# 6

# Halogens and
# Politics and Deep Space

While all of this was going on there were a lot of people who were not convinced that peroxide, or acid, or nitrogen tetroxide was the last word in storable oxidizers, nor that something a bit more potent couldn't be found. An oxygen-based oxidizer is all very well, but it seemed likely that one containing fluorine would pack an impressive wallop. And so everybody started looking around for an easily decomposed fluorine compound that could be used as a storable oxidizer.

"Easily decomposed" is the operative phrase. Most fluorine compounds are pretty final—so final that they can be thought of as the ash of an element which has been burned with fluorine, and are quite useless as propellants. Only when fluorine is combined with nitrogen, or oxygen, or another halogen, can it be considered as available to burn something else. And in 1945 not very many compounds of fluorine with these elements were known.

$OF_2$ was known, but it was difficult to make and its boiling point was so low that it had to be considered a cryogenic. $O_2F_2$ had been reported, but was unstable at room temperature. $NF_3$ was known, but its boiling point was too low for a storable. ONF and $O_2NF$ both had low boiling points, and couldn't be kept liquid at room temperature by any reasonable pressure. (It was specified, arbitrarily, a few years later, that a storable propellant must not have a vapor pressure greater than 500 psia at 71° (160°F). Fluorine nitrate and perchlorate, $FNO_3$ and $FClO_4$, were well known, but both were sensitive and treacherous explosives. Of the latter it had been reported that it frequently det-

onated "upon heating or cooling; freezing or melting; evaporation or condensation; and sometimes for no apparent reason."

That left the halogen fluorides. $IF_5$ and $IF_7$ both melted above 0°C, and the thought of carrying that heavy iodine atom around was not appealing. BrF was unstable. $BrF_3$ and $BrF_5$ were known. If either of these were to be used, the pentafluoride was obviously the better bet, since it carried the more fluorine. ClF was low boiling, and didn't have enough fluorine in it. That left $ClF_3$, and maybe $BrF_5$ in a pinch, or when density was all important. (It has a density of 2.466 at 25°.)

And that was it, although JPL in 1947 was dreaming wistfully of such improbabilities as $F_2O_7$, and the Harshaw Chemical Co. spent a good deal of time and money, in 1949 and 1950, trying to synthesize things like $HClF_6$ and $ArF_4$,* and naturally (as we say now, with 20–20 hindsight) got nowhere. They *did* learn a lot about the synthesis and properties of $OF_2$.

So $ClF_3$ it had to be. Otto Ruff had discovered the stuff in 1930 (as he had also discovered the majority of the compounds listed above) and the Germans had done a little work with it during the war, and so quite a lot was known about it. The efflorescence of fluorine chemistry sparked by the Manhattan Project led to studies in this country, and the Oak Ridge people, among others, investigated it exhaustively during the late 40's and early 50's. So it wasn't exactly an unknown quantity when the rocket people started in on it.

Chlorine trifluoride, $ClF_3$, or "CTF" as the engineers insist on calling it, is a colorless gas, a greenish liquid, or a white solid. It boils at 12° (so that a trivial pressure will keep it liquid at room temperature) and freezes at a convenient −76°. It also has a nice fat density, about 1.81 at room temperature.

It is also quite probably the most vigorous fluorinating agent in existence—much more vigorous than fluorine itself. Gaseous fluorine, of course, is much more dilute than the liquid $ClF_3$, and liquid fluorine is so cold that its activity is very much reduced.

All this sounds fairly academic and innocuous, but when it is translated into the problem of handling the stuff, the results are horrendous. It is, of course, extremely toxic, but that's the least of the problem. It is hypergolic with every known fuel, and so rapidly hypergolic that no ignition delay has ever been measured. It is also hypergolic with such things as cloth, wood, and test engineers, not to mention asbestos, sand, and water—with which it reacts explosively. It can be

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* It has recently been shown that an argon fluoride, probably $ArF_2$, *does* exist, but it is unstable except at cryogenic temperatures.

kept in some of the ordinary structural metals — steel, copper, aluminum, etc. — because of the formation of a thin film of insoluble metal fluoride which protects the bulk of the metal, just as the invisible coat of oxide on aluminum keeps it from burning up in the atmosphere. If, however, this coat is melted or scrubbed off, and has no chance to reform, the operator is confronted with the problem of coping with a metal–fluorine fire. For dealing with this situation, I have always recommended a good pair of running shoes. And even if you don't have a fire, the results can be devastating enough when chlorine trifluoride gets loose, as the General Chemical Co. discovered when they had a big spill. Their salesmen were awfully coy about discussing the matter, and it wasn't until I threatened to buy my RFNA from Du Pont that one of them would come across with the details.

It happened at their Shreveport, Louisiana, installation, while they were preparing to ship out, for the first time, a one-ton steel cylinder of CTF. The cylinder had been cooled with dry ice to make it easier to load the material into it, and the cold had apparently embrittled the steel. For as they were maneuvering the cylinder onto a dolly, it split and dumped one ton of chlorine trifluoride onto the floor. It chewed its way through twelve inches of concrete and dug a three-foot hole in the gravel underneath, filled the place with fumes which corroded everything in sight, and, in general, made one hell of a mess. Civil Defense turned out, and started to evacuate the neighborhood, and to put it mildly, there was quite a brouhaha before things quieted down. Miraculously, nobody was killed, but there was one casualty — the man who had been steadying the cylinder when it split. He was found some five hundred feet away, where he had reached Mach 2 and was still picking up speed when he was stopped by a heart attack.

This episode was still in the future when the rocket people started working with CTF, but they nevertheless knew enough to be scared to death, and proceeded with a degree of caution appropriate to dental work on a king cobra. And they never had any reason to regret that caution. The stuff consistently lived up to its reputation.

Bert Abramson of Bell Aircraft fired it in the spring of 1948, using hydrazine as the fuel, NACA and North American followed suit the next year, and in 1951 NARTS burned it with both ammonia and hydrazine.

The results were excellent, but the difficulties were infuriating. Ignition was beautiful — so smooth that it was like turning on a hose. Performance was high — very close to theoretical. And the reaction was so fast that you could burn it in a surprisingly small chamber. But. If your hardware was dirty, and there was a smear of oil or grease

somewhere inside a feed line, said feed line would ignite and cleverly reduce itself to ashes. Gaskets and O-rings generally had to be of metal; no organic material could be restrained from ignition. Teflon would stand up under static conditions, but if the CTF flowed over it with any speed at all, it would erode away like so much sugar in hot water, even if it didn't ignite. So joints had to be welded whenever possible, and the welds had to be good. An enclosure of slag in the weld could react and touch off a fire without even trying. So the welds had to be made, and inspected and polished smooth and reinspected, and then all the plumbing had to be cleaned out and passivated before you dared put the CTF into the system. First there was a water flush, and the lines were blown dry with nitrogen. Then came one with ethylene trichloride to catch any traces of oil or grease, followed by another nitrogen blow-down. Then gaseous CTF was introduced into the system, and left there for some hours to catch anything the flushing might have missed, and *then* the liquid chlorine trifluoride could be let into the propellant lines.

It was when the stuff got into the motor that the real difficulties began, for a chlorine trifluoride motor operates at a chamber temperature close to 4000 K, where injectors and nozzle throats have a deplorable tendency to wash away, and unless the materials of which they are made are chosen with considerable astuteness, and unless the design is *very* good, the motor isn't going to last long. The propellant man liked CTF because of its performance, and the engineer hated the beast because it was so rough on motors and so miserable to handle. Although he had to learn to live with it, he postponed the learning process as long as he could. It is only recently, as the customers have been demanding a better performance than can be wrung out of IRFNA-UDMH, that CTF has been the subject of much intensive, large scale, testing.

Bromine pentafluoride, $BrF_5$ is very similar to $ClF_3$ as far as its handling properties are concerned, except that its boiling point (40.5°), is a little higher. Oddly enough, it never seems to perform as well as it should, and it's much harder to get a reasonable percentage of its theoretical performance out of it on the test stand than it is with CTF. Nobody knows why.

Very early in the game it was apparent to several of us in propellant chemistry that there really wasn't any fuel available that was right for $ClF_3$. Ammonia's performance was too low, and hydrazine, with an excellent performance and density, froze at a temperature that was much too high. And everything else had carbon in it. And with a fluorine type oxidizer that is bad. (See the chapter on performance.) It

degrades the performance, and produces a conspicuous smoky exhaust stream. So in the latter part of 1958 Tom Reinhardt of Bell, Stan Tannenbaum of RMI and I at NARTS, unknown to each other, tried to do something about it. And since chemists with similar problems are likely to come up with similar answers, we went about it in very much the same way. Stan and Tom considered that the best place to start was with MMH, $CH_6N_2$, which was about as close to hydrazine as you could get, and then get enough oxygen into the system to burn the single carbon to CO. And they did this by mixing one mole of water with one of MMH, to get a mixture equivalent to $COH_8N_2$. When this was burned with CTF the carbon and oxygen went to CO and the hydrogens burned to HCl and HF. The performance was somewhat below that of hydrazine, since considerable energy was wasted in decomposing the water, but it was still better than that of ammonia. And they found that they could add considerable hydrazine (0.85 moles to one of MMH) to the mixture without raising the freezing point above −54°. Bell Aerosystems now calls the mixture BAF-1185.

I started with MMH, too. But I remembered all the work we had done with hydrazine nitrate, $N_2H_5NO_3$, and used that as my oxygen carrier, mixing one mole of it with three of MMH. And I found that I could add a mole or two of straight hydrazine to the mix without ruining my freezing point. I wanted to do performance calculations, to see how it would compare with hydrazine, and phoned Jack Gordon of RMI to get the heat of formation of MMH and hydrazine nitrate. He was (and is) a walking compendium of thermodynamic data, so I wasn't too surprised that he had the figures on the tip of his tongue. But my subconscious filed the fact for future reference.

Anyway, I did the performance calculations, and the results looked good—about 95 percent of the performance of straight hydrazine, and no freezing point troubles. So we made up a lot of the stuff and ran it through the wringer, characterizing it as well as we could, which was pretty well. We ran card-gap tests * on it, and found that it was

* The card-gap test is used to determine the shock sensitivity of a potentially explosive liquid. A 50-gram block of tetryl (high explosive) is detonated beneath a 40 cc sample of the liquid in question, contained in a 3″ length of 1″ iron pipe sealed at the botton with a thin sheet of Teflon. If the liquid detonates, it punches a hole in the target plate, of ³⁄₈″ boiler plate, sitting on top of it. The sensitivity of the liquid is measured by the number of "cards," discs of 0.01″ thick cellulose acetate, which must be stacked between the tetryl and the sample to keep the latter from going off. Zero cards means relatively insensitive, a hundred cards means that you'd better forget the whole business. As may be imagined, the test is somewhat noisy, and best done some distance from human habitation, or, at least, from humans who can make their complaints stick.

quite shock insensitive, in spite of all that oxidizing salt in it. It seemed to be a reasonably good answer to the problem, so we code-named it "Hydrazoid N," and stuck it on the shelf for the engineers when they would need it.

Then, one day, I got a phone call from Stan Tannenbaum. "John, will you do some card gaps for me?" (RMI wasn't equipped to do them, and RMI and my outfit always had a comfortable, off-the-cuff, forget the paperwork and what the brass don't know won't hurt them, sort of relationship, so I wasn't surprised at the request.)

"Sure, Stan, no problem. What's the stuff you want me to fire?"

He hesitated a moment, and then, "It's proprietary information and I'm afraid I can't tell . . ."

"(-bleep-) you, Stan," I interrupted amiably. "If you think I'm going to tell my people to fire something without knowing what's in it you've got rocks in the head."

A longer pause. I suspect that my reaction wasn't unexpected. Then, "Well, it's a substituted hydrazine with some oxidizing material . . ."

"Don't tell me, Stan," I broke in. My subconscious had put all the pieces together. "Let me tell you. You've got three moles of MMH and one of hydrazine nitrate and—"

"Who told you?" he demanded incredulously.

God forgive me, but I couldn't resist the line. "Oh, my spies are everywhere," I replied airily. "And it doesn't go off at zero cards anyway." And I hung up.

But two minutes later I was on the phone again, talking to the people in the rocket branch in Washington, and informing them that RMI's MHF-1 and NARTS's Hydrazoid were the same thing, that Stan Tannenbaum and I had come up independently with the same answer at the same time and that nobody had swiped anything from anybody. The time to stop that sort of rumor is before it starts!

A few years later (in 1961), thinking that if hydrazine nitrate was good, hydrazine perchlorate ought to be better, I put together Hydrazoid P, which consisted of one mole of the latter, $N_2H_5ClO_4$, four of MMH, and four of straight hydrazine. It was definitely superior to Hydrazoid N, with a performance 98 percent of that of hydrazine itself, and a somewhat higher density. In putting it together, though, I remembered previous experience with hydrazine perchlorate, and figured out a way to use it without ever isolating the dry salt, which is a procedure, as you may remember, to be avoided. Instead, I added the correct amount of ammonium perchlorate (nice and safe and easy to handle) to the hydrazine, and blew out the displaced

ammonia with a stream of nitrogen. Then I added the MMH, and I was in business. The mixture turned out to be somewhat corrosive to stainless steel at 71° (hydrazine perchlorate in *hydrazine* is a strong acid) but its behavior when it was spilled was what scared the engineers. If it caught fire as it lay on the ground, it would burn quietly for some time, and then, as the hydrazine perchlorate became more concentrated, it would detonate—violently. (Hydrazoid N, or any similar mixture, it turned out, would do the same thing.)

It seemed likely that if the burning rate of the mixture could be increased so much that the combustion would take place in the liquid and not in the vapor phase, the perchlorate would never have a chance to get concentrated, and the problem might be licked. I knew, of course, that certain metal oxides and ions catalyzed hydrazine decomposition, but I didn't want this to happen except under combustion conditions. The answer seemed to be to wrap the ion in a protective structure of some sort, which would be stripped off at combustion temperatures. So I told one of the gang to make the acetylacetonate complex of every metal ion he could find in the stockroom.

He came up with a dozen or so, and we tried them out. Some of them did nothing at all. Others started decomposing the Hydrazoid P as soon as they got into solution. But the nickel acetylacetonate did a beautiful job. It did nothing at all at room temperature or in storage. But half a percent or so speeded up Hydrazoid P combustion, either in the air, or when we burned the stuff under pressure as a monopropellant, by orders of magnitude. But when we did fire tests in the open, the results weren't so good. An uncertainty factor had been introduced into Hydrazoid burning, and instead of detonating every time it did it about one time in three. So the engineers were still afraid of it.

A pity, too. For the nickel complex gave the fuel a peculiarly beautiful purple color, and somehow I'd always wanted a purple propellant!

Other fuels for $ClF_3$ have been developed, but they're generally rather similar to those I've described, with the carbon in them balanced out to CO by the addition of oxygen, somehow, to the mixture. On the whole, the problem can be considered to be pretty well under control. The detonation hazard after a spill is important on the test stand, but *not* with a prepackaged missile.

While the preliminary work with CTF was going on, and people were trying to come up with a good fuel for it, they were also looking very hard at the oxides of chlorine and their derivatives. $Cl_2O_7$, with an endothermic heat of formation of +63.4 kcal/mole, was one of

the most powerful liquid oxidizers known in the early 50's, and preliminary calculations showed that it should give a remarkably high performance with any number of fuels. It had, however, one slight drawback—it would detonate violently at the slightest provocation or none at all. From first to last, at least five laboratories tried to domesticate it, with no success at all. The approach was to hunt for additives which would desensitize or stabilize it—Olin Mathieson, alone, tried some seventy—and was a dismal failure.

The closely related perchloric acid, at first, appeared to be a more promising candidate. Its heat of formation was exothermic, at least, and so the acid should show little tendency to decompose to the elements. However, 100 percent perchloric acid, like nitric acid, is not entirely what it seems. An equilibrium exists in the concentrated acid:

$$3HClO_4 \leftrightarrows Cl_2O_7 + H_3OClO_4$$
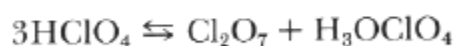
so that there is always some of the very sensitive oxide present waiting to make trouble. And when it triggers the perchloric acid, the latter decomposes, not to the elements, but to chlorine, oxygen, *and* $H_2O$, with the release of enough energy to scare anybody to death.

I had been ruminating on this fact, and had had an idea. The structure of perchloric acid can be written $H{-}O{-}\overset{\displaystyle O}{\underset{\displaystyle O}{\overset{\|}{\underset{\|}{Cl}}}}{=}O$. Now, if the HO group were replaced by an F, to give $F{-}\overset{\displaystyle O}{\underset{\displaystyle O}{\overset{\|}{\underset{\|}{Cl}}}}{=}O$, what could the stuff decompose to? Certainly there weren't any obvious products whose formation would release a lot of energy, and the compound ought to be reasonably stable. And it should be a real nice oxidizer.

So, one day in the spring of 1954, Tom Reinhardt, then the chief engineer of NARTS, Dr. John Gall, director of research of Pennsalt Chemicals, and I were sitting around the table in my laboratory shooting the breeze and discussing propellants in general. John was trying to sell us $NF_3$, but we weren't interested in anything with a boiling point of $-129°$. Then I brought up the subject of this hypothetical derivative of perchloric acid, added my guess that it would probably be low boiling, but not so low that it couldn't be kept as a pressurized liquid at room temperature, and my further guess that it should be rather inert chemically "because of that hard shell of electrons around it." And then I asked, "John, can you make it for me?"

His reply, delivered with considerable self-satisfaction, was enough to break up the meeting—and start a new one. "It *has* been made, its properties are as you predicted, and, just by coincidence, we just hired the man who discovered it."

My delighted whoop woke up the firehouse dog half a mile away —and was the beginning of the perchloryl fluoride program. It seems that in 1951, some workers in Germany had treated sodium chlorate, $NaClO_3$, with fluorine gas and had obtained sodium fluoride and various unidentified gaseous products which they did not identify—but one of them, in hindsight, must have been perchloryl fluoride. Then, in 1952, Englebrecht and Atzwanger, in Austria, dissolved sodium perchlorate in anhydrous hydrofluoric acid, HF, and electrolyzed the solution, mainly, I suspect, to see what would happen. They collected the gases involved, sorted them out, and isolated perchloryl fluoride among them. Since hydrogen, fluorine, and a few other items were all mixed together, they were plagued by explosions, but managed to survive the process somehow. (Englebrecht was just naturally ventursome to the point of lunacy. One of his other exploits was the development of a fearsome cutting torch burning powdered aluminum with gaseous fluorine. He could slice through a concrete block with it, to the accompaniment of an horrendous display of sparks, flames, and fumes which suggested an inadequately controlled catastrophe.) I had missed the report of the discovery (it appeared in an Austrian journal which I didn't normally see) but Pennsalt apparently had not, and decided that Englebrecht was just the sort of person they wanted on their staff.

In June BuAer authorized NARTS to investigate perchloryl fluoride, and Pennsalt sent us thirty-three grams of it in October—painfully produced by Englebrecht's method. And then, while we tried to characterize the material, they started looking for a simpler way to make it. Dr. Barth-Wehrenalp of their laboratories came up with— and patented—a synthesis by which it could be made rather easily and cheaply. It worked by the reaction $KClO_4 + (\text{excess}) \, HSO_3F \rightarrow KHSO_4 + FClO_3$, which looks simpler than it is. Nobody really understands the reaction mechanism.

While we were characterizing it, Pennsalt was doing the same, and passing their results over to us, and in a few months we knew just about everything we wanted to know about it. It was a pleasure working with that outfit. I'd phone one day asking, say, for the viscosity as a function of temperature, and within a week they would have made the measurements (and measuring the viscosity of a liquid under its own vapor pressure isn't exactly easy) and passed the results on to me.

In 1955 we were ready for motor work, and Pennsalt shipped—or

rather hand-carried—ten pounds of perchloryl fluoride to us. (It was made by the old process, since the new one wasn't yet ready, and cost us $540 per pound. We didn't mind. We'd expected it to cost a thousand!)

With ten pounds of it we were able to make small motor tests (the fuel was MMH) and found that we had a very fine oxidizer on our hands. Its performance with MMH was very close to that of $ClF_3$ with hydrazine, and there wasn't any freezing point trouble to worry about. It was hypergolic with MMH, but starts were hard,* so we used a starting slug of RFNA. Later, Barth-Wehrenalp tried mixing a small amount of chloryl fluoride, $ClO_2F$ with it, and got hypergolic ignition that way.† But what made the rocket mechanics happy·was the fact that it varied from all other oxidizers in that you just couldn't hurt yourself with it, unless, as Englebrecht suggested, "you drop a cylinder of it on your foot." Its toxicity was surprisingly low, it didn't attack either inflammables or human hide, it wouldn't set fire to you—in fact, it was a joy to live with.

What did it in, finally, was the fact that its density at room temperature was rather low, 1.411 compared to 1.809 for CTF, and since its critical temperature was only 95°, it had a very high coefficient of expansion. Its volume would increase by 20 percent between 25° and 71°, so your tanks always had to be oversized. It is, however, completely miscible with all-halogen oxidizers such as CTF, and can be added to the latter to help them burn carbon-containing fuels, which need oxygen. This will probably be its future role.

While PF (so called for security and in deference to the engineers, who were apparently quite incapable of pronouncing the word "perchloryl") was being investigated, the next candidate was about to make its appearance. Several laboratories, at this time, were trying to come up with storable oxidizers with a better performance than $ClF_3$, and in 1957, Colburn and Kennedy, at Rohm and Haas, reacted nitrogen trifluoride ‡ with copper turnings at 450° and produced $N_2F_4$ by the reaction $2NF_3 + Cu \rightarrow CuF_2 + N_2F_4$.

* It seems that liquid perchloryl fluoride reacts with liquid amines, hydrazines, or ammonia, $FClO_3 + H_2N—R \rightarrow HF + O_3Cl—NH—R$ and the perchloramide-type compound is remarkably and violently explosive. Hence the hard starts.

† Chloryl fluoride, $ClO_2F$, was first reported by Schmitz and Schumacher in 1942. It is indecently reactive, and the hardest to keep of all the Cl-O-F compounds, since it apparently dissolves the protective metal fluoride coatings that make the storage of $ClF_3$ comparatively simple.

‡ Making $NF_3$ is tricky enough. It's done by electrolyzing molten ammonium bifluoride, using graphite electrodes. They have to be graphite—if you use nickel you don't get any $NF_3$—and the yield depends upon who manufactured the graphite. Don't ask me why.

Here was something interesting, and the propellant community leaped into the act with glad cries and both feet. Research went off in two directions—improving the synthetic method of hydrazine tetrafluoride, as it was called,* for one, and determining its physical properties and its chemistry for another.

Rohm and Haas came up with a somewhat esoteric, not to say peculiar, synthesis when they reacted $NF_3$ with hot arsenic, of all things. Stauffer Chemical reacted $NF_3$ with hot fluidized carbon in a reaction which was easy to control, but which gave a product grossly contaminated with large amounts of $C_2F_6$, just about impossible to remove. Du Pont developed a completely different synthesis, in which $NF_3$ and NO are reacted at 600° in a nickel flow tube to form $N_2F_4$ and NOF. Other syntheses took a route through difluoramine, $HNF_2$, which was made by reacting urea in aqueous solution with gaseous fluorine to form $F_2NCONH_2$, and then hydrolyzing this with hot sulfuric acid to liberate the $HNF_2$. The final step was to oxidize the difluoramine to $N_2F_4$. Callery Chemical Co. did this with sodium hypochlorite in a strongly alkaline solution; Aerojet, as well as Rohm and Haas, did it with ferric ion in acid solution. The Du Pont process, and the $HNF_2$ –route syntheses are those used today.

(There was some desire to use $HNF_2$ itself as an oxidizer—its boiling point is −23.6° and its density is greater than 1.4—but it is so violently explosive that the idea never got very far. When it is used as an intermediate, the drill is to make it as a gas and use it up immediately.)

Dinitrogentetrafluoride was definitely a high-energy oxidizer, with a high theoretical performance with fuels such as hydrazine. (Marantz and his group at NBS soon determined its heat of formation so that accurate calculations could be made) and when Aerojet, in 1962, burned it with hydrazine and with pentaborane they measured 95 to 98 percent of the theoretical performance. And it had a fairly good density—1.397 at its boiling point. But that boiling point was −73°,† which put it out of the class of storable propellants.

* $N_2F_4$ is an inorganic compound, and should have been named according to the nomenclature rules of inorganic chemistry, "dinitrogen tetrafluoride" in strict analogy to "dinitrogen tetroxide" for $N_2O_4$. Instead it was named by the nomenclature rules of organic chemistry, as a derivative of hydrazine. This sort of thing was happening all the time, as organic chemists tried to name inorganic compounds, and inorganic chemists made a mess of naming organics!

† This boiling point was a surprise to many, who had expected that it would be somewhere near that of hydrazine, or around 100°. But some of us had noted that the boiling point of $NF_3$ was very near that of $CF_4$, and hence expected that of $N_2F_4$ to be not too far from that of $C_2F_6$, which is −79°. So some of us, at least, weren't disappointed, since we hadn't hoped for much.

And this fact led to the concept of "space-storable propellants." As you will remember, 1957 was the year of Sputnik 1, when the public suddenly realized that there might be something to this science-fiction foolishness of space travel after all. Anything remotely connected with space had suddenly become eminently salable, and if the services weren't able to use $N_2F_4$ in missiles, perhaps the space agencies (NACA, later NASA) could use it in space. After all, the hard vacuum of space is a pretty good insulator, and when you have, in effect, a Dewar flask the size of the universe available, you can store a low-boiling liquid a long time. An arbitrary upper limit ($-150°$) was set for the boiling point of a space-storable, but the custom is to stretch this limit to include the propellant you want to sell. $OF_2$, boiling at $-144.8°$ is considered a space storable, but if you want to call its ideal partner, methane, $CH_4$, boiling at $-161.5°$ one too, nobody is going to complain too loudly.

$NF_3$ is a rather inert material, and its chemistry isn't too complicated, but $N_2F_4$ turned out to be a horse of another color, with a peculiarly rich and interesting chemistry. The propellant men were not exactly overjoyed by this development, since they much prefer to deal with an unenterprising propellant, which just sits in its tank, doing nothing, until they get around to burning it.

$N_2F_4$ reacts with water to form HF and various nitrogen oxides, with nitric oxide to form the unstable and brilliantly colored (purple) $F_2NNO$, and with a bewildering number of oxygen-containing compounds to form $NF_3$, NOF, $N_2$ and assorted nitrogen oxides, by reactions which are generally strongly dependent upon the exact conditions, and frequently affected by traces of water or nitrogen oxides, by the material of the reactor, and by everything else that the experimenter can (or cannot) think of. Many of its reactions result from the fact that it is always partially dissociated to $2NF_2$, just as $N_2O_4$ is always partially dissociated to $2NO_2$, and that the extent of the dissociation increases with the temperature. This is the way a halogen, such as $Cl_2$, behaves, and $N_2F_4$ can be considered to be a pseudo-halogen. Niederhauser, at Rohm and Haas, thought that as such, it should add across a double bond, and reacted it, in the vapor phase, with ethylene—and came up with $F_2NCH_2CH_2NF_2$. The reaction proved to be general, and it led to many things, some of which will be described in the chapter on monopropellants.

The handling and characteristics of $N_2F_4$ are fairly well understood now, and it is undeniably a high-performing oxidizer, but it is difficult to assess its future role as a propellant. It's not going to be used for any military application, and liquid oxygen is better, and cheaper, in the big boosters. It *may* find some use, eventually, in deep

space missions. A Saturn orbiter would have to coast for years before
the burn which puts it in orbit, and even with the thermal insulation
provided by empty space liquid oxygen might be hard to keep for
that long. And $N_2O_4$ would probably be frozen solid.

When Kennedy and Colburn found dinitrogentetrafluoride they
knew what they were hunting for. But the next oxidizer was dis-
covered by people who were looking for something else.

It seems that at the beginning of 1960, Dr. Emil Lawton of Rocket-
dyne, armed with an Air Force contract, had an idea that looked
wonderful at the time. It was to react chlorine trifluoride with di-
fluoroamine,

$$ClF_3 + 3HNF_2 \rightarrow 3HF + Cl(NF_2)_3$$
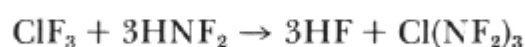
thusly. He put Dr. Donald Pilipovich, "Flip," on the job. Flip built
himself a metal vacuum line and started in. But he didn't get what he
wanted. He got mainly $ClNF_2$, plus a small quantity of "Compound
X." Compound X showed a strong $NF_2O^+$ peak on the mass spectrom-
eter, and the question was the source of the oxygen. He investigated,
and found that the chlorine trifluoride he was using was heavily con-
taminated with $FClO_2$ and $ClO_2$.

Meanwhile, Dr. Walter Maya, of the same group, was making $O_2F_2$
by an electical discharge in a mixture of fluorine and oxygen. And
he got some air in his line, by accident, and came up with Compound
X too.

Flip was tied up with another job at that time, so Maya took over the
Compound X problem. He found that an electrical discharge in a
mixture of air and fluorine would give X, but that a discharge in a
mixture of oxygen and $NF_3$ did even better. Dr. Bartholomew Tuffly
of their analytical group invented a gelled fluorocarbon gas chroma-
tograph column to separate the X from the $NF_3$, and its mass spectrum
and molecular weight identified it unambiguously as $ONF_3$ or the
long-sought $F_2NOF$.

In the meantime a group at Allied Chemical, Drs. W. B. Fox, J. S.
Mackenzie, and N. Vandercook, had been investigating the electrical
discharge reaction of $OF_2$ with $NF_3$, and had taken the IR spectrum of
an impure mixture around the middle of 1959, but had not identified
their products. The two groups compared their results and spectra
around January 1961, and found that they had the same compound.
Nuclear magnetic resonance (NMR) spectroscopy showed that it was
$ONF_3$, and not $F_2NOF$.

And the moral of this story is that it's always worth trying an elec-
trical discharge on your mixtures when you're hunting for new com-

pounds. You *never* know what will happen. Almost anything can.

Bill Fox's group soon found that $ONF_3$ could be synthesized by the photochemical fluorination of ONF, and by the flame fluorination of NO, with a fast quench. The last synthesis is best for relatively large scale production.

A little later, I was chairing a session on propellant synthesis at one of the big meetings, and found, on the program, that both Rocketdyne and Allied were reporting on $ONF_3$. I knew that they differed widely in their interpretations of the chemical bonding in the compound, so I rearranged the program to put the two papers back to back, in the hope of starting a fight. No luck, though—they were both too polite. Too bad.

Another meeting, some years later, had more interesting results. In June 1966, a symposium on fluorine chemistry was held at Ann Arbor and one of the papers, by Professor Neil Bartlett of the University of British Columbia, was to be on the discovery and properties of $ONF_3$. Bartlett, a virtuoso of fluorine chemistry, the discoverer of $OIF_5$ and of the xenon fluorides, had, of course, never heard of Rocketdyne's and Allied's classified research. But Bill Fox, seeing an advance program, hurriedly had his report on the compound declassified, and presented it immediately after Bartlett's, describing several methods of synthesis, and just about every interesting property of the compound. Bill did his best not to make Bartlett look foolish, and Bartlett grinned and shrugged it off—"well, back to the old vacuum rack"—but the incident is something that should be noted by the ivory tower types who are convinced of the intellectual (and moral) superiority of "pure" undirected research to the applied and directed sort.

The compound has been called nitrogen oxidetrifluoride, nitrosyl trifluoride, and trifluoroamine oxide. The first is probably preferable. It boils at $-87.5°$, and its density at that temperature is 1.547. It is much less active chemically than dinitrogentetrafluoride, and is hence much easier to handle. It is stable in most metals, reacts only very slowly with water or alkalis, or with glass or quartz even at $400°$. In these respects it is very similar to perchloryl fluoride, which has a similar compact and symmetrical tetrahedral structure, with no reactive electrons. It reacts with fluorinated olefins to form $C-O-NF_2$ structures, and with $SbF_5$ to form the interesting salt $ONF_2^+SbF_6^-$.

Its potential as an oxidizer seems to be similar to that of $N_2F_4$, and it should be useful in deep space missions.

Rocket motors designed to operate only in deep space are generally designed to have a comparatively low chamber pressure—150 psia or less—and it takes less energy to inject the propellants than would be

the case with motors designed for sea-level use, whose chamber pressure is usually around 1000 psia. (In a few years it will probably be 2500!) And for the low injection pressure requirements of the deep space motors, some of the "space storables" seem peculiarly well suited. During the coast period, they could be kept below their normal boiling points. Then as the time for their use approached, a small energy source (a small electrical heating coil or the like) could be employed to heat them up to a temperature at which their vapor pressure would be well above the low chamber pressure of the motor, and could itself, be the injection pressure source, just as an aerosol spray is expelled by its own vapor pressure. Dinitrogentetrafluoride, nitrogen oxidetrifluoride, as well as the long known nitryl fluoride, $FNO_2$, seem to be particularly suitable for this sort of application. Aerojet, during 1963, did a great deal of work along these lines, with complete success.

It's a good idea, when choosing a pair of "space storables," to choose a fuel and an oxidizer that have a common liquid (temperature) range. If they are stored next to each other during a mission that lasts several months, their temperatures are going to get closer and closer together, no matter how good the insulation is. And if the temperature toward which the two converge is one at which one propellant is a solid and the other is a gas, there are going to be difficulties when it comes time for them to go to work. Likewise, if the self-pressurizing type of injection is used, design problems are simplified if the two have vapor pressures that are pretty close to each other. So, if the designer intends to use $ONF_3$, with a boiling point of $-87.5°$, ethane, whose boiling point is $-88.6°$, would be a good choice for the fuel.

Two space-storable systems have been investigated rather intensively. RMI and JPL, starting in 1963 or so, and continuing into 1969, worked out the diborane–$OF_2$ system, while Pratt and Whitney, Rocketdyne, and TRW, with NASA contracts, as well as NASA itself, have concentrated their efforts on $OF_2$ and the light hydrocarbons: methane, ethane, propane, 1-butene, and assorted mixtures of these. (In most of their motor work, they used a mixture of oxygen and fluorine as a reasonably inexpensive surrogate for $OF_2$.) All the hydrocarbons were good fuels, but methane was in a class by itself as a coolant, transpiration or regenerative, besides having the best performance. The $OF_2$–methane combination is an extremely promising one. (It took a long time for Winkler's fuel of 1930 to come into its own!)

The last part of the oxidizer story that I can tell without getting into trouble with Security is the saga of "Compound A." If I tell it in more detail than usual, the reasons are simple. The discovery of "A" is probably the most important achievement to date of the chemists who have made propellants a career, the story is well documented, and it illustrates admirably the nontechnical, but bureaucratic and personal obstacles they had to surmount.

While Walter Maya was doing electrical discharge experiments in 1960–61 (he made $NF_3$ that way, something that no one else had been able to do, and was trying to get things like $N_3F_5$) he occasionally got trace quantities of two compounds, with absorption bands at 13.7 and 14.3 microns, respectively, in the infra red. And for convenience he called them "Compound A" and "Compound B." At that point, he got tied up in another job, and Lawton put Dr. Hans Bauer to the problem of identifying them. Bauer made slow progress, but finally got enough A to subject it to mass spectroscopy. And found that it had chlorine in it. Since only nitrogen and fluorine had been put into the apparatus, this took some explaining, and it seemed likely that the chlorotrifluorohydrocarbon (Kel-F) grease used on the stopcocks of the apparatus was entering into the reaction. Lawton had Bauer (much against his will) introduce some chlorine into the system, and it soon was obvious that only chlorine and fluorine were needed to make "A." From this fact, from the further fact that "A" reacted with traces of water to form $FClO_2$, and from the IR spectrum, Lawton suggested in a report submitted in September 1961, that "A" was $ClF_5$. At that precise moment Rocketdyne's contract (supported by the Advanced Research Projects Administration — ARPA — and monitored by the Office of Naval Research — ONR) was canceled.
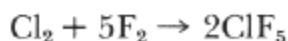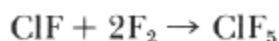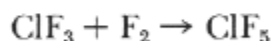
It seems that somebody in Rocketdyne's solid propellant operation in Texas, several hundred miles away, had made a security goof regarding the ARPA program, and Dr. Jean Mock of ARPA felt that something had to be done by way of reproof. Besides, as he remarked to Dr. Bob Thompson, Lawton's boss, "Lawton claimed he made $ClF_5$ and we know that's impossible." So the project lay dormant for half a year.

Then, about March 1962, Dr. Thompson scraped up some company R and D money, and told Lawton that he'd support two chemists for three months, doing anything that Lawton wanted them to do. Maya was put back on the job, and with Dave Sheehan's help, managed to make enough "A" to get an approximate molecular weight. It was 127 —as compared with the calculated value of 130.5.

Armed with this information, Lawton went back to ARPA and pleaded with Dick Holtzman, Mock's lieutenant. Holtzman threw him out of the office. By this time it was the middle of 1962.

At this time Lawton had an Air Force research program, and he decided, in desperation, to use their program — and money — to try to solve the problem. The catch was that the AF program didn't allow for work on interhalogens, but apparently he figured that if he succeeded all would be forgiven. (In the old Royal Spanish Army there was a decoration awarded to a general who won a battle fought against orders. Of course, if he *lost* it, he was shot.) Pilipovitch was Lawton's Responsible Scientist by that time, and he put Dick Wilson on the job. And within a week he had come up with

$$ClF_3 + F_2 \rightarrow ClF_5$$

$$ClF + 2F_2 \rightarrow ClF_5$$

$$Cl_2 + 5F_2 \rightarrow 2ClF_5$$

$$CsClF_4 + F_2 \rightarrow CsF + ClF_5,$$

all four reactions requiring heat and pressure.

The next problem was to explain all this to the Air Force. It wasn't easy. When Rocketdyne's report got to Edwards Air Force Base in January 1963 the (bleep) hit the fan. Don McGregor, who had been monitoring Lawton's program, was utterly infuriated, and wanted to kill him — slowly. Forrest "Woody" Forbes wanted to give him a medal. There was a fabulous brouhaha, people were shifted around from one job to another, and it took weeks for things to settle down. Lawton was forgiven, Dick Holtzman apologized handsomely for ARPA and gave Lawton a new contract, and relative peace descended upon the propellant business. And when I heard, a few weeks later, of the discovery of $ClF_5$ (the code name, Compound "A" was kept for some years for security reasons) I sent Emil a letter which started, "Congratulations, you S.O.B.! I only wish I'd done it myself!" He was inordinately proud of it, and showed it to everybody at Rocketdyne.

$ClF_5$ is very similar to $ClF_3$, but, with a given fuel, has a performance about twenty seconds better. It boils at $-13.6°$, has a density of 1.735 at 25°. And all of the techniques developed for using and handling CTF could be applied, unchanged, to the new oxidizer. To say that the propellant community was enthusiastic would be a mad understatement.

On their ARPA contract the Rocketdyne group, by grace of Dick Wilson's tremendous laboratory skill, came up with "Florox" — but

that one's still classified, and I can't talk about it without getting into trouble.* But nobody has yet come up with what $OClF_5$, which I called "Compound Omega," because it would be just about the ultimate possible storable oxidizer. It would be particularly useful with a fuel containing carbon, such as monomethyl hydrazine, $CH_6N_2$, with which it would react, mole for mole, to produce $5HF + HCl + CO + N_2$—a set of exhaust species to warm the heart of any thermodynamicist. Lawton and company tried, and are presumably still trying to get it, and Dr. Sam Hashman and Joe Smith, of my own group, hunted for it for more than three years, without any luck, although they employed every known synthetic technique short of sacrificing a virgin to the moon. (A critical shortage of raw material held that one up.) If anybody ever *does* synthesize Omega, it will probably be Neil Bartlett or somebody in Lawton's group.

A good deal of work has been done with mixed oxidizers, tailoring the mixture to match the intended fuel. NOTS for one, experimented in 1962 with "Triflox," a mixture of $ClF_3$, $FClO_3$ and $N_2F_4$, and Pennsalt, for another, examined "Halox," comprising $ClF_3$ and $FClO_3$. In this connection, it seems to me that a suitable mixture of $ClF_5$ and $FClO_3$ might be almost as good as the elusive Omega to burn with MMH.

One attempt to upgrade the performance of $ClF_5$ by adding $N_2F_4$ to it came to an abrupt end when the vapor pressure of the liquid mixture (stored in steel pressure bottles) started to rise in an alarming manner. It seems that the two oxidizers reacted thus:

$$ClF_5 + N_2F_4 \rightarrow ClF_3 + 2NF_3.$$
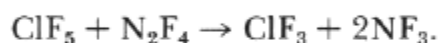
And there was absolutely nothing that could be done about it.

Oh, yes. About "Compound B." That's a sad story. It turned out to be tungsten hexafluoride—$WF_6$—apparently from the tungsten filament in the mass spectrometer. Even Lawton can't win 'em all!

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* Emil Lawton has recently informed me (9/71) that Florox has been declassified since a Frenchman reported it independently late in 1970. It is $OClF_3$, and is made by the fluorination of $Cl_2O$ or, of all things, chlorine nitrate, or $ClONO_2$. Its boiling point is 30.6°, and it has a high density, 1.852. And since it contains oxygen, it can be used with a carbon-containing fuel, such as UDMH.