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The Hunting of the Hypergol . . .

As the American interrogators moved into Germany close behind—and sometimes ahead of—the armies, they found the German rocket scientists more than willing to surrender (and get new jobs) and more than anxious to tell everything they knew. Not only did the Americans get almost all the top scientists—they got everything else that wasn't nailed down, including the complete Peenemunde archives (which von Braun's crew had thoughtfully deposited in an abandoned mine) and all the A-4 rockets, complete or otherwise. And, red-blooded young Americans all, with larceny in their hearts, they liberated every milligram of hydrazine hydrate and high-strength hydrogen peroxide that they could find in Germany. Plus, naturally, the special aluminum tank cars built to carry the latter. Everything was promptly shipped to the United States.

These steps were obvious. The next step was not.

The alcohol–oxygen combination seemed all right for long-range missiles, but the United States had no immediate plans for building such things. The Tonkas and Visols were no improvements on monoethylaniline, or on the aniline-furfuryl alcohol mixtures that had been developed in the U.S. And there was nothing new about nitric acid. The Americans thought they knew all about it—as had the Germans. Unwarranted euphoria and misplaced confidence are international phenomena.

They had no doubt that missiles, guided and ballistic, were to be the artillery of the future. The question—or one of many—was the identity of the optimum propellant combination for a given, or projected, missile. And so everybody even remotely connected with the business made his own survey of every conceivable fuel and oxidizer, and tried to decide which ones to choose. Lemmon, of JPL, presented the results of such a comprehensive survey to the Navy in the spring of 1945, and a half a dozen more, by North American Aviation, Reaction Motors, the Rand Corporation, M. W. Kellogg Co., and others, appeared in the next few years. Each survey listed the characteristics of every propellant, or prospective propellant, that the compiler could think of, and presented the results of dozens of tedious performance calculations. To the surprise of nobody with any chemical sophistication at all, everybody came to just about the same conclusions.

There were two sets of these. The first related to long-range ballistic missiles, or to rockets designed to orbit an artificial satellite. (As early as 1946 both the Air Force and the Navy were making serious studies of the problem of orbiting an artificial Earth satellite.) In these applications, cryogenics (substances that cannot be liquefied except at very low temperatures) could be used. And here everybody agreed that:

1. The optimum oxidizer is liquid oxygen. ("Fluorine might be good, but its density is too low, and it's a holy terror to handle.")
2. As far as performance is concerned, liquid hydrogen is tops as a fuel. (But it was extremely hard to handle, and to come by, and its density is so low that the necessary tankage would be immense.) Below hydrogen it didn't much matter. Alcohol, gasoline, kerosene—they'd all work pretty well, and could be lived with. ("But maybe somebody could do something with things like diborane and pentaborane?" Their performances, as calculated, looked awfully impressive. "Sure, they were rare and expensive and poisonous to boot, but—?")

The second set of conclusions—or the lack of them—concerned things like JATO's and short range tactical missiles, which had to use storable propellants. Here the conclusions were less definite.

1. The available oxidizers were nitric acid, hydrogen peroxide (as soon as it could be got into production in the United States) and nitrogen tetroxide. (But N_2O_4 and 90 percent peroxide both froze at −11°C, and if you want to fight a war in, say, Siberia in February, or in the stratosphere—?) It looked as though nitric acid, in one of its variants, was the most likely candidate. ("Of course, if the freezing points of the other two could be reduced somehow—? And what about weirdies like ClF_3—?")

2. The conclusions were much less clean-cut when storable fuels were considered. With few exceptions, none of the possible fuels had a performance much better than any of the others. Decisions would have to be made based on their secondary characteristics: availability, hypergolicity, smoothness of combustion, toxicity, and so on. The one important exception was hydrazine. (Not the hydrazine hydrate the Germans had been using, but anhydrous N_2H_4. Dave Horvitz, at RMI, fired the hydrate with oxygen in 1950, but I am not aware of any other experiments, in this country at least, in which it was involved. Almost all the hydrazine hydrate looted from Germany was converted to the anhydrous base before being distributed for testing. One method of conversion was to reflux the hydrate over barium oxide, and then to distil over the anhydrous hydrazine under reduced pressure.) Hydrazine was hypergolic with the prospective oxidizers, it had a high density for a fuel (1.004) and its performance was definitely better than those of the other prospective fuels. But —its freezing point was 1.5°C higher than that of water! And it cost almost twenty dollars a pound. So two things obviously had to be done—get the price of hydrazine down, and somehow, lower the freezing point. (And again, there was that haunting thought of pentaborane—?)

There was one subject on which everybody agreed. Nobody was going to put up with the aniline–RFNA combination for one moment longer than he had to. The acid was so corrosive to anything you wanted to make propellant tanks out of that it had to be loaded into the missile just before firing, which meant handling it in the field. And when poured it gives off dense clouds of highly poisonous NO_2, and the liquid itself produces dangerous and extremely painful burns when it touches the human hide. And . . . but nitric acid and the struggle to domesticate it deserve, and will get, a chapter all to themselves.

The aniline is almost as bad, but a bit more subtle in its actions. If a man is spashed generously with it, and it isn't removed immediately, he usually turns purple and then blue and is likely to die of cyanosis in a matter of minutes. So the combination was understandably unpopular, and the call went out for a new one that was, at least, not quite so poisonous and miserable to handle.

Kaplan and Borden at JPL suggested one at the beginning of 1946. This was WFNA and straight furfuryl alcohol. Furfuryl alcohol was about as harmless as any propellant was likely to be, and WFNA, while it was just as corrosive as RFNA, and was just as hard on the anatomy, at least didn't give off those clouds of NO_2. They fired the combination in a WAC Corporal motor, comparing it to the 20 percent furfuryl alcohol, 80 percent aniline mixture and RFNA, and found no measurable difference in performance between the two systems. (The WAC Corporal was conceived as a sounding rocket, the "Little Sister" to the 20,000 pound thrust "Corporal" then under development. It was the ancestor of the Aerobee.) And, as a bonus, they found that ignition was fast and smooth, and much more tolerant to water in the acid than was the Corporal combination.

At about the same time, RMI was making a similar set of tests. These were all run in a 220-pound thrust Lark motor, whose mixed-acid, monoethylaniline combination was the reference propellant system. They used three fuels – 80 octane gasoline, furfuryl alcohol, and turpentine; and three types of nitric acid oxidizer – mixed acid, WFNA, and RFNA containing 15% N_2O_4.* They used a hypergolic starting slug on the gasoline firings, and rather surprisingly, got good results with all three acids. Furfuryl alcohol was no good with mixed acid. The combination was smoky and messy, and the reaction of the sulfuric acid of the MA with the alcohol produced a weird collection of tars, cokes, and resins, which quite clogged up the motor. But furfuryl alcohol was excellent with RFNA and WFNA, starting considerably smoother than did their reference propellants. And turpentine gave hard starts with RFNA and WFNA, but with MA started off like a fire hose. So that was one of the two combinations that they preferred. The other was furfuryl alcohol and WFNA (the RFNA performed a little better, but those NO_2 fumes!), although neat furfuryl alcohol freezes at −31°C – rather too high for comfort.

Many other fuels were tried during the late 40's and early 50's. At JPL mixtures of aniline with ethanol or with isopropanol were investigated and burned with RFNA. Ammonia was fired there (with RFNA) as early as 1949, and the next year Cole and Foster fired it with N_2O_4. The M. W. Kellogg Co. burned it with WFNA, and by 1951, R. J. Thompson of that company was beating the drum for this combination as the workhorse propellant for all occasions. Reaction Motors experimented with mixtures of ammonia and methylamine (to reduce the vapor pressure of the ammonia) and showed that the addition of 1.5 percent of dekaborane made ammonia hypergolic with WFNA, while the Bendix Corp., in 1953, showed that the same

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* Interestingly enough, the first stage of Diamant, which put the first French satellite into orbit, burns turpentine and RFNA.

end could be achieved by flowing the ammonia over lithium wire just upstream of the injector.

JPL fired various oddities with RFNA, such as furfural and two methylated and partially reduced pyridines, tetrapyre and pentaprim. The object of these tests is not readily apparent, nor is the reason why RMI bothered to fire cyclooctatetraene with WFNA. The fuel is not only expensive and hard to get, but it has a very high freezing point and has nothing in particular to recommend it. And the reason that the Naval Air Rocket Test Station went to the trouble of burning ethylene oxide with WFNA is equally baffling. The Edisonian approach has much to recommend it, but can be run into the ground. One of the oddest combinations to be investigated was tried by RMI, who burned d-limonene with WFNA. d-limonene is a terpene which can be extracted from the skins of citrus fruits, and all during the runs the test area was blanketed with a delightful odor of lemon oil. The contrast with the odors of most other rocket propellants makes the event worth recording.

It had long since become obvious to everybody concerned that firing a combination in a rocket motor is not the ideal way to find out whether or not it is hypergolic—and, if it is, how fast it ignites. By the nature of research more tests are going to fail than are going to succeed, and more combinations are going to ignite slowly than are going to light off in a hurry. And when the result of each delayed ignition is a demolished motor, a screening program can become a bit tedious and more than a bit expensive. So the initial screening moved from the test stand into the laboratory, as various agencies built themselves ignition delay apparatus of one sort or another. Most of these devices were intended not only to determine whether or not a combination was hypergolic, but also to measure the ignition delay if it was. In construction they varied wildly, the designs being limited only by the imagination of the investigator. The simplest tester consisted of an eyedropper, a small beaker, and a finely calibrated eyeball—and the most complicated was practically a small rocket motor setup. And there was everything in between. One of the fancier rigs was conceived by my immediate boss, Paul Terlizzi, at NARTS. He wanted to take high-speed Schlieren (shadow) movies of the ignition process. (What information he thought they would provide escaped me at the time, and still does.) * There was a small ig-

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* An incurable inventor of acronyms, he called it "STIDA," for Schlieren Type Ignition Delay Apparatus.

nition chamber, with high-speed valves and injectors for the propellants under investigation. Viewing ports, a high-speed Fastex camera, and about forty pounds of lenses, prisms, and what not, most of them salvaged from German submarine periscopes, completed the setup. Dr. Milton Scheer (Uncle Milty) labored over the thing for weeks, getting all the optics lined up and focused.

Came the day of the first trial. The propellants were hydrazine and WFNA. We were all gathered around waiting for the balloon to go up, when Uncle Milty warned, "Hold it—the acid valve is leaking!"

"Go ahead—fire anyway!" Paul ordered.

I looked around and signaled to my own gang, and we started backing gently away, like so many cats with wet feet. Howard Streim opened his mouth to protest, but as he said later, "I saw that dog-eating grin on Doc's face and shut it again," and somebody pushed the button. There was a little flicker of yellow flame, and then a brilliant blue-white flash and an ear-splitting crack. The lid to the chamber went through the ceiling (we found it in the attic some weeks later), the viewports vanished, and some forty pounds of high-grade optical glass was reduced to a fine powder before I could blink.

I clasped both hands over my mouth and staggered out of the lab, to collapse on the lawn and laugh myself sick, and Paul stalked out in a huff. When I tottered weakly back into the lab some hours later I found that my gang had sawed out, carried away, and carefully lost, some four feet from the middle of the table on which the gadget had rested, so that Paul's STIDA could never, never, never be reassembled, in *our* lab.

Other agencies had their troubles with ignition delay apparatus, although their experiences weren't often as spectacular as ours, but they eventually started cranking out results. Not too surprisingly, no two laboratories got the same numbers, and from 1945 until 1955 one would be hard put to find a period when there wasn't a cooperative ignition delay program going on, as the various laboratories tried to reconcile their results. One of the difficulties was that the different testers varied widely in the speed and the efficiency with which they mixed the two reactants. And another lay in the fact that different criteria for ignition were used by various experimenters. One might take the first appearance of flame (as shown by a photo cell or an ionization gage or a high-speed camera) as the moment of ignition, while another, with a micro-motor setup, might take the moment at which his motor arrived at full thrust or the design chamber pressure.

But although the various investigators didn't often come up with the same numbers, they generally rated propellant combinations in the same order. While they seldom agreed on the number of milliseconds it took combination A to light off, they were generally in complete agreement that it was a Hell of a lot faster than combination B.

Which was enough for many purposes. After all, everybody knew that WFNA and furfuryl alcohol were fast enough to live with, and obviously, if something shows up on the tester as faster than that combination it's probably worth trying in a motor.

Many laboratories worked in the field but Don Griffin at JPL and Lou Rapp at RMI were early comers in ignition delay work. The former organization, as was natural since Corporal was their baby, did a lot of work on the aniline–furfuryl–alcohol mixture, and in 1948 determined that the mixture with the minimum ignition delay consisted of 60 percent of the alcohol and 40 of aniline. This was close to the 49FA, 51 aniline eutectic (melting point −43°C) and the Corporal fuel (the missile was still under development) was changed from the 20 percent FA mixture to a 50–50 one.

Otherwise, they confirmed the hypergolic reaction of furan compounds and of aromatic amines with nitric acid, and demonstrated the beneficial effect of N_2O_4 in the latter case. And they showed that amines, particularly tertiary amines, and unsaturated compounds were generally hypergolic, while aliphatic alcohols and saturates generally were not. Most of their work was done with nitric acid, but a good deal, from 1948 on, was done with N_2O_4, whose hypergolic nature generally resembled that of acid.

Reaction Motors investigated the hypergolicity of similar compounds, as well as such things as the furans, vinyl and allyl amines, and polyacetylenics, such as di-propargyl, with the skeleton structure (without the hydrogens) $C{\equiv}C{-}C{-}C{-}C{\equiv}C$. And they found that many silanes were hypergolic with acid. The University of Texas, in 1948, also worked with these, and showed that 30 percent of tetra-allyl silane would make gasoline hypergolic. The University of Texas also investigated the zinc alkyls, as Sänger had done sixteen years earlier.

Standard Oil of California was the first of the oil companies to get into rocket propellant research in a big way, when Mike Pino, at the company's research arm, California Research, started measuring ignition delays in the fall of 1948.

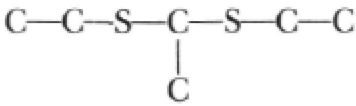
At first his work resembled that of the other workers, as he demonstrated fast ignition with dienes, acetylenics, and allyl amines. (Some years later, in 1954, Lou Rapp at RMI assembled the results of all the early ignition delay work, and attempted to make some generalizations. His major conclusion was that the ignition of a hydrocarbon or an alcohol involved the reaction of the acid with a double or triple bond, and that if none existed it had to be created before the ignition could take place. Later, in speaking of nitric acid, the plausibility of this postulate will be examined.)

But then Pino, in 1949, made a discovery that can fairly be described as revolting. He discovered that butyl mercaptan was very rapidly hypergolic with mixed acid. This naturally delighted Standard of California, whose crudes contained large quantities of mercaptans and sulfides which had to be removed in order to make their gasoline socially acceptable. So they had drums and drums of mixed butyl mercaptans, and no use for it. If they could only sell it for rocket fuel life would indeed be beautiful.

Well, it had two virtues, or maybe three. It was hypergolic with mixed acid, and it had a rather high density for a fuel. And it wasn't corrosive. But its performance was below that of a straight hydrocarbon, and its odor—! Well, its odor was something to consider. Intense, pervasive and penetrating, and resembling the stink of an enraged skunk, but surpassing, by far, the best efforts of the most vigorous specimen of *Mephitis mephitis*. It also clings to the clothes and the skin. But rocketeers are a hardy breed, and the stuff was duly and successfully fired, although it is rumored that certain rocket mechanics were excluded from their car pools and had to run behind. Ten years after it was fired at the Naval Air Rocket Test Station—NARTS—the odor was still noticeable around the test areas. (And at NARTS, with more zeal than judgment, I actually developed an analysis for it!)

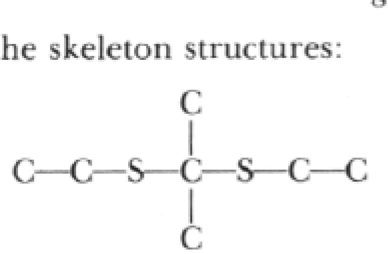
California Research had an extremely posh laboratory at Richmond, on San Francisco Bay, and that was where Pino started his investigations. But when he started working on the mercaptans, he and his accomplices were exiled to a wooden shack out in the boondocks at least two hundred yards from the main building. Undeterred and unrepentant, he continued his noisome endeavors, but it is very much worth noting that their emphasis had changed. His next candidates were not petroleum by-products, nor were they chemicals which were commercially available. They were synthesized by his own crew, specifically for fuels. Here, at the very beginning of the 50's, the chemists started taking over from the engineers, synthesizing new propellants (which were frequently entirely new compounds) to order, instead of being content with items off the shelf.

Anyhow, he came up with the ethyl mercaptal of acetaldehyde and the ethyl mercaptol of acetone, with the skeleton structures:



$$\mathrm{C-C-S-\underset{\underset{C}{|}}{C}-S-C-C}$$

and



$$\mathrm{C-C-S-\overset{\overset{C}{|}}{\underset{\underset{C}{|}}{C}}-S-C-C}$$

respectively. The odor of these was not so much skunk-like as garlicky, the epitome and concentrate of all the back doors of all the bad Greek restaurants in all the world. And finally he surpassed himself with something that had a dimethylamino group attached to a mercaptan sulfur, and whose odor can't, with all the resources of the English language, even be described. It also drew flies. This was too much, even for Pino and his unregenerate crew, and they banished it to a hole in the ground another two hundred yards farther out into the tule marshes. Some months later, in the dead of night, they surreptitiously consigned it to the bottom of San Francisco Bay.

To understand the entry of the next group of workers into the propellant field, it's necessary to go back a bit and pick up another thread. From the beginning, the services had disliked the fuels that the researchers had offered them, not only because of their inherent disadvantages, but above all because they weren't gasoline. They already had gasoline and used huge quantities of it – and why should they have to bother with something else? But, as we have seen, gasoline is not a good fuel to burn with nitric acid, and the services had to accept the fact. Which they did, grudgingly. But all through the late 40's and early 50's the Navy and the Air Force were busily changing over from piston airplane engines to turbojets. And they started buying jet fuel instead of gasoline, and the whole thing started all over again. They demanded of the people designing their missiles that said missiles be fueled with jet fuel.

Now, what is jet fuel? That depends. A turbojet has a remarkably undiscriminating appetite, and will run, or can be made to run, on just about anything that will burn and can be made to flow, from coal dust to hydrogen. But the services decided, in setting up the specifications for the jet fuel that they were willing to buy, that the most important considerations should be availability and ease of handling. So since petroleum was the most readily available source of thermal energy in the country, and since they had been handling petroleum products for years, and knew all about it, the services decided that jet fuel should be a petroleum derivative – a kerosene.

The first fuel that they specified was JP-1, a rather narrow cut, high paraffinic kerosene. The oil companies pointed out that not many refineries in the country could produce such a product with their available equipment and crudes, and that the supply might thus be somewhat limited. So the next specification, for JP-3 (JP-2 was an experimental fuel that never got anywhere), was remarkably liberal, with a wide cut (range of distillation temperatures) and with such permissive limits on olefins and aromatics that any refinery above the level of a Kentucky moonshiner's pot still could convert at least half of any crude to jet fuel. This time they went too far, allowing such a large fraction of low boiling constituents that a jet plane at high altitude boiled off a good part of its fuel. So the cut was narrowed to avoid this difficulty, but the permitted fractions of aromatics and olefins (25 and 5 percent respectively) were not reduced. The result was JP-4, with just about the most permissive specifications to appear since the days of Coal Oil Johnny Rockefeller the First. It is NATO standard, and the usual fuel for everything from a Boeing 707 to an F-111. (JP-5 and 6 have arrived since, but haven't replaced JP-4. And RP-1 is another story, which will be told later.)

But trying to burn JP-3 or JP-4 in a rocket motor with nitric acid was a harrowing experience. In the first place, the specifications being what they were, no two barrels of it were alike. (A jet engine doesn't care about the shape of the molecules it burns as long as they give up the right number of BTU's per pound, but a nitric acid rocket is fussier.) It wasn't hypergolic with acid, but reacted with it to produce all sorts of tars, goos, weird colored compounds of cryptic composition —and troubles. And if you got it going—using a hypergolic slug, say— sometimes everything went well, but usually not. It was acid-gasoline all over again—a coughing, choking, screaming motor, that usually managed to reduce itself to fragments, and the engineers to frustrated blasphemy. Everything was tried to make the stuff burn smoothly, from catalysts in the acid down—or up—to voodoo. The farthest-out expedient that I heard of was tried at Bell Aeronautic. Somebody had the bright idea that the sonic vibrations of a rocket motor might promote combustion. So he made a tape recording of the sound of a running motor and played it back at the interacting propellants in the hope that they might be shaken—or shamed—into smooth combustion. (Why not? He'd tried everything else!) But alas, this didn't work either. Obviously JP was a lost cause as far as the rocket business was concerned.

It was with this background that the Navy's program on "Rocket Fuels Derivable from Petroleum" came into being in the spring of 1951, although it wasn't called that officially until the next year. If you couldn't make JP work, maybe you could derive something else (cheaply, for choice) from petroleum that would. Or, one hoped, that could be mixed with JP and make the latter burn smoothly over a reasonable mixture-ratio range.

The title of the program was deceptive. "Derivable" is an elastic term, and it is to be doubted that the higher-ups of the Bureau of Aeronautics realized what they had authorized. But the lower-level chemist types in the Rocket Branch were perfectly aware of the fact that a good chemist, given a little time and money, can derive just about anything organic, up to RNA, from petroleum if he wants to. The contractors were being told, in effect, "Go ahead, Mack—see what you can come up with. And if it's any good, we'll find a way to make it from petroleum—somehow!"

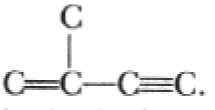
The contractors now joining their endeavors to those of California Research were the Shell Development Co., Standard Oil of Indiana, Phillips Petroleum, and the Chemical Engineering Department of New York University (NYU). And for the next two or three years there was a continuous ignition delay project going on. Each laboratory, as it came up with a new hypergolic additive, would ship samples to all the others, who would mix it with standard nonhypergolic fuels and then measure the ignition delay of the mixtures. The standard nonhypergols were generally toluene and n-heptane, although NYU, presumably to assert its academic independence, used benzene and n-hexane. (JP wasn't much use as a reference fuel, since no two lots of it were alike.)

As for the fuels and/or additives that they synthesized, Shell and NYU concentrated on acetylenic compounds, and Phillips put their major effort into amines. As for Standard of Indiana, that organization went off on a wild tangent. Apparently jealous of their sister company of California and determined to do them one better, they went beyond mere sulfur compounds, and came down hard on phosphorous derivatives. They investigated assorted substituted phosphines, from the timethyl phosphine, through butyl and octyl phosphines, on to monochloro (dimethylamino) phosphine, and then they settled happily on the alkyl trithiophosphites, with the general formula $(RS)_3P$, where R could be methyl, ethyl, or whatever. The one they gave the greatest play was "mixed alkyl trithiophosphites," which was a mixture of, mainly, the ethyl and methyl compounds. Its virtues were those of the mercaptans—hypergolicity and good density and no corrosion problems—but its vices were also those of the mercaptans—exaggerated. The performance was below that of the mercaptans, and the odor, while not as strong as those of the Pino's creations, was utterly and indescribably vile. Furthermore, their structures had an unnerving resemblance to those of the G agents, or "nerve gases" or of some of the insecticides which so alarmed Rachel Carlson. This disquietude was justified. When some of the alkylthiophosphites were fired at NARTS, they put two rocket mechanics in the hospital, whereupon they were summarily and violently thrown off the station. Standard of Indiana plugged them hard, and there was even a conference devoted to them in March of 1953, but somehow they, like the mercaptans, never roused the enthusiasm of the prospective users. Neither type of propellant, now, is anything but a noisome memory.

The rationale behind the acetylenic work was clear enough. It had been shown (by Lou Rapp and Mike Pino, among others) that double and triple bonds aided hypergolic ignition, and it was reasonable to assume that they might promote smooth combustion, if only by furnishing the fuel molecule with a weak point where the oxidation might start. Furthermore, the parent molecule of the family, acetylene itself, had always been regarded hopefully by the workers in the field. The extra energy conferred upon it by the triple bond should lead to good performance, although the low percentage of hydrogen in the molecule might work against it. (See the chapter on performance.) But pure liquid acetylene was just too dangerous to live with—having a lamentable tendency to detonate without warning and for no apparent reason. Perhaps some of its derivatives might be less temperamental. And these was another reason for looking at the acetylenics.

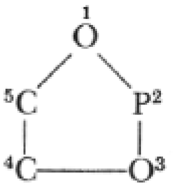
A good many people, in the early 50's, were considering some unusual, not to say bizarre, propulsion cycles. Among these was the ram rocket. This is a rocket, generally a monopropellant rocket, inside of and surrounded by a ramjet. A ramjet will not function except at high speed relative to the atmosphere, and hence has to be boosted into operation by a rocket or some other means. If the enclosed rocket of the ram rocket could get the device up to operating velocity, and if the rocket exhaust gases were combustible and could act as the fuel for the ramjet—well, then you could build a cruising missile that didn't need a booster and with a lower specific fuel consumption than a straight rocket. Say that you burned propyne, or methyl acetylene, in a monopropellant rocket, and that the exhaust products were largely methane and finely divided elementary carbon. Then the carbon and the methane could be burned with air in the ramjet, going to water and carbon dioxide, and you would be making the best of both worlds. (Ethylene oxide, C_2H_4O, whose major decomposition products are methane and carbon monoxide, was considered for the same sort of cycle.) So the acetylenics looked good for the ram rocket.

And finally, the acetylenics are rather easy to produce from petroleum feed-stock, by cracking and partial oxidation. The approaches of NYU and of Shell to the acetylenic problem were completely dissimilar. NYU tried dozens of compounds of the family, while Shell concentrated on just two, and then went hunting for additives which would make them into useful fuels. One of the two was 1,6-heptadiyne, with the skeletal structure $C{\equiv}C{-}C{-}C{-}C{-}C{\equiv}C$. And the other was 2-methyl-1-buten-3-yne, otherwise known as "isopropenyl acetylene" or "methyl vinyl acetylene," whose skeleton is


$C{=}\overset{\overset{\displaystyle C}{|}}{C}{-}C{\equiv}C$. One source of confusion in the history of the acetylenics is the multiplicity of systems by which they were named!

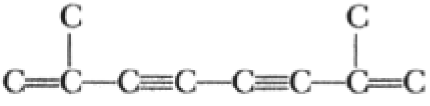
The first additives that they investigated thoroughly were methyl derivatives of phosphorous triamide, $P(NH_2)_3$, with methyl groups substituted for from three to six of the hydrogens. They worked, but so much of the additive was needed for proper ignition that it became a major component of the mixture, and even then explosive ignition was common.

Then they tried the derivative of 1,3,2-dioxaphospholane,



and finally settled on 2-dimethylamino-4-methyl-1,3,2-dioxaphospholane, which was usually, and mercifully, known as "Reference Fuel 208." Again, it wasn't a success as an additive, but taken neat, it was one of the fastest hypergols ever seen. It wasn't particularly toxic, and might have made a fairly good workhorse fuel, but before much work had been done on it, events made it obsolete. It's all but forgotten now.

Between 1951 and 1955 Happell and Marsel at NYU prepared and characterized some fifty acetylenics: hydrocarbons, alcohols, ethers, amines, and nitriles. They varied in complexity from propyne, or methyl acetylene, $C{-}C{\equiv}C$ to such things as dimethyldivinyldiacetylen


$C{=}\overset{\overset{\displaystyle C}{|}}{C}{-}C{\equiv}C{-}C{\equiv}C{-}\overset{\overset{\displaystyle C}{|}}{C}{=}C$ with no less than four multiple bonds. The climax of unsaturation came with butyne di-nitrile, or dicyano-

acetylene, N≡C—C≡C—C≡N which had no hydrogen atoms at all, but rejoiced in the possession of three triple bonds. This was useless as a propellant—it was unstable, for one thing, and its freezing point was too high—but it has one claim to fame. Burning it with ozone in a laboratory experiment, Professor Grosse of Temple University (who always liked living dangerously) attained a steady state temperature of some 6000 K, equal to that of the surface of the sun.

Many, if not most, of the acetylenics had poor storage properties, and tended to change to tars or gels on standing. They also tended to form explosive peroxides on exposure to the atmosphere. Many of them were shock sensitive, and would decompose explosively with little or no provocation. Something like divinyldiacetylene can fairly be described as an accident looking for a place to happen. While some of them were fired successfully in a rocket (RMI burned propyne, methylvinylacetylene methyldivinylacetylene, and dimethyldivinylacetylene, all with oxygen) they turned out not to be suitable fuels for nitric acid. They usually detonated on contact with the oxidizer, as several possessors of piles of junk that had originally been ignition delay equipment could testify, and did.

But some of them showed promise as monopropellants and as additives, and the Air Reduction Co., which had entered the field around the middle of 1953, had propyne, methylvinylacetylene, and dimethyldivinylacetylene in commercial production by 1955.

Some of them were excellent additives for JP-4. By August, 1953, RMI had shown that as little as 10 percent of methylvinylacetylene in JP-4 led to smooth combustion with RFNA over a wide range of mixture ratios, and greatly improved ignition. If a hypergolic slug was used, transition to the working fuel was smooth and without incident, and, for that matter, ignition could easily be achieved with a powder squib, and without a starting slug at all. Several of the others had the same effect, but by the time that this was determined the acetylenics had been overtaken by history, and had been developed only to be abandoned.

Homer Fox and Howard Bost ran the amine program at Phillips Petroleum. The relationship of amines to petroleum is exiguous at best, but they had been used as fuels for some time (triethylamine had been used in the Tonkas) and looked good, although they had never been examined systematically for propellant use. This Phillips proceeded to do, and investigated amines in infinite variety. Primary, secondary, and tertiary amines. Saturated and unsaturated amines, allyl and propargyl amines. Monoamines, diamines, even triamines and tetramines. They must have synthesized and characterized at least forty aliphatic amines, including a few with other functional groups —OH groups and ether linkages.

They concentrated on the tertiary polyamines. This was logical enough. They knew that tertiary amines were generally hypergolic with nitric acid, and it was reasonable to think that a di- or tri-tertiary amine might be more so. (Their guess turned out to be right, but one is reminded of E. T. Bell's remark that the great vice of the Greeks was not sodomy but extrapolation.) The compounds they investigated ranged from 1,2 bis (dimethylamino) ethane, up to such curiosities as 1,2,3, tris (dimethylamino) propane and tetrakis (dimethylaminomethyl) methane, which can be visualized as a neopentane molecule with a dimethylamine group on each corner. Incidentally, it turned out to have an unacceptably high freezing point, which, considering the symmetry of the molecule, might have been expected. One is led to suspect that some of the fancier amines were synthesized, not because there was any reason to believe that they would be an improvement on the ones they already had, but to demonstrate the virtuosity of the bench man, who wanted to prove that he could do it.

The tertiary diamines were the ones that really got a workout. Just about every possible structural change, and its consequences, were investigated. Thus they investigated the consequences of varying the terminal groups, as in the series:

1,2 bis (dimethyl, or ethyl, or allylamino) ethane.

Or, of varying the length of the central hydrocarbon chain, as in:

$$\left.\begin{array}{l}1,1\\1,2\\1,3\\1,4\\1,6\end{array}\right\}\text{-bis (dimethylamino)}\left\{\begin{array}{l}\text{methane}\\\text{ethane}\\\text{propane}\\\text{butane}\\\text{hexane}\end{array}\right.$$

They moved the amino groups around, as in:

$$\left.\begin{array}{l}1,2\\1,3\end{array}\right\}\text{ bis (dimethylamino)-propane and}$$

$$\left.\begin{array}{l}1,2\\1,3\\1,4\end{array}\right\}\text{ bis (dimethylamino) butane.}$$

They examined the effect of unsaturation, in series like

$$\text{1,4 bis (dimethylamino)}\left\{\begin{array}{l}\text{butane}\\\text{2 butene}\\\text{2 butyne}\end{array}\right.$$

And they tried every conceivable permutation and combination of these changes, as well as adding OH groups or ether linkages.

As might have been expected, introducing an hydroxyl group produced a compound which was excessively viscous at low temperatures. (Triethanolamine, which had been considered as a fuel, is an extreme example of this effect, and therefore was never used.) The allyl-terminated amines were also rather viscous, and were subject to atmospheric oxidation. Otherwise, as might have been expected, they were all very much alike, the complicated ones being in no way superior to the simple compounds, as might also have been expected.

None of them was any good as a jet fuel additive. They neither improved combustion nor, except in overwhelming proportions, made the jet fuel hypergolic. However, they looked promising as straight fuels, and Phillips shipped samples of four of them to the Wright Air Development Center to be test fired. They were all of the bis (dimethylamino) type, the 1,2 ethane, the 1,2, and 1,3 propane, and the 1,3-1 butene.

At WADC, in 1956, Jack Gordon checked out their properties and logistics, and fired them with RFNA. They were good fuels. Ignition was hypergolic and fast, combustion was good and performance was respectable, and the saturated ones, at least, were quite stable to heat and suitable for regenerative cooling.

And they, too, were obsolete at birth.

For all this work had been done, as it were, with the left hand. Hydrazine was the name of the big game. That was the fuel that everybody wanted to use. High performance, good density, hypergolic with the storable oxidizers—it had everything. Almost.

Its price was high, but the nature of the chemical industry being what it was, and is, one could be confident that it would come down to a reasonable figure when anybody wanted it in quantity. It was somewhat sensitive to catalytic decomposition, but if you used the right materials to make your tanks of, and were reasonably careful about cleanliness, that was no real problem. But that freezing point −1.5°C—was just too high for anything that was going to be used in a tactical missile. The services were awfully coy about setting definite limits on the freezing point of propellants that they would accept—one had the feeling that they would demand the impossible and then settle for what they could get—but they finally decided that −65°F, or −54°C, would be acceptable for most purposes. (Although the Navy, during one whimsical period, demanded a freezing point no higher than −100°F. How they would fight a war at that temperature they didn't specify. One is tempted to believe that they were carried away by the magnificent evenness of the number.)

So everybody was trying to bring the freezing point of hydrazine down to −54°. And without adversely affecting its other—and good—properties. Which turned out to be impossible. This could have been predicted, but at that time we were all hoping for miracles.

From first to last, at least eight agencies were involved in the effort, Aerojet, JPL, the Metalectro Co., NARTS, Naval Ordnance Test Station (NOTS), North American Aviation, Reaction Motors, and Syracuse University.

The first freezing point depressant to be tried—although involuntarily—was water. Hydrazine hydrate, which is 36 percent water; has a freezing point of −51.7°, and a mixture containing 42 percent water freezes at −54°. (V. I. Semishin, in Russia, had determined part of the hydrazine-water phase diagram in 1938, and Mohr and Audrieth, in this country, in 1949, and Hill and Summer, in England, in 1951 completed the job.) But water was an extremely bad additive for a fuel. It contributed nothing to the energetics of the system, and the mass of the water, just going along for the ride, seriously degraded the performance.

Ammonia wasn't quite as bad. F. Fredericks, in 1913 and in 1923, had reported on the hydrazine-ammonia phase diagram, which was also investigated by D. D. Thomas, at JPL, in 1948. Ammonia, unlike water, was a fuel, but it is a very stable compound and its heat of combustion is not what might be desired. And it took something like 61 percent of ammonia in the hydrazine to reduce its freezing point to −54°! This not only reduced the performance sharply, but decreased the density of the fuel, and, on top of that increased its vapor pressure so much that it boiled at about −25° instead of at the +113.5° boiling point of pure hydrazine. Dave Horvitz of RMI investigated ternary mixtures of hydrazine, water, and ammonia in 1950, but couldn't find any mixture that possessed both an acceptable freezing point and a large fraction of hydrazine. Water and ammonia were not the answers.

Another additive investigated by RMI (in 1947) was methanol. A mixture containing 44 percent of the hydrazine and 56 of the alcohol freezes at −54°, and its other physical properties are acceptable, but it yields a performance considerably below that of the neat hydrazine. Some years later, under circumstances which will be described, interest in the mixture was revived.

Don Armstrong, of Aerojet, came up with something in the summer of 1948 that for a time looked extremely promising. He found that the addition of 13 percent of lithium borohydride to hydrazine produced a mixture whose (eutectic) freezing point was −49°. Not the magic −54°, but still something. The density was reduced somewhat, from 1.004 to about 0.93, but as the borohydride itself is such an energetic compound there was no reason to expect any appreciable degradation of the performance. But, alas, his triumph was illusory. After some time had elapsed the mixture was found to be inherently unstable, and slowly and inexorably to decompose, with a steady evolution of hydrogen. They gave the whole idea up around 1952, but RMI was looking at it as late as 1958, and only around 1966 or 1967 somebody else suggested using $LiBH_4$ as a freezing point depressant for hydrazine! This may indicate something beyond a profound and depressing ignorance of the history of one's own technology, but I'm not exactly sure what.

At about the same time T. L. Thompson, of North American, came up with another freezing point additive, whose major drawback, although its thermal stability was poor, was that it scared everybody to death. He found that 15 percent of hydrocyanic acid, HCN, would reduce the freezing point of hydrazine to −54°. But the mere thought of the HCN so alarmed everybody (although much more toxic compounds had been and would be investigated, and without any particular notice being taken of it) that the mixture was never accepted.

At about this time (1949–50) the LAR missile was being developed at NOTS, and E. D. Campbell and his associates came up with a low freezing fuel for it—a mixture of 67 percent hydrazine and 33 ammonium thiocyanate, with a freezing point of −54°. This could be lived with, although the performance was somewhat degraded and the vapor pressure was inconveniently high.

Early in 1951, Dave Horvitz at the Metallectro Co. (where he had moved from RMI) investigated hydrazine–aniline mixtures, and found that the eutectic composition, with a freezing point of −36°, contained only 17 percent hydrazine. He then started adding methylamine to the mixture, to reduce the viscosity as well as the freezing point, and finally came up with a hydrazine–aniline–methylamine mixture (regrettably called "HAM Juice"), which froze at −50°, but contained only 9.1 percent of hydrazine, with 19.3 of methylamine and 71.6 of aniline. This was investigated rather thoroughly, and was test fired, but it wasn't the answer that people were looking for. (But the Army, in 1953 added 5 percent of hydrazine to their aniline–furfuryl alcohol Corporal fuel, and three years later raised the percentage to seven.)

One of the most thoroughly investigated additives was hydrazine nitrate. The ammonia analogue of the mixture—ammonium nitrate in ammonia, Diver's solution—had been around for years, so the idea was obvious enough, and apparently several people thought of it independently at about the same time. Dwiggins at the Naval Ordnance Laboratory (NOL) and my group at NARTS investigated the system in 1951, and by the end of 1953 J. M. Corcoran and his colleagues at NOTS had worked out the whole hydrazine–hydrazine nitrate–water system. A mixture containing 55 percent hydrazine and 45 hydrazine nitrate froze below −40°, and the magic −54° could be attained with one containing 54 percent hydrazine, 33 of the nitrate, and 13 water. This was not bad, but there was, as usual, a catch or two. The mixtures were quite viscous at low temperatures, and had a tendency to froth, which could lead to trouble if a pumped feed system were used. And, particularly, most of the really useful mixtures, with low percentages of water, could be detonated with alarming ease. (And the dry hydrazine nitrate, if mistreated, could produce a very plausible simulation of a turret fire. The NARTS group found that out!) But some of the mixtures could be used as monopropellants, and as such, were studied extensively for some years, and some of them were tried as liquid gun propellants.

The NARTS group, not content with mere nitrates, tried hydrazine perchlorate as a depressant in 1951, and found that a mixture containing 49 percent hydrazine, 41.5 of the perchlorate, and 8.5 water was still liquid at −54°. But it was even more likely to detonate than were the nitrate mixtures (while attempting to investigate its thermal stability we blew a hole in the ceiling of the laboratory), and I discovered, nearly blowing my head off in the process, that it is not advisable to attempt to dehydrate the hydrazinium perchlorate hemihydrate (the form in which it crystallizes) to the anhydrous salt. So, although the perchlorate mixture was more energetic than the nitrate mixtures, its use was outside of the range of practical politics. Nevertheless, Walker, at Syracuse University, tried sodium perchlorate monohydrate a year or so later, and found that a 50-percent mixture with hydrazine froze at approximately −46°. Somehow, he managed to do it without killing himself.

Many other freezing point depressants were tried by various groups, with little or no success, and it was rapidly becoming obvious that the additive approach wasn't going to get anywhere. You either ruined your performance or were likely to blow your head off. Something new had to be added to people's thinking.

It was a Navy program that led to the breakout. At the beginning of 1951 the Rocket Branch of the Bureau of Aeronautics granted contracts to Metallectro and to Aerojet to synthesize certain hydrazine derivatives, and to determine their suitability as rocket propellants.

The three derivatives were monomethylhydrazine, symmetrical dimethyl hydrazine, and unsymmetrical dimethyl hydrazine. The hope was that a very slight alteration to the structure – and you can hardly alter it less than by adding a methyl group – might give it a reasonable freezing point without changing its energetics enough to matter.

At NARTS, I had the same idea, and managing to lay my hands on a pound of monomethylhydrazine – it cost $50.00 – I investigated its mixtures with hydrazine, and before the end of the year recommended the eutectic, which contained 12 percent hydrazine and froze at −61°, as *the* fuel to concentrate on.* The performance with HNO_3 was about 98 percent of that of straight hydrazine, the density was not too bad (0.89) the freezing point was beautiful, the viscosity was nothing to worry about, and storage and handling didn't seem to involve any particular problems, although the methyl hydrazine appeared to be a bit more sensitive to catalytic decomposition than the parent compound.

It didn't take Metallectro and Aerojet very long to discover that they were on to something good. Symmetrical dimethyl hydrazine turned out to be a dog (it's freezing point was only −8.9°), but monomethylhydrazine (to be referred to from now on as MMH) melted at −52.4°, and unsymmetrical dimethyl hydrazine (UDMH) melted at −57.2°. And Dave Horvitz at Metallectro found that the 60–40 UDMH-MMH eutectic mixture froze only at −80°, or −112°F, thus exceeding the Navy's mystic goal. What's more, its viscosity at their magic −100°F was only 50 centipoises, so that it could really be used at that temperature. In the meantime, Aston and his colleagues at Pennsylvania State College had been determining the thermodynamic properties (heat of formation, heat capacity, heat of vaporization, etc.) of the substituted hydrazines, and by 1953 just about every useful piece of information about UDMH and MMH had been firmly nailed down.

They were both magnificent fuels – and the question that had to be decided was which one to concentrate on. A symposium on hydrazine and its derivatives and applications was held in February 1953, and the question was argued at length and with heat. MMH was a little denser than UDMH, and had a slightly higher performance. On the other hand, UDMH was less liable to catalytic decomposition, and had such good thermal stability that it could easily be used for regenerative cooling. Either one could be used as a combustion additive for JP-4, but UDMH was more soluble, and would tolerate a

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*MHF-3, introduced by Reaction Motors a few years ago, is 86% monomethyl hydrazine and 14% hydrazine. "And there is nothing new under the sun."

larger percentage of water in the fuel without separating. Both were hypergolic with nitric acid, the UDMH being the faster—after all, it was not only a hydrazine, but also a tertiary amine. And they both performed well as propellants, with performances superior to those of the tertiary diamines or of any of the phosphorous or sulfur compounds or of the old aniline type or furfuryl alcohol fuels. My MMH-hydrazine mixture was fired at NARTS early in 1954, UDMH at WADC at about the same time, MMH a little later and the UDMH-MMH eutectic at the same agency during 1955—all with red fuming nitric acid. And UDMH in JP-4 was so successful in smoothing out combustion that the fuel decided upon for the Nike Ajax missile was 17 percent UDMH in JP-4. The substituted hydrazine program was a resounding success. It had made all the other storable fuels completely obsolete.

The final decision to concentrate on UDMH was made on economic grounds. The two competitors for the first production contract for the substituted hydrazines were Metallectro and the Westvaco Chlor-Alkali division of Food Machinery and Chemical Co. (FMC). Metallectro proposed using a modification of the classic Raschig process for hydrazine, by reacting chloroamine with mono or dimethyl amine, according to which of the two hydrazines the customer wanted. And in their bid they proposed a carefully worked out sliding scale of prices, depending on the size of the order.

Westvaco took another approach. They proposed using another synthesis in which nitrous acid reacts with dimethyl amine to form nitrosodimethylamine, which can easily be reduced to the UDMH. The process cannot be used for MMH, and so Westvaco ignored the latter, and being prepared to take a loss on the initial orders (after all, the money involved was trivial from the point of view of a company the size of FMC), drastically underbid Metallectro. They got the order, and Metallectro dropped out of the picture for good. The first military specifications for UDMH were published in September 1955.

But that didn't inhibit Westvaco's advertising department. Intoxicated with success, and military specification or no, they tried to get away with a trade name, and called their stuff "DIMAZINE—the Westvaco brand of UDMH" and insisted that all of their people refer to it by that name. I pitied some of their chemists, visiting various agencies in the rocket business, dutifully and blushingly obeying orders, amidst the ribald hoots from their highly sophisticated audiences, who were as aware as they were themselves of the fact that

Westvaco UDMH was absolutely indistinguishable from that made by Olin Mathieson or anyone else.

Some attempts were made to improve upon UDMH. Mike Pino at California Research had, as we have seen, worked with allyl amines, and in 1954 he carried this a bit further, and came up with the mono and the unsymmetrical diallyl hydrazines. These were interesting, but no particular improvement over UDMH, and were sensitive to oxidation and polymerization. And the people at Dow Chemical, a little later, produced monopropargyl hydrazine and unsymmetrical dipropargyl hydrazine. Again, no improvement, and both of them were horribly viscous at low temperatures. And McBride and his group, at NOTS, studying the oxidation chemistry of UDMH, in 1956 came upon tetramethyl tetrazene $(CH_3)_2N—N{=}N—N(CH_3)_2$. But its performance advantage over UDMH was trivial, and its freezing point was quite high.

So UDMH, for several years, was *the* fuel to be burned with nitric acid or N_2O_4. But, as designers have been trying to wring the last possible second of performance out of their motors, MMH has been growing in popularity. (It, too, has a Mil. Spec. now!) And, in applications which do not require a low freezing point, hydrazine itself is used, either straight or mixed with one of its derivatives. The fuel of the Titan II ICBM doesn't have to have a low freezing point, since Titan II lives in a steam-heated hole in the ground, but it *does* need the highest possible performance, and hydrazine was the first candidate for the job. But, as hydrazine has an unfortunate tendency to detonate if you try to use it as a regenerative coolant, the fuel finally chosen was a 50–50 mixture of hydrazine and UDMH, called "Aerozine 50" by Aerojet who came up with it first, and "50–50" by everybody else.

Today there are a bewildering lot of hydrazine-type fuels around, with names like MAF-3 (Mixed Amine Fuel-3) or MHF-5 (Mixed Hydrazine Fuel-5) or Hydyne, or Aerozine-50, or Hydrazoid N, or U-DETA or whatever. But whatever the name, the fuel is a mixture of two or more of the following: hydrazine, MMH, UDMH, diethylene triamine (DETA, added to increase the density), acetonitrile (added to reduce the viscosity of mixtures containing DETA) and hydrazine nitrate. And, for one special application (a vernier motor on Surveyor) enough water was added to MMH to form the monohydrate, whose cooling properties were much superior to those of the anhydrous compound. A candidate for entry to the list is ethylene di-hydrazine $(H_3N_2C_2H_4N_2H_3)$ synthesized by Dow early in 1962. By itself it wouldn't be particularly useful—its freezing point is 12.8°C—but its density is high (1.09), and it might well be superior to DETA as a density additive.

So now the designer has a family of high performing fuels at his disposal—reliable, easy to handle, and available. Which mixture he chooses—or composes for the occasion—depends upon the specific requirements of the job at hand. And he knows that it will work. That, at least, is progress.