

. . . and Its Mate

The RFNA of 1945 was hated by everybody who had anything to do with it, with a pure and abiding hatred. And with reason. In the first place, it was fantastically corrosive. If you kept it in an aluminum drum, apparently nothing in particular happened—as long as the weather was warm. But when it cooled down, a slimy, gelatinous, white precipitate would appear and settle slowly to the bottom of the drum. This sludge was just sticky enough to plug up the injector of the motor when you tried to fire it. People surmised that it was some sort of a solvated aluminum nitrate, but the aversion with which it was regarded was equaled only by the difficulty of analyzing it.

If you tried to keep the acid in stainless steel (SS-347 stood up the best) the results were even worse. Corrosion was faster than with aluminum, and the acid turned a ghastly green color and its performance was seriously degraded. This became understandable when the magnitude of the change in composition was discovered. Near the end of 1947, JPL published the results of two acid analyses. One was of a sample of RFNA fresh from the manufacturer, which had scarcely started to chew on the drum in which it was shipped. The other was a sample of “old” acid, which had been standing for several months in a SS-347 drum. The results were eloquent. And, if my own experience is any criterion, there was a bit of insoluble matter of cryptic composition on the bottom of the drum. Acid like that might have been useful in the manufacture of fertilizer, but as a propellant it was not.*

* Note to the sophisticated reader: Don't take the exact percentages too seriously. Acid analysis wasn't really that good in 1947. Also, most of the iron really shows up in the ferrous and not in the ferric state, as I discovered in my own laboratory (and to my complete surprise) some years later.

Constituent	New acid	Old acid
HNO ₃	92.6 percent	73.6 percent
N ₂ O ₄	6.3 percent	11.77 percent
Fe(NO ₃) ₃	.19 percent	8.77 percent
Cr(NO ₃) ₃	.05 percent	2.31 percent
Ni(NO ₃) ₂	.02 percent	.71 percent
H ₂ O	.83 percent	2.83 percent

So the acid couldn't be kept indefinitely in a missile tank—or there wouldn't be any tank left. It had to be loaded just before firing, which meant handling it in the field.

This is emphatically not fun. RFNA attacks skin and flesh with the avidity of a school of piranhas. (One drop of it on my arm gave me a scar which I still bear more than fifteen years later.) And when it is poured, it gives off dense clouds of NO₂, which is a remarkably toxic gas. A man gets a good breath of it, and coughs a few minutes, and then insists that he's all right. And the next day, walking about, he's just as likely as not to drop dead.

So the propellant handlers had to wear protective suits (which are infernally hot and so awkward that they probably cause more accidents than they prevent) and face shields, and frequently gas masks or self-contained breathing apparatus.

An alternative to RFNA was mixed acid, essentially WFNA to which had been added some 10 to 17 percent of H₂SO₄. Its performance was somewhat lower than that of RFNA (all that stable sulfuric acid and that heavy sulfur atom didn't help any) but its density was a little better than that of the other acid, and it was magnificently hypergolic with many fuels. (I used to take advantage of this property when somebody came into my lab looking for a job. At an inconspicuous signal, one of my henchmen would drop the finger of an old rubber glove into a flask containing about 100 cc of mixed acid—and then stand back. The rubber would swell and squirm a moment, and then a magnificent rocket-like jet of flame would rise from the flask, with appropriate hissing noises. I could usually tell from the candidate's demeanor whether he had the sort of nervous system desirable in a propellant chemist.) Mixed acid, of course, didn't give off those NO₂ fumes, and everybody was convinced, as late as 1949, that it didn't corrode stainless steel. In that year the Navy purchased several hundred 55-gallon drums and several tank cars, all expensively (the drums cost about \$120 each) made from SS-347, and designed to contain mixed acid.

Well, everybody had been wrong. The acid doesn't corrode stainless—at first. But after an induction period, which may vary from minutes to months, and which depends upon the acid composition and particularly the percentage of water, the temperature, the past history of the steel, and presumably upon the state of the moon, the corrosion starts and proceeds apace. The eventual results are worse than with RFNA. Not only is the quality of the acid degraded and the drum damaged, but a thick, heavy, greenish-gray sludge of loathsome appearance, revolting properties, and mysterious composition forms and deposits. I have seen drums of mixed acid with twelve solid inches of sludge on the bottom. To make things worse, pressure gradually builds up in the drum or tank car, which has to be vented periodically. And the water breathed in then (mixed acid is extremely hygroscopic) accelerates the corrosion. Within two years all the Navy's expensive tank cars and drums had to be junked.

Another possibility was white fuming nitric acid, which, at least, didn't give off lethal clouds of NO_2 when it was poured. But its freezing point was too high to be acceptable. (Pure HNO_3 freezes at -41.6° , the commercial WFNA a few degrees lower.) It was just as corrosive as RFNA, if not more so, and was less hypergolic with many fuels than the red acid. And it had another trick up its sleeve. For years people had noted that a standing drum of acid slowly built up pressure, and had to be vented periodically. But they assumed that this pressure was a by-product of drum corrosion, and didn't think much about it. But then, around the beginning of 1950, they began to get suspicious. They put WFNA in glass containers and in the dark (to prevent any photochemical reaction from complicating the results) and found, to their dismay, that the pressure buildup was even faster than in an aluminum drum. Nitric acid, or WFNA at least, was inherently unstable, and would decompose spontaneously, all by itself. This was a revolting situation.

The fourth possibility was N_2O_4 . True, it was poisonous, but if you could avoid handling it in the field that didn't much matter. And, as long as you kept water out of it, it was practically noncorrosive to most metals. You didn't even have to keep it in aluminum or stainless—ordinary mild steel would do. So the tanks of a missile could be filled at the factory, and the operators would never see, or smell, or breathe, the N_2O_4 . And it was perfectly stable in storage, and didn't build up any pressure. But its freezing point was -9.3° , which the services would not accept.

Thus, with four oxidizers available, we had four sets of headaches—and nothing that we could use with any degree of satisfaction. The

situation led to what might be called "the battle of the acid," which went on for some five years, and involved just about every chemist in the rocket business—and a lot who were not.

There were certainly problems enough for everybody, more than enough to go around. As a result, research went off in a dozen different, and at times contradictory, directions. Several groups attacked the freezing point of WFNA directly, using all sorts of additives to bring it down to a reasonable (or, in the case of those shooting for -100°F , an unreasonable) figure. R. W. Greenwood at Bell Aircraft, and R. O. Miller, of the Lewis Flight Propulsion Laboratory of NACA, both investigated ammonium nitrate and a 50 percent aqueous solution of the salt; 72 percent perchloric acid (the anhydrous stuff was entirely too touchy to handle) and a 50 percent solution of potassium nitrate (the dry salt was almost insoluble in WFNA), which had been suggested by WADC. They got their freezing points down where they wanted them, but at an intolerable cost. Ignition in a motor was slow and frequently explosive, and combustion was rough and unsatisfactory. And the KNO_3 solution had another disadvantage, which had not been anticipated. When it was fired, the exhaust stream contained a high concentration of potassium ions and free electrons—a plasma, in fact—which would absorb radio waves like mad and make radar guidance of a missile quite impossible. Greenwood tried a few organic additives, acetic anhydride and 2,4,6 trinitrophenol among them, but that approach was a blind alley. Nitric acid *does* react with acetic anhydride in time—and as for the trinitrophenol, loading a propellant up with a high explosive isn't a very appealing idea.

W. H. Schechter, of the Callery Chemical Co., with more courage than judgment, investigated anhydrous perchloric acid, but found that he couldn't get the depression he wanted with a percentage of the additive that could be lived with, and also tried nitronium perchlorate. He didn't get any freezing point depression to speak of, the stability of the mixture was worse than that of the straight WFNA, and its corrosivity was absolutely ferocious. One other additive that he tried was nitromethane, as did A. Zletz, of the Standard Oil Company of Indiana, who also investigated the ethyl and 2 propyl homologues. Nitromethane, naturally, was the best depressant of the lot, and a freezing point of -100°F was reached without any trouble, but the mixture was too sensitive and likely to explode to be of any use.

Mike Pino, of California Research, tried sodium nitrite (it worked, but slowly reacted with the acid to form sodium nitrate, which precipitated out) and sodium cobaltinitrite and found that 4 percent of the salt plus 1 percent of water reduced the freezing point of *anhydrous* acid to -65°F , but he couldn't get to the magic -100°F with any

reasonable amount of water. He was always very conscious of the effect (pernicious) of water on ignition delay, and shied away from any system that contained any great amount of it. The mixture was unstable, too. So he took another tack, and went to work to see if he could do anything with mixed acid. He had already tried nitrosyl sulfuric acid, NOHSO_4 , and had found that it was a better freezing point depressant than sulfuric acid, but that it was even worse as a sludge producer. He turned then to the alkane sulfonic acids, particularly methane sulfonic acid, and found that 16 percent of this in WFNA gave a mixture that froze only at -59° , although upon occasion it could be supercooled considerably below that before solidifying. This looked promising. It gave good ignition with the fuels he was considering at the time (mixtures of allyl amines and triethylamine). Its corrosivity was similar to or a little less than that of WFNA or of ordinary mixed acid, but it had one shining virtue—it didn't produce any sludge. A similar mixed acid was investigated at North American Aviation at about the same time (1953). This used fluoro-sulfonic acid instead of the methanesulfonic, and most of its properties were very similar to those of the other mixture. But by this time nobody cared.

Many people were more interested in the ignition delay of WFNA than in its freezing point, and they tried to get the driest acid that could be got, in order to determine, exactly, the effect of water on the delay. The General Chemical division of Allied Chemical and Dye Co. could, and would, oblige. Apparently one of their acid stills was unusually efficient, and would turn out acid with less than 1 percent water in it. You could get it, on special order, shipped in 14-gallon glass carboys inside a protective aluminum drum. When it arrived, it was advisable to keep the carboy in a cold box—the colder the better—to slow down the decomposition of the acid.

The work with this "anhydrous" acid extinguished any remaining doubt that ignition delay with WFNA was critically and overwhelmingly dependent on its water content. Nothing else really mattered.

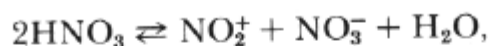
It had become painfully obvious that you had to know how much water you had in your acid before you could load it into a missile and push the button without disaster. It was equally obvious that setting up an analytical chemistry laboratory in the field wasn't practical politics. So a great cry went out for a "field method" for analyzing nitric acid. What the customer wanted, of course, was a little black box into which he could insert a sample of the acid in question (or preferably, that he could merely point at the sample!) whereupon the box would flash a green light if the acid could be used, or a red one if it couldn't.

Little black boxes like that aren't too easy to come by. But two people tried to invent such a gadget.

The first was Dr. L. White, of the Southern Research Institute, working for the Air Force. His idea was simple and direct. Water, dissolved in nitric acid, has an absorption line in the near infrared. You merely shine IR of the correct wave length through your sample, measure the absorption, and there you are. (Another IR absorption band could be used to measure the N_2O_4 content.) Neat, simple—any rocket mechanic can do it.

But things didn't turn out that way. There were the expected difficulties (only they were worse than expected) that stemmed from the corrosive nature of the acid and its fumes, both of which did their best to chew up the black box. But then something much more disconcerting showed up. White would take a sample of acid which was, as far as he could tell, absolutely anhydrous, with no water in it at all. And the IR absorption band was still there, as large as life, and twice as natural. Nitric acid appeared to be a somewhat more complicated substance than most people thought.

It is. Take 100 percent nitric acid—pure hydrogen nitrate. (I won't go into the question of how you go about getting such a substance.) Does it appear as HNO_3 , period? It does nothing of the sort. Studies by Ingold and Hughes, by Dunning, and by others during the 30's and 40's had shown that there is an equilibrium:



so that there is some—not much, but some—“species” water present even in absolutely “anhydrous” acid. So the relation between “analytical” water, which was what people were interested in, and optical absorption is not linear, and you have to analyze dozens of samples of acid in order to establish a calibration curve. White embarked upon the calibration.

At NARTS, working for the Navy, I was the other black-box builder. I based my method on the electrical conductivity of the acid. If you take pure water and start adding nitric acid to it, queer things happen. The conductivity increases at first, from the practically zero conductivity of pure water, to reach a broad maximum at about 33 percent acid. Then it declines, reaching a minimum at about 97.5 percent acid, and then starts to rise again and is still increasing when you get to 100 percent HNO_3 . To make the whole thing more complicated, the presence of N_2O_4 in the acid changes the conductivity, too, since N_2O_4 is partially ionized to NO^+ and NO_3^- .

After blundering about a bit, in the spring of 1951 I took the

following approach: I would divide a specimen of acid into three parts. Part 1 was left alone. To part 2 I added a small amount of water, 2.5 cc to 50 cc of acid. Part 3 was diluted more liberally, 30 cc of water to 10 of acid. I then measured the conductivities of all three parts and derived two ratios: conductance 1:conductance 2, and conductance 2:conductance 3. (Taking these ratios eliminated the conductivity cell-constant and reduced the effect of temperature variations.) The water and N_2O_4 content of the acid could then, in principle, be deduced from the two ratios. *After*, of course, the method had been calibrated, by measuring the conductivities of 150 or so samples of acid of varying but *known* composition.

And how do you get to know the composition of an acid? By analyzing it, of course. Everybody knows that. So it was something of a shock to the black-box builders to learn that nobody could analyze nitric acid accurately enough to calibrate the field methods.

Obviously, a calibration method has to be better than the method calibrated—and nobody could determine the water content of nitric acid—routinely—to a tenth of a percent. The N_2O_4 was easy—titration with ceric sulfate was fast and accurate. But there was no direct method for determining the water. You had to determine the total acid (HNO_3 plus N_2O_4) and then determine the N_2O_4 , and then get the water by difference—a small difference between two large quantities.

Suppose that your analysis said that you had 0.76 percent N_2O_4 , and 99.2 percent, plus or minus 0.2 percent, nitric acid (and it was a good man who could be sure of the acid to 0.2 percent!), then what was your water content? 0.04 percent? Minus 0.16 percent? 0.24 percent? You could take your choice—one guess was as good as another.

Many attempts, all unsuccessful, were made to find a direct method for water, but I chose to apply brute force, and set out grimly to refine the classical method until it could be used to calibrate the field methods. Every conceivable source of error was investigated—and it was surprising to learn in how many ways a classical acid-base titration can go wrong. Nobody would have believed, until he learned the hard way, that when you make up five gallons of 1.4 normal NaOH, you have to stir the solution for an hour to make sure that its concentration is uniform to within one part in 10,000 throughout the whole volume. Nor that when air is admitted to the stock bottle it has to be bubbled through a trap of the same solution. If it isn't, the moisture in the laboratory air will dilute the upper layer of the NaOH and foul you up. Nor that when you get to a phenolphthalein end-point with your 1.4 N alkali, it's advisable to back-titrate with 0.1 N HCl (thus

splitting the last drop) until the pink color is the faintest discernible tint. But all those precautions and refinements are necessary if you need results that you can believe.

The most important refinement was the use of specially made precision burettes, thermostated and held at 25°. (The coefficient of expansion of 1.4 N NaOH was *not* well known, and even if it were, somebody would be sure to put it in backwards!) The burettes were made for me by the Emil Greiner Co., and cost the taxpayer seventy-five dollars a throw. They worked so well that certain other agencies acquired the deplorable habit of borrowing one from me and then forgetting to return it.*

The job took almost a year, but when it was done the water in the acid could be determined, by *difference*, to 0.025 percent. And the analysis took no longer than the crude analysis of a year before.

The calibration then went like a breeze, complicated only by the difficulties encountered when absolutely anhydrous acid was needed. The classical way of making such a substance was to mix P₂O₅ with WFNA, and then distill the dry acid over under vacuum. This was an infernal nuisance—three hours work might get you ten cc of anhydrous acid—and in our case we needed it by the liter. So we hit on a simple method that required no effort or attention whatsoever. Into a big flask we would load about two liters of 100 percent sulfuric acid, and then three times as much WFNA. Then, holding the flask at about 40°, we would blow dry air through it, and try to condense as much acid as we could out of the exhaust stream. We'd start the gadget going in the evening, and by next morning there would be a liter or two of water-white acid (the N₂O₄ had all been blown out) waiting to be stored in the deep freeze. It would analyze from 99.8 percent to more than 100 percent acid—the last, of course, containing excess N₂O₅. The method was horribly inefficient—we lost two-thirds of the acid in the exhaust—but with acid at nine cents a pound, who cared?

White published his complete optical method for water and N₂O₄ at the end of 1951, and I published my conductivity method nine months later.† Both black boxes worked fine. And, then, naturally, everybody lost interest in WFNA.

* I name no names, but God will punish Doc Harris of WADC!

† Dave Mason and his associates at JPL, about sixteen months later, in January 1954, described another conductimetric method, which would work with both WFNA and RFNA. Two conductivity measurements were made, both at 0°C—one of the straight acid and one of the acid saturated with KNO₃. From these two measurements the N₂O₄ and H₂O could be derived using a calibration chart.

There were a few other analytical problems connected with nitric acid that were cleaned up at about this time. Dr. Harris, at WADC, designed an ingenious glass and Teflon sample holder for RFNA, which made it possible to prevent any loss of N_2O_4 when the acid was diluted before titration, and let it be analyzed with an accuracy equal to that possible with WFNA. And I devised analyses for mixed acid and for Mike Pino's mixture of WFNA and methane sulfonic acid. These are worth recording, if only to show the weird expedients to which we were driven to get the results we needed. In both cases, the N_2O_4 and the total acid were determined exactly as in the refined WFNA analysis, and the problem was to determine the additive acid. In the case of the mixed acid, the major part of the nitric acid in the sample was destroyed with formaldehyde, and any formic acid formed was reacted with methanol and boiled off as methyl formate. (The emerging fumes invariably caught fire and burned with a spectacular blue flame.) What was left, then, was dumped into a boiling mixture of water and n-propanol, and titrated, conductimetrically, with barium acetate. This sounds like a weird procedure, but it worked beautifully, and gave as precise results as anybody could wish. Mike Pino's mixture had to be treated differently. The nitric acid was destroyed by reacting it with warm formic acid, and what was left was titrated, potentiometrically, with sodium acetate in acetic acid, in a medium of glacial acetic acid. One electrode was a conventional glass electrode as used for pH determination, the other a modified calomel electrode, using saturated lithium chloride in acetic acid. Again, a peculiar but effective analysis. And as soon as these methods had been worked out, everybody stopped using either mixed acid!

In many ways N_2O_4 was more appealing as an oxidizer than nitric acid. Its performance was a little better, and it didn't have so many corrosion problems. Its main drawback, of course, was its freezing point, and several agencies tried to do something about that. The prime candidate for a freezing point depressant was nitric oxide, NO. Wittorf, as early as 1905, had examined the phase behavior of the mixture, as had Baumé and Roberts in 1919. But mixtures of NO and N_2O_4 have a higher vapor pressure than the neat nitrogen tetroxide, and several optimists tried to find an additive that would reduce the freezing point without increasing the vapor pressure. This turned out to be rather easy to do—lots of things are soluble in N_2O_4 —but at an unacceptable price. L. G. Cole, at JPL, in 1948, tried such things as mono and di nitrobenzene, picric acid, and methyl nitrate, and discovered, upon examining his mixtures, that he had some

extremely touchy and temperamental high explosives on his hands. T. L. Thompson, at North American, three years later, tried nitromethane, nitroethane, and nitropropane, and made the same discovery. Collins, Lewis, and Schechter, at Callery Chemical Co., tried these same nitro-alkanes in 1953, as well as tetranitromethane, and worked out the ternary phase diagram for nitrogen tetroxide, nitromethane, and TNM. Again—high explosives. At about the same time, S. Burket, at Aerojet, went them one better by trying not only these compounds, but even the notoriously treacherous nitroform, plus diethyl carbonate, diethyl oxalate, and diethyl cellosolve. And his mixtures, too, were nothing more than catastrophes looking for a place to happen. It appeared that about the only thing that could safely be dissolved in a nitrogen oxide was another nitrogen oxide.

T. L. Thompson had tried nitrous oxide in 1951, and reported that it wasn't particularly soluble in N_2O_4 , and this was confirmed by W. W. Rocker of du Pont. So nitric oxide it had to be.*

NO is an extremely effective freezing point depressant for N_2O_4 . It combines, under pressure or at low temperatures, with the latter to form the unstable N_2O_3 , so that the eutectic appears between pure N_2O_4 and the composition corresponding to N_2O_3 , so that a small addition of NO has an inordinately large effect on the freezing point. G. R. Makepeace and his associates, at NOTS, were able to show, in 1948, that 25 percent of NO would bring the freezing point of nitrogen tetroxide down below the required -65°F , and that 30 percent would depress it well below the magic -100°F . However, the vapor pressure of the latter mixture at 160°F was unacceptably high, about 300 psi. Several investigators examined the system, among them T. L. Thompson of North American and T. J. McGonnigle of, appropriately, the Nitrogen Division of Allied Chemical and Dye Co., but the definitive work came from JPL and NOTS.

Between 1950 and 1954, Whittaker, Sprague, and Skolnik and their group at NOTS, and B. H. Sage and his colleagues at JPL investigated the nitrogen tetroxide–nitric oxide system with a thoroughness that left nothing to be discovered that could conceivably be worth the trouble of discovering. Their meticulous investigations were to bear fruit years later, when Titan II, with its N_2O_4 oxidizer, was developed.

Several agencies tried the mixed oxides of nitrogen (MON-25 or

* Cole, at JPL, had reported in 1948 that a mixture of 41.5 percent N_2O and the remainder N_2O_4 had a freezing point of -51° and a boiling point of 33° . These figures so thoroughly contradicted the experience of everybody else that they are completely inexplicable.

MON-30 or whatever, with the number designating the percentage of NO in the mix) with various fuels, and discovered that it was more difficult to get a good performance (a high percentage of the theoretical performance) with MON than with neat nitrogen tetroxide. Apparently the great kinetic stability of the NO slowed down the combustion reaction. For this reason, and because of its high vapor pressure, investigators turned away from MON for some years. (Certain space rockets, today, use MON-10.) *

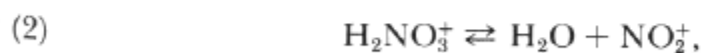
And there was another reason. RFNA had been domesticated. Two things had done it: A series of meticulous studies at Ohio State University and at JPL solved the problem of decomposition and pressure buildup, and a completely unexpected breakthrough at NARTS reduced the corrosion problem to negligible proportions. With these problems solved the acid could be "packaged" or loaded into a missile at the factory, so that it didn't have to be handled in the field. And that solved the problem of those toxic fumes, and eliminated the danger of acid burns.

By the beginning of 1951 the nature and behavior of nitric acid had become comprehensible. True, it was a fiendishly complicated system — one could hardly call it a substance — but some sense could be made out of it. The monumental work of Professor C. K. Ingold and his colleagues, published in a series of articles in 1950, had clarified the equilibria existing among the various species present in the system, and Frank and Schirmer, in Germany, in the same year, explained its decomposition. Briefly, this is what their work showed:

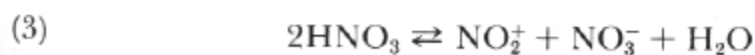
First, in very strong nitric acid, there is an equilibrium:



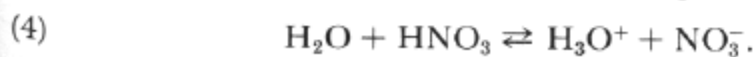
However the concentration of H_2NO_3^+ is extremely small at any time, since it, too is in equilibrium:



so that for all practical purposes we can write:



and ignore the H_2NO_3^+ . In dilute acid, the equilibrium is



Thus, in acid containing less than about 2.5 percent of water, NO_2^+

* And "green" N_2O_4 , containing about 0.6% of NO and green by transmitted light, has recently been developed. The NO seems to reduce stress corrosion of titanium, and also scavenges dissolved oxygen in the N_2O_4 .

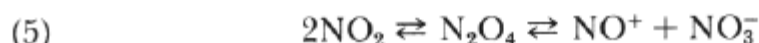
is the major cation, and in acid containing more than that, H_3O^+ takes that role. Exactly at 2.5 percent water, very little of either one is present, which very neatly explains the minimum in the electrical conductivity observed there. If NO_2^+ is the active oxidizing ion in strong acid (and in the course of some corrosion studies I made a couple of years later I proved that it is) the effect of water on ignition delay is obvious. Equation (3) shows that adding water to dry acid will reduce the concentration of NO_2^+ which is the active species. The addition of NO_3^- will do the same thing—which explains the poor combustion observed with acid containing NH_4NO_3 .

The nitronium (NO_2^+) ion would naturally be attracted to a negative site on a fuel molecule, such as the concentration of electrons at a double or triple bond—which goes far to justify Lou Rapp's remarks as to the desirability of multiple bonds to shorten ignition delay.

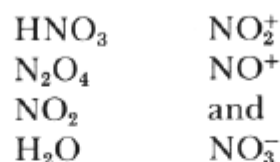
The NO_2^+ ion also explains the instability of nitrites in strong acid by the reaction:



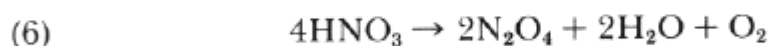
If N_2O_4 is present in strong acid, another set of equilibria show up.



The result of all of this is that (even neglecting solvation) in strong acid containing N_2O_4 have appreciable quantities of at least seven species:



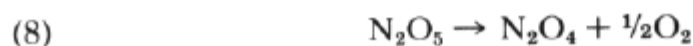
Plus possible traces of H_3O^+ and H_2NO_3^+ . And all of them in interlocking equilibria. But this didn't explain the pressure buildup. Nitric acid decomposes by the gross reaction.



But how? Well, Frank and Schirmer had shown that there is yet another equilibrium present in the system, and another species:



And N_2O_5 was well known to be unstable and to decompose by the reaction.



Then as O_2 is essentially insoluble in nitric acid, it bubbles out of it and the pressure builds up and your acid turns red from the NO_2 .

What to do about it? There were two possible approaches. The obvious one is suggested by equation (6): increase the concentration (or, in the case of the oxygen, the pressure) of the species on the right hand side of the equation, and force the equilibrium back. It soon became obvious that merely putting a blanket of oxygen over your WFNA wouldn't help. The equilibrium oxygen pressure was much too high. I have actually seen the hair-raising sight of rocket mechanics trying to determine the oxygen pressure developed over decomposing WFNA by measuring the bulging of the drums—and shuddered at the sight! The equilibrium oxygen pressure over 100 percent acid at zero ullage (no appreciable unfilled volume in the tank) at $160^\circ F$ turned out to be well over 70 atmospheres. Nobody wants to work with a bomb like that.

To reduce the equilibrium oxygen pressure, you obviously have to increase the N_2O_4 or the water concentration or both. WFNA and anhydrous acid were definitely out.

It was D. M. Mason and his crew at JPL and Kay and his group at Ohio State who undertook—and completed—the heroic task of mapping the phase behavior and equilibrium pressure and composition of the nitric acid- N_2O_4 - H_2O system over the whole composition range of interest, up to 50% N_2O_4 and up to 10 percent or so H_2O —and from room temperature up to $120^\circ C$. By the time these groups were finished (all of the work was published by 1955) there was nothing worth knowing about nitric acid that hadn't been nailed down. Thermodynamics, decomposition, ionetics, phase properties, transport properties, the works. Considering the difficulties involved in working with such a miserable substance, the achievement can fairly be classified as heroic.

And it paid off. An RFNA could be concocted which had a quite tolerable decomposition pressure (considerably less than 100 psi) even at $160^\circ F$ ($71^\circ C$). The General Chemical Co. came up with one containing 23% N_2O_4 and 2% H_2O , while the JPL mixture, which they called SFNA (Stable Fuming Nitric Acid) contained 14 percent and 2.5 percent respectively.

The freezing points of the HNO_3 - N_2O_4 - H_2O mixtures were soon mapped out over the whole range of interest. R. O. Miller at LFPL, G. W. Elverum at JPL, and Jack Gordon at WADC among others, were involved in this job, which was completed by 1955.

Their results were not in the best of agreement (the mixtures frequently supercooled and, as I have mentioned, RFNA is not the

easiest thing in the world to analyze) but they all showed that both the General Chemical Co. mixture and JPL's SFNA froze below -65°F . About this time the Navy decided to relax and enjoy it and backed off from their demand for the mystic -100°F and everybody and his brother heaved a deep sigh of relief. One job done!

The solution to the corrosion problem turned out to be simple—once we had thought of it. In the spring of 1951 we at NARTS were concerned about—and studying—the corrosion of 18-8 stainless steel, specifically SS-347, by WFNA. Eric Rau, who had been with me for only a few months (the chemistry lab had been functioning only since the previous summer) thought that a coating of fluoride on the steel might protect it from the acid. (Don't ask me why he thought so!) So, he talked a friend of his who worked at the General Chemical Co. division of Allied Chemical and Dye into taking some of our sample strips of 347 and leaving them for some days inside one of the pipelines that conveyed HF from one part of the plant to another. Then Eric tested these samples for corrosion resistance, and found that they corroded just as badly as did the untreated steel. *But*, this corrosion was delayed, and didn't start, apparently, until a day or two had passed. The inference was that (1) a fluoride coating was protective, but (2) it didn't last long in WFNA. He thought then that it might be possible to make the fluoride coating self-healing by putting some HF in the WFNA. However the only HF that we had in the lab was the common 50 percent aqueous solution of that acid, and Eric didn't want to add any water to his WFNA. So I suggested that he try ammonium bifluoride, $\text{NH}_4\text{F}\cdot\text{HF}$, which is more than two-thirds HF anyway, and a lot easier to handle. Also, we had it on the shelf. He tried it, and to our incredulous delight it worked—worked with an effectiveness beyond our wildest hopes. A few weeks of messing around showed us that 0.5 percent of HF in the acid, no matter how introduced, reduced the corrosion rate of the steel by a factor of ten or more, and that more than 0.5 percent didn't improve things measurably. We reported this finding in our quarterly report, on 1 July, 1951, but NARTS was just two years old then, and apparently nobody bothered to read our reports.

But there was a meeting at the Pentagon devoted to the problems of nitric acid on October 10–11–12, attended by about 150 propellant-oriented people from industry, government and the services. I went, and so did Dr. Milton Scheer ("Uncle Milty") of our group, and on the afternoon of the 11th he reported Eric's discovery. What made the occasion delightful (for us) was the fact that that very morning, in discussing another paper, R. W. Greenwood, of Bell Aircraft, had stated that he had tried ammonium bifluoride as a freezing point

depressant for WFNA, and then, three papers later, T. L. Thompson of North American Aviation reported on using both anhydrous and aqueous HF as freezing point depressants for R.F.N.A. And both of them had completely missed the corrosion-inhibiting effect!

Then everybody got into the act—North American, JPL, and just about everybody else. (We were already there.) As it turned out, HF was even more effective in inhibiting the corrosion of aluminum than reducing that of SS-347: inhibition was just as good with RFNA as with WFNA; and it was effective not only in the liquid phase but in the gas phase, where the metal was in the acid vapor above the liquid level.

But while HF was a good inhibitor for aluminum and for 18-8 stainless steels, it wasn't universally effective. It had no particular effect on the corrosion of nickel or chromium, while it *increased* the corrosion rate at tantalum by a factor of 2000 and that of titanium by one of 8000.

There was a great deal of interest in titanium at that time, and as many rocket engineers wanted to use it, the question of its resistance to RFNA couldn't be neglected. But these corrosion studies were interrupted by a completely unexpected accident. On December 29, 1953, a technician at Edwards Air Force Base was examining a set of titanium samples immersed in RFNA, when, absolutely without warning, one or more of them detonated, smashing him up, spraying him with acid and flying glass, and filling the room with NO_2 . The technician, probably fortunately for him, died of asphyxiation without regaining consciousness.

There was a terrific brouhaha, as might be expected, and JPL undertook to find out what had happened. J. B. Rittenhouse and his associates tracked the facts down, and by 1956 they were fairly clear. Initial intergranular corrosion produced a fine black powder of (mainly) metallic titanium. And this, when wet with nitric acid, was as sensitive as nitroglycerine or mercury fulminate. (The driving reaction, of course, was the formation of TiO_2 .) Not all titanium alloys behaved this way, but enough did to keep the metal in the doghouse for years, as far as the propellant people were concerned.

In spite of the titanium debacle, the rocket business now had a usable nitric acid, and a rewriting of the military specifications for WFNA and RFNA seemed appropriate.

During 1954, then, a group representing the services and industry got together under Air Force sponsorship to do just that. I was there, as one of the Navy representatives.

Various users still argued over the relative merits of 14 percent RFNA and 22 percent RFNA, and a few still liked WFNA. The chem-

ical industry was amiably willing to go along with anything – “Hell, it’s just as easy to make one sort of acid as another – just tell us what you want!” So we decided to write one specification which would make everybody happy. We officially threw out the terms WFNA and RFNA and described no less than four types of nitric acid, which we designated, with stunning unoriginally as “Nitric Acid, Type I, II, III and IV.” These contained, in the order named, nominally 0 percent, –7 percent, 14 percent, and 21 percent N_2O_4 . If you wanted HF inhibited acid, you asked for I-A or III-A, or whatever, and your acid would contain 0.6 percent HF.

I was against describing the nature of the inhibitor in the openly published specifications, since the inhibition was such an unlikely – though simple – trick that it might well have been kept secret for some time. I had friends in the intelligence community, and asked them to try to learn, discreetly, whether or not the trick was known on the other side of the iron curtain. The answer came back, with remarkable speed, that it was not, and that, in fact, the Soviet HF manufacture was in trouble, and that the director of the same was vacationing in Siberia. So I protested violently and at length, but the Air Force was running the show and I was overruled. And when the specs were published, the gaff was blown for good.

Included in the specs were the procedures for analyzing the acids. These were conventional, except the one for HF, which was a complicated and tricky optical method involving the bleaching of a zirconium-alizarin dye by fluoride ion. In my own lab I declined to have anything to do with it, and whomped up a simple – not to say simple-minded – test that required no effort or intelligence whatever. You put one volume of acid and two of water in a polyethylene beaker, and dropped into it a magnetic stirring rod enclosed in soft glass tubing and weighed. You then let the thing stir overnight and reweighed the stirring rod. If you had calibrated that particular piece of glass with an acid containing a known concentration of HF, that was all you needed. Accuracy quite good enough for the purpose.

Dave Mason of JPL came up with another quick-and-dirty method for estimating the HF – almost as simple as mine, and a lot faster. It was a colorimetric method, which depended upon the bleaching effect of fluoride ion on purple ferric salicylate.

As it turned out, the type III-A gradually edged out the others, and is now *the* nitric acid oxidizer.* The engineers call it IRFNA, inhibited Red Fuming Nitric Acid, and very few of the current crop are even

* Just one important motor – that for the second stages of Vanguard and of Thor Able used type I-A acid (IWFNA) which it burned with UDMH.

aware that there ever was another sort—or of what “inhibited” means. A few years ago I saw one alleged rocket engineer fill a stainless steel tank with RFNA *without* any HF in it—and then wonder why his acid turned green.

The only other sort of acid worth mentioning is “Maximum Density Nitric Acid.” This was proposed by Aerojet for applications in which density is all-important and freezing point requirements are not too strict. It contains 44 percent N_2O_4 and has a density of 1.63. Once a satisfactory acid had been found, interest in its analysis dropped to zero. III-A was so smoothly hypergolic with UDMH, and a little water more or less didn’t make any difference, and you could keep it sealed so it wouldn’t pick up water—and with the HF in it there wasn’t any corrosion to worry about—so why bother? An occasional purchasing agent may have a drum analyzed now and then, but the general custom is to accept the manufacturer’s analysis—slap the acid into the tank—and fire it. And it works.

The situation today, then, is this: For tactical missiles, where the freezing point of the propellants matters, IRFNA type III-A is the oxidizer. The 47,000-pound thrust Lance, whose fuel is UDMH, is an example, as is the Bullpup, which burns a mixture of UDMH, DETA and acetonitrile. In space, Bell’s remarkably reliable Agena motor, of 16,000 pounds thrust, also uses IRFNA, along with UDMH.

For strategic missiles, which are fired from hardened—and heated—sites, N_2O_4 , with a somewhat greater performance, is the oxidizer used. Titan II is, of course, the largest of the US ICBMS, and its first stage is driven by two 215,000-pound thrust motors, using N_2O_4 and the 50–50 hydrazine-UDMH mixture.

Many other N_2O_4 motors are used in space, ranging from the 21,500-pound Apollo service engine, which also uses 50–50, down to tiny one-pound thrusters used for attitude control. The fuel is invariably a hydrazine or a hydrazine mixture. And the users have reason to be happy with their performance and reliability.

As have the chemists, and engineers, who don’t have to go through it again.

Afterword

Another symposium on liquid propellants was held at the Pentagon on May 23 and 24, 1955. If the October 1951 meeting was devoted

mainly to difficulties, the May 1955 meeting described a series of battles fought and triumphantly won.

The high points were the narration by Bernard Hornstein of ONR of the development of MMH and UDMH, and that by S. P. Greenfield, of North American, of the vicissitudes of NALAR.

NALAR was a 2.75" diameter air-to-air missile for the Air Force. The requirements were rough. The liquid propellants had to be hypergolic. They also had to be packageable, so that the missile could be stored, fully fueled, for five years and be in a condition to fire. And they had to perform at any temperature from -65°F to $+165^{\circ}\text{F}$. North American started development in July 1950.

The first oxidizer they tried was RFNA, 18% N_2O_4 . From the beginning they were contending with a pressure buildup, and with corrosion. However, trying to get good ignition and smooth combustion, they fired it with:

- Turpentine
- and Decalin
- and 2Nitropropane plus 10-20% turpentine
- and Isopropanol
- and Ethanol
- and Butylmercaptan
- and Toluene
- and Alkyl thiophosphites
- and got nowhere.

Then they shifted to MON-30 for their oxidizer, 70% N_2O_4 , 30% NO, and resumed their quest for smooth ignition and smooth combustion with:

- Turpentine
- and Butyl mercaptan
- and Hydrazine
- and Isopropanol
- and Toluene
- and 2Methyl furan
- and Methanol
- and Aviation gasoline
- and Turpentine plus 20-30% 2Methyl furan
- and Butyl mercaptan plus 20-30% 2Methyl furan
- and Isopropanol plus 30% turpentine
- and Methanol plus 20-25% 2Methyl furan
- and Methanol plus 30-40% Hydrazine

- and Alkyl thiophosphites
- and Turpentine plus Alkyl thiophosphites
- and JP-4 plus Alkyl thiophosphites
- and JP-4 plus 10–30% Xylidine
- and achieved a succession of hard starts, usually followed by rough combustion.

By this time the spring of 1953 had arrived, and the engineers learned of the uses of HF in inhibiting nitric acid corrosion. (The fact that this effect had been discovered two years before, and that North American's own chemists had been working with HF for at least a year suggest that there was a lack of communication somewhere, or, perhaps, that engineers don't read!)

Be that as it may, they returned, probably with a sense of *déjà vu*, to turpentine and RFNA—but inhibited this time. To improve ignition they added up to 20 percent of Reference Fuel 208, the alias of 2-dimethylamino-4-methyl-1-3-2-dioxaphospholane, to the turpentine. Then the Air Force, who, you will recollect, was paying for all of this, suggested that they substitute UDMH for the RF-208. They did, and the results were so good that they went to straight UDMH, and to Hell with the turps.

It had taken them four years to arrive at today's standard workhorse combination of UDMH-IRFNA, but they had finally arrived. And recently, a NALAR missile which had been sitting around for about twelve years was hauled off the shelf and fired. And it worked. The hypergol and his mate had been captured and tamed. (Fade out into the sunset to the sound of music.)