data in Table XXVII, the dielectric strength of SF_6 and C_3F_8 are equal, each being 2.2 greater than that of nitrogen. The dielectric strengths of the fluorocarbon compounds, C_4F_{10} and c-C_4F_8 is about 25% greater than that for C_3F_8 or SF_6. The percentage increase over SF_6 increases with increasing gap distance in nonuniform fields, with C_3F_8 also being better than SF_6 under these conditions.

The fluorocarbon gases have several advantages over sulfur hexafluoride. Among these are much greater thermal stability. For SF_6 an upper limit of 150°C is recommended. When properly purified, a fluorocarbon dielectric such as C_3F_8 may be used at temperatures of 450°C. The fluorocarbon gases are also essentially nontoxic. For example, C_3F_8 as used in power transformers will not kill mice when mixed with oxygen at 70% by volume even when the mice are exposed for 16 hr. Even when subjected to voltage breakdown, the degradation products are not appreciably toxic, although if the arcing proceeds in the presence of moisture or hydrocarbon vapors, trace quantities of acidic or other noxious products may result.

The C_4 fluorocarbon gases all boil within a few degrees of 0°C, consequently are limited in their service to temperatures higher than 0°C if the full dielectric strength of the medium is to be maintained.

Bashara(23) has reported on the dielectric strength of a number of fluorocarbon type gases. Typical data is included in Figs. 25 and 26.

The essential equivalence of $(C_2F_5)_2O$, c-C_4F_8O, and C_4F_{10} are noted.

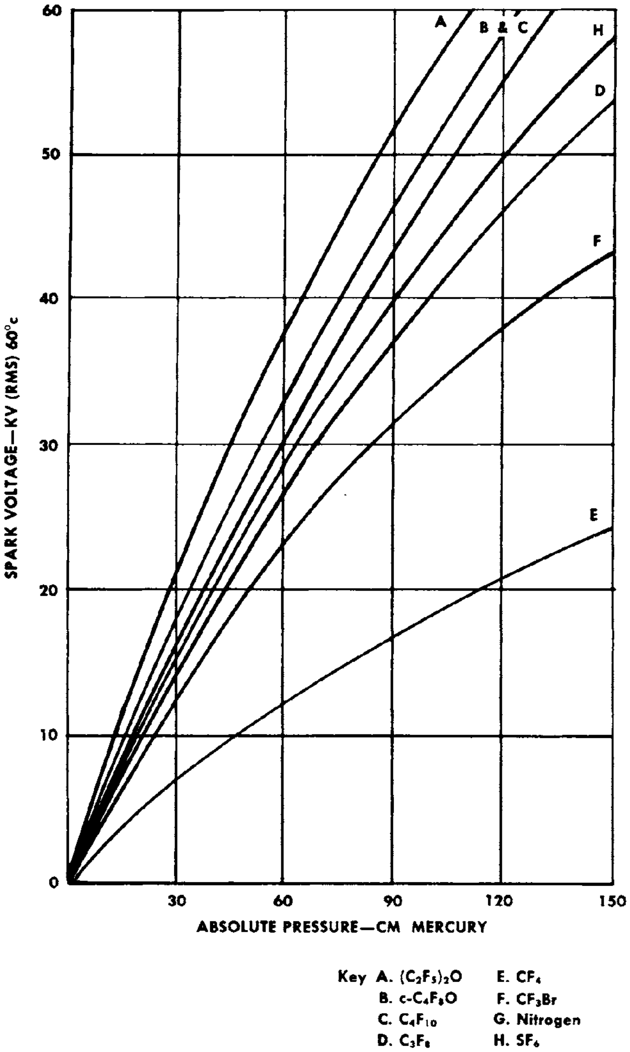


FIG. 25. Dielectric strength of fluorocarbon gases with 1-in. diameter spherical electrodes at 0.2-in. gap.

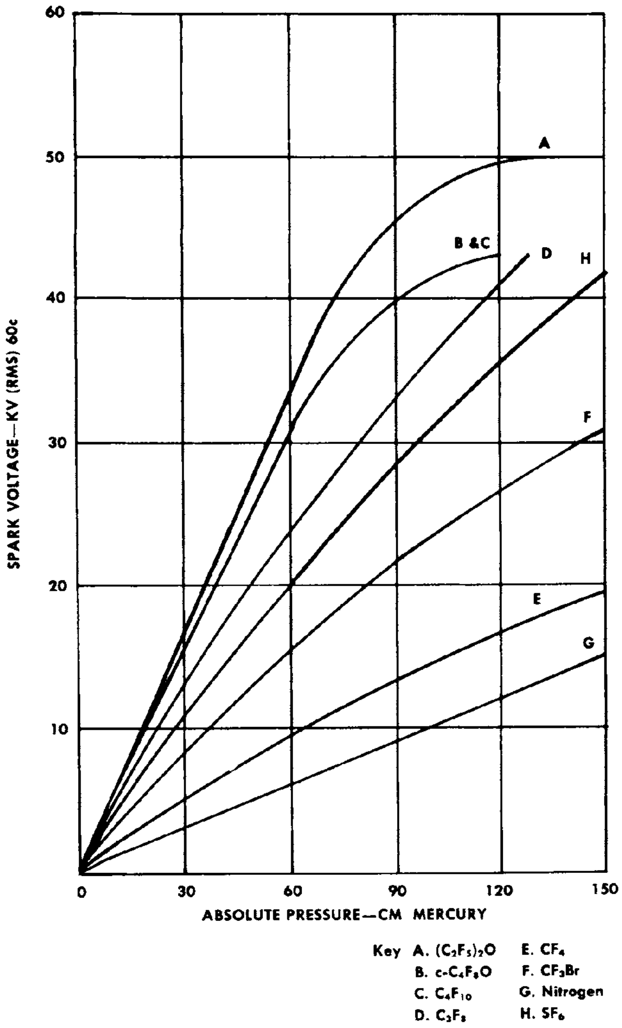


FIG. 26. Dielectric strength of fluorocarbon gases with 0.3-in. gap between electrodes, one of which is a 1-in. diameter sphere, the other being a 0.1-in. diameter rod of 0.05-in. radius.

The equivalence of C_3F_8 and SF_6 in a relatively uniform field is seen from Fig. 25; on the other hand, in the nonuniform field, the C_3F_8 has considerably higher breakdown voltage than the SF_6.

VII. Fire Extinguishing Agents

Fires may be extinguished by either physical or chemical mechanism. However, while different extinguishing effects can be separated in principle, the action of a given extinguishing agent does not have to fall exclusively in the realm of one or another of the mechanisms. In general, there are three types of flames: a diffusion flame, in which the oxygen or air must diffuse to the combustible gas for its combustion; a premixed flame in which air is streaming through the fuel; and a monofuel in which only one type of molecule is involved and its decomposition results in sufficient heat to sustain a flame.

A. Physical Extinguishment

A diffusion flame can be extinguished if the combustible is isolated from the supply of oxidant. This is generally known as blanketing or smothering the flame. Another physical means involves cooling. If the flame zone is cooled, heat-producing reactions are slowed, and may be carried to the point where insufficient heat is produced to maintain the reaction. The fire is then extinguished. Other physical means of extinguishment involve an aerodynamic disturbance of the flame zone.

B. Chemical Extinguishment

It is well established in many cases that preflame and flame reactions involve radicals and are chain reactions. To be effective in chemical extinguishment, the extinguishing agent must serve to break the chains.

To consider the action of flame inhibition, it is necessary first to define the criteria for classifying a substance as an inhibitor.

Broadly speaking, an inhibitor is a substance which makes it more difficult for the flame to burn. Many substances which would not ordinarily be considered as flame inhibitors do this. Thus, the addition of nitrogen, argon, or any inert gas to a premixed flame lowers the flame temperature and flame speed and contracts the flammability range until at some concentration of additions, the flame will not propagate for any combination of fuel and air. These effects are relatively well understood and can be explained in terms of heat capacities of the additives and the dilution of the flame. In general, these effects are physical in nature, and accordingly, fairly large amounts of the additive are needed for extinguishment.

In general, chemical inhibitors are effective in amounts much smaller than those required for inert gases. There are two types of chemical inhibitors: one group is made up of inorganic salts; the other group includes the halides of nonmetallic elements such as carbon, silicon, phosphorus, sulfur, and nitrogen. Table XXX shows a comparison of data,

TABLE XXX

COMPARISON OF THE EXTINGUISHING POWER OF METHYL BROMIDE, NITROGEN, AND CARBON DIOXIDE(55,56)

Combustible (in air)	Peak percentage		
	Methyl bromide	Nitrogen	Carbon dioxide
Hydrogen	13.7	75	61
Carbon monoxide	6.2	68	52
Ethylene	11.7	50	41
Methane	4.7	38	25
n-Hexane	7.1	42	29
Benzene	7.8	44	31

obtained by Burgoyne and Williams-Leir for the peak percentages of methyl bromide for various fuel systems with the peak percentages of the inert gases, nitrogen and carbon dioxide, as taken from the tabulation by Coward and Jones(55,56).

For all systems, methyl bromide is effective in amounts much smaller than those for the inert gases. Both nitrogen and carbon dioxide are purely physical extinguishers; whereas methyl bromide is a chemical extinguisher.

C. ACTION OF SPECIFIC COMPOUNDS

A group at Purdue University has made a systematic evaluation of 56 compounds as fire extinguishing agents. The compounds included in Table XXXI are mostly monohalogenated and polyhalogenated hydrocarbons, but halides of a few other nonmetals were also included. The flame system used was *n*-heptane in air, and the peak percentage values were evaluated(57).

Comparing the compound, CCl_4, CF_4, CF_3Cl, and CF_3Br with peak percentages of 11.5, 26, 12.3, and 6.1 respectively, it appears that bromine is more effective than chlorine; while chlorine is more effective than fluorine.

Molecular weight and boiling point definitely affect the ability of a fire extinguishing agent to extinguish fires at least physically. Chemical inhibition, on the other hand, appears to be associated with the ability of the compound to dissociate at certain critical temperatures in the flame, producing free radicals. These radicals presumably enter into the combustion process and terminate the chain reactions. From the data in Table XXXI, it is apparent that compounds such as CF_2Br_2 and CF_3Br are very

TABLE XXXI

FIRE EXTINGUISHING AGENTS FOR *n*-HEPTANE—AIR
(Room temperature, 300–500 mm Hg absolute pressure)

Compound	Peak in flammability curve (volume %)
CF_2Br_2	4.2
$CFBr_3$	4.3
$CF_3CHBrCH_3$	4.9
$CBrF_2CBrF_2$	4.9
CF_2ICF_2I	5.0
CH_2Br_2	5.2
CF_3CF_2I	5.3
$CF_3CH_2CH_2Br$	5.4
CF_3CF_2Br	6.1
CF_3Br	6.1
$CH_2BrCF_2CH_3$	6.3
$CHBr_2F$	6.4
$CBrF_2CH_2Br$	6.8
CF_3CH_2Br	6.8
$C_6F_{11}C_2F_5$	6.8
1, 3-$C_6F_{10}(CF_3)_2$	6.8
CF_3I	6.8
$CClF_2CH_2Br$	7.2
$C_6F_{11}CF_3$	7.5
C_7F_{16}	7.5
$CHBrF_2$	8.4
$CClF_2CCl_2F$	9.0
$CBrClF_2$	9.3
CH_3Br	9.7
$CF_2{=}CHBr$	9.7
C_4F_{10}	9.8
$CBrF_2CBrClF$	10.8
$CClF_2CClF_2$	10.8
CCl_4	11.5
$CF_3CHClCH_3$	12.0
CF_3Cl	12.3
CF_3CF_3	13.4
CF_2Cl_2	14.9
CF_3H	17.8
$CHClF_2$	17.9
C_4F_8	18.1
SF_6	20.5
BF_3	20.5
CF_4	26
CO_2	29.5

effective. It may be presumed that the cleavage of the C—Br bonds yield —CF_2 and —CF_3 radicals as well as bromine atoms. The fact that chlorine-substituted compounds are not as effective suggests that the C—Cl bonds are not as readily broken due to their greater energy of formation. On the other hand, compounds such as CF_4, SF_6, are not active chemically, but have a purely physical effect in extinguishing the fire.

D. CF_2Br_2 AND CF_3Br

The two fluorine-containing compounds which have received most attention in recent years have been CF_3Br, bromotrifluoromethane, and CF_2Br_2, dibromodifluoromethane. These compounds which boil at −58°C and 25°C respectively, have been shown to be highly efficient fire extinguishing agents(58,59). Both are considerably more thermally stable than the typical nonfluorine-containing agents, such as carbon tetrachloride, CCl_4, methyl bromide CH_3Br, and methylene chlorobromide ("CB"), CH_2ClBr.

The CF_3Br especially is much less toxic than conventional agents, both initially and after exposure to combustion. The approximate lethal concentration of CF_3Br, the concentration necessary to kill mice or rats as a result of a 15 min exposure, was found to be 8.3×10^6 ppm (5070×10^3 mg per m^3), which is equivalent to 83% by volume in air. The hydrocarbon agent "CB" CH_2ClBr, on the other hand, is toxic at 30,000 ppm (160×10^3 mg per m^3) or 3% by volume in air. In chronic toxicity tests, exposures to vapors of CF_3Br at concentrations of 23,000 ppm (140×10^3 mg per m^3) for eighteen weeks did not show any toxic effects on mice or rats. No evidence was found for either pulmonary edema or pulmonary necrosis. On the other hand, the maximum prolonged toleration for CH_2ClBr appears to be about 1000 ppm (5.3×10^3 mg per m^3) for fourteen weeks(61,62).

It is reported that when a half pound of gasoline was poured into a 1 in. high, 12 sq-in. pan in a 20 m^3 test chamber and ignited, only 0.3 lb of CF_3Br extinguished the fire in 15 sec; whereas 1.3 lb. of CH_2ClBr were required(60).

Although both CF_3Br and CF_2Br_2 have been used in military and commercial aircraft in the protection of aircraft engine nacelles, and other confined spaces, CF_3Br has achieved the greatest usage. Besides its generally lower order of toxicity, it is considerably more effective in extinguishing fires at low temperatures (−65°F) than CF_2Br_2.

These compounds have also been found effective in extinguishing fires from liquid rocket fuels such as white fuming nitric acid and JP-3. Table XXXII compares several fire extinguishing agents(63).

TABLE XXXII

EXTINGUISHMENT OF WHITE FUMING NITRIC ACID AND JP-3 LIQUID FUELS

Agent	Pounds of agent used	Remarks
CH_3Br	9.0	fire not affected
CH_2BrCl	5.5	fire not affected
CF_2Br_2	1.5	fire immediately extinguished
CF_3Br	0.7	fire immediately extinguished

With further reduction in cost and greater emphasis on maximum fire extinguishing efficiency, it appears obvious that there will be increased usage of fire extinguishing agents such as CF_3Br and CF_2Br_2.

VIII. Lubricants

In this section two types of fluorocarbon lubricants will be reviewed: Those that are liquids in character, such as oils, greases; and those that are used as surface coatings. The low coefficient of friction of polytetrafluoroethylene will be reviewed in a later section. This polymer has found considerable use as an oil-less bearing, or in the form of thin films on a metal substrate(64).

A. FRICTION

Sliding friction is almost certainly due to the exceedingly strong adhesion between those parts of the surfaces which come into real contact with each other, when two solid bodies touch. That friction is present at high speeds is evidence that the point to point contacts between the two surfaces are formed very rapidly. It is also well known that friction results in the liberation of a large amount of heat, which may, of course, be calculated from the work required to slide the faces over each other.

Lubricants separate the solid surfaces so that the slightly elevated portions which come into contact cannot seize with the same intensity as when they were clean. While a considerable degree of lubrication can be obtained with films of various organic or inorganic substances only one molecule thick, the engineer aims whenever possible at separating the moving surfaces by a film of oil thick enough to have the properties of the oil in bulk.

B. TWO TYPES OF LUBRICATION

Two states of lubrication can be distinguished: hydrodynamic and boundary lubrication. In the hydrodynamic lubrication, there is a comparatively thick layer of oil everywhere between the faces; whereas with boundary lubrication, the surfaces come into contact except for an invisible film which may often be monomolecular.

In hydrodynamic lubrication a high viscosity hinders the oil being squeezed out and aids dragging the oil in. As the only friction is fluid friction, the viscosity should not be higher than is necessary to maintain the complete fluid film, with a reasonable margin of safety after providing for any likely lowering of viscosity through heating of the oil, decomposition, etc. The ability of a lubricating oil to lubricate and perform a number of its assigned functions is largely determined by its viscosity. The chemical characteristics of the oil are mainly important in ensuring chemical stability and a favorable temperature coefficient of viscosity, which is not too high. A high degree of adhesion between the oil and the metal surfaces is desirable.

The conditions at the surface being lubricated are also important—the so-called region of "boundary lubrication". The ability of a lubricating oil to wet the surface is easily influenced by absorbed monolayers. Clean metallic surfaces, for example, are generally quite easily wetted by lubricating oils, the contact angle being usually less than 50°.

A monomolecular film of a long-chain substance on a solid surface diminishes the friction very greatly. Langmuir transferred a monomolecular film of oleic acid from the surface of water to a glass plate, thereby lowering the coefficient of friction from about unity to 0.13(65). As friction is due to seizure, to the adhesions between the molecules when they really touch, a principal reason for the lubricating effect of layers only one molecule thick is that they cover the regions which would otherwise come into real contact. The strength of the adhesive forces between the two solids can no longer be the strength of the solids themselves, but the much smaller strength of adhesion between the molecules which have been absorbed.

C. Halofluorocarbon Oils, Waxes, and Greases

When the polymerization of $CF_2 = CFCl$ is carried out in the presence of solvent or other agents which can function as chain transfer agents, then a series of low molecular weight oils and greases are formed(66). This telomerization reaction may be represented:

$$\text{Peroxide} \xrightarrow{\text{heat}} R\cdot \tag{10}$$

$$R\cdot + n(CF_2 = CFCl) \rightarrow R(CF_2\text{-}CFCl)_n\cdot \tag{11}$$

$$R(CF_2\text{-}CFCl)_n\cdot + CHCl_3 \rightarrow R(CF_2\text{-}CFCl)_nH + CCl_3. \tag{12}$$

$$CCl_3\cdot + n(CF_2 = CFCl) \rightarrow CCl_3(CF_2\text{-}CFCl)_n \tag{13}$$

TABLE XXXIII

TYPICAL PROPERTIES OF STANDARD "KEL-F" BRAND (CTFE) OILS AND WAXES[67]

Grade designation	1	3	10	40	10–200	200
Description	light oil	medium oil	heavy oil	soft wax	medium wax	hard wax
Formula	← $Cl(CF_2—CFCl)_xCl$ →					
Molecular weight	500	630	780	940	—	—
Color	← colorless →					
Clarity (room temperature)	clear	clear	clear	opaque	opaque	opaque
Odor	sweet	← odorless →				
Refractive index, n_D						
25°C	1.400	1.405	1.410	—	—	—
70°C	—	—	—	1.398	1.401	—
Viscosity (cs)						
38°C	2	25	220	—	—	—
100°C	0.8	3	10	40	55	—
130°C	—	—	—	—	—	145
Viscosity (cp)						
38°C	3.6	47	425	—	—	—
130°C	—	5	18	75	105	—
Viscosity-temperature coefficient[a]	0.67	0.88	0.96	—	—	—
Pour point (°F)	< −70	−45	+30	+90	—	—
Melting point, ASTM D-127 (°F)	—	—	—	100	150	200
Specific gravity						
20°C/4°C	1.84	1.93	1.96	—	2.02	2.11
38°C/4°C	1.81	1.90	1.93	—	1.99	—
70°C/4°C	—	1.85	1.88	1.92	1.94	—

Density (lb per gal)						
20°C	15.4	16.1	16.3	—	16.8	17.6
38°C	15.1	15.8	16.1	—	16.6	—
70°C	—	15.4	15.7	16.0	16.2	—
Volume expansivity (ml per ml per °F × 10^4) relative to 20°C						
4– 38°C	4.0	—	—	—	—	—
38– 70°C	—	4.8	4.8	—	4.4	—
70–100°C	—	—	—	4.6	—	—
Vapor pressure constants[b]						
A	7.4991	8.4976	9.0503	10.2123	9.6116	—
B	2351	3161	3743	4863	4313	—
Heat of vaporization						
cal per gm	21	23	22	23	—	—
kcal per mole	10.7	14.5	17.1	22	—	—
Surface tension (dynes per cm)	23	28	30	—	—	—
Specific heat (cal per gm)	—	—	0.22	—	—	—
Thermal conductivity (BTU per hr per ft² per °F per ft)	—	—	0.080	0.110	—	—

---

[a] V. T. Coefficient = 1 − viscosity at 100°C/viscosity at 100°F.

[b] $\log P_{(\text{mm Hg})} = A - B/T$ °K.

In the above n can be controlled so that distribution of telomer products ranges from $n = 2$ to $n = 20$ are readily obtained with a number averaging 12 carbon atoms. As might be expected, it is difficult to control the reaction so as to obtain narrow boiling range products.

A second procedure has also been used to prepare chlorofluorocarbon oils. This involves the thermal cracking of the high molecular weight polychlorotrifluoroethylene resins. When carried out under proper conditions of temperature and pressure, high yield of products boiling in the same range as the telomer products are produced.

The crude product resulting from either the telomerization or the thermal cracking processes must generally be stabilized by reaction with chlorine or various fluorinating agents such as F_2 or CoF_3.

Vacuum distillation of this product leads to a series of products ranging from light oils to heavy greases and waxes. Such products are available from several sources and are known as "Kel-F" Brand halofluorocarbon oils and greases (Minnesota Mining and Manufacturing

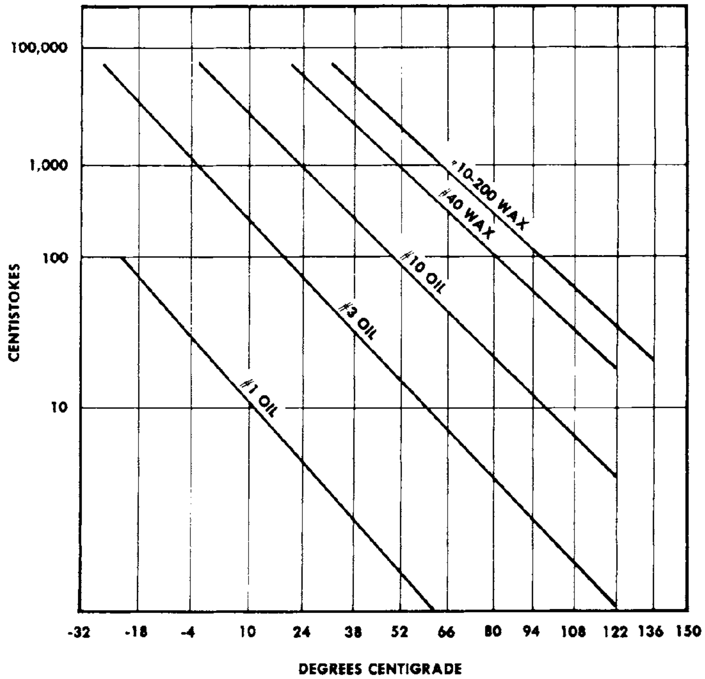


FIG. 27. Kinematic viscosity of chlorofluorocarbon oils.

Company), Fluorolubes (Hooker Chemical Corporation), and Halocarbon Oils (Fluorochem Corporation).

Typical properties for such a commercial series of products is included in Table XXXIII. It will be seen that the products range from light oils to hard waxes at room temperature.

The kinematic viscosity of the chlorofluorocarbon oils as a function of temperature is shown in Fig. 27. Figures 28 and 29 show the variation in specific gravities and vapor pressures respectively for representative members of these chlorofluorocarbon products.

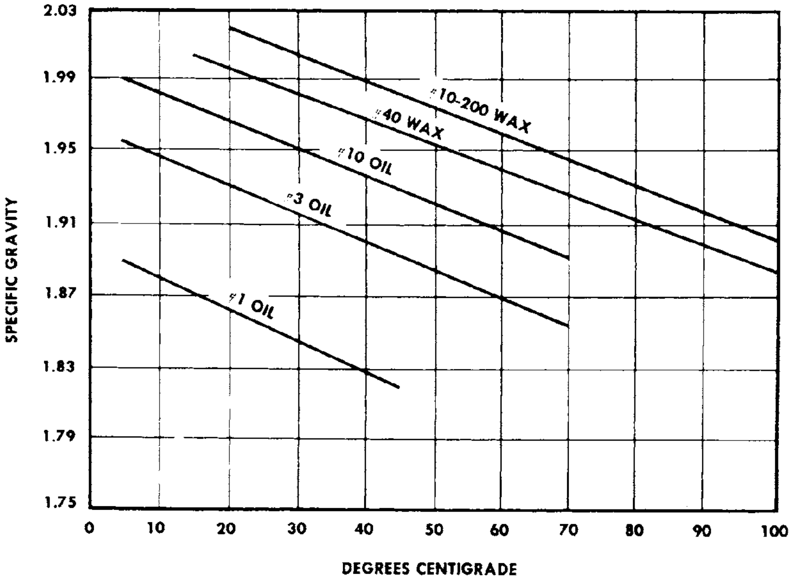


FIG. 28. Specific gravity of chlorofluorocarbon oils and waxes.

As can be seen from the data in Table XXXIII, all the products when properly prepared, are colorless and odorless. Since these products are substantially free of hydrogen, they are transparent in the 2 to 4 μ infrared region, where most organic liquids are strongly absorbing.

Because of their high fluorine content, these oils are very resistant to all types of oxidation whether by combustion by air or chemical action of liquid oxygen, hydrogen peroxide, or fuming nitric or sulfuric acids. They are also not attacked by ClF_3 at 150°C or concentrated H_2SO_4 at 200°C. They do not attack metals used in normal construction such as steels, copper, nickel, or alloys of these metals. Under conditions of high heat, they can react vigorously with light metals such as aluminum and magnesium. Under normal service conditions, the oils are stable up to temperatures of 260°C.

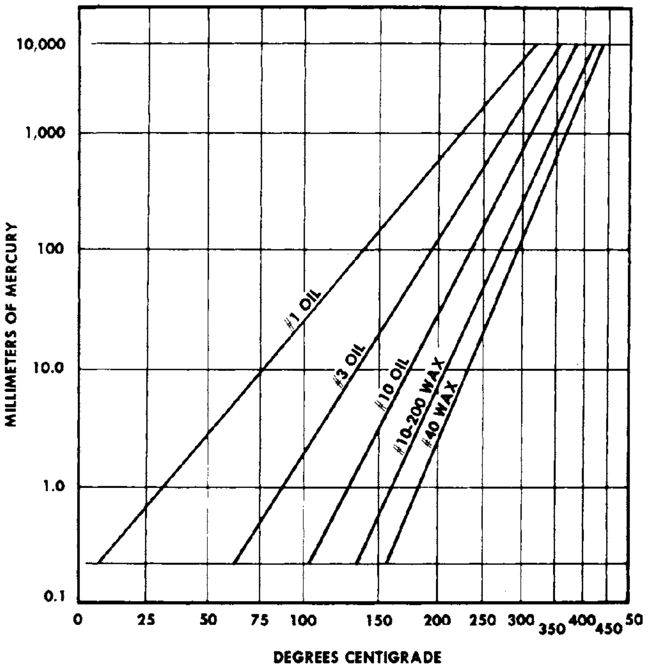


FIG. 29. Vapor pressure of CTFE oils and waxes.

The oils and waxes are soluble in aromatic, aliphatic, and chlorinated hydrocarbons, alcohols, ketones, esters, and fluorocarbons. They are insoluble in water. The degree of solubility, of course, varies widely with molecular weight, the high molecular weight waxes being less soluble than the oils. It should be noted that the relatively high solubilities of these oils are due to the presence of the chlorine atom. Comparison with the fluorocarbon liquids, such as FC-75 and FC-43 containing no chlorine, as discussed earlier under Coolants, will emphasize this difference.

The oils are excellent lubricants. Under certain conditions they exhibit the properties of a pure extreme pressure additive. The mean Hertz load as measured by 10-sec run in the Shell 4-ball E. P. Tester[68] is 120 kg, a value which compares favorably with typical values of 70–80 kg for commercial hydrocarbon type gear lubricants.

The chlorofluorocarbon oils have found extensive use as lubricants for highly corrosive service. They were originally developed for use in handling the separation of the hexafluorides of the isotopes of uranium(68). They are also being used extensively to lubricate compressors, valves, seals, etc., in handling liquid oxygen, and a varicty of highly oxidizing and corrosive missile and rocket propellants.

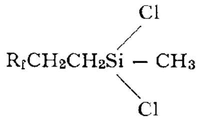
These oils have also found extensive use as flotation fluids in gyroscopic devices. While high density is the primary property in this use, chemical inertness, as well as the ability to attain specific density values by blending the different oils, are also important. A typical gyroscopic device is shown in Fig. 30.

FIG. 30. Gyroscope utilizing clorofluorocarbon oils as flotation fluids.

When thickened with various inorganic thickeners, such as silica, a variety of greases may be made from the chlorofluorocarbon oils.

D. Other Fluorine-Containing Fluids

Although they have not achieved any extensive usage at the time of writing, several fluorine-containing fluids have been introduced as special lubricants. Included are a series of fluorosilicone fluids and greases designated as FS-1265, FS-1280, FS-1281, FS-1290, and FS-1291 (Dow Corning Corporation). These presumably are low molecular weight polymers based on fluorosilicone derivatives of the type



$$R_fCH_2CH_2Si(Cl)_2-CH_3$$

where R_f is a fluorocarbon group such as CF_3, C_3F_7, etc. Typical properties are shown in Table XXXIV.

TABLE XXXIV

Typical Properties

Fluorocarbon Fluids FS 1265

	Viscosity grade		
	250 cs	1000 cs	10,000 cs
Color	water white to straw		
Viscosity, cs at 25°C	250	1000	10,000
Viscosity, cs at			
−18°C	3900	22,000	440,000
37°C	140	510	5400
100°C	24	74	690
205°C	5	11.5	80
Specific gravity at 25°C	1.24	1.28	1.30
Freeze point	−51°C	−40°C	−32°C
Flash point, open cup	225°C	275°C	275°C
Fire point	275°C	>325°C	>325°C
Volatility (wt %)			
4 hr at 200°C	4.1	1.5	1.5
48 hr at 200°C	13.5	3.1	3.0
120 hr at 200°C	20.0	5.0	4.9
240 hr at 200°C	25.0	8.0	6.0
Gel time, hr at 200°C	350	350	350
Acid number	trace	trace	trace
Surface tension (dynes per cm)	25.7	26.1	28.7

E. Fluorocarbon Monolayers

Zisman has studied a series of hydrocarbon and fluorocarbon derivatives adsorbed on clear glass surfaces(70). He measured the contact angles, θ, exhibited by methylene iodide (surface tension 50.8 at 20°C) on the adsorbed surfaces. He also measured the coefficient of friction for a stainless steel ball sliding at the speed of 0.01 cm per sec while pressing against the coated glass plate. Typical data are plotted in Fig. 31 comparing the contact angle for homologues of $CH_3(CH_2)_nCOOH$, $HCF_2(CF_2)_n$-$COOH$, and $CF_3(CF_2)_nCOOH$.

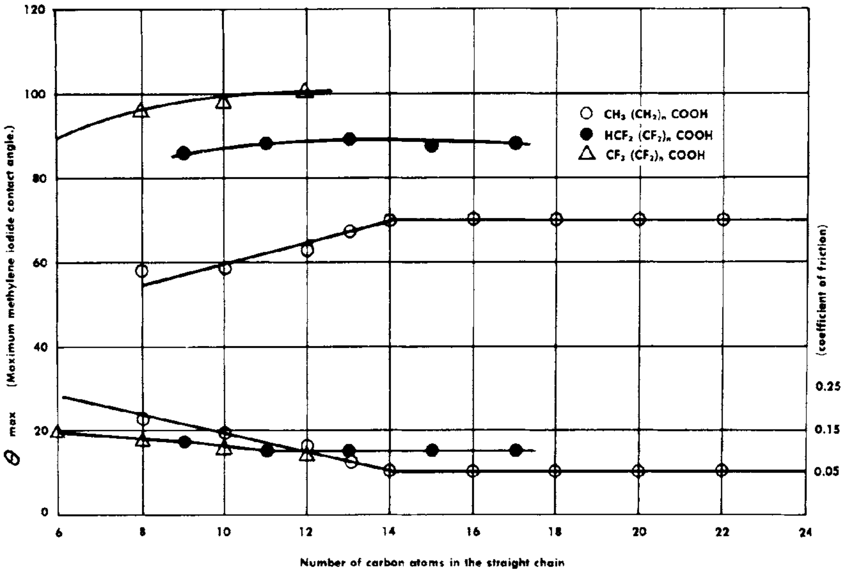


FIG. 31. Frictional and wetting properties of condensed monolayers.

Whereas the plots of θ_{max} vs number of carbon atoms differ quite markedly, the plots of μ_K, the coefficient of friction, vs the number of carbon atoms lie quite closely together. It is particularly noteworthy that the HCF_2^- and CF_3^- terminal groups cause major differences in the wettability of these condensed monolayers, but these groups cause no essential difference in frictional behavior. As might also be expected, the hydrocarbon compounds show much lower contact angles, θ_{max}, to methylene iodide. The coefficient of friction, μ_K, however, does fall to a value lower than that for the fluorocarbon derivatives.

It is concluded from this work that while wettability of the surface is determined by the substituents on the terminal group, these substituents play a very insignificant part in boundary lubrication. The coefficient of friction of either a fluorocarbon or hydrocarbon derivative is most influenced by the ability of the molecules in the monolayer to close pack through the strong adlineating effects of intermolecular cohesive forces.

It is noted that the μ_K vs number of carbon atoms curve for the hydrocarbon fatty acids crosses the curve for the fluorocarbon compounds at between 12 and 13 carbon atoms and thus has a lower asymptotic value. This means that for chain length greater than 12, the mechanical strength of the condensed monolayer of the fatty acids is greater than that of the corresponding fluorocarbon derivatives.

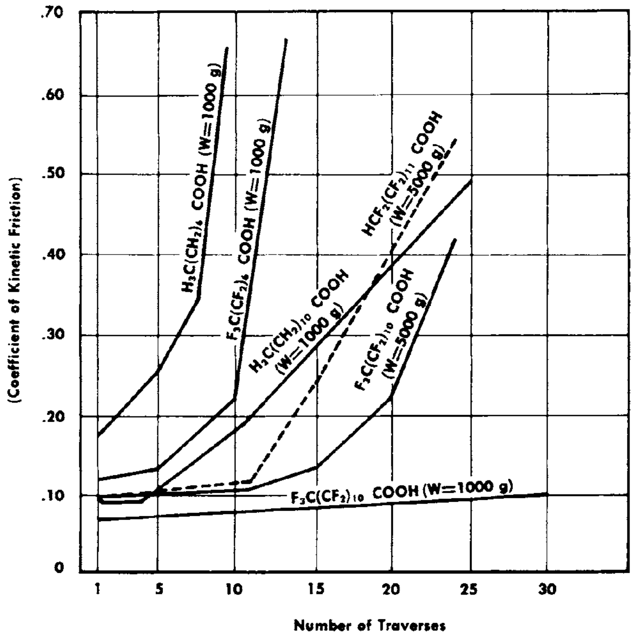


FIG. 32. Comparative durabilities of straight chain fluorocarbon and hydrocarbon carboxylic acids when adsorbed on solid surface.

Zisman has also studied the durability of adsorbed films, by making a series of successive unidirectional traverses of the steel ball over a 2 mm path on the film-coated glass plates. The ball was held firmly in one position in its holder so that the same area of the ball was always in contact with the glass plate. Using this procedure Zisman has shown that for a homologous series of fatty acid, there was no change in the coefficient of friction even after 35 traverses for $C_{13}H_{27}COOH$ and higher homologues. Lower homologues showed coefficient of friction increases at progressively fewer traverses.

In Fig. 32 data is plotted showing the changes in coefficient of friction for straight chain hydrocarbon and fluorocarbon carboxylic acids of equal chain length.

It will be noted that a monolayer of $CH_3(CH_2)_{10}COOH$ under a load of 1000 gm will break down after only 3 or 4 traverses, whereas a monolayer of $CF_3(CF_2)_{10}COOH$ has essentially the same coefficient of friction even after 30 traverses. This means that a condensed monolayer of the fluorocarbon acid is a solid, whereas lauric acid is a liquid. Similarly, a condensed monolayer of $CF_3(CF_2)_6COOH$ is so much less durable than a solid monolayer of $CH_3(CH_2)_{10}COOH$ that it must be classified as a liquid monolayer. On the other hand, the eight-carbon fluorocarbon acid is more durable than a liquid monolayer of its hydrocarbon analog. Presumably this greater durability is associated with the stronger bond to the glass because of the much greater acidity of $CF_3(CF_2)_{10}COOH$.

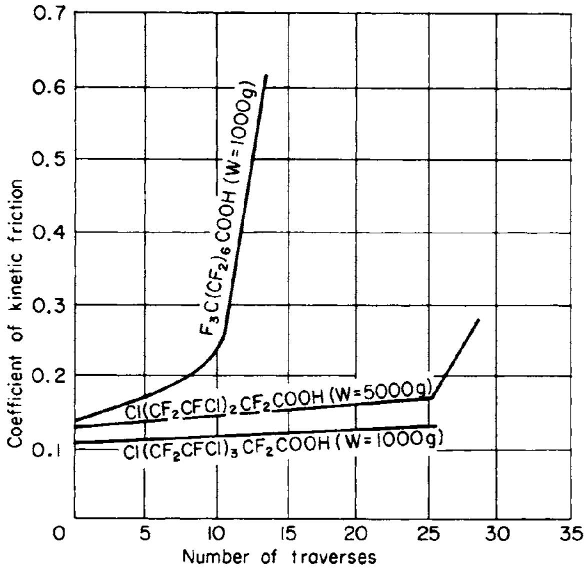


FIG. 33. Effect of halogen substituent on the durability of a condensed monolayer.

The data in Fig. 32 also shows that the CF_3 terminated 12-carbon fluorocarbon acid is somewhat more durable than the —CF_2H terminated 13-carbon acid.

Figure 33 shows the comparison between the fluorocarbon acid, $CF_3(CF_2)_6COOH$, and the chlorine-substituted analog, $Cl(CF_2CFCl)_3$-CF_2COOH. It is apparent that there is a large and beneficial effect on film strength caused by the substitution of covalent bonded chlorin-atoms for fluorine. Thus, whereas the fluorocarbon acid forms a liquid monolayer, the chlorine-containing analog forms a plastic monolayer. The greater mechanical strength of the chlorinated film is attributed to the larger energy of intermolecular cohesion.

It may be concluded from Zisman's work that fluorocarbon derivatives can show excellent lubricant properties, but that it is necessary to select the proper chain length so as to have good adlineation of the oriented molecules. It is also important to select a functional group that will show maximum bonding to the substrate to be lubricated.

IX. Fluorocarbon Surfactants

In the section on Characteristic Properties it was seen that as a class the fluorocarbons have the lowest surface tensions of any known materials. When a functional group is attached to a fluorocarbon tail, a new class of compounds is formed which are extremely surface active. Surface activity, of course, is defined as the ability of a compound, when dissolved in a liquid medium, to migrate to and orient on the surface, thereby reducing the surface energy (or surface tension) of the liquid. A fluorocarbon surfactant is defined as a molecule, one end of which is a solubilizing functional group, while the other end consists of a fluorocarbon group containing a minimum of four carbon atoms and terminated by a —CF_3 group. They have the general formula

$$CF_3(CF_2)_n - X$$

TABLE XXXV

MINIMUM SURFACE TENSION VALUES IN WATER FOR SUBSTITUTED FLUOROCARBON SURFACTANTS

Compound	Concentration (gm per 100 ml)	Minimum surface tension (dynes per cm at 25°C)	Reference
$CF_3(CF_2)_6COOH$	0.35	15.3	(13)
$HCF_2(CF_2)_5COOH$	0.50	21.8	(72)
$Cl(CF_2 \cdot CFCl)_3CF_2COOH$	0.50	24.0	(71)

When either a hydrogen atom or another halogen Cl, or Br, are substituted for any of the fluorine atoms in the fluorocarbon group, this will be defined as a substituted fluorocarbon group. From the data in Table XXXV it is seen that when the substitution takes place in the terminal CF_3 group, there is a very significant increase in the minimum surface tension lowering possible. The surface activity of the hydrogen and chlorine substituted fluorocarbon compounds is approximately the same as that of conventional hydrocarbon surfactants terminated by a terminal CH_3 group. This, of course, is consistent with the Zisman critical surface tension values reported earlier when the same groups are adsorbed on solid surfaces.

A. Surface Active Nature of Fluorocarbon Compounds

Scholberg, Guenthner, and Coon reported on the surface active properties of a homologous series of fluorocarbon carboxylic acids, namely, CF_3COOH, C_2F_5COOH, C_3F_7COOH, $C_5F_{11}COOH$, $C_7F_{15}COOH$, and $C_9F_{19}COOH$(13). As was shown in Fig. 4 of a previous section, these compounds are able to reduce the surface tension of a water to 16 to 18 dynes per cm. The concentration required decreases sharply as the chain length increases. For practical purposes, only those compounds with a carbon chain of six or more can be considered as effective surface active agents.

The fluorocarbon carboxylic acids are also important as chemical intermediates in deriving a vast array of other fluorocarbon surfactants. The carboxylic acid group may be altered in many ways by conventional chemical reactions. Examples of this are shown in Fig. 34. In this case the compound, $C_7F_{15}COF$, may be prepared using the Simons electrochemical cell. From this compound a wide variety of surface active compounds may be produced, all of which contain the same C_7F_{15}- group(74).

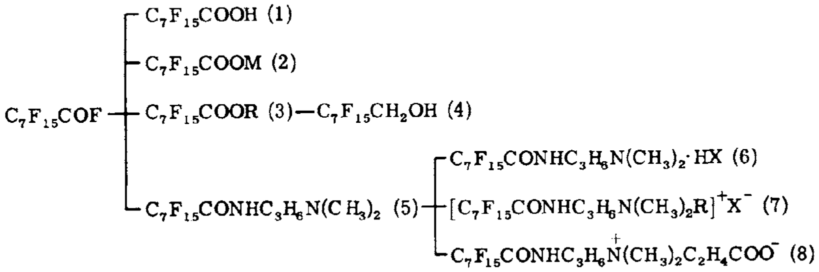


FIG. 34. Surface active compounds based on fluorocarbon carboxylic acid.

Brice and Trott reported the preparation of a homologous series of fluorocarbon sulfonyl fluorides, which by hydrolysis may be converted to the corresponding fluorocarbon sulfonic acids(172). Besides showing the typical properties of a fluorocarbon surfactant, the above compounds are all exceptionally strong acids, having acid strength greater than the strong mineral acids, HCl, HNO_3, and H_2SO_4.

Fluorocarbon sulfonic acids are also important as a starting material for the synthesis of many additional surface active compounds containing the same fluorocarbon tail, but with greatly varying functional groups. Guenthner and Vietor have reported on a number of these compounds, examples of which are included in Fig. 35(75). In the figure the starting material is the compound, R_fSO_2F, which is a product of the Simons electrochemical process. In the figure the example chosen is $C_8F_{17}SO_2F$ which, as was shown earlier, has a fluorocarbon tail of the right chain length to show good surface activity. Direct hydrolysis of the $C_8F_{17}SO_2F$ leads to the acid, $C_8F_{17}SO_3H$, or its salts. The two sulfonamido types are derived by direct reaction with a primary or secondary amine. These amines can then be converted to a sulfonamido aliphatic acid and its salts or the alcohols. Reaction of the alcohol with ethylene oxide gives a nonionic type. Quaternization of the tertiary amino sulfonamide gives the quaternary cationic. The reaction with a lactone leads to an amphoteric betaine. From the alcohol, on the other hand, normal sulfate or phosphate esters can be prepared.

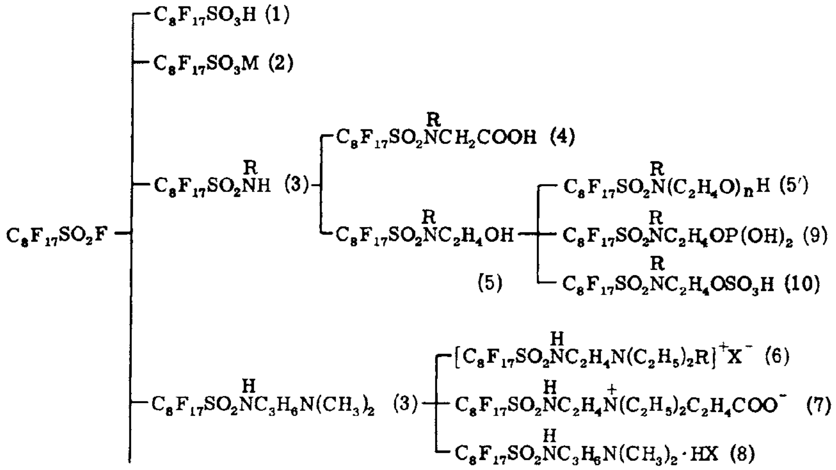


FIG. 35. Surface active compounds based on fluorocarbon sulfonic acids.

Thus, a very large number of compounds can be made in which the fluorocarbon group, R_f, and the functional group, X, are varied. For a given fluorocarbon group, i.e., C_8F_{17} the solubility of the whole molecule can be varied by changing the character of the functional group X. The sulfonic group, the carboxyl group, the quaternary nitrogen group, etc., all impart a degree of solubility in aqueous solutions. On the other hand, the introduction of hydrocarbon groups will give solubility in a variety of organic liquids.

B. SURFACE ACTIVITY IN WATER

The data in Fig. 36 shows the effect of changing of the solubilizing group for a series of fluorocarbon sulfonic acid derivatives containing the C_8F_{17} group. Of particular note are the extremely surface active compounds,

$[C_8F_{17}SO_2NHC_3H_6N(CH_3)_3]^+I^-$ and $C_8F_{17}SO_2N(C_2H_5)(C_2H_4O)_{14}H$

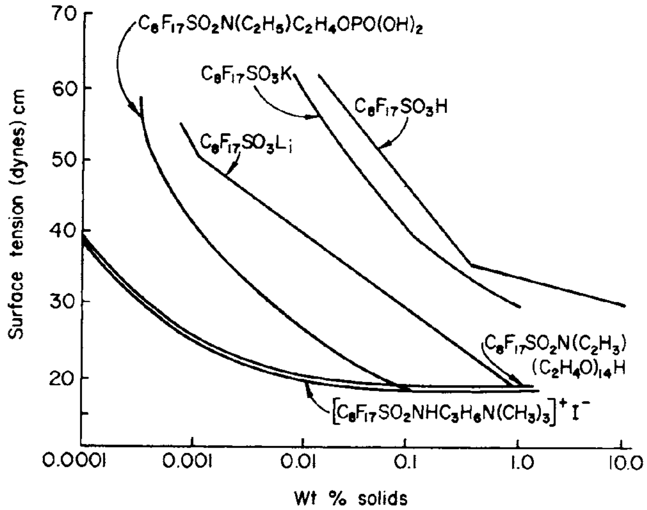


Fig. 36. Surface activity of various fluorocarbon sulfonic acid derivatives in water.

On the other hand, the free acid and its salt are much less effective. It is interesting to note that the lithium salt is much more surface active than the potassium salt.

A similar relationship exists for a variety of derivatives of $C_7F_{15}COOH$; again the properties are very greatly dependent on the nature of the functional group. Fig. 37 shows the relationship between surface tension and concentration for a number of specific compounds.

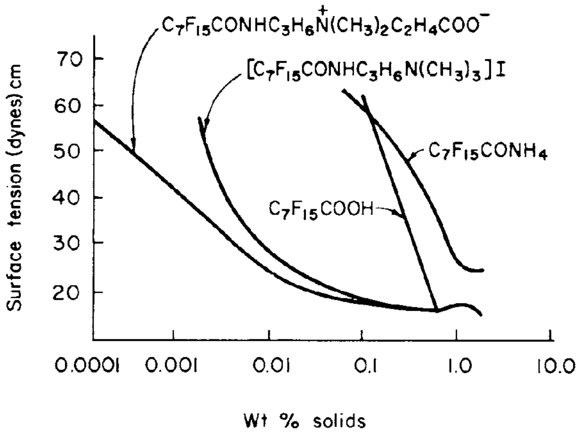


FIG. 37. Surface activity of various fluorocarbon carboxylic acid derivatives in water.

C. Surface Activity in Strong Acids and Bases

The longer chain fluorocarbon sulfonic acids illustrate rather graphically some of the unique qualities of the fluorocarbon surfactants. Typical

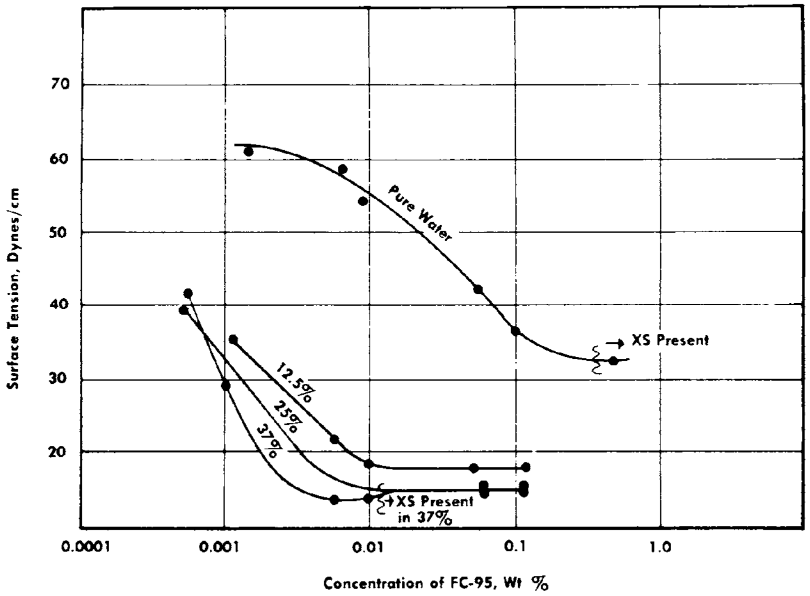
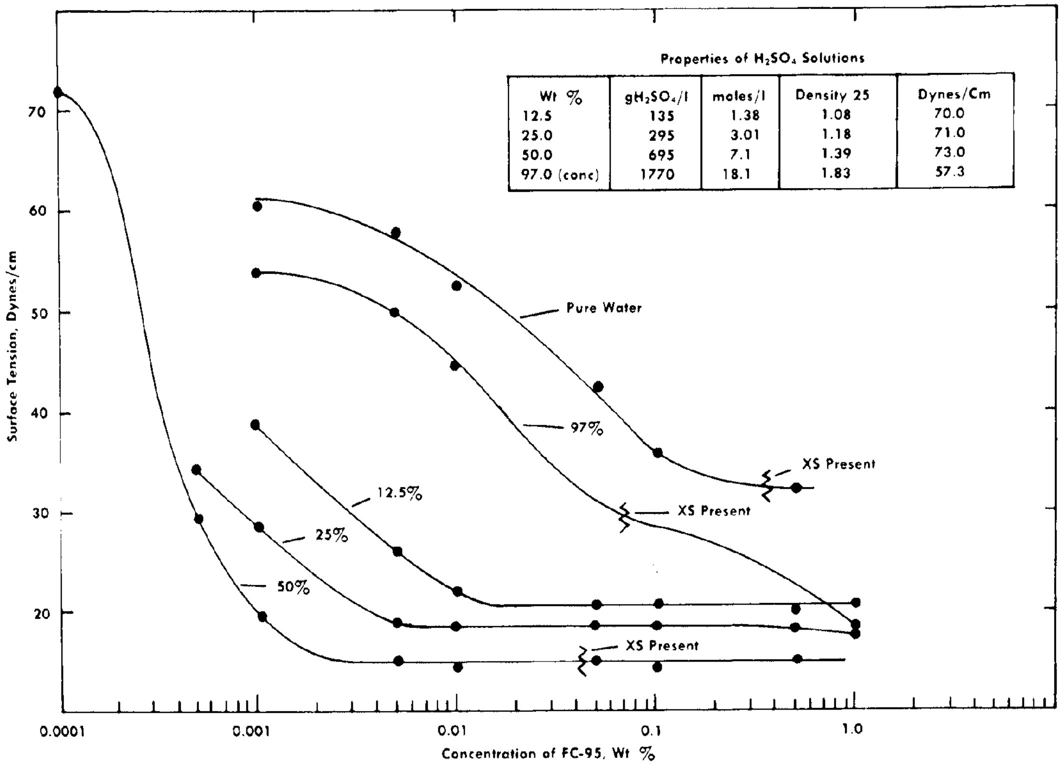


FIG. 38. Surface activity of $C_8F_{17}SO_3K$ in aqueous hydrochloric acid.



Properties of H_2SO_4 Solutions

Wt %	gH_2SO_4/l	moles/l	Density 25	Dynes/Cm
12.5	135	1.38	1.08	70.0
25.0	295	3.01	1.18	71.0
50.0	695	7.1	1.39	73.0
97.0 (conc)	1770	18.1	1.83	57.3

FIG. 39. Surface activity of $C_8F_{17}SO_3K$ in aqueous sulfuric acid.

examples are $C_8F_{17}SO_3H$ or $C_2F_5C_6F_{10}SO_3H$, both of which may be readily converted into their salts. The fluorocarbon acids are among the strongest acids known. It may not be too surprising to find that compounds such as those above have unusual surface properties in solutions of strong mineral also. In Figs. 38, 39, 40, and 41 the data shows the potassium salt of the one of the acids mentioned above, $C_8F_{17}SO_3K$, is very surface active in hydrochloric acid, sulfuric acid, phosphoric acid, and nitric acid(76). It is interesting to note that whereas the above compound is not very surface active in pure water, there is a marked increase in the surface activity as the concentration of the mineral acid increases, at least up to 37% for HCl, 50% for H_2SO_4, and 25% for HNO_3. The surface active nature of compounds such as $C_8F_{17}SO_3K$ in these strong mineral acids is due to a combination of several factors. In the first place, the compounds are completely stable; secondly, the very strong sulfonic acid group enables the compound to be sufficiently soluble in the strong mineral acid and at the same time maintain a relatively high level of the ionized form. It will be noted in all cases that the surface tensions are reduced below 20 dynes per cm at concentrations in the range of 0.001 to 0.01 wt %.

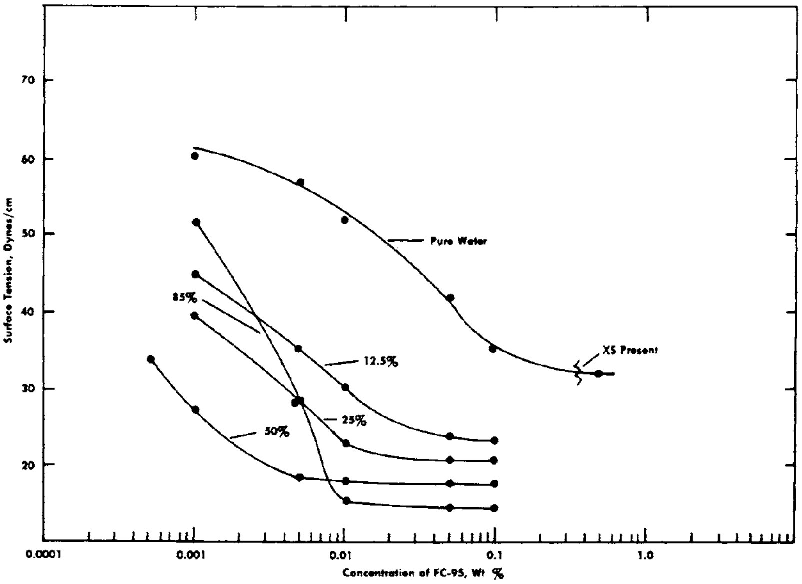


FIG. 40. Surface activity of $C_8F_{17}SO_3K$ in aqueous phosphoric acid.

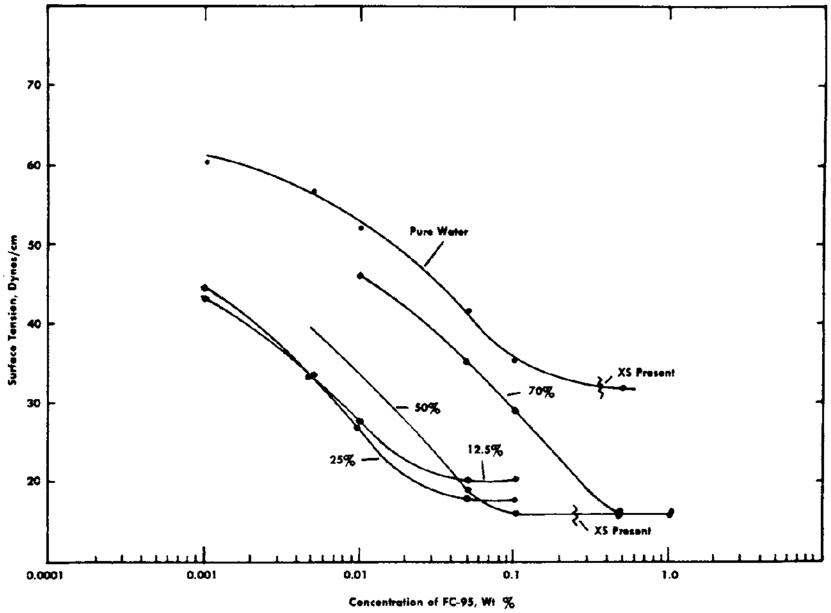


FIG. 41. Surface activity of $C_8F_{17}SO_3K$ in aqueous nitric acid.

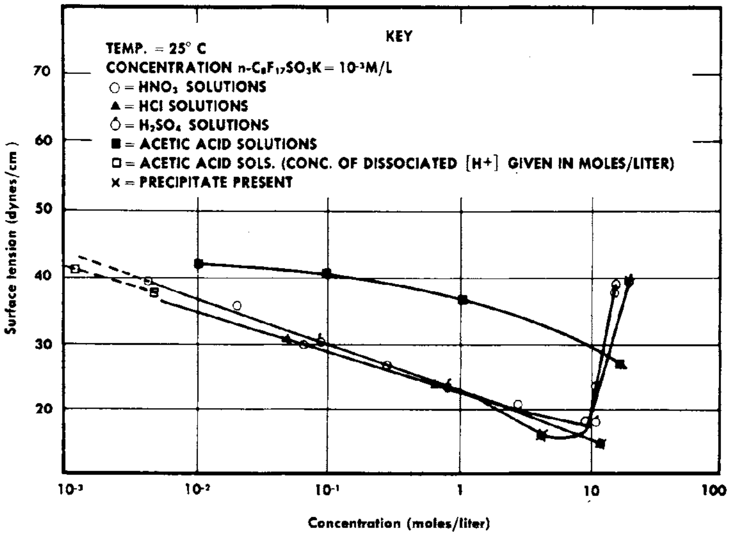


FIG. 42. The concentration effect of various acid media on the surface tension of $C_8F_{17}SO_3K$ solutions.

Talbot(73) has measured the surface tensions of the fluorocarbon sulfonic acid potassium salts, $C_8F_{17}SO_3K$, $CF_3C_6F_{10}SO_3K$ and $C_2F_5C_6F_{10}SO_3K$ in dilute and concentrated acid solutions. The data in Fig. 42 shows that the compound shows the same increase in surface activity with acid strength for the strong mineral acids, HNO_3, HCl, and H_2SO_4 over the concentration range of 10^{-3} to 10 M. On the other hand, $C_8F_{17}SO_3K$ is much less surface active in a weak acid such as acetic acid. These effects are consistent with the very strongly acid nature of the fluorocarbon sulfonic acids.

The fluorocarbon sulfonic acids also show pronounced surface activity in strong base solutions. The data in Fig. 43 shows the surface tension depression of $C_8F_{17}SO_3K$ in a 25% sodium hydroxide solution.

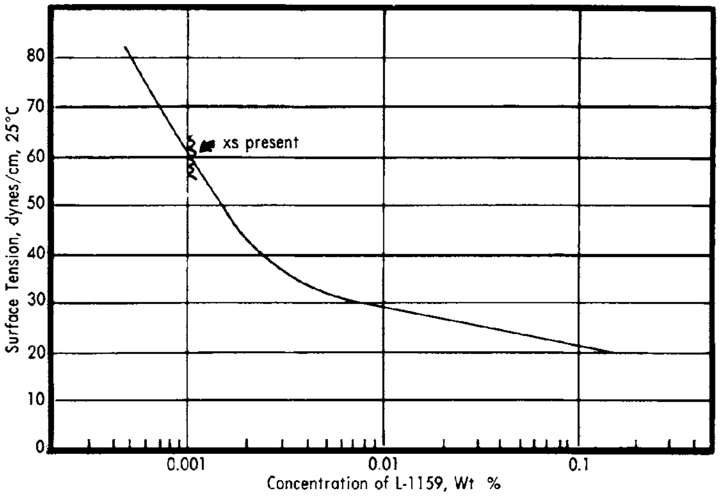


FIG. 43. Surface tension of $C_8F_{17}SO_3K$ in 25% NaOH.

In Fig. 44 the nonionic surfactant, $C_8F_{17}SO_2N(C_3H_7)(C_2H_4O)_nH$ is shown to be very surface active in a variety of acid, base, and salt solutions. All the surface tension measurements were made after the solutions had been allowed to stand for 24 hours at room temperature. The bar represents the surface tension of the electrolyte solution; the shaded area the reduction in surface tension which was measured.

Examples of the variety of media in which the salts of fluorocarbon sulfonic acids are completely stable are shown in Fig. 45. Surface activity is indicated by the reductions in surface tension as shown by the shaded

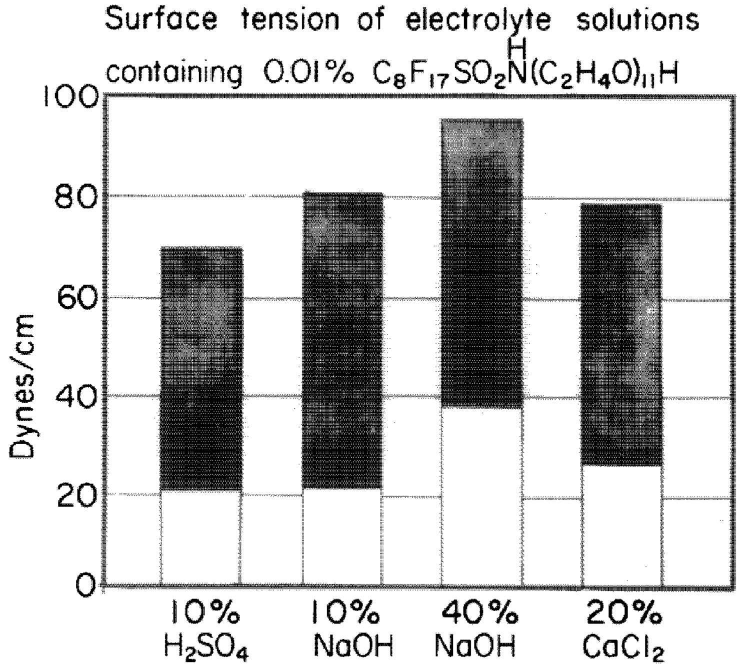


FIG. 44. Surface activity of nonionic surfactant in various media.

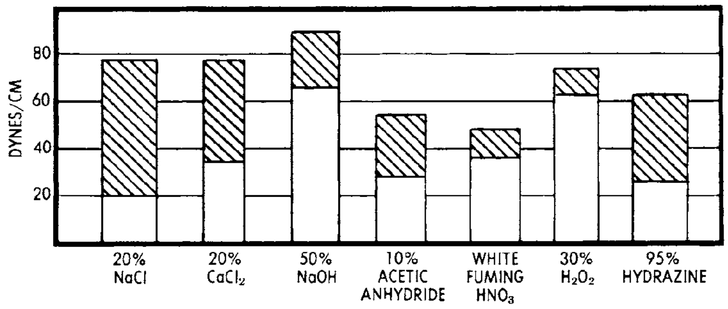


FIG. 45. Surface activity of $C_8F_{17}SO_3K$ in various chemical media. The tops of the columns represent surface tension without surfactant added. The shaded areas indicate the surface tension reductions obtained with $C_8F_{17}SO_3K$.

area. Maximum depression is not always obtained with the type of structure indicated by $C_8F_{17}SO_3K$. The compound, $C_7F_{15}COOH$, or its salts, are, for example, more surface active and equally stable in hydrogen peroxide.

D. THERMAL STABILITY

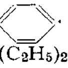
The fluorocarbon group is stable to temperatures in excess of 400°C. The thermal stability of a given fluorocarbon surfactant will, however, be dependent upon the thermal stability of the attached functional group. The fluorocarbon sulfonates are exceptionally stable, showing no decomposition below 350°C. The fluorocarbon carboxylic acids and salts, on the other hand, decompose by elimination of carbon dioxide at temperatures of 175° to 250°C(77).

E. SURFACE ACTIVITY IN ORGANIC MEDIA

When the functional group which is attached to the fluorocarbon tail is of such a nature that it will solubilize the resulting compound to a definite, though small degree in an organic media, a unique class of surfactants results. Ahlbrecht, Blake, and Bryce were the first to report on such fluorocarbon surface active agents(78). They were able to show that a series of substituted amides of $C_7F_{15}COOH$ and $C_9F_{19}COOH$ could be modified to show surface activity in a number of hydrocarbon type materials. The compounds studied are shown in Table XXXVI. Fig. 46 gives typical results. The right ends of the bars indicate the normal surface tensions as plotted along the bottom of the chart. The striped areas represent the magnitudes of the lowerings obtained. It can be seen that decreases in

TABLE XXXVI

TYPICAL FLUOROCARBON SURFACTANTS

Chemical formula	Code
$C_8F_{17}SO_3H$	F-1
$C_7F_{15}CONHC_3H_6N(CH_3)_3I$	F-2
$C_7F_{15}CONHC_3H_6N(CH_3)_2C_{10}H_{21}Br$	F-3
$C_7F_{15}CONHC_3H_6N(CH_3)_2C_2H_5I$	F-4
$C_9F_{19}CONHC_3H_6N(CH_3)_3I$	F-5
$C_7F_{15}CONHC_2H_4N$  · Cl	F-6
$C_7F_{15}CONHC_3H_6N(C_2H_5)_2CH_3I$	F-7
$C_7F_{15}CONHC_2H_4N(C_2H_5)_2CH_3I$	F-8
$C_7F_{15}CONHC_3H_6N(CH_3)_2$	F-9
$C_7F_{15}CONHC_2H_4N(C_2H_5)_2$	F-10

surface tension range from about 5 dynes per cm in Stoddard solvent to 14 or 15 dynes per cm in molten microcrystalline wax, linseed oil, and lubricating oil.

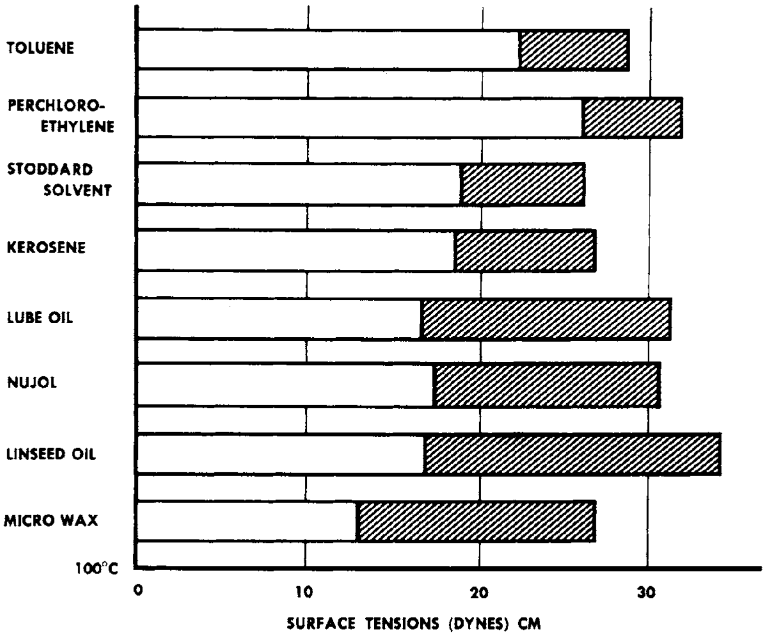


FIG. 46. Surface tension depression for a fluorocarbon surfactant in a variety of organic liquids.

Several fluorocarbon surfactants are quite effective in lowering the surface tensions of melted petroleum waxes. Data is shown in Fig. 47 for a fully refined paraffin wax with a melting range of 52–55°C. The normal surface tension of this wax at 100°C is 24.3 as measured using a DuNuoy Tensiometer. The minimum effective concentrations are at the knees of the curves and occur at between 0.006 and 0.03%. The compound F-2, $C_7F_{15}CONHC_3H_6N(CH_3)_3I$, is the most effective of the compounds containing the $C_7F_{15}^-$ group, giving a surface tension of 15 dynes per cm at 0.01%. On the other hand, the compound F-5, $C_9F_{19}CONHC_3H_6N(CH_3)_3I$ will reduce the surface tension to 12 dynes per cm at 0.01% concentration. Fig. 48 shows the effect of temperature; as would be expected, the surface tension vs temperature curve for 100°C is displaced downward from the curve at 75°C.

As shown in Fig. 49, the compounds F-3, F-4, F-9, and F-10 all have the ability to reduce the surface tensions of a mineral oil by 10 or more dynes per cm. In this case a base stock lubricating oil, SAE 20, was used for the experiments. All the compounds appear to be effective in the 0.002 to 0.008% by weight concentration range.

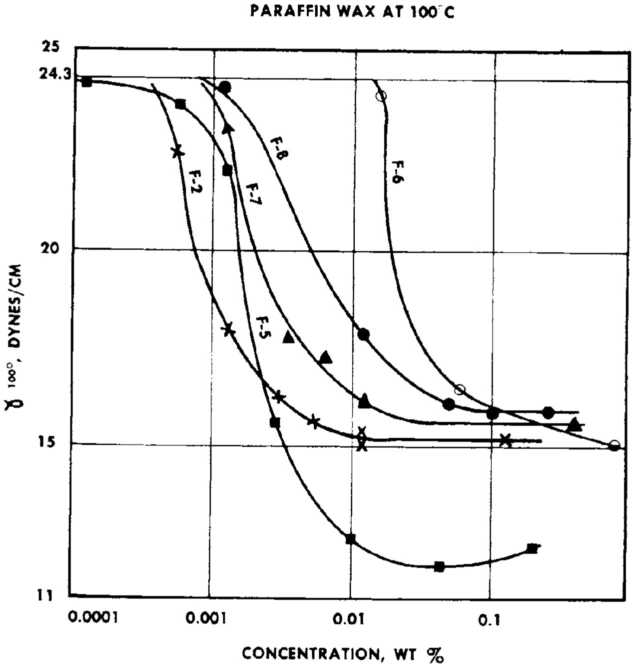


FIG. 47. Surface tension of paraffin wax containing various concentrations of fluorocarbon surfactant.

Guenthner and Vietor have shown that various derivatives of $C_8F_{17}SO_3H$ also produce a marked reduction in surface tension of a variety of organic liquids(75). It is apparent from the examples cited that the choice of the proper solubilizing group is of paramount importance in developing maximum surface activity. Zisman and co-workers have reported on the surface tension depressions in solvents such as *n*-hexadecane, hexachlorobutadiene, and trichlorodiphenyl, by a number of esters of fluorocarbon carboxylic acids, including $C_3F_7COOC_2H_5$, $C_7F_{15}COOC_4H_7$(79).

Some very interesting effects have been reported in which certain fluorocarbon surfactants produce a surface barrier at an organic surface, which tends to prevent the migration of the organic material through the interface. Ahlbrecht, *et al.* have reviewed the effect of such fluorocarbon surfactants inhibiting the evaporation of volatile hydrocarbons such as gasoline, heptane, etc.(78). Guenthner and Vietor have reviewed the influence of organic active surfactants in decreasing the migration of plasticizers or other migratory components from such systems as plasticized vinyl polymers, asphalt, adhesives, etc.(75).

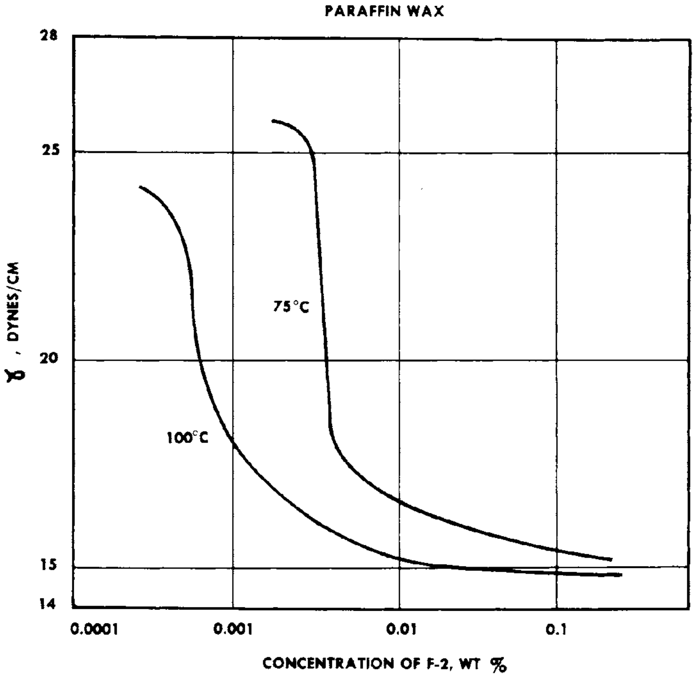


FIG. 48. Effect of temperature on surface tension depression of a fluorocarbon surfactant.

In many arid regions of the world hydrocarbon surfactants such as cetyl alcohol have been used to reduce the evaporation of water from outdoor ponds. In this case it appears that the nonvolatile surface active compound forms a "skin" of molecular dimensions on the liquid surface and thereby interferes with the escape of the volatile water molecules.

Ahlbrecht, Blake, and Bryce were able to produce very marked reductions in the evaporation of gasoline, through the use of the fluorocarbon surfactant, $C_7F_{15}CONHC_3H_6N(CH_3)_3^+I^-$(F-2). Fig. 50 shows the effect

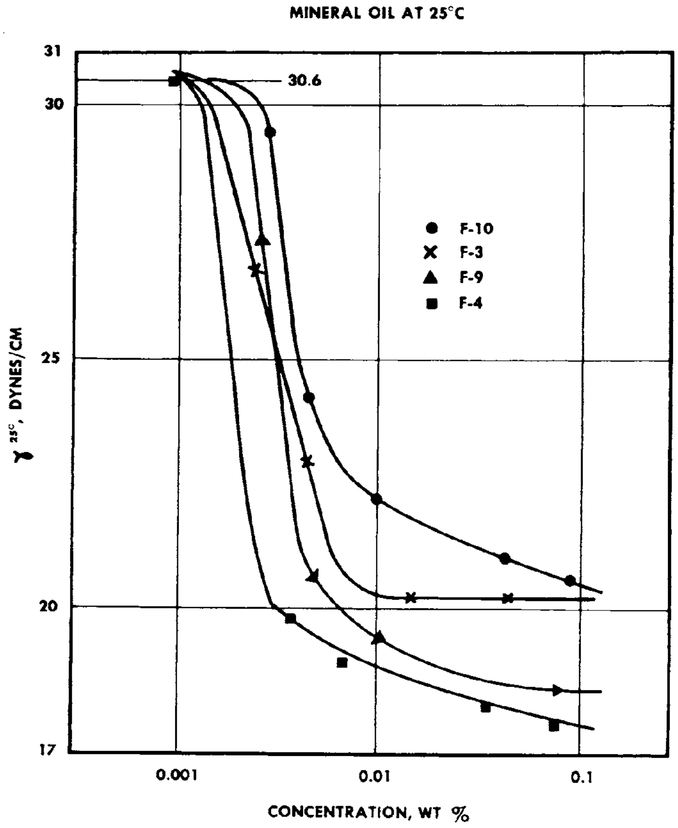


FIG. 49. Surface activity of fluorocarbon surfactants in mineral oil.

of 0.003% by weight of this compound in inhibiting the evaporation of gasoline. In the example shown, the beakers were placed in an open hood with a constant air flow. When the per cent of liquid remaining is plotted against time, results such as those in Fig. 50 were obtained. It will be noted that the rate of evaporation is quite rapid initially in both cases; however, there is an abrupt decrease in evaporation rate for the F-2 treated gasoline. The initial rapid evaporation in this case is probably due to the time

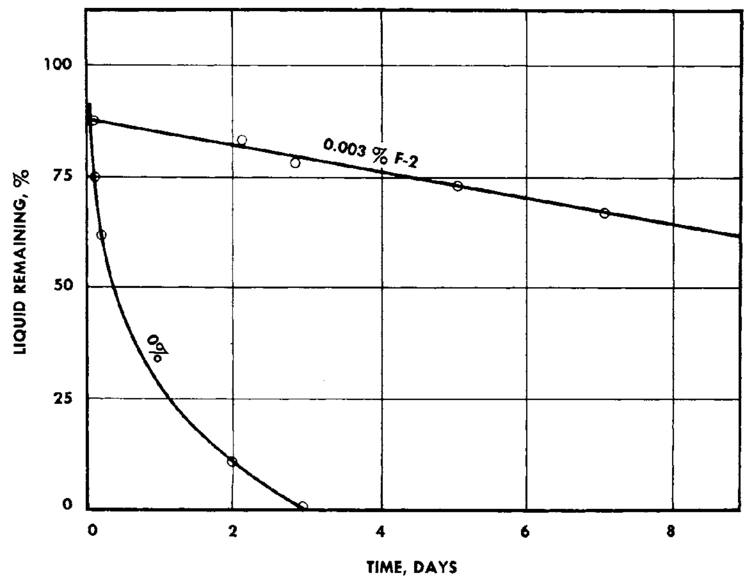


FIG. 50. Inhibition of rate of evaporation of gasoline by a fluorocarbon surfactant.

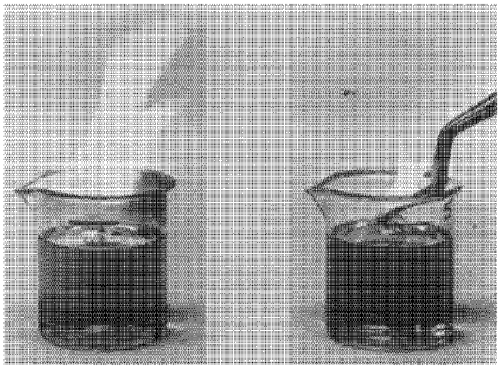


FIG. 51. Decrease in flammability of gasoline containing 0.003 wt % of a fluorocarbon surfactant.

required to form the barrier film on the surface which requires migration of the F-2 molecules to the surface and then orientation to form a close-packed film. When the treated gasoline is stirred, there is a sudden increase in evaporation rate, which appears in the case of F-2 to require 10–15 min to return to the inhibited condition. It has been found that F-2 forms a condensed or solid film on the surface of the gasoline, which accounts for the length of time required to form initially and to restore itself when stirred(80). From a practical point of view, compounds which would form liquid films would be much more rapid in forming at the surface. The much lower rate of evaporation is graphically illustrated in Fig. 51, where untreated gasoline is shown to ignite rapidly when a match is placed over the beaker, while a treated gasoline cannot be ignited.

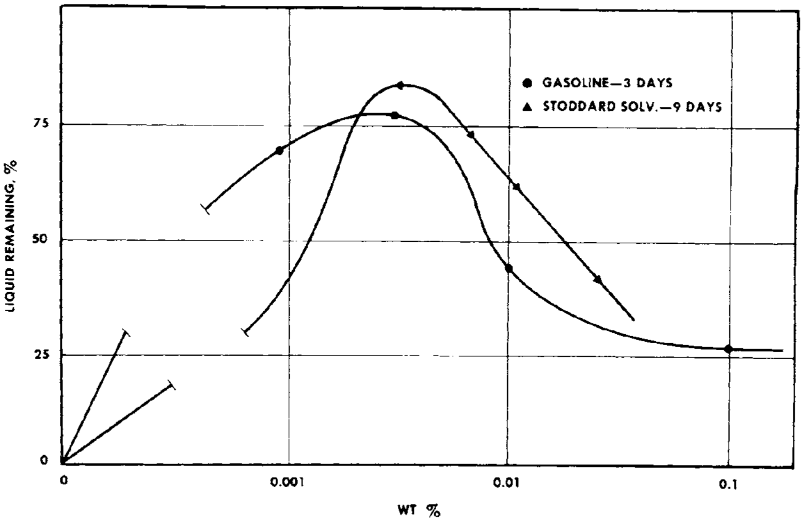


Fig. 52. Effect of concentration of surfactant F-2 on inhibiting action of rate of evaporation.

As might be expected, any given compound has a rather specific effect on a given hydrocarbon solvent. Through the proper choice of solubilizing group, however, compounds can be made which will have a pronounced effect on a wide variety of organic solvents.

The relationship between concentration of F-2 in the gasoline and effectiveness in inhibiting evaporation is shown in Fig. 52. It is interesting to note that there is an optimum concentration of about 0.003% by weight.

This presumably is the concentration required to completely saturate the surface layer; higher concentrations in the gasoline tend to produce adsorbed layers at the surface that are too thick and which contain many fissures and cracks.

Small-scale field tests using the F-2 compound at about 0.005% in regular gasoline showed a reduction in evaporation losses of about 30% in a simulated refinery storage tank. With the development of specific surfactants, especially one giving a liquid surface film and having a lower cost, it is anticipated that these fluorocarbon surfactants should find many applications where volatile organic solvents are involved.

A second type of "barrier" effect has been observed in a variety of thermoplastic systems(75). Asphalt, for example, consists of a rather broad range of compounds ranging from relatively low boiling light oils to nonvolatile resins. It has been reported that when a fluorocarbon surfactant is dissolved in the hot asphalt, there is a marked reduction in the migration of the light oils to the surface of the asphalt. Tests have shown that, while the asphalt as initially poured does not show a contact angle to a hydrocarbon mineral oil, on standing for a few hours the surface becomes quite oil repellent. In this case the fluorocarbon surfactant would appear to be soluble in the light oils, which as they migrate to the surface of the asphalt, carry the surfactants with them. At the surface the fluorocarbon tails orient themselves and eventually form a condensed film with the CF_3 terminal groups extending outward. When this condition occurs, the light oils can no longer migrate to the surface. Not only are they blocked by the heavy fluorocarbon molecules, but they are not able to wet the low energy $—CF_3$ surface.

Several graphic examples of this have been shown. When treated and untreated asphalts are formed into sheets, and these sheets placed in a weatherometer, it has been noted that the asphalt containing the fluorocarbon surfactant resists the weathering action of the water and ultraviolet light much more effectively than the untreated asphalt.

Another example involves the use of asphalt in producing paper to asphalt laminates. If a fluorocarbon surfactant has been added to the asphalt at a concentration of 100 to 300 ppm, and this asphalt is used to prepare a laminate with a white paper, it has been observed that the migration and wicking of the light oils by the white paper is reduced to essentially zero even when the laminate is heated. A control using an untreated asphalt, on the other hand, shows severe wicking of the light oils by the white paper so that it is changed to a yellowish-brown color in only a few hours at room temperature.

Other examples of this second type of barrier which have been studied include plasticized vinyl polymers and plasticized adhesives.

F. ADSORPTION ON SOLIDS

Surface active fluorocarbon compounds can be either physically or chemically adsorbed on a solid surface. In either case the resulting films exhibit both oil and water repellency, lower coefficients of friction, low adhesive qualities, and other effects associated with low energy films(70). Figure 53 shows the contact angles of water, methylene iodide, and hexadecane on a film of $C_8F_{17}SO_2NHCH_2COOH$ which has been chemisorbed on aluminum. These contact angles in the range of 110°–160° are among the highest ever measured. The decyl bromide quaternary of the sulfonamide amine, $[C_8F_{17}SO_2NH(C_3H_6)N(CH_3)_2C_{10}H_{21}]^+Br^-$, for example, shows strong adsorption on glass and silica surfaces.

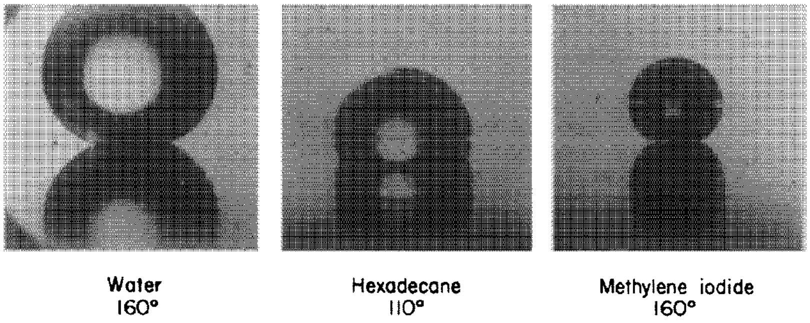


FIG. 53. Advancing contact angles for various liquids on an aluminum surface coated with a fluorocarbon surfactant.

Using the Shell 4-Ball Wear Test(81), it has been shown that fluorocarbon derivatives adsorbed on metal surfaces show improvements in both point B (load vs wear) and also wear vs time values. It has been reported that fluorocarbon extreme pressure additives show efficiencies comparable to the best additives known(75,82).

Again, when the compound $C_8F_{17}SO_2NC_2H_5C_2H_4OP(OH)_2$ is adsorbed on aluminum, there is an 80% reduction in the adhesion of ice compared to untreated aluminum(75).

The combined properties of adsorption and stability of the fluorocarbon surfactants makes it possible for them to function effectively as corrosion inhibitors in a wide variety of systems and conditions(75). These compounds can function both as solution inhibitors and as protective surface films. For example, the compound $C_8F_{17}SO_2N(C_2H_5)C_2H_4OP(OH)_2$, adsorbed on aluminum as a protective film, completely inhibits the surface attack of 3% hydrochloric acid. When the same compound is used as a solution inhibitor at 200 ppm, there is over a 75% reduction in the rate of reaction with dilute sodium hydroxide. Copper, brass, steel, etc., can also be protected by the use of specific fluorocarbon derivatives. The surface active compounds can also modify the reaction of metals with brightening or etching compositions. As an example, the addition of 25–50 ppm of $C_8F_{17}SO_3K$ to a conventional aluminum bright dip solution improves the brightening action of the solution as well as increasing the rate.

G. MICROBIOCIDAL ACTIVITY

Fluorocarbon compounds have shown some interesting microbiocidals activity. As might be expected, the fluorocarbon portion of the molecule is physiologically inert; but by varying the functional group, some compounds have been shown to have unusually high activity as bactericides and algaecides. Therefore, the application of such compounds in insecticide, herbicides, or fungicides can be viewed from either of two desirable approaches. Those which are inert may be used as wetting agents or dispersants in microbiocides where biological activity of the surfactant would be an undesirable side effect; or those with activity can serve in a dual role as a surfactant-biocide.

H. INTERFACIAL TENSIONS

Fluorocarbon surfactants are also effective in reducing the interfacial tensions between aqueous and organic media(76). For example, the interfacial tension between concentrated hydrochloric acid and an organic ester, tributyl aconitate, was lowered from 12.6 to 1.8 dynes per cm by the addition of 0.5% $C_8F_{17}SO_3K$ to the acid phase. Figure 54 shows the effect of

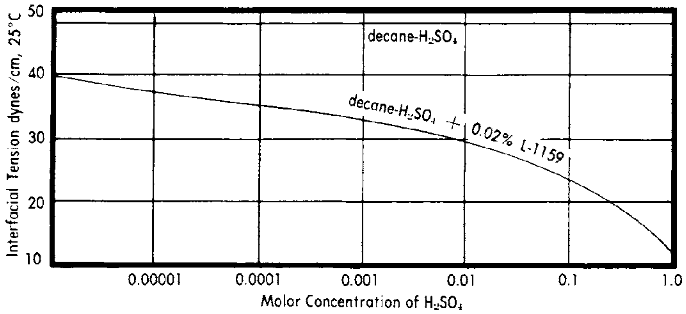


FIG. 54. Effect of $C_8F_{17}SO_3K$ on the interfacial tension between *n*-decane and dilute sulfuric acid.

$C_8F_{17}SO_3K$ in the interfacial tensions between *n*-decane and dilute solutions of sulfuric acid of various strengths. This fact, combined with their chemical stability, enables these materials to be used to increase the rates of reaction in a heterogeneous system where a hydrocarbon type surfactant would be destroyed. In the case of the hydrolysis of ethyl malonate by refluxing in concentrated hydrochloric acid, the ester was completely hydrolyzed in three hours when $C_2F_5C_6F_{10}SO_3H$ or its salts were added. The control, on the other hand, was incomplete after eight hours. In another example, the addition of $C_2F_5C_6F_{10}SO_3H$ or its salts reduced the time by one-third in the sulfonation of benzene with sulfuric acid(75).

I. COMMERCIAL ASPECTS

1. *Chromium Plating*

Hama, Frederick, Millage, and Brown have reported results on the suppression of chromic acid mist and spray from chromium plating baths through the use of a fluorocarbon surface active agent(83). Chromium-plating is in world-wide use for decorative and engineering purposes, due to the superlative properties of chromium plate from the standpoint of tarnish and atmospheric corrosion resistance, its outstanding resistance to heat and wear, and its low coefficient of friction.

The baths for the electrodeposition of chromium consist of rather concentrated solutions of chromic acid (about 150 to 400 gm per liter of CrO_3) and contain in addition definite small percentages of sulfate, fluoride, or fluorosilicate anions. Insoluble lead or lead alloy anodes are used. High current densities are required for the deposition of chromium, about 140 to 280 amp per sq ft. The cathode efficiencies vary from 10 to 20%; and therefore, a large volume of hydrogen is liberated during plating; and since insoluble anodes are used, oxygen is evolved at the anodes.

These gases are evolved during electrolysis in the form of multitudinous bubbles of higher surface tension bursting violently at the surface of the concentrated chromic acid solution and throwing out a fine mist of chromic acid droplets. The spray and mist resulting from this bubble bursting is of considerable volume and requires large volume and efficient local exhaust ventilation since chromic acid is both corrosive and toxic. These exhaust systems are expensive and have high maintenance costs due to coating and corroding of the hoods, ducts, and fans.

The loss of chromic acid through mist and spray amounts to approximately 30% of the total chromic acid used. In order to avoid outdoor air pollution, the chromic acid mist must be removed by expensive air-washing equipment.

Various attempts have been made to form "blankets" on the surface of the bath to trap the mist and spray, including layers of various hydrocarbon oils, organics, foaming agents, such as cresylic acid, etc.; but because they are rather rapidly oxidized, requiring frequent or continuous additions, and because they also contaminate the bath as well as the plated part, such materials have never been used extensively. Floating objects, such as paraffin-dipped corks, plastic bubbles, etc. have also been tried; but although they help to reduce the mist losses, they are confined to "hard" chromium plating, where thick deposits of plate are formed and the parts to be plated are left in the bath for several hours. However, in decorative or bright chromium plating, the plating time is usually around 5 min or less, and it is too difficult to keep the bead layer properly distributed over the surface with the very frequent entry and removal of plating racks.

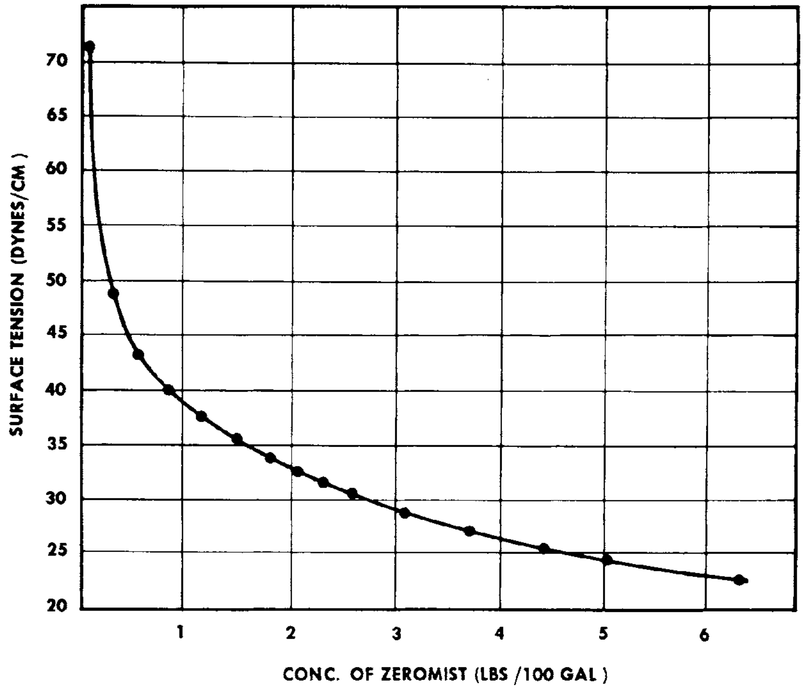


FIG. 55. Variation of surface tension of a chromium plating solution with concentration of a commercial product "zeromist", which contains a fluorocarbon surfactant.

Even though plastic bubbles or beads have proved useful in "hard" chromium plating, no decrease in ventilation is recommended for such systems.

Silverman and Thompson reported on the use of certain hydrocarbon surfactants to lower the surface tension of the chromic acid solution and hence form a foam blanket on the surface of the plating bath; however, the surface active agents used were not sufficiently stable to the powerful anodic oxidation during plating to be of practical value(84).

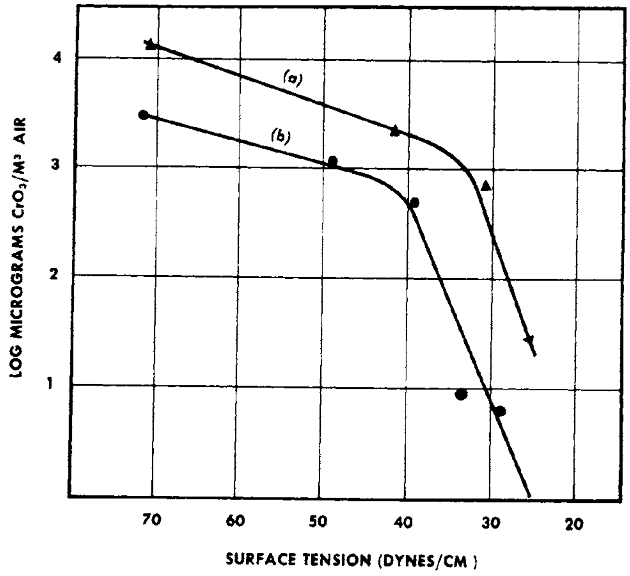


FIG. 56. Effect of fluorocarbon surface active agent concentration on the reduction of chromic acid mist in a discharge duct. (*a*) Plating bath at 55°C; (*b*) plating bath at 38°C.

It was found that a surface active agent with a fluorocarbon "tail" was not only stable to boiling concentrated chromic acid and the highest oxidizing conditions at the anodes during chromium plating, but that they were very effective in reducing the surface tension of the plating solution with the formation of a relatively stable foam blanket(83). Figure 55 shows the variation in surface tension of a chromium plating solution with concentration of a proprietary product, "Zeromist"(85) in which the fluorocarbon surfactant is an eight-carbon sulfonic acid salt. Figure 56 shows the relationship between surface tension of the bath and the micrograms of CrO_3 in the exhaust gases from a plating bath. Figure 57 shows the effect of temperature on the micrograms of CrO_3 in the exhaust gases for three surface tension conditions, namely, 50 dynes per cm, 35 dynes per cm, and 25 dynes per cm.

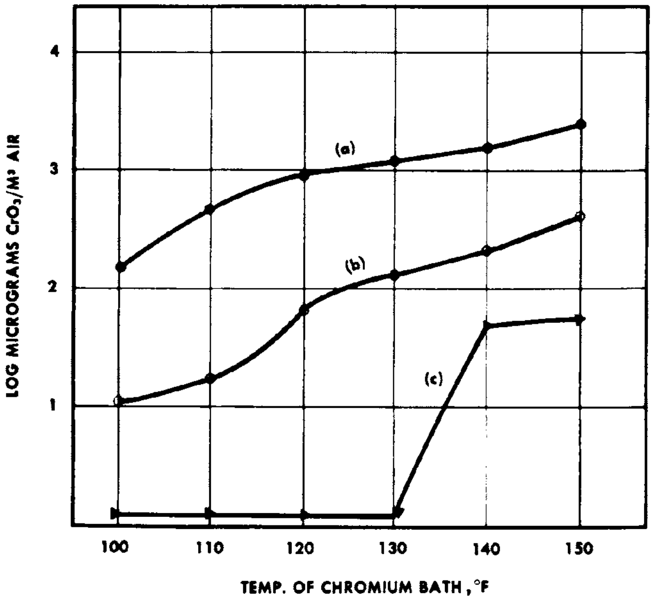


Fig. 57. Effect of bath temperature on the concentration of chromic acid mist in the discharge duct. (*a*) Surface tension of bath is 50 dynes per cm; (*b*) 35 dynes per cm; (*c*) 25 dynes per cm.

Figure 58 shows the foam blanket present on a chromium plating tank, just after the plated work has been removed.

The fluorocarbon surface active agent is lost from the bath only by "drag-out" (in the film of solution on plated articles withdrawn from the bath); hence, only infrequent additions are needed to maintain the desired concentration so that essentially no loss of chromic acid occurs through misting or spraying. In an actual plating plant test where the tank ventilation was turned off, maximum concentrations of CrO_3 of 0.01–0.02 mg per m^3 of air were observed; whereas the maximum allowable levels are 0.1 mg CrO_3 per m^3 of air.

In summary, the use of the fluorocarbon surface active agent has solved several problems associated with chromium plating; namely, (1) reduced toxicity hazards to personnel; (2) eliminated expensive special ventilation facilities; (3) reduced losses of chromic acid through elimination of mist

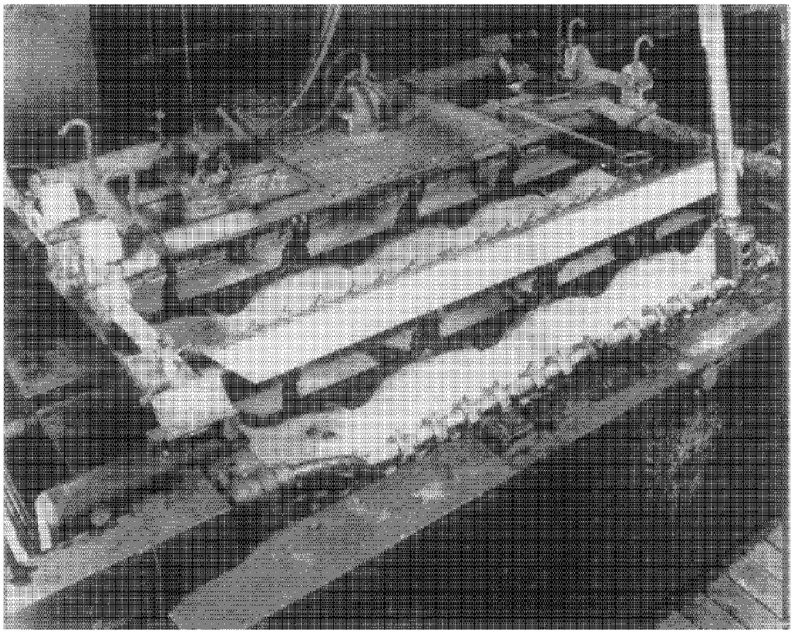


FIG. 58. A chromium plating bath showing the foam blanket produced by a fluorocarbon surfactant immediately after removal of plated objects. (Courtesy Udylite Corp.)

and spray and also reductions even in "drag-out" due to better run-off of plating solution from the plated part; and (4) reduction in heat losses from plant area due to reduction of ventilation requirement.

2. *Levelling of Liquid Floor Waxes*(86)

The floor being the integral part of the interior of a building which must withstand most of the wear, it is logical that it should receive special attention and care. The application of waxes to wooden floors for the purpose of preservation dates back many centuries. Many floors are covered with a soft pliable material, such as linoleum, rubber tile, congoleum, and vinyl plastics, which are cemented or otherwise fixed to the original flooring. Quite often a layer of felt is laid between the underflooring and the floor covering to act as a cushion. The application of wax to such flooring materials retards the penetration of air and moisture, thereby increasing the life of the cushioning material, as well as preventing deterioration of the surface by abrasion from grit.

There are two main types of floor waxes, solid or paste waxes and liquid waxes. Carnauba wax, from the leaves of the carnauba palm, has been the mainstay of wax preparation, and remains today the base for the best paste wax formulas. Paste waxes are used for wood floors.

The emulsion or water-type liquid waxes, also called "self-polishing," enjoy the largest sales volume in the floor wax field and are used extensively for polishing such floor coverings as asphalt tile, vinyl plastic, linoleum, etc. Many of the original products contained carnauba wax or other luster-producing hard waxes, emulsifiers, and a considerable proportion of shellac, a typical formula being:

Sodium soap	1.3 parts
Carnauba wax	8.75 parts
Shellac	2.45 parts
Sodium borate	1.05 parts
Water	86.45 parts

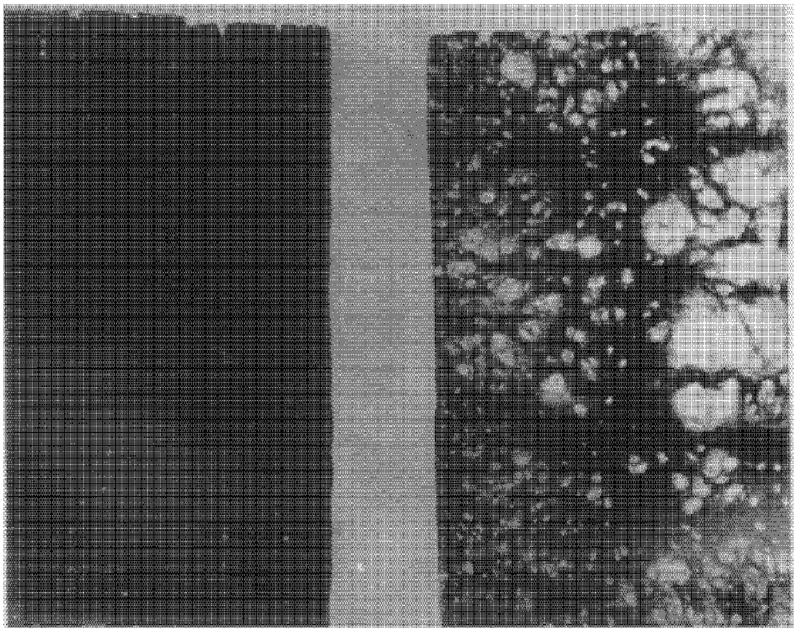


FIG. 59. Effect of fluorocarbon surfactant on leveling of a liquid emulsion type floor wax. The sample on the right contained no fluorocarbon surfactant; whereas the one on the left contained 0.01% of a fluorocarbon surfactant.

Shellac is less expensive than carnauba and is used to aid the levelling properties of the polish, give a quick luster, and increase slip resistance(86).

In recent years several developments have brought about the replacement of a considerable portion of both the carnauba and the shellac by a variety of synthetic resins in emulsion form. Included are the polyethylenes, the polystyrenes, the polyacrylates, and the polyvinylacetates. These synthetic resins are, for the most part, less expensive, less subject to quality variance, and in many cases more resistant to yellowing and aging, especially in comparison to shellac.

The use of these synthetic resins, however, introduced new problems in getting self-polishing, high gloss properties, and yet maintain high water resistance. The fluorocarbon surfactants have solved this problem in a unique fashion. They are many times more effective than hydrocarbon surfactants in producing good "leveling" of the emulsion wax, being effective at concentrations of 0.005–0.010% by weight. Because of their effectiveness at these extremely low concentrations, they do not interfere with the development of good water resistance of the wax film.

Figure 59 shows the improvement in leveling (or gloss) of a commercial aqueous emulsion type floor wax through the addition of 0.01% of the fluorocarbon surfactant, FC-134(76). In addition, the effect of concentration of the surfactant is also shown.

A typical formula is as follows(87a,b):

Polystyrene emulsion (40% solids)	85 parts
Wax emulsion	5–10 parts
Alkali soluble resin	5–10 parts
Plasticizer	2 parts
Fluorocarbon surfactant (FC-128) (1% solution)	1 part

3. *Emulsion Polymerization*

As emulsifiers the fluorocarbon surfactants have been used in a variety of vinyl type polymerizations(88,89).

X. Textiles

A. Surface Treatments for Fibers

As has been reviewed earlier, the low surface energy of a fluorocarbon surface is one of the unique features of this class of compounds. The work of Zisman and co-workers has shown that the least wettable surface is one with a close packed arrangement of oriented fluorocarbon tails with their CF_3^- groups extended outward(18). To wet such a surface Zisman has determined that a liquid with a surface tension of 6 dynes per cm or less would be required. On the other hand, a highly oriented closely-packed hydrocarbon surface would be wet by liquids having surface tensions less than 23 dynes per cm. Zisman prepared the close packed structures which he studied under ideal conditions using the Langmuir film balance to first orient and pack the molecules together. The close packed films were then transferred to scrupulously clean glass or platinum surfaces.

It will be the purpose of the following sections to review the application of fluorocarbon materials to textiles, paper, and leather fibers and to show how these modified surfaces affect the properties of textile fabrics, paper, and leather.

B. INTRODUCTION TO FIBERS

In general, any material capable of existing in a fiber form may be used to prepare a woven fabric. These materials range quite broadly in origin and in chemical and physical nature. Table XXXVII lists a number of these including those which occur naturally and those which are man-made(90,p.18).

TABLE XXXVII

CLASSIFICATION OF TEXTILE FIBERS

Natural fibers	
Vegetable:	cotton, jute, linen
Animal:	wool, silk, hair
Mineral:	asbestos
Man-made	
Regenerated cellulosics:	rayon, acetate
Synthetic organic:	polyvinyls—"Saran" polyamides—"Nylon" polyesters—"Dacron" polyacrylics—"Orlon" "Acrilan" "Dynel"
Mineral:	glass
Metallic:	fine wire filaments
Fluorocarbon:	polytetrafluoroethylene

Although tremendous strides have been made in introducing man-made fibers in the past twenty years, cotton and wool continue to be the fibers most used for clothing and general household uses. The modified cellulosics, such as rayon and acetate, have attained large usage and are often competitive with cotton in price range as well as end use.

The synthetic organic fibers have become a very important factor in those countries of the world with well developed chemical industries.

With the exception of metals, all fiber-producing materials are polymeric in character, and have predominantly linear structures which are oriented in the longitudinal direction of the fiber. The properties of these fibrous materials differ widely and in consequence are used for many purposes including wearing apparel, furniture, upholstery, bedding, tents and awnings, filter cloths, reinforced plastic, and many laminated constructions, etc.

The first man-made fibers to achieve commercial significance were the modified cellulosics or rayons. Nylon, the first true synthetic, was developed during the 1930's, and the rapid acceptance of this fiber around 1940 was based on its use in filament form to replace the expensive and quality variable silk fiber in women's hosiery.

In many aspects these synthetic organic fibers, such as nylon, differ quite markedly from their naturally occurring counterparts, such as cotton and wool. The synthetic fibers have rather smooth surfaces and well defined cross-sections, whereas a fiber such as cotton or wool has an extremely rough surface. Unlike the naturally occurring fibers of vegetable or animal origin or the modified cellulosics, the synthetic fibers have relatively low absorptive power for water vapor. A comparison of the average moisture regain values of various fibers is shown in Table XXXVIII. While high moisture absorption is desirable from the comfort

TABLE XXXVIII

AVERAGE MOISTURE REGAIN OF VARIOUS FIBERS(90, p.965)

Fiber	Approximate average regain at 65% r.h. and room temperature (Wt %)
Wool	16
Viscose rayon	13
Mercerized cotton	11
Cotton and linen	8
Acetate	6
Nylon	4
Orlon acrylic	1–2
Dacron polyester	0.4

standpoint when in contact with the body, this property also results in a definite tendency to wrinkle and also to lose desired creases put in by pressing. The synthetic fibers have found much favor, either alone or in blends with cotton, rayon, or wool, because they are relatively resistant to wrinkling both when dry or wet.

During the past ten years, a number of treatments have been developed which have markedly increased the ability of cotton to resist wrinkling. These treatments involve reactive resin systems such as substituted melamine-formaldehyde, triazine derivatives, or specifically catalyzed formaldehyde or vinyl sulfones.

It will be obvious that textiles and textile fibers are rather complex structures, both from a chemical as well as physical point of view. Especially is this true of the fiber surfaces which may range from being relatively smooth to being extremely rough. These surfaces may also be modified in numerous ways by chemical action, such as mercerization or bleaching or through the application of a vast array of dyestuffs, resins, and textile auxiliaries.

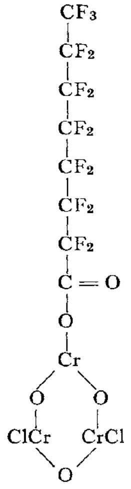
A number of hydrocarbon-type materials have been used for many years to impart water repellency to such items as tent and rainwear fabrics. Earlier formulations contained a variety of animal, vegetable, and mineral waxes and aluminum soaps of stearic acid. In more recent years, a number of synthetic products have been developed including pyridinium derivatives of stearic acid, and a variety of silicone resins and oils. These products give excellent water repellent treatments, but—as might be expected—offer no repellency to oils and greases of any origin.

During the past five years, textile finishes based on fluorocarbons have been developed and introduced commercially. Besides water repellency, these new finishes impart a high degree of oil repellency and consequently increase the resistance to most staining and soiling conditions(91).

C. Chemical Nature of Fluorocarbon Finishes

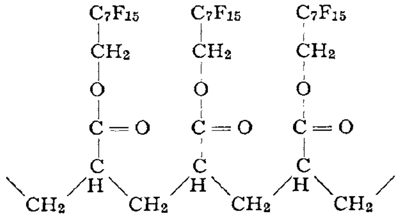
Previous considerations have established the point that in order to produce an oil and water repellent surface on a fiber, it is necessary to have the surface covered at least in part by fluorocarbon groups which are oriented so as to have their terminal —CF_3 groups exposed.

This has been accomplished in several ways. One approach is to use a fluorocarbon compound with a functional group which will be either adsorbed strongly to the surface or which will undergo a chemical reaction with the fiber surface. Examples of this type of bonding would be chromium complex of various acids containing long chain fluorocarbon groups. A typical structure of this type may be illustrated, viz.,



Such chromium complexes are easily soluble and stable in solvents such as isopropyl alcohol. The alcohol solutions may be diluted with water, but the aqueous solution react slowly at room temperature to hydrolyze off the chlorine as HCl. If this reaction occurs on the surface of a fiber, such as cotton, wool, or nylon, the chromium will complex with carboxyl, hydroxyl, or amino groups, thus anchoring the fluorocarbon tail to the fiber surface. As might be expected, such "complex" linkages are relatively unstable and hence are not generally durable to normal laundering or drycleaning processes(92,93).

Another approach has been to attach the fluorocarbon groups to conventional hydrocarbon polymer structure, the polymer backbone being chosen so as to provide good adhesion to the substrate and also be of sufficiently high molecular weight to be insoluble in both aqueous laundry systems and drycleaning solvents. Thus, 1, 1-dihydrooctforyl alcohol, $C_7F_{15}CH_2OH$, may be reacted with acrylic acid to form the acrylate monomer, which when polymerized, forms the polyacrylate,



Depending on the molecular weight and other characteristics of the polymer, it may either be dissolved in a suitable solvent or dispersed as an aqueous emulsion with either nonionic, cationic, or anionic agents.

D. Methods for Measuring Repellency

At this point it would be well to consider some of the standard methods which have been used to determine the degree of oil and water repellency on the treated fabric. A flat, clean surface such as glass or metal which has been treated with a repellent material may be classified according to its degree of oil or water repellency by measuring the contact angle of a drop of oil or water on the surface. On the other hand, a complex structure such as a woven textile fabric presents an entirely different type of surface.

1. *Water Repellency*

Several methods are available for measuring the water repellency or water resistance of a treated fabric. The procedure most commonly used in the United States is the standard spray test as developed by the American Association of Textile Chemists and Colorists, and designated as Test Method 22-1961(94,p.152). The procedure is illustrated in Fig. 60. The piece of fabric is stretched over a darning hoop which is then placed on an inclined plane at a 45° angle to the horizontal. Approximately 250 ml of water are then sprayed on the surface through a standard nozzle. After tapping the fabric, the amount of water clinging to or remaining on the surface is determined by visual observation using a standard chart. Corresponding water repellency ratings are given on this basis; namely, if no water is retained, a reading of 100, whereas with increasing amounts of water on the surface, values decrease 90, 80, 70, 50, and 0. This method is the most convenient to utilize and gives a simpler expression of the actual surface repellency.

A second method, which is used particularly in the evaluation of rainwear fabrics, is the Rain Test (Test Method 35-1961, see 94, page 143). In this case, water is forced through a nozzle at a given hydrostatic head so as to impinge on a piece of fabric. The fabric is backed by a weighed blotter, which is reweighed after the test to determine the amount of water which has leaked through the specimen during the test.

A third method is the Bundesmann Test(95) which is used predominantly in Europe. In this case, the fabric is placed in a holder; and while water is applied through a spray nozzle at a considerable height and pressure, the fabric is rubbed from the reverse side by a smooth rotating object. The water resistance values are expressed in terms of water adsorbed by the fabric and also the amount of water actually transmitted by the fabric.

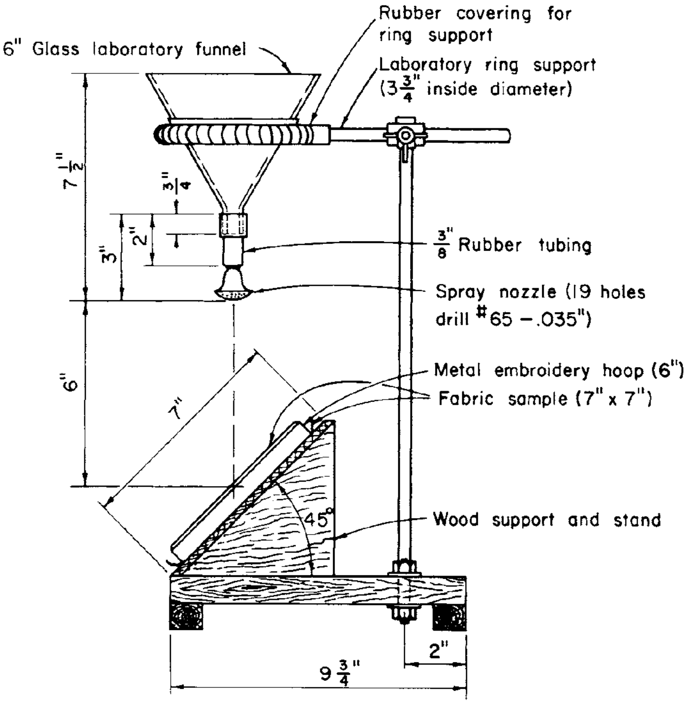


FIG. 60. Standard test apparatus for measuring spray rating of a treated fabric.

2. *Oil Repellency*

Oil repellent treatments were unknown prior to the use of the fluorocarbon finishes. The simplest and most reliable method developed to date is that utilizing mixtures of white mineral oil and heptane(96,97). A rating scale has been devised so as to give repellency values for oily materials which are comparable on a repellency basis with those of the A.A.T.C.C. Spray Test described above. This test method is based on the different penetrating properties of two miscible hydrocarbon liquids, a white mineral oil and normal heptane. Mixtures of these two liquids are miscible in all proportions and exhibit greater wetting power as the amount of *n*-heptane in the mixture is increased. As might be expected, the surface tension values for the mixtures are relatively linear with respect to the composition.

Table XXXIX gives the oil repellency rating assigned to each of the eleven test oils, which range in composition from pure mineral oil by

TABLE XXXIX

COMPOSITION OF LIQUID MIXTURES FOR THE STANDARD OIL REPELLENCY TEST

Oil Rating	Per cent by volume at 20°C		Surface tension (dynes per cm)	Viscosity (cs)	Specific gravity
	Mineral Oil[a]	n-Heptane[b]			
150	0	100	20.0	0.534	0.679
140	10	90	20.5	0.668	0.701
130	20	80	21.2	0.862	0.722
120	30	70	21.9	1.15	0.741
110	40	60	22.8	1.60	0.761
100	50	50	23.8	3.31	0.780
90	60	40	24.9	3.63	0.799
80	70	30	26.3	6.16	0.817
70	80	20	28.1	11.7	0.840
60	90	10	30.4	26.6	0.860
50	100	0	32.8	78.6	0.880
0	(no holdout to mineral oil)				

[a] "Nujol" (Plough, Inc.) Saybolt viscosity 360/390 at 100°F; Specific gravity 0.880/.900 at 60°F.

[b] Heptane (Matheson, Coleman & Bell) b.p. 98–99°C.

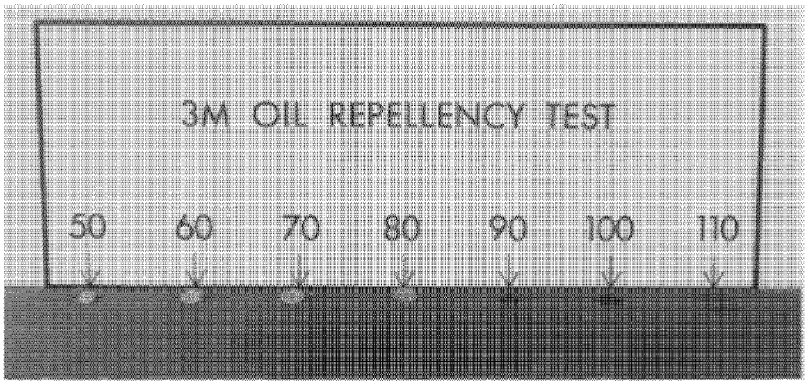


FIG. 61. Oil repellency test, showing fabric with an oil rating of 80.

ten per cent increments to pure heptane. It will be noted that on reading up the table from oil ratings of 50 to 150, the test oils exhibit a gradual lowering of surface tensions, decreasing specific gravities, and decreasing viscosities. It is believed that the controlling variables in the wettability characteristics of these, and other liquids, are surface tension and vapor pressure.

To measure oil repellency of a treated fabric using the above test oils, drops of these oils are gently placed on the fabric and allowed to stand undisturbed for three minutes. The number corresponding to that mixture containing the highest percentage of heptane, which does not penetrate or wet the fabric, is considered the oil repellency rating of the fabric. Figure 61 shows the behavior of a series of the test oils on a treated fabric. In the case illustrated the fabric would be given an 80 rating. The distinction between failure or resistance of successive mixtures is usually quite sharp and presents no problem in determining the break point.

3. *Stain Resistance*

The oil repellency values determined by this test have been found to correlate with practical resistance to common animal, vegetable, or mineral oil stains. When typical oily stains are dropped on treated fabrics and subsequently blotted off, those fabrics with an oil repellency rating

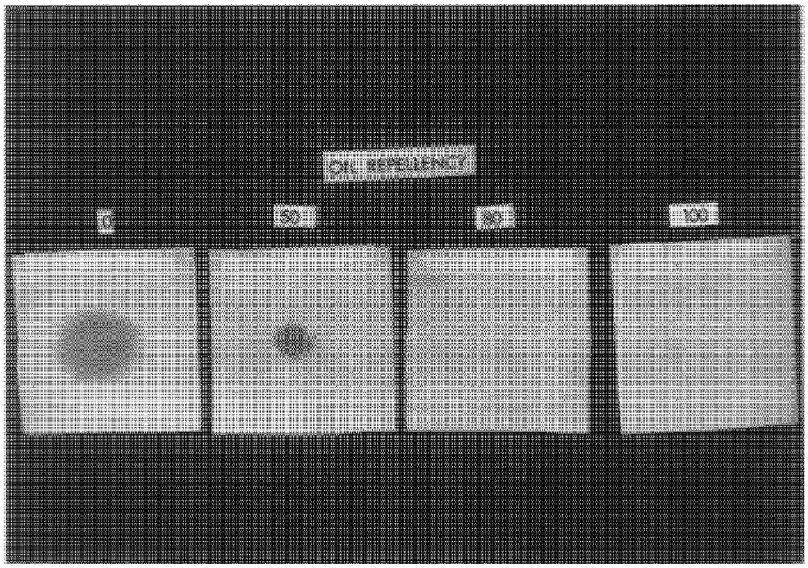


FIG. 62. Oil repellency and its relation to stain resistance.

of 50–70 will exhibit only fair resistance to staining; those fabrics with an oil repellency rating of 80–90 will show good resistance to staining; and those with oil ratings of 100 and up will give excellent resistance. In Fig. 62 the correlation between oil repellency rating of the fabric, and stain resistance is clearly demonstrated when one cubic centimeter of dyed mineral oil is dropped on the fabric sample and blotted off.

E. Factors Affecting Behavior of Fluorocarbon Derivatives on Fabrics

1. *Chemical Structure*

The chain length of the fluorocarbon group is an important factor in determining the repellency properties imparted to a surface. In close-packed structures, such as those studied by Zisman and co-workers(16,18), the CF_3 terminal group is the prime factor. On the other hand, on rough and irregular fiber surfaces where close packing is not achieved, the length of the fluorocarbon chain governs the degree of orientation and hence the effectiveness of the surface treatment.

TABLE XL

Repellency Properties of a Cotton Print Cloth Which Is Treated with a Series of Substituted Polyacrylates

Substituent group	Oil repellency	Water repellency
CF_3-	0	50
C_2F_5-	60	70
C_3F_7-	90	70
$C_5F_{11}-$	100	70
$C_7F_{15}-$	120	70
$C_9F_{19}-$	130	80
$HCF_2(CF_2)_7-$	50	80
$Cl(CF_2CFCl)_3CF_2-$	0	80

In Table XL are shown data for the oil and water repellency on an 80 × 80 cotton print cloth for a series of polyacrylates with differing chain lengths of the fluorocarbon group, the monomers for which have the general structure, $R_fCH_2OOCCH{=}CH_2$. In each case the materials were applied at an add-on of 1% by weight to the fabric. As can be seen, the oil repellency increases progressively from 0 to 130 as the fluorocarbon chain increases from $-CF_3$ to $-C_9F_{19}$. On the other hand, the water repellency values vary only from 50–80. This relative insensitivity as far as water repellency is concerned is believed to be due to the influence of the ester linkage in this polymer system. The data shown in Fig. 63 shows a similar relationship for a homologous series based on a modified acrylate polymer. In this case there is a marked increase in oil repellency with chain length from —C_4F_9 to —C_8F_{17}, while the water repellency values are relatively constant, though this time in the 90–100 range. The modification is of such a nature as to block the influence of the ester linkage, and hence the higher water repellency values. Included in Table XL are data for fluorocarbon groups in which one of the terminal fluorine atoms has been replaced by a hydrogen or a chlorine atom. There is a marked decrease in the oil repellency indicating a considerably higher surface energy. These results are in line with the observation of Zisman and co-workers as reviewed in the section on Characteristic Properties.

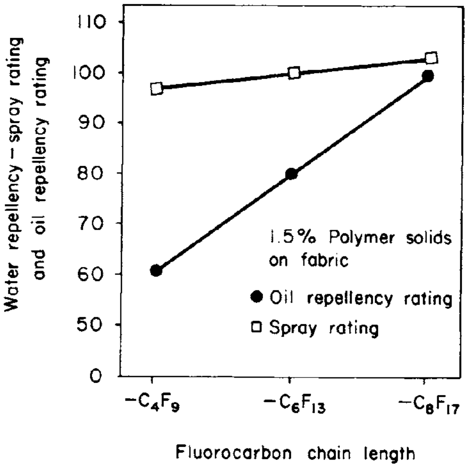


FIG. 63. Water and oil repellency ratings as a function of chain length for a homologous series.

From a practical point of view, perhaps the most important factor in determining the behavior of a fluorocarbon group on a fiber surface is the chemical grouping by which the fluorocarbon group is attached to the fiber. Among the properties desired on fabrics treated with fluorocarbon-type finishes are oil repellency, water repellency, durability of these properties to both drycleaning and laundering, dry soil resistance, and abrasion resistance. Depending on the end use, some of the above properties will be more important than others. It is apparent, therefore, that the most versatile means of varying these properties is to incorporate the fluorocarbon groups into specific molecules which, when applied to a fabric, will give the balance of properties desired.

From earlier results, it has been shown that a prime requisite for good oil repellency is a fluorocarbon group of at least four carbon atoms, terminated by a CF_3— group. If such a fluorocarbon group is complexed with a chromium compound, one set of properties will result; on the other hand, when this same fluorocarbon group is attached to a polyacrylate structure, different levels of performance will result. It is indeed true that it is possible with many types of functional groups to have very low oil and water repellencies and poor durability even though long chain fluorocarbon groups are attached to the fiber.

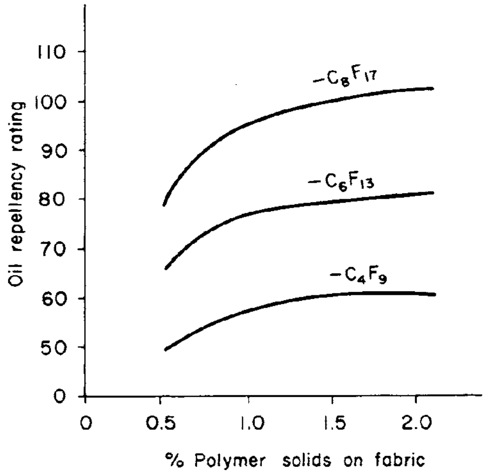


FIG. 64. Oil repellency vs solids on fabric for a series of polymers containing varying fluorocarbon groups of different chain lengths.

The portion of the molecule to which the fluorocarbon group is affixed, namely, the bonding group, provides the physical or chemical bonding between these groups and the substrate. As indicated above, the type and nature of this bonding group can influence most of the properties associated with the fluorocarbon group. In particular, however, it determines the durability of the attachment to cleaning processes, abrasive action, and exposure to heat or sunlight. In addition, this bonding group will also largely determine the ease of and degree of orientation and the density of packing of the fluorocarbon group on the surface. The proper orientation of the fluorocarbon groups on the surface is most important in attaining the maximum repellency values with the minimum number of fluorocarbon groups per unit area.

A bonding group which is hydrophilic can offset the inherent water repellent properties of the oriented fluorocarbon group with resulting lower than expected water repellency ratings. Similarly, a bonding group which has either a dry or tacky surface will very strongly affect the ability of the treated surface to resist the adhesion of dry soil particles.

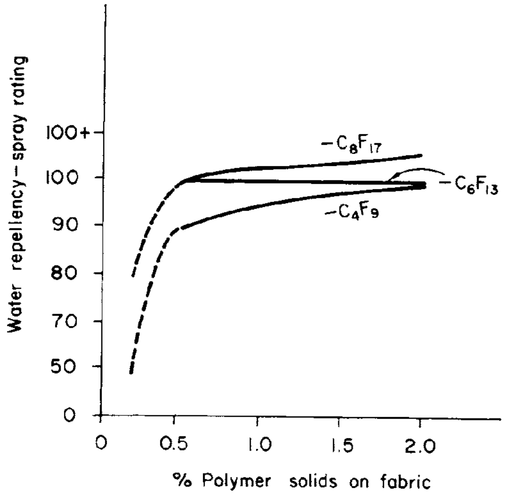


FIG. 65. Water repellency vs solids on fabric for a series of polymers containing varying fluorocarbon groups of different chain lengths.

In Figs. 64 and 65 the oil and water repellency for a homologous series of fluorocarbon groups which are attached to the same modified acrylate polymer bonding group are shown. The maximum oil and water repellency ratings are reached at approximately 1.0–1.5% of solids on the fabric. It is apparent that no matter how much material is applied to the surface, the oil repellency obtained with a C_4F_9— group will never reach that of a C_8F_{17}— group.

F. COMMERCIAL PRODUCTS

The results shown in Figs. 66 and 67 are those for a commercially available fluorocarbon textile finish designated commercially as Textile Chemical FC-208(98). As noted, both oil repellency and spray ratings rise steeply as the concentration increases from 0.2 to 1.0% by weight solids on the fabric. Above the 1.0% level, the curves flatten out and give essentially constant repellency values.

Fluorocarbon type finishes can be applied from aqueous or organic solvent systems. They may be in the form of true solutions or may be

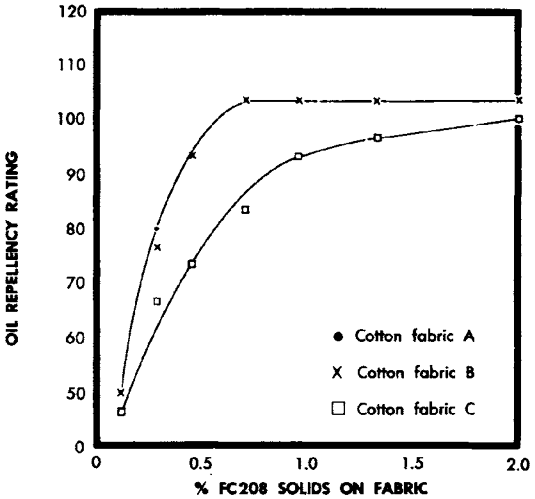


FIG. 66. Oil repellency vs FC-208 solids for different cotton fabrics.

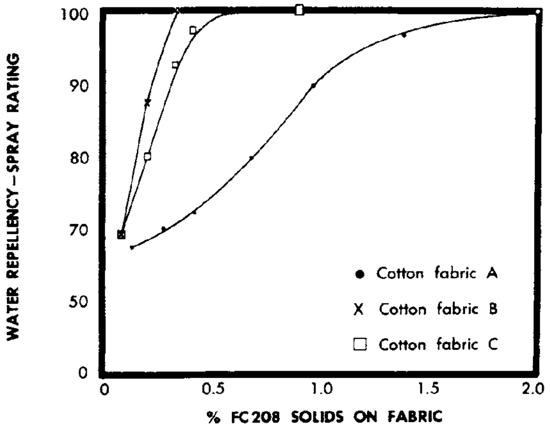


FIG. 67. Water repellency vs FC-208 solids for different cotton fabrics.

emulsified or dispersed in a finely divided state in a liquid medium. In general, the use of an organic solvent will present fewer problems in obtaining maximum performance from a given species. The solvent gives a more uniform treating medium and also permits better wetting and penetration of the fiber surface without excessive swelling of the fiber and hence, disruption of the fiber surface. Such solvent applications are practical under limited circumstances but for the most part, however, are not consistent with standard textile mill practices. A commercial product of this type is available and is known as Textile Chemical FC-310(98). It is used primarily in the finishing of high grade upholstery and decorator fabrics.

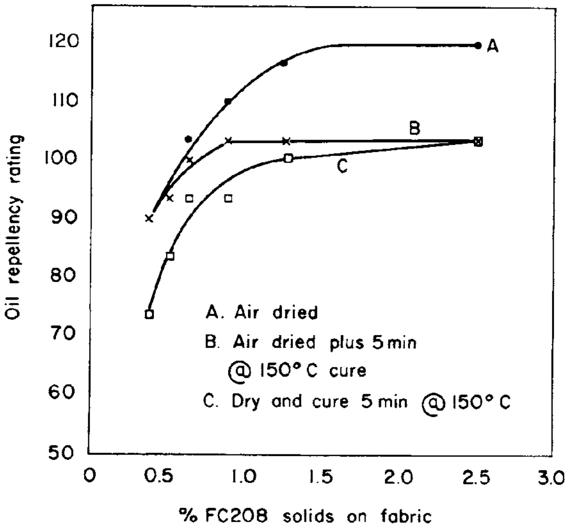


FIG. 68. Effect of varying drying and curing conditions on oil repellency of a treated cotton fabric.

Aqueous systems, such as Textile Chemical FC-208, are used in general textile mill applications to a wide variety of apparel, upholstery, automotive, and industrial fabrics. Such aqueous emulsions, of course owe their stability to a variety of emulsifying agents. Depending on the choice of emulsifier, they may be anionic, nonionic, or cationic. It will be readily seen that the ultimate performance attainable on a given fabric will depend very greatly on the relationship of the charges on the fluorocarbon finish emulsion and the charges associated with the fiber, as well as other electrolytes present. For example, anionic latices perform best on wool fabrics at pH values less than the isoelectric point of wool (pH = 4.2), whereas cationic and nonionic latices are most suitable for cotton fabrics generally and for wool fabrics at pH values above their isoelectric point.

When a fluorocarbon finish is applied to a fabric, some drying or curing of the treated fabric is required. In general, this procedure has a marked effect on the degree of repellency obtained. In Figs. 68 and 69 typical data are shown when samples of an 80 × 80 cotton print cloth are treated with FC-208. The higher oil repellency ratings at all concentrations occur when the fabric is air dried, i.e., Curve A. The lowest oil repellency ratings result when the fabric is rapidly dried for five minutes at 150°C. Intermediate values result when the fabric is air dried and subsequently oven cured. These results are best understood in terms of maximum orientation of the fluorocarbon groups on the surface. A slow drying process allows the most time for migration of the fluorocarbon groups to the surface and their proper orientation on the surface; hence, the lowest surface energy and consequently highest degree of oil repellency.

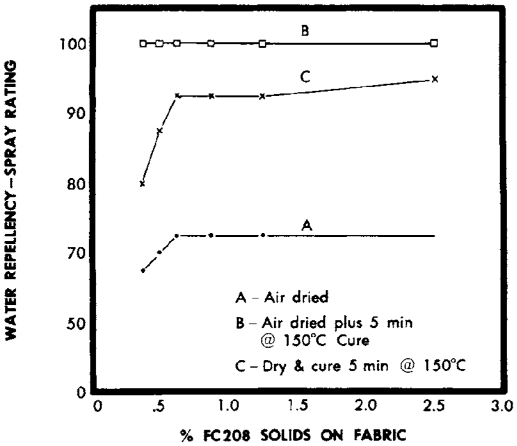


FIG. 69. Effect of varying drying and curing conditions on water repellency of a treated cotton fabric.

As can be seen from Fig. 69, however, the maximum water repellency is attained when the drying process is most complete, i.e., air drying plus 5 min at 150°C. This is undoubtedly due to the need to remove as completely as possible from the cotton fiber the absorbed water associated with the treating medium.

Some interesting effects have been observed through the use of fluorocarbon type textile treatments in combination with a number of crosslinking textile treating resins and other products such as water repellents. For example, the data in Fig. 70 shows that there is a definite

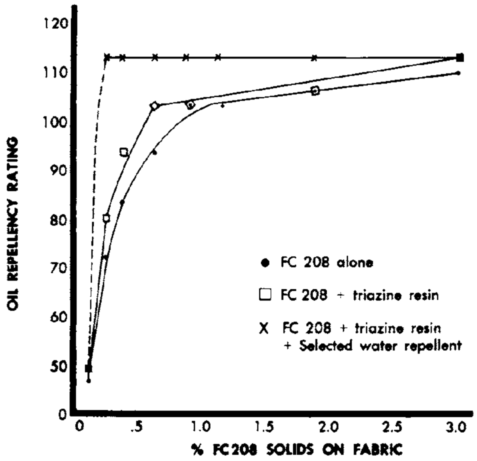


FIG. 70. The effect of a triazine resin and a hydrocarbon water repellent on oil repellency of a cotton fabric treated with a commercial fluorocarbon resin FC-208.

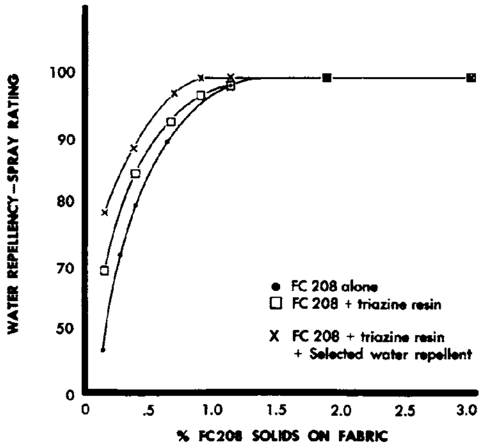


FIG. 71. The effect of a triazine resin and a hydrocarbon water repellent on water repellency of a cotton fabric treated with a commercial fluorocarbon resin FC-208.

improvement in the repellency rating for oil when the FC-208 is used in combination with both a triazine resin and also a commercial hydrocarbon type water repellent as a treatment for cotton. Figure 71 shows that, although to a lesser degree, there is also an improvement in the spray rating for water repellency in the presence of selected reactive type resins and hydrocarbon water repellents. It would appear from these results that the presence of such auxiliary materials makes it easier for the fluorocarbon groups to migrate to and orient on the surface of the cotton fiber. As stated earlier, the cotton fiber possesses an extremely rough surface with a very large surface area.

From a practical point of view, there are many factors which may influence the ability of a fluorocarbon textile finish to produce optimum oil or water repellency ratings on a fabric. In general, these factors may be correlated with the ability of the material to migrate to the surface and subsequently orient so as to give maximum exposure of fluorocarbon groups on the surface. In consequence of this, extreme care must be taken in being sure that the fabric is properly prepared so as to be free of deleterious contaminants. It is also important that other materials which are used in conjunction with the fluorocarbon finish be of such a nature as not to interfere with the proper orientation of the fluorocarbon groups on the surface(97).

G. Stain Resistance of Fluorocarbon Treated Fabrics

Fabrics which have been properly treated with a fluorocarbon type textile finish will show good stain resistance to both water and oil based stains. Thus, for the first time it is practical to have resistance to all common staining materials including aqueous systems such as ink, fruit juices, coffee, soft drinks, and also a wide variety of greasy or oily materials of either vegetable, animal, or mineral origin. Generally speaking, water and oil repellency ratings of 90 or more give excellent resistance to aqueous or oil-borne stains. Ratings of 70 to 80 give fair stain resistance, while ratings of 50 or less have poor or no resistance. When attached to the surface of a fabric through the proper linkage, a fluorocarbon group will impart a significant resistance to the adhesion of dry soil particles. Particularly noteworthy are such materials as the chromium complexes of fluorocarbon carboxylic acids(92,93). A piece of fabric when treated with such a material at a level of 0.5% by weight of solids, will resist soiling by a synthetic soil mixture such as described by Salsbury and co-workers(99).

H. Durability to Cleaning Processes

Fabrics may be cleaned by several procedures. They may be laundered in water containing a variety of soaps and detergents at temperatures up to the boiling point. They may be "drycleaned" by immersion in solvents such as perchloroethylene or a hydrocarbon fraction known as "Stoddard solvent". Today "drycleaning" processes almost universally use a 3% detergent charge with the above solvents. There are also a variety of special cleaning methods such as spot cleaning with special solvents or shampooing with foamed detergent solutions.

There are a number of factors which affect the ability of a given repellent finish, whether hydrocarbon or fluorocarbon, to retain its repellency after laundering or drycleaning. Naturally, the finish must not be soluble in the cleaning medium; it must also be either bonded chemically to the fiber or else be sufficiently insoluble and be so tightly attached that it will not be removed during the exposure to the cleaning solution. It is also obvious that in normal cleaning processes there is considerable abrasive action which the finish must withstand. A cotton fiber will swell in hot water so as to increase its cross-sectional area by as much as 50% with a corresponding increase in surface area.

It has become generally accepted that a "durable" finish is one that is not significantly removed from the fiber surface at least through several cleanings.

TABLE XLI

COMMERCIAL DRYCLEANING RESISTANCE OF VARIOUS WATER REPELLENTS

	Water repellency—spray rating			
Water repellent	Initial	After 1 dry cleaning	After 5 dry cleanings[a]	After 5 dry cleanings[b]
A	100	0	0	0
B	100	50−	0	0
C	100	50−	0	0
Fluorochemical (FC-208)	100	90	80	80

[a] Perchloroethylene—3% soap; rinse contains < 0.5% soap.
[b] Stoddard solvent—2% soap; no rinse.

The durable hydrocarbon or silicone type water repellents appear to have a strong affinity for the soaps and detergents used in standard drycleaning procedures. Because of this "poisoning" action by the soaps, the water repellency of the fabric disappears almost completely even after one cleaning. Typical data is included in Table XLI, which emphasizes the rapid fall-off in water repellency on the hydrocarbon pyridinium and substituted melamine types, as well as a commercial silicone-type repellent. By contrast, the fluorocarbon type retains a water repellency rating of 80 even after five commercial type drycleanings.

TABLE XLII

Durability of Water Repellents

	Initial			After 5 drycleanings[a]			After 5 launderings[b]	
Water repellent	Oil	Spray	Bund.[c]	Oil	Spray	Bund.[c]	Oil	Spray
Fluorochemical (FC-208) (0.3–0.5% solids on fabrics)	100	100	7 cc	70	70	14 cc	50	90
Pyridinium water repellent (2–3% on fabric)	0	100	5 cc	0	0	210 cc	0	100
Fluorochemical and pyridinium (concentration as above)	70	100	24 cc	50	0	314 cc	50	100
"Quarpel" (2% fluorochemical solids, 2% pyridinium solids on fabric)	100	100	2 cc	100	90	3 cc	90	100

[a] Commercial drycleaning. Perchloroethylene, 4% soap charge, < 0.5% soap in rinse.

[b] Home automatic washer—moderate settings; "Tide" soap.

[c] Bundesmann test—cc penetration through fabric.

The U.S. Army Quartermaster Corps have developed a water repellent finish which has been shown to possess outstanding durability(100). This finish, known as "Quarpel", is based on a combination of certain fluorocarbon type resins, such as FC-208, with the standard commercially available pyridinium durable water repellents. In actual practice the treating bath is made up so that 2% on solids basis of both the fluorocarbon resin and the pyridinium compound are put on the fabric. As the data in Table XLII shows, not only are initial properties excellent; but even using the extremely rigorous Bundesmann test, both oil and water repellencies are retained at essentially the initial levels after both laundering and drycleaning.

I. Commercial Treating Procedures

At this point it will be in order to review some of the technology which is specific to a commercially available fluorocarbon finish, which has found widespread usage in treatment of many textile fabrics. The product chosen has been designated as Textile Chemical FC-208 which is an aqueous dispersion of a resin(98).

FC-208 is recommended for treating cottons, cotton-synthetic blends, rayons, and rayon-synthetic blends in "Wash-and-Wear" resin systems to produce oil and water repellency which is durable to both laundering and drycleaning. FC-208 is also used, in conjunction with selected resins and auxiliaries, on most upholstery and drapery fabrics.

Specific formulas for treating typical fabrics of the types mentioned above vary widely depending on reactive resin used and the various other textile auxiliaries required to give the desired fabric finish. A typical treating formula for a typical apparel cotton fabric might be as follows:

Component	Wt%*
Reactive cross-linking resin	10.0
Catalyst	2.0
Auxiliary Water Repellent	1-5
Nonionic wetting agent	0.05
FC-208 fluorocarbon finish	2.5

*For all materials, weights per cent are based on the commodity basis.

As a commercial commodity, FC-208 is supplied as an essentially nonionic aqueous emulsion with a minimum of 28% active solids. Assuming that in treating the cotton fabric, the wet pick-up is 70%, then the actual fluorocarbon resin solids deposited would be 0.5% by weight. It should be noted that because of the highly surface active nature of the fluorocarbon groups, the fluorocarbon properties, i.e., oil and water repellency, are developed on the surface even in a complex mixture such as the formula given above. For optimum results, treating, drying, and curing conditions should be such as to maximize the opportunity for migration to and orientation on the surface.

Reactive cross-linking resins or chemicals which are commonly used include a variety of types including urea-formaldehyde, substituted and unsubstituted melamine derivatives plus formaldehyde, triazine and triazone resins, and specially catalyzed formaldehyde and vinyl sulfone solutions. As a general rule, proprietary hydrocarbon type water repellents can be incorporated in treating formulas and in some cases actually enhance the development of oil and water repellency. Many variations in resins, catalysts, softeners, water repellents, wetting agents, etc. are possible; but for optimum results on a specific fabric, it is essential that each combination be tested under specific conditions.

On woolens, worsteds, and wool-synthetic blends, FC-208 is used without resins and will develop oil and water repellency which withstands repeated drycleaning.

In many applications, there is a definite reduction in the retention of airborne dry household type soils. DeMarco, McQuade, and Kennedy have made air permeability measurements which show essentially no change in the porosity of the fabric(100), hence, staining materials may be forced into the fabric. Oil-borne stains, which normally are particularly troublesome, can be readily removed with a hydrocarbon solvent without leaving the typical solvent "ring" since the solvent will not wick along the fibers.

FC-208 is also used in many applications to provide functional properties to fabrics. For example, on automotive upholstery fabrics, in addition to oil and water repellency, it makes possible the removal of in-plant stains without leaving a solvent ring. For the same reason, it is used on glass fabrics and filament knit nylon fabrics used in the auto industry. The fluorocarbon textile finishes are unique in that they do not adsorb conventional hydrocarbon detergents. From a practical point of view, this means that these finishes are resistant not only to pure water but to aqueous solutions containing a wide variety of wetting agents. As a consequence, retention of both water and oil repellency after drycleaning in the presence of soap and detergents is much better than for hydrocarbon or oleophibic type water repellents(96).

In the normal finishing process for textile fabrics, the best procedure involves the immersion of the fabric in the treating bath, followed by passage through squeeze rolls where a controlled amount of the treating solution remains in the fabric. The wet fabric is then introduced into an oven which removes the water and also permits the reactive resins to cure and the fluorocarbon groups to migrate to and orient on the fiber surface(98).

In general, at the textile mill the use of aqueous treating baths is preferred for almost any type of fabric. This would include all types of fibers including cotton, rayon, synthetics, and wool. For application on manufactured items, such as furniture or wearing apparel, it is possible to achieve excellent results using solvent solutions of fluorocarbon derivatives. Such treatments may be effective either by immersion in the solvent system and removal of excess solution, or by direct application of a desired quantity of solution by a spraying procedure.

Although the use of fluorocarbon type textile finishes is new and much progress has been made in a relatively short time, it is anticipated that many new developments will be forthcoming in the near future.

XI. Leather

Leather is animal hide or skin converted by chemical treatment and processing, known as tanning, to a stable and nonputrifiable state. The objectives of tanning are to render hides and skins resistant to decomposition or bacterial decay, particularly when wet; to achieve specified physical properties in the tanned hides or skin, such as tensile strength, flexibility, resilience, abrasion resistance; and to impart to the leather chemical properties such as nonsolubility in water at relatively high temperatures. Untanned hides or skin substance become soluble in water at approximately 140°F, while many types of leather remain stable at the boiling point of water. All leather possesses a common physical property, water vapor permeability, which is attributable to the internal capillary action of the fibers composing leather and to surface evaporation. The principal hides or skins used in the manufacture of leather are cattle hides, calfskin, goat and kidskins, sheep and lambskins, pigskins, and a variety of other animal skins. These hides are obtained as major raw materials from meat consumption.

The uses for leather are quite wide and varied. The principal consumption is in shoes of all types and varieties. Other major uses include garment leathers, handbags, and brief cases, luggage, upholstery, harnesses, and saddles, and for certain industrial uses such as belts, seals.

A. LEATHER PROCESSING

Excellent reviews of leather and leather processing have been written in recent years(101,102).

1. *Preparation of Hides*

Upon removal of the skin from the animal at the slaughter house, it is necessary to preserve it from decomposition through the application of coarse salt. In most cases where the transportation costs are not too high, the skins are kept in a wet condition. Where overseas shipments are involved, it is necessary to dry the skin to remove excess moisture. Upon arrival at the tannery, the hides are washed and soaked to remove the excess salt and other foreign contaminants. They are then subjected to a variety of operations involving removal of excess flesh, dehairing, and liming. The liming operation results in the loosening of the hair in the hair follicles. After the liming, the hair is scraped off and the excess lime is removed by washing. The leather is subjected to enzymatic action, called bating, to remove the degradation products of the epidermal system. The leather may then be subjected to a pickling process, which consists of bringing the stock to a condition of equilibrium in a bath of sulfuric acid and other salts.

2. *Tanning*

Following the preparations reviewed above, the hides and skins are now ready for the chemical conversion to leather, which process is known as tanning. The oldest system of tanning relied on the action of vegetable extracts containing tannin or tannic acid, but modern technology has developed a large range of chemical agents and processes to produce leather.

Vegetable tanning is still used for certain specific types of leather, particularly those used in shoe soles and upholstery leathers. In general, the vegetable tanning processes involve soaking the leather for long periods of time in solutions of a variety of vegetable or synthetic tanning agents, including extracts of Quebracho, oak, and commercially synthesized products based on phenols and naphthalenes in various combinations with formaldehyde.

Although a variety of mineral tannages have been developed, including those based on aluminum compounds and zirconium compounds, the most important systems are based on chromium. In fact, the chrome tanning process produces the largest volume of leather today. The advantages of the chrome tanned procedure, as contrasted to the vegetable or synthetic tannins, are that the leather may be made by the chrome process in matters of hours and days instead of weeks by vegetable tanning. Also much greater precision is afforded the tanner in controlling the nature of his output. Chrome tanned leather has exceptionally good wearing properties, high tensile strength, and resistance to chemical agents, and will also stand high temperatures in a wet or dry condition without detrimental effect.

The usual procedure in preparing a chrome tan liquor is to mix together equal parts of sodium bichromate and concentrated sulfuric acid, after dissolving the bichromate in a small quantity of water. A reducing agent, such as glucose, is then added resulting in the formation of the bright green chromic ion. This tanning solution is then reacted with the leather in a large rotating drum, the solution being added gradually until complete penetration of the leather has been effected.

3. *Dyeing and Fat-Liquoring*

Following the tanning operation, the leather is dyed to the desired shade and then "fat-liquored" through the addition of emulsions of oils and tallows to produce the necessary lubricity and softness. In the case of chrome tanned leather, the dyeing and fat liquoring are also carried out in the tanning drum.

After removal from the drum, the leather is then prepared for drying either by "pasting" to a metal panel or by "toggling" or stretching the leather on a frame. In either case the drying process involves a circulating air oven at a temperature of about 65°C.

4. *Finishing*

The leather is then finished. For side leathers this may involve sanding to remove imperfections followed by the application of a variety of resin finishes to give lustre and abrasion resistance. For suede leathers this involves buffing to restore nap.

5. *Application of Fluorocarbon Derivatives*

The most suitable fluorocarbon products to date for application to leather are the chromium complexes of the fluorocarbon carboxylic acids, in which the fluorocarbon group is at least 6 carbon atoms in length(103). These compounds are similar to those reviewed earlier. A commercially available product of this type is Leather Chemical FC-146, produced by Minnesota Mining and Manufacturing Company(104). It consists of a 30% solids solution of the fluorocarbon type chromium complex dissolved in isopropyl alcohol.

FC-146 is applied in the tanning drum either in place of or in conjunction with the normal "fat liquors" after the dyeing and coloring operations. When added with water to the wet hides, the FC-146 is absorbed by or exhausted into the leather while the drum is rotated. Subsequent hydrolytic reactions of the chromium complex with the protein matter in the leather effect a permanent linkage of the fluorocarbon groups to the leather fibers. In order to achieve optimum properties and to minimize interference with the proper orientation of the fluorocarbon groups at the surface of the leather fiber, it is necessary to evaluate the other auxiliary chemicals used including dyestuffs, fat liquors, etc. In general, the process is quite simple and easy to control. After removal from the drum, the leather is dried and finished in the same manner described earlier(104).

B. PROPERTIES OF FLUOROCARBON TREATED LEATHER

1. *Durable Lubricity and Softness*

The leather fiber is one of the most durable and chemically resistant known. This is especially true of the chromium tanned leather fiber. In order to produce a soft and pliable piece of leather, it is necessary to lubricate these fibers; otherwise they form a hard compact mass. Until recent years the only available lubricants were a variety of mineral, vegetable, or animal type oils and greases in a modified or unmodified state, generally given the term, "fat liquors". Many of the shortcomings of leather are due to these oils and greases. In the first place these "fat liquors" are generally drummed into the leather in the form of aqueous emulsions and are not in any way chemically bonded. Furthermore, in order to get better penetration and better absorption by the leather fibers, many of these "fat liquors" are modified chemically to introduce sulfonate or sulfate groups. Such groups, of course, are water receptive and may cause the leather to absorb and retain water. Mechanical working of the wet leather will cause the oils to be displaced from the wetted area; and hence, upon drying, the leather will harden and crack. In recent years commercial products based on chromium complexes of stearic and myristic acid and a variety of silicone derivatives have been used to provide more durable lubrication for leather. These products also provide resistance to water absorption.

Fluorocarbon derivatives, such as FC-146, are being used quite extensively in leather processing(103). The fluorocarbon group imparts a number of very desirable properties to the finished leather. When properly attached to the leather fiber, the fluorocarbon "tail" provides a type of lubricity which gives leather a soft, yet springy feel—or in leather language, good "roundness." This quality is important in shoes, especially in shape retention. Side leathers containing a fluorocarbon type treatment also exhibit a fine "break". "Break" refers to the nature of the creases formed in the grain when the leather is doubled over on itself with the grain side inside. A good break is indicated by fine, yet not deep, penetrating creases; conversely, a poor break shows up in the form of large, but not plentiful creases.

2. *Chemical Resistance*

Perhaps one of the most striking contributions of the fluorocarbon treatment to the leather fiber is the great improvement in resistance to chemicals. This can be most graphically represented by placing a drop of concentrated hydrochloric acid on the surface of thin strips of treated and untreated side leather. This is illustrated in Fig. 72. With untreated leather the strip folds up as indicated until it doubles back on itself with a curl angle of greater than 90°. Leather properly treated with FC-146 will show essentially no curl angle. Similarly, boiling caustic will burn completely through a piece of untreated leather, whereas the fluorocarbon treated leather will resist the attack of the hot caustic. Besides the obvious advantages of making leather much more resistant to chemicals, the fluorocarbon treated leathers are more resistant to perspiration than untreated leathers. Shoe leathers, for instance, become impregnated with perspiration, which contains a variety of acidic materials such as lactic and butyric acids. These acidic materials ultimately cause the leather to harden and crack.

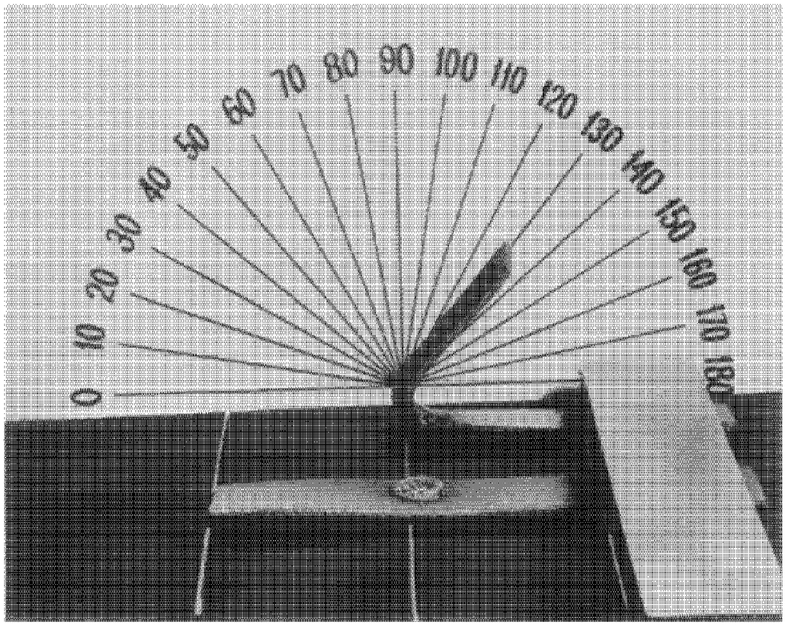


FIG. 72. Acid curl test for leather.

3. *Fungus Resistance*

The normal fat liquors used as lubricants in the leather are destroyed by many bacteria and fungi, being nutrients for these organisms. When this happens, regular leather hardens and cracks in service such as shoes. As has been mentioned earlier, the fluorocarbon derivatives are completely inert to such biological action and, hence, remain as lubricants in the leather indefinitely.

4. *Water and Oil Resistance*

The commercially available fluorocarbon derivative, FC-146, imparts a high degree of resistance to the absorption and penetration of water and also a high degree of resistance to the absorption of oils. Table XLIII shows the properties of both a pigskin suede leather and a typical cowhide

TABLE XLIII

PERFORMANCE OF FC-146 TREATED COWHIDE LEATHER VS UNTREATED

Reference	Water resistance			Oil resistance	Chemical resistance		Surface oil repellency	Water spray rating
	Flexes	% Absorbed dynamic	% Absorbed static	% Absorbed Static	Degrees curl to concentrated HCl	Effect of hot (90°C) NaOH		
FC-146 treated cowhide	10,000	17	25	28	0°	slight stain		
Untreated (regular) cowhide	100	92	90	71	130°	hole		
Fluorochemical properties imparted to Brushed Pigskin								
FC-146 Treated pigskin			47	22	0°	slight stain	70	90

side leather which have been treated with FC-146. Included for comparison is a typical regular cowhide.

5. *Rate of Drying*

Leather treated with a fluorocarbon treatment such as FC-146 resists wetting by water to a high degree. However, if immersed in water and flexed, it can be wet. As the data in Fig. 73 shows, the fluorocarbon treated leather dries much more rapidly than the untreated leather. Not only does the treated leather dry faster, but it also remains soft and pliable even after repeated wetting and drying.

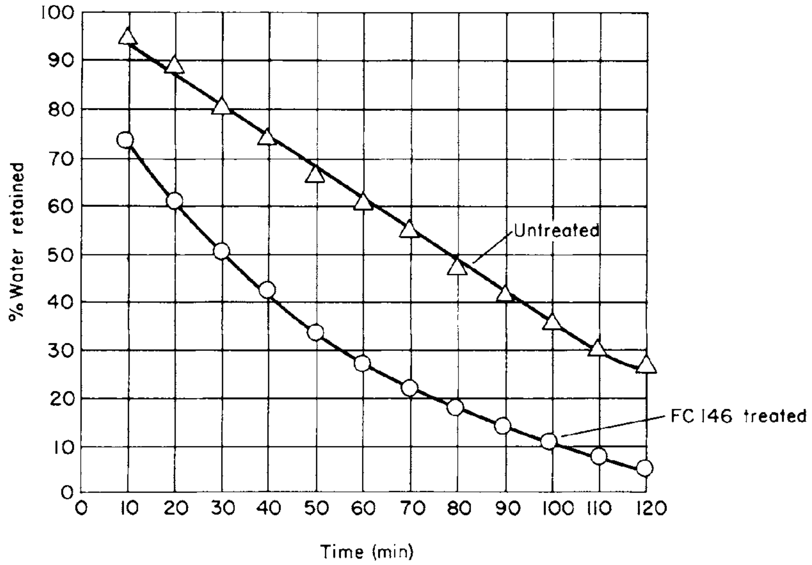


FIG. 73. Drying rate of brushed pigskin at room temperature; one sample has been treated with a fluorocarbon chromium complex, FC-146, and the other is untreated.

6. *Soil Resistance*

Particularly in the case of suede leathers, which have a rough surface and are normally rather absorbent to all types of wet or dry soils, the fluorocarbon treatments impart a high degree of resistance to soiling. They also permit the easy release of any soil which may be attached to the leather, and in addition, facilitate cleaning by normal soap and water treatment without injury to the leather, either in effect on the softness or appearance.

C. COMMERCIAL APPLICATIONS

1. *Pigskin Suedes*

A striking example of this type of application is afforded by the recently introduced sueded pigskin leather casual shoes. Pigskin leather has excellent wearing quality and produces a soft, breathable leather with good abrasion resistance; however, in the conventionally tanned state this leather is highly absorbent to water and oils. After it becomes saturated with water, it shrinks on drying and becomes rather hard. Treatment of this leather with FC-146 results in an excellent leather for casual shoes with good wearing qualities, excellent retention of softness and shape, and easy cleanability.

2. *Cowhide Side Leathers*

The illustration in Fig. 74 shows the high degree of serviceability which has been imparted to cowhide side leathers, as used in shoes, which have

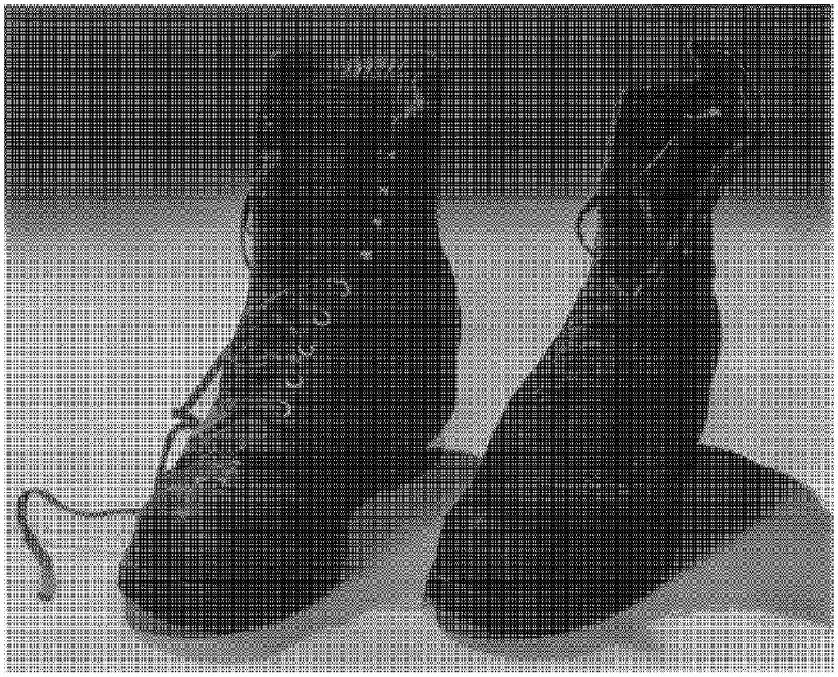


FIG. 74. A pair of matched shoes, one shoe made from leather treated with FC-146, other regular leather, after having been worn by a chemical plant operator.

been treated with a fluorocarbon product. Both shoes were worn by an operator in a chemical plant, where occasional spillages of acids or other chemicals took place. It will be noted that the chemicals have burned holes in the shoe on the left, which is made from conventional leather, while the other shoe made from leather treated with FC-146 has no holes. It will also be seen that the shoe made from treated leather has retained its shape considerably better than the other shoe.

XII. Paper

A. Introduction to Paper

Wood, in general, is made up of long fibers of cellulose $(C_6H_{10}O_5)_x$ cemented together by a gummy substance called lignin. In the preparation of paper pulp, this lignin may or may not be removed, depending on the type of paper being produced. The main processes used for producing pulp are as follows: (a) mechanical grinding of the wood to produce "groundwood"; (b) cooking with caustic soda under pressure to produce soda pulp; (c) cooking with calcium, magnesium, or ammonium bisulfite with excess sulfur dioxide to produce sulfite pulp; (d) cooking of wood chips in approximately equal parts of caustic soda and sodium sulfide to produce sulfate or Kraft pulp. Kraft, sulfite, and soda pulps are relatively free from lignin, whereas groundwood pulp contains essentially all the lignin in the original wood. In all cases the water is removed from the pulp suspension, resulting in a relatively thick felt of dried pulp.

In paper making, the pulp is dispersed by mechanical means such as a "beater", and often various sizing agents, pigments, colors, etc. are added. The beater pulp is converted to paper on a paper machine. Ordinarily, there are two machines used, the Fourdrinier and the cylinder machine(105). In either case the pulp slurry is brought in contact with a wire screen through which the water passes, the wet fibers are picked off by a wool felt, where more water is removed by squeezing. From the felt section the paper web passes over one or more heated rolls or "hot cans" where it is dried. In many cases, where a large number of "hot cans" are used, there is a separation in the dry section, where a "size press" is introduced. This size press is used for the addition of other ingredients to the paper.

The common paper fiber is both hydrophilic and oleophilic, hence, absorbs both water and oily materials very readily. It is common practice to apply to the paper such water resistant sizings as rosin, or other hydrocarbon derivatives, either in the "beater" or at the "size press".

With the development of fluorocarbon sizes it is possible to produce paper which is both hydrophobic and oleophobic. As we have seen from the previous discussion on textiles, all that is required is that the fluorocarbon compound be one containing a fluorocarbon tail, preferably with between 6 and 10 carbon atoms, which compound is capable of being solubilized or dispersed in a suitable media. While solvents can be used in experimental work, in a paper mill it is impractical to consider any other medium than water, especially if the treatment is to apply to the paper while on the paper machine. It is furthermore desirable to have the fluorocarbon material become either chemically bonded to the surface, or upon evaporation of the water, sufficiently insolubilized so that it will not be readily removed by either solvents, chemicals, or abrasive action.

B. Fluorocarbon Paper Sizes

1. *Chemical Nature*

The chromium complexes of certain fluorocarbon type carboxylic acids have been used commercially to treat paper(106,107,108). A typical product of this type is known as Paper Chemical FC-805 which has been used commercially for several years(109). These chromium complexes are soluble in various hydrocarbon alcohols and are supplied commercially as a 30% solids solution in isopropyl alcohol. The concentrated solution, which is dark green in color due to the chromium, is readily diluted to any desired concentration with water to give the proper treating level.

TABLE XLIV

Typical FC-805 Treating Solution

1.67 ml FC-805[a] Commodity
1.67 gm urea
Dilute to 100 ml with water

[a] FC-805 Commodity contains 30% active solids in isopropyl alcohol.

A typical treating solution is described in Table XLIV. Using this solution, a sheet of Kraft paper would be treated in the laboratory by dipping in the solution, then putting the sheet through a set of squeeze rolls so as to obtain a wet pick-up of 60%, and then drying. The dried paper would then have a treatment level amounting to 0.30% by weight add-on of FC-805 solids. As has been mentioned earlier, during hydrolysis of the chromium complexes there is liberation of hydrochloric acid which, of course, would have a pronounced tenderizing effect on the cellulosic fibers of the paper. In order to counteract this acid, urea is added at the level indicated.

Due to the hydrolysis process in water, the chromium complex has a limited useful shelf life after make-up. Table XLV gives minimum shelf life data for the commercial product, FC-805. It is seen that there is a rather marked increase in the rate of hydrolysis or consequent decrease in shelf life as the temperature is increased from 21°C to 55°C. There are other factors which affect the solution stability, among which are pH of the solution and the hardness of the water. The rate of hydrolysis of the chromium complex increases markedly with pH; in fact, it is too rapid for practical use at pH values in excess of 4.5. While hardness of the water below 200 ppm is not troublesome, there is a general decrease in stability of the complex with increasing hardness.

TABLE XLV

Stability of FC-805 Solutions as a Function of Temperature

Temperature (°C)	Solution life minimum (hr)
21	48
38	8
55	4

Aqueous solutions of FC-805 have low surface tensions, generally in the neighborhood of 20 dynes per cm. In consequence, there is a strong tendency to foam, especially when agitated or pumped as in the case of a typical paper mill size press. This foaming tendency can be controlled by the use of certain specific antifoaming agents(109).

2. *Influence of Chain Length*

From the data plotted on Fig. 75, there is a marked increase in oil resistance as the chain length of the fluorocarbon acid is increased. In this case the oil repellency is measured by standard test which makes use of the penetration power of turpentine. This test is a very severe measure of oil resistance(110). The results show that whereas the chromium complexes of $C_7F_{15}COOH$, $C_8F_{17}COOH$, and $C_9F_{19}COOH$ (when applied to paper at 0.5% by weight) resist the penetration of turpentine for 3 min, there is an abrupt decrease in penetration resistance at chain lengths less than eight carbons. For example, the complex of $C_6F_{13}COOH$ requires a solids concentration of 2.0% to reach a 3-min resistance; whereas the $C_5F_{11}COOH$

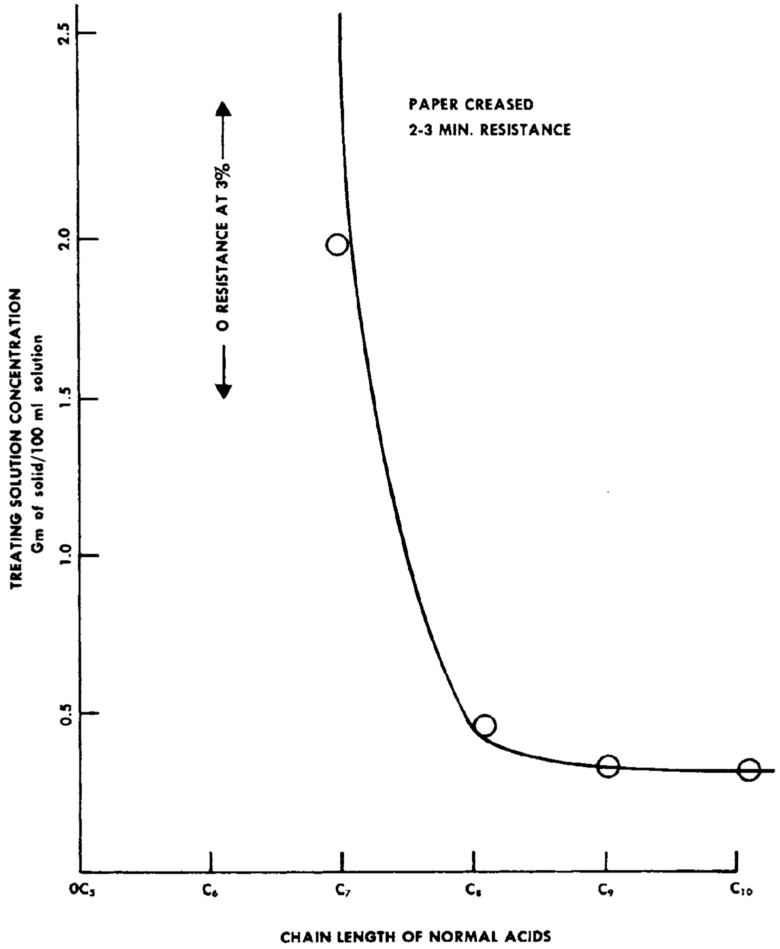


FIG. 75. Oil resistance imparted to paper by chromium complexes of fluorocarbon carboxylic acids of differing chain lengths.

complex has 0-min resistance even at 3.0% on the paper. In line with previous conclusion (see Textiles), it is necessary to utilize fluorocarbon groups which have eight or more carbons to effect efficient orientation of the fluorocarbon tails on the very rough and porous surface of a paper fiber.

3. *Performance vs Amount on the Paper*

In Fig. 76 is plotted the degree of oil resistance which is attainable on a Kraft paper at increasing levels of FC-805. Approximately 0.6% by weight is required to resist the highly penetrating turpentine. On the other hand, lesser amounts provide resistance to penetration by mineral oil, asphalt, or molten wax. These results have much practical significance since it enables the degree of oil repellency to be varied to meet the requirements of any given application. In general, the lower the surface tension of the oil or grease, the greater the concentration of fluorocarbon tails of a given chain length that will be required to prevent the oil from wetting the paper fiber. It is also obvious that a longer fluorocarbon tail will be more effective at a given concentration than a shorter one in preventing wetting, at least up to the point where the surface energy of the fiber surface has been reduced below that of the surface tension of the fluid.

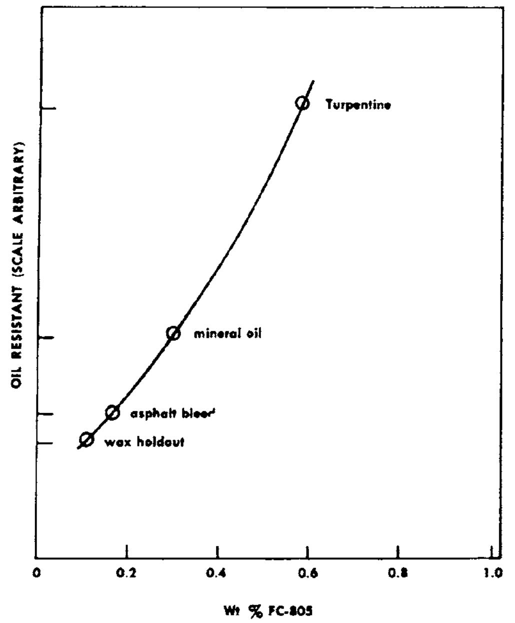


FIG. 76. Oil resistance vs concentration for a Kraft paper treated with different concentrations of a chromium complex of a fluorocarbon carboxylic acid FC-805.

4. *Performance vs Drying Conditions*

On a laboratory scale it is comparatively easy to treat a sheet of paper, using a treating solution as given in Table XLIV, following the procedure outlined earlier. The drying may be done in any convenient fashion, but preferably it should be done so as to avoid cockling and wrinkling. Drying conditions can have a marked effect on the degree of oil repellency attained on the treated paper. Figure 77 shows the influence of drying temperature on the efficiency of FC-805 in giving the paper resistance to turpentine for 30 min. For example, at 0.5 wt % of FC-805 on the paper and drying at 20°C, the paper will resist penetration of turpentine for 30 min. On the other hand, when dried at 130°C, approximately twice as much FC-805 solids is required to give the same penetration resistance. These results are consistent with the fact that the rate of drying is greater at the higher temperatures; and, of course, the more rapidly the drying occurs, the less efficient will be the migration of the fluorocarbon tails and their subsequent orientation on the surface. In general practice it has been established that the best results are attained by removing the bulk of the water at temperatures as low as possible, less than 100°C, followed by final drying at higher temperatures.

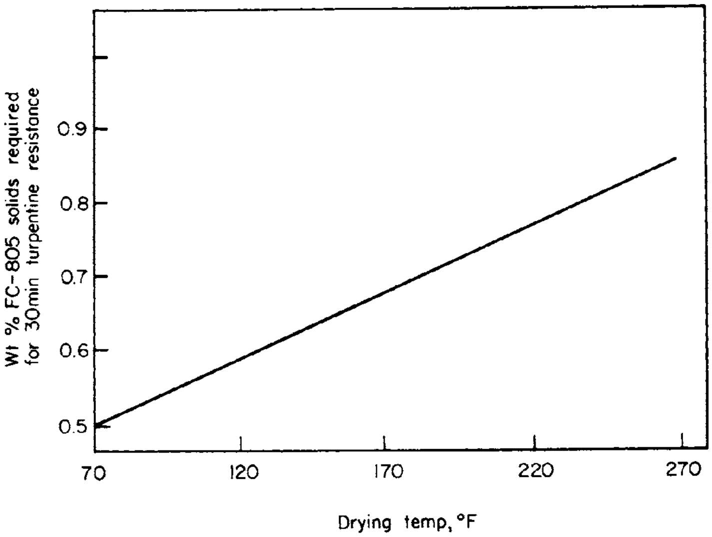


FIG. 77. Effect of drying temperature on the oil repellency of paper treated with FC-805.

5. *Performance vs Type of Pulp*

Depending on the particular process used to prepare the paper fibers prior to conversion to a sheet of paper, there may be various naturally occurring ingredients which will be more or less compatible with the fluorocarbon. Table XLVI gives a general classification of common types of paper pulp based on the processes by which they are prepared. The order of listing is from sulfate kraft at the top to the groundwood and jutes at the bottom, and also corresponds to the order of increasing content of other ingredients than the cellulosic fibers. In other words, sulfate kraft pulps are relatively free of natural rosins and lignins, whereas the other pulps contain increasing amounts of other contaminants in the order listed. The types listed under D, Jute, Newsboard, and Chipboard often contain rather large amounts of reclaimed newsprint, etc.

TABLE XLVI

Type of Pulp

A. Sulfate
B. 1. Sulfite
    2. Semi-chemical
    3. Soda
C. Groundwood
D. 1. Jute
    2. Newsboard
    3. Chipboard

As a general rule, it is possible to achieve higher performance levels from a given concentration of a fluorocarbon sizing, such as FC-805, on the purer sulfate type pulps than on the less pure varieties. It would appear that the naturally occurring contaminants interfere with the maximum orientation of the fluorocarbon tails on the fiber surfaces. From a practical point of view the above statement may only be significant if a high degree of oil resistance is required for a particular application. If low levels of resistance to wetting or spreading are sufficient, the impurities and contaminants are not as harmful.

C. COMMERICAL TREATING PROCEDURES

On a commercial paper machine the most convenient method of applying FC-805 is to use a size press. Figure 78 shows a typical size press as used in paper manufacturing, which is usually installed part way through the drying section.

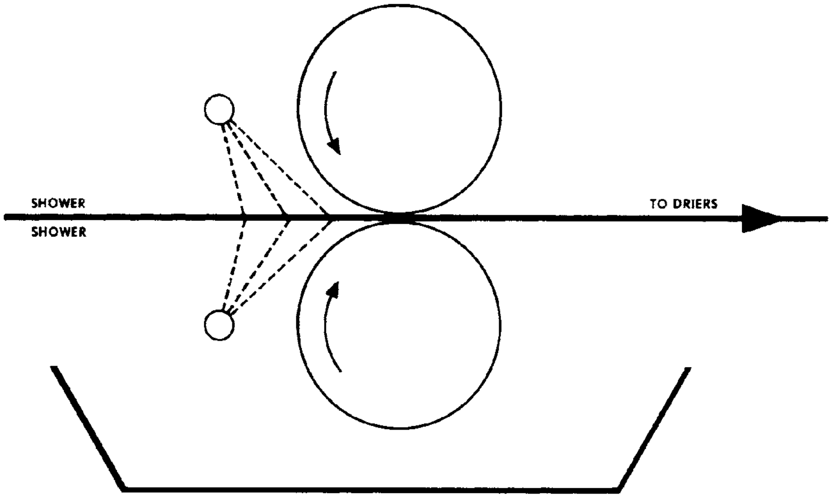


FIG. 78. Sketch showing a typical size press as used on a paper machine.

D. PROPERTIES OF TREATED PAPER

The application of fluorocarbon sizings to paper offers the paper maker, the converter, and the end-use designer a new tool in making paper and paper products which are resistant to penetration of oily (as well as aqueous) materials. Grease resistant papers have been available to the paper trade for long periods of time; however, these papers are formed by highly hydrated pulp which then forms a continuous or nonporous film. These papers are known as parchment, greaseproof, and glassine papers. In many cases it is also possible through the use of grease resistant films to produce a laminated structure which affords a certain degree of resistance to the penetration of greasy materials depending on the grease resistance of the film. The use of the fluorocarbon sizing, however, offers an entirely new approach, since this is the first time that grease resistance is possible without loss of porosity in the sheet since the paper fiber is given a truly non-oil and non-water wettable surface.

The fact that this degree of resistance may be varied by controlling the amount of fluorocarbon material added to the paper, of course, has much practical significance. For example, treatments that are at such a high level that they prevent the penetration of such fluids as turpentine or volatile hydrocarbon liquids, will also interfere seriously with the adhesion of inks or such coatings as waxes and lacquers. On the other hand, a degree of resistance, which is sufficient to prevent the penetration of molten wax or the bleeding of the oils from asphalt, will not interfere with good printing character.

There are three properties imparted to a sheet of paper by the use of these fluorocarbon treatments. The sheet becomes oleophobic, hydrophobic, and also shows a definite resistance to the pick-up of dry soils. At normal treating levels the water resistance imparted to the paper is at least equivalent to conventional rosin, wax, or synthetic sizes. The resistance to the adhesion of dry soil particles is a significant property and indicates again the low energy characteristics of the fluorocarbon surface which is created on the paper fiber.

Since the oil or grease resistance imparted by a fluorocarbon sizing to paper is that of coating the individual fibers so that they resist wetting or wicking, this concept must be appreciated in actual end use application. As stated earlier, conventional grease-proof or glassine papers or plastic films resist penetration by forming a continuous film or barrier through which the oil or grease cannot pass, even when significant pressure is applied. However, in the case of the fluorocarbon sizes, due to the retention of the porous nature of the sheet, it is possible to force the oil or grease through the sheet, even though the fibers themselves will not be significantly wetted. In other words, such sheets may resist wicking or wetting, but being porous, will not have sufficient pressure resistance to prevent the liquid from being forced through the paper.

In a similar manner, the distinction must also be made with regards to the passage of vapors. Obviously due to the porous nature of the fluorochemically treated sheet, the rate of transmission of vapors through the extremely thin fluorochemical layer on each fiber is not materially affected over that of untreated fibers. In consequence, a sheet of treated and untreated paper shows a similar moisture regain rate after drying and then equilibrating under given humidity conditions. Similarly, under varying humidity conditions, the fluorochemically treated paper does not show any significant improvement in dimensional stability over untreated paper. While this may be a disappointment in the case of many uses for paper, it is a very important asset in the application of these same materials to cotton wearing apparel where such factors as comfort and ease of drying are related to the ready moisture vapor absorption and transmission.

The conditions represented in Fig. 79 indicate some interesting effects depending upon the manner in which the paper is treated. The uppermost sheet has been treated from both sides; the middle sheet has been treated from the top; whereas the bottom sheet has been treated from the under side. If the desired objective is to minimize wetting of the paper by the oils, then obviously the two-sided saturation type treatment (Example A) is best. On the other hand, if the objective is to minimize actual strikethrough or penetration of a thermoplastic hydrocarbon or oil through the sheet, then Example C, in which the treatment is applied to the side opposite to that which is in contact with the hydrocarbon material, is best. This will be explained below. In example B when an oil drop is placed on the same side of the paper which has been treated, it will resist penetration indefinitely unless forced into the sheet. However, if the drop is forced into the sheet, it will continue to wick its way through because it is in an environment in which there is a gradient in the treatment level on the paper fibers which decreases in the direction of the arrow in Example B. On the other hand, when the oil is placed on the untreated or only slightly treated side of the sheet, Example C, it may wet the surface almost immediately; but instead of penetrating against the "wettability gradient" represented by the arrow, it merely spreads along the surface. Even when forced into the sheet, the oil will often wick back again in the direction of the "wettability gradient". These effects are, of course, due to the fact that the concentration of fluorocarbon groups is highest on the surface of that side to which the treating solution was applied; and there is a consequent decrease in concentration of fluorocarbon groups on the fiber surfaces as the solution penetrated into the interior of the paper.

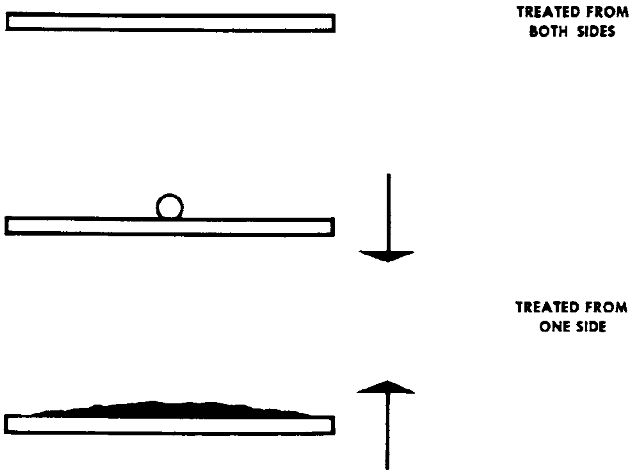


Fig. 79. Oil resistance of paper treated with FC-805 as a function of method of treatment, i.e., one-side vs two-side treatment.

E. Applications for Treated Paper and Paper Board

As indicated earlier, the use of a fluorocarbon sizing agent offers the paper manufacturer a new tool by which to attain resistance to penetration of many hydrocarbon based materials including oils, greases, waxes, and plastic-based lacquers. Not only is it possible to produce truly oil-repellent papers, but also to control the degree of oil repellency, which may be required for a given application.

1. *Asphalt Laminates*

When two sheets of Kraft paper are bonded together by a layer of asphalt, a packaging barrier is produced which has considerable strength and also excellent resistance to both moisture and moisture vapor. Asphalt, however, is a complex mixture of lighter oils and heavy waxes and insoluble resins. Under normal use in paper laminates, there is a gradual migration of the oily constituents of the asphalt through the paper to the outside. This not only causes a considerable discoloration and unsightly appearance, but may contaminate an article next to it. As shown in Fig. 80, FC-805

Fig. 80. Asphalt laminated seed corn bag. Bag on right has outer ply treated with FC-805; bag on left has untreated kraft.

is used commercially for asphalt laminates to prevent the asphalt bleed. In this case the fluorocarbon size is applied to one side of the paper as indicated earlier. In the manufacture of the laminate, the paper is laminated so as to apply the asphalt to the untreated side. As we have seen from earlier considerations, this one-sided treatment is effective in giving good adhesion to the asphalt and yet preventing the migration of the oils against the "wettability gradient." Such asphalt laminates are not only more useful at room temperatures, but also maintain freedom from staining even at elevated temperatures or in the presence of oily materials. Figure 81 shows an example of treated and untreated laminates which have been exposed for one hr at 125°C.

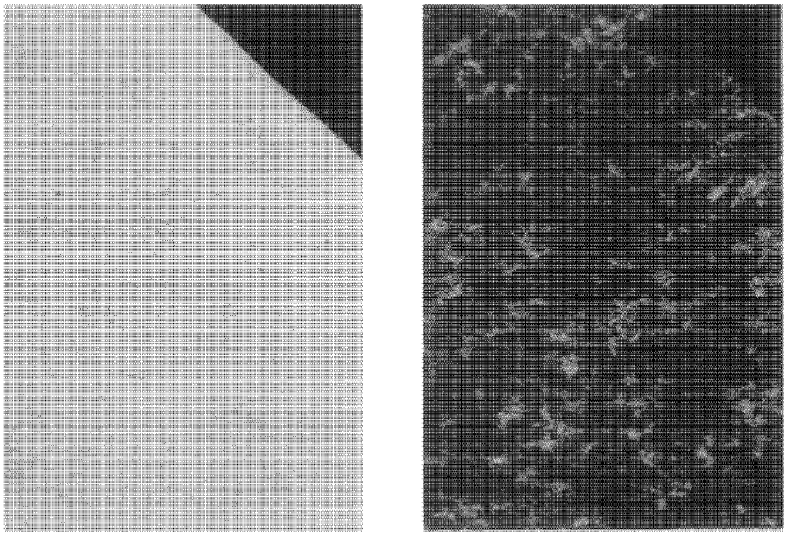


FIG. 81. Shows resistance of FC-805 treated paper to asphalt bleed. Sample on left is treated with FC-805 at 0.25 wt %; one on left is untreated. Both were exposed to 125°C for 1 hr.

2. *Waxed Papers and Boards*

Large quantities of paraffin and microcrystalline waxes are used to coat paper to provide a moisture vapor barrier and also to give resistance to liquid water. Such coated products find extensive use in such items as bread wraps, frozen food packages, bakery boards, and the like. In addition, it is common practice in many package constructions, where moisture vapor barrier is required, to laminate two sheets of paper or a sheet of paper and a sheet of paper board together using a layer of microcrystalline wax. Fluorocarbon treatments, such as FC-805, have been used quite extensively in conjunction with these molten wax coatings to prevent unnecessary wax penetration and yet permit the wax to form a continuous smooth film with good anchorage. Generally, it has been found advantageous to use a one-sided treatment for maximum opacity. The molten wax is generally applied to the treated side. Besides the reduction in the absorption of the molten wax into the paper and hence, a saving, it is also possible to retain the opacity of the sheet. Figure 82 shows how the opacity of a bleached kraft treated with FC-805 and with no filler remains the same as the unwaxed sheet. On the other hand a normal waxed sheet must be filled with a titanium pigment to the extent of 5% to retain even 69% of the original opacity; while the unfilled sheet retains only 45% of its original opacity.

3. *Carbonizing Tissues*

In the modern business world, in fact, in everyday living, the role of paper in transmitting information is extremely vital. Not only do the electronic computers grind out enormous volumes of data, many copies of which must be circulated, but the modern secretary is required to make many copies of information for general circulation. One of the growing uses for paper has been one-time carbon papers which are used to reproduce copies of the original impression at the same time the original is made. To maximize the number of copies which can be made, this paper must be as thin as possible, yet relatively strong. They must also resist penetration by the hot molten carbon dope which is coated on one side since the other side must be free of this dope. The application of fluorocarbon sizing, such as FC-805, to such sheets permits the application of the dope without strike-through, even when the sheet is very thin and relatively porous, thus effecting superior performance at lower cost than with conventional highly beaten and rather expensive carbonizing grades.

4. *Polyethylene Laminates*

Perhaps one of the most interesting developments involving these fluorocarbon sized papers is their use in the combination with polyethylene. Large quantities of polyethylene coated papers are used for a variety of packaging problems where the strength and formability characteristics of the paper or paper board, combined with the moisture vapor and liquid barrier characteristics of the polyethylene, offer an excellent packaging material. In general, these combinations have been restricted to uses where

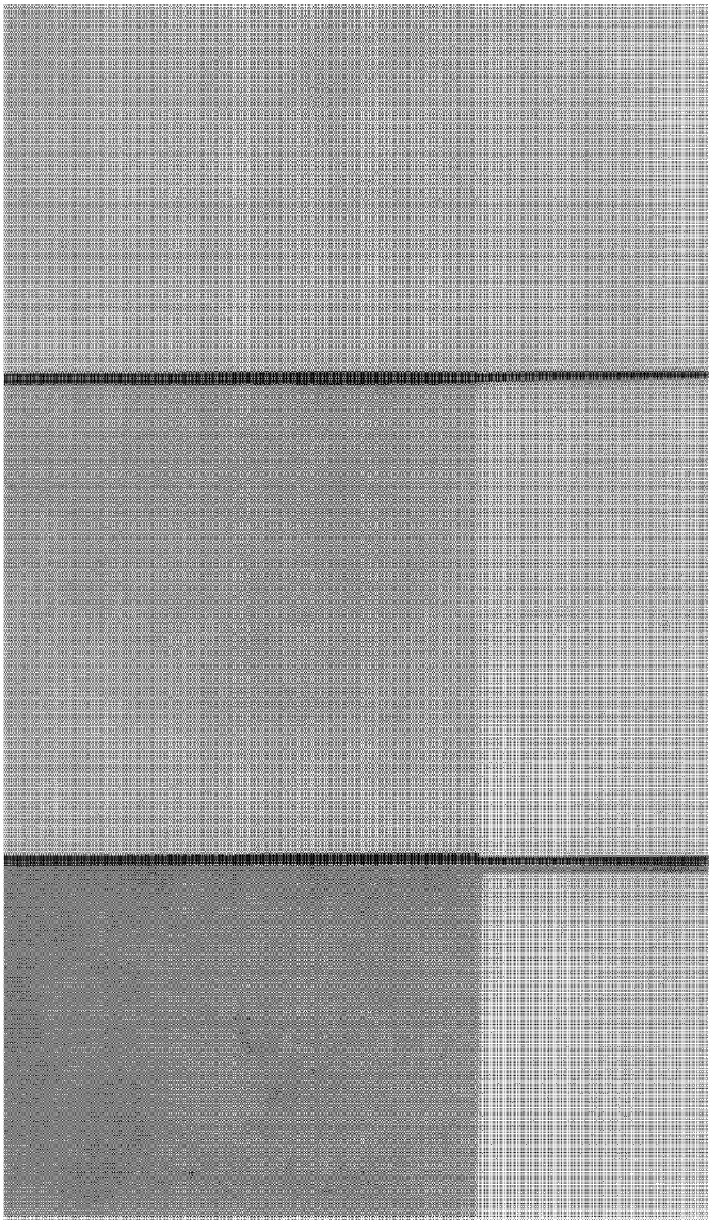


FIG. 82. Shows resistance to wax penetration by FC-805 treated paper, as measured by opacity retention. Sample on left is untreated paper; sample in middle is a paper containing TiO_2, and sample on right has been treated with 0.20% FC-805.

they are free from excessive exposure to oily or greasy materials. When the polyethylene coating is applied to paper, on the untreated side, and a fluorocarbon sizing is applied to the opposite side, a construction results which has excellent resistance to penetration of a wide variety of oils, greases, etc. The data in Table XLVII illustrates this point quite clearly;

TABLE XLVII

OIL RESISTANCE OF POLYETHYLENE—PAPER LAMINATES

Construction	Wt % FC-805 (solids) on paper	Lard oil resistance	
		Flat	Creased
0.5 mil polyethylene on 50 lb kraft	0	10 days	11 hr
1.0 mil polyethylene on 50 lb kraft	0	18 days	
0.5 mil polyethylene on 45 lb kraft treated with FC-805	0.25	30+ days	6 days

whereas neither the FC-805 treatment alone, nor the polyethylene film of even 2 mils is effective for any long period of time in resisting the penetration of the oils, the combination of 1/2 mil of polyethylene combined with 0.25 wt % solids of FC-805 achieves a very high level of resistance to oils and greases, even when folded or creased.

5. *Corrugated Cartons*

Treatment of either the inside or the outside liner of a corrugated carton has been found to greatly increase the serviceability of corrugated cartons. In particular, such cartons have given excellent performance in the packaging of many greasy items such as binder twine, spare parts, sweeping compound, etc.

It is anticipated that besides the present commercial usages described above, there will be many more uses for these fluorocarbon sizings.

XIII. Fluorocarbon Polymers—Plastics

A. INTRODUCTION TO POLYMERS

According to accepted definition, a polymer is the result of a reaction in which many small molecules combine to form a very large molecule. The reactions by which these unit molecules combine to form the larger molecules may take place in two general ways: namely, addition reactions and condensation reactions. The addition reactions involve compounds possessing unsaturated character such as double bond. A typical example involves the monomer ethylene, the molecules of which react together to form polyethylene which may be represented as follows:

$$n(CH_2 = CH_2) \rightarrow -(CH_2\text{-}CH_2)_n- \qquad (14)$$

On the other hand, condensation reactions involve linkages of unit molecules containing reactive groups which are polyfunctional and in which the polymerization reaction involves the loss of some simple molecule such as water, hydrogen, chloride, ammonia, etc., thereby forming a macro molecule. For example, a polyester results from the reaction of a dibasic carboxylic acid, such as adipic acid and a dihydric alcohol such as ethylene glycol which may be represented ($HOOC(CH_2)_4(COO(CH_2)_2OOC(CH_2)_4$-$COO(CH_2)_2O$---).

As might be expected in the case of the condensation polymers, a combining linkage such as the ester linkage in the above example retains the essential characteristics of this type of bond, and except for the influence of increasing molecular weights, follow most of the conventional chemistry for this type of reaction.

Although the chemist may describe these polymer species in simple formulas, such as that given for polyethylene above, these simple structures are at best only approximations to understanding some of the essential "polymer" characteristics. Such factors as end groups, impurities which lead to branching and other disturbances in the structure are obvious points of deviation. It is well established that defects in the assumed structure affect significantly the properties of most hydrocarbon type polymers such as depolymerization to monomer, low temperature or low energy chain cission and also cross-linking. As will be seen, however, in the case of fluorocarbon type polymers, these defects have even greater effect on properties.

Although there are numerous references in the literature to fluorine-containing condensation polymers, none of these has attained any commercial significance at the present time. This appears in large part to be due to an incomplete understanding of the chemistry of fluorocarbon compounds, and it is presumed that the next decade will see many breakthroughs in determining ways and means of combining the smaller fluorocarbon units in such fashion as to produce high molecular weight products with exceptional stability and chemical resistance.

Several fluorocarbon type polymers of the addition type have obtained considerable commercial importance. For the most part, these involve polymers formed from the tetrafluoroethylene, chlorotrifluoroethylene, vinylidene fluoride, and hexafluoropropylene, either as homopolymers or in various combinations as copolymers. These monomers are prepared from various chlorine and fluorine-substituted derivatives of methane and ethane, some of which have already been reviewed in the section on refrigerant and aerosol propellants.

B. POLYTETRAFLUOROETHYLENE

Tetrafluoroethylene, C_2F_4, was first isolated by Ruff and Bretschneider in 1933 from the product of decomposition of carbon tetrafluoride in the electric arc(111). C_2F_4 can also be prepared by the general method for the synthesis of fluoro-olefins using the compound, CF_2ClCF_2Cl. The modern commercial production of tetrafluoroethylene is by the noncatalytic pyrolysis of CHF_2Cl in a silver or platinum tube at temperatures above 650°C. The reactions involved are represented by the following equations:

$$CHCl_3 \rightarrow CHF_2Cl \tag{15}$$

$$2CHF_2Cl \rightarrow CF_2 = CF_2 + 2HCl \tag{16}$$

The yield from this reaction is reportedly 90 to 95%(112). Tetrafluoroethylene is a colorless, odorless gas with a boiling point of −76.6°C and a freezing point of −102.5°C, which can be stored under pressure in the absence of oxygen and with various stabilizers such as pinene.

Tetrafluoroethylene polymerizes very readily to produce polytetrafluoroethylene (TFE) which is a white, dense, highly crystalline linear polymer. On a commercial scale, the polymerization is carried out in the presence of water with efficient mixing and temperature control and with initiators such as potassium, sodium, or ammonium persulfates, oxygen, hydrogen peroxide, and peroxy organic compounds(113). The first successful polymerization was reported by Plunkett in 1941(114). In this case, the polymerization of tetrafluoroethylene occurred under superatmospheric conditions while the monomer was being stored in a cylinder. Brubaker reports the first aqueous emulsion polymerization system using catalysts on a commercial scale(115). Polytetrafluoroethylene (TFE) has relatively high molecular weights, ranging from 400,000 to as high as 9,000,000. The heat of formation of polytetrafluoroethylene from the monomer, appears to be in the range of 20 to 35 kcal per mole. This fact should be carefully borne in mind in considering the properties of the polymer of tetrafluoroethylene. It will be recalled that the energy required to break a carbon-to-carbon bond in a fluorocarbon is about 83 kcal per mole and that of the carbon–fluorine bond is approximately 116 kcal per mole. It is then not surprising that the polymer of tetrafluoroethylene is less stable to high temperatures or high energy radiation sources than a simple fluorocarbon such as C_8F_{18}, since the energy of formation of the polymer from the monomer is much lower than that of either the C—C or C—F bonds. These points will be considered further in the light of some of the properties of fluorocarbon polymers in a later section.

Of course, these same energy relationships also exist among hydrocarbon polymers as compared to true hydrocarbon molecules, at least so far as thermal or radiation degradation are concerned, but are often masked due to the presence of the highly reactive —C—H bond as contrasted to the very inert —C—F bond.

TABLE XLVIII

Weight Loss of TFE at Various Temperatures(116)

Temperature (°C)	Weight loss (%/hr)
204	0.0002[a]
260	0.0002[a]
316	0.0002[a]
360	0.001[b]
390	0.006[b]
420	0.09[b]

[a] Test conducted on granular molding powder.
[b] Test conducted on molded sheet.

The data in Table XLVIII illustrates the fact that there are definite, though small, changes occurring in the polytetrafluoroethylene molecules even at temperatures as low as 200°C(116). It has been determined that these weight losses are associated with the evolution of gaseous decomposition products and at least at temperatures below 400°C may be due to structural defects introduced during polymerization with energies of formation lower than either the —C—C— or —C—F bonds. The principal product formed is the monomer, C_2F_4, with trace amounts of products such as CF_4, C_3F_6, C_4F_8.

1. *Mechanical Properties*

Typical mechanical properties for TFE plastic are given in Table XLIX. The lower energy characteristics of the polymer are exhibited in the extremely low coefficients of friction(116), approximately one-fifth that of the analogous hydrocarbon plastic.

Table L shows that TFE resins remain tough and strong over an extremely wide temperature range, from −200°C to over 250°C. At

−196°C, for example, TFE polymers deform at approximately the same yield stress as a ductile metal, such as annealed copper(118).

While the elongation value of 6% at −196°C is substantially lower than the value at room temperature, namely 40%, it is adequate for most low temperature applications.

TABLE XLIX

TYPICAL MECHANICAL PROPERTIES OF POLYTETRAFLUOROETHYLENE AT 25°C(116)

Property		ASTM method
Specific gravity	2.13–2.20	D-792-50
Tensile strength (psi)	1500–3000	D-638-52T
Modulus of elasticity in tension	58,000 psi	D-747
Elongation (%)	100–350	D-638-52T
Flexural strength (psi)	Did not break	D-790-49T
Flexural modulus (psi)	50,000–90,000	D-747-50
Compressive strength at 1% offset (psi)	600	D-695-52T
Deformation under load, 1200 psi, 50°C, 24 hr (%)	4–8	D-621-51
Impact strength (IZOD) ft lb per in.	3.0	D-256-47T
Hardness, Rockwell D	50–65	D-676-49T
Coefficient of friction against polished steel	0.04	

TABLE L

EFFECT OF TEMPERATURE ON PROPERTIES OF TFE RESINS(118)

Property	−196°C	−80°C	−40°C	23°C	100°C	260°C
Compressive yield strength (psi)	(1) 11,000	(1) 4200	(1) 2800	(2) 1600	(2) 700	(2) 220
Elongation (%)	5–6	8	30	40	—	—
Flexural modulus (psi)	850,000	277,000	—	80,700	28,700	6500

Unlike many hydrocarbon or organic derived materials, fluorocarbon polymers do not become brittle at low temperatures. At temperatures throughout their service range—both high and low—they show elastic behavior up to the elastic limit. When the limit is reached, plastic deformation takes place.

2. *Chemical Resistance*

It is obvious that polytetrafluoroethylene is an outstanding member of the plastics family. Besides being chemically inert to all types of ordinary chemicals with the exception of molten alkali, it is also nonabsorptive to water, nonflammable, and has exceptional resistance to deteriorating effects of weathering.

3. *Electrical Properties*

As is shown in Table LI, TFE polymers possess unusually low dielectric constants and dissipation factors even over very wide frequency ranges. They also have high dielectric strength, volume resistivities, and arc resistance.

TABLE LI

ELECTRICAL PROPERTIES OF POLYTETRAFLUOROETHYLENE AT 25°C

Dielectric constant 60–10^6 cycles	2.2
Dissipation factor 60–10^6 cycles	< 0.0002
Dielectric strength (volts per mil)	400–600
Volume resistivity (ohms per cm)	$> 10^{16}$
Arc resistance (sec)	> 300

4. *Radiation Resistance*

The data in Table LII shows the effect of X-ray and gamma radiation on polytetrafluoroethylene(117). It is obvious that with radiation doses exceeding 0.1 megarads there is a rather severe action on the polymer, resulting in rather pronounced changes in both the electrical and mechanical properties of the polymer. If the dosages included in Table LII are compared with those reported for a known fluorocarbon structure, such as

TABLE LII

EFFECT OF RADIATION OF PROPERTIES OF POLYTETRAFLUOROETHYLENE(117)

50 kv X-radiation in 10^{-6} mm Hg vacuum

Radiation dosage (megarads)	Dielectric constant		Dissipation factor		Surface resistivity (ohms per cm²)	Volume resistivity (ohm per cm)
	60 cps	1 kc	60 cps	1 kc		
0	2.08	2.08	< 0.001	< 0.001	5×10^{17}	10^{18}
0.5	2.08	2.08	0.024	0.003	4.8×10^{14}	1.1×10^{17}
2.1	2.12	2.08	0.144	0.017	1.9×10^{13}	3.1×10^{16}
4.3	2.23	2.12	0.239	0.036	2.0×10^{13}	6.9×10^{15}
9.9	2.33	2.12	0.408	0.048	4.1×10^{13}	2.3×10^{16}
17.6	2.20	2.08	0.168	0.019	5.3×10^{13}	1.7×10^{16}

(*Continued on following page*)

TABLE LII (Continued)

Gamma radiation—Co 60 Isotope Source(119)

Radiation dosage (megarads)	In air at 1 atm		In 10^{-6} mm Hg vacuum	
	Tensile strength (psi)	Elongation (%)	Tensile strength (psi)	Elongation (%)
0	3000	165	3000	165
0.1	1882	152	—	—
0.5	1539	37	—	—
1.0	1388	21	2481	92
5.0	1322	—	1972	73
51.0			1462	38

C_8F_{18}, it is obvious that the polymer of tetrafluoroethylene is much less stable to degradation by radiation than would be expected for a simple —CF_2—CF_2—CF_2—CF_2— structure. For example, even at 100 megarads there is less than 20% change produced in the C_8F_{18} molecule. It is reported that polytetrafluoroethylene is considerably more stable to degradation by radiation in the absence of oxygen or in a vacuum(120).

5. *Crystallinity*

As produced commercially, polytetrafluoroethylene exists in a partially crystalline state. Depending on previous heating or cooling history, the degree of crystallinity ranges generally from 40 to 60%.

The relationship of per cent crystallinity to true specific gravity of TFE-fluorocarbon resins is shown in Fig. 83. It should be pointed out that many of the true properties of polytetrafluoroethylene polymers are somewhat difficult to attain. This is due to the inherent low energy properties of fluorocarbon molecules, which—as has been shown earlier—results in very low intermolecular forces. In consequence, it is difficult to force the very large polymer molecules to stick to each other; hence, polytetrafluoroethylene, unless handled very carefully, may contain a relatively large percentage of microvoids ranging down in size to molecular dimensions. Therefore, although the relationship between true specific gravity and per cent crystallinity is very direct, in actual practice the measured specific gravity may not correlate at all. Obviously, the presence of voids may very seriously affect many of the properties of any shape or form of the TFE polymer(136).

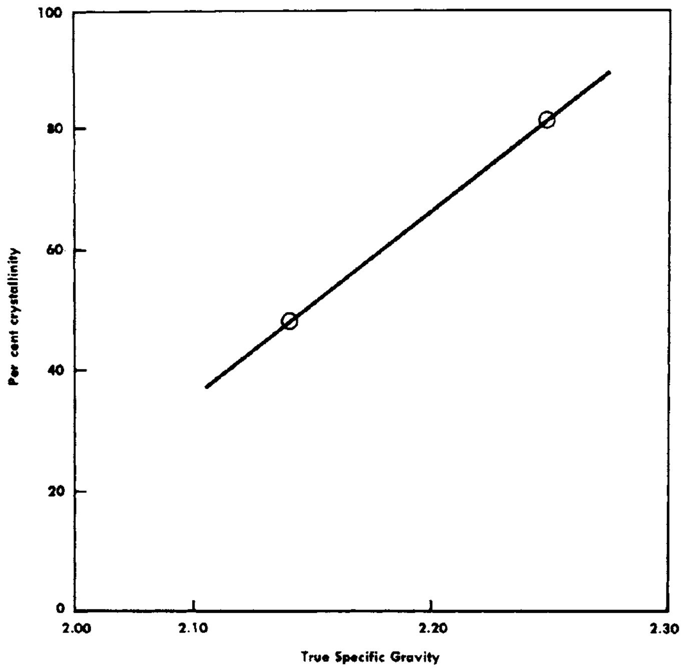


FIG. 83. True specific gravity of polytetrafluoroethylene as a function of crystallinity.

TABLE LIII

COMMERCIALLY AVAILABLE FORMS OF POLYTETRAFLUOROETHYLENE

Type	Description
1	General purpose molding powder.
5	Molding powder specifically granulated for molding cylinders of skive type.
6	Powder for use in extrusion of thin-wall tubular goods and tapes.
7	Special purpose ultrafine molding powder for use in molding shapes and molding cylinders for skieve tapes.
30	Aqueous dispersion for use in coating, impregnation, and casting processes.

The degree of crystallinity is controlled by molecular weight and by the length of time during fabrication that the material is maintained within the temperature range for rapid crystallization (300–327°C). Several workers have discussed at length the influence of degree of crystallinity and voids on the properties of fabricated TFE-fluorocarbon resins(121,122).

Polytetrafluoroethylene is made available commercially under the trademark, "Teflon" Fluorocarbon Resin, by the E. I. duPont de Nemours and Company. It is available in several forms, the most important of which are indicated in Table LIII.

6. *Fabrication Techniques*

a. Compression Molding

The molding of polytetrafluoroethylene (TFE) plastics is accomplished with techniques similar to those used in powder metallurgy and in the processing of ceramics. Granular powder is compressed at room temperature under a pressure of 2000 to 10,000 psi; and the resulting preform is baked or sintered in an oven or fluid bath maintained at a temperature of 370 to 395°C until the entire piece has reached the gel state. This resin does not have a true melting point but does have a transition temperature at 327°C, at which temperature it changes from an essentially crystalline polymer to the amorphous or gel form. For thin sections which do not require accurate control of dimensions, the preform is removed from the mold and placed in an oven where it is baked free without pressure applied. However, where accurate control of shape and dimensions are important, the piece is transferred directly from the oven to a cold coining die where pressure of the order of 2000 psi is applied to control dimensions while the piece is cooling. Where very complex shapes are required, the preform may be removed from oven while still in the gel state and quickly placed in a cold die cavity and forced under pressure to 10,000 to 20,000 psi into shape. For heavy sections, such as rods and tubes, having thicknesses greater than 3/4 in. the preform is left in the mold during the baking step and the preform pressure is maintained while cooling to avoid shrinkage cracks and other imperfections. A finished, molded part may be readily machined to give accurate dimensions.

b. Ram Extrusion

Besides the use of compression molding procedures, such as those indicated above, various forms can be made using ram extrusion procedures. This process involves compacting the cold powder with either a reciprocating ram or a screw and then forcing the compacted powder through a heated die where it is sintered. A variety of shapes and forms can be produced by this method; for example, coatings may be applied to wire which have thicknesses of 0.060 to 0.30 in. or relatively thick rods or tubes may likewise be satisfactorily formed.

c. Aqueous Dispersions

The aqueous dispersion form of polytetrafluoroethylene is supplied as a milky-white liquid consisting of very small particles of the polymer resin suspended in water. This is a convenient method of applying a coating to the surface of a substrate such as metal or ceramic glass or any material which can later be subjected to a baking temperature 350°C to 360°C.

Since the polytetrafluoroethylene does not have a true melting point, it cannot be extruded or injection molded using conventional techniques available for melt processible resins.

C. CHLOROTRIFLUOROETHYLENE POLYMERS

Chlorotrifluoroethylene is a colorless, odorless gas which boils at $-28°C$ and is prepared in almost quantitative yields from the fluorinated product, $CF_2ClCFCl_2$. The reaction may be represented as follows:

$$CF_2ClCFCl_2 \xrightarrow{Zn\text{-}ETOH} CF_2 = CFCl \qquad (17)$$

Chlorotrifluoroethylene may be stabilized during storage by inhibitors and is readily polymerized by peroxide catalysts to the polymer. A variety of methods are available, including polymerization in mass, in solution, or in aqueous emulsion systems(125).

Polychlorotrifluoroethylene has a melting point of 213°C; it is, therefore, classified as a melt processible resin with typical thermoplastic properties. Like polytetrafluoroethylene, this fluorocarbon type polymer also exhibits some characteristics which are more typical of its polymeric nature than the properties which are usually associated with fluorocarbons. The presence of the chlorine atom does introduce a bond of lower energy than either the C—C or C—F bonds. The chlorotrifluoroethylene polymers of commerical significance have molecular weights in the range of 300,000 to 400,000 which are much lower than those of the commercially available homopolymers of tetrafluoroethylene.

1. *Mechanical Properties*

Typical mechanical properties are included in Table LIV(126). Of note is the fact that CTFE polymer has a relatively high tensile strength with elongation in the 100–200% range. It has a relatively high compressive strength; namely, 5440 psi at 0.2% offset. As compared to poly-TFE, poly-CTFE has a much higher compressive strength; it is considerably harder, and has much higher resistance to deformation under load.

CTFE polymers have definite crystalline character. The data in Fig. 84 shows the difference in resistance to deformation under an applied load of 1000 psi as a function of temperature for a specimen of the plastic which is approximately 40% crystalline compared to one that is about 65% crystalline(126). Obviously, the crystalline state provides much greater lateral bonding between polymer chains; hence, the much greater resistance to deformation under load and higher densities.

TABLE LIV

TYPICAL MECHANICAL PROPERTIES OF POLYCHLOROTRIFLUOROETHYLENE AT 25°C (ZST: 250 sec)

Property	Crystalline	Amorphous	ASTM test Method
Specific gravity	2.1312	2.1047	D792-50
Tensile strength (psi)	4900	5070	D638-56T
Elongation (%)	105	175	
Yield point (psi)	5710	4650	
Yield strength (psi, 0.2% offset)	2660	1940	
Modulus of elasticity tensile (psi)	186×10^3	162×10^3	
Flexural strength (psi)	10,700	7810	D790-59T
Modulus of elasticity flexure (psi)	254×10^3	190×10^3	
Compressive yield strength (psi, 0.2% Offset)	5440	—	D695-54
Modulus of elasticity compressive (psi)	180×10^3	—	
Deformation under load (24 hr 1000 psi)			D621-59
% at 25°C	0.20	0.37	
% at 70°C	0.40	7.32	
% at 125°C	3.57	25.00	
Impact strength (Izod ft lb per in. notch)	3.1	7.3	D256-56
Hardness, knoop KNP	10.7	8.2	D1474-57T
Rockwell S-Scale	85	80	D785-51
Thermal conductivity (cal per cm^2 per sec per °C per cm)	6.32×10^{-4}	6.12×10^{-4}	D696-44
Coefficient of linear expansion			
−196°C	1.8×10^{-5}		
0−50°C	4.8×10^{-5}		
Coefficient of friction on steel		0.43	

The data in Table LV shows the variation in mechanical properties of poly-CTFE as a function of temperature(126,127). Like poly-TFE this polymer also retains useful mechanical properties below −200°C, particularly with respect to flexing and resisting deformation up to the limit of the small but definite elongation limits. In the case of poly-CTFE, there is a rather rapid fall-off in properties above 125°C, particularly as the melting point of 213°C is approached.

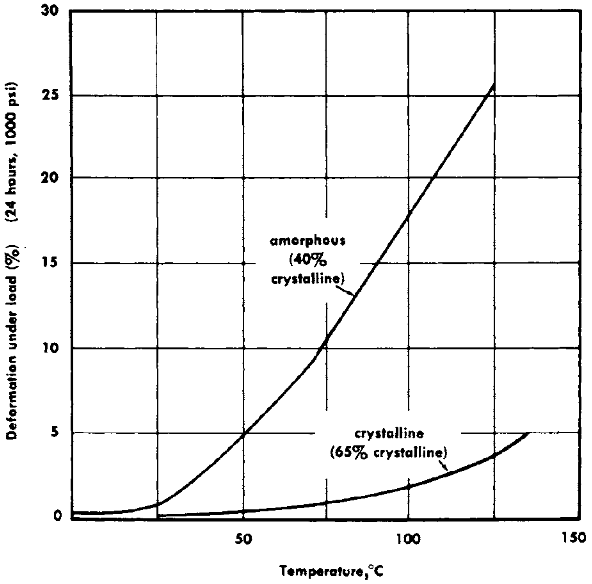


Fig. 84. Deformation under load as a function of crystallinity and temperature for polychlorotrifluoroethylene.

The presence of chlorine in this otherwise fluorocarbon plastic contributes to much greater cohesive forces between the polymer molecules. For example, comparing the compressive strengths of the polymer of tetrafluoroethylene, which contains only —CF_2 groups, and the polymer of chlorotrifluoroethylene with—CF_2—and—CFCl—groups, the CTFE polymer gives values of 5400 psi at 0.2% offset as compared to 1000 psi at 1% offset for TFE. Thus, there is a much greater tendency for the polymer chains in the case of the TFE polymer to slip and slide over each other; whereas the chlorine atoms in the CTFE type tend to bond the chains together, hence resist the slipping and sliding. This greater cohesive force between

TABLE LV

VARIATION IN MECHANICAL PROPERTIES OF POLYCHLOROTRIFLUOROETHYLENE AS A FUNCTION OF TEMPERATURE

Property	Temperature (°C)							
	−253	−196	−73	−40	23	70	125	150
Tensile strength (psi)		23,000	16,000	12,000	5,200	3,250	530	300
Elongation (%)		6	—	—	150	375	450	>500
Modulus of elasticity in tension (psi)		1,200,000	400,000	320,000	186,000	83,000	15,000	
Compressive yield strength (psi)	44,000	—	—	—	5,440	—	—	
Impact strength Izod (ft lb per in. notch)		1.7			3–7	—	—	—
Flexural strength (psi)		24,400	—	—	10,700	4,950	1,650	—
Flexural modulus (psi)		565,000	—	—	254,000	149,000	32,000	

the polymer chains in CTFE polymers is also evidenced by the fact that these materials tend to maintain a much higher density. This is illustrated by the fact that the CTFE polymers are much less permeable to a variety of gaseous materials than the polymers of tetrafluoroethylene or the copolymer of tetrafluoroethylene and hexafluoropropylene. Data for permeability to water vapor is shown in Table LVI.

TABLE LVI

WATER VAPOR TRANSMISSION OF VARIOUS PLASTICS

Material	Caliper of film (mils)	Duration of test (days)	Permeability gm per mil per 100 in^2 per 24 hr	Reference
CTFE homopolymer				
Grade II	5	30	0.030	
	1	3	0.034	(126)
CTFE homopolymer				
plasticized[a] (25%)	3.4	3	0.20	(126)
(C_2F_4-C_3F_6) copolymer (FEP)	—	—	0.46	(189)
($CH_2 = CCl_2$) homopolymer	—	3	0.80	
($CH_2 = CH_2$) homopolymer				
(low density)	—	3	1.0	

[a] Plasticizer used is low molecular weight polymers of CF_2CFCl.

The rather strong intermolecular cohesive forces for CTFE are also shown by the fact that even for relatively low weight of 300,000, the polymers have tensile strength in excess of 5000 psi. TFE polymers, on the other hand, even with molecular weights of 2,000,000 or more, have tensile strengths of 2000 to 4000 psi.

2. *Thermal Stability*

While the presence of the chlorine atom does contribute to greater tensile and compressive strength and also to closer packing between polymer chains, it also introduces inherent weak spots in the polymer systems. For example, at temperatures above 260°C, the CTFE polymer undergoes degradation reaction resulting in the formation of lower molecular weight polymer. In Fig. 85 we see results which are expressed in terms of the decrease in zero strength time as a function of temperature and time. It will be noted that there is a rapid decrease in the ZST as the temperature exceeds 315°C.

In this case, the ZST or zero strength time is a measure of molecular weight and has been shown to correlate with the dilute solution viscosity method(128). The test method is outlined in A.S.T.M. D-1430-58T(129). Briefly, the ZST is measured as the number seconds required for a notched specimen of the plastic having a carefully defined cross-section to be pulled apart by a fixed weight when placed in a furnace at 250°C.

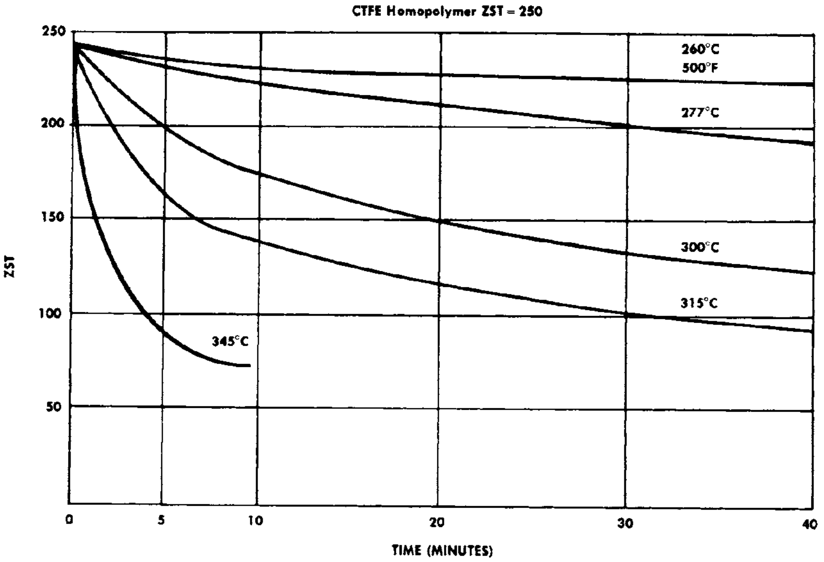


FIG. 85. Change in ZST as a function of time and temperature for chlorotrifluoroethylene homopolymer.

This degradation into lower molecular weight fragments is presumably due to the cission of the polymer chains at weak spots along the chain. These weak spots may arise for a number of reasons such as irregularities introduced during the polymerization process caused by impurities, influence of terminal groups, etc. The fact that the heat of formation of the carbon-to-chlorine bond is only 78.5 kcal per mole as compared to that for the carbon-to-fluorine bond of 116 kcal per mole respectively is also a point of weakness.

The presence of chlorine in the polymer molecule also introduces certain dipolar structures as evidenced by the higher dielectric constant of 2.60 over that of polytetrafluoroethylene which has a value of approximately 2.0. This is also indicated in Table LVII by the much larger dissipation factor for the CTFE over the TFE polymer; i.e., 0.0215 at 100 cycles per sec vs less than 0.0005 for the TFE.

TABLE LVII

ELECTRICAL PROPERTIES OF CTFE HOMOPOLYMER AT 25°C
(ZST = 250 sec)

Frequency (cps)	Dielectric constant	Dissipation factor
10^2	2.59	0.0215
10^4	2.41	0.0229
10^5	2.34	0.0144
Dielectric strength		500 volts per mil
Electrical resistivity		
Volume		$>10^{16}$ ohm cm
Surface		$>5 \times 10^{17}$ ohms per cm^2
Arc resistance		>360 sec

TABLE LVIII

CLASSIFICATION OF COMMERCIAL POLYCHLOROTRIFLUOROETHYLENE HOMOPOLYMER
(ASTM D-1430-58T)

Grade	ZST range	Intended usage
2	176 to 300	Extrusion of film, tubing, and wire coating, injection molding
3	301 to 750	Compression molding, injection molding, Rod, and thick-walled tubing extrusion

The homopolymer of CTFE is made available in several grades based on the molecular weights. These are described in Table LVIII, again using the A.S.T.M. designation for grades based on the ZST.

The homopolymer of CTFE is manufactured by the Minnesota Mining and Manufacturing Company under the trademark, "KEL-F" Brand Plastic.

3. *Chemical Resistance*

Resistance of CTFE polymers to a variety of solvents and chemicals is shown in Table LIX. As can be seen from the table, this material is highly resistant to a wide variety of chemicals and solvents. It is unaffected

TABLE LIX

CHEMICAL RESISTANCE OF CHLOROTRIFLUOROETHYLENE HOMOPOLYMER

ASTM test method	Property	Crystalline		Amorphous	
		% weight change	% volume change	% weight change	% volume change
	Chemical resistance (7 days/25°C)				
D543-56T	Acetone	0.1	−1.1	0.3	0.2
	Benzene	0.1	−1.2	0.3	−0.3
	Ethanol, 95%	0.0	−0.8	0.0	−0.7
	Methyl ethyl ketone	0.2	−0.5	0.4	0.1
	Trichloroethylene	1.8	1.5	3.0	1.9
	Ammonium hydroxide, 10%	0.0	−0.7	0.0	−0.3
	Ethyl ether	4.4	7.6[a]	5.8	11.2[a]
	Freon 113	0.9	0.6	0.9	0.4
	Hydrochloric acid, 10%	0.0	−0.5	0.0	−0.6
	Sodium hydroxide, 10%	0.0	−0.9	0.0	−0.6
	Nitric acid, 90% fuming	0.0	−0.2	0.0	−0.4
	Hydrofluoric acid, anhydrous	0.0	−0.1	0.0	−0.8
	Nitrogen tetroxide (5°C)	8.2	9.4[a]	9.9	10.5[a]
	Unsymmetric dimethyl hydrazine	0.0	0.8	0.1	0.1
D570-59T	Water absorption (21 days/25°C)	0.0	0.0	0.0	0.0
RMD Tester	Liquid oxygen impact sensitivity (ft lb per sq in. for 0.010 in. thick)	162		162	

[a] Becomes rubber-like.

by all types of strong acids and bases even at elevated temperatures. It is not soluble in any of the conventional solvents being only very slightly swollen by such materials as trichloroethylene, ethyl ether, and nitrogen tetroxide. By the standard test procedures for plastic materials, the polymer shows no absorption of water.

4. *Radiation Resistance*

CTFE polymers have been investigated recently as to their radiation resistance, particularly under conditions which approximate those in outer space(117). Results were obtained by exposure to 50 kv X-rays in a vacuum of 10^{-6} mm Hg. The data is included in Table LX. These results correspond quite closely to values which were obtained by other workers using gamma radiation in air(126). As can be seen from the data, the dissipation factor actually shows a slight decrease in value upon exposure

TABLE LX

EFFECT OF RADIATION ON POLY-CTFE(117) (50 KV X-RADIATION AT 10^{-6} MM HG)

Radiation dosage (megarads)	Tensile strength (psi)	Elongation (%)	Dielectric constant 60 cps	Dielectric constant 1 kc	Dissipation factor 60 cps	Dissipation factor 1 kc	Surface resistivity (ohms per cm²)	Volume resistivity (ohm-cm)
0	5200	180	2.73	2.65	0.008	0.025	$>5 \times 10^{17}$	$>1 \times 10^{18}$
4.4	—	—	—	—	0.005	0.029	4.5×10^{16}	2.3×10^{17}
9.8	4270	200	—	—	0.005	0.028	4.2×10^{16}	5.7×10^{17}
17.5	—	—	—	—	0.005	0.028	5.4×10^{16}	2.3×10^{17}
GAMMA RADIATION—SPENT FUEL ELEMENTS IN AIR AT ATMOSPHERIC PRESSURE(126)								
0	5440	180						
8	4090	165						
16	3520	80						
24	3410	80						

to X-rays, while the tensile and other physical properties show losses of less than 20%.

5. *Visible and Infrared Transmission*

CTFE polymers have high transmission properties in both the visible and infrared regions. Typical *IR* absorption curves are shown in Fig. 86.

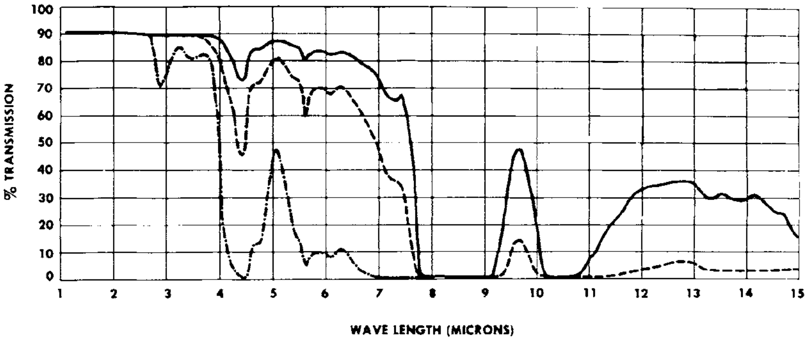


FIG. 86. Infrared absorption spectrum for chlorotrifluoroethylene homopolymer.

6. *Processing of CTFE*

Polychlorotrifluoroethylene molding powder may be converted to a variety of forms by several procedures. As has been stated earlier, the resin has a definite melting point, therefore, may be converted by processes common to all true thermoplastic resins. Included are compression molding injection molding, transfer molding and extrusion.

At the melting point, poly-CTFE has a very high viscosity; hence, during compression molding it is necessary to heat the molding powder to a temperature of 260°C under a pressure of 5000 psi before it can be converted to a dense uniform mass. Injection molding and extrusion processes require considerably lower viscosities; hence, require even higher temperatures, generally in excess of 315°C. Care must be taken to avoid overheating the polymer for excessive periods of time; otherwise serious degradation occurs, with resulting poor mechanical properties.

The mechanical properties of the finished article are also a function of the degree of crystallinity. At least in relatively thin sections it is possible to vary the crystallinity by heat treatment followed by quick quenching or slow cooling. Quick quenching from above the melting point, of course, leads to forms having the most amorphous character. On the other hand, slow cooling results in relatively high degrees of crystallinity.

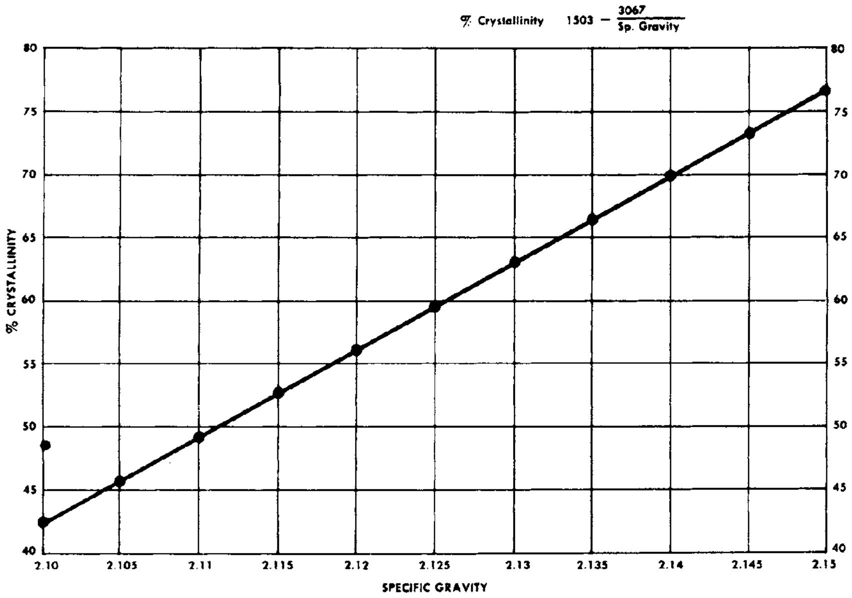


FIG. 87. Per cent crystallinity vs specific gravity for chlorotrifluoroethylene homopolymer.

The degree of crystallinity may be determined by several means such as X-ray diffraction and density. Figure 87 shows the relationship between per cent crystallinity and density for the CTFE homopolymer.

D. POLYVINYLIDENE FLUORIDE

The homopolymer of vinylidene fluoride has recently been introduced on a commerial scale by the Pennsalt Chemical Corporation. The monomer may be prepared by the dehydrohalogenation of 1, 1, 1 chlorodifluoroethane(130,131) or the dehalogenation of 1, 2 dichloro 1, 1-difluoroethane(132). The highly regular structure of the resulting polymer and the similar sizes of the appending fluorine and hydrogen atoms permits close packing of the polymer chains. As might be expected, there is considerable hydrogen bonding between the hydrogen atoms, which produces cross-bonding of high lattice energies. As in the case of chlorotrifluoroethylene polymers, this polymer is characterized by the high tensile strength which can be improved by orientation and exhibits rather rigid structure with high compressive strength. Typical data are included in Table LXI. The polymer has a melting point of 171°C compared to 213°C for CTFE. The highly dipole nature of the polymer is shown up in the unusually high dielectric constant of 8.4 at 60 cps and the high dissipation factors at 10^6–10^9 cps. Typical electrical properties are included in Table LXII.

TABLE LXI

MECHANICAL PROPERTIES OF POLYVINYLIDENE FLUORIDE AT 25°C[133]

Tensile strength (psi)	7000
Elongation (%)	300
Modulus of elasticity in tension	120,000
Compressive strength	10,000
Modulus of elasticity in compression	120,000
Impact strength (Izod, notched)	3.8
Coefficient of sliding friction to steel	0.14–0.17
Specific gravity	1.76

TABLE LXII

ELECTRICAL PROPERTIES OF POLYVINYLIDENE FLUORIDE AT 25°C[133]

Dielectric constant	
60 cps	8.40
10^3 cps	7.72
10^6 cps	6.43
10^9 cps	2.98
Dissipation factor	
60 cps	0.050
10^3 cps	0.019
10^6 cps	0.159
10^9 cps	0.110
Volume resistivity (ohm-cm)	2×10^{14}
Dielectric strength (volts per mil, 0.125 in. thickness)	260

While this polymer has greater resistances to solvent and chemicals when compared to the hydrocarbon analogue, it is considerably less resistant than the more highly fluorinated or hydrogen-free polymers such as those based on tetrafluoroethylene or chlorotrifluoroethylene. It is severely degraded by fuming sulfuric acid and by certain organic bases, such as *n*-butyl amine. It can be swelled and partially dispersed by acetone and will form colloidal solutions with such strongly polar solvents as dimethylacetamide.

E. Polyvinyl Fluoride

The polymer of vinyl fluoride, $(CH_2—CHF)_n$, has been made available recently in film form(134). The polymer has a glass transition temperature point of 150°C. Film is reported to have outstanding weatherability, being unaffected even after seven years' exposure to Florida sunlight. Polyvinyl chloride, on the other hand, showed serious degradation in six months. It is also reported to have high ultraviolet transmission. The film has excellent flex resistance and high dielectric strength. As might be expected, polyvinyl fluoride is, relatively, quite a polar material and exhibits high dielectric constant of 7.5 at 60 cps. The product is being offered under the tradename of "Tedlar" by E. I. duPont de Nemours and Company.

F. Copolymer of Tetrafluoroethylene and Hexafluoropropylene

A copolymer of tetrafluoroethylene and hexafluoropropylene has been introduced commercially by the E. I. duPont de Nemours and Company under the tradename, "Teflon 100 FEP"(135). As might be expected, the hexafluoropropylene group introduces the $—CF_3$ side group into the polymer molecule; hence, altering some of the physical characteristics from that of the polytetrafluoroethylene (TFE) polymer. In particular, this produces higher strength characteristics at lower molecular weights, probably by reducing the slippage of one polymer chain against the other. The $—CF_3$ group also tends to inhibit crystallization of the polymer chain. The $—CF_3$ side group, of course, does not introduce any significant lateral chain to chain binding; in consequence, the general properties of the polymer are very similar to those of the homopolymer of tetrafluoroethylene. Typical data comparing the two materials are included in Table LXIII.

The primary difference between the two materials exists in the fact that the copolymer of FEP is a melt processible resin and hence may be extruded or injection molded by conventional thermoplastic techniques. It will be noted, however, that even this melting point is considerably higher than the homopolymer of chlorotrifluoroethylene. In consequence, it is necessary in order to handle the resin in the melt condition to use temperatures in excess of 370°C.

Both polytetrafluoroethylene and the copolymer of tetrafluoroethylene and hexafluoropropylene are more stable to chain cission or molecular degradation than the polychlorotrifluoroethylene. In consequence of this,

TABLE LXIII

COMPARISON OF PROPERTIES OF POLY TFE AND THE COPOLYMER OF TETRAFLUOROETHYLENE AND HEXAFLUOROPROPYLENE (FEP)(136)

Property	TFE	FEP
Melting point	none	285–290°C
Specific gravity	2.13–2.20	2.14–2.17
Refractive index	1.350	1.338
Tensile strength (psi)	3000	2500
Elongation (%)	100–350	250–330
Modulus of elasticity	58,000	50,000
Coefficient of friction	0.04	0.08
Dielectric constant	2.10	2.10
Dissipation factor		
60–10^6 cycles	<0.0002	<0.0002
10^6 cycles	<0.0002	0.0007
Compressive strength at 25°C	600 (1% deformation)	1400 (2% deformation)

TFE and FEP can be held at temperatures of 400°C for periods of time required for fabrication or in certain end use service without excessive loss of physical properties.

Both polymers are relatively soft and have rather low compressive stresses as shown in Table LXIII. Tensile strengths and elongation are in the same general range, and both have extremely low coefficients of friction.

G. COPOLYMERS CONTAINING CHLOROTRIFLUOROETHYLENE

Several copolymers have obtained commercial significance which are based on combinations of chlorotrifluoroethylene and vinylidene fluoride. As might be expected, the properties of the copolymers are affected in several ways as the percentage of the vinylidene fluoride is increased. There is a marked decrease in the resistance to various solvents and chemicals due apparently to the presence of $—CH_2—$ group in the backbone of the polymer. Depending upon the particular range of composition, the polymers may be hard plastics or at higher vinylidene fluoride compositions, may approach those of elastomers. The various points of difference are illustrated in the data in Table LXIV.

As has been stated earlier, the homopolymer of chlorotrifluoroethylene is quite highly crystalline; and if the molecular weights are on the low side, there is a strong tendency for the polymer to crystallize upon exposure to slightly elevated temperatures. In many applications, such as extrusion of films, thin-walled tubing, or insulation coatings on wire, this crystallization phenomenon leads to embrittlement and ultimately cracking and crazing. The incorporation of small percentages of vinylidene fluoride provides sufficient interference with normal crystallization phenomenon as to materially increase resistance to embrittlement and cracking; hence improve the basic performance of the polymer as far as aging is concerned.

TABLE LXIV

PROPERTIES OF COPOLYMERS OF VINYLIDENE FLUORIDE AND CHLOROTRIFLUOROETHYLENE

Mole % vinylidene fluoride	Melting point	Form of polymer
0	213	Hard plastic
5	192	Hard plastic
7	183	Hard plastic
25	no true T_m	Rubbery plastic
50	no true T_m	Tough elastomer
65	no true T_m	Tough elastomer
100	171°C	Hard plastic

Polymers of this type are being made commercially under the "KEL-F" Brand trademark by Minnesota Mining and Manufacturing Company or as "Halon" Plastics by the Allied Chemical Corporation.

H. SUMMATION

The preceding review of the characteristics of a variety of polymer materials based on fluorine-containing monomers demonstrates several characteristics of fluorocarbon material. Those plastics, which contain only carbon-fluorine bonds other than the inter-connecting carbon-to-carbon linkages, exhibit the highest thermal stability, the greatest chemical and solvent resistance, and the lowest coefficient of friction. They also possess the lowest dielectric constants and the least degree of residual polar character as evidenced by their very low dissipation factors. The introduction of somewhat more polar linkages such as the carbon-to-chlorine or the carbon-to-hydrogen bonds results in the lowering of melting points and also increases very greatly the lateral cohesive bonds between polymer chains. This effect results in much harder and more dense polymer structures, with lower permeability to a variety of gases, vapors, and solvents.

I. APPLICATIONS

1. *Electrical*

The electrical industry has made widespread use of the fluorocarbon resins, particularly the homopolymers of tetrafluoroethylene and chlorotrifluoroethylene and, in recent years, the copolymer of hexafluoropropylene and tetrafluoroethylene. This usage, of course, is obvious from review of the properties given previously; namely, high heat resistance, zero moisture resistance, excellent dielectric properties, high dielectric strengths. Insulation uses include primary wire coating, as well as cable jacketing. These polymers have also found uses in a variety of specialized electrical equipment including coil forms, switchgears, resistor coatings, and many others. See Fig. 88.

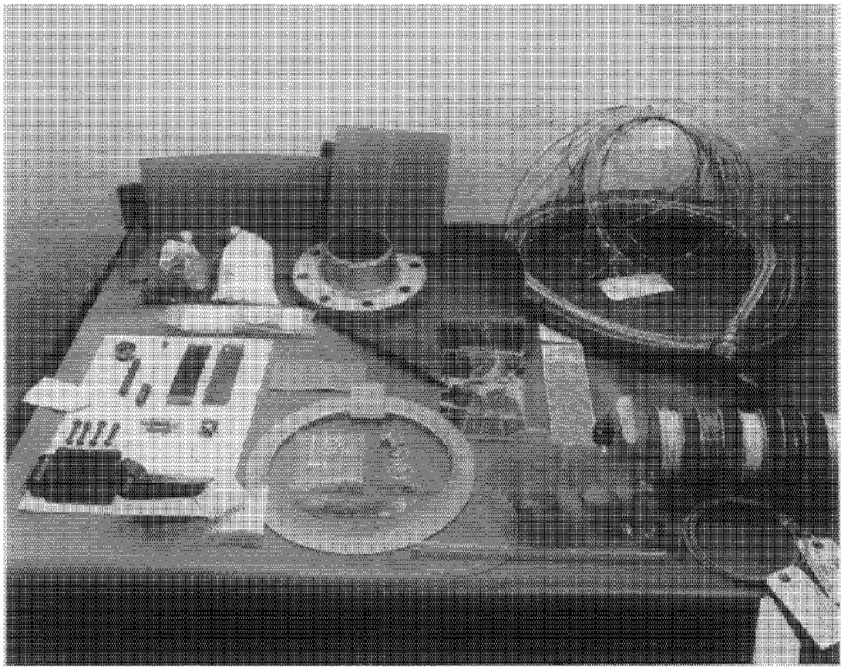


FIG. 88. Applications for polychlorotrifluoroethylene.

2. *Chemical Resistance*

The excellent combination of chemical resistance and thermal resistance has led to the use of these fluorocarbon-type resins for a variety of applications in which their chemical resistance is of prime importance. Included are gaskets and seals for many chemical process operations and in the handling of a variety of missile and rocket fuels, such as jet fuels, fuming nitric, nitrogen tetroxide, hydrazines, etc. In some applications, the flow properties of the TFE type polymer, combined with the higher heat resistance, makes this material a desirable choice. In other applications, where greater resistance to cold flow is concerned and less permeability to vapors or fumes is required, the chlorine-substituted polymers, such as CTFE, are generally preferred. Extensive use of all types has been made for the lining of pipes and valves, tanks, etc., to protect the base metal, usually steel, from attack from the chemical agents. In small items, such as pipes, valves, the linings are often molded in place; while other items, such as tanks or agitator paddles, are generally coated by using suitable dispersion coating system—either based on aqueous or nonaqueous systems.

3. *Lubricity*

The TFE and FEP polymers are unique in possessing extremely low coefficients of friction as contrasted to the rather high values for the chlorine or hydrogen substituted counterparts (see Tables XLIX, LIV, and LXIII). This, again, points out the fact that the C—Cl or C—H bonds introduce polar characteristics which greatly increase the coefficient of friction. This low coefficient of friction has led to many uses for the TFE and FEP products wherein their use in bearings and packings for sleeves in valves has become extremely important. Where higher loads are required on bearing materials, fillers are often incorporated in order to give greater compressive strength and resistance to flow and yet maintain the low coefficients of friction.

4. *Anti-Stick*

The low adhesive qualities of the fluorocarbon resins have also become extremely important. Many items used in handling bakery doughs are coated with products such as TFE or FEP to give a high degree of resistance to stick. During the last few years, extensive use has been made of TFE in coating such items as frying pans to prevent the sticking of food. Many types of industrial rollers, which are used to apply or handle items which normally are sticky, are given a coating of TFE to prevent this adhesion.

An interesting application involves the use of TFE fabric impregnated with phenolic resins as permanent bearing for automobile steering gear knuckle joints. These are reported not to need normal lubricants.

5. *Moisture Vapor Transmission*

The packaging field has made considerable use of films, particularly those based on chlorotrifluoroethylene. In this case, the primary factors have been relative ease of heat sealing and the extremely low vapor transmission characteristics for both moisture and organic material. Typical example of such a use involves the packaging of sterilized sutures in alcohol solutions. This use replaces glass with considerable greater ease of handling and much less danger of breakage. A significant application has developed for the use of CTFE type films as a protective covering for electroluminescent panel lights. In this application the extremely low moisture vapor transmission of the film combined with toughness and good abrasion resistance offer protection to the sensitive chemical coatings.

6. *Cryogenics*

Many applications in the cryogenic field for the use of both TFE and CTFE plastics have been developed. Of particular note is the fact that these products retain their flexibility even at temperatures as low as liquid hydrogen or liquid helium. In addition, they are not sensitive to impact in the presence of liquid oxygen or highly oxidizing fuel systems. Specific applications involve seats for valves, the valve body itself, lipseals, and a variety of special parts.

Needless to say, these new fluorocarbon-type materials are just in their infancy. With increasing research and development, new and different types are to be expected in the near future. It is obvious that these materials satisfy many requirements which are not met by any conventional hydrocarbon resin.

XIV. Fluorine-Containing Elastomers

A. Introduction to Rubbers

All the synthetic rubbers, as well as natural rubber, are formed from long, flexible chain-like molecules which are usually subsequently crosslinked to form a three-dimensional network. There is approximately one cross link to every few hundred chain atoms in a typical rubber of good properties. Linear polymers of sufficiently high molecular weight also show rubbery properties in a suitable temperature interval. In these cases the "entanglements" between the chains act as transient cross-links, but the linear polymer will flow at sufficiently high temperatures. Unvulcanized natural rubber is a linear polymer which, though rubbery at room temperature, has only limited uses as such because it flows at high temperatures. To make a more useful product, natural rubber must be vulcanized by mixing with various chemical agents, such as sulfur or peroxides, and curing at elevated temperatures.

The most obvious and also the most important characteristic of the rubber-like state is, of course, a high degree of elastic deformability under the action of comparatively small stresses. A typical stress-strain curve for rubber is shown in Fig. 89. The maximum extensibility normally falls within the 500 to 1000% range, with the Young's modulus for small extension of the order of 14 lb per in^{2}(137).

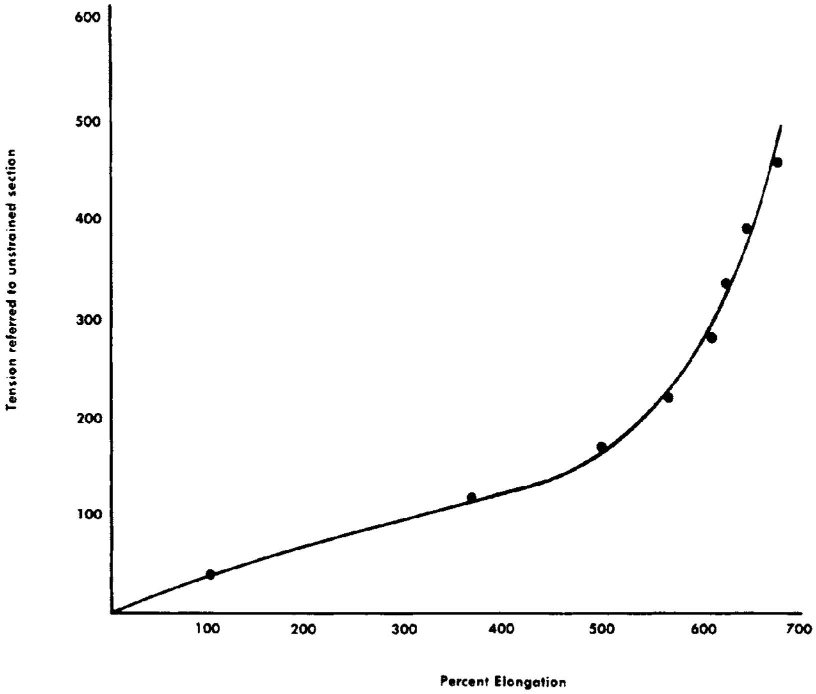


FIG. 89. Typical force-extension curve for a vulcanized rubber.

B. FLUORINE-CONTAINING ELASTOMERS

The outstanding chemical and thermal properties of polymers of tetrafluoroethylene and chlorotrifluoroethylene, together with the increasing importance of ever higher temperatures in military and other applications, have resulted in a very large research and development effort to make fluorine-containing elastomers. Many systems have been studied, but only four have attained any commercial significance. These are:

(1) Copolymers of chlorotrifluoroethylene and vinylidene fluoride ("KEL-F" Brand Elastomers*).

(2) Copolymers of hexafluoropropylene and vinylidene fluoride ("VITON"† and "FLUOREL"* Brand Elastomers).

(3) Homopolymer of 1, 1-dihydrobutylacrylate (lF4 Brand Elastomer*).

(4) Polymer of methyl 3, 3, 3-trifluoropropyl siloxane, viz, $(CF_3C_2H_4Si(CH_3)—O)_n$, ("Silastic LS-53"‡).

C. COPOLYMERS OF CHLOROTRIFLUOROETHYLENE AND VINYLIDENE FLUORIDE

Two elastomers are available, one known as "KEL-F" Brand Elastomer 5500, and the other known as "KEL-F" Brand Elastomer 3700(138,139,140). The former is a 50: 50 copolymer of chlorotrifluoroethylene and vinylidene fluoride, whereas the latter is a 30: 70 of the same monomers. Elasticity has been attained by incorporation of methylene groups, $—CH_2—$, in the normally rigid, highly fluorinated polymer chain.

X-ray diagrams have shown that the polymers are amorphous at temperatures as low as −40°C. On stretching to 300%, typical fiber diagrams are observed, indicating susceptibility to orientation and crystal formation.

TABLE LXV

GUM PROPERTIES OF TYPES 3700 AND 5500 CH_2CF_2 AND CF_2CFCl COPOLYMER ELASTOMERS

Property	Grade 3700	Grade 5500
Specific gravity	1.85	1.85
% Fluorine by weight	50	50
Color	Off-white	Off-white
Shore A hardness	45	45
Tg (°C)	−15	0
Embrittlement temperature (°C)	−64	−51
Tensile properties of pressed gum:		
Tensile strength (psi)	350–600	350–600
Elongation (%)	500–800	500–800
Low temperature stiffness, ASTM D-1053-52T:		
Gehman (°C)		
T_2	−7	+7
T_5	−11	+3
T_{10}	−14	+1

---

*Minnesota Mining and Manufacturing Company, St. Paul, Minnesota.

†E. I. duPont de Nemours and Company, Inc., Wilmington, Delaware.

‡Dow Corning Corporation, Midland, Michigan.

The polymers are stable to temperatures of 227°C, there being no chain scission or halogen loss.

Table LXV gives data on the gum properties of the two copolymers. As can be seen from the data, both polymers contain about 50% fluorine and have embrittlement temperatures below −50°C. Grade 3700 has a glassy state transition temperature of −15°C, while that for Grade 5500 is 0°C. The Gehman temperature show a similar 15°C difference for the two grades.

Both grades of "KEL-F" Elastomer can be mixed with curatives, fillers, and other compounding ingredients on standard rubber processing equipment. Although they can both be banded readily on a rubber mill, the gums do not break down on prolonged milling. Grade 5500 should be milled at 50–65°C, while Grade 3700 should be handled at 75–90°C.

1. *Vulcanization*

Since these polymers do not possess any unsaturation, they are not readily vulcanized by normal rubber curatives such as sulfur. However, they can be vulcanized with organic peroxides, polyamines, polyisocyanates, and isocyanate-amine combinations. A comparison of these curing systems is shown in Table LXVI. From these data it can be clearly seen that peroxide and polyamine cure are to be preferred, both from the standpoint of cure time and physical properties of the vulcanizates(138).

The peroxide vulcanizing system takes advantage of the presence of the hydrogen atoms on the chain, which in a basic system are abstracted by decomposing organic peroxides, thus generating active sites. Under proper conditions, these active chains are interreacted to form —C—C— linkages between chains. The metal oxides in the formula provide the base strength required to accelerate the cure.

Benzoyl peroxide is the most effective and convenient peroxide curative. The recommended curing conditions are 15–30 min at 110–125°C for the initial or molding stage. The press cure is followed by an after-cure in an oven at 150°C for times up to 16 hr depending on thickness.

The other reactive atom on the polymer is the —Cl, which reacts readily with strongly basic, sterically unhindered amines. Of the amines listed, hexamethylene diamine, tetraethylene pentamine, and triethylene tetramine impart the highest tensile strength. With hexamethylene diamine the best balance in stress–strain properties is achieved with three parts of amine. Metal oxides, such as zinc oxide and lead salts, such as dibasic lead phosphate, are used to moderate the amine vulcanization and to neutralize acidic by-products.

Amine stocks should be cured in the press for 0.5 hr at 150–175°C and in the oven at 175°C for 5–16 hr.

TABLE LXVI

CURING SYSTEMS FOR TYPES 3700 and 5500 CH_2CF_2 AND CF_2CFCl COPOLYMER ELASTOMERS

Type of cure— (stock number)	Peroxide 89	Polyamine 282	Isocyanate 1	Isocyanate-amine 98
Compound				
Elastomer 3700	100	100	—	—
Elastomer 5500	—	—	100	100
Zinc oxide	10	10	5	5
Dyphos	10	10	—	—
Benzoyl peroxide	3	—	—	—
MID-100[a]	—	—	5	5
TEPA[b]	—	—	—	1
HMDA[c]	—	3	—	—
Low molecular weight polyethylene[d]	—	0.25	—	—
Cure				
Press (hr/°F)	1/2/300	1/4/350	1/260	1/260
Oven (hr/°F)	16/300	16/300	72/212	16/212
Physical properties				
Stress at 300% elongation (psi)	1300	1500	600	630
Tensile strength (psi)	3500	2000	800	1280
Elongation (%)	500	400	320	580
Hardness (Shore A)	58	58	61	60
Compression set (16 hr at 212°F)	25	29	rupture	rupture

[a] di(4-phenyl isocyante)methane.
[b] tetraethylene pentamine.
[c] Hexamethylenediamine.
[d] Plaskon 8416.

2. *Physical and Chemical Properties*

Among the chemical and heat resistant rubbers, "KEL-F" Brand Elastomers are notable for their high tensile strength (2000–3500 psi), good extensibility (300–600%) and good abrasion resistance. These rubbers have been aged for 60–80 days at 400°F without losing more than 25% of their tensile strength and elongation and with no appreciable increase in hardness.

The high degree of stiffness developed at its corresponding T_g value (0 to -15°C) may be a detriment to some applications of these materials.

The polymers are not affected by fuming nitric acid and the peroxide vulcanizates of Grade 5500 are swelled only about 20–30%. The vulcanizates are also quite resistant to hydrocarbon mineral oils, silicone oils, and silicate-based synthetic fluids. However, the gum and vulcanizates are highly swollen by the diester and phosphate ester-based fluids. The elastomers are also highly swollen by chlorofluorocarbons used as refrigerants and propellants and also fluorocarbon fluids such as FC-75 and FC-43. They are also attacked quite severely by hydrazine and other strongly basic amines. Typical data are included in Table LXVII.

TABLE LXVII

CHEMICAL RESISTANCE OF CH_2CF_2 AND CF_2CFCl COPOLYMER ELASTOMER VULCANIZED (ASTM D-471, Method B; Type 5500, Peroxide Cure)

Media	Time (days)	Temperature (°C)	Volume swell (%)
Red fuming nitric acid	27	25	24
Fuming sulfuric acid	27	25	1
Hydrochloric acid (36.5%)	27	25	16
Phosphoric acid (85%)	27	25	1
Hydrofluoric acid (48%)	32	20	15
Petroleum ether	27	25	13
Ethyl alcohol	27	25	6
Toluene	27	25	55
Aniline	27	25	5
Carbon tetrachloride	27	25	33
Iso-octane/toluene (70/30)	27	25	30
ASTM Oil No. 1	7	150	−2
Silicate ester fluid	14	150	25
Phosphate ester fluid	14	150	70
Diester lubricant	27	25	600
Sour crude	7	150	10
Silicone DC-200	7	150	1
$CF_2ClCFCl_2$	1	25	180

Although the viscosity of the "KEL-F" Elastomers is comparatively high, they can be compression molded, transfer molded, extruded, calendered, dipped, and spread coated using standard rubber processing equipment. Coating and dipping solutions or cements have been made from both Grades 3700 and 5500. Ketones, esters, and cyclic ethers are used as the primary solvents; and aliphatic and aromatic hydrocarbons and alcohols are satisfactory diluents.

3. *Applications*

The "KEL-F" Elastomers have found uses in both unvulcanized and vulcanized states. In the unvulcanized form, it is used as a binder for certain propellant and explosive systems, where the stability, as well as the high density and its high fluorine content, are important. In the vulcanized state, it has found service as a liner for a chemical pump used to pump a variety of corrosive acidic materials including red fuming nitric acid, fuming sulfuric acid, titanium tetrachloride. On handling red fuming nitric acid, it has been reported that a "KEL-F" Elastomer lined pump has been running continuously for 14,700,000 flex cycles without any noticeable swelling or corrosion. It has also found use as seals in systems handling corrosive chemicals including those mentioned above.

As we shall see later, the chlorotrifluoroethylene-vinylidene fluoride copolymer elastomers are superior to other fluorocarbon type elastomers in the area of resistance to strong corrosive mineral acid. The copolymers of hexafluoropropylene and vinylidene fluoride are generally superior to both high and low temperature service as well as general solvent resistance.

D. COPOLYMERS OF HEXAFLUOROPROPYLENE AND VINYLIDENE FLUORIDE

At the present the most useful elastomers of this type are the 20: 80 mole ratio copolymers of hexafluoropropylene and vinylidene fluoride. These elastomers are available commercially under the trade names, "VITON" Fluorocarbon Elastomer (E. I. duPont de Nemours & Co., Inc.) and "FLUOREL" Brand Elastomer (Minnesota Mining and Manufacturing Company). They are usable over the wide temperature range of −50° to 300°C.

TABLE LXVIII

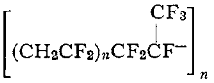
TYPICAL RAW GUM PROPERTIES OF C_3F_6,CH_2CF_2 COPOLYMER ELASTOMERS

Specific gravity	1.85
% Fluorine by weight	>60%
Color	off-white
Hardness (Shore A)	40
Embrittlement temperature	−45
Low temperature stiffness ASTM D1053-52T)	
Gehman	
T_2	−10°C
T_5	−15°C
T_{10}	−17°C

Typical properties of the raw gum stock are included in Table LXVIII.

1. *Vulcanization*

The copolymer structure consists of alternating methylene and difluoromethylene groups interspersed with very short branched fluorocarbon chains, the latter resulting from the hexafluoropropylene molecule. The structure may be represented as:



$$\left[(CH_2CF_2)_nCF_2\overset{CF_3}{\overset{|}{C}}F-\right]_n$$

The chemical stability conferred by this structure, while valuable in the cross-linked molded elastomer, makes the problem of forming cross links difficult(141).

Three general methods are known by which cross links may be introduced into these elastomers. They are: (1) the action of aliphatic amines; (2) the action of high energy radiation; and (3) the action of peroxides. For this class of elastomers the action of amines is by far the most important. Except for some specialty peroxide cures, all the commercial curing formulations contain organic bases of some kind.

Smith has shown that the cross linking of C_3F_6 and $CH_2=CF_2$ copolymers takes place by a three-stage process(142). Bases, high energy radiation, and other radical generators, in conjunction with metal oxides, react with the elastomer chain at the poly(vinylidene fluoride) segments to form double bonds. During press cures at or around 150°C difunctional cross-linking agents such as diamines or dithiols may react with these double bonds to form some partially cross-linked structures. During the oven post-curing cycle at 200°C, conjugated double bonds systems are formed by dehydrofluorination at points adjacent to the double bonds formed in the first stage. These unsaturated centers then react to form direct carbon to carbon linkages between chains. The resulting vulcanizate is largely stable to heat, the centers of instability having been removed by the oven cure. For example, these rubbers maintain their properties well even when subjected to temperatures of 300°C for times up to 100 hr.

Oven post-curing is recommended for all fluorocarbon elastomers, not because good properties cannot be obtained by a direct press cure, but because the centers of instability produced during press curing must be removed in order to obtain a vulcanizate which is stable at high temperature. After the post cure, subsequent heating of the vulcanizate at 200°C for prolonged periods of time causes no further degradation or cross-linking.

Amine cures are the best method for processing the polymer to a vulcanizate which is stable, both to high temperatures and to chemical attack, and has the best obtainable physical properties. Amine compounds such as the carbamates and diamines confer additional advantages of processibility and are thus preferred.

2. *Compounding*

The gum can be easily compounded on a two-roll mill and can be successfully extruded on standard rubber tubers. A typical general purpose compound with good mechanical properties is shown in Table LXIX.

TABLE LXIX

General Purpose Formula and Properties for C_3F_6,CH_2CF_2 Elastomers

Recipe	Parts by weight
Base Elastomer	100
Magnesium oxide	20
Medium Thermal Carbon black	15
Hexamethylene diamine Carbamate	1
Cure	
½ hr in press	150°C
24 hr in oven	205°C
Properties at 25°C	
Stress at 100% elongation	320 psi
Tensile strength	2300 psi
Elongation (%)	320
Hardness (Shore A)	65
Tear strength	180 lb per in.

The formula represented in the above Table has a Mooney scorch rating of 8 min to a 10-point rise. For safer processing, modifications can be made so as to increase the scorch rating to the 20–30 min range for a 10-point rise(144,145,146).

All compounds for these elastomers contain at least three different types of compounding ingredients. These are acid acceptors, fillers, and curing agents. Plasticizers may also be used. Metal oxides such as magnesium and lead and combinations of zinc oxide and dibasic lead phosphate are commonly used as acceptors. A number of fillers, including both carbon black and mineral fillers, can be used. Generally, smaller amounts of filler are used than in conventional elastomers to avoid excessive stiffness.

A wide variety of polyamines will cure the $C_3F_6,CH_2=CF_2$ elastomers, but one of the most practical is the hindered polyamine, hexamethylene carbamate. Since this curing agent tends to react rapidly, to increase processing safety a copper inhibitor (retarder) is used in some formulas.

Peroxides, such as benzoyl peroxide, will also cure these elastomers but with some difficulty encountered in preventing porosity in the vulcanizate. Peroxide cured stocks generally have poor compression set resistance, but do exhibit good resistance to red fuming nitric acid. A high state of cure can also be developed by exposure to high intensity beta or gamma radiation. For example, a β-radiation dosage of 1×10^7 REP followed by heating at 200–250°C yields physical properties comparable to those obtainable with benzoyl peroxide.

3. *Physical Properties and Chemical Resistance of Vulcanizates*

In Table LXIX are included typical values for some of the physical properties of the vulcanizate. Table LXX shows the per cent swell of a

TABLE LXX

Chemical Resistance of C_3F_6,CH_2CF_2 Elastomers in Vulcanized State, Polyamine Cure (seven-day immersion)

Media	Temperature (°C)	Volume swell (%)
Sodium hydroxide (46.5%)	25	2.1
Fuming Sulfuric acid	25	4.8
Hydrofluoric acid (48%)	25	4.8
Hydrochloric acid (36.5%)	25	7.3
Glacial acetic acid	25	61.6
Red fuming nitric acid	25	74.0
Carbon tetrachloride	25	1.3
Ethyl alcohol	25	1.7
Aniline	25	3.0
Benzene	25	19.6
Tricresyl phosphate	300	24.0
Methyl ethyl ketone	25	287.0
Isooctane-toluene (70/30)	25	2.5
ASTM#3 Oil	300	4.3
Silicate ester fluid	300	1.8
Silicate ester fluid	400	11.1
Diester lubricant	400	19.6
Phosphate ester fluid	300	270.0

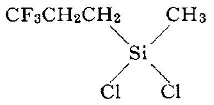
polyamine-cured vulcanizate, after seven-day immersion in the medium at temperatures specified. It will be noted that the solvent resistance is generally very good with the exception of ketones and a phosphate ester fluid. Another outstanding characteristic is ability to recover following compression at 150–200°C.

4. *Applications*

The $C_3F_6,CH_2=CF_2$ elastomers are relatively easy to process and also the vulcanizates possess good all-round physical properties. They have useful properties between the temperature extremes of $-50°C$ to 300°C and generally resist chemical and solvent attack. Consequently, these elastomers have attained considerable commercial usage for both military and civilian applications. Included among the many applications are O-rings, seals for valves, seals for contact with aircraft fuels and automotive transmission fluids, aircraft and industrial hose, pump components, tank linings, and gasketing materials.

E. FLUORINE-CONTAINING SILICONE RUBBER

The commercially available product is derived from the fluorine containing silane,



and is designated as "Silastic LS-53". (Dow Corning Corporation). This product has the typical very low operating temperatures of silicone rubbers; it can be used over the range $-70°C$ to 250°C.

TABLE LXXI

PROPERTIES OF FLUOROSILICONE RUBBER

Specific gravity	1.4
Hardness (Shore A)	50
Tensile strength (psi)	800
Elongation (%)	250
Brittle point	−68°C
Low temperature stiffness	
Gehman	
T_2	−18°C
T_5	−47°C
T_{10}	−60°C

The polymer consists of long chains of alternate silicon and oxygen atoms, heat stable groups being attached to each silicon atom.

The commercial product is supplied as a fully compounded material, which can be vulcanized in 5 min at 125°C. The recommended post oven cure is 24 hr at 150°C. Typical properties of the cured elastomer are shown in Table LXXI.

TABLE LXXII

SOLVENT RESISTANCE OF FLUOROSILICONE ELASTOMER

Media	Conditions	Volume swell (%)
Iso-octane	7 days at 25°C	+15
Xylene	7 days at 25°C	+19
Carbon tetrachloride	7 days at 25°C	+21
Ethyl alcohol	7 days at 25°C	+5
Acetone	7 days at 25°C	+180
Iso-octane/toluene (70/30)	3 days at 25°C	+20
ASTM oil # 3	3 days at 150°C	300
Diester lubricant	3 days at 175°C	+5
Phosphate ester	3 days at 120°C	+11
Silicate ester	3 days at 175°C	−5

The fluorine-containing silicone elastomer has much improved solvent resistance over the general purpose silicone elastomers. Typical data are shown in Table LXXII.

1. *Applications*

The fluorine-containing silicone elastomer has found application in certain seals for aircraft where a combination of solvent resistance and extreme low temperature flexibility are important. It is generally, however, not as serviceable as the $C_3F_6,CH_2=CF_2$ elastomers(150).

F. FLUORINE-CONTAINING ACRYLATE ELASTOMER

The homopolymer of 1, 1-dihydroheptafluoroacrylate was introduced commercially as "FLUORORUBBER 1F4" by Minnesota Mining and Manufacturing Company. The best physical properties are attained by the use of polyamines as curing agents. A typical recipe is shown in Table LXXIII.

This elastomer has considerably lower tensile strengths than the $C_3F_6,CH_2=CF_2$ elastomers. It has a maximum useful temperature range of −13°C to 200°C.

TABLE LXXIII

CHARACTERISTICS OF 1, 1,-DIHYDROPERFLUOROBUTYL ACRYLATE ELASTOMER

Recipe	Parts
Polymer	100
Stearic acid	1
Sulfur	1
Carbon black	35
Triethylamine tetramine	1
Cure—60 min at 155°C	
Physical properties at 25°C	
Specific gravity	1.54
Tensile strength	1250 psi
Elongation	300%
Hardness (Shore A)	55
Gehman Stiffness, T_{10}	−9°C
Brittle point	−7°C

TABLE LXXIV

CHEMICAL RESISTANCE OF 1, 1,-DIHYDROPERFLUOROBUTYL ACRYLATE ELASTOMER

Media	Conditions	Volume swell (%)
Benzene	72 hr at 25°C	25
Acetone	72 hr at 25°C	60
Iso-octane/toluene (70/30)	72 hr at 25°C	15
ASTM oil # 3	72 hr at 150°C	0
Diester base oil	500 hr at 150°C	6
Phosphate ester	100 hr at 100°C	25
Silicate ester	750 hr at 150°C	15
Hydrochloric acid (36.5%)	72 hr at 25°C	5
Concentrated nitric acid	72 hr at 25°C.	49
Concentrated sulfuric acid	72 hr at 25°C	100
Sodium hydroxide (50%)	72 hr at 25°C	60

It has been reported that cross-linking occurs in this polymer at unesterified acrylic acid monomer units, which are present in the original monomer or are formed during the curing process(151,152).

The chemical resistance is illustrated in Table LXXIV.

1. *Applications*

"Fluororubber IF4" is inferior to $C_3F_6,CH_2=CF_2$ elastomers in flexibility at low temperatures, is much inferior at high temperature, and is attacked much more by concentrated nitric and sulfuric acids. It has, however, the greatest resistance to a wide range of solvents of any of the fluoroelastomers. It has found limited use in specialty military service in diester type lubricants.

XV. Missiles and Rockets

A. PRINCIPLES GOVERNING JET ENGINES

In general, jet engines are propellant devices which are based on Newton's Third Law of Motion which states that the mutual action of any two bodies are always equal and opposite. The propulsive force is generated in these devices by the reaction of masses which are ejected in a direction opposite to the direction of motion of the device. The ejection of mass requires a source of energy and then the conversion of this energy into kinetic energy of the mass to be ejected. Although there are many sources of energy which offer considerable promise, including nuclear reactions, solar radiation and charged ions, to date the chemical propellants are the most highly developed.

The development of missile and rocket devices has been characterized by requirements for increased performance from the propellant system. Fluorine is an especially attractive component of a rocket system since its oxidizing power is the highest of any known element. The energy release with fluorine is also favorably effected because of the low molecular weight of the combustion products. In recent years research and development work has been very extensive, and it appears that liquid fluorine is quite practical to use. In addition, the theoretical performance of liquid fluorine and other fluorine compounds has been clearly demonstrated(153,157). An excellent summary of recent work is given by Kit and Evered(154).

Newton's Second Law of Motion states that force is proportional to the time rate of change of momentum. This law is a convenient method for the evaluation of rocket engine thrust. Assuming steady state operation, with both propellant flow rate and exhaust velocity being constant, then the thrust, F, is given by the following equation:

$$F = \frac{WC_e}{g} + A_e(p_e - p_a) \tag{18}$$

where

W = propellant flow rate, lb per sec
C_e = exhaust velocity, ft per sec
g = gravitational acceleration, ft per sec^2
A_e = nozzle exit area, ft^2
p_e = nozzle exhaust pressure, psi
p_a = ambient pressure, psi

In the theoretical calculations the thrust is greatest when $p_e = p_a$, hence,

$$F = \frac{WC_e}{g} \tag{19}$$

The specific impulse I_{sp} is defined as the thrust in pounds force resulting from the expulsion of one pound mass per second.

$$I_{sp} = \frac{F}{W}\left(\frac{\text{lb force-sec}}{\text{lb mass}}\right). \tag{20}$$

Pounds force and pounds mass are generally canceled, and hence, I_{sp} is expressed in seconds.

Combining equations (19) and (20) above, the equation for specific impulse takes the form,

$$I_{sp} = \frac{C_e}{g}\text{ sec} \tag{21}$$

Using the law of conservation of energy, it can be easily shown that the specific impulse is related to the heat energy made available for propulsion by the following equation:

$$I_{sp} = \sqrt{2\frac{J}{g}(h_c - h_e)} = \sqrt{\frac{2J\Delta H}{\bar{M}}}, \tag{22}$$

where

h_c = specific enthalpy of propellant gases within rocket chambers, BTU per lb
h_e = specific enthalpy of gases after they have been discharged from rocket nozzle, BTU per lb
J = mechanical equivalent of heat, 778 ft lb per BTU
ΔH = heat per mole released during expansion, BTU per mole
$\bar{M}$ = average molecular weight of the gases, lb per mole.

According to the Eq. (22) above, the specific impulse obtained from a chemical propellant is proportional to the square root of the heat made available by the operation of the rocket.

Usually the chemical reaction consists in burning a fuel with an oxidizer, but there are certain types of monopropellants which develop heat by decomposing into simpler products. In general, the combustion process can be visualized as starting with the disruption of molecules into atoms, and a concomitant absorption of energy, followed by combination of the atoms with the products of combustion, resulting in the release of energy. Values for the energy released in a number of oxidation processes is given in Table LXXV(156).

TABLE LXXV

LIBERATION OF HEAT DURING OXIDATION PROCESSES(156)

Reaction	Heat released kcal per gm mole
$H_2 + \frac{1}{2} O_2 \rightarrow H_2O$ (g)	57.8
$\frac{1}{2} H_2 + \frac{1}{2} F_2 \rightarrow HF$ (g)	64.2
$\frac{1}{2} H_2 + \frac{1}{2} Cl_2 \rightarrow HCl$ (g)	21.9
$B + 1\frac{1}{2} F_2 \rightarrow BF_3$ (g)	256.9
$2 Al + 1\frac{1}{2} O_2 \rightarrow Al_2O_3$ (c)	398.0
$Al + 1\frac{1}{2} F_2 \rightarrow AlF_3$ (g)	329.0[a]
$Si + 2 F_2 \rightarrow SiF_4$ (g)	360.1
$2 P + 2\frac{1}{2} O_2 \rightarrow P_2O_5$ (c)	360.0[a]

[a] This is not a good value for propellant systems, since AlF_3 (c) never occurs as a solid in the exhaust of a conventional rocket. Also entropy effects cause dissociation of complex molecules such as AlF_3, SiF_4, and P_2O_5.

Equation (22) also indicates that the specific impulse increases with decreasing molecular weight of the products. This requirement makes it practically always desirable to operate at a fuel-rich mixture ratio, so that some of the hydrogen contained in the fuel remains as such in the combustion products.

In general, there are a number of requirements which govern the choice of efficient rocket propellants, viz.:

(1) A high heat value in order to give high specific impulse.

(2) Low molecular weight of the combustion products.

(3) A high heat of combustion per unit volume in order to permit reducing the size of the rocket.

(4) High heat capacity of combustion products.

(5) Combustion products in a gaseous form, in order to insure satisfactory conversion of heat energy into kinetic energy.

There are, of course, many other operational or economic requirements specific to both solid and liquid propellant systems.

B. LIQUID PROPELLANTS

Liquid propellant power plants delivering one million or more pounds of thrust are now being constructed and tested. These developments have not been without difficulties; in fact, liquid propellant rocket engines are extremely complex devices, and the propellants used frequently present serious handling problems(158).

TABLE LXXVI

THEORETICAL PERFORMANCE OF SOME LIQUID PROPELLANTS

Oxidizer	Fuel	O/F ratio (weight)	I_{sp} (sec)
HNO_3 (red fuming)	JP-4	3.50	242
HNO_3 (red fuming)	Hydrazine	1.20	260
H_2O_2	JP-4	7.00	243
H_2O_2	Hydrazine	1.89	256
ClF_3	Hydrazine	2.20	246
N_2O_4	Hydrazine	1.03	266

A liquid propellant, by definition, is one which is introduced into the combustion chamber as a liquid. Most liquid propellant rocket engines now in operation use liquid bipropellant systems, consisting of a liquid oxidizer and a liquid fuel, each of which is injected separately. Liquid bipropellant systems may be divided into two classes, spontaneously (hypergolic) or nonspontaneously ignitable systems. The hypergolic systems ignite spontaneously on contact in the combustion chamber, whereas the nonspontaneous systems require suitable igniters.

In Table LXXVI are shown the specific impulse values for a number of presently used liquid propellant systems.

C. SOLID PROPELLANTS

The main advantage of solid propellant rockets over liquid propellants is their simplicity. They have no moving parts, no tanks, no injection systems, and they require as a rule, no cooling. They do not have to be fueled before launching. As a result, they are easily stored, handled, and fired.

Solid propellant rockets also have a number of disadvantages in comparison to liquid propellant rockets. They have in general a lower performance, poor thrust control, and precise termination is difficult. However, improvements are rapidly being made in these deficiencies, and solid propellant rocket systems are often first choice because of specific rocket requirements and usage.

A typical solid propellant rocket engine has three parts: (1) the propellant grain; (2) the igniter; and (3) hardware. The hardware includes the combustion chamber and exhaust nozzle.

There are several important characteristics of solid propellants which must be considered, among the most important of which are linear burning rate, rate of propellant consumption, grain shape, and thrust(154).

Besides the general requirements for rocket propellants reviewed earlier, a solid propellant must also possess good mechanical properties, which must be uniform through the grain and must be maintained over the temperature ranges involved during storage or actual operation.

D. Elemental Fluorine

Elemental fluorine is the most powerful of all chemical rocket oxidants, which have been investigated in the U.S.A. This element has maximum energy release during combustion and at the same time maintains low molecular weight of the combustion products. With hydrazine, which is a noncarbonaceous material, the specific impulse, I_{sp}, is substantially higher than with systems using O_2 or O_3. With carbonaceous fuels, such as JP-4 or gasoline, CF_4 forms during combustion and decreases performance. Hence, it is good practice to use mixtures of fluorine and oxygen with sufficient oxygen to oxidize the carbon, thus leaving free fluorine to react with hydrogen.

The specific gravity of liquid fluorine is considerably greater than that of liquid oxygen or liquid ozone; viz., the specific gravity of fluorine is 1.51, while that of oxygen is 1.14, and ozone is 1.46 at normal boiling points. This is also a favorable factor in the performance of fluorine in rocket fuels. Experience indicates that fluorine is hypergolic upon contact with all practical fuels, thus obviating special ignition systems. Therefore, in addition to the higher performance, fluorine-powered rockets may be mechanically simpler and more reliable than their oxygen counterparts.

Table LXXVII gives the theoretical performance of fluorine with various fuels. Comparison with the data given previously in Table LXXVI shows that the use of fluorine as an oxidizer results in a fifty per cent increase in specific impulse of conventional liquid systems. A direct comparison between liquid fluorine and liquid oxygen is shown in Table LXXVIII.

In spite of the extreme reactivity of elemental fluorine, it may be safely stored and handled using common construction materials. In the case of most metals, a metal fluoride film is formed which protects the base metal from further attack. Metals which may be used safely with fluorine even

TABLE LXXVII

THEORETICAL PERFORMANCE OF FLUORINE WITH VARIOUS FUELS

Fuel	O/F ratio	Bulk (Specific gravity)	Specific impulse
H_2	4.5	0.32	373
Li	2.19	0.83	335
N_2H_4	2.0	1.30	318
B_2H_6	5.0	1.07	309
NH_3	3.0	1.16	307
CH_3OH	2.37	0.99	297
JP-4	2.9	1.19	280

TABLE LXXVIII

COMPARISON OF THEORETICAL PERFORMANCES OF FLUORINE AND OXYGEN WITH VARIOUS FUELS(159,160,161)

Fuel	I_{sp} with fluorine	I_{sp} with oxygen
JP-4	276	262
NH_3	320	268
N_2H_4	324	281
H_2	376	363

at elevated temperatures include nickel, Monel, copper, aluminum, and steel. High silicon-containing alloys are not recommended due to the liberation of the gaseous SiF_4. The fluorocarbon plastics, polytetrafluoroethylene and polychlorotrifluoroethylene, are satisfactory for use at relatively low combustion temperatures and pressures. Similarly, fluorocarbon type oils and greases are useful as lubricants under certain temperature and pressure conditions.

For rocket fuel use, fluorine can be supplied as a liquid. Transportation and storage involve the use of tanks which are similar to those used for transportation and storage of liquid oxygen. Although the handling of liquid fluorine is generally the same as for liquid oxygen, some basic differences, particularly in regards to venting the atmosphere, must be noted. In the case of fluorine, venting to the atmosphere must be avoided and, hence, systems which are closed to the atmosphere must be used with equipment for condensing the gaseous fluorine boil-off. Also rocket exhaust gases from fluorine combustions require special handling since HF is one of the principal products. This can usually be readily accomplished by washing with water, chemical neutralization, or if at high altitudes of outer space, simple dilution in the atmosphere. Since the spillage of liquid fluorine would also be a hazard, designs are usually best which prevent spills as much as possible.

E. Compounds of Fluorine

A number of compounds of fluorine have been considered as oxidizers due to their ease of handling, and because of this, may offer advantages over liquid fluorine. Included among the most important are chlorine trifluoride, ClF_3; perchloryl fluoride, ClO_3F; nitrosyl fluoride, NOF(167); nitryl fluoride, NO_2F(167); nitrogen trifluoride, NF_3; dinitrogen tetrafluoride, N_2F_4; and difluorine monoxide, F_2O.

1. *Chlorine Trifluoride*

Chlorine trifluoride offers most of the qualities of liquid fluorine in terms of performance with fewer storage and handling problems because of its higher critical temperature and boiling point. This compound has a boiling point of 11.3°C. It also has a high specific gravity, namely, 1.82 at 20°C. ClF_3 can be prepared by a one-step process whereby chlorine and fluorine gases are passed through a reaction chamber filled with silver-plated copper chips at 280°C. It is estimated that a large volume of production chlorine trifluoride could be made for less than $1 per lb.

Handling and storage of ClF_3 requires much the same precautions as for fluorine with obvious care to avoid contact with organic compounds including greases, oils, paints, etc. The general toxicology is also very much like fluorine(162,163,164).

2. *Perchloryl Fluoride*

Perchloryl fluoride, ClO_3F, is a colorless gas with a sweet odor. It is one of the fluorine compounds which offers some of the attractive features of liquid fluorine, in terms of reactivity, while presenting much fewer problems of storage, handling, and toxicity. It boils at −46.8°C and has a density of 1.66 at the boiling point. ClO_2F is not sensitive to shock and is not flammable. However, it readily supports combustion and forms flammable and explosive mixtures with oxidizable vapors. When dry, ClO_3F can be stored in glass or metal systems; when wet, however, it is very corrosive. This compound is much lower in performance in rocket systems than liquid fluorine(165,166).

3. *Nitrogen Trifluoride*

Nitrogen trifluoride, NF_3, is a colorless gas which is much more stable than other nitrogen-containing halides. It is also relatively easy to prepare and hence, potentially inexpensive. NF_3 does not react with water, caustic alkalies, etc. It is best prepared by the electrolysis of molten ammonium bifluoride at as low temperatures as possible. Purification can be accomplished by passing over manganese dioxide. It has a boiling point of $-129°C$(168).

4. *Dinitrogen Tetrafluoride*

The compound, N_2F_4, has recently been prepared and appears of definite interest as a rocket fuel(169).

F. Solid Propellants

There would appear to be advantages to be gained by incorporating fluorine compounds in the binders of solid propellant systems, particularly those which contain light metals such as lithium, aluminum, or boron, and hydrogen-containing compounds.

The early solid propellants were adapted from the explosives industry and consisted of materials compounded from nitroglycerine and nitrocellulose. These materials formed the basis for present-day *double-base* propellants. Other oxidizing materials, such as potassium perchlorate and ammonium nitrate, were mixed with various liquids, such as asphalt and tars, which would harden upon standing or heating. These propellants became known as composites.

More suitable substitutes for the asphalts and tars have been developed in the form of polymerizable binders, including butyl and thiokol-type elastomers, polyurethanes, polyacrylates, polydienes, etc. Initially, the composites consisted primarily of an oxidizing salt held togeher with the polymerizable binder. Recently, the addition of a light metal, such as aluminum in a finely divided state, to both the double-base and composite propellants has improved their performance. The increase has been chiefly due to the high energy per unit weight resulting from the combustion of the aluminum to its oxide. This energy heats the combustion gases to a higher temperature than that produced by the binder and oxidizer present.

As was reviewed earlier, the important parameter for propellant energy is the maximum value for the expression in Eq. (22). This means propellant ingredients must include compounds that will yield high heat of reaction with low molecular weight combustion gases, together with a minimum amount of solid or liquid particles.

To obtain a solid propellant which will yield a high performance, the following criteria must be met:

(1) The material must have a high heat of reaction per unit weight.

(2) The amount of liquid or solid particles formed during the combustion process must be small.

(3) All propellant ingredients should enter the combustion process and contribute to the available energy.

(4) The average molecular weight of the gases must be low.

The search for suitable gaseous metal combustion products with high available energies again leads to the fluorine atom. Most metal oxides have high vaporization temperatures and are solids or liquids at rocket combustion temperatures. The metal fluorides, on the other hand, are usually present in a highly stable gaseous form at these same temperatures. Therefore, the chief advantage of using fluorine in a solid-propellant formulation is the resultant formation of highly energetic gaseous metal fluorides as exhaust products. Table LXXIX gives the heats of formation of some light metal oxides and fluorides.

TABLE LXXIX

HEATS OF FORMATION OF SEVERAL LIGHT METAL OXIDES AND FLUORIDES(170)

Oxide	$H_{298°K}$	Fluoride	$H_{298°K}$
Li_2O	−142	LiF (c)	−146
BeO (c)	−146	BeF_2 (c)	−227
B_2O_3 (c)	−302	BF_3 (g)	−265
MgO (c)	−143	MgF_2 (c)	−264
Al_2O_3 (c)	−399	AlF_3 (c)	−356

It might appear that a fluorocarbon might not contribute in a positive fashion to the energy output due to the very stable C—F bond. However, when utilized in a propellant formulation as a binder for other oxidizing and reducing components, it is the net available energy which is of importance. Consequently, when light metals are added to binder systems which contain both C—F and C—H bonds, it is possible to show a net increase in energy release, due to the formation of HF or metal fluorides. When a fluorocarbon binder is used in a rocket propellant system, there should be other favorable effects. In the first place, the higher atomic weight of fluorine, 19, vs that of hydrogen, 1, decreases the concentration of the relatively ineffective carbon atoms in the system. In addition, the fluorocarbons have higher densities and are thermally more stable than hydrocarbons.

It may be anticipated, therefore, that future research will see the development of new types of polymerizable fluorine-containing materials for use in solid propellant rocket propulsion systems.

XVI. Catalysis

A. Hydrogen Fluoride

1. *Physical and Chemical Properties*

As has been pointed out by Simons, the chemical and physical properties of hydrogen fluoride do not follow those of other hydrogen halides—HI, HBr, or HCl(173). In general, the properties of hydrogen fluoride are more closely related to water and ammonia than the other hydrogen halides. This is shown in Table LXXX.

TABLE LXXX

Comparison of Physical Properties(173)

	Freezing point °C	Boiling point °C	Molar heat of fusion kcal	Molar heat of vaporization kcal	Dielectric constant
HF	−83	19.9	1.09[a]	6.02[b]	85.3 (0°)
HCl	−114	−85.8	0.50	3.6	4.60 (27.7°)
HBr	−86	−67.1	0.62	4.0	3.82 (24.7°)
HI	−53.6	−36.0	0.72	4.4	2.9 (21.7°)
H_2O	0	100	1.34	9.72	80 (20°)
NH_3	−77	−38.5	1.84	5.6	14.9 (24.5°)

[a] For 20 gm.

[b] For 63.36 gm from vapor pressure curve. Calorimetrically measured value is 97.5 cal per gm. This varies with both temperature and pressure. See the "Heat of Vaporization of Hydrogen Fluoride" by Simons and Bouknight.

The high dielectric constant enables hydrogen fluoride to be a good solvent for salts, and the resulting salt solutions are good conductors of electric current. Hydrocarbons and similar nonpolar liquids are not usually soluble in a liquid of this type. Anhydrous hydrogen fluoride, however, is a very strong acid, and all compounds capable of exhibiting basic character in it are made soluble through chemical interaction. As a consequence, many organic compounds that are only very slightly soluble in water are soluble in hydrogen fluoride. For example, alcohols, phenols, carboxylic acids, etc., act as bases to hydrogen fluoride and hence form ionizing salts. Examples are:

$$CH_3COOH + HF \rightleftharpoons CH_3CO_2H_2^+ + F^- \qquad (23)$$

$$C_2H_5OH + HF \rightleftharpoons C_2H_5OH_2^+ + F^- \qquad (24)$$

Of the three liquids, ammonia, water, and hydrogen fluoride, ammonia is the most basic, while hydrogen fluoride is the most acidic.

In the vapor state, hydrogen fluoride exists in a number of molecular forms one of which has an apparent formula, H_6F_6(174) (see Chapter 1).

While anhydrous hydrogen fluoride is a very strong acid, when dissolved in water it exhibits the properties of a weak acid. Hydrogen fluoride is also a very powerful dehydrating agent for free water. It also forms a wide variety of molecular complexes, some of which are very strong.

2. *Catalytic Effects*

The first disclosure of the use of hydrogen fluoride as a catalyst for an organic reaction was made by Simons(175).

Simons and co-workers have published a series of papers on the general subject of hydrogen fluoride as a condensing agent. A good review of this work has been published(176).

a. Alkylation. One of the reactions for which hydrogen fluoride is a very effective catalyst is alkylation. This is essentially the preparation of a product that contains one or more alkyl groups in its molecules than were in the molecules of the source material. Using hydrogen fluoride, it was found that a great many source materials could be alkylated and that many materials could be used to supply the alkyl groups including alkyl halides, olefins, alcohols, esters, ethers, etc.

As an example, benzene may be reacted with butyl chloride. In the case of tertiary butyl chloride, the reaction takes place at 0°C; if secondary butyl chloride, at 25°C; and if *n*-butyl chloride at 100°C. In these reactions, the hydrogen chloride escapes as a gas, and only a relatively small amount of hydrogen fluoride is necessary for the reaction.

Benzene may also be alkylated using an olefin. Butylene or propylene may be reacted at relatively low temperatures. As the olefins polymerize readily, they are added with stirring to the benzene; hence, the alkylation will proceed much more rapidly than the polymerization.

Alcohols may also be used to alkylate benzene; tertiary alcohols react most readily; and primary the least. Considerably more hydrogen fluoride is required when alcohols are used than when alkyl halides or olefins are used. In the first place water is formed which tends to dilute the hydrogen fluoride; and secondly, alcohols tend to add hydrogen fluoride; both of these reduce the catalytic activity.

When an ester is used, such as propyl acetate, the reaction proceeds in a manner similar to propyl alcohol; however, in this case, acetic acid is produced in place of water.

Ethers may also be used to alkylate benzene; for example, dipropyl ether will react in either of two ways—it may react so as to add one propyl group, leaving propyl alcohol as a by-product. On the other hand, it may also react so as to add two propyl groups, leaving only water as the product.

It is not necessary to use highly purified compounds, for common impurities do not deactivate the catalytic action of hydrogen fluoride. The catalyst is readily recovered. The equipment is relatively simple. In general, the yields are very high with little loss of product due to side reactions.

Any substance that contains atoms of hydrogen that are sufficiently active for replacement reactions can be reacted. This includes phenols, naphthalene, and many other aromatic compounds.

b. Acylation. Hydrogen fluoride is also an effective catalyst for acylation. For example, benzene may react with a carboxylic acid, an acid halide, an acid anhydride, or an ester. For either alkylation or acylation reaction, the group introduced into the benzene ring goes primarily into the para position.

c. Rearrangements. Hydrogen fluoride can also be used as a catalyst for such reactions as ring closures and rearrangements. It is also a useful catalyst in sulfonation. Benzene reacts with sulfuric acid in the presence of hydrogen fluoride to form benzene sulfonic acid. At higher temperatures diphenyl sulfone is formed. For example, in the presence of hydrogen fluoride, toluene reacts with benzene sulfonic acid to form the mixed sulfone, *p*-tolyl phenyl sulfone.

d. Nitration. Hydrogen fluoride also catalyzes nitration. Nitric acid reacts with benzene at subzero temperatures to form mononitrobenzene.

e. Commerical Usage. On a commercial scale, hydrogen fluoride has achieved its largest usage in the alkylation of isoparaffins, which are important in producing high octane aviation and automotive gasolines.

B. TRIFLUOROACETIC ACID AND ANHYDRIDE

1. *Properties*

Trifluoroacetic acid is a very strong acid, comparable in strength to the mineral acids such as HCl(177,178). This strong acidity is due to the presence of the trifluoromethyl group with its strong electron attracting power. Trifluoroacetic acid also has high solvent power for many materials. It is reported to have good solvent power for halogens(179).

Many salts are dissolved in trifluoroacetic acid. It also readily dissolves proteins; upon evaporation of the solvent, the proteins were recovered in a water soluble condition(180). Trifluoroacetic acid is an excellent solvent for specific polymers. Its use to dissolve terephthalate polyesters has been described(181).

2. *Catalytic Effects*

Trifluoroacetic acid has been reported to be an excellent catalyst for certain organic reactions. Morgan found that CF_3COOH effectively catalyzed the esterification of many alcohols as well as cellulose with acetic anhydride(182,183).

Coover *et al.*, found that CF_3COOH or its anhydride promoted the esterification of polyvinyl alcohol without the introduction of CF_3CO-groups into the polymer(184).

C. BORON TRIFLUORIDE

1. *Properties*

Boron forms the very stable compound, BF_3, with fluorine. It is noteworthy that the B—F bond is reported as having a bond energy of 140.6 kcal per mole, compared to 116 kcal per mole for the C—F bond. BF_3 boils at $-101°C$ and has a melting point of $-130.7°C$. It is very soluble in water and like silicon tetrafluoride is only partially hydrolyzed to fluoroboric acid, HBF_4. BF_3 is soluble in most organic liquids; for example, it is soluble in *n*-pentane to the extent of 30 gm per liter at 55°C and 3 atm pressure. It forms coordination compounds with a very large number of organic nitrogen and oxygen compounds, such as ammonia, amines, hydrocyanic acid, ethers, aldehydes, and ketones. This power of coordination undoubtedly accounts for the effectiveness of boron trifluoride as a catalyst in many organic reactions.

2. *Catalytic Effects*

BF_3 as a catalyst resembles aluminum chloride in the Friedel-Crafts reaction(185). However, instead of occurring with organic halides with the elimination of HCl, BF_3 acts with oxygen compounds such as alcohols, ethers, esters and splits off water.

Boron trifluoride is effective as a catalyst in the formation of esters from alcohols and acids; ethers + acids; and alcohols + amides(186). It is also effective in transferring an alkyl or an acyl group from an oxygen attachment to one with carbon. Many examples of this are reported in the literature(186).

BF_3 will also catalyze direct additions to olefins. For example, propylene can be added to acids to form isopropyl esters; olefins can also be reacted with benzene to form alkyl substituted benzene. BF_3 will also catalyze the polymerization of olefins.

Isomeric changes can also be catalyzed by BF_3 in a manner similar to $AlCl_3$. Examples are the Beckmann reaction, the benzidine transformation, and the equilibrium of cis- and *trans*-stilbene(186).

Boron trifluoride is used extensively in organic synthesis, based primarily on reactions of the type listed above.

BIBLIOGRAPHY

1. Stacey, M., Tatlow, J. C., and Sharpe, A. G. (1961). *Advances in Fluorine Chem.* **2,** 35.
2. Weyl, W. A. (1950). "Fluorine Chemistry", (J. H. Simons, ed.), Vol. 1, p. 553, Academic Press, New York.
3. Finger, G. C., Risser, H. E., and Bradburg, J. C. (1960). *Survey, Illinois State Geol. Circ.* **296.**
4. Stuewe, A. H. (1958). *Chem. Eng. News.* **36,** 34.
5. Editorial Article. (1960). *Chem. Eng. News* July 18.
6. Editorial Report. *Ind. Eng. Chem.* (1960). **52,** 25a.
7. Latimer, W. M. (1926). *J. Am. Chem. Soc.* **48,** 2868.
8. Pauling, L. C. (1960). "The Nature of the Chemical Bond". Cornell Univ. Press, Ithaca, New York.
9. Cottrell, T. L. (1958). "The Strengths of Chemical Bonds". 2nd ed. Academic Press, New York.
10. Rohrbach, G. H., and Cady, G. H. (1949). *J. Am. Chem. Soc.* **71,** 1938.
11. Hazeldine, R. N., and Smith, F. (1951). *J. Chem. Soc.*, p. 603.
12. Private communication. (1952). Minnesota Mining and Manufacturing Co., St. Paul, Minnesota.
13. Scholberg, H. M. Guenthner, R. A., and Coon, R. I. (1953). *J. Phys. Chem.* **57,** 923.
14. Fox, H. W., Hare, E. F., and Zisman, W. A. (1953). *J. Colloid Sci.* **8,** 194.
15. Hare, E. F., Shafrin, E. G., and Zisman, W. A., (1954). *J. Phys. Chem.* **58,** 236.
16. Zisman, W. A. (May, 1957). "Relation of Chemical Constitution to the Wetting and Spreading of Liquids on Solids". NRL Report 4932.
17. Bennett, M. K., and Zisman, W. A. (Oct. 1958). "Relation of Wettability by Aqueous Solutions to the Surface Constitution of Low-Energy Solids". NRL Report 5207.
18. Zisman, W. A. (Nov. 1961). "Constitutional Effects of Adhesion and Abhesion" NRL Report 5699.
19. Heine, R. F. (1960). "Some Effects of Ionizing Radiation on Fluorocarbon Liquids", presented at Fluorine Symposium. 138*th Natl. Meeting of Am. Chem. Soc.*, New York.

20. Kinderman, E. M. (July 1957). WADC Tech. Report 57–465, Stanford Research Inst.
21. Simons, J. H., and Taylor, E. H. (1959). *J. Phys. Chem.* **63,** 636.
22. Florin, R. E., Wall, L. A., and Brown, D. W. (1960). *J. Research Natl. Bur. Standards.* **64A,** 269.
23. Bashara, N. M. (May 5–7, 1952). Paper presented at the Meeting on Progress on Quality Electronic Components, Washington, D.C.
24. Bryce, H. G. (1953). *Chem. in Can.* p. 29.
25. Hildebrand, J. H., and Scott, R. L. (1950). "The Solubility of Nonelectrolytes". Reinhold, New York.
26. Scott, R. L. (1948). *J. Am. Chem. Soc.* **70,** 4090.
27. Hildebrand, J. H., Fisher, B. B., and Benesi, H. A. (1950). *J. Am. Chem. Soc.* **72,** 4348.
28. Midgley, T., Jr., Henne, A. L., and McNary, R. E. (1930). U.S. Patent 1,833,847.
29. Midgley, T., Jr., Henne, A. L., and McNary, R. E. (1934). U.S. Patent 1,968,049.
30. Thompson, R. J. (Jan. 9 and Jan. 16, 1950). *Air Conditioning and Refrigeration News.*
31. Underwriters Laboratories, Reports MH-2256, MH-2375, MH-2630, MH-3134, and MH-3072.
32. *Chem. Eng. News* (1961). **39,** No. 42, 26.
33. Olyphant, M., Jr., and Brice, T. J. (1954). *Proc. Electronic Component Symposium, Washington, D.C.*
34. Kilham, L. F., Jr., Ursch, R. R., and Ahearn, J. F. (Feb. 24, 1953, to Jan. 1, 1956) Navy Dept., Bureau of Ships Contract NObsr-63239, Index NE-110915. Raytheon Corp., Waltham, Massachusetts.
35. Kilham, L. F., Jr., and Ursch, R. R. (April 1956). *Proc. I.R.E.* **44,** 515.
36. Narbut, P., and Monito, G. A. (Nov. 1959). *Westinghouse Eng.* p. 162.
37. Etter, R. E. (March 1957). Interim Tech. Report, RCA Contract AF33 (635) 7359.
38. Renaud, L. (Aug. 1960). *EDN Packaging Symposium, Boulder, Colorado.*
39. Drexel, W. H. (May 1961). *Electronic Design.* p. 40.
40. Technical Bulletin. (1953). Inert Fluorochemical Liquid FC-75, Y-IFLFC (49.15)M. Minnesota Mining and Manufacturing Co., St. Paul, Minnesota.
41. Hildebrand, J. H. (1959). Private communication.
42. Marcellus, M. C., Spilhaus, A. F., Jr., and Troeltzsch, L. A. (1961). *J. Chem. Eng. Data.* **6,** 459.
43. Hsu, S. T. (1961). Univ. of Winconsin. Private communication.
44. Yarrington, R. M., and Kay, W. B. (1959). *J. Chem. Eng. Data.* **4,** 24.
45. Technical Bulletin. (1957). Inert Fluorochemical Liquid FC-43. H-FIH(475)S. Minnesota Mining and Manufacturing Co., St. Paul, Minnesota.
46. Camilli, G., and Plump, R. E. (1953). *A.I.E.E. Trans.* **72,** Part I, Communications in Electronics.
47. Massey, H. S. W. (1950). "Negative Ions". Cambridge Univ. Press, London and New York.
48. Charlton, E. E., and Cooper, F. S. (1937). *Gen. Elec. Rev.* **40,** 438.
49. Pollock, H. C., and Cooper, F. S. (1939). *Phys. Rev.* **56,** 170.
50. Camilli, G. (1956). *Gen. Elec. Rev.* **59,** 41–44.
51. Henry, E. B., Friedrich, R. E., and Reese, F. L. (Nov. 14, 1957). *A.I.E.E. Trans. Paper* 58–128.
52. Anderson, T., Reeves, A. L., Mears, W. H., and Orfeo, S. R. (Submitted Nov. 8, 1956). *A.I.E.E. Conf. Paper* 57–82.

53. Sutherland, J. E. (Dec. 1954). *Elec. Eng.*, pp. 538–540.
54. Technical Brochure. (1960). General Electric Co. Bull. GEA-6790A. Medium Transformer Division, Rome, Georgia.
55. Burgoyne, J. H., and Williams, L. G. (1948). *Proc. Roy. Soc.* **A193,** 525.
56. Coward, H. F., and Jones, G. W. (1952). *U.S. Bur. Mines, Bull.* **503.**
57. Purdue University Foundation and Dept. of Chemistry. (July 1950). "Final Report on Fire Extinguishing Agents for the Period 1 September, 1947 to 30 June, 1950", Purdue University.
58. *Fire Eng.* p. 357. (May 1950).
59. Coleman, E. H. (1952). *Fuel.* **31,** 445.
60. Comstock, C. C., and Oberst, F. W. (1953). *Arch. Ind. Hyg. Occup. Med.* **7,** 157.
61. Comstock, C. C., Kirschner, J., and Oberst, F. W. Research Report 180. Army Chemical Center, Missouri. (ASTIA No. AD-11563).
62. Svirbely, J. L., Highman, B., Alford, W. C., and von Oettingen, (1947). *J. Ind. Hyg. and Toxicol.* **29,** 382.
63. Rosenberg, H., and Mosteller, J. C. (April 1955). WADC Tech. Report 54-580.
64. Fitzsimmons, V. G., and Zisman, W. A. (1956). NRL Report 4753.
65. Langmuir, I. (1920). *Trans. Faraday. Soc.* **15,** 68.
66. Miller, W. T., Jr., Dittman, A. L., Ehrenfeld, R. L., and Prober, M. (1947). *Ind. Eng. Chem.* **39.** 333.
67. Technical Bulletin. (1957). "KEL-F" Brand Halofluorocarbon Oils, Waxes, Greases, and Alkanes. J-OPB (68.5) W.G.A. Minnesota Mining and Manufacturing Co., St. Paul, Minnesota.
68. *In. Eng. Chem.* (1947). **39,** 236–434.
69. Technical Bulletin 15-200. (Sep. 1961). Dow Corning Corp.
70. Davies, R. (1957). "Friction and Wear", a Symposium held at General Motors Research Center, Detroit.
71. Technical Bulletin. (1955). M. W. Kellogg Co.
72. Bennett, M. K., and Zisman, W. A. (1959). *J. Phys. Chem.* **63,** 1912.
73. Talbot, E. L. (1959). *J. Phys. Chem.* **63,** 1666.
74. Ahlbrecht, A. H., and Blake, G. B. (1954). Paper presented at Fluorine Symposium (Division of Ind. and Eng. Chem.), 126 Meeting of Am. Chem. Soc., New York.
75. Guenthner, R. A., and Vietor, M. L. (1961). Paper presented at Fluorine Symposium (Division of Ind. and Eng. Chem.), 140th Meeting of Am. Chem. Soc., Chicago, Illinois.
76. Technical Bulletin. (1959). Fluorochemical Surfactants. F-L46 (128.03)M. Minnesota Mining and Manufacturing Co., St. Paul, Minnesota.
77. LaZerte, J. D., Hals, L. J., Reid, T. S., and Smith, G. H. (1953). *J. Am. Chem. Soc.* **75,** 4525.
78. Ahlbrecht, A. H., Blake, G. B., and Bryce, H. G. (Sep. 1954). Paper presented before the Petroleum Division, 126th Meeting of Am. Chem. Soc., New York. (p. 131, No. 32, *Preprints.*)
79. Ellison, A. H., and Zisman, W. A. (1959). "Adsorption of Soluble Fluorocarbon Derivatives at the Organic–Liquid/Air Interface". NRL Report 5256.
80. Lamer, V. K. Columbia University, private communication.
81. Test method developed by the Shell Oil Development, Emeryville, California.
82. Kawahara, F. K. (1961). U. S. Patent 3,006,741.
83. Hama, G., Fredrick, W., Millage, D., and Brown, H. (1954). *Am. Ind. Hyg. Assoc. Quart.* **15,** 3.

84. Silverman, L., and Thompson, R. M. (1948). *J. Ind. Hyg. and Toxicol.* **30,** 303.
85. "Zeromist" is a registered trade mark of the Udylite Corp., Detroit, Michigan.
86. Warth, A. H. (1956). "Chemistry and Technology of Wax", 2nd Ed. Reinhold, New York.
87a. Technical Bulletin No. 9. (1957). N.B.S. Chemical Corp., Cambridge, Massachusetts.
87b. Technical Bulletin. (July 1959). Rohm and Haas Co., Philadelphia.
88. Berry, K. L. (1951). U.S. Patent 2,559,752.
89. Bolstad, A. N., and Herbst, R. L., (1959). U.S. Patent 2,874, 152.
90. Mauersberger, H. R. (1954). "Matthews' Textile Fibers". Wiley, New York.
91. Grajeck, E. J., and Petersen, W. H. (1959). *Am. Dyestuff Reptr.* **48,** 37.
92. Phillips, F. J., Segal, L., and Loeb, L. (1957). *Textile Research J.* **27,** 369.
93. Segal, L., Phillips, F. J., Loeb, L., and Clayton, R. L. Jr. (1958). *Textile Research J.* **28,** 233.
94. Technical Manual No. 37. (1961). Am. Assoc. Textile Chemists and Colorists.
95. British Standards Handbook No. 11. (1956). 190–196.
96. Petersen, W. H., and Grajeck, E. J. (Nov. 9, 1961). Paper presented before the 10th Chemical Finishing Conference of the National Cotton Council.
97. Technical Literature, Textile Products. (1959). F-LA46 (128.03)M. Minnesota Mining and Manufacturing Co., St. Paul, Minnesota.
98. Product of Minnesota Mining and Manufacturing Co., St. Paul, Minnesota.
99. Salsbury, J. M., Cooke, T. F., Pierce, E. S., and Roth, P. B. (1956). *Am. Dyestuff Reptr.* **45,** No. 7, 199.
100. DeMarco, C. G., McQuade, A. J., and Kennedy, S. J. (Feb. 1960). *Modern Textile Mag.* p. 50.
101. O'Flaherty, F., Roddy, W. T., and Lollar, R. M. (1956). "The Chemistry and Technology of Leather". Reinhold, New York.
102. Gustavson, K. H. (1956). "The Chemistry of the Tanning Process". Academic Press, New York.
103. Olson, M. H., (1961). *Leather and Shoes.* **141,** 24.
104. Technical Literature. (1960). 3M Brand Leather Chemical FC-146, F-L46 (128.03) M. Minnesota Mining and Manufacturing Co., St. Paul, Minnesota.
105. Calkin, J. B., and Witham, G. S. (1957). "Modern Pulp and Paper Making". Reinhold, New York.
106. Ernlund, J. H. (1957). *TAPPI* **40,** No. 3.
107. Ernlund, J. H., and Hessburg, L. J. (Aug. 1957). *Modern Packaging.*
108. Toensmeier, P. A. (May 1960). *Paperboard Packaging.*
109. Technical Bulletin. (1959). 3M Brand Paper Chemical FC-805, F-L46 (128.03)M. Minnesota Mining and Manufacturing Co., St. Paul, Minnesota.
110. TAPPI. (1955). Tentative Standard T 454M-44, Turpentine Test for Grease Resistance.
111. Ruff, O., and Bretschneider, O. (1933). *Z. anorg. u. allgem. Chem.* **210,** 173.
112. Park, J. D., Benning, A. F., Downing, F. B., Laucius, J. F., and McHarness, R. C. (1947). *Ind. Eng. Chem.* **39,** 354.
113. Hanford, W. E., and Joyce, R. M. (1946). *J. Am. Chem. Soc.* **68,** 2082.
114. Plunkett, R. J. (1941). (to Kinetic Chemicals, Inc.), U.S. Patent 2,230,654.
115. Brubaker, M. M. (1946). U.S. Patent 2,393,967.
116. Technical Literature. (1955). "TEFLON", Tetrafluoroethylene. E. I. duPont de Nemours and Co.

117. U.S. Army Signal Research and Development Report No. 2. (May 1960 to Feb. 1961). Contract DA-36-039-SC-78321, DA Project 3A-99-15-001.
118. E. I. duPont de Nemours and Co. (1961). *J. of Teflon.* **2,** No. 3,6.
119. *Elec. Manuf.* (Feb. 1959). p. 112.
120. Wall, L. A., and Florin, R. E. (1959). *J. Appl. Polymer Sci.* **2,** 251.
121. Sperati, C. A., and McPherson, J. L. (Sep. 1956). Meeting of Am. Chem. Soc., *Atlantic City.*
122. *Machine Design.* (Jan. 21 and Feb. 18, 1960).
123. Shooter, K. V., and Tabor, D. (1952). *Proc. Phys. Soc.* **65B,** 661.
124. Bowden, F. P. (1953). *Proc. Roy. Soc.* **A217,** 462.
125. British Patent 465,520. (1937).
126. Technical Data. (1961). "KEL-F" 81 Brand Plastic. Minnesota Mining and Manufacturing Co., St. Paul, Minnesota.
127. Mowers, R. E. (June 26, 1961). Paper presented to 64th Annual ASTM Meeting, Atlantic City.
128. Kaufman, H. S., Kroncke, C. O., and Giannotta, C. R. (1954). *Modern Plastics.* **32,** 146.
129. Book of Am. Soc. Testing Materials Standards. (1961). Part 9, p. 32.
130. Downing, F. B., *et al.* (1951). U.S. Patent 2,551,573.
131. Mantell, R. M., and Barnhart, W. S. (1956). U.S. Patent 2,774,799.
132. Benning, A. F., *et al.* (1953). U.S. Patent 2,628,989.
133. Technical Literature. (1961). Bulletin VF 2R-61, "KYNAR", Pennsalt Chemicals Corp.
134. Simril, V. L., and Curry, B. A. (1959). *Modern Plastics.* **36,** 121.
135. Technical Literature. (1961). Bulletin X-90a, "TEFLON 100 FEP". E. I. duPont de Nemours and Co., Wilmington, Delaware.
136. E. I. duPont de Nemours and Co. (1961). *J. of Teflon.* **2,** No. 1, p. 1.
137. Tobolsky, A. V. (1960). "Properties and Structure of Polymers". Wiley, New York.
138. Wolf, D. R. (1958). "The Vanderbilt Rubber Handbook". p. 136. R. T. Vanderbilt Co., New York.
139. Robb, L. E., Honn, F. J., and Wolf, D. R. (Nov. 1957). *Rubber Age.*
140. Montermoso, J. C., Griffis, C. B., Wilson, A., and Oesterling, J. F. (1958). *Proc. Inst. Rubber Ind.* **5,** 97.
141. Miles, D. C. (Oct. 7, 1961). *Rubber and Plastics World.*
142. Smith, J. F. (Nov. 1959). Paper 70 presented at International Rubber Conf. (Am. Chem. Soc.), Washington D.C.
143. Stivers, D. A., Honn, F. J., and Robb, L. E. (1959). *Ind. Eng. Chem.* **51,** 1465.
144. Stivers, D. A., Peterson, D. L., and Meier, G. R. (1960). *Rubber Age.* **88,** 292.
145. Rugg, J. S., and Stevenson, A. C. (1957). *Rubber Age.* New York. **82,** 102.
146. Moran, A. L. (1957). *Rubber World.* **137,** 250.
147. Technical Literature: (*a*) Moran, A. L., and Eubank, T. D. (1958). Report 58-3; (*b*) Moran, A. L. (1959). Report 59-4. E. I. duPont de Nemours and Co., Wilmington, Delaware.
148. Technical Literature. (1959). "FLUOREL" High Temperature Elastomer. Y-TTDC (Fluorel) 19.35 W. Minesota Mining and Manufacturing Co., St. Paul, Minnesota.
149. Technical Literature. (9-370 Sep. 1956). "SILASTIC LS-53". Dow Corning Corp., Midland, Michigan.

150. Konkle, G. M. (June 1958). Paper presented before the Soc. Mech. Engineers (Rubber and Plastics Division), Semi-Annual Meeting, Detroit. Paper 58-SA-66.
151. Stedry, P. J., Abere, J. F., and Borders, A. M. (1955). *J. Polymer Sci.* **24,** 33.
152. Postelnek, W. (1958). *Ind. Eng. Chem.* **50,** 1603.
153. Zachringer, A. J. (May 1958). *Missiles and Rockets.* p. 104.
154. Kit, B., and Evered, D. S. (1960). "Rocket Propellant Handbook". Macmillan, New York.
155. Gall, J. F. (1957). *Ind. Eng. Chem.* **49,** 1331.
156. Paushkin, Y. M. (1958). "Chemical Composition and Properties of Rocket Propellants". Acad. Sci. U.S.S.R., Moscow.
157. Means, P. (May 1959). *Missiles and Rockets.* p. 42.
158. Tormey, J. F., (1957). *Ind. Eng. Chem.* **49,** 1339.
159. Annual Report of the British Interplanetary Society. (1952). London.
160. Reuel, N. C., and Friedman, J. (1947). Liquid Rocket Design Manual. Report AL-259, Missile Division, North American Aviation, Downey, California.
161. From chart entitled, "Theoretical Performance of Several Propellant Combinations". (1956). By Rocketdyne, a division of North American Aviation.
162. Grisard, J. W., Bernhardt, H. A., and Oliver, G. D. (1951). *J. Amer. Chem. Soc.* **73,** 5725.
163. Evans, W. H., Munson, T. R., and Wagman, D. D. (1955). *National Bur. Standards J. Research.* **55,** 147.
164. Horowitz, D. (1950). Report RMI-293-55, Reaction Motors. Rockaway, New Jersey.
165. Gall, J. F. (Feb. 1959). *R.S. Journal*, pp. 95–103.
166. Technical Literature. (1957). Manual PF-1. "Perchloryl Fluoride, Properties and Handling". Pennsalt Chem. Corp., Philadelphia.
167. Falloon, V. A., and Kenna, B. W. (1951). *J. Am. Chem. Soc.* **73,** 2937.
168. Ruff, O., Fischer, J., and Luft, F. (1928). *Z. anorg. Chem.* **172,** 417.
169. Colburn, C. B., and Kennedy, A. (1958). *J. Am. Chem. Soc.* **80,** 5004.
170. *Natl. Bur. Standards* (*U.S.*). (1950). *Circ.* **500,**
171. Frear, D. E. H. (1948). "Chemistry of Insecticides, Fungicides, and Herbicides". 2nd ed. Van Nostrand, Princeton.
172. Brice, T. J., and Trott, P. W. (1956). U.S. Patent 2,732,398.
173. Simons, J. H. (1931). *Chem. Rev.* **8,** 213.
174. Simons, J. H., and Hildebrand, J. H. (1924). *J. Am. Chem. Soc.* **46,** 2183.
175. Simons, J. H., and Archer, S. J. (1938). *J. Am. Chem. Soc.* **60,** 986.
176. Simons, J. H. (1943). *Petroleum Refiner.* **22,** 83.
177. McBee, E. T., Pierce, O. R., and Smith, D. D. (1954). *J. Am. Chem. Soc.* **76,** 3722.
178. Henne, A. L., and Fox, C. J. (1951). *J. Am. Chem. Soc.* **73,** 2323.
179. Buckles, R. E., and Mills, J. F. (1953). *J. Am. Chem. Soc.* **75,** 552.
180. Katz, J. J. (1954). *Nature.* **174,** 509.
181. Sweet, S. S., Van Horn, M. H., and Newsome, P. T. (1955). U.S. Patent 2,710,848.
182. Morgan, P. W. (1953). U.S. Patent 2,629,716.
183. Morgan, P. W. (1951). *Ind. Eng. Chem.* **43,** 2575.
184. Coover, H. W., Jr., Stanin, T. E., and Dickey, J. B. (1950). U.S. Patent 2,525,526.
185. Meerwein, H. (1933). *Ber.* **66,** 411.
186. Sedgwick, N. V. (1950). "The Chemical Elements and Their Compounds". Vol. I. Oxford Univ. Press (Clarendon), London and New York.
187. Yarrington, R. M., and Kay, W. B. (1959). *J. Chem. Eng. Data* **4,** No. 4, 24.

188. Technical Literature: (*a*) Buffington, R. M., and Gilkey, W. K. (Oct. 1932). Report of A.S.R.E. circ. No. 12, Tech. Paper No. 12; (*b*) Thompson, R. J. (Oct. 1932). Report of Tech. Paper No. 11; (*c*) Benning, A. F., and McHarness, R. C. (Copyright, 1938). "The Thermodynamic Properties of "FREON-II (CCl_3F)"; (*d*) Benning, A. F., and Markwood, W. H., Jr. (Copyright, 1942). "Thermodynamic Properties of "FREON-11 Trichloromonofluoromethane (CCl_3F)"; (*e*) Benning, A. F., and Markwood, W. H. Jr. (Copyright 1942). "Thermodynamic Properties of "FREON-22" Monochlorodifluoromethane ($CHClF_2$)". E. I. duPont de Nemours and Co., Wilmington, Delaware.

189. Technical Brochure, (1961). FEP-fluorocarbon Film. E. I. duPont de Nemours and Co., Wilmington, Delaware.

190. Editorial Review (1963), *Chem. and Eng. News* **41,** 36.