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Texas Tech Lessons

Explosion highlights need to improve safety culture at university, initiates government oversight

Jyllian N. Kemsley

Texas Tech U

REPERCUSSION The blast that injured Brown also damaged the lab.

Texas Tech U

EXPLOSIVE The purple compound made by the students was likely nickel hydrazine perchlorate.

On Jan. 7, 2010, Texas Tech University (TTU) graduate student Preston Brown was working with another graduate student to synthesize and characterize an energetic material, most likely nickel hydrazine perchlorate. Despite being told by their adviser, chemistry professor Louisa J. Hope-Weeks, to make no more than 100 mg of the material, the students synthesized 10 g.

They then divided up the product: Brown took half to prepare the sample to run characterization tests, and the other student took half for solubility studies. Because the product was lumpy, Brown placed his portion into a mortar. He believed that the compound was safe when "wet," so he added some hexane and—wearing safety goggles but working at a bench in the middle of the lab, with no blast shield—"very gently, very, very gently" used a pestle to try to break up the chunks, Brown told TTU environmental health and safety (EH&S) officers, according to an interview transcript.

When Brown thought he was done, he set down the mortar and took off his goggles. Then he decided to give the compound one last stir. The mortar exploded in Brown's hands. Brown "lost three digits on his left hand, severely lacerated his right hand, perforated his left eye, scratched his right eye and had superficial cuts to the parts of his body that were exposed," says an investigation report prepared by Randy Nix, TTU's EH&S director. The other student was not injured.

The students' laboratory notebooks and the TTU police and EH&S investigation reports, along with related interview transcripts and summaries, collectively reveal a lack of attention to safety at TTU at all levels—lab, department, and university. The incident has prompted changes in TTU's laboratory safety program as well as new oversight of laboratories funded by the Department of Homeland Security (DHS), which funded Brown's research through Northeastern University's Center of Excellence for Awareness & Localization of Explosives-Related Threats (ALERT).

"This was a very unfortunate and unnecessary accident that could have resulted in loss of life very easily," says T. Taylor Eighmy, a civil engineer and TTU's vice president of research. "I think that the graduate student in question has culpability here of carelessness in the lab." And beyond that, at the department and institutional level, "the culture around safety was just not as prevalent as it should have been," Eighmy says.

Chemical engineering professor Brandon Weeks told police that the Hope-Weeks lab was working on a project to characterize energetic compounds that could be used to produce improvised explosives, according to the TTU police report, one of several documents obtained by C&EN through a public records request. Results from the research were to be used by collaborators to develop new detection and mitigation techniques for the explosives. Weeks is the lead principal investigator for the effort, and Hope-Weeks is a co-principal investigator.

Brown was training the other student to take over his project in anticipation of Brown's graduation, according to the EH&S interview transcript. Brown's laboratory notebook provides no detail about what exactly the two were doing in the lab on the day of the incident. Brown used 14 pages in his lab notebook to document his lab work from Sept. 9, 2009, through the date of the incident. During that time, the notebook includes seminar notes, other notes seemingly unrelated to his research, and only vague descriptions of experimental work: One apparent synthesis is documented in an undated entry simply as "$Ni(NO_3)_2$ + hydrazine / 10 g / purple ppt forms immediately / also an exothermic rxn." The other student's "notebook" is a typed summary of reaction protocols and observations, also without dates. TTU has declined to identify the other student because of student privacy laws; Brown's identity became public at the time of the incident.

Brown told Nix and TTU laboratory safety specialist Jared Martin that he and the other student were making "cobalt perchlorate hydrazinate," the interview transcript says. But on the day of the incident, the other student told police that they were working with nickel hydrazine perchlorate and told Martin that the compound they were working with was blue or purple—a color consistent with his notebook description of nickel hydrazine perchlorate. Hope-Weeks believes the students made nickel hydrazine perchlorate, "but due to conflicting reports and the fact that the compound was destroyed in the explosion and subsequent emergency disposal, she can't be absolutely certain," says Alice M. Young, TTU faculty fellow for research integrity and a pharmacology professor. Hope-Weeks did not respond to a C&EN interview request.

Policies & Procedures

Chemical Hygiene Plan Violations

An internal investigation determined that Texas Tech University violated many of its own policies and procedures. Some of the findings were as follows:

The chemistry department did not
• Implement university health and safety policies
• Maintain a current list of OSHA-regulated substances
• Ensure that personal protective equipment was worn in laboratories
• Appoint a department chemical hygiene coordinator
• Train employees
• Maintain availability of material safety data sheets
• Develop a department-specific CHP (which led to other violations, including a lack of standard operating procedures and policies for reducing chemical exposure)

The principal investigators did not
• Ensure that containers were properly labeled
• Perform a hazard determination of chemicals generated in the lab
• Ensure that workers knew and followed chemical hygiene rules
• Prepare written procedures for use of carcinogens
• Conduct regular chemical hygiene and housekeeping inspections
• Ensure that adequate facilities and training were available for use of lab materials

TTU EH&S investigation interviews with other researchers who worked in the lab indicate that Brown's labmates were disturbed by his conduct in the lab prior to the incident. His space was disorganized, items were not labeled, and "there had been conflicts over work space, cleanliness of the lab and use of chemicals," one researcher told the investigators.

Another researcher told EH&S investigators that Brown started scaling up syntheses in June 2009, first to 1 to 3 g and then to 5 g. The researcher told Brown the scale-up was inappropriate; Brown reportedly responded that things were "just fine." The researcher apparently did not report the scale-up to either Weeks or Hope-Weeks. Brown later told investigators that he scaled up syntheses because he was concerned about batch-to-batch consistency.

"There was no logical reason for anyone involved in the research to utilize 10 grams of the substance for workbench testing," Weeks told police. Under typical circumstances, 50 to 100 mg of a compound would be enough to fully characterize material with methods such as spark tests, flame tests, pressure hammer tests, and infrared spectroscopy, the police report says.

The instrumentation for some of those tests was in other buildings on campus. Brown transported as much as "several grams of compounds" at a time in glass vials in a backpack or coat pocket, a researcher who helped Brown told EH&S investigators. Brown "was told that a metal container would be better for the transport, but he continued to bring them in a glass vial," the researcher said.

Weeks also told police that a student reported to him that Brown "would often avoid necessary steps to characterize compounds in order to save time," the police report says.

None of the researchers interviewed by EH&S officials, including Brown and the student he was training, reported receiving either general safety training or specific instruction on how to handle energetic materials. The Hope-Weeks lab had neither blast shields nor a safe in which to store energetic materials, Eighmy says.

As for communication with Hope-Weeks, Brown told investigators that he would see her at weekly group meetings or go to her office to ask questions. Hope-Weeks told EH&S investigators that she assumed the students were synthesizing compounds in the quantities she told them to make—50 to 100 mg—and that she never checked on the amounts.

After the incident, personnel from the Lubbock County Sheriff's Office Bomb Squad and the Bureau of Alcohol, Tobacco, Firearms & Explosives removed several vials of material from Brown's home. The containers were largely unlabeled, except for one marked "TATP," most likely for triacetone triperoxide. The bomb squad destroyed the items. Brown later told Nix and Martin that he brought vials home from the lab because he absent-mindedly left them in his pockets.

A further search of the Hope-Weeks lab turned up additional nickel hydrazine perchlorate "in both powder and liquid form in several places around the laboratory, with a number of the containers thought to be in various stages of production," the police report says. Other powders and liquids found in the lab could not be identified because of improper labeling. Everything was removed and destroyed by bomb squad personnel.

Brown is now recovering from his injuries and is writing his dissertation, according to a TTU press release.

C&EN provided the TTU documents to several energetic materials experts to get their input on the incident.

"In light of the disregard for housekeeping and a cluttered work space, the lack of hazard-specific training, and the lack of direct supervision by experienced scientists, this research group was fortunate not to have had an incident earlier," says Keith Butler, chief chemist at ammunition manufacturer American Ordnance.

"What appears to have happened was that students got complacent because they didn't have any accidents and started scaling up without the knowledge of the professors," says Charles A. Wight, dean of the graduate school and a chemistry professor at the University of Utah. "You need to have enough one-on-one training to make sure that doesn't happen."

INCIDENT INFORMATION (PDFs)

Students' lab notebooks

Texas Tech EH&S accident report

Texas Tech police report

With regard to training, "In laboratories that routinely synthesize and characterize novel explosive compounds, it is a general practice to evaluate new researchers by assigning them tasks with less sensitive, well-characterized explosives," Butler says. Researchers who show a lack of respect for the compounds or lack the skills to manipulate them are given other projects or dismissed. Researchers who demonstrate proficiency are allowed to work with increasingly hazardous materials, he says.

Even after researchers demonstrate proficiency, however, the first rule of handling energetic materials is to keep quantities low, says Michael A. Hiskey, who formerly synthesized explosives at Los Alamos National Laboratory (LANL) and now runs pyrotechnics company DMD Systems. At LANL, in a dedicated energetic materials facility, "I wouldn't have been allowed to make more than 0.5 g," Hiskey says, adding that safety goggles and blast shields were used at all times. In Wight's group at Utah, the limit for sensitive explosives is 10 mg.

Energetic materials experts also say that peer review is common in labs synthesizing particularly dangerous materials. "The worker would write up the proposed reaction, and another approved worker would review the work with special emphasis on safety," says James R. Stine, a former high-energy-explosives group leader at LANL who is now retired.

The experts further highlight the need to fully characterize energetic materials, especially if reactions are scaled up. "Inorganic synthesis can be straightforward, but sometimes there are side reactions," Butler says. The lumps that Brown was trying to break up "may have been contaminated with impurities that showed up in a 5- or

10-g batch that didn't show up in 100 mg," he says. Alternatively, the lumps could have contained unreacted perchlorate or may have been a different, more hazardous crystal form of the intended compound. Lead azide, for example, has one crystal form that is fairly stable and another that is very dangerous, Butler says. He would have separated the lumps from the larger sample and characterized them independently instead of trying to mix them in.

As for transporting energetic materials, Lawrence Livermore National Laboratory (LLNL) requires that small containers of samples less than 10 mg each must be packaged inside a carton or box that is marked as containing explosives, says lab spokeswoman Anne M. Stark. For quantities greater than 10 mg, samples must be packaged inside an ammunition can, with additional specifications for quantities between 300 mg and 2 g. People transporting explosives must have training to handle the materials and must hand-carry the containers or place them in a government vehicle, Stark says.

The internal TTU investigation identified multiple violations of the university's chemical hygiene plan (CHP). A CHP is required by the federal Occupational Safety & Health Administration for laboratories that use hazardous chemicals. OSHA sets requirements for what must be covered in a CHP, but it is up to the organization to decide how those requirements are addressed, says Russell W. Phifer, a safety consultant and past-chair of ACS's Division of Chemical Health & Safety. The organization then must comply with the policies and procedures it establishes. In TTU's investigation, the university found a lack of training and standard operating procedures, among other deficiencies.

So far, OSHA itself has not investigated the incident. OSHA typically does not get directly involved unless there is a fatality or multiple injuries requiring hospitalization or unless an institution or company has an accident rate that is much higher than comparable establishments, Phifer says. If an employee complains to OSHA, the agency sends a letter to the employer asking for a response to the charges and will investigate if the response is deemed inadequate, Phifer says.

"What appears to have happened was that students got complacent because they didn't have any accidents."

The U.S. Chemical Safety & Hazard Investigation Board (CSB), on the other hand, did investigate the incident—its first ever of an academic lab (C&EN, Feb. 1, page 25). Its report on the TTU incident is expected to come out this fall and will be more of a bulletin than a full analysis, a CSB official says. CSB Chairman Rafael Moure-Eraso is scheduled to discuss the board's interest in academic labs and give an update on its TTU investigation in a talk during the Presidential Event on Laboratory Safety on Tuesday, Aug. 24, at the ACS national meeting.

The investigation results released so far have prompted changes in safety protocols and programs at TTU from the lab to the institutional level. At the lab level, Hope-Weeks told TTU investigators in January that she planned to have each of her students write up experimental protocols, which both she and EH&S officials would review. Once the protocols were finalized, Hope-Weeks and the students would sign them, and copies would be kept in the lab for all to review. Hope-Weeks also said she planned to have students sign a contract that they would abide by lab rules or risk being dismissed from her group, according to the interview summary.

The Hope-Weeks lab is also now equipped with blast shields and a safe for storage of energetic materials, TTU's Young says. Brandon Weeks's lab has developed a standard operating procedure for logging and transporting energetic materials.

In addition to addressing the CHP violations, the university appointed a working group to review lab safety policies and training compliance. Chaired by Young, the group released its report in July (*C&EN Online* Latest News, July 23). The group's recommendations included that TTU establish a university-wide research safety committee, commission an outside panel to review the university's safety culture, identify research programs that require more than usual monitoring, develop or expand roles of ombudsmen to include safety, and add safety information to faculty annual reports and tenure and promotion packages as well as undergraduate research reports, master's theses, and doctoral dissertations.

University officials subsequently established the safety committee and charged it with implementing all of the working group recommendations. Young is chair of the committee; the EH&S department will also start reporting to her on Sept. 1.

Research safety will also be a cornerstone of the university's responsible conduct of research (RCR) program, Young says. RCR training is now required for all undergraduates, graduate students, and postdoctoral researchers supported by National Science Foundation grants. The National Institutes of Health requires similar training for researchers receiving grants for research training, career development, or research education.

The incident has also prompted DHS to set up a safety oversight program for projects it funds. "I was a combination of hurt and furious" in response to the TTU incident, says Matthew Clark, director of university programs at DHS. "I don't want to see it happen again on my watch."

The risks involved in DHS-funded research go beyond energetic materials, Clark says. DHS is also concerned about things such as researchers doing surveys in foreign countries. "I don't want lab accidents, and I also don't want one of my researchers kidnapped in Pakistan or Indonesia," Clark says. "We have to make sure that, whatever type of research is done, people have adequate protocols."

Although DHS has always required that researchers follow university rules and any federal regulations that might apply to their work, the agency had never asked researchers to prove they were doing so, Clark says. Most DHS money is awarded through 12 Centers of Excellence, such as Northeastern's ALERT, and those centers will now have to set up review panels to oversee research safety at the 200 institutions involved in the consortia. The panels "will have to go and look at the type of research being done at each of their subcontractors and make sure it meets the highest standard of safety," Clark says.

An ALERT team did investigate TTU, and Clark says the safety oversight program the center has put in place is the model DHS will ask other centers to emulate. ALERT staff did not respond to interview requests from C&EN, but according to the center's website, the center has established a six-member safety review board that will annually review and edit ALERT safety protocols and standard operating procedures. The board will also visit each ALERT subcontractor annually to audit each institution's safety program.

The website also describes a "Safety Awareness Education Program" being created by the center, with an "Explosive Safety Protocols & Procedures" course to be offered every six months. Everyone participating in ALERT is to attend the course within six months of joining the program and at least every other year afterward.

Eighmy hopes that ultimately TTU will come out of the incident, investigations, and reviews with a safety program based on best practices that can be a model for other institutions. "What you really need to do is promote a face-to-face, interactive, solution-based training and culture," Eighmy says, adding that if safety is not treated as important, it won't be considered important. "The private sector gets this, and the government labs probably get this, but universities are late to the game about ownership of safety culture."

Additional reporting was done by Jeff Johnson.

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1DOC7

Copies of Researchers' Laboratory Notebooks

11/1/09 – 1/7/10

1DOC7

Part A.

9/9/09

Washed carbon nanotube gels
Washed ferrite gels
Vented gels in desiccator Rula - CuZn
Sameer - CNT Al

Tom made Tron gels in water

Attended Dr. Shi Seminar

9/10/09

Washed carbon nanotube and ferrite gels
XRD analysis on ferrites

#1,5 - ZnFe	Start 5	Div 1/3°
#2,6 - CoFe	Stop 80	Div HL 10mm
#3,7 - CuFe	Sampling W 0.02	Sct 2/3°
#4,8 - NiFe	Speed 2	Recs 0.30
		5°V Rx

SEM is still not working will check tomorrow

	Zn	Co	Cu	Ni	
[illegible]	✓	✓	✓	O	In additive
DMSO	✓	✓	✓	✓	4 prop
Water	✓	✓	✓	✓	pH
Ethanol	✓	✓	✓	O	

1. Gas must be ON before instrument.

2. Regulator at 10 psi (dont mess with regulator valve)

to switch off.

3. Boot the software

4. Power on ~~side~~

5. TPRW — signal — He flowing ⓘ Green.
— Tells the status.

6. 30 mins of warm up time.

TCD — 150 mAmps (milli amples).
TCD — sensitivity — step up or down attenuation.

7. Choose function — Reduction
— Ti at 400, flow for ½ hr.

8. CO Pulse titration. (2) Left to right.
Reduction (3) 1, 2, 3
AUX — No function.

9. Reduction at higher attenuation

10. Pulse titration — CO on surface
- Very sensitive
- Low attenuation.

11. Attenuation goes to all the way up.

12. Do zero adjust.

13. Solenoid — automatic titration. (not on ours)

14. 50, 100, 200 μl loops inject.

15. 2 ways — loop
- Gas syringe.

16. 5-10 pulses  3 peaks same height

- titration done
- do average.

17. Wrench for solenoid loop
- Be careful — can get stripped easily.

18 Take sample -- treat with (Clean) helium
- reduce
- titrate with CO.

19. Every order
- Data acquisition. (always for
- Manual analysis (titration)

* titration is NOT MANUAL
TPR is automated.

2 Stages - Automatic sample prepation.

- Titrate manually.

Sample prep (Build a macro)

(1) Change Gas - Helium (Steps given in manual)

(2) Hit OK

(3) Ramp temp by rate (20 degree per min. target 120)
(5 min target)

(4)

→ Manual Analysis
- Titration.

Go to your attenuation & Use coarse & fine to zero it out again.

4-14

- Zero adjust for ∞
- Coarse & fine — Sample or Fine attenuation.
- Do the adjust just before sample analysis.

Out gas station of left side (Opp to power switch).

Hear click for release.

Flow rate between 80 & 90 on bubble meter

Calibration gas done not flow through. — put couple inbetween

- adjust 1-2 bubble every 2 seconds.

Open screws — get thermocouple out (DONT BEND IT)
- load sample

0.98~~23~~ g

Data acquisition — ChemBET ~~NO~~
~~Waiting~~ X — Instrument setup — Part

5-14

- CO gas to titration not the parts.

Data Acq — Chem BET
— Analysis program
—
} for expert question Quantachrome.

6-14

~~[illegible]~~

my dad dis
this factorial
design

WOW

How can silver just
leave the structure?

$AgCl_{(s)}$ in H_2O

AgCl

Ag^+ catalyst in presence
of HCl?

7-14

#1 Sako   Micropor. mesopor Mater.

Silver ions w/ nanoparticles

TiO_2 - p25?

$O_2 \rightarrow O_2^-$

keep electrons & holes apart.
Ag + ZnO

Role of Silver Ni^{2+}/Ni^0
Pb^{2+}/Pb^0

Microporous zeolite
TiO_2 chains quantum wires
Si Matrix
Ti

Slurry Reactor   ETS-10 is visible

multipole plasmon resonance @ 350 nm

500 W Xenon Lamp
pH ~ 5.2

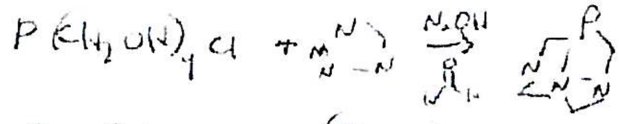
photo assisted reaction

8-14

Nevada Reno

Heterogenous catalysis is prefered to homogeneous aqueous catalysis

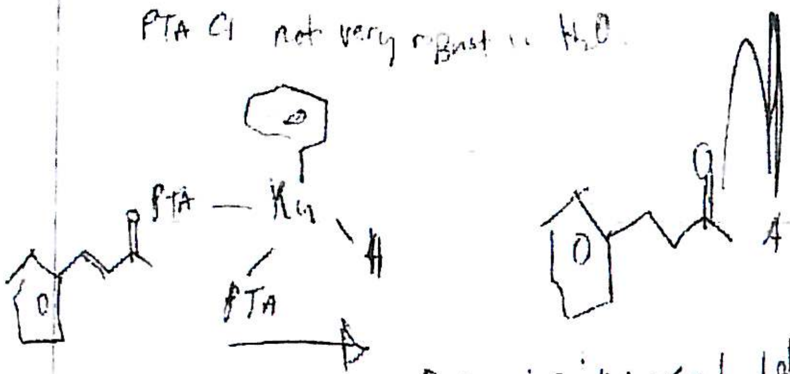
water soluble phosphines.
ligand TPPTS
PTA



Ru·PTA arene (Dyson)
anti cancer agents

PTA can bind by either N or P depending on metal.

PTA Cl not very robust in H_2O.



Potential MOF building Block.

9-14

Oct 14 2009

Trial synthesis of Bitetrazole:

- 0.464 g KCN + 1.64 g H_2O 5C
  add 35% HCl 0.35 mL slowly
- 0.51 g $NaNO_2$ in 1.3 mL of H_2O
- Add 17 mg $CuSO_4$

42 mg HAC.

After removal from ice and stirring yellowish liquid darkened to greenish black rxn flask was warm
possible need to slow rxn rate by temp control

pH check during synthesis

10-14

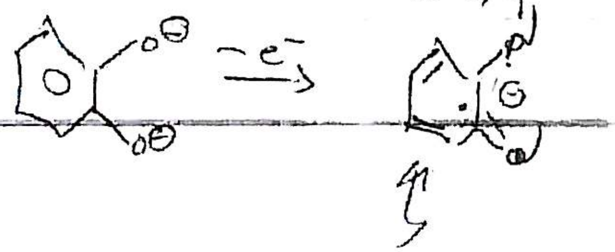
11/11

UC Irvine

Metal Catalysis — Metal Redox
d8 square planar

use d0 to reduce the ambiguity of where the e⁻ are coming from to only ligand.

Catechol Quinone   Berry Spider



Stable

~~metathese~~
metathesis

12/4

Have made complexes of

$Co(NO_3)_2$ and hydrazine and

$Ni(NO_3)_2$ and hydrazine

The nickel compound NHN is known and reported but the cobalt compound on the other hand is not reported.

Other metals (Zn, Y, Fe) that we have tried appear to give hydroxide ppt upon addition of hydrazine.

12/8/04

Observed formation of two complexes when working with

Co perchlorate:

$Co(NO_3)_2$ + NaOH → $Co(OH)_2$ ppt

↓ $HClO_4$

$Co(ClO_4)_2$

↙ red mother liquor yields red "crystals" after sitting 1-2 days

↘ green powder forms quickly

12-14

Both compounds burn very well.

~~Co~~ $Co(NO_3)_2$ + hydrazine
8.7 g

↓

Co hydrazinate nitrate?
peach orange color ppt.
exotherm.

$Ni(NO_3)_2$ + hydrazine
10 g

purple ppt forms immediately
also an exothermic rxn.

Cation – ~~Co~~

Co: NO_3, Per

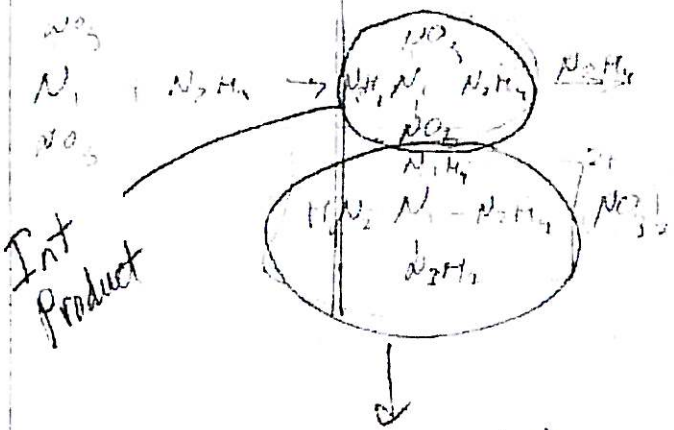
Ni: NO_3, Per

Coordination

M – A

Co: NO_3, Per

Ni: NO_3, Per



Final Product

1. Crystal F + Elemental F, I + EC & I + F

2. Crystal F + EC & F

14-14

1DOC7

Part B.

Bitetrazole synthesis

KCN 0,5 g dissolved in 10 ml of water, NaN_3 in 10 ml added with stirring, + several drops of acetic acid and 20mg of $CuSO_4$ (cat). Temp 5-8C. Heats on its own, don't let to heat up to much. Leave at 45C for 40 minutes, then heat to 90 for 4 hours.

Heated vigorously developing dark green colour , colour change: green at 45 to blue after 3-4 hours at 90C. Crystals of mixed K Na salt filtered from the mother liquor. NH_3 added , NH_4 salt less soluble than Na filtered after that. Yield ~60%.

Doesn't burn, doesn't work on drop-hammer..

Repeated twice with 0,5g of KCN. Regardless of what we do, heats when we take it out of the ice bath. It looks like it influences the result.

2-aminopyridine

0,5 g of pyridine + 1,1 excess of NaNH2, in 10 ml of toluene, reflux 4 hours. Black resin. Add water to precipitate product, no result.

Repeated 2 times with bigger excess 2.5 of amide and Fe(NO3)3 as catalyst. No product.

Amide looks bad, doesn't really react with water.

Reordered amide

NHN Nickel hydrazine nitrate

0.5g $Ni(NO_3)_2$ reacting with hydrazine (excess, until precipitation stops)– 2-3ml of hydrazine. Immediately forms pink suspension, filtered, yield is high, but hard to tell, stochiometry is unknown. Insoluble in water, ethanol, acetone, DMFA.

Burns nicely.

Drophammer full height full weight works 50%

CHN

Same as NHN, suspension forms slowly, orange colour, yield less than NHN, takes some time and stirring for precipitation to occur, but still insoluble in all solvents.

Burns.

Works on drophammer with the same weight an height as NHN.

CuHN

Cu nitrate reacts with hydrazine immediately. Managed to get CuHN in alcohol ice bath at around -5C upon treatment with cold diluted hydrazine. Dark blue precipitate, burns nicely but worse than NHN. Colour of flame greenish yellow. Maybe hydrazine perchlorate will be good for fireworks..

Decomposes when dry overnight. Useless.

Other metal hydrazine nitrates

Fe, Zn, Al give precipitates looking very like hydroxides. Do not burn, do not dissolve.

NHP $(NiClO_4)_2$ hydrazine

0,5 g $Ni(NO_3)2$ treated with NaOH to get NiOH. Add $HClO_4$ to dissolve precipitate, controlling pH. Hydrazine added, solution changes colour to green, then blue(precipitate forms), then purple, precipitate dissolves.

Both Blue and purple dried up, both burn. Blue one explodes on the match when compressed.

CHP $(CoClO_4)_2$ hydrazine

0,5 g $Co(NO_3)_2$ treated as Ni, to get perchlorate, then hydrazine added. Colour changes to green, precipitates, does not burn. Too little, no more than 10% If add more hydrazine colour slowly changes to pink, no precipitate. Let it dry up. Product burns and sparkles on the match

CHP works on Drophammer, minimal weight, maximum height (50%)

Flame test good. NHP doesn't burn on flam test.

Tried TGA for CHP, broke the wire, 5 mg too much for it. Apparently exploded at 180C

~25mg spark in mortar!!! Apparently should be ground wet. No problems with grinding wet.(water added, couple drops) But some of it dissolves.

Dissolves in water and hydrazine. trying to get crystals.

Got crystals from water and hydrazine mixture. Took one week, then precipitated overnight.

$Cu(ClO_4)_2$ Hydrazine

Cannot get even at -8C. Reacts immediately with any concentration of Cu and hydrazine.

Flame tests

4 hydrazinates tested on for flame propagation. NHN and CHP ~2m/s, CHN 0.5m/s. NHP sparks or explodes but doesn't burn steadily. Results and video: folder \Flame test.

Amination of bypyridine

0.5g of bypyridine with 2.2 excess of $NaNH_2$ in 10 ml of toluene 12 hours. New amide reacts with water. Distilled toluene before reaction. After reaction no bypyridine left (TLC) but bad mixture of many products. Nothing got as crystals.

Metal bitetrazolates

0.2g of Cu, Ni, Co nitrates treated with bitetrazole + couple of drops of HNO_3, got Blue, dark blue and orange precipitates. All spark on the match, do not really burn, do not work on drophammer with full weight and height. Maybe need more weight.

Diazominotetrazole

Plastic vial!! 0.2 g of 5-aminotetrazole dissolved in 5 ml of 10% acetic acid, treated with equimolar $NaNO_2$ in 5 ml of water. $NaNO_2$ added at ice bath temp, slowly with stirring. Left for 20 mins, then 0.2 more g of 5-aminotetrazole added slowly at 0C.

Cu salt

Olive green precipitate formed after addition of Cu nitrate. Burns.

Will be interesting to try with Ni and Co.

NHP exact procedure

g of $Ni(NO_3)_2$ reacted with g of NaOH. Precipitate centrifuged, water decanted, then precipitate washed with distilled water, again centrifuged. Repeated 3 times. $Ni(OH)_2$ reacted with HClO4 , pH checked all the time to avoid adding too much acid (and potential formation of hydrazine perchlorate afterwards). Solution transferred to plastic weighing container and there treated with hydrazine. Upon adding blue colour develops and precipitation occurs. At this stage divided into 2 container, one container treated with excess of hydrazine until complete dissolution of precipitate. Colour changes to purple. Both container left overnight in the hood to evaporate solvent without heating. Second Day. In both containers have some solvent left. In the first container, which had less hydrazine initially added hydrazine until precipitates becomes purple and no change occurs upon further addition. So, at this point first container contained **NHP** + **hydrazine** + left from previous day **water** and looked as wet as it might seem.