10

"Exotics"

Fifteen years ago people used to ask me "What *is* an exotic fuel anyway?" and I would answer "It's expensive, it's got boron in it, and it probably doesn't work." I had intended, originally, to entitle this chapter "The Billion Buck Boron Booboo," but decided against it on two grounds. The first was that such a title might conceivably be considered tactless by some of the people who authorized the programs concerned. The second reason is that it would not be completely accurate. Actually, the boron programs did *not* cost a billion dollars. It just seemed that way at the time.

The boranes are compounds of boron and hydrogen, the best known (although there are many others) being diborane, B_2H_6; pentaborane, B_5H_9; and decaborane, $B_{10}H_{14}$. At room temperature the first is a gas, the second a liquid, and the third a solid. Alfred Stock discovered most of the better known boranes between 1912 and 1933, while H. I. Schlesinger, starting about 1930, contributed vastly to the field of borane chemistry, and in particular to the development of synthetic routes.

Boranes are unpleasant beasts. Diborane and pentaborane ignite spontaneously in the atmosphere, and the fires are remarkably difficult to extinguish. They react with water to form, eventually, hydrogen and boric acid, and the reaction is sometimes violent. Also, they not only are possessed of a peculiarly repulsive odor; they are extremely poisonous by just about any route. This collection of properties does not simplify the problem of handling them. They are also very expensive since their synthesis is neither easy nor simple.

But they possess one property which attracted rocket people to them as hippies to a happening. They have an extremely high heat of combustion — gram for gram about 50 percent more than jet fuel. And from 1937 on, when Parsons at JPL had first considered decaborane, propellant men had been considering them wistfully, and lusting after the performance which might, with luck, be wrung out of that heat of combustion.

Nothing could be done about it, of course, until World War II was over. But in 1946 the U.S. Army Ordnance Corps awarded a contract to GE (Project Hermes), to investigate the boranes in depth, and to develop methods of large scale synthesis. The primary objective was not the development of rocket propellants, but the exploitation of the boranes as fuels for air-breathing engines, primarily jets. But the rocket people, as was inevitable with their preoccupations, got involved anyway.

It was Paul Winternitz, at Reaction Motors, who in 1947 made what were probably the first performance calculations on the boranes. He calculated the performance of diborane, pentaborane, and aluminum borohydride, $Al(BH_4)_3$, all with liquid oxygen. Considering the scantiness and general unreliability of the thermodynamic data, not only on these would-be propellants but on their combustion products as well, not to mention the complexity of the calculations (no computers around then, remember!), my admiration of his industry is only equaled by my astonishment at his courage.

At any rate, the numbers that came out at the other end of the calculation, whatever their validity or lack of it, looked encouraging. The next step was to confirm them with motor firings. Diborane (the most available of the boranes) was to be the fuel, and liquid oxygen the oxidizer.

Diborane was the most available of the boranes, but it wasn't exactly abundant. In fact, there were precisely forty pounds of it in existence when RMI started work. So the firings were necessarily at a very low thrust level (perhaps fifty pounds) and were extremely short. At that, as the engineer in charge confessed to me many years later, "Every time I pushed the button I could feel the price of a Cadillac going down the tailpipe!"

The results, not to put too fine a point on it, did not encourage euphoria. The performance was dismally bad — far below theoretical — and solid glassy deposits appeared in the throat (changing its size and shape) and in the diverging (downstream) section of the nozzle. These consisted, apparently, mostly of B_2O_3, but appeared to contain some elemental boron as well. This was a sure indication of poor combustion, and was not encouraging.

Ordian and Rowe, at NASA-Lewis, fired the same combination in 1948, and got much the same sort of results. Nor were the results any better when they used hydrogen peroxide as the oxidizer. The glassy deposits seemed to be as characteristic of borane firings as was the bright green exhaust flame.

The next fuel that RMI tried was the dimethylamine adduct of diborane—not exactly a borane, but a close relative. But when they fired it with oxygen, in 1951, the results were borane results—and discouraging. So were their results with pentaborane, which Jack Gould fired the next year in a fifty-pound thrust motor, using oxygen and hydrogen peroxide as oxidizers. It would be some twelve years before anybody could get good results with that last combination. One with better combustion efficiency was fired by Ordin in 1955—diborane and fluorine. Here, at least, there weren't any deposits in the nozzle—BF_3 is a gas—but the combination was a fiendishly hot one, and very difficult to handle.

The early borane firings weren't, on the whole, too successful, but enthusiasm, hopes, and expectations were all high, and two meetings on boron fuels and would-be fuels were held in 1951 alone. Some awfully dubious chemistry was presented at these meetings—the big breakthroughs in boron chemistry were yet to come—but everybody had a good time and came home inspired to renewed efforts.

And very soon they had the money to make these efforts. Project "Zip" was started in 1952, by BuAer of the Navy. It was designed to carry on from where the Hermes project had left off, and to develop a high-energy, boron-based fuel for jet engines. This was before the day of the ICBM's, the long-range bomber-carrying nuclear bombs was the chosen weapon of deterrence in the cold war, and anything that would increase the range or the speed of that bomber was very much to be desired. The major prime contractors, each with multi-million-dollar contracts, were the Olin Mathieson Chemical Corporation and the Callery Chemical Co., but by the end of the decade many more organizations, propulsion, chemical, academic—you name it—had become involved, either as minor prime contractors or as subcontractors to the primes. By 1956 the program had become so unwieldy that it had to be split, with the Air Force monitoring Olin Mathieson's work and the "HEF" program and Navy's BuAer watching over Callery's "Zip." The trade journals played up the Zip and "Super" fuels (omitting, naturally, the classified chemical details—which, if published, might give some people pause) and legions of trusting and avaricious souls went out and bought boron stocks. And, eventually, lost their shirts.

It soon became evident that in order to attain the desired physical properties (similar to those of jet fuel) the fuels would have to be alkyl derivatives of the boranes. In the end, three of these were developed and put into fairly large-scale production. Mathieson's HEF-2 was propyl pentaborane. Callery's HiCal-3, and Mathieson's HEF-3 were mixtures of mono-, di-, and triethyl decaborane, and HiCal-4 and HEF-4 were mixtures of mono-, di-, tri-, and tetramethyl decaborane. Both -3 and -4 contained traces of unsubstituted decaborane. (The missing numbers represented the fuels in an intermediate stage of synthesis.)

The chemistry of the borohydrides was investigated as it had never been investigated before, process details were worked out on the pilot-plant level, two full-sized production facilities, one Callery, one Mathieson, were built and put on stream, handling and safety manuals were written and published — and the whole thing was done on a crash basis. Never had one poor element been given such concentrated attention by so many chemists and chemical engineers.

And then the whole program was brought to a screeching halt. There were two reasons for this, one strategic, one technical. The first was the arrival of the ICBM on the scene, and the declining role of the long-range bomber. The second lay in the fact that the combustion product of boron is boron trioxide, B_2O_3, and that below about 1800° this is either a solid or a glassy, very viscous liquid. And when you have a turbine spinning at some 4000 rpm, and the clearance between the blades is a few thousandths of an inch, and this sticky, viscous liquid deposits on the blades, the engine is likely to undergo what the British, with precision, call "catastrophic self-disassembly."

All sorts of efforts were made to reduce the viscosity of the oxide, but to no avail. The HEF's and the HiCal's just could not be used in a jet engine. The plants were put on stand-by, and eventually sold for junk. The Zip program was dead, but the memory lingers.

It was by no means a total fiasco. The small fraction of the total cost which went for research added more to the corpus of boron chemistry in ten years than otherwise would have been learned in fifty.[*] One of the most interesting discoveries was that of the "Carboranes," by Murray Cohen, of Reaction Motors, in 1957. The parent

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[*] Dick Holzmann was at ARPA at the time, and it is due to him that all this chemistry is available, and not buried forever in the files of the contractors and the services. He had all the information collected, heckled Ronald Hughes, Ivan Smith, and Ed Lawless of Midwest Research Institute into putting it together in one volume, and finally edited *Production of the Boranes and Related Research*, which was published by Academic Press in 1967.

compound, $B_{10}C_2H_{12}$, has the structure of a closed, symmetrical, icosahedral cage, and it and its derivatives exhibit a surprisingly high stability against oxidation, hydrolysis, and thermal decomposition. Neff, of Hughes Tool, took advantage of this stability when he attempted to make a monopropellant based on a carborane derivative. (See the monopropellant chapter.) Derivatives may also be useful in high-energy solid propellants, and even, possibly, as high-temperature-resistant plastics.

As far as rocket propulsion itself was concerned, the result of the Zip program was that there were now large stocks of diborane (the starting point for the synthesis of all the boranes and their derivatives) pentaborane, decaborane, and the HEF's and HiCal's available, so that their usefulness as fuels could be investigated on something more than the frustrating fifty-pound level. Aerojet, starting about 1959, worked with HEF-3 and pentaborane, burning them with N_2O_4 or hydrogen peroxide, and Reaction Motors had most of the bugs out of the pentaborane-peroxide system by 1964. With proper injector design the systems could be made to work, and to yield something close to their theoretical specific impulse. And the problem of the solid deposits in the nozzle wasn't too important when the motor was of a respectable size. It didn't arise at all, of course, when a fluorine oxidizer was used. Don Rogillio, at Edwards Air Force Base, in 1962–64 burned pentaborane with NF_3 and with N_2F_4, and got quite a good performance, although, as the combination is a fiendishly hot one, he had a lot of trouble with burned-out injectors and nozzles.

But once pentaborane was made to work, nobody could find any particular use for it. The performance was good, yes, but the density of pentaborane is low—0.618—which militated against its use in a tactical missile. Further, the (oxygen type) oxidizers with which it performed best, peroxide and N_2O_4, had unacceptable freezing points. And if you used nitric acid, you lost a good deal of its performance advantage. And, of course, with any of these oxidizers, the exhaust contained large quantities of solid B_2O_3, and a conspicuous exhaust stream may be undesirable. And if you used a halogen oxidizer, such as ClF_3, the performance wasn't enough better than that of a hydrazine to be worth the trouble. And finally, it was still expensive.

The situation was otherwise with diborane. It couldn't be used in a missile, of course (its boiling point is $-92.5°$) but might well be used in certain deep-space applications where its low density (0.433 at the boiling point) wouldn't matter. Its natural partner was OF_2 (although ONF_3 would also be suitable) and from 1959 to the present that combination has been under investigation by several agencies, among

them Reaction Motors, and NASA-Lewis. The combination is a hot one, and it isn't easy to design injectors and nozzles which will stand it, but the difficulties are far from insurmountable, and an operational system does not seem far away. The combination, by the way, is an unusually hairy one to work with, both propellants being remarkably poisonous, but rocket men usually know how to stay alive, and it hasn't killed anybody—yet.

One thing that might have kept pentaborane in the picture was the advent of BN system, early in 1958. Callery Chemical was the originator of the idea, but within a year *every* propulsion contractor in the country, plus JPL, NASA, and EAFB had got into the act.

This is the idea: Boron nitride, BN, is a white, crystalline solid, with a hexagonal crystal structure like that of graphite.* It is a very stable molecule, with an exothermic heat of formation of some sixty kilocalories per mole. Now, imagine the reaction of a borane with hydrazine.

$$B_2H_6 + N_2H_4 \rightarrow 2BN + 5H_2$$

or

$$2B_5H_9 + 5N_2H_4 \rightarrow 10BN + 19H_2$$
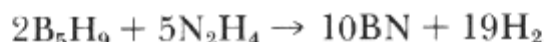
The heat of formation of the BN would be the energy source, and the hydrogen would comprise the working fluid—dragging the solid BN along with it, of course. Performance calculations indicated that the pentaborane–hydrazine combination should have the astounding performance of 326 seconds, and brought out the even more astounding fact that the chamber temperature should be only about 2000 K —1500 K or so, cooler than anything else with that sort of performance. The thought of a *storable* combination with a performance above 300 seconds, and with such a manageable chamber temperature sent every propulsion man in the country into orbit.

Getting enough pentaborane to work with was no problem, of course, in 1958–59. The Air Force had tons and tons of the stuff, from their Mathieson operation, and hadn't the foggiest idea of what to do with it. So it was practically free for the asking, and everybody leaped into the act, uttering glad cries. Callery, NASA-Lewis, Reaction Motors, and EAFB were some of the first to try the combination —most of them, at first, at approximately the hundred-pound thrust level.

* Carbon, of course, occurs both as graphite and diamond. And some recent work indicates that BN can be had, not only with the graphite structure, but with a diamond-like structure, and as hard, or harder, than diamond itself.

Reaction Motors' experience is typical. Hydrazine/pentaborane was hypergolic, although ignition was a bit hard. Combustion efficiency was ghastly, about 85–88 percent C* efficiency.* And specific impulse efficiency was worse; the engineers considered themselves lucky when they got 75 percent of the 326 seconds the calculations said they should get.

Obviously, the combustion efficiency was the first problem to be tackled, for unless that was brought up to a reasonable figure nothing could be done about the specific impulse — or anything else.

Part of the difficulty stemmed from the fact — soon discovered — that the reaction does not go neatly to BN and hydrogen, as the equations say it should. Instead, some of the boron is exhausted as elemental boron, and the leftover nitrogen combines with some of the hydrogen to form ammonia. This, naturally, does not help performance.

Another problem lay in the difficulty of mixing the pentaborane and the hydrazine so that they could react. Hydrazine is a water-soluble substance, and pentaborane is oil-soluble, and the two were remarkably stubborn about getting together. (This led to the BN-monopropellant work, described in the monopropellant chapter.) Additives to the propellants were no help — and everything from hydrazine nitrate to UDMH was tried. To get good mixing you simply have to use a remarkably sophisticated injector. Love, Jackson, and Haberman learned this the hard way, at EAFB, during 1959–60–61. As their thrust level rose from 100 to 5000 pounds, and they laboriously dragged their C* efficiency from 76 percent up to 95 percent, they experimented with no less than thirty different injectors, each one more sophisticated and complicated than the last.

While this was going on, the problems involved in handling pentaborane were still around — and hairy. It was remarkably poisonous, as I have mentioned. And it is hypergolic with the atmosphere, and the fires are brutes to extinguish. If you spray a burning pool of the stuff with water, the fire goes out eventually — if you're lucky. But then the remaining unburned pentaborane is covered with a layer of solid boron oxide or perhaps boric acid, which protects it from the air. And

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* C*, pronounced "see star," is a measure of combustion efficiency. It is derived by multiplying the measured chamber pressure by the area of the throat of the nozzle, and dividing this by the mass flow of the propellants. It comes out in feet per second or meters per second, depending on the system you use. Its theoretical value can be calculated, just as theoretical specific impulse can, and the percentage of theoretical C* that you measure experimentally is a good measure of the completeness of combustion, and of the efficiency of the injector.

if that crust is broken (which is certain to happen), the fire starts all over again. Even disposing of leftover pentaborane is a problem, but not one I'll go into here. Holzmann's book tells all about it, if you're interested.

Considering all this, I asked some of Rocketdyne's people — Rocketdyne was working closely with EAFB on their BN work — how they managed to live with the stuff. "Oh, it's no problem," they answered. "You just follow the directions in our safety manual!" I asked them to send me a copy of said manual, and in due time it arrived. It would be a misstatement to say that it was the size of the Manhattan phone book, but I've seen a great many municipalities with smaller ones. And even with the help of the manual, one of their rocket mechanics, a little later, managed to get himself hospitalized because of pentaborane.

The final step in the BN work was to scale up to a larger motor, of some 30,000 pounds thrust, and this was done at Edwards during 1961–62–63. (Incidentally, a lot of the work with hazardous propellants has been done at Edwards. It's located in the middle of the Mojave desert, and you don't have to worry about the neighbors. Even if you spill a ton of liquid fluorine — and that's been done there, just to see what would happen — the only thing that's likely to be damaged is the peace of mind of a few jack rabbits and rattlesnakes.) I saw movies of some of the test runs, and they were spectacular, with dense white clouds of solid BN rising two miles into the sky.

The results with the big motor were poor at first — about three-quarters of the theoretical specific impulse — but they improved with injector design, and before the end of 1963 the magic 300 seconds had been reached. (The final injector comprised some *six thousand* carefully drilled orifices! It was not cheap to manufacture.) But the BN system had finally been made to work, and was a success.

The only fly in the ointment was that the system was obsolete at birth. CIF_5 arrived on the scene just as BN succeeded — and the CIF_5–hydrazine combination performs as well as the hydrazine–pentaborane system, is much denser, and much easier to handle, works in a much simpler and cheaper motor, has an invisible exhaust stream — and is cheaper by at least an order of magnitude. Five years of work had been a frustrating exercise in expensive futility. Sometimes rocket men wonder why they ever got into the business.

However, there does seem to be some hope for the BN system, in a rather specialized application. Aerojet, fairly recently (1966–67) has been investigating the usability of the combination in a ram rocket, where the exhausted hydrogen, BN, elemental boron, and ammonia would be burned by the intake air, to give extra thrust, and has found

that it works very well indeed in such an arrangement. So perhaps the Edwards people didn't labor entirely in vain.

The borohydrides were related fuels that never quite made it. Here a word of explanation seems to be in order. Borohydrides come in two, or perhaps three types. The first type comprises the alkali metal borohydrides, $LiBH_4$, $NaBH_4$, and so on. These are straightforward ionic salts—white crystalline solids, with no nonsense about them. They are reasonably stable—$NaBH_4$ is *almost* stable in water—and can be handled easily.

Lithium borohydride, as has been mentioned, was tried as a freezing point depressant for hydrazine by Don Armstrong at Aerojet as early as 1948. He found that the mixture was unstable, but nevertheless Stan Tannenbaum, at RMI, tried it again in 1958, with the same results. And then, back at Aerojet, Rosenberg lit on the same mixture in 1965. And *he* found that 3 percent of the borohydride decomposed in 200 days at 69°. All of which gives one a feeling of "this is where I came in."

Sodium borohydride is much more stable than is the lithium salt, and its solution in liquid ammonia is quite stable, and Aerojet fired this, with oxygen, in 1949, but its performance was inferior to that of hydrazine and the work wasn't followed up. And Patrick McNamara, at EAFB, fired a hydrazine solution of the sodium salt with chlorine trifluoride in 1965, but got a performance inferior to that of pure hydrazine.

The second type (the "perhaps") includes ammonium and hydrazinium borohydride, which can be made *in situ* in liquid ammonia or hydrazine, but which would be unstable if isolated at room temperature. Aerojet burned a solution of hydrazinium borohydride in hydrazine (with oxygen) in 1949. I suspect that the mixture was unstable, for nothing more ever came of it.

The third type includes the aluminum and beryllium borohydrides, $Al(BH_4)_3$ and $Be(BH_4)_2$. These are covalent compounds, with unusual bonding, liquids at room temperature, and violently hypergolic with air. Nobody has ever had enough beryllium borohydride all together in one place and at one time for a motor firing, but Armstrong and Young at Aerojet fired aluminum borohydride with oxygen in 1950, and the next year Wilson, also at Aerojet, burned it with liquid fluorine. The results were not sufficiently encouraging to outweigh the difficulties involved in handling the fuel, and aluminum borohydride lay more or less dormant for some ten years.

Then, starting about 1960, Dr. H. W. Schulz and J. N. Hogsett, at

Union Carbide, started the development of the "Hybalines." And—
something rare in the propellant business—they did it with company,
not government, money. Aluminum borohydride forms a mole for
mole addition compound—an adduct—with amines. And these ad-
ducts are *not* spontaneously inflammable in the atmosphere, but with
reasonable precautions, can be handled without any particular diffi-
culty.

Schulz and Hogsett experimented with dozens of different amines,
but the fuel they settled on, as having the best combination of proper-
ties, was a mixture of the adducts of monomethyl amine and of di-
methylamine. They called it Hybaline A_5. (They also made some ad-
ducts of beryllium borohydride. These they called "Hybaline B.")
They plugged the Hybalines for some four years, quoting calculated
performance figures which were a wonder to behold. The only diffi-
culty was that they assumed—on the basis of certain very doubtful
experimental figures—a heat of formation for their mixture of ad-
ducts which was incompatible with that generally accepted for alumi-
num borohydride, and which generated a certain skepticism in their
audiences. The question was finally settled when EAFB made a series
of full-scale (5000 pound thrust) firings with Hybaline A_5/N_2O_4.
And got a maximum of 281 seconds, much less than would have been
delivered by, say, ClF_5 and hydrazine. So, by 1964, the Hybalines were
finished.

The latest excursion into the realm of the exotic was made by F. C.
Gunderloy, at Rocketdyne. He discovered that certain linear poly-
mers of beryllium hydride and dimethyl beryllium, with the chains
terminated with BH_3 groups (since the work is classified, I can't be
more specific in describing them) were viscous liquids, and worked
on them for four or five years. The chemistry involved is interesting
for its own sake, but it doesn't appear likely to lead to a useful pro-
pellant. The liquids are extremely poisonous, and beryllium oxide,
which would be one of the exhaust products if one of them were used
as a fuel, is so toxic as to rule out any use in a tactical missile; and there
are better fuels for space work. Setting to one side the problems of
working with a high-viscosity propellant, beryllium is a comparatively
rare and quite expensive material, and there appear to be better uses
for it. The development of these compounds would have been an
admirable academic exercise well worth several PhD's in inorganic
chemistry. As a propellant development program it can be classified
only as an unfortunate waste of the taxpayer's money.

So what's ahead for the "exotics?" As I see it, just two things.

1. Diborane will probably be useful in deep space work.
2. The pentaborane/hydrazine, BN system should be very good in ram-rocket and similar systems.

And the people who lost their shirts on boron stocks will have to discover a better way of getting rich from other people's work. For them, my heart does not bleed.