

High Density and the Higher Foolishness

The idea of a hybrid rocket, one using a solid fuel and a liquid oxidizer is a very old one; in fact, Oberth had tried to make one for UFA back in 1929, and BMW had experimented with such a device during 1944–45. Configurations vary somewhat, but the usual arrangement is a cylinder of fuel, solid except for a longitudinal passage down the center line, fitted tightly into a cylindrical chamber. Oxidizer is injected at the upstream end, and reacts with the fuel as it travels down the passage, and the combustion products eventually emerge through the nozzle just downstream of the fuel grain. (Even if it weighs two hundred pounds, it's still a "grain.")

On the face of it, the idea looks attractive. Solid fuels are denser than liquid fuels, for one thing, and for another, the rocket can be throttled just like a pure liquid device, while there is only one liquid to handle. From the point of view of safety, it looks ideal, since there just isn't any way for the fuel and the oxidizer to get together until you want them to.

Soon after the end of the war, then, several organizations set out confidently to design—and fire—hybrid rockets, and fell flat on their corporate faces. The experience of GE (in 1952, on Project Hermes) was typical. Their intention was to use a polyethylene fuel grain, with hydrogen peroxide as the oxidizer. And when they fired their rocket, the results were worse than depressing—they were disastrous. Combustion was extremely poor, with a measured C^* to make an engineer weep. And when they tried to throttle their motor, the oxidizer-fuel ration varied madly, and was never anywhere near the

optimum for performance. (This is hardly surprising, since the oxidizer consumption depends upon the rate at which it is injected, while the fuel consumption depends on the area of the fuel grain exposed.) And tinkering with the injector and the exact shape of the fuel grain did very little good.

The engineers had been guilty of a sin to which engineers are prone—starting their engineering before doing their research. For it had become devastatingly clear that *nobody* knew *how* a solid fuel burned. Did it evaporate, and then burn in the vapor phase? Or was a solid-state reaction involved? Or what? There were lots of questions, and very few answers, and hybrid work languished for some years. Only the Navy, at NOTS, kept at it, trying to learn some of the answers.

The revival started in 1959 when Lockheed, with an Army contract, started hybrid work. In 1961 ARPA got into hybrids in a big way, and by 1963 there were at least seven hybrid programs going.

I was greatly amused by the behavior of each new contractor as it got into the act. The pattern was invariable. First, they would get themselves a computer. Then, they would calculate the performance of every conceivable liquid oxidizer with every conceivable solid fuel. And then they would publish a huge report containing all the results of all of these computations. And to the surprise of nobody who had been in the business any length of time (we had all made these calculations for ourselves years before) everybody came out with the same numbers and recommended practically identical combinations. Thus, the fuel grains recommended by three different contractors, Lockheed, United Technology Co., and Aerojet, comprised:

1. Lithium hydride plus a hydrocarbon (rubber) binder;
2. Lithium hydride plus lithium metal plus a binder;
3. Lithium hydride plus powdered aluminum plus a binder.

And the oxidizers recommended (not necessarily in the same order) consisted of:

1. Chlorine trifluoride plus perchloryl fluoride;
2. The same two plus bromine pentafluoride;
3. Or, plus N_2F_4 ;
4. Or, finally, and a little further out, straight OF_2 .

All of which made some of us wonder whether or not the taxpayer had got his money's worth from all that expensive computer time.

Rohm and Haas investigated an entirely different type of hybrid, one which would still burn and produce thrust even when the oxi-

dizer was completely cut off. The grain consisted of aluminum powder, ammonium perchlorate, and a plastisol binder. (Plastisol is a castable and quick-curing double-base mixture, consisting largely of nitrocellulose and nitroglycerine, and was a solid propellant in its own right.) Its combustion products included a large fraction of hydrogen and carbon monoxide, and the liquid oxidizer, N_2O_4 , was intended to react with this and to increase the energy output and the thrust. NOTS performed a long series of combustion studies with a similar system, RFNA oxidizer and a fuel rich composite grain (ammonium perchlorate and a hydrocarbon or similar binder). As the hybrid system is a compromise between a solid and a liquid system, these and similar combinations can be considered as combining hybrid and solid features.

Steve Tunkel at Reaction Motors investigated a much more esoteric system in 1962–63—a reverse hybrid in which the oxidizer was in the grain, which consisted of nitronium perchlorate, NO_2ClO_4 or hydrazine di-perchlorate, $N_2H_6(ClO_4)_2$, in a fluorocarbon (Teflon-type) binder. The liquid fuel was hydrazine, and powdered aluminum or boron could either be suspended in the fuel or incorporated into the grain. The idea was to let the fluorine in the fluorocarbon react to form aluminum or boron trifluoride, while the carbon was oxidized to CO. (The other combustion products would depend upon the exact grain composition, the fuel flow, and so on.) The idea was interesting, but their hopes were never realized. Nitronium perchlorate turned out to be inherently unstable, for one thing, and Tunkel was never able to achieve efficient fluorocarbon-metal combustion. The system was just too precious to work.

Much more important, in the long run, was some of the work at UTC, who had a Navy contract to investigate the basic mechanism of hybrid combustion. (This, of course, should have been done at least ten years earlier, and before a lot of money had been sunk into hybrid work. But it's always easier to get money for engineering than for fundamental research. Don't ask me why.)

Most of this work was done with a simplified model of a hybrid motor, consisting of a flat slab of fuel with the oxidizer flowing across its surface, the whole in a transparent chamber so that the investigators could see what was happening, and take pictures of it. The fuel was usually polyethylene or methyl methacrylate (Plexiglass) and the oxidizer was oxygen or OF_2 . They learned that the oxidizer reacts with the fuel only in the vapor phase, and that the rate was controlled by diffusion, while the rate of regression (consumption) of the fuel depended largely upon heat transfer from the hot reacting gases.

(This, of course, was not strictly true when the fuel grain contained oxidizer of its own.) They learned that proper injector design could keep the regression rate uniform across the whole grain surface, but that the mixing of the fuel vapor and the oxidizer was so slow that additional mixing volume downstream of the grain was usually necessary to get reasonable combustion efficiency. This extra volume did much to reduce the density advantage claimed for the hybrid systems. But they learned how to build a hybrid motor that would work with reasonable efficiency.

Thus, although all the work with the lithium hydride grains and the chlorine trifluoride oxidizers never led to anything in particular, the fundamental research done at UTC led eventually to one hybrid motor which is operational and flying—the UTC power plant of a target drone. The oxidizer is N_2O_4 , and the fuel is a very fuel-rich composite solid propellant. A hybrid motor could be made and made to work—but the hybrid was not the answer to everything, and its place in the propulsion spectrum is, and will be, very limited.

The “Arcogels” were another attempted approach to a high-density system. These were conceived in 1956 by the Atlantic Research Co., who worked on them for some five years. They were a mixture comprising mainly powdered ammonium perchlorate, aluminum, and a relatively nonvolatile liquid fuel and carrier, such as dibutyl phthalate. They had the consistency, approximately, of toothpaste. They obviously couldn’t be brought into a chamber through a normal injector, but had to be forced in through special burner tips, which spread the pasty ribbon out to expose the maximum burning area. They burned all right, at least on a small scale, but their high density wasn’t enough of an advantage to outweigh the horrendous problem of designing an injection system that could be carried in a flyable missile, and they never got anywhere.

All sorts of efforts were being made, during the late 50’s, to increase propellant densities, and I was responsible (not purposely, but from being taken seriously when I didn’t expect to be) for one of the strangest. Phil Pomerantz, of BuWeps, wanted me to try dimethyl mercury, $Hg(CH_3)_2$, as a fuel. I suggested that it might be somewhat toxic and a bit dangerous to synthesize and handle, but he assured me that it was (a) very easy to put together, and (b) as harmless as mother’s milk. I was dubious, but told him that I’d see what I could do.

I looked the stuff up, and discovered that, indeed, the synthesis was easy, but that it was extremely toxic, and a long way from harmless. As I had suffered from mercury poisoning on two previous occasions and didn’t care to take a chance on doing it again, I thought that it

would be an excellent idea to have somebody else make the compound for me. So I phoned Rochester, and asked my contact man at Eastman Kodak if they would make a hundred pounds of dimethyl mercury and ship it to NARTS.

I heard a horrified gasp, and then a tightly controlled voice (I could hear the grinding of teeth beneath the words) informed me that if they were silly enough to synthesize that much dimethyl mercury, they would, in the process fog every square inch of photographic film in Rochester, and that, thank you just the same, Eastman was *not* interested. The receiver came down with a crash, and I sat back to consider the matter. An agonizing reappraisal seemed to be indicated.

Phil wanted density. Well, dimethyl mercury was dense, all right— $d = 3.07$ —but it would be burned with RFNA, and at a reasonable mixture ratio the total propellant density would be about 2.1 or 2.2. (The density of the acid-UDMH system is about 1.2.) That didn't seem too impressive, and I decided to apply the *reducto ad absurdum* method. Why not use the densest known substance which is liquid at room temperature—mercury itself? Just squirt it into the chamber of a motor burning, say, acid-UDMH. It would evaporate into a monatomic gas (with a low C_p , which would help performance), and would go out the nozzle with the combustion products. *That* technique should give Phil all the density he wanted! Charmed by the delightful nuttiness of the idea, I reached for the calculator.

For my calculations I used the monopropellant Cavea A, not only because it had a good density by itself (1.5) but because it would be simpler to handle two liquids than three in the wildly improbable event that things ever got as far as motor work. I calculated the performance of Cavea A with various proportions of mercury—up to six times the mass of the primary propellant. (It was easy to fit mercury into the NQD calculation method.) As expected, the specific impulse dropped outrageously as mercury was added to the system, but the density impulse (specific impulse \times propellant density) rose spectacularly, to peak at 50 percent above that of the neat monopropellant with a mercury/propellant ratio of about 4.8.

The next thing was to set up the boost velocity equation: $c_b = c \ln(1 + \varphi d)$, and to plug in the results of the performance calculations. I did this for various values of φ ,* plotting the percentage increase in boost velocity over that produced by the neat propellant

* φ , as you may remember, is a loading factor: the propellant tank volume divided by the dry mass (all propellants gone) of the missile. If there are ten kilograms of dry mass per liter of tank volume, $\varphi = 1/10$, or 0.1.

against the percentage of the (fixed) tank volume filled with mercury rather than propellant. The result was spectacular. With $\varphi = 0.1$, and 27.5 percent of the tank volume filled with mercury instead of propellant, the bulk density was 4.9 and the boost velocity was about 31 percent above that of the neat propellant; at $\varphi = 0.2$ there was a 20 percent increase with 21 volume percent of mercury. At $\varphi = 1.0$, on the other hand, the best you could get was a 2 percent increase in boost velocity with 5 volume percent of mercury. Obviously, a missile with a low φ , such as an air-to-air job, was where this system belonged—if anywhere.

I solemnly and formally wrote the whole thing up, complete with graphs, labeled it—dead pan—the “Ultra High Density Propellant Concept,” and sent it off to the Bureau. I expected to see it bounce back in a week, with a “Who do you think you’re kidding?” letter attached. It didn’t.

Phil bought it.

He directed us, forthwith, to verify the calculations experimentally, and NARTS, horrified, was stuck with the job of firing a mercury-spewing motor in the middle of Morris County, New Jersey.

Firing the motor wouldn’t be any problem; the problem lay in the fact that all of the mercury vapor in the atmosphere would not be good for the health of the (presumably) innocent inhabitants of the county—nor for our own. So a scrubber had to be built, a long pipe-like affair down which the motor would be fired, and fitted with water sprays, filters, and assorted devices to condense and collect the mercury in the exhaust before it could get out into the atmosphere. We had it built and were about ready to go, when the Navy decided to shut down—“disestablish”—NARTS, and ordered us to ship the whole mercury setup to NOTS. With a sigh of relief, we complied, and handed them the wet baby. Saved by the bell!

At NOTS, Dean Couch and D. G. Nyberg took over the job, and by March 1960 had completed their experiments. They used a 250-pound thrust RFNA-UDMH motor, and injected mercury through a tap in the chamber wall. And the thing *did* work. They used up to 31 volume percent of mercury in their runs, and found that at 20 percent they got a 40 percent increase in density impulse. (I had calculated 43.) As they were firing in the middle of the desert, they didn’t bother with the scrubber. And they didn’t poison a single rattlesnake. Technically, the system was a complete success. Practically—that was something else again.

A more practical way to get a high-density system (or so people thought) was to use a metallized fuel, one with a light metal suspended

in it. As we have seen, this was an old idea, going back at least to 1929. BMW in Germany tried it about 1944, without noticeable success, and Dave Horvitz at Reaction Motors made a long series of tests, in 1947-51, burning a 10 to 20 percent suspension of powdered aluminum in gasoline, with liquid oxygen. Again, his success was not spectacular. It was difficult to get decent combustion efficiency, and a good part of the metal never burned at all, but was exhausted unchanged out the nozzle. Designing an injector which would handle a suspension wasn't easy, particularly as the viscosity of the suspension varied outrageously with temperature. And if the mixture stood around a while, the aluminum had a strong tendency to settle to the bottom of the tank.

So, although Boeing, in 1953, considered using a suspension of magnesium in jet fuel, and burning it with WFNA (the project never got anywhere) interest in such things languished for some years. What revived it, late in the 50's, was a safety problem.

The Navy had always been reluctant to store loaded liquid rockets in the magazines of its beloved airplane carriers. What would happen if one of them sprung a leak, and disgorged a load of highly corrosive oxidizer, or highly inflammable fuel (or even worse, both of them!) onto the magazine deck? The point being, of course, that below decks on a carrier ventilation is difficult, and furthermore, aboard ship there's no place to run. Somebody—nobody now remembers who it was—came up with the idea that if the propellants were gelled—given the consistency of a not particularly stiff gelatine dessert—leakage would be extremely slow, and the situation would be manageable. As for the problem of injecting a gelled propellant, that could be solved by making the gel thixotropic. Whereupon everybody concerned demanded an explanation of *that* word.

A thixotropic gel, or "thixotrope," is a peculiar beast. Left to itself, it sets up to a comparatively stiff jelly, and if it is pushed gently it resists and flows very slowly, as though its viscosity were very high. If, however, it is subjected to a *large* force, as it would be if shaken violently, or forced under high pressure through an injector, its resistance suddenly collapses as though it had decided to relax and enjoy it, its viscosity drops precipitously, and it flows like a civilized liquid. A thixotropic propellant, then, would reduce the leakage hazard, while still being injectable.*

* A jellied, or thixotropic, fuel is much less of a fire hazard than the straight liquid if it is spilled. It evaporates and burns much more slowly, and doesn't have a tendency to spread the fire all over the surroundings. Considerable work has been done, recently, on applying the principle to jet fuel in commercial airliners, to reduce the fire hazard in case of a crash.

As it turned out, it wasn't particularly difficult to turn most of the common propellants into thixotropes. Five percent of so of finely divided silica would do it to nitric acid, and the hydrazines could usually be gelled the same way or by the addition of a small percentage of certain cellulose derivatives. And the results *could* be fired, although filling the tank beforehand was a frustrating and infuriating job. Combustion efficiency left something to be desired, and the dead weight of the silica naturally reduced the performance; but the system could be made to work—more or less. The real trouble showed up when an attempt was made to gel the halogen oxidizers. Silica, obviously, was impossible, as were the carbohydrate cellulose type agents. At Aerojects they tried to gel a mixture of ClF_3 and BrF_5 with a pyrolytic carbon black, and thought that they had solved the problem, particularly when the gelled mixture showed a card-gap value of zero cards. I was dubious about the whole thing though, and warned their Bill Tarpley and Dana McKinney that the system was inherently unstable, and that they were hunting for trouble. Unfortunately, I was proved right almost immediately. Fred Gaskins, was working with some of the material late in 1959, when it detonated. He lost an eye and a hand, and suffered fluorine burns which would have killed most people. Somehow, he survived, but that was the end of the attempt to mix interhalogens and carbon black. Later attempts used completely fluorinated substances, such as SbF_5 , for the gelling agent. Unfortunately, an inordinate amount of the agent was required to do the job.

A few years later, gelling appeared to be the answer to another problem, that of propellant sloshing in space vehicles. If, for some reason, the propellant in a partly full tank starts to slosh back and forth, the center of gravity of the rocket will shift in an unpredictable manner, and directional and attitude control can be lost. A gelled propellant, obviously, isn't subject to sloshing, and in 1965 A. J. Beardell of Reaction Motors, then investigating the diborane/ OF_2 system for deep space work, looked into the problem of gelling OF_2 . He found that he could do it with finely divided LiF , which, of course, would not react with the oxidizer. However, since several percent of LiF were needed to form the gel, the performance was appreciably degraded. R. H. Globus of Aerojet discovered a much more elegant solution to the problem three years later. He simply bubbled gaseous ClF_3 through liquid OF_2 . The chlorine trifluoride froze instantly to microscopic crystals which acted as the gelling agent. Five or 6 percent of the additive made a very fine gel, and the effect on performance was microscopic. For some reason or other, ClF_5 wouldn't work.

The gelled propellants revived the interest in metallized fuels. Many people thought that, by gelling a fuel, it might be possible to load it up with 50 percent or so of aluminum, or boron, or perhaps even beryllium—if you could ever get your hands on enough of the last—without having the metal settle out. It was soon discovered, too, that if your metal were finely enough divided, with particle sizes of the order of a micrometer, so that the Van der Waals forces became important, it would itself tend to gel the mixture. So there was a great burst of effort and people all over the country started to investigate the rheological properties of various metallized slurries (these have no gelling agent besides the metal), gels, and even emulsions. (These have two liquid phases—like mayonnaise—besides the metal.) Most of the investigators used Ferranti-Shirley viscosimeters, which can measure the viscosity of such substances as a function of the shear rate. (I was always getting the name confused with “Ferrari,” which is not unreasonable, since not only the names, but also the prices were similar.)

These investigators discovered that making a stable gel or slurry was not a science, but a black art, accomplished reliably only with the aid of witchcraft, and that getting two batches of gel with the same rheology was a miracle. But they persisted and in the early 60's several mixtures were ready for test firing.

Boron, aluminum, and beryllium were the metals investigated. Reaction Motors came up with a slurry of boron in a hydrocarbon, intended to be used in a ram-rocket, with chlorine trifluoride as the primary oxidizer. The idea was to maximize the propellant density, and since BF_3 is a gas, combustion problems were not serious. Most of the work, however, was directed towards aluminized fuels, and Rocketdyne, as early as 1962, had fired an aluminum-hydrazine mixture with N_2O_4 . It contained almost 50 percent of aluminum, and they called it “Alumizine.” It was designed for an improved Titan II, but, although they have been working on it ever since, it hasn't yet become operational. Reaction Motors fired an aluminized hydrazine-hydrocarbon emulsion with N_2O_4 two years later, but it, too, has failed to make the grade. And although the Naval Ordnance Test Station has fired their “Notsgel” (aluminum in gelled hydrazine mixtures) successfully many times, it hasn't yet found an application.*

* One of their hydrazine mixtures was a three to one mix of monomethyl hydrazine and ethylene di-hydrazine. This has a freezing point of -61° , and the viscosity of the EDH improves the stability of the gel. This is one of the few propellant applications that EDH has found to date.

And there have been other aluminized fuels, but none of them are ready for operational use.

In my own opinion, it will be a long time before they are operational, if they ever are. For the problems are horrendous. They come in two sorts, those arising when you try to store the fuels, and those which show up when you try to fire them, and it's hard to say which resist solution more stubbornly.

A shelf life of five years is specified for a prepackaged missile, and a lot of things can happen to a metallized gel in five years, particularly if the storage temperature varies considerably during that time—as it would if the missile were stored out of doors—or if it is subjected to vibration, which it is certain to be if it is shipped from point A to point B. There is always the tendency for the metal to settle out, and this tendency is abetted by wide temperature variations, which drastically and sometimes irreversibly change the rheology of the gel. And vibration, of course, has a tendency to reduce the viscosity, of a thixotropic gel, temporarily, of course, but possibly long enough to permit appreciable sedimentation. Or syneresis—a peculiar vice to which some gels are addicted—may set in. If this happens, the gel starts to shrink and to squeeze the liquid out of its structure, and the end of the process may be a comparatively small volume of a very dense and stiff solid phase surrounded by a volume of clear liquid. None of these things may happen—but on the other hand, they may—and the state of the art has not advanced to the point at which one can be assured that a metallized gel will survive, unchanged, five years of storage in climates ranging from that of Point Barrow to that of the Mojave Desert.

Most of the gels and slurries which have been considered have been based on hydrazine or hydrazine mixtures, which fact is the cause of another—and very peculiar—problem. Missile tanks are usually made of very pure aluminum. But there are always some impurities, and some of these impurities are likely to be transition metals such as iron which catalyze the decomposition of hydrazine. However, if the concentration of the catalytic metals is only some parts per million, very few of the offending atoms will be on the tank surface itself, where they can make trouble, and the decomposition and gas evolution will be negligible. However, if the hydrazine is loaded with very finely divided aluminum, the surface volume ratio of the metal will be increased by many orders of magnitude, as will be the number of catalytic atoms in contact with the hydrazine. Under these circumstances, the decomposition is increased enormously, and even if it is insufficient to change the composition of the fuel appreciably in a

reasonable length of time, the accompanying gas evolution can have serious, and disconcerting, results. For the gas cannot escape from the gel, which thereupon swells up exactly like a cheese soufflé. And try to run *that* through an injector!

Assuming, however, that the storage problems have been coped with, somehow, the operational problems remain. The first of these is that of forcing the fuel out of its tank. If a metallized gel is pressurized—that is, high pressure gas is let into the tank to force the fuel out—a sort of tunneling process takes place. The gas simply blows a hole for its own passage down through the gel to the outlet, and leaves most of the fuel untouched and sitting quietly around the sides of the tank, instead of flowing, as it should, through the feed line to the motor. The fuel has to be completely enclosed, as in a flexible bladder (to which the expulsion pressure is applied), or a large fraction of it simply won't leave the tank. Once the fuel leaves the tank, the rate at which it flows through the fuel line and the injector into the motor is strongly dependent on its viscosity, and the viscosity of a metallized gel varies madly with the temperature. Since the viscosity of the oxidizer doesn't vary nearly as much, the result of this is that the mixture ratio if you fire the motor at -40° will be quite unlike that which you will get if you fire it at $+25^\circ$ —and it certainly won't be the one that you want.

Then, once the fuel is in the motor—and I won't go into the problem of designing an injector which will disperse a gel properly—there's the problem of burning the aluminum. Unless the chamber temperature is well above the melting point of aluminum oxide (about 2050°) or, preferably above the considerably higher temperature at which it decomposes, the aluminum particle will simply coat itself with a layer of solid or liquid alumina, and refuse to burn to completion. When burned with N_2O_4 the chamber temperature is just about high enough to burn an aluminized gel properly. It's highly probable that combustion with nitric acid would be marginal, with a chamber temperature not quite high enough to make the metal burn to completion. (With a halogen oxidizer, such as ClF_3 , this particular problem doesn't arise, since AlF_3 is a gas at the temperatures we're talking about.) And, naturally, the dense clouds of solid Al_2O_3 resulting from the combustion of an aluminized gel leave a very conspicuous exhaust trail.

There is one final problem which should be mentioned—final because it comes up when the motor is shut down. The heat from the hot motor soaks back into the injector, and the gel in the injector holes sets up to something resembling reinforced concrete, which has to be

drilled out before the motor can be fired again. So, restarts are out of the question.

The problems with beryllium-loaded gels are the same as those with aluminized ones, only more so, and with one or two peculiar to themselves. The exhausted BeO, of course, is violently poisonous, producing something resembling a galloping silicosis, but the most serious problem is in the combustion. Beryllium oxide melts at a considerably higher temperature than does aluminum oxide, and doesn't vaporize until the temperature is near 4000°, so that burning it is even more difficult than burning aluminum. Rosenberg, at Aerojet, burned a beryllium-hydrazine slurry ("Beryllizine") with hydrogen peroxide in 1965, and got a C* efficiency of some 70 percent, which indicated that *none* of the beryllium had burned. At Rocketdyne, they had the same experience with the combination. When Rosenberg used N₂O₄ as his oxidizer, his C* efficiency was some 85 percent, showing that *some* of the metal had burned. His performance was particularly bad at what should have been the optimum mixture ratio. Various expedients designed to improve combustion, such as vapor-coating the beryllium powder with chromium, didn't improve the situation appreciably.

Aluminum hydride was a compound that aroused a flurry of interest in the early 60's. It had long been known, but not as pure or relatively pure AlH₃, since it had always been prepared solvated with ether, which couldn't be removed without decomposing the hydride. However, Dow Chemical and Metal Hydrides, late in 1959 or early in 1960, devised methods of obtaining it without ether, and Olin Mathieson soon made important contributions to the synthetic methods. Its intended use was as an ingredient in solid propellants, but the liquid people tried to use it in gels. It wasn't sufficiently stable, but reacted with the hydrazines, evolving hydrogen in the process, so the idea was soon abandoned.

Beryllium hydride, BeH₂ had more staying power. It had been known since 1951, but again, in an impure state. In 1962, however, G. E. Coates and I. Glocking of the Ethyl Corporation managed to prepare it in a fairly pure (about 90 percent) state. It, too, was intended for solid propellant use. It was nicknamed "Beane" (pronounced "beany"), as a security measure. (A little later it was discovered that its stability could be improved by heating it, and the result was called "Baked Beane.") But code name or no, the secret was soon out. I was in Dick Holzmann's office in the Pentagon when an assistant came in with the latest issue of *Missiles and Rockets*. And there was BeH₂, spread all over the page. It appears that a congress-

man who wanted to show how knowledgeable he was had blown security and had told a reporter everything he knew. I have heard – and used – some spectacular language in my time, but Holzmänn's remarks were a high point in the history of oral expression.

Naturally, the liquid people had to see if BeH_2 could be used in a gel. It appeared to be much more stable than aluminum hydride, particularly when it was in the amorphous, rather than the crystalline, state. Rocketdyne reported that the former reacted very little even with water. Texaco, Aerojet, and Rocketdyne investigated it in monomethyl hydrazine gels between 1963 and 1967. Aerojet claimed the mixture was stable, but Rocketdyne's gel, which had some straight hydrazine in it, displayed the soufflé syndrome. Its longtime stability in hydrazine appears very doubtful; certainly it is thermodynamically unstable.

With liquids which do not have active hydrogens, the situation is different. Grelecki at Reaction Motors, in 1966, made a 55 percent slurry of BeH_2 in dodecane, and burned it with hydrogen peroxide, getting good combustion and a high C^* efficiency. That same year the Ethyl Corporation made an apparently stable slurry of the material with pentaborane, and Gunderlory, at Rocketdyne, has investigated mixtures of the hydride with his beryllium semiliquids.

However, even if they are stable – and not all countries have been heard from – BeH_2 gels and slurries don't appear to be the wave of the future. The toxicity of the exhaust and the high price of the propellant appear to rule them out as far as tactical missiles are concerned, and there doesn't seem to be any other rôle for them that can't be filled better by something else.

A rather far-out concept, even in the fields of gels and slurries and monopropellants, is that of the heterogeneous monopropellant – a solid fuel slurried or gelled in a liquid oxidizer. The Midwest Research Institute came up with the first of these in 1958, when they suspended powdered polyethylene in RFNA. Unfortunately, its sensitivity was more than 120 cards, and it was thermally unstable to boot, so it was hurriedly abandoned before anybody got hurt. About five years later Reaction Motors introduced a similar mixture, with boron carbide, B_4C suspended in a special high density RFNA containing about 40 percent N_2O_4 . This was insensitive to the card-gap test, but was thermally unstable, and it, too, had to be junked. In 1965 they tried mixing boron carbide with ClF_5 (!), and found that it was apparently stable at 65° , although there was some reaction at first when the two compounds were mixed. Nevertheless, apparently remembering what had happened to Fred Gaskins, they didn't carry their experi-

ments any further. And for some years Rocket Research Co., a small organization in Seattle, has been industriously plugging "Monex," a mixture of powdered aluminum, hydrazine, hydrazine nitrate, and water, and, ignorant of or ignoring the work on hydrazine and hydrazine nitrate done nearly twenty years before at NOTS, claiming an outstanding and original contribution to rocketry. Recently they have been experimenting with beryllium instead of aluminum. Combustion efficiency with these propellants, particularly the beryllium-based ones, is bound to be bad, since the chamber temperature is comparatively low. Rocketdyne, in 1966, did some work with similar beryllium mixtures, with no notable success. The heterogeneous monopropellants can only be considered an aberration, off the main line of propellant development, and highly unlikely ever to lead to anything useful. About all it proves is the willingness of rocket people to try *anything*, no matter how implausible, if they can con NASA or one of the services into paying for it.

This may explain the work on the "Tribrid" (an etymological monstrosity, if there ever was one!). These are propellant systems involving three propellants, and the name derives vaguely from "hybrid." Sometimes the term "tripropellant" is used. Performance calculations made in the early 60's showed that for space use, there were two propellant systems whose specific impulses exceeded those of any other system that could be dreamed up—and exceeded them by a spectacular margin. The first of these was the Be-O-H system, in which the beryllium was burned to BeO by the oxygen, and the hydrogen provided the working fluid. It started to arouse considerable interest in 1963 or so, and Atlantic Research and Aerojet started programs designed to prove it out.

Atlantic Research's approach was an extension of the hybrid system. Powdered beryllium was made into a solid grain with the help of a small amount of hydrocarbon binder. This was burned, as in a hybrid, with the oxygen, and then hydrogen was fed into the chamber downstream of the grain. (In a variant arrangement, some of it was introduced upstream with the oxygen, and the rest farther down.) A scrubber was needed, of course, to take the BeO out of the exhaust stream—and the totality of the precautions taken to avoid poisoning the bystanders was fantastic. In any case, although the motor could be and was fired, combustion efficiency was extremely poor, and the system never, practically, approached its theoretical potential.

G. M. Beighley, at Aerojet, tried another approach, this one resembling the usual bi-propellant arrangement. His two propellants were liquid hydrogen and a slurry of powdered beryllium metal in

liquid oxygen. He was able to report his results by 1966, and they were not encouraging. He never got more than 70 percent combustion efficiency, and was plagued by "burnbacks" of his Be-O₂ slurry through the injector. It's really surprising that he didn't manage to kill himself.

At any rate, he didn't continue the work, and as little has been heard of the Be-H-O system in the last few years, it is probably dead. When the combustion difficulties are added to the toxicity of BeO and the price of beryllium, there isn't really much point in continuing with it.

The Li-F-H system looks much more promising, and has been investigated rather thoroughly by Rocketdyne. Here, two approaches are possible. Lithium has a low melting point for a metal—179°—so it is possible to inject lithium, fluorine, and hydrogen into the motor, all as liquids, in a true tripropellant system. Or, the lithium can be slurried in the hydrogen, so that the motor can be run as a bi-propellant system. Rocketdyne started investigating Li-H₂ gels in 1963, and three years later Bill Tarpley and Dana McKinney of Technidyne (Aeroprojects renamed) reported gelling liquid hydrogen with lithium and with lithium borohydride. Satisfactory and stable gels were produced with 61.1 weight percent (17.4 volume percent) of lithium or 58.8 weight percent (13.3 volume percent) of lithium borohydride. The evaporation rate of the hydrogen was reduced by a factor of 2 or 3, and gelling the fuel eliminated the propellant sloshing problem.

Their work was, however, only on the liter scale, and in the meantime Rocketdyne went ahead with the other approach, and fired the combination in a true tripropellant motor. They used liquid lithium and liquid fluorine, but used gaseous hydrogen instead of liquid. I presume that they considered that handling two such hairy liquids as fluorine and lithium at the same time was enough, without adding to their misery by coping with liquid hydrogen. I have described some of the problems associated with liquid fluorine, and liquid lithium has its own collection of headaches. You have to keep it hot, or it will freeze in the propellant lines. You must also keep it from contact with the atmosphere, or it will burst into brilliant and practically extinguishable flame. Add to this the fact that liquid lithium is highly corrosive to most metals, and that it is incompatible with anything you might want to use for gaskets and sealing materials (it even attacks Teflon with enthusiasm), and you have problems.

But somehow the Rocketdyne crew (H. A. Arbit, R. A. Dickerson, S. D. Clapp, and C. K. Nagai) managed to overcome them, and made their firings. They worked at 500 psi chamber pressure, with a high

expansion nozzle (exit area/throat area = 60) designed for space work. Their main problem stemmed from the high surface tension of liquid lithium, orders of magnitude higher than that of ordinary propellants, which made it difficult to design an injector that would produce droplets of lithium small enough to burn completely before going out the nozzle. Once this problem was overcome, their results were spectacular. Using lithium and fluorine alone (no hydrogen) their maximum specific impulse was 458 seconds. But when they proportioned the lithium and fluorine to burn stoichiometrically to LiF, and injected hydrogen to make up 30 percent of the mass flow, they measured 542 seconds—probably the highest measured specific impulse ever attained by anything except a nuclear motor. And the chamber temperature was only 2200 K! Performance like that is worth fighting for. The beryllium-burning motor is probably a lost cause, but the lithium–fluorine–hydrogen system may well have a bright future.