Journal of Fluorine Chemistry, *32* (1986) 29–40

THE SIMONS ELECTROCHEMICAL FLUORINATION PROCESS (COMMERCIAL DEVELOPMENT AT 3M)

W.H. PEARLSON

3M Center, St. Paul, MN 55144 (U.S.A.)

First came the idea. Joe Simons wanted to make carbon-fluorine compounds. He figured the easiest way might be to pass a direct electrical current through a solution of an organic compound in anhydrous hydrogen fluoride.

Then came the invention. A solution was prepared, placed between an anode and a cathode, the gases produced condensed and analyzed -and carbon-fluorine compounds and hydrogen were identified.

But from the invention, the ability to make some compounds, to the industrial achievement of making, in large quantities, products that people want to buy, is a long path. It is not the kind of trail that a lone inventor, or even a small group, can break. The odds against success are tremendous. But in this case they were overcome and we might look at how it was that a relatively small company, with gross sales of about $ 50 million dollars, knowledgeable in glueing particles to paper to make sandpaper, glueing glass beads on paper to make reflective sheeting, glueing big particles on paper to make Safety-Walk® surfaces, combining glue and paper to make tape, was willing and able to successfully carry out the necessary research and development program.

It took a lot of people, and there is no way to do justice to even the major contributors in the space available so names will be skipped, with a very few exceptions. It took a lot of selling. A number of eminent chemical and electrochemical companies had a shot at the process and turned it down cold. Dr. H.N. Stephens, director of Central Research of 3M, thought it looked good. He carried the concept back to 3M, and over many hours of discussion convinced Mr. Carlton, vice president in charge of Research and Manufacturing, and Mr. McKnight, president of the company, that this was a venture worth undertaking. The challenge was sold honestly, and they were told it was going to take about five years, and maybe a half-a-million

0020-1139/86/$3.50

dollars, before they would know if there was anything to it at all. It was going to take another five years, and maybe a million dollars, before they would know if they could make a profitable venture out of it. Mr. McKnight summed it up: "Here is a new process that will make new compounds appear to do things that nothing else can do and we can get good patent coverage so let's go!".

Expenditures at 3M really began in about 1946, when several laboratory cells were put into operation and construction was begun on a major pilot plant cell. This was quite a gamble for a company the size of Minnesota Mining. After all, even though at Penn State at that time we had made grams of a number of different substances, we really had produced pounds only of CF_4, boiling at minus 130°; C_2F_6, boiling about minus 80°; and C_3F_8, boiling about minus 40°C. The Pilot Plant accordingly was designed to produce these gases, which we anticipated would be useful replacement for the Freons® and hydrocarbons as refrigerants. It took us several years before we had the thermodynamics run to show there was a problem with retrograde condensation that made it unlikely that these would ever be commercial refrigerants.

We had another problem, analytical data was hard to come by. We could run fluorine analysis by reaction with elemental sodium, plus or minus 20%. We could run infrared spectra but of course we were preparing the original library. We could determine molecular weights with a vapor density balance, sensitive perhaps to five percent. We could determine boiling points and liquid densities.

For example, we tried dibutyl ether in the cell. The product by all the tests we could run was C_8F_{18}, previously prepared from octyl alcohol and octyl amine. Nobody liked to believe that one could pull out an oxygen from the middle of a molecule and tie the two pieces together again, but the density, the boiling point, the molecular weight, the infra-red spectrum, within our precision, were all about the same. Novel methods for novel compounds. We got Professor Al Nier of the University of Minnesota to pass the product through the new mass spectrometer he had developed for ions with high molecular weight. Every fragment having more than four carbon atoms had this nice little 16 moiety within it. We had a perfluoro-dibutyl ether, and he, incidentally, had a method of calibrating his equipment with ions of up to 400 and higher.

It was pretty clear that we weren't going to be able to go very far in synthetic chemistry with the kind of materials we could then make. They showed all the characteristics of the fluorocarbons, incompatibility with oil and water, thermostability, etc., but there was no good way of converting these stable compounds into the kinds of organic molecules that could be commercial products. We needed a "hook" so that we could transform this type of material into polymerizable molecules, or into molecules that would be the raw materials for organic syntheses but fluorocarbons with functional groups were virtually unknown at that time. To find some was the job I was assigned when I came up from Penn State to St. Paul. We started out with brute force, pyrolyzing our simple fluorocarbons and sometimes making unsaturated compounds.

Fortunately, serendipity reared its head. Down in the Pilot Plant they were running butyric acid to make C_3F_8, but were plagued with large amounts of oxygen difluoride from the water liberated. We had to use a train of a catalyst tube in which the hydrogen gas could reduce the OF_2, followed with an aqueous ammonia tower that could take out the HF and CO_2, and then condense the fluorocarbons out of the gas stream. One of the engineers had the bright idea of using butyric anhydride to get rid of some of the water and perhaps cut down the OF_2.

It worked, and OF_2 was minimized, but, apparently unfortunately, there was a slight side-effect. The ammonia column kept plugging up with a white solid; pounds of it were actually found. Some of it was sent up to the analytical lab and we played around with it for a couple of days, and identified perfluorobutyramide. Out of the cell was coming a fluorinated carboxylic acid derivative in recoverable quantities. Now we had the 'hook', we had the reactive group we needed. The new acid went over to the organic chemists. They could esterify it, they could make an acid chloride out of it, they could make vinyl esters, they could reduce it to the alcohol and make acrylates, and we began to look at the library of compounds that could come out of a reactive fluorochemical.

In spring of '49 a meeting was called in the laboratory, with all 31 of the professional people associated with the fluorocarbon project, and present was Mr. Carlton. He pointed out that he was shortly going to have to make a request for the budget for next year, and he thought we were the most knowledgeable group to give him information as to whether he should increase the budget, decrease it, or drop the project as a whole. It was a very voluble group, and, even to the number two man in the company, we expressed our opinions at length as is why we thought it was a good project, and why we thought it would work.

To sum it up Mr. Carlton said, "Look, I'm going to have to make a recommendation for next year, and I'm going to have to sign my name to it. I would like each of you to project the future of this program, make your recommendation and sign your name to it." And we did. There were two notes for dropping back to perhaps a two- or three-man program, until we could find a product that could be sold and from the profits we could build up the research the standard 3M pattern. The rest of us felt we had a bear by the tail. The only way we were going to survive was by going at the project full bore, until we could develop it to where it would stand on its own feet. We were given the chance to continue.

That was the year that the papers on the Simons process were first presented to the American Chemical Society, at the Portland meeting, creating a vast amount of interest. The rest of the chemical world immediately became interested. From a major chemical house came an invitation: "You people know how to make sandpaper, but we are chemists. Let us develop a joint venture, and carry out the development of this program together." From one of the foremost of the chlor-alkali companies came the comment: "You people know how to make sandpaper, but we know electrochemistry. Together we can develop this invention properly."

To the 3M company, chronically short on capital, and to enthusiasts in other fields denied funds for pet projects they knew would develop faster if less money were "poured down that fluorocarbon rat hole," the temptation was strong. However, satisfied that such interest from the outside experts merely confirmed the potential value of the process, the management decided to carry on as before.

The Air Force then came into the picture. They wanted us to try to create an oil-resistant elastomer stable at high temperatures and flexible at low temperatures. Eventually, we got a suitable contract and we were on that course for several years. The best polymer that we got was poly-(perfluorobutyl acrylate) which was a pretty good oil resistant rubber, fairly stable at elevated temperatures, but about 80° short of reaching the minus 100° goal that the Air Force had in mind. Nevertheless, the contract did allow us to expand the laboratory program by about 50 percent, further developing the chemistry of these novel fluorochemicals.

The year 1950 was very significant, one of the major chemical companies came to us after the '49 ACS meeting and said, "We need a surfactant. Would you make for us the ammonium salt of a nine-carbon carboxylic acid, completely fluorinated except for a hydrogen on the far end?" We looked at it and had to say we couldn't, but asked if they would care to try an eight-carbon carboxylic acid with fluorine on the end.

At first they declined, they had technical experience that showed their compound worked and a theoretical basis for saying they needed it. We said that we could make the completely fluorinated acid and it was worth a trial. They tried it and they liked it, and, as a matter of fact, they are still buying it.

Now at last we had our first repeat sale. For the first time we had a customer out there who was going to buy the materials today, and next week, and, optimistically, next year even: we were in business! Actually, we had one fulltime salesman.

We could make four-carbon, six-carbon, and eight-carbon carboxylic acids; at ten carbons, the yields dropped so that it was no longer feasible to isolate the material. Incidentally, there are a few interesting papers out speculating on why the Simons process can make only even-numbered carboxylic acids. It apparently didn't occur to some that those are the fatty acids commercially available.

We started on surface treatments about this time. Toluene wets glass, but if a diluted toluene solution of perfluorooctanoic acid is poured into a flask, swirled around and then poured out, the flask is almost dry, just a few small droplets are left and the glass is no longer wetted by toluene.

There were obvious commercial possibilities in this. A paint might be so treated so that it then would drain clean. All the waste could be eliminated, and it takes only a very little material to coat that can so we tried it. We coated the can, poured the toluene out, poured the paint in, poured the paint out, and it drained dry beautifully. We had to show Mr. McKnight. We prepared the can, put the paint in, and a day or two later we were able to sit down with him across the desk (fortunately I was not there) and poured the paint out of the can, and it stuck to the can just like any other paint you ever saw. In the few days interval, the deposited film had dissolved in the paint. Mr. McKnight was not impressed. But he didn't kick us out!

We knew that a chromium complex of stearic acid could be deposited onto fabric which would then shed water beautifully. If we could use a fluorocarbon acid it should shed both oil and water; in fact be stain resistant. We made such a complex, and it worked, oil and water both beaded up on the treated fabric. We had fair business, not big. You could treat upholstery with it, you could treat drapery with it but it didn't go so far in textiles. Our marketing man used to come around pleading: "Please, can't you give us a white chrome complex?" However chromium stayed green, and there is a 'very' limited market for green fabric.

There we were then, with no really good leads to highly marketable products; salesmen called on various industries, raising an occasional show of curiosity from the field, but we clearly had to make the world better acquainted with what we could do, and create more interest in these unique compounds. We gave seminars in any company that would give us the time. We were invited on ACS tours. We would present examples of these stable materials and demonstrate their unique low temperature fluidity; their low surface tension; their stability to oxidation or reduction. I'd end my presentation something like this: "Now you know something about these unusual compounds, all the possibilities for solving up-to-now intractable problems. Have you any such problems?"

At one meeting in Detroit, as was usual, many came up after the meeting and asked questions, and toward the end when the crowd had thinned out, one man came up to me and almost furtively said, "I don't want my competitors to know what I'm asking, but you've got what I've been looking for for the last ten years, can I have a sample of your perfluorocarboxylic acid?" Because that material was awfully expensive to make, we weren't lightly giving away the pounds that everyone seemed to expect, but he said, "If I had a couple of grams I think I could show whether or not it would work, and with ten grams, I think I could run a program." We gave him the sample. Within two weeks, we had a four- or five-page handwritten letter coming back to us praising the product to the sky. They would pay any price for this material, and, we immediately sent a couple of salesmen down there - we then had two salesmen.

What the customer company wanted to do was to add this acid to a chrome plating bath, consisting of hot concentrated sulfuric and chromic acid. The gas bubbles coming up through the surface create a rather vicious mist which even takes paint off the cars in the parking lot. They spent more on the ventilation to make the plant livable than they did on the power to do their plating. They put the C_8 acid in the bath and it formed a beautiful bed of bubbles on top, almost no mist came out; they could turn off the ventilation.

We were in business, or almost! It seemed that while they would be willing to pay almost any price, there actually were some limits. This material evaporated so rapidly, that they couldn't afford the necessary replacement and had to have something less volatile. There was a stir in the laboratory at that point. If we had the corresponding amine it probably would stay in the bath but it was very difficult to find a practical method of making this amine. While working on that tack, we tried others, too. Sulfonic acids are essentially non-volatile. We had tried three times to make perfluorosulfonic acids as we had the carboxylics but we had never got a trace. However, we had learned something in the last year or two, and thought we ought to try again.

Paratoluenesulfonic acid was readily available at a reasonable price, and this time we did make the perfluorosulfonic acid. It performed beautifully; it went in the bath and stayed there and they had their foam blanket. However, too much of it still had to be used to make it really practicable. Could we add just one more carbon atom? We set out to sulfonate ethylbenzene. We couldn't wait for the proper equipment to be installed, and in a Minnesota winter, we did our sulfonating in a 50-gallon drum in a tent. We had some real earnest process engineers and, they worked and it worked. We had a satisfied plating outfit, and we were off and running with a major repeat customer. We were in business and we had sales.

Our top management team was sent down to discuss price on the sulfonic acids, vice presidents in charge of sales and managers, and they had a wonderful time down there for three days. So good a time in fact that when they came back we found that they had accepted a price that was two-thirds of what we had told them was the minimum that we must have. But we too had pulled a fast one in the three days they had been gone, we had been able to double the yield of the sulfonic acid out of the cell. While the carboxylic acids could fill the technical needs, their cost was too high. The sulfonic acids were a bit better, and now we had low-cost product, at least, low-cost by our standards. Further, through the sulfonyl group we could tie onto almost any reactive functional organic group, and move right into known organic synthesis, with a little modification to compensate for the oddities of the fluorocarbon moiety.

With about a hundred people in the laboratory, we were now reaching sales of $ 100,000 per year. Our vice president came down to one of our Friday morning meetings, and he put the sales curve on the board and said, "That is a nice steep curve, I'm sure you are proud of it." Then he put another curve on, just a little bit steeper, and he said, "That's your expense curve, and I'm not sure that we can afford to build up your sales any further." It was very clear that the honeymoon was over, and we had to get more sales, without any significant increase in laboratory work.

Obviously economics favored using our materials to produce a very thin film on a surface. The chrome complex had shown that a low energy stain repellant surface could be created, but left something to be desired. However, the dream of the Man in the White Suit, the fabric that would shed soil and stain, was still alive.

The elastomer that we were developing, poly (perfluorobutylacrylate) was made as a latex, and a technician spilled a little of this onto her tennis shoe. A couple of weeks later, she had a spot on the tennis shoe, a clean spot: everything else was dirty. When the tennis shoes were washed, the spot stayed there and stayed clean. We had a couple of observant chemists, and they now set to work to find a suitable acrylate polymer that could be put on fabric and provide the resistance to staining we had been looking for.

When they had succeeded we were able to go to the textile mills and convince them that they should run through yards of fabric that would have these fantastic properties. Everybody on the project of course obtained some of the fabric and had it made into suits, even Mr. McKnight. Our suits worked just like advertised. You put oil on the fabric, the drops stood right up; you put water on it, and it rolled right off; if you got a stain, you could remove it without leaving a ring. In contrast, Mr. McKnight's suit seemed to act like a sponge and soaked dirt up. We had taken our material to a local tailor and he had cut it and made into suits, and it worked! Mr. McKnight sent his down to his Chicago tailor, who used what I think is termed 'The London Boil', something that required it be boiled in soapy water for hours so that it would have dimensional stability when the suit was completed. It had dimensional stability, but no finish. We left Mr. McKnight out of the experimental loop from then on.

But he still appreciated us, though the textile industry didn't. They conceded that we could do everything that we said; they were willing to make hundreds of yards of treated cloth, but had no real appetite.

Our sales people were frantic, and couldn't understand why they couldn't sell products with such marvelous properties. We had a cost accountant who constantly criticised them, until they finally told him to get out there and sell it himself! And he did; he spent a week or so out in the field and came back with the story. He said "this industry is not like the chemical industry. They don't buy on performance. They buy on gimmicks, they buy on advertising, and if we are going to sell anything, we're going to have to play it their way. Devise an advertising campaign, and we're going to have to pay for a lot of it." This was strictly against 3M principles like so much else on this project, but we set out to do it. We promoted the Scothgard name, we got some advertisements to grab attention, and at last we had customers demanding to buy treated garments. We were at long last in that delightful state of having to expand capacity to meet demand.

And of course, just about at this time, everything else broke. Always, when we produced these nice reactive materials we also produced 'inerts,' liquids boiling from room temperature up to several hundred degrees that had no reactivity. They were just nice stable fluids. Because of their high thermal expansion, because of their electrical resistance, because of their chemical stability, we knew that they should be wonderful for heat transfer. As a matter of fact, Westinghouse had a patent in the late '40's that used fluorocarbon as direct contact coolant for a transformer. It worked but somehow or another, it didn't work well enough for anybody to want to keep on building them. We talked to a lot of people, and after about four years of extensive engineering development, Raytheon was finally able to create a radar generator that weighed one-third and occupied one-half the volume of the best previously available, and for the Air Force, that is eminently marketable. We now had a totally new line of business.

Once the electronic people got hold of these fluids, they found that they could be adapted to all kinds of things. The fluids were highly stable, and non-conducting, ideal for test equipment. Hermetically sealed units could be immersed in the heated fluid and if bubbles arose, taken out and resealed and then retested. If there were no bubbles, they could be sold directly, no clean-up being involved. A whole new field of testing technology arose.

More recently, Western Electric became concerned about the difficulties in soldering the myriad of connections on circuit boards. A soldering iron couldn't be used anymore: little collets of solder were placed where needed, the board was put in an oven, and hopefully it reached the right temperature and the solder flowed, but not too much. The temperature had to be high enough to melt the solder, but not high enough to warp the board, which was taken out just at the time when it reached maximum temperature. Even if you had 99% completion, you still had an awful lot of boards to be re-worked.

If on the other hand, you have an inert fluid that boils just a few degrees above the melting point of the solder, and you put the circuit board cold into the condensing vapors, and let them condense on the board, you have beautiful heat transfer. The solder melts, but it doesn't get any hotter than necessary, and you pull the board out and shake it off, no clean-up is necessary, and it's ready for use.

Consider another market sector. Aircraft carriers, out on the ocean are floating bombs, with tanks and pipes and hoses full of flammable fuel; every plane is a potential ignition source.

Some Naval Officers have devoted their lives to trying to find methods for successfully fighting this class of fires, and they will try anything. They tried some of our surfactants, thinking they might have better effects than the silicone material they had been working with. They found instead that, with the fluorochemical surfactant, water would float on gasoline, cut off the escape of vapors and the fire was extinguished almost immediately, at least in an experiment in a petri dish. Of course, it took about five years of laboratory work to develop that concept into salable products, products that would put out fires dependably and at an affordable price.

There has been in all this an interesting pattern of product concept generation, not unique to fluorochemicals. Except for the fabric treating, the markets all came from outside; emulsifier, plating bath foamer, transformer coolant, electronic testing, fire extinguishing, and many others. Why didn't we ourselves start these projects? Pure ignorance, it is not possible to know all the intricacies of everybody's art.

Once we were shown a particular problem-solving application, we should usually come up with a better-fitting composition that did the job efficiently and at a reasonable cost. However, we needed the initial clue tha can come only from one familiar with the problem.

I've indicated many different people who contributed to the commercial success of Joe Simons' concept, and I've omitted far more. In fact, the presentation has been almost egocentric. Admittedly, until you have a working process, and a useful product, you have nothing, but with just these you haven't much more.

All has to start in the research laboratory, but then engineers to design and build the plants that can make tons instead of grams are needed, and a production team to keep a stream of quality products going from the shipping dock, a marketing team, and a sales team. The proverbial path to the door of the inventor of the better mousetrap just doesn't get beaten in practice, especially in truly new technologies!

Most importantly, all these team members must be hired, trained, clothed and fed. They must be kept in an environment which encourages and stimulates, and all this with no money coming in and no assurance that any ever will.

Our original estimates were not too far off. It took almost ten year before we broke even (- the year expenses equalled income -) and not until the late '50's were we able to say that the profits contributed to 3M equalled the many dollars that had gone down that fluorocarbon rathole.

It took a management with patient money that would encourage and assist and observe, and could recognize when the information and skills and technical developments had reached the critical point, when they could apply the screws, insist that now we could and now we must respect that bottom line in the balance sheet.

3M had such a management and Joe Simons' original concept is now an industry with more than 250 commercial items.