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From: G. Huvard, M. Burt, HRC

Date: 12/14/15

Re: H&H ClearCool Hydrogel vs. White Phosphorus

Summary

The ability of ClearCool hydrogel to extinguish burning white phosphorus (WP) was evaluated *in vitro* by using a raw chicken breast as a test tissue. In each of the four experiments we completed, the hydrogel extinguished the white hot phosphorus instantly. When the hydrogel was allowed to remain in contact with the white phosphorus for about 30 seconds, the hydrogel apparently coated the WP with enough water to slow reignition. In all tests, the integrity of the hydrogel was maintained—there were no "burn through" holes and there was no shrinkage of the hydrogel in the area of contact.

White phosphorus is especially resistant to spontaneous ignition after submersion in methyl alcohol (MeOH); a discovery we made during the tests. The stability unexpectedly allowed us to handle the WP with relative ease and safety. As discussed in the report, we think this behavior is due to the ability of MeOH to easily wet the surface of WP.

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Experimental

Preparation of White Phosphorus

In 2001, the U.S. Drug Enforcement agency declared red and white phosphorus as List I precursor chemicals under 21 CFR 1310.02. While WP cannot legally be obtained in the U.S., red phosphorus can be purchased in small quantities from Sigma-Aldrich. Although it required more than a year to complete the purchase, we did finally receive a sample of red phosphorus.

We placed red phosphorus in 1" diameter crucibles, heated to 200°C in a nitrogen-purged tube furnace, and used the nitrogen to carry phosphorus vapor to the exit of the furnace. At the exit, we bubbled the phosphorus–laden gas through cold distilled water to precipitate white phosphorus (P_4). According to Kuck and Gersten, red phosphorus should be heated to about 450°C to produce white phosphorus[1]. However, a short extrapolation of the vapor pressure equation given by MacRae and Ven Voorhis[2] led us to expect a significant vapor pressure at much lower temperatures (ie., ~130 mm Hg at 200°C) and carryover to the water quench as long as the transfer lines remained above about 250°C. This occured as expected and we observed white phosphorus crystals in the scrubber as the furnace temperature rose to 200°C.

The water scrubber we employed was not efficient enough to capture all of the WP vapors. WP crystals formed on the glass tubing at the outlet of the scrubber and burst into flame during the preparation. We used a squirt bottle of water to force the WP back into the scrubber and were able to control the fires and complete the preparation. After quickly cooling the furnace and eliminating WP vapors from the outlet stream, we collected the WP and quench water in 50 cc centrifuge tubes. The WP centrifuged to the bottom of the tubes easily and formed a waxy solid. By repeatedly decanting, mixing, combining, and respinning, the contents of all of the centrifuge tubes were combined into a single tube. The water in the final tube was removed and replaced with methyl alcohol by decanting and filling with MeOH several times. Figure 1 is a photo of the sample of WP (~ 3 g) obtained.

Figure 1

[1] M. Kuck and S. Gersten, US 4,618,345 (1986). *"Method of preparing high purity white phosphorus."*

[2] D. MacRae and C. Ven Voorhis, JACS, 43(3), 547 (1921). *"Vapor pressure of white phosphorus from 44° to 150°."*

ClearCool Hydrogel Testing

A raw chicken breast was placed in a Pyrex dish in our flammability hood. This hood is lined with Duroc cement paneling and will easily withstand the 5000°F white heat when white phosphorus burns. We carefully removed a small piece of white phosphorus from the tube in Figure 1, placed the WP on the chicken breast, and quickly moved back from the fume hood. Nothing happened. We waited...nothing happened. We tried blowing on the WP using canned air and...nothing happened. So we very cautiously used a stainless steel spatula to poke the WP around a bit, stood back again, and watched. Still, nothing happened. It finally occured to us to burn off the methyl alcohol and we did so by lighting a long wooden stick and touching the flame to the area next to the WP. It burst into flame as expected and then the WP ignited with the spectacular result recorded in Figure 2.

Figure 2: Ignition of white phosphorus. The apparent diameter of the burn is overstated from the camera exposure to burning MeOH around the WP. The area around the white hot WP was actually about 2 cm in diameter. Once ignited, the WP burned as intensely as expected. The large beaker in the background was to be used as a safety quench in case the WP tube caught fire. As it turned out, the beaker of water was not needed and the MeOH-coated WP was quite easy to work with safely in the hood.

The phosphorus was allowed to burn for about ten seconds before a sample of ClearCool was placed over the WP (Figure 3). The ClearCool sample was used as-received from the packaging at room temperature. When dropped into place over the WP, the intense white flame disappeared immediately. There was no afterglow, fumes, or any indication of an incompletely quenched reaction. We used a hand-held infrared temperature gun to measure the temperature of the hydrogel directly over the quenched WP and obtained a reading of ~18°C. We could not detect any temperature change of the hydrogel—apparently, the ClearCool extinguished the white phosphorus so rapidly that negligible heat transfer to the hydrogel occurred. The oxidation was instantly and completely stopped by covering the WP with ClearCool.

After smothering the WP, we removed the hydrogel and waited for the WP to reignite (Figure 4). When the hydrogel was removed quickly after asphyxiating the WP, the phosphorus reignited immediately. If the hydrogel was left in contact with the WP for 15–30 seconds after quenching, the WP did not immediately reignite but had to be encouraged to do so by our flaming stick. The short wait of 15–30 seconds apparently allowed the surface of the WP to wet enough to block oxygen

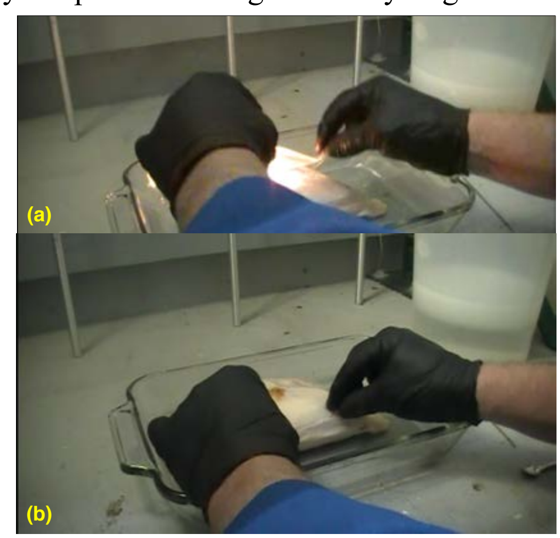

Figure 3: ClearCool hydrogel was applied directly over the top of burning WP. The white hot glow of the WP can be seen in (a) as the ClearCool is situated over the WP. As soon as the ClearCool is lowered over the WP (b), the flame is instantly and completely extinguished. The reddish dot in (b) is from charred chicken skin on the contact side of the ClearCool.

flow to the surface and pacify the phosphorus. There also seemed to be enough residual methanol in the chicken skin to enable reignition of the area near the WP by a touch with open flame from the burning stick.

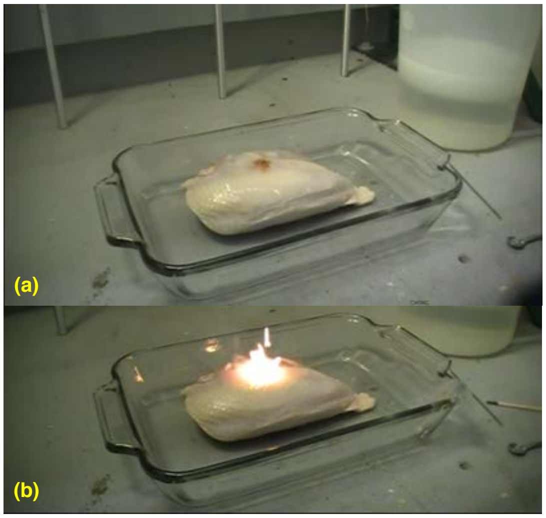

Figure 4: After applying ClearCool to extinguish the WP, the hydrogel was left in place for approximately 15 seconds, during which time the surface of the WP was cooled and rewetted. When the ClearCool was removed, the WP was stabilized against instantaneous reignition. We used a burning stick to get the WP to reignite and demonstrate that there was a significant amount of the phosphorus remaining to burn.

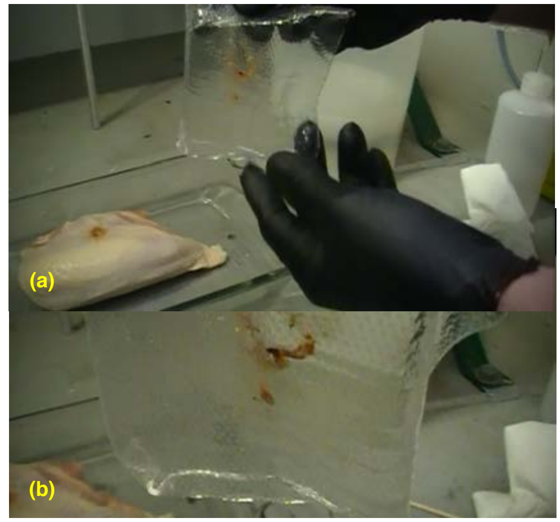

Figure 5: The appearance of the hydrogel was essentially normal after use on the WP. The ClearCool remained intact (a) and exhibited mild staining from the charring of the chicken (b).

We examined the ClearCool after use and found the hydrogel to be fully intact and essentially unharmed (Figure 5). The area of contact with the WP showed some staining from charring of the chicken but was otherwised undamaged. The ClearCool integrity was not compromised and the hydrogel was still usable. Examination of the burned spot on the chicken showed complete consumption of the WP with no noticeable residue. As described below, this was to be expected given the ready availability of water from the chicken and the hydrogel as the WP burned.

Results and Discussion

The chemistry of white phosphorus oxidation is given in Eq. 1.

$$P_4 + 5O_2 \longrightarrow P_4O_{10} \qquad [1]$$

The product of the oxidation is phosphorus oxide, P_4O_{10}. Often, the compound is referred to using its empirical formula, P_2O_5, or phosphorus pentoxide. Pure phosphorus oxide is a non-flammable, white crystalline solid. The solid sublimes when heated and its liquid boils at about 360°C. Under the white hot conditions of white phosphorus oxidation, much of the reaction product vaporizes.

However, under the reaction conditions presented by the wet surface of raw chicken, P_4O_{10} is short-lived if any escapes boiling or sublimation. The reaction product combines rapidly with water to form phosphoric acid which presents as a clear, slightly viscous solution. For this reason, there is no visable residue after burning white phosphorus in the presence of excess water.

$$P_4O_{10} + 6H_2O \longrightarrow 4H_3PO_4 \quad [2]$$

Path Forward

Originally, we presumed methanol to be a fast evaporating stabilizer for WP compared to water. Therefore, white phosphorus removed from methanol was assumed to ignite more quickly than white phosphorus removed from water. Surprisingly, WP samples removed from MeOH submersion were very stable and could be handled with ease. In fact, we had to ignite the MeOH and burn it from the WP in order to get sufficient oxygen to the solid surface to ignite the WP. In retrospect, we suspect that the low surface tension of MeOH results in complete wetting of the WP surface. Although we have not found any contact angle data to support this, water probably wets WP poorly. If so, water should bead on the surface of WP and expose the solid to air once removed from submersion.

Rapid ignition of water–wet WP exposed to air was the behavior we observed when we synthesized the white phosphorus. The WP accumulation at the end of our crystallizer outlet burst into flame three times during the process and squirting the solid with water did little to extinguish the fire. It was necessary to force the solid back into the nitrogen atmosphere within the glassware to maintain control. In contrast, methanol apparently wet the surface of WP and excluded oxygen from the surface very effectively. As a result, WP could be handled easily and safely and would not ignite until we ignited and burned/evaporated the alcohol from the surface of the phosphorus. Once oxygen from the air was allowed to contact the WP, the phosphorus immediately ignited and burned as expected.

As shown in the video of the tests (supplied separately), thoroughly wetted WP is not prone to instantaneous reignition but must be encouraged to burn again by the brief application of an external flame. These observations should help guide the direction of future research.

Conclusions

- ClearCool hydrogel is a very effective medium for the instantaneous quenching of burning white phosphorus.

- ClearCool hydrogel is not ruined or compromised after being used to smother a burning fragment of white phosphorus.
- The propensity of white phosphorus to spontaneously reignite after removal of ClearCool hydrogel is mitigated by adequate contact time. If the hydrogel remains in place long enough to fully rewet the surface of the phosphorus, oxygen is effectively blocked from the surface for an extended period.