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Technical Notes

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Compatibility of Injector Materials with Hydrogen Peroxide Propellant

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Introduction

ROCKET grade hydrogen peroxide (RGHP) is receiving renewed interest as a monopropellant and as the oxidizer for bipropellant systems. These applications are characterized as involving human proximity to the propulsion systems either as ground crew or within a vehicle. RGHP is considered to have much less toxicity than other monopropellants and oxidizers when stored and yields innocuous products when decomposed for propulsion. Proposed uses[1–4] of RGHP have included crew vehicle escape and orbital maneuvering, space station orbit maintenance, hybrid concepts, combined-cycle concepts, upper-stage propulsion, satellite station keeping, and military target vehicles. RGHP is hydrogen peroxide in concentrations ranging from 85 to 98%, with a defined aerospace set of additives. All surfaces wetted by RGHP must be evaluated for compatibility with the fluid. In the case of tanks, lines and valves compatibility is required to preserve the RGHP oxygen and energy content and to avoid overpressurization due to decomposition. With injectors and regenerative cooling passages, shorter exposure time reduces these concerns. However, phase changes from fluid to gas impact heat transfer and become the dominant compatibility concern. Isothermal microcalorimetry (IMC) provides a convenient, sensitive, and reproducible means to observe the decomposition of RGHP when exposed to structural materials. Calorimetry was earliest proposed (see Ref. 5) by Hess to evaluate the stability of energetic materials including explosives and propellants. The first IMC instrument comparable to modern heat conduction devices was designed by Calvet (see Ref. 6) incorporating a thermopile detector. This instrument was refined to measure smaller samples with parallel analysis.

IMC was chosen for this study because of its high sensitivity (microwatt) allowing comparison of slower reacting[7,8] and, therefore, more compatible materials. This sensitivity is at least one order of magnitude better[9] than that of a more commonly used calorimetry method, differential scanning calorimetry (DSC). The obvious limitation[6] of all calorimetry techniques including DSC is detection of total heat flow without information regarding its source. However, the decomposition of hydrogen peroxide is well characterized thermodynamically and any other source of heat in the experiments is not plausible.

In a previous paper,[10] the author discussed how this technique has been used to evaluate RGHP compatibility with propulsion system materials and specifically the effect of welding on this compatibility. The instrument provides heat flow values in terms of watts that may be converted to a reaction rate given the heat of reaction for the decomposition of hydrogen peroxide. These values are then converted to percent active oxygen loss per week (%AOL/wk) to preserve an earlier convention for quantifying RGHP compatibility. Additionally, qualitative designations of compatibility[11] have been assigned to these values. This scheme consists of four classes with class 1 being the most compatible. To relate the quantitative measurements to the qualitative compatibility designations, metal samples having a %AOL/wk of ≤ 5 are assigned to class 1, whereas those having a value between 5 and 80 are considered class 2. Class 3 materials have a %AOL/wk > 80. Although archive compatibility data are available,[11] its current applicability is in question due to subtle changes in the compositions of both RGHP and structural materials. Trace levels of molecules can have significant influence on compatibility. Therefore, representative samples of materials must be evaluated with current RGHP formulations. In this work seven RGHP injector candidate materials were selected for compatibility evaluation. The materials were evaluated by the IMC technique.

Experimental Approach

IMC instrumentation and method described in an earlier work[10] was also used in this investigation. Accuracy of a particular experiment is expected to be within $\pm 0.2\%$ based on the manufacture's specifications. Rocketdyne Propulsion and Power supplied samples of Inconel 625, nickel 200, A-286, and corrosion resistant steel (CRES) 347. A manufacturer of specialized alloys, Foster–Miller, Inc., furnished three proprietary metals (batch 1, 2, and 3) for evaluation. All samples were prepared to have surface roughness between 0.8 and 1.6 R_q μm, where R_q is the root mean square deviation from mean line. RGHP (98%, FMC, Inc.) and the metal samples were used as provided.

Results and Discussion

As shown in Table 1, two of the generally available materials (Inconel 625 and nickel 200) and one of the proprietary formulations (Foster–Miller batch 2) had poor compatibility with RGHP and would be immediately excluded from this application. The alloy A-286 has marginal compatibility and would likely also have inadequate heat transfer characteristics because much of the propellant would be decomposing into gas-phase products. The stainless

Table 1 Percent active oxygen loss per week

Material	%AOL/wk[a,b]	Class
Inconel 625	Over[c]	4, 4[d]
Nickel 200	Over[c]	4
Foster–Miller batch 2	Over[c]	4
A-286	82.4 ± 1.6	3
CRES 347	12.7 ± 1.5	2, 2[d]
Foster–Miller batch 1	2.8 ± 0.2	1
Foster–Miller batch 3	2.2 ± 0.3	1

[a]Average of three coupons.
[b]Confidence level of 90%.
[c]Over maximum instrument measurable value 680,000 μW (73 %AOL/day).
[d]Reference 11 value.

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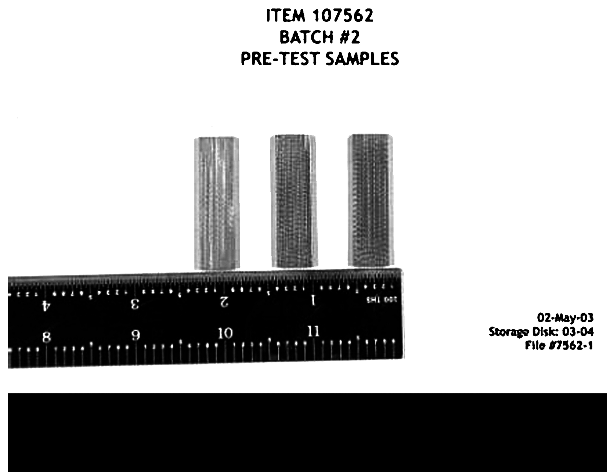

Fig. 1 Foster–Miller batch 2 material, pretest.

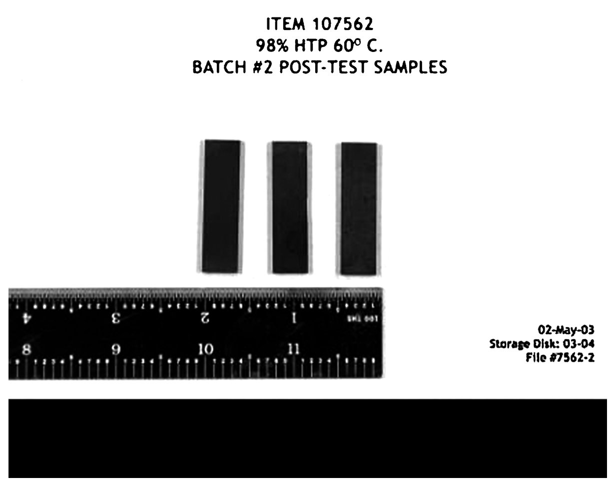

Fig. 2 Foster–Miller batch 2 material, posttest.

steel CRES 347 has acceptable compatibility considering the short residence time it would be wetted. Two Foster-Miller specimens (batch 1 and 3) displayed exceptional compatibility. If other requirements are met, such as high-temperature strength, these materials are a clear choice for construction of a RGHP injector.

Nearly all of the class 3 and 4 materials showed visible signs of incompatibility following exposure to RGHP. Observable change was most dramatic with Foster–Miller batch 2. In Fig. 1 is a sample coupon of this material before exposure. In contrast, Fig. 2 shows the same coupon after 568 h of exposure to RGHP at 60°C during an IMC experiment. In this case, the entire coupon is uniformly discolored. However, visual inspection is not a reliable evaluation of compatibility because nickel 200 showed no perceivable sign of reaction, yet was clearly observed in the IMC experiment to decompose RGHP.

Finally, considering the earlier mentioned caveat that representative samples of materials must be evaluated with current RGHP formulations, it is reassuring that archive[11] consistent compatibility designations were found for Inconel 625 and for CRES 347 as indicated in Table 1.

Conclusions

The isothermal microcalorimeter provides a simple, reproducible, and sensitive means to assess quantitatively compatibility of injector materials with RGHP propellant. In contrast, visual inspection is not adequate to determine compatibility.

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