

Communications

Brief technical articles, comments on prior articles and book reviews

Comment on:

High-Nitrogen Pyrotechnic Compositions, Summer 1998, Issue 7.

Rutger Webb posed the following questions:

1. Did you measure the color (spectra) of the flames? Or was the color quality determined by visual comparison?
2. Why was increased burn rate of most copper salts undesirable? Did it "wash out" the color?
3. Did you try copper(I) chloride (CuCl) as a color agent? It is, as far as I know, the only desired emitter that does not have to be formed *in situ*.
4. Do you have more detail on the stability of the Hz₂Tz compositions?

Michael Hiskey's Reply:

Thanks for your inquiry, and I'll be glad to tell you what we know so far about our pyrotechnic compositions. First, all color quality determinations were done with the naked eye and compared to the color of traditional formulations. Since we wrote the paper last fall, we have made some improvements.

Reds are now using nontoxic Li₂CO₃; orange CaCO₃, which give much better depth of color compared to sodium; green uses H₃BO₃, which is superior to Ba(NO₃)₂ and is also nontoxic; and very nice canary yellows utilize NaNO₃ and H₃BO₃. Hot pink uses orange with smaller amounts of green and blue. Blues and purples still use copper as sulfide or oxide. As you are probably aware, hydrazine is used as a monopropellant by spraying through a palladium or platinum gauze. Other transition metals have varying degrees of activity; so it is not too surprising that copper acts as a burn rate catalyst for our substituted hydrazine. Very fine Fe₂O₃ (i.e., nanocat) is exceptional in this regard and increases the burn rate by at least an

order of magnitude with only 1% added. The blue colors with CuS or CuO are good. When stars are burned stationary, they have orange tips, but while flying through the air in an indoor mine, the blue is very nice with no flame tip discoloration. However, we must make these stars slightly larger as they burn faster. The increase in burn rate does not wash out the color. Regarding the stability of di-hydrazino-tetrazine, we have found that as long as the mixtures containing copper salts are dry, they age quite well. We make cut stars by first wetting the formulations with water into a mud-like mass and cutting small pieces. Large stars made by this method air-dry very quickly in New Mexico. Again, the stars have shown no decomposition as long as they remain dry. When copper mixtures are wet for extended periods, the situation is not good. Discoloration and gassing occur after several hours. At your suggestion, we mixed up some star composition containing 2% CuCl. The blue was very nice, but not significantly superior to what we already have, and the burn rate was faster than with CuS. It was worth a try; thanks for the suggestions.

We have currently not found a viable replacement for copper; we tried CsCl and Ni(NH₃)₆Cl₂ with no luck. The replacement of copper for blues and purples would definitely be an advancement as this is the only toxic (although not very toxic) metal left in our formulations. We are currently thinking about the possibilities of low or even zero signature rocket propellants utilizing di-hydrazino-tetrazine. As mentioned above, nanocat is an extremely powerful burn rate catalyst, and this may allow us to use ammonium nitrate as an oxidant in a non-aluminized propellant and still achieve reasonable burn rates. Please keep in mind that we plan to publish our most recent observations in the *Journal of Pyrotechnics* in the near future.

Follow-up from Rutger Webb:

I'm curious. In the article you wrote that you had examined a large number of materials, such

as nitroguanidine, guanidine nitrate, etc. How did you evaluate their “degree of usefulness”? Did you create color compositions containing guanidine nitrate? How did these compare to those made with Hz_2Tz ?

In your reply above, you mention “... we tried CsCl and $\text{Ni}(\text{NH}_3)_6\text{Cl}_2$ with no luck.” Interesting! Atomic emission of cesium is used in covert infrared (IR) illuminant flares, as you probably know. Yes, that is not of any use for color compositions, but there seems to be demand for it. If I may suggest, try to measure the IR/VIS (visible) spectrum of your compositions, too. [See: C.W. Lohkamp, “Black Nite Flare”, AD-A030713 (NWSC/CR/RDTR-39), 2 Sep 1996 and C.W. Lohkamp, “Black Nite Flare”, 5th *IPS Proceedings* (1976)pp 307–315.]

What desired emitting species were you aiming for with $\text{Ni}(\text{NH}_3)_6\text{Cl}_2$?

In your reply above, you mention “...Please keep in mind that we plan to publish our most recent observations in the *Journal of Pyrotechnics* in the near future.” Would it be possible that I could have a preview of your article? I’d really appreciate it. Please ask me anything in return. As you see, your article made me very curious.

Mike Hiskey’s reply to the above:

We had problems with the burn rate of the other high-nitrogen energetic materials. They burned slow and smoky, even when mixed with oxidizer. The real advantage of Hz_2Tz is zero signature and reasonable burn rate, even when using ammonium nitrate as an oxidizer.

With regard to $\text{Ni}(\text{NH}_3)_6\text{Cl}_2$, we thought that NiCl^+ could possibly give interesting color, but it was not acceptable. Other more exotic colorants have been examined with some degree of success, for instance AgNO_3 gave an acceptable purple and Au_2O_3 gave a nice green. There’s a whole periodic table out there and most of it is metals, and I don’t think the final word has been written on coloring pyrotechnic flames.

With regard to “... preview of your article ...”, Not a problem, you must realize that I’m a terrible writer, and I haven’t even started to put this paper together in my head yet. Our pyrotechnic work has been done essentially with no funding, and therefore only in our spare time, which is almost non-existent these days.

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