

## Peroxide— Always a Bridesmaid

Hydrogen peroxide can be called the oxidizer that never made it. (At least, it hasn't yet.) Not that people weren't interested in it—they were, both in this country and, even more so, in England. Its performance with most fuels was close to that of nitric acid, as was its density, and in certain respects it was superior to the other oxidizer. First, no toxic fumes, and it didn't chew on skin as the acid did. If you received a splash of it, and didn't delay too long about washing it off, all the damage you got was a persistent itch, and skin bleached bone white—to stay that way until replaced by new. And it didn't corrode metals as the acid did.

But (as is usual in the propellant business, there were lots of “buts”) the freezing point of 100 percent  $\text{H}_2\text{O}_2$  was only half a degree below that of water. (Of course, 85 or 90 percent stuff, which was the best available in the 40's, had a better freezing point, but diluting a propellant with an inert, just to improve its freezing point, is not a process that appeals to men interested in propulsion!) And it was unstable.

Hydrogen peroxide decomposes according to the equation  $\text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \frac{1}{2}\text{O}_2$ , with the evolution of heat. Of course, WFNA also decomposed, but *not* exothermically. The difference is crucial: It meant that peroxide decomposition is self-accelerating. Say that you have a tank of peroxide, with no efficient means of sucking heat out of it. Your peroxide starts to decompose for some reason or other. This decomposition produces heat, which warms up the rest of the peroxide, which naturally then starts to decompose faster—producing more heat. And so the faster it goes the faster it goes until the whole thing

goes up in a magnificent whoosh or bang as the case may be, spreading superheated steam and hot oxygen all over the landscape.

And a disconcerting number of things could start the decomposition in the first place: most of the transition metals (Fe, Cu, Ag, Co, etc.) and their compounds; many organic compounds (a splash of peroxide on a wool suit can turn the wearer into a flaming torch, suitable for decorating Nero's gardens); ordinary dirt, of ambiguous composition, and universal provenance; OH ions. Name a substance at random, and there's a 50–50 chance (or better) that it will catalyze peroxide decomposition.

There were certain substances, stannates and phosphates, for instance, that could be added to peroxide in trace quantities and would stabilize it a bit by taking certain transition metal ions out of circulation, but their usefulness and potency was strictly limited; and they made trouble when you *wanted* to decompose the stuff catalytically. The only thing to do was to keep the peroxide in a tank made of something that didn't catalyze its decomposition (very pure aluminum was best) and to keep it clean. The cleanliness required was not merely surgical—it was levitical. Merely preparing an aluminum tank to hold peroxide was a project, a diverting ceremonial that could take days. Scrubbing, alkaline washes, acid washes, flushing, passivation with dilute peroxide—it went on and on. And even when it was successfully completed, the peroxide would *still* decompose slowly; not enough to start a runaway chain reaction, but enough to build up an oxygen pressure in a sealed tank, and make packaging impossible. And it is a nerve-wracking experience to put your ear against a propellant tank and hear it go “glub”—long pause—“glub” and so on. After such an experience many people, myself (particularly) included, tended to look dubiously at peroxide and to pass it by on the other side.

Well, early in 1945, we laid our hands on a lot of German peroxide, about 80–85 percent stuff. Some of it went to England. The British were very much interested in it as an oxidizer and in the German manufacturing process. In that same year they fired it in a motor using a solution of calcium permanganate to decompose the peroxide, and with furfural as the fuel, and for several years they worked with it and various (mainly hydrocarbon) fuels.

The rest of it came to this country. However, it contained considerable sodium stannate (as a stabilizer) and was not too suitable for experimental work. So the Navy made a deal with the Buffalo Electrochemical Co., which was just getting into production itself making high-strength peroxide. The Navy turned over most of the German

peroxide to Becco, who diluted it down to 2 or 4 percent mouthwash or hair bleach (where the stabilizer was a help) and Becco furnishing the Navy with an equivalent amount of new 90 percent stuff without any stabilizer. And then the Navy distributed this to the various workers in the field.

JPL was one of the first agencies in this country to look at peroxide seriously. From late 1944 through 1948 they worked it out, using 87 percent to 100 percent peroxide, and a variety of fuels, including methanol, kerosene, hydrazine, and ethylene diamine. Only the hydrazine was hypergolic with the peroxide; all the other combinations had to be started with a pyrotechnic igniter. One very odd combination that they investigated during this period was peroxide and nitromethane, either straight or with 35 percent nitroethane or with 30 percent methanol. One oddity was the very low O/F ratio, which ran from 0.1 to 0.5 or so. (With hydrazine as a fuel, it would be about 2.0! The large amount of oxygen in the fuel explains the low O/F.)

Other agencies, MIT and GE and the M. W. Kellogg Co. among them, burned peroxide with hydrazines of various concentrations — from 54 percent up to 100 percent, and Kellogg even tried it with  $K_3Cu(CN)_4$  catalyst in the hydrazine, as the Germans had done.

In general, everybody got respectable performances out of peroxide, although there were some difficulties with ignition and with combustion stability, but that freezing point was a tough problem, and most organizations rather lost interest in the oxidizer.

Except the Navy. At just that time the admirals were kicking and screaming and refusing their gold-braided lunches at the thought of bringing nitric acid aboard their beloved carriers; they were also digging in their heels with a determined stubbornness that they hadn't shown since that day when it had first been suggested that steam might be preferable to sail for moving a battleship from point A to point B.

So NOTS was constrained to develop a "nontoxic" propellant system based on hydrogen peroxide and jet fuel, and with acceptable low temperature behavior.

A lot of information was available—on the shelf. Maas and his associates, during the 20's, had investigated hydrogen peroxide up and down and sideways, and had dissolved all sorts of things in it, from salt to sucrose. And many of these things were excellent freezing point depressants: 9.5 percent of ammonia, for instance, formed a eutectic which froze at  $-40^\circ$ , and a mixture containing 59 percent froze at  $-54^\circ$ . (In between, at 33 percent, was the compound  $NH_4OOH$ , which melted at about  $25^\circ$ .) And one containing 45 percent of

methanol froze at  $-40^{\circ}$ . These mixtures, however, had one slight drawback—they were sensitive and violent explosives.

The British, as has been mentioned, were intensely interested in peroxide, and Wiseman, of ERDE (Explosives Research and Development Establishment) at Waltham Abbey, pointed out in 1948 that ammonium nitrate was a good freezing point depressant and didn't make it into a high explosive. So the NOTS team (G. R. Makepeace and G. M. Dyer) mapped out the relevant part of the peroxide-AN-water field, and came up with a mixture that didn't freeze above  $-54^{\circ}$ . It was 55 percent peroxide, 25 percent ammonium nitrate and 20 percent water. They fired it successfully with JP-1 early in 1951, but the performance was not impressive. Other peroxide-AN mixtures were fired by NOTS, and, a little later, by NARTS. In the meantime, L. V. Wisniewski, at Becco, had been adding things like ethylene glycol, diethylene glycol, and tetrahydrofuran to peroxide. These mixtures were designed as monopropellants, but they froze at  $-40^{\circ}$ , and RMI tried them as oxidizers for gasoline and JP-4, with indifferent success. Below  $+10^{\circ}\text{C}$ , RMI just couldn't get the mixtures to ignite. Also, they were dangerously explosive.

So, the only low-freezing peroxide mixtures which could be used were those containing ammonium nitrate—and these had serious limitations. One of these was that adding AN to the peroxide increased its instability so much that it was likely to detonate in the injector, and was almost certain to go off, taking the motor with it, if you tried to use it for regenerative cooling.

Ignition of a hydrogen peroxide system, particularly one burning gasoline or jet fuel, was always a problem. In some cases, a solution of calcium permanganate was injected along with the propellants at the start of the run, but this was an awkward complication. In some tests (at MIT) a small amount of catalyst (cobaltous nitrate) was dissolved in the peroxide, but this reduced its stability. The fuel was kerosene with a few percent of *o*-toluidine. A hypergolic or easily ignited starting slug (generally hydrazine, sometimes containing a catalyst) could lead the fuel. An energetic solid-propellant pyrotechnic igniter was used in some cases. Probably the most reliable, and hence the safest, technique was to decompose part or all of the peroxide in a separate catalyst chamber, lead the hot products into the main chamber, and inject the fuel (and the rest of the oxidizer, if any) there. (A stack of screens made of silver wire was an efficient catalyst array.) NARTS designed and fired a motor which incorporated the catalyst chamber in the main chamber.

Most of the Navy work on peroxide was not directed toward missiles, but toward what was called "super performance" for fighter planes—an auxiliary rocket propulsion unit that could be brought into play to produce a burst of very high speed—so that when a pilot found six Migs breathing down his neck he could hit the panic button and perform the maneuver known as getting the hell out of here. The reason for the jet fuel was clear enough; the pilot already had it aboard, and so only an oxidizer tank had to be added to the plane.

But here an unexpected complication showed up. The peroxide was to be stored aboard airplane carriers in aluminum tanks. And then suddenly it was discovered that trace quantities of chlorides in peroxide made the latter peculiarly corrosive to aluminum. How to keep traces of chloride out of *anything* when you're sitting on an ocean of salt water was a problem whose solution was not entirely obvious.

And there was always the problem of gross pollution. Say that somebody dropped (accidentally or otherwise) a greasy wrench into 10,000 gallons of 90 percent peroxide in the hold of the ship. What would happen—and would the ship survive? This question so worried people that one functionary in the Rocket Branch (safely in Washington) who had apparently been reading Captain Horatio Hornblower, wanted us at NARTS to build ourselves a 10,000-gallon tank, fill it up with 90 percent peroxide, and then drop into it—so help me God—one rat. (He didn't specify the sex of the rat.) It was with considerable difficulty that our chief managed to get him to scale his order down to one test tube of peroxide and one quarter inch of rat tail.

Carrier admirals are—with good reason—deadly afraid of fire. That was one of the things they had against acid and a hypergolic fuel.

A broken missile on deck—or any sort of shipboard accident that brought fuel and acid together—would inevitably start a fire. On the other hand, they reasoned that jet fuel wouldn't even mix with peroxide, but would just float on top of it, doing nothing. And if, somehow, it caught fire, it might be possible to put it out—with foam perhaps—without too much trouble.

So, at NARTS we tried it. A few drums of peroxide (about 55 gallons per drum) were poured out into a big pan, a drum or two of JP-4 was floated on top, and the whole thing touched off. The results were unspectacular. The JP burned quietly, with occasional patches of flare or fizz burning. And the fire chief moved in with his men and his foam and put the whole thing out without any fuss. End of exercise.

The Lord had his hands on our heads that day—the firemen, a couple of dozen bystanders, and me.

For when we—and other people—tried it again (fortunately on a smaller scale) the results were different. The jet fuel burns quietly at first, then the flare burning starts coming, and its frequency increases. (That's the time to start running.) Then, as the layer of JP gets thinner, the peroxide underneath gets warmer, and starts to boil and decompose, and the overlying fuel is permeated with oxygen and peroxide vapor. And then the whole shebang detonates, with absolutely shattering violence.

When the big brass saw a demonstration or two, the reaction was "Not on *my* carrier!" and that was that.

The Super-P project was dropped for a variety of reasons, but the pan-burning tests were not entirely without influence on the final decision.

It is amusing to note that when actual tests were made of the effects of a big spill of acid and UDMH, the results weren't so frightening after all. There was a big flare, but the two propellants were so reactive that the bulk liquids could never really mix and explode, but were, rather, driven apart. So the flare was soon over, and plain water—and not much of it, considering—was enough to bring things under control. And so acid-UDMH propelled missiles finally got into the carriers' magazines after all.

But peroxide didn't. Research on it continued for some years, and the British designed and built a rocket-driven plane and a missile or two around the peroxide-JP combination, but that was about all, and for some ten years peroxide, as an oxidizer, has been pretty much out of the picture. (Monopropellant peroxide is another story.)

Higher concentrations (you can buy 98 percent stuff now) have appeared in the last few years, and they appear to be rather more stable than the 90 percent material, but all the drum beating indulged in by the manufacturers hasn't got the bridesmaid into a bridal bed. Peroxide just didn't make it.