

Chapter 5

THE MANHATTAN PROJECT

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Introduction

The story of the development of the atomic bomb during the Second World War has been told many times in both official government histories [1] and popular accounts [2]. The Manhattan Project is the name often applied to the U.S. Government's participation in the production of nuclear weapons at that time. Descriptions of the Project have generally covered the nuclear physics background in some detail together with the political and strategic considerations surrounding the decision to manufacture and use atomic bombs. The remarkable feats of engineering that led to the production of the nuclear explosives have also been well described, but in these writings about the Project the key role played by fluorine chemistry in the realization of nuclear weapons has received relatively scant attention. There are comprehensive scientific and technological surveys of many aspects of this fluorine chemistry, in which any narrative or historical element is incidental [3]. It is the objective of this chapter to provide such a narrative history, concentrating primarily on the part that fluorocarbon chemistry played in the quest for the atomic bomb. This narrative is based principally on the written record, supplemented where possible by recollections of some of those who worked on fluorocarbon chemistry in the Manhattan Project.

Nuclear fission, 1939 - 40 [1]

By early 1939 the puzzling results that had been obtained during the preceding five years of investigation into the bombardment of uranium by neutrons were finally clarified. Otto Frisch and Lise Meitner, theorizing from the observations of Hahn and Strassman that a barium isotope was a product of the bombardment, suggested that neutron bombardment of uranium sometimes led to the breakup or fission of the uranium nucleus, with the consequent release of a large amount of energy. (It is historically interesting that the first suggestion of uranium nuclear fission seems to have been made by Ida Tacke Noddack, co-discoverer of rhenium, in 1934, to explain the results of Enrico Fermi's first experiments on neutron interactions with uranium.) At a meeting in late January 1939, Fermi discussed with Niels Bohr the possibility that neutrons might be emitted during the

fission of uranium, and that consequently a chain reaction might ensue under appropriate conditions. By early 1940 some 100 articles had already appeared on the subject of fission. Among them was the experimental confirmation, by Joliot and his collaborators, that about three neutrons were emitted each time uranium fission took place. In March 1940, collaborative experiments involving Nier, Booth, Dunning and Grosse in the United States proved that it was the rare (0.7%) isotope of uranium of mass 235 that was undergoing fission. It was also becoming clear, by mid-1940, that the abundant uranium isotope of mass 238 could probably react with slow neutrons producing a new transuranium element (later dubbed plutonium 239) which might show fission characteristics analogous to those of U-235.

The Second World War had erupted in Europe in September 1939, and perceptive scientists in Britain and the United States were speculating on the possibility that atomic fission could lead to weapons of unprecedented power. By early 1940 Frisch and Peierls had done rough calculations on the amount of fissile uranium needed for such a weapon, and had arrived at a figure of between one and one hundred kilograms. It was also clear that the separation of this amount of the 0.7% abundant U-235 from natural uranium was going to be a formidable task.

The threat of war in Europe in mid-1939 led a group of expatriate scientists in the United States to worry about the consequences of Germany winning the race to produce an atomic bomb. Szilard and Wigner met with Einstein and drafted a letter to President Roosevelt urging a rapid buildup of research in nuclear processes, and the acquisition of a stockpile of uranium. The letter was delivered in October 1939, and Roosevelt appointed an Advisory Committee on Uranium, chaired by Lyman Briggs, which received modest funding, and began to acquire uranium and graphite, a moderator of neutron velocity, for the fabrication of a pile. This was to be an experimental assemblage to explore the reactions between slow neutrons and uranium.

By the middle of 1940 remarkably parallel developments in nuclear research programs, and their administrations, were taking place in Britain and the United States. In Britain a Government Committee chaired by Professor Sir George Thomson was asked to determine the feasibility of producing an atomic bomb, and to coordinate work already in progress in a number of laboratories. The group soon concluded that the most economical method of producing a bomb would be by separation of fissile U-235, and that gas diffusion of uranium hexafluoride would be the method of choice for the separation. By mid-1941 the Committee had prepared a summary report concluding that the manufacture of an atomic bomb was feasible; that it would be a very powerful weapon, with an explosive effect equivalent to that of several thousand tons of conventional explosives; and that separation of U-235 on the necessary scale could be accomplished by gas diffusion of UF_6 .

In the United States, the National Defense Research Committee was established in June 1940 with the charge of using the nation's scientific

resources in the national defense. It became the oversight group for the Committee on Uranium, initiated a ban on any further publication in the open literature of work related to nuclear weapons, and began funding support of a number of research projects. Among these were studies of chain reactions in uranium, leading to either power generation or a weapon, and an isotope separation program. Initially separation by a centrifuge seemed an attractive method, and was examined by a group at Columbia led by Urey. Kistiakowski suggested gas diffusion, and the Columbia group, including Dunning, Booth and Grosse, finally settled on that as the most promising approach. Nevertheless the uranium work in the United States was still proceeding at a rather slow pace in early 1941, by which time France had fallen and Britain was essentially alone in the struggle against Nazi Germany in Europe.

Lawrence, at the University of California at Berkeley, began urging a faster pace for nuclear weapons research on two fronts. His colleagues at Berkeley, led by Seaborg, isolated the new element of atomic number 94 (soon to be named plutonium) which was produced by the reaction of neutrons with the abundant isotope U-238. If plutonium were fissionable, and the nuclear model of Bohr and Wheeler suggested it would be, then in principle all the uranium in a pile could be converted into the new fissile element. Furthermore, since plutonium and uranium were different elements and not isotopes, a chemical separation of them might be possible. This should be a much simpler process than the gas diffusion separation of isotopes. Lawrence also had a new approach to isotope separation. Why not use one of his Berkeley cyclotrons as a large-scale mass spectrometer to separate substantial quantities of the uranium isotopes?

Developments in 1941 [1]

During 1941, work continued steadily in all the most promising directions that might lead to nuclear explosives. By July, Fermi and his associates had assembled an experimental graphite-moderated pile at Columbia University. This was to be used to gather further experimental data on the fission process, and to explore the possibility of plutonium production. Also at Columbia, Urey and his group were doing further experimental and theoretical studies of isotope separation. They established that a plant based on gas-diffusion separation of UF_6 would require some 5000 stages; would need acres of some as-yet undeveloped barrier material; and would probably cost upwards of 10^7 dollars. Centrifuge separation was also given some consideration, but seemed less attractive than, and at least as costly as, gas diffusion. British scientists had reached similar conclusions, and throughout the year information continued to be exchanged between U.S. and British groups. By the end of the year Lawrence had managed to scale-up his cyclotron/mass spectrometer to the point where it was producing 1 μ g of fairly pure U-235 per hour.

Late in 1941, a National Academy of Sciences Committee, that had been appointed to review the nuclear effort, reported that it should be possible to produce an atomic bomb based on U-235 in a three to four year period, and that the research effort should continue. In December 1941 the United States entered the Second World War, and work on atomic bombs acquired a new urgency.

With this background the rest of this chapter will concentrate on the part that fluorine chemistry in general, and fluorocarbon chemistry in particular, played in the gas-diffusion project which finally resulted in viable nuclear weapons in 1945.

Organic fluorine chemistry in the U.S.A. in 1941

The work of the European pioneers of organic fluorine chemistry, like Ruff and Swarts, led to active research and development in America in the 1930s. A deliberate search for an alternative to the toxic and odorous refrigerant gas ammonia, led Midgley and Henne to dichlorodifluoromethane, which was introduced in 1930 [4]. The compound had exceptional properties as a refrigerant, being nontoxic, chemically inert and relatively inexpensive. It was widely and rapidly accepted, and began to displace ammonia in refrigeration equipment. The introduction of CCl_2F_2 had another important consequence. It established an organic fluorine chemical industry in America and led to continued activity in research in this area (see Chapter 4).

Henne continued to work on chlorofluoro compounds, building up a repertoire of methods for their preparation [5]. Bigelow and his students studied the vapor-phase direct reaction between elemental fluorine and hydrocarbons, and found ways to control the reactions [6]. Simons and Block worked on the reaction between elemental fluorine and carbon, and found that a trace of mercury would catalyze the reaction, allowing it to proceed smoothly, without explosions, at elevated temperatures (see p. 91). From this reaction small quantities of a number of saturated fluorocarbons became available [7]. As a consequence of these and other developments, by mid-1941 there was a group of chemists experienced in organic fluorine chemistry in the U.S. ready to face the challenges posed by the nuclear weapons project.

A key figure in the recognition of the possible utility of organic fluorine compounds in the Project was Aristide V. Grosse, who had a versatile background as a chemist. Russian-born, he earned his doctorate in Berlin, worked with Paneth on radioactivity, and was a discoverer of the element protoactinium. He emigrated to America in 1930 and worked with Ipatieff at Universal Oil Products in Chicago on the catalytic chemistry of hydrocarbons, including the use of HF as a catalyst. He came to Columbia University as a Guggenheim Fellow in 1940 to work on nuclear-related research. With his background in both radioactivity and areas of fluorine chemistry, Grosse appreciated that in order to use the highly reactive and

corrosive UF_6 it would be necessary to find a range of compounds that would be inert to it. He suggested to Urey that Simons' fluorocarbons might fit the bill, so Urey requested samples of some of Simons' higher-boiling compounds for testing. A few precious grams of fluorocarbons — essentially the world's total supply at the time — soon arrived at Columbia, and Grosse quickly showed that they did not react with UF_6 [8]. It thus became clear that a research effort in fluorocarbon chemistry would have to be mounted as part of the gas-diffusion separation project.

Grosse continued work in the nuclear area for only a short time after this. In the summer of 1942 his expertise was needed in another area, namely the production of synthetic rubber. He was part of a delegation that went to the U.S.S.R. to discuss joint projects in this field, and the rest of his war effort was on synthetic rubber.

By the end of 1941 the Office of Scientific Research and Development (OSRD) had decided that the uranium project was so important that it needed a new, more direct, administrative structure. Accordingly, in December 1941, the S-1 Section of OSRD was established to oversee an intensified effort. The scientific side of the work was separated from the engineering aspects, and three program chiefs were appointed for various facets of the scientific research. They were Urey, whose responsibilities included uranium separation by gas diffusion; Lawrence, who was to direct the electromagnetic separation research; and Compton, who was in charge of the more basic physical aspects of the project. In the summer of 1942 the Army Corps of Engineers organized the Manhattan District as the unit that would take charge of the procurement and engineering aspects of the nuclear weapons program [1].

In the field with which this chapter is concerned, it was clear by early 1942 that there were some formidable problems to be solved. Uranium hexafluoride was almost as reactive as elemental fluorine. In order to use it in a gas-diffusion plant a wide range of materials which would not react with UF_6 would have to be developed. These would include relatively low-molecular-weight liquids, for use as coolants; higher-molecular-weight materials that could act as liquid and solid lubricants; and polymers that could be fabricated into such essential items as gaskets, valve packings and tubing. The chemically distinct paths that were taken to produce the necessary materials are outlined in the next sections of this chapter.

Direct production of fluorocarbons

The first samples of fluorocarbons found by Grosse to be inert towards UF_6 had been made by Simons and Block by direct reaction between elemental fluorine and carbon, catalyzed by mercury [7] (see p. 91). Naturally, when intensive research on fluorocarbon preparation began at Columbia in early 1942, this was one of the first reactions re-examined. The results confirmed those of the earlier workers; but although small amounts of liquid fluoro-

carbons were formed, including C_4F_{10} and C_5F_{12} , the main product was CF_4 , a gas which was of no immediate use. Consequently, this reaction was not studied further [9].

Bigelow and Fukuhara had published in 1941 the results of a study of the direct reaction of elementary fluorine with benzene in the vapor phase over a copper gauze catalyst. They had obtained perfluorocyclohexane, C_6F_{12} , with only moderate degradation of the starting compound to materials with shorter chains [10]. This method seemed to the Columbia group to be a promising one for the preparation of fluorocarbons, and a detailed investigation was undertaken (see Fig. 5.1). The factors that were varied included the feedstock hydrocarbon; the F_2 /hydrocarbon ratio; the reaction temperature; and the metal catalyst. A protocol was finally developed which gave optimum yields and which included the following factors. Both the hydrocarbon and the fluorine were diluted with an inert carrier gas, normally nitrogen, in the proportion of two volumes of diluent to one of fluorine; fluorine was also used in slight excess of the stoichiometric amount, to reduce the proportion of partly fluorinated product. The reaction was run at temperatures ranging from $200^\circ C$ to $325^\circ C$; lower temperatures prolonged catalyst life, but the higher temperatures were needed for feedstocks of lower volatility. Finally, the most effective catalyst was found to be finely-divided copper coated with silver fluoride, prepared *in situ* by passing fluorine over silver-coated copper turnings. This fluorination technique gave up to a 58% yield of

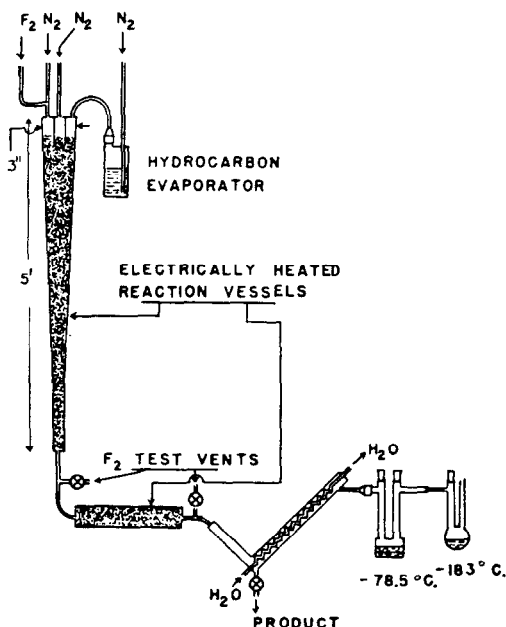


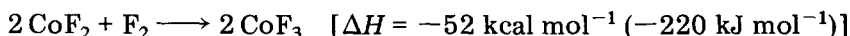
Fig. 5.1. Apparatus for catalytic fluorination of hydrocarbons. (Reproduced by courtesy of the American Chemical Society.)

perfluorocyclohexane from benzene, 62% of perfluoroheptane from n-heptane and 87% of C_8F_{16} from bis(trifluoromethyl)benzene. Yields from higher-boiling hydrocarbons were lower but still reasonable. Anthracene gave a 43% yield of $C_{14}F_{24}$, while a light Pennsylvania paraffinic lubricating oil, fluorinated at 300 °C, gave a 12% yield of a fluorinated product boiling from 150 °C to 200 °C at 11 mmHg pressure [9, 11]. The last product showed promise as a fluorinated lubricant.

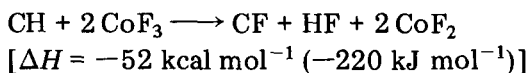
Vapor-phase catalytic fluorination was a versatile technique which gave a range of fluorinated products from one relatively uncomplicated piece of equipment. It was particularly valuable in giving samples of fluorocarbons for testing in the early phase of the Project, and showed promise for the production of fluorinated lubricants. Nevertheless the simultaneous development of the cobalt trifluoride method indicated that this was the method of choice for the direct preparation of C_6 - C_8 fluorocarbons in quantity.

The cobalt fluoride process

The cobalt trifluoride method was developed by a group working at Johns Hopkins University, in Baltimore [12]. Initially this group also tried to improve the Simons and Block reaction between fluorine and carbon, and explored various different sources of carbon in the reaction. Their efforts were fruitless because invariably over 80% of the product was gaseous, and the yields of useful fluorocarbons were very small. The group then began to explore some observations that the pioneering German fluorine chemist Ruff had reported in his monograph on fluorine chemistry, which was published in 1920 [13]. Ruff had discovered that a number of transition metals formed fluorides of their higher oxidation states which were powerful oxidants and fluorinating agents. These fluorides were only formed by direct action of elemental fluorine on compounds of the metals. Among the compounds Ruff studied were AgF_2 , CoF_3 and MnF_3 . These compounds had been prepared in the Johns Hopkins laboratories in 1941 as reagents for the conversion of UF_4 to UF_6 . It occurred to the workers at Johns Hopkins that these high-oxidation-state fluorides might be effective in converting hydrocarbons to fluorocarbons. This would be equivalent to a two-step process for the conversion of CH to CF. To use cobalt fluorides as an example, in the first step fluorine would be used to convert CoF_2 (obtainable by treatment of Co^{II} salts with hydrogen fluoride) to CoF_3 :



In the second step, treatment of a hydrocarbon with cobalt trifluoride would yield a fluorocarbon; symbolically:



This second step would clearly be less vigorous and exothermic than the direct reaction of F_2 with a hydrocarbon (see pp. 93, 263), because the enthalpy of the reaction has been divided into two parts. In fact, the Johns Hopkins group, after establishing the utility of the CoF_3 process, did determine the enthalpy changes for the two steps, with the approximate results shown above. Thus the enthalpy change for the direct replacement of a hydrogen atom bonded to carbon by a fluorine atom is roughly halved when the transformation is carried out by using CoF_3 rather than F_2 .

A variety of reactors was tested for the cobalt trifluoride process. The design finally adopted allowed for stirring of the cobalt trifluoride, to prevent it caking during the reaction, and for a temperature gradient in the reactor, ranging from around 200 °C at the point where the hydrocarbon substrate was introduced, to around 300 °C at the gas exit (see Fig. 5.2). Of course, the precise temperatures were optimized for individual substrates [12]. After obtaining very promising results with small test reactors, a number of large-scale reactors were built at Johns Hopkins, and by workers at the Du Pont Company in Wilmington, Delaware [12, 14] (see Fig. 5.3). A typical large reactor might contain 60 kg of CoF_3 when charged. Passage of 1300 g of n-heptane through the reactor at a rate of 4 g min^{-1} (ca. 1 l min^{-1} of vapor, diluted with 0.5 l min^{-1} of nitrogen) gave a yield of 4600 g of crude product; this was washed with dilute sodium hydroxide then water, dried and fractionated to give 3500 g (69%) of pure perfluoro-n-heptane, b.p., 82.4 - 82.6 °C. A further 10% of product could be obtained by a second passage of the higher-boiling fractions of the crude product, which still contained some hydrogen, through the 'regenerated' reactor.

The reactor was regenerated ($CoF_2 \rightarrow CoF_3$) between runs by heating it to 250 °C and passing F_2 through it. Although satisfactory product yields

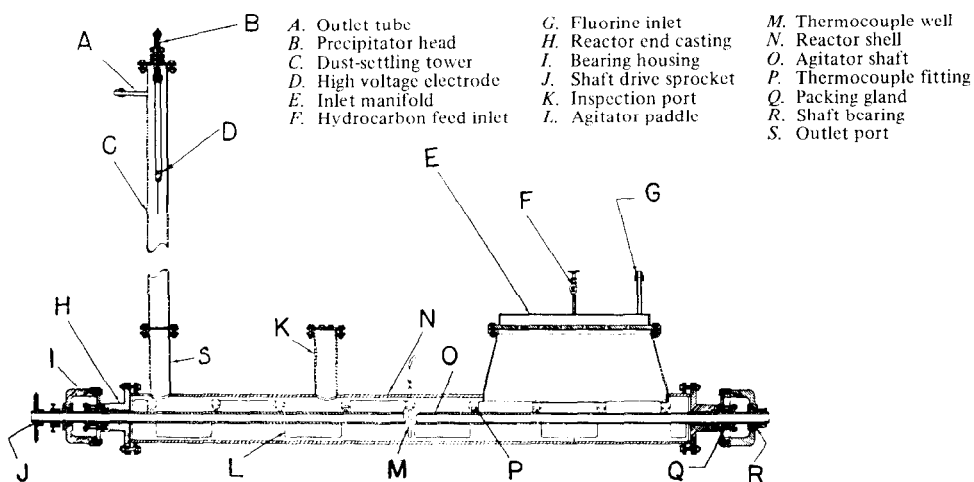


Fig. 5.2. Schematic view of a cobalt fluoride reactor. (Reproduced by courtesy of the American Chemical Society.)

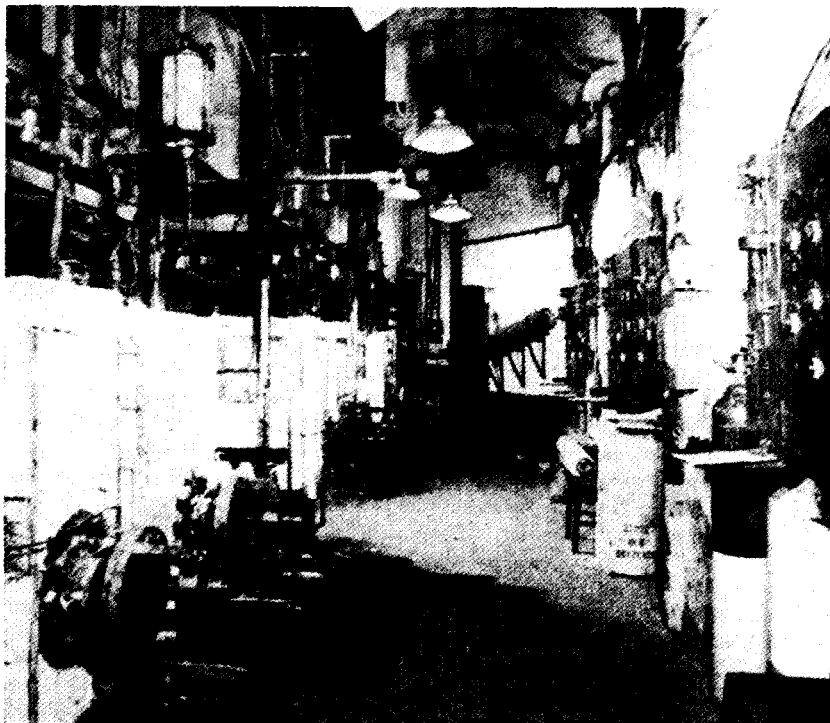


Fig. 5.3. Large cobalt fluoride reactors. (Photograph by courtesy of the American Chemical Society.)

could be obtained by using the reactor until 85% of the CoF_3 was 'exhausted', *i.e.* converted to CoF_2 , better yields were produced if only 30% of the CoF_3 charge was used, and this became the standard operating limit.

The cobalt trifluoride reaction became a major contributor to the production of volatile fluorocarbons for the Manhattan Project. It was scaled-up to a pilot plant for the production of materials ranging from low-boiling gases, like perfluorobutane, b.p., $-2\text{ }^\circ\text{C}$, to fully-fluorinated lubricating oils, with boiling points above $350\text{ }^\circ\text{C}$, in amounts as high as 35 kg d^{-1} [14]. Since the process was a major consumer of elementary fluorine (for the reversion of CoF_2 to CoF_3), and since fluorine was a critical material in several phases of the Project, the next section of this chapter will be a brief account of the production of F_2 and its uses in the Project.

Fluorine production and use [15]

From 1886 until 1919, elemental fluorine was produced by essentially Henri Moissan's original method, namely the electrolysis of mixtures of metal fluorides and HF containing more than 60% of hydrogen fluoride, at

temperatures below room temperature. The cells had metal electrodes, and the anode invariably underwent severe corrosion during cell operation. The first fluorine cell of the modern type was introduced by Argo, Mathers, Humiston and Anderson in 1919. It was a high-temperature cell with molten KHF_2 (m.p., $239\text{ }^\circ\text{C}$) as the electrolyte. The cell body, which functioned as the cathode, was copper; the anode was graphite. This cell became the model for further development, but it was not free from operating problems. Hydrogen fluoride had to be added to the electrolyte at intervals, to prevent its melting point from becoming too high. In addition, the cell was subject to a phenomenon known as anodic polarization, in which a rapid rise in anode resistance is followed by a rapid fall in the rate of fluorine production. (The current interpretation of anodic polarization is that it is due to the formation of a layer of the nonconducting fluorine intercalation compound of graphite on the anode.) In 1925, Lebeau and Damiens introduced a new medium-temperature cell operating at around $100\text{ }^\circ\text{C}$. The electrolyte contained *ca.* 2 - 3 mol hydrogen fluoride per 1 mol potassium fluoride, and the anode was made of nickel. This cell proved reliable, and was not subject to anodic polarization. The nickel anode did, however, suffer steady corrosion, and a sludge of nickel fluoride slowly accumulated at the bottom of the cell, so that periodically the cell would have to be taken apart for cleaning and replacement of the anode. This type of cell was improved by Cady, who made careful studies of the HF/KF system and mapped out its phase diagram. Cady, who was recruited for the Manhattan Project by Grosse in the Fall of 1941, developed the medium-temperature cell with a nickel anode into a reliable source of fluorine for the catalytic fluorination process [15].

While nickel anode cells were useful for the laboratory production of fluorine, they were not promising for larger industrial-scale uses. Their current efficiency was low, only around 60 - 70%, and they were subject to frequent shut-down, so that the nickel fluoride sludge could be removed. Consequently a good deal of research effort was put into improving the operation of carbon anode cells [16]. It was found that anodic polarization in these cells could be minimized by using strictly anhydrous hydrogen fluoride in the electrolyte. The addition of 1 - 2% lithium fluoride to the electrolyte also inhibited anodic polarization. It was also found that the nature of the carbon used for the anode influenced polarization. So-called nongraphitized high-density low-permeability carbon gave better results than graphite. Successful anodes were also made from copper-impregnated graphite. While a variety of different large-scale electrolytic fluorine cells was constructed and used successfully in the Project, they can all be characterized as medium-temperature cells with carbon anodes (see Fig. 5.4). It is also worth mentioning that poly(tetrafluoroethylene), which will be discussed in more detail later in this chapter, was found to be extremely useful as an insulator in the fabrication of fluorine cells.

After the start-up of an electrolytic fluorine cell, the major contaminant in the fluorine produced was hydrogen fluoride. This was removed from the gas stream by cooling to *ca.* $-70\text{ }^\circ\text{C}$ (dry ice) and absorbing the final traces

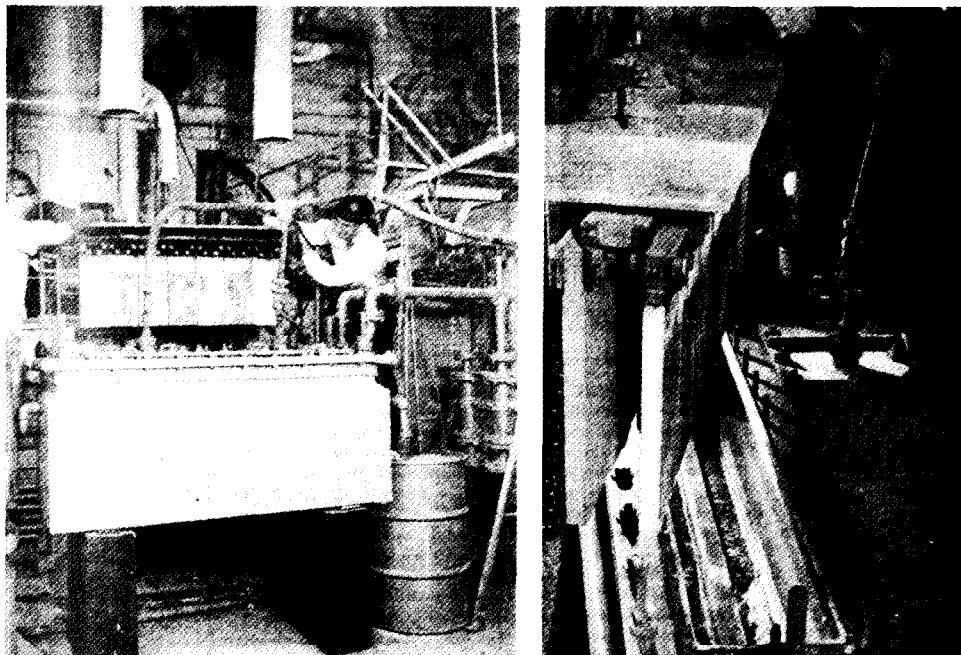
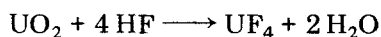


Fig. 5.4. (Left) 2000-A carbon-anode fluorine cell with one anode assembly removed. (Right) Looking down on the cell with one anode assembly removed. (Photographs by courtesy of the American Chemical Society.)

of hydrogen fluoride on sodium fluoride pellets held at 100 °C. Methods also had to be worked out for the storage of fluorine. The gas could be compressed to moderate pressures by using a diaphragm pump [17]. Storage at higher pressures in nickel or steel cylinders was accomplished by liquefying the fluorine in a metal trap and transferring it to the cylinder, and then allowing it to become gaseous. A protective fluoride coating formed on the inner surfaces of the cylinders [17].

The need for elemental fluorine in reactions for the production of fluorocarbons has been discussed in earlier sections of this chapter, and will be referred to further below. Another essential role for fluorine was in the production of the substrate compound for the gas-diffusion process, *viz.* uranium hexafluoride. This compound was produced during the Project by a two-step sequence starting from uranium dioxide [18]. In the first step, uranium tetrafluoride was produced by reaction with hydrogen fluoride at 550 °C:



The involatile, green, anhydrous uranium tetrafluoride was then converted into colorless, volatile uranium hexafluoride by reaction with fluorine at temperatures above 250 °C. This UF_6 was then used as the substrate in the gas-diffusion process for uranium isotope separation.

Haloaromatic precursors

Fluorocarbon production by either direct catalytic fluorination or the cobalt trifluoride process involved the costly and often difficult preparation of elementary fluorine in large amounts. Consequently, a number of research projects were mounted to discover ways of producing highly-fluorinated compounds that would be more economical in terms of fluorine consumption.

One such way, explored by McBee and his coworkers at Purdue University, involved chlorinated aromatic compounds as precursors to fluorocarbons [19]. The strategy made use of the well-established chemistry for the conversion of trichloromethyl groups attached to aromatic rings into trifluoromethyl groups (see Chapter 4). This could be readily carried out using hydrogen fluoride in the presence of an antimony salt catalyst. Commercial xylenes were chosen as starting materials. They were readily available and relatively cheap. Since *ortho*-bis(trichloromethyl)benzene is highly sterically hindered, and cannot be made by direct chlorination of *o*-xylene, the research was carried out on xylene mixtures free of the *ortho* isomer.

The Purdue group first developed a photochemical method for converting an *m-p*-xylene mixture to a mixture of bis(trichloromethyl)benzenes by treating it with an excess of chlorine while irradiating the reaction vessel with a mercury arc lamp and steadily raising the temperature to 100 - 110 °C. This gave excellent yields of chlorinated products which were principally bis(trichloromethyl)benzenes, though they did contain small amounts of ring-chlorinated materials. The conversion of the bis(trichloromethyl)- to bis(trifluoromethyl)benzenes involved many trials of different reaction conditions. The most successful conversions were achieved by using a nickel-lined autoclave at around 150 °C with a substantial excess of HF. Antimony salts did not improve product yields under these conditions, though at lower temperatures SbCl₅ catalysis was helpful.

The bis(trifluoromethyl)benzene mixture proved to be an excellent feedstock for the cobalt trifluoride fluorination process, and so the production of this starting material was scaled-up to pilot-plant level by a group at the Hooker Electrochemical Company at Niagara Falls, NY [20]. The manufacturing conditions were adapted from the laboratory techniques developed by the Purdue group. The process started with a 137.5 - 139.5 °C xylene fraction rich in *p*-xylene, which the Purdue group had shown to be the isomer which gave the best overall yields. This was chlorinated with irradiation at temperatures rising to 110 °C until it contained 67.7% chlorine, and had a density at 25 °C of between 1.600 and 1.605 g cm⁻³. The product was then batch-fluorinated in an agitated 110 gal (415 l) steel autoclave containing an excess of anhydrous hydrogen fluoride. The operating temperature was 110 - 120 °C, and the autoclave pressure was 90 - 100 atm. The development of a pressure seal for the agitator was a critical step in the realization of this process, and the availability of a fluorinated polymer, namely poly(tetrafluoroethylene), finally allowed an effective seal to be produced.

The crude fluorinated product was washed with sodium hydroxide solution, filtered, steam-distilled, dried over sodium carbonate and vacuum fractionated to give the desired bis(trifluoromethyl)benzenes. Higher-boiling partly-fluorinated products were re-fluorinated. In a typical batch run, 890 kg of xylenes gave 2511 kg of bis(trichloromethyl)benzenes, a 96% yield. The efficiency of chlorine use was 80%. When 234 kg of the chlorinated benzenes were fluorinated, 94 kg of the desired fraction, b.p., 113 - 116.5 °C, was obtained. Overall product yields ranged from 40 - 65% and were quite acceptable.

Chloroalkane precursors

A second possible approach to minimizing the consumption of elemental fluorine was also explored by McBee and his collaborators at Purdue. The strategy of this approach was to chlorinate an alkane as fully as possible, and then to fluorinate the chlorinated product with HF in the presence of an antimony salt. The chlorofluoro material thus obtained could then be used as feedstock for the final cobalt trifluoride process. Since a highly desired end-product was C_7F_{16} , the starting material explored most fully was n-heptane [21].

The chlorination of the hydrocarbon was carried out in the liquid phase under irradiation from a medium-pressure mercury arc while the temperature was steadily raised from 25 to 100 °C. The final product of this process contained 83% chlorine, corresponding to an empirical formula of roughly $C_7H_4Cl_{12}$. (Attempts to chlorinate this product further, by raising the temperature, extending the time, or adding Lewis acid catalysts or free-radical initiators led only to chlorinolysis.) This polychloroheptane was fluorinated by heating with hydrogen fluoride in a stirred autoclave at 100 - 125 °C in the presence of antimony pentachloride. During the fluorination the antimony catalyst was reduced to Sb^{III} salts, but attempts to re-oxidize the catalyst back to Sb^V by adding Cl_2 to the autoclave periodically did not improve the yield in the laboratory-scale runs. The fluorinated product was distilled directly from the antimony salts and had the approximate composition $C_7H_xCl_3F_9$. It contained unsaturated components, as revealed by its ready reaction with a solution of potassium permanganate in acetone. Fractionation of the fluorinated product gave, as the lower-boiling components, C_7F_{12} , $C_7F_{11}Cl$ and $C_7F_{10}Cl_2$, which could be used directly in the cobalt trifluoride process for the production of perfluoroheptane. Higher-boiling fractions, containing three or more chlorine atoms per molecule, were re-fluorinated.

This successful laboratory route to C_7F_{16} was scaled-up directly to pilot-plant level by a group at the Hooker Electrochemical Company [22]. They encountered a number of difficulties. For example, there were often small explosions in the initial stages of the chlorination, which were traced to the presence of molecular oxygen dissolved in the heptane; it was also

harder to reach the desired degree of chlorination. It was found that quite pure (>98%) n-heptane had to be used as the starting material. Finally all the difficulties were resolved and the following working protocol was adopted. A 570 l vessel with a light well containing a 1200 W mercury arc was charged with 118 kg of heptane, which was then purged with HCl (byproduct of the chlorination, and saved for this purpose) and then treated at 35 °C with a mixture of HCl and Cl₂ at such a rate as to keep the temperature constant. Then, after a few hours, undiluted chlorine was introduced at a rate of 16 kg h⁻¹. After 40 h the pressure was increased to *ca.* 2 - 2.5 atm (this pressure change greatly improved the pilot-plant process), and the temperature was slowly raised. After 72 h, with the temperature at 90 °C, the product contained about 9.5 atoms of chlorine per molecule; after 120 h, with the temperature at 115 °C, the product was the desired Cl₁₂ material, containing 83.6% chlorine, and the chlorination was terminated. This chlorine content in the product gave good results in the fluorination step; if the chlorine level was only 78%, a great deal of tar formed during fluorination.

Fluorination was carried out with hydrogen fluoride in the presence of Sb^V catalysts. The major change from the laboratory conditions was the successful re-oxidation of the catalyst by periodic injection of chlorine into the reaction vessel. Typical fluorination conditions were as follows. A 38 l nickel-lined reactor was charged with 27 kg of C₇H₄Cl₁₂ and 2.7 kg of SbCl₅, together with 24.5 kg of used catalyst from a previous fluorination run. The mixture was heated to between 50 and 70 °C, then treated with 1.4 kg of Cl₂ per hour for 5 h to re-oxidize the used catalyst. Then during a 17 h period, 14 kg of HF was added to the reactor. The chlorination treatment was then repeated, followed by another HF treatment of the same kind as the first. These conditions yielded 88% of crude product analyzing approximately as C₇H₂Cl_{2.5}F_{9.5}. Fractionation of this gave about 45% of material suitable for cobalt trifluoride treatment, and 52% which was recycled for further reaction with HF.

Chlorotrifluoroethylene polymers

The routes to fully-fluorinated hydrocarbons via chloro-aromatics or chloroalkanes produced relatively volatile fluorocarbons, and could not be adapted to the preparation of either lubricants or greases. The only ways described so far to make sufficiently high-molecular-weight materials that were resistant to UF₆ were the direct treatment of lubricating oils with F₂ (the catalytic fluorination process) or with CoF₃. Both approaches used large amounts of elementary fluorine, and the methods were not really capable of producing the relatively large quantities of involatile lubricants needed for the Project. However a solution to this dilemma was provided by the work of William T. Miller (see Fig. 5.5) and his associates, initially at Cornell University of Ithaca, NY, and later at Columbia University [23].

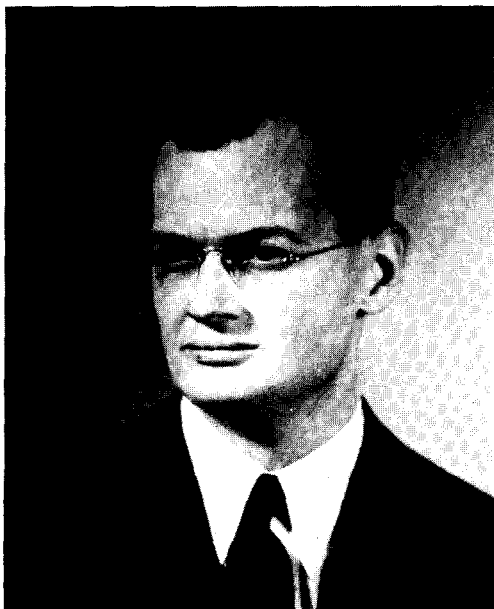


Fig. 5.5. William T. Miller in 1941.

In the Fall of 1941, Miller was contacted by the N.D.R.C. about the possibility of his engaging in research connected with the national interest. He was told that the Government was seeking ways to produce fully-fluorinated organic materials that could be used for war purposes such as noncombustible hydraulic fluids for naval gun recoil mechanisms, lubricants for machine-gun bullets and coolants for applications under extreme conditions. Miller suggested a novel approach to this problem, namely the controlled combination or polymerization of small units, e.g. fluoro-olefins, to give larger molecules which were fluorocarbons, or could be converted to fluorocarbons, with molecular weights ranging from light oils, to greases and waxes, to high polymers with useful mechanical properties. The project was approved, and the group worked on the problem at Cornell for the next year and a half, moving to Columbia University during the period April to June 1943. (At Columbia basic research for the diffusion process was located under the code name of SAM laboratories.) It was only then that Miller realized the actual applications for which his polymers were intended.

Poly(chlorotrifluoroethylene) was not the first highly-fluorinated polymer to be made available to the Project. Poly(tetrafluoroethylene) had been discovered serendipitously in 1938 by Plunkett at Du Pont. It had many valuable applications, particularly in handling UF_6 and F_2 , but its plant use was limited by its extreme melt viscosity, which meant it could not be moulded, and its tendency to undergo cold flow under load. Because of its great chemical stability and unusual physical properties it was regarded by its producers as a unique, and somewhat mysterious, product.

From the outset Miller was searching for a range of fluorocarbon polymers formed from different monomers. The first monomer explored was hexafluorobuta-1,3-diene, but the major effort shifted to chlorotrifluoroethylene when it was found that compounds containing some chlorine in addition to fluorine were stable to UF_6 . The monomer $F_2C=CFCl$ was far more easily prepared than hexafluorobutadiene, and gave saturated products upon polymerization. It was readily made by zinc dechlorination of the commercially available 1,1,2-trichlorotrifluoroethane, Freon[®] 113. The production of this halogenated ethane involved no elementary fluorine, only the reaction of hydrogen fluoride with hexachloroethane. Solid polymers of chlorotrifluoroethylene had been described previously, and were initial targets of the research. They were prepared by free-radical polymerization of the monomer, and were brittle solids of no utility. The way to reduce the molecular weight of the polymers was indicated by Flory's theoretical discussions of polymerization mechanisms. Fast polymerization with a high concentration of initiator, in the presence of an excess of a solvent that could act as a chain-transfer agent, should give telomeric products of low molecular weight. Extensive research led to the choice of benzoyl peroxide as the initiator. Acetyl or chloroacetyl peroxides were quite as effective, but were not commercial products at the time; the benzoyl compound was. The best solvent and chain-transfer agent found was chloroform, which had to be ethanol-free, since ethanol inhibited polymerization. A typical test run, carried out in a steel cylinder, involved a solution of 300 g of C_2F_3Cl in 2700 g of $CHCl_3$ containing 15 g of benzoyl peroxide. The pressure vessel was heated at 100 °C for 100 min, then cooled and vented when some unreacted monomer was recovered. Distillation of the chloroform solution gave an 86% yield of volatile product, based on unrecovered C_2F_3Cl , which was collected as two main fractions: 26% as an oil of boiling range 120 - 220 °C at 0.3 mmHg, and 51% as a thick grease boiling above 220 °C at 0.3 mmHg. The polymers contained carbon-hydrogen bonds derived from the initiator and the solvent, and relatively reactive carbon-chlorine bonds. These reactive end-groups could be removed, and the polymers stabilized, by heating the polymers with a roughly equal mass of cobalt trifluoride. The resulting oils and greases were quite inert to UF_6 .

The mechanism of the polymerization reaction advanced by Miller's group was as follows:

Initiation: Peroxide $\longrightarrow R\cdot$ ($CCl_3\cdot$ and $CHCl_2\cdot$ from chain transfer may also function as initiators)

Propagation: $R\cdot + nCF_2=CFCl \longrightarrow R(CF_2CFCl)_n\cdot$

Chain transfer: $R(CF_2CFCl)_n\cdot + CHCl_3 \longrightarrow R(CF_2CFCl)_nH + CCl_3\cdot$
 $R(CF_2CFCl)_n\cdot + CHCl_3 \longrightarrow R(CF_2CFCl)_nCl + CHCl_2\cdot$

Termination: Radical pairing and/or disproportionation.

The lower-boiling polymer oil fraction (b.p., 120 - 220 °C/0.3 mmHg) contained 39 - 41% chlorine and *ca.* 0.25% hydrogen before cobalt trifluoride treatment. It was quite soluble in a range of organic solvents — halogenated hydrocarbons, ethers — and had a number average molecular weight, determined ebullioscopically, of around 770 g mol⁻¹, corresponding to an average chain length of C₁₂. The higher-boiling polymer fraction could be cracked thermally to give both lower-boiling oils and monomer. Thus the yield of useful oils could be increased. Long-duration mechanical wear tests of pumps and motors lubricated by the stabilized fluorinated oils showed them to be excellent lubricants (at least as effective as standard hydrocarbon lubricants) which exhibited no signs of breakdown over long periods of use.

Within three months, this attractive process for producing a range of useful products from a single easily-prepared monomer was being carried out on pilot-plant scale by a group at the Hooker Electrochemical Company, Niagara Falls, NY [24]. Initially the group made its own monomer, but later used chlorotrifluoroethylene supplied by the Du Pont Company. To increase productivity, the monomer was polymerized at a higher temperature for a shorter time than in the laboratory experiments. For example, a charge of 45 kg of C₂F₃Cl, 409 kg of CHCl₃ and 3.6 kg of benzoyl peroxide was heated at 150 °C for 15 min. This gave a lower average molecular-weight product than under the laboratory conditions described above, but about as much usable oil fraction was produced. After unreacted monomer, some 7.7 kg, had been vented, the chloroform solution was washed with sodium carbonate solution, filtered, then heated to 150 °C under vacuum whilst being purged with oxygen. The resulting oil was subjected to molecular distillation at Distillation Products Incorporated (part of the Eastman Kodak Company). The oil fractions of the distillate were treated with an equal mass of CoF₃ (prepared, as usual, by reaction of F₂ with CoF₂), added in portions with agitation as the temperature was raised to 200 °C and held there for 2 h. The fluorinated, stabilized product was extracted with carbon tetrachloride then, after recovery via removal of the solvent from the filtered extract *in vacuo*, purified by molecular distillation at Distillation Products Inc.

The yields at the various stages of the pilot-plant process were approximately as follows: 100 parts of monomer gave 66 parts of crude polymer and 34 parts of distilled polymer. This yielded 29 parts of crude stabilized product, and 18 parts of the final distilled fluorinated oil. This yield does not take into account the use of higher-boiling fractions for cracking and further production of recovered monomer and oil fractions. It is noteworthy that polymer oils derived from chlorotrifluoroethylene are still in production by essentially the method described here. They are used to lubricate oxygen compressors, and presumably in the processing of UF₆ in the nuclear industries.

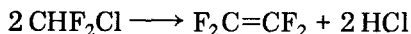
Poly(tetrafluoroethylene) [25]

In 1938, R.J. Plunkett, working for the Du Pont Company, was exploring the properties of tetrafluoroethylene, C₂F₄, the fully-fluorinated analog

of ethylene. The compound was prepared by metal dechlorination of 1,2-dichlorotetrafluoroethane. On one occasion Plunkett condensed a substantial amount of tetrafluoroethylene into a steel pressure vessel for storage. When he next needed the compound he cracked open the cylinder valve, only to find that there was no gas left in the vessel. Curious to find out what had become of the C_2F_4 he cut open the cylinder to find that it contained a waxy solid. His tetrafluoroethylene had spontaneously polymerized. Incidentally, Plunkett was fortunate in two ways in this instance. Not only had he accidentally discovered an extremely valuable polymer, but he had also fortunately avoided a dangerous accident. The polymerization of tetrafluoroethylene can be violent, even explosive, if it is not carefully controlled. Traces of molecular oxygen can act as an initiator for this hazardous reaction.

The properties of the solid poly(tetrafluoroethylene) discovered by Plunkett were remarkable. Most notable was its chemical inertness; it was unaffected by virtually all reagents, including highly aggressive ones like boiling sulfuric acid and molten potassium hydroxide. In addition, it had an extraordinarily low coefficient of friction — things simply did not stick to its surface. It also had high dielectric strength and low dielectric loss. This combination of properties made the polymer potentially very useful in the chemical and electrical industries, and Plunkett's discovery was protected by a 1941 patent.

The fact that poly(tetrafluoroethylene) was inert to compounds like hydrogen fluoride and antimony pentachloride made it a target of Project research also. It could clearly serve useful functions as an inert gasket or valve-packing material. An improved method for producing the monomer was worked out as follows [26]. Treatment of chloroform with hydrogen fluoride, with antimony pentachloride as a catalyst, gave good yields of chlorodifluoromethane, CHF_2Cl ; pyrolysis of this compound, diluted with around 7-10 volumes of steam, at around 700 °C gave excellent yields of tetrafluoroethylene:



The monomer was polymerized in an aqueous dispersion at a pressure of between 10 and 70 atm, using a soluble peroxydisulfate salt as a free-radical initiator. This process gave a good yield of the polymer as white granules composed of very highly crystalline, linear homopolymer. The polymer began to decompose before it melted, consequently conventional melt techniques could not be applied to its fabrication. The technology that was finally worked out was very similar to that of powder metallurgy. The dry powder was pressed into appropriately shaped moulds at 100 - 400 atm to give a mechanically weak preform. This was then sintered at 365 - 385 °C and slowly cooled to give the final product.

Large pieces of poly(tetrafluoroethylene) made in this way could be cut and machined to desired final forms. Gaskets, valve packings and insulators made of this remarkable material were of inestimable value to the operations of the Project.

High polymers of chlorotrifluoroethylene

Although poly(tetrafluoroethylene) did possess the chemical inertness desirable for a high polymer to be used under many of the chemically aggressive conditions found in Project processes, it was difficult to fabricate, and its physical properties made it unsuitable for some important applications. The most successful, and most widely used, alternative was high-molecular-weight poly(chlorotrifluoroethylene), which was developed and produced in amounts of over 100 kg by W.T. Miller and his group [23] at the SAM laboratories, and then put into larger-scale production by a group at Linde Air Products Company, a division of the Union Carbide and Carbon Corporation, which had by this time assumed responsibility for operating the Oak Ridge gas-diffusion plant.

Miller's group had already achieved notable success in the production of lubricants from chlorotrifluoroethylene polymers, as described above. They believed that since the introduction of a chlorine atom in place of one of the fluorines in tetrafluoroethylene would lead to high polymers containing a different dipolar group, they might be less crystalline. Also, it seemed that the lower symmetry of $(C_2F_3Cl)_n$ compared to $(C_2F_4)_n$ might make the former less crystalline than the latter, thus making it a more conventional thermoplastic material.

The conditions that were finally worked out for the preparation of useful high polymers of chlorotrifluoroethylene with the desired mechanical properties were unusual. They involved bulk polymerization of the monomer at low temperature for a long time, a quite new technique. The monomer had to be scrupulously pure to avoid thermal instability of the polymer, so it was carefully fractionated in a low-temperature distillation unit. A new initiator was synthesized for the reaction, namely trichloroacetyl peroxide. This was made by reaction between trichloroacetyl chloride and a 2% solution of sodium peroxide in aqueous (20%) sodium chloride solution at -15°C . The precipitated product was extracted with $CFCl_3$ (Freon[®] 11), crystallized by cooling the extract with dry ice, and redissolved in $CFCl_3$ ready for use. The pure peroxide was a crystalline shock-sensitive solid. In $CFCl_3$ solution its half-life at -16°C was *ca.* 70 h.

Pure chlorotrifluoroethylene, contained in 15 cm diameter stainless-steel cylinders, was treated with a solution of the peroxide in $CFCl_3$, with the initial peroxide concentration in the reaction vessel being 0.03%. The vessel was held at -16°C for 7 d. Under these conditions 30% of the monomer was converted into high polymer. Unreacted monomer and other volatiles were removed by distillation, and the polymer core, which was mechanically quite robust, was cut into roughly 2 cm cubes and heated in a current of filtered air at $125 - 150^\circ\text{C}$ to remove the last traces of volatile materials. The polymer thus produced was chemically very resistant. In fact, polymer scrap which had been contaminated with hydrocarbon oils could be cleaned by heating it with fuming nitric acid or with a dichromate/concentrated sulfuric acid mixture.

The polymer was code-named MFP (Miller's group suggested this stood for *Mighty Fine Product*) and was a high-temperature thermoplastic, so that conventional polymer processes, like pressing into sheets or extruding into tubing, could be applied to it. It was processed at 250 - 300 °C even though it still had a high melt viscosity at the upper end of this range, because it began to decompose back to monomer if the temperature were much higher. Different batches of the polymer were characterized by their No Strength Temperatures (NST). In the NST test a notched sheet of polymer of specified dimensions and carrying a small weight was heated with the temperature increasing steadily at 1.5 °C min⁻¹ until the sheet tore in half. The temperature at which this occurred, normally reproducible to within a degree or two, was called the NST. The most widely used polymer had an NST in the range 300 - 325 °C, and mechanically useful polymers were made with NSTs ranging from 215 °C (though these were rather brittle) to 340 °C (though these had very high melt viscosities).

Control of the crystallinity of the high polymers led to a range of physical properties. Slow cooling from melt temperature gave a harder product that was translucent or milky. Rapid quenching of thin sheets led to a transparent, more flexible, material. A more flexible polymer could also be made by plasticizing high polymer with low-molecular-weight poly(chlorotrifluoroethylene) oils of the type described earlier. The whole range of high-molecular-weight polymers of chlorotrifluoroethylene found a wide range of applications in the Project in situations where a chemically resistant seal, gasket or tube was essential.

A number of other interesting highly-fluorinated polymers were also examined by the Miller group during the Project, but none of them was produced for plant use at the time. These included chlorotrifluoroethylene/tetrafluoroethylene and fluoroethylene/hexafluoropropene copolymers, and homopolymers of perfluorobutadiene [23].

Conclusion

The years 1943 and 1944 saw steady development of the processes discussed above, which made reliable supplies of fluorocarbon derivatives available for the production needs of the Project. It is beyond the scope of this chapter to detail the many problems encountered in both the U-235 gas diffusion separation process and the plutonium production operation. As late as June 1944 the supply of fissile materials from the plants was just a trickle. But the difficulties of production were steadily overcome, and it became clear that nuclear weapons would be ready by late 1945.

On May 7th, 1945, the German High Command agreed to an unconditional surrender. The war in Europe was over, but the Pacific war still raged fiercely, and it became clear that if a successful atomic bomb could be produced, it would be in the Pacific region that it might be used. By now a steady flow of fissile uranium and plutonium was issuing from the produc-

tion lines. It was decided that the plutonium weapon, which was of a novel design involving implosion of a mass of plutonium in order to make it critical, would have to be tested. The test was arranged for a remote site at Alamogordo in the New Mexico desert, and was code-named 'Trinity'. The device tested was not a combat weapon, but its charge was similar to that planned for actual bombs. The test took place just after 5 a.m. on July 16th, 1945. It was technically a spectacular success. The explosive yield of the device was well above that estimated by the scientists involved, and was the equivalent of over 5000 tons of TNT.

By late July two combat weapons had been assembled. 'Little Boy' was the code-name of the uranium-235 gun-type weapon, 'Fat Man' that of the plutonium-implosion bomb. On August 6th, 1945, 'Little Boy', with an explosive yield equivalent to greater than 20 000 tons of TNT, was exploded over Hiroshima, Japan, with devastating effect. On August 9th, 1945, 'Fat Man', with a similar explosive yield, was exploded over Nagasaki, Japan, and wreaked awesome destruction. On August 10th, 1945, Japan agreed to accept the surrender terms of the Allies, and the Second World War was at an end. For good or ill a new age of weaponry had been initiated, the age of nuclear weapons, and the World had had an awful illustration of the devastation these new weapons could wreak.

Fluorine chemistry came of age during the Manhattan Project. Of course it did make an indispensable contribution to the development of nuclear weapons, but it also paved the way to the peaceful uses of atomic energy. And it provided a remarkable model of a cooperative, multinational, government-supported, large-scale scientific undertaking that has been followed widely since.

Acknowledgements

I wish to thank Professors G. H. Cady and W. T. Miller for their willingness to discuss details of those phases of the Manhattan Project in which they were involved; Professor Miller also provided helpful comments on parts of this chapter. I am also grateful to W. T. Miller and the American Chemical Society for permission to reproduce illustrations. The preparation of this chapter was aided by a grant from California State University, Los Angeles.

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BIOGRAPHIC NOTE

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