Independent Panel Evaluation of Dry Sludge PISA Program

by

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INDEPENDENT PANEL EVALUATION OF DRY SLUDGE PISA PROGRAM

**F. F. Fondeur
W. R. Wilmarth**

August 30, 1999

**Westinghouse Savannah River Company
Savannah River Site
Aiken, SC 29808**

SAVANNAH RIVER SITE

INDEPENDENT PANEL EVALUATION OF DRY SLUDGE PISA PROGRAM

SUMMARY

Dr. Kirk Yeager and Mr. Marvin Banks from Energetic Material Research and Technology Center (EMRTC) evaluated Savannah River Site (SRS) efforts in the Dry Sludge program. They evaluated four program areas: energetic material formation, stability, initiation, and propagation. The panel evaluation included a site visit (July 13 and 14) as well as a review of various reports¹⁻¹⁰ and presentations by researchers involved in the program. A summary of their findings follows. Attachment 1 contains the full report. Attachment 2 includes the agenda for the meetings and copies of the presented materials.

- The panel endorses SRS efforts in the Dry Sludge Program
- The panel agrees with selecting mercury fulminate as a surrogate energetic compound and mercury oxalate as a possible energetic compound in the tank farm. They recommend a similar study of stability of Millon's base if synthesis proves feasible. The panel recommends no additional work -- except perhaps radiation studies -- on silver nitride.
- The panel concurred with SRTC conclusions that caustic environment and radiation destroyed energetic compounds. However, the panel recognized that the addition of a caustic solution to the dry-sludge tanks might not effectively re-wet all the sludge and, therefore, reliance should be placed in degradation due to the radiation environment.
- The panel strongly recommends additional stability tests of energetic compounds -- mercury fulminate, mercury oxalate, and Millon's base -- in a high radiation field (1 Mrad/h) as a first priority. If an energetic material survives this test, then propagation studies may prove necessary to fully resolve safety concerns.
- The panel recommended additional impact test to determine the minimum impact energy and the highest fraction of energetic material in sludge if the radiation studies do not show marked (e.g. >90%) reduction in decomposition energy for the material over a relatively short period of time.
- The panel recommended contacts with Peter Hefferan and Gerald Laib as additional energetic material experts. They suggested review of additional literature work for completeness.
- The panel as well as SRS personnel found vendor test results inconclusive and confusing. The panel members, after further consultation with an additional expert in this technology, believes the vendor synthesis failed to

yield as pure a mercury fulminate as used by SRTC personnel (the X-ray diffraction and thermal analysis data support this interpretation). As such, the panel members found the SRTC findings more credible. The panel recommends radiation stability testing of the vendor synthesized material only if readily available.

REFERENCES:

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- [2] D. T. Hobbs, "Possible Explosive Compounds in the Savannah River Site Waste Tank Farm Facilities," WSRC-TR-91-444, Rev. 1, April 30, 1995.
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- [7] Mercury Oxalate," SRS Material Safety Data Sheet Equivalent #26988.00.
- [8] "Mercury Fulminate," SRS Material Safety Data Sheet Equivalent # 26970.00.
- [9] "Silver Nitride," SRS Material Safety Data Sheet Equivalent # 26970.00.
- [10] L. O. Dworjanyn, "Vendor Testing Of Sensitive Compounds In Simulated Dry Sludge," WSRC-RP-99-00428, June 1999.

ATTACHMENT 1

New Mexico Tech

Dr. Kirk Yeager
New Mexico Tech/EMRTC
Socorro, NM 87801
July 22, 1999

Bill,

Here is our final report on your efforts. I have enclosed a bound copy for archive purposes and a loose copy for replication. The general report emphasizes the suggestions that Marv and myself made when we were on site. If you have any questions, please feel free to contact either me or Marv. Thanks for the hospitality while we were out there. We both enjoyed our visit.

Sincerely,

Kirk Yeager, PhD
(Acting Associate Director of Research and Development)

R C E M

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EMRTC

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**ANALYSIS OF RESEARCH EFFORTS EXAMINING ENERGETIC
COMPOUND FORMATION IN DRY HIGH-LEVEL WASTE SLUDGE**

EMRTC Report No. FR 99-14

Final Report Submitted to:

**Bill Wilmarth
Savannah River Technology Center
773-43A
Aiken, SC 29808**

by

**Dr. Kirk Yeager and Mr. Marvin Banks
Principal Investigators**

July 1999

Introduction: From 6/13/99 to 6/14/99 both Dr. Kirk Yeager and Mr. Marvin Banks visited the Savannah River Site (SRS) to receive briefings on their efforts to study the potential of energetic material formation in dry high level waste sludge. This report will provide impressions of the research covered, analysis of results presented, and suggestions for future experimentation to complete the study described.

Background: The overall impression of EMRTC researchers was that the major concerns being addressed by SRS could be broken into two categories. Of initial importance is whether or not energetic materials could exist at all in the dry sludges. This concern encompasses two main issues; a.) whether or not conditions in the tanks would allow for formation of explosives, and b.) what would be the survivability of suspected explosives under the hostile tank environments. Presupposing that explosive compounds could both be formed and maintain integrity in the tanks, the second concern would be what hazards these materials could introduce. Under this area of study come the issues of a.) what amount of energy it would take to initiate entrapped explosives, and b.) what potential exists for propagation of an explosion through the sludge body if some of the material is initiated.

The overall problem can be viewed as a decision hierarchy with four stages. Each stage poses a question, with the answer dictating whether work has to be conducted on the stage below it. Figure 1 gives an overview of this hierarchy.

Figure 1 – Decision making hierarchy

Each stage in the hierarchy will be addressed in terms of analysis of the experiments conducted to date and suggestions for work needed to provide closure to the issues. An overview of concerns was provided to EMRTC researchers by SRS personnel. Specific areas were highlighted for comment. Before their departure from SRS, EMRTC personnel provided an "out-brief" addressing the concerns given to them. The outline of Questions posed by SRS, followed by the EMRTC briefing is provided in Appendix A. All concerns called out in the original SRS listing of questions will be addressed in this report.

Discussion: Each stage in the hierarchy will be covered as a separate unit.

Stage 1 – Can explosives form in sludge?

A tremendous body of work was done addressing this issue. In general it looked as if the chemical environment needed to produce a significant amount of explosives was not present. However, it was not possible to discount this possibility. Due to the high degree of certainty required in this situation, it was not possible to dismiss the presence of some level of explosive contamination. The past history of silver nitride alone makes it hard to argue against the freak production of energetics.

The relatively low levels of silver present in the dry tanks would argue against the formation of any *significant* amounts of silver compounds. For this reason, the detailed study of silver nitride may very well be overkill. A concentrated effort on the other potential explosives seems more prudent.

Study of mercury compounds does seem reasonable. The scenario of mercury combining with waste constituents to form primary explosives remains a remote possibility. SRS provided a well thought out overview of potential explosives which might exist in the tanks. Selection of mercury oxalate and fulminate for further study seemed logical. As pointed out by SRS scientists, the use of fulminate as a surrogate for the more likely (albeit unstable) mercury compounds formed brings certain problems with it. Care must be taken in both stressing that

fulminate is only intended as a surrogate, and in generalizing fulminate data to reach conclusions about the other compounds suspected present.

Concern was raised over potential literature references which might have gone unnoticed. As most of the research covered was dedicated to the mercury-based explosives, a review of two well respected literature sources was conducted for these materials [1,2]. The results are provided in Appendix B, and will be used later in the report to support various conclusions drawn. Both oxalate and fulminates were stressed. No references could be found to Millon's base or related compounds. Vendor information for procurement of the literature sources utilized is given in Appendix C.

Stage 2 – Will the tank environment destroy any explosives formed?

Detailed studies of both mercury fulminate and oxalate were conducted to see if these compounds could withstand the hostile tank environments of high radioactivity and strong alkalinity. As both compounds were able to survive neutral dry sludge, extreme simulations had to be tested to determine their reaction to more realistic conditions.

Tests of the effects of caustic conditions on both materials showed promise. It seemed that neither mercury compound held up well to this environment. Unfortunately, the debate as to whether the compounds in the dry tanks saw sufficient caustic environments, or could be re-wetted effectively to introduce additional caustic, made the logistics of this scenario too tentative.

In all cases it was agreed upon that high levels of radioactivity were present in the tanks. It is the opinion of EMRTC researchers that tests examining this effect showed the most promise of all of the research conducted. As both compounds showed significant decay (as displayed by DSC exotherms) with a dosage equivalent to only 1.5 hours in a tank, logic dictates that the time span of months or years should essentially eradicate them.

One important experiment that remains to be done is a greater dosing of the explosives being studied. Oxalate displayed the greatest extent of decomposition under the dosing tested, with a

decrease to 1/3 of its initial energy output. To feel fully confident in the ability of radiation to remove these explosives, it would be desirable to see a decrease in their presence on the scale of an order of magnitude or greater. This would serve as a much more definitive result.

At this point, the research results of the vendor should be mentioned. Whereas SRS scientists conducted a sound series of experiments in the opinion of EMRTC reviewers, vendor results tended to obscure some issues. Most importantly was the difference in the vendor fulminate. Again, it must be borne in mind that fulminate is not anticipated to exist in the tanks, but its use as a surrogate does require consistent results between SRS and its vendor.

After consulting other experts in the field, the behavior of SRS fulminate was confirmed to match that ideally expected [3]. The high temperature decomposition and complicated peak shape exhibited by the vendor fulminate shows that they did not obtain a pure form of the explosive. Of the literature presented in Appendix B, the experiments that best corroborate the results of SRS are given by Davis [4]. In the test described, mercury fulminate heated in a glass tube at 20°C per minute gave explosive decomposition at 175°C. Both the conditions of the test and the results obtained closely match SRS data. No explanation can be given for the cause of the discrepancies displayed by the vendor fulminate.

External vendor data was sought to validate in-house testing at SRS. Unfortunately, the fulminate issues cloud this goal. It is the opinion of EMRTC reviewers that SRS fulminate was the better of the two compounds tested, and the results obtained with this material the more believable. The complexity of the vendor product makes interpretation of their results problematic. Two approaches seem to be available to resolve the issues raised. First, vendor data on fulminate can be ignored, as majority opinion favors the SRS product. Second, if any minor doubts remain, vendor "fulminate" can be irradiated to see if it also rapidly decomposes under doses expected in the tanks. Unavailability of vendor product would limit the options.

It should be stressed that of all the stages being examined, the explosive survivability issue exists as the most "black and white". If the suspected materials are found to be unable to survive under the harsh tank conditions, all other issues become moot. Studies of initiation and propagation

become much more complex and difficult to relate to "real-world" conditions. The potential for explosives to segregate out in strata (or pockets) creates complexity in any analyses conducted in these next two stages.

Stage 3 – Will explosives diluted in the sludge initiate?

The main thrust of the research in this stage was to determine if sampling techniques designed to get cores of the sludge would initiate entrained explosives. As mentioned above, this area becomes much more difficult to interpret as problems arise in simulating the sludge body with small scale tests. Most tests used to measure sensitivity of explosives to insult operate with relatively small samples (20-40 mg). Reproducing conditions present in the tank body may not be possible with such a small sample. Therefore, the results of these tests must be taken in the context of the broader problem.

Use of the drophammer to probe sensitivity to impact seemed valid. This is the industry standard test, and provides good data. SRS chose to gently mix sludge with fulminate crystals. There is little else that can be done in terms of mixing. SRS researchers also chose to run the impact tests at full energy input. The use of lower insults might be advisable, as will be discussed below.

EMRTC reviewers were told of the problems that occurred in judging whether or not the explosively spiked sludges initiated. The production of smoke and color change was utilized to determine if the pure fulminate initiated. Color change was not a good indicator for the sludge samples, as they started out a similar color to the reacted fulminate. This left the presence of smoke as the only indicator. No smoke was seen for the sludge samples, which was taken as a sign that they did not initiate. Unfortunately, some SRS data seemed to point towards the presence of elemental mercury in the impact tested samples. This would be a sign of initiation. The net result of these tests introduces some unwanted ambiguity.

It is suggested that a few additional experiments be conducted to resolve some of the issues that arose during these impact tests. Of prime importance is gaining a better consensus of whether a sample has initiated or not. To do this, several approaches can be taken. First the percentage of fulminate in the sludge can be increased until an obvious sign of initiation is observed (such as

visible smoke). The 3 mg of pure fulminate may not produce enough smoke when surrounded by all the particulate matter of the sludge. Another way to judge a reaction would be to make a surrogate sludge out of white solids such as sodium nitrate and alumina. This would make it easier to see any dark spots in the impacted sample. Once a level of comfort is reached with the ability to judge whether or not a sample was initiated, quantification of the energy needed to create reaction should be done. Some idea of how much energy input is needed to create an initiation of the fulminate in sludge would be valuable. This number would provide a base-line value for types of sampling that could be undertaken with a margin of safety. It should be noted that there is almost no way that pockets or strata of explosive in the sludge can be accounted for with the small-scale tests. At best a bracketing region of energy could be derived with pure fulminate on one end, and the fulminate diluted in the sludge at the other extreme. The uncertainty surrounding the exact nature of the sludge introduces an unavoidable uncertainty.

Stage 4 – If initiated, can the resulting explosion propagate through the sludge?

A shock, caused by a hand tool being dropped into the sludge (or by a natural disaster) could initiate an explosion. There is a concern that if concentrated areas of mercury or silver formed into primary explosive that these concentrated pockets could be initiated by a shock and the resulting explosion propagate through the sludge layer. At present, no tests have been conducted to examine the potential of this scenario. If the further testing recommended above shows that explosives are not destroyed by tank conditions, testing for propagation feasibility would be recommended.

Although the concentration of the mercury or silver compounds would be low (7% or less), detonation tests could be run on a "worst-case" surrogate sludge to determine if propagation would occur. Tests of this type are performed in a steel pipe (high confinement) to reproduce a "worst-case" scenario. The sludge could be loaded to 150% or greater concentration with mercury fulminate, thus allowing a rather large safety factor. The device would be initiated with a booster and detonator or hot wire. Velocity pins would be mounted on the tube wall to track the progress of the shock wave inside the tube. Velocity pins increase the confidence level of results because, in many instances, fragments are hard to recover if the shock propagates to a full detonation.

The steel confinement tube (pipe) should be as large as possible, but because the surrogate sludge has to be manufactured in the laboratory, it would be necessary to limit the inside diameter and the length. Two tests on each mixture, using a tube with an inside diameter of 2-inches and a length of 10 times the diameter, is suggested. Figure 2 shows the general test hardware after a non-propagation.

Figure 2. Results of "High Temperature Gap Test" that did not propagate a detonation. The booster caused the banana peeling effect at the left hand side of the tube. Broken heating belts (red) can be seen.

One method of initiating the experiment is with a detonator and a booster. The booster would have the same diameter as the shock tube and have a length $1 \frac{1}{2}$ times the diameter. The booster would be packed with Composition C-4 high explosive. An alternative method is to load the end of the device with mercury fulminate and initiate the primary explosive with a hot wire. The hot wire would be made from a short piece of resistance wire connected to a power source.

Ancillary Issues: To ensure complete understanding, the questions posed by SRS (and provided in Appendix A) will be addressed sequentially.

1. Do you recommend any additional tests?

Several additional tests were outlined in the report above. The most important of all tests recommended would be the increased dosage of the test explosives. As the destruction of these materials through irradiation would mitigate all other concerns, this should be top priority. In addition, if possible, it would be a good follow through to irradiate both the vendor fulminate and a sample of Millon's base (if it could be successfully made). This would aid in closing all potential concerns. Additional drophammer tests were discussed, as well as tests for propagation. Whether these should be pursued simultaneously with radiation tests remains a decision that SRS needs to make. The testing scheme to date at SRS has addressed multiple issues at the same time. This approach seems wise if resources allow its continuation, as time will be saved if one avenue proves fruitless.

2. Do the proposed tests with silver nitride add significant value to the current data?

The problems described by SRS personnel in isolation of this compound seem to indicate that its existence would imply that no handling procedures could be implemented at all in its presence. Fortunately the low concentration of silver seems to dictate that little of the material should be able to form. At present, tests with the nitride might only serve to complicate the main issues. If any tests should be conducted with it, they should be limited to radiation experiments. Great care is recommended if work is continued in this area.

3. Should we consult with other individuals or organizations?

Two individuals with unique talents in the area of primary explosives were mentioned. Peter Hefferan has already been contacted by EMRTC researchers, and was given contact information for Bill Wilmarth. Perhaps one of the nation's experts on primary explosives is Gerald Laib. He can be reached for consulting work on energetic materials at (301)-774-5049.

4. Do you know literature data that we overlooked or sources we should investigate?

Relevant literature has been included in Appendix B, with vendor sources to procure it given in Appendix C.

5. Have we investigated at sufficient scale to conclude safety of operations?

The DSC scale experiments are ideal to determine the survivability of materials in different configurations. In general, these experiments will provide good reliable data for Stage 2 concerns. Drophammer results are more problematic. The issue of replicating tank conditions with milligram scale samples was addressed. Short of moving on to larger scale propagation techniques, little can be done to compensate for this shortcoming of small-scale testing methodologies. If it is determined that explosives can survive in tank conditions, larger experiments will be deemed of significant value.

6. Would you recommend alternate sample preparation of handling methods?

Overall methods described by SRS seemed safe and adequate for the operations. The use of glass for explosives synthesis poses inherent risks. Most importantly, glass does not show up on an X-ray. This may make for unpleasant exploration of wounds if glassware becomes shrapnel. Lead glass, plastic, or metal are used in most EMRTC operations when feasible. Keep sample size in the region discussed in the briefings. Scaling up to even the gram level can create a tremendous increase in hazards.

7. Do any specific test results cause concern?

The presence of significant amounts of explosives after short-term irradiation shows the need for larger dosage experimentation. The data produced by SRS seemed sound and well analyzed. Discrepancies in vendor data did not produce much confidence overall. Ideas were provided to overcome this shortfall.

The overall use and interpretation of the Carius tests conducted by the vendor did create some concern. The vendor reported the results of five tests and submitted a profile for a sixth. The Association of the British Pharmaceutical Industry furnished the guidelines for the Carius tube tests ". The appropriateness of this test for explosive materials is not known.

In order to evaluate the vender data, Table 1 was constructed. The final pressure at 250°C (from the vendors Carius tube profiles) was added to the table in order to try and form a trend caused by the addition of MF to the sludge. The pressure readings were taken from the graphs found in Appendix 5 of the vendors report. References will be made to pages 26 and 27 of 32 found in "Report No.: WE1905RP". Any data added to the table by EMRTC will be in bold script.

Sample Name	W _{MF} (grams)	T _{onset} (°C)	T _{gas (onset)} (vendors P _o) (°C)	Pressure at 250°C (psig)
Mercury Fulminate (MF)	2.37	186.34	185.57	319
10% MF in CS Run 1	0.3026	N/D No exotherm	140.1 Onset ???	23
10% MF in NS Run 2	0.3067	N/D No exotherm	140.1 No onset	37
10% MF in CS Run 3	1.020	114.63	141.96	209
10% MF in NS Run 4	0.991	117.5 No exotherm	148.79 No onset	603
Run 5 (Repeat of Run 4)		No exotherm	No onset	517

Table 1. Data from the vender report with additions made by EMRTC

The following comments can be made about the specific results:

- a.) The cook-off profile of the mercury fulminate (MF) test provided by the vender is very good. This would be normal for this kind of material.
- b.) Run 1 has no onset temperature, but an onset temperature of 140.1°C is given for the pressure. This pressure rise may or may not have a relationship to the reaction of MF.
- c.) Run 2 profiles do not appear to have an onset temperature, but an onset temperature of 140.1°C is given for the pressure. There is no obvious pressure acceleration shown on graph CWE1965e/f.txt. Moisture and many non-energetic materials will result in profiles similar to this. It would seem difficult to identify a temperature/pressure threshold without a temperature response caused by a reaction.
- d.) For Run 3, the vendor identified an onset temperature of 114.63°C and a temperature at which gas generation began to accelerate (141.96°C). From the profile, it appears that the onset temperature starts at 127 to 130°C rather than the temperatures reported.

- e.) The profile for Run 4 shows neither an onset temperature nor a point of accelerating gas production. No conclusions can be drawn from this test. The profile of the repeat of Run 4 (Run 5) shows no reaction occurred.

The conclusions drawn by the vender seem hard to justify after carefully reviewing the data. Since no baseline tests were performed on the caustic sludge or the neutral sludge, it is hard to judge the effects of the addition of small amounts mercury fulminate. If consideration is given to the pressure at 250°C, the results become even more confusing.

If the thermal data is needed to support the (SRTC) DSC data, the above series should be repeated. The small sample sizes limits the amount of gas that can be produced. It is suggested that larger sample sizes be used for the next round of tests. One-liter tests would introduce sample sizes which would allow any reactions taking place to be easily identified. It is imperative that at least one baseline test be run on both the caustic sludge and the neutral sludge. There is no way to interpret profiles from the "loaded" cook-off tests without knowing how the sludge behaves without mercury fulminate added.

The tests should have been run in triplicate. Experience has shown that making a judgment on the results of only one test is risky. One baseline test on each of the "unloaded" surrogate sludge samples should be sufficient.

The SRTC research group has obtained very good data from their DSC tests. It would be valuable to have data from a larger scale tests to support their findings. EMRTC does not feel that the vender data contributes much support.

8. *Would you recommend testing with any alternate energetic compound?*

Testing with surrogates of suspected mercury compounds may lead to "philosophical" debates about their applicability to real-world problems. If possible, some additional tests with the most likely candidates would be prudent. These tests should be limited to radiation survivability, as this is the most definitive experiment. Fulminate will provide a worse case scenario in other test areas.

9. *Do you know of other instances of energetic materials formed in highly alkaline solutions?*

Normally a basic environment is used to dispose of most energetic materials. Their formation in this type of situation is not common.

10. *Do you know of any industry analogies we should consider?*

Your industry has too many unique variables (such as high levels of radioactivity) to readily compare to any others.

11. *Do you believe any energetic compounds likely survive these environments (i.e. caustic and radiation)?*

EMRTC reviewers would find the likelihood of any of these materials forming in the first place remote. Data for both caustic and radiation destruction of explosives makes it unlikely that these materials would survive. The logical tests to provide more definitive proof of this have been suggested.

References:

1. Tenney L. Davis, The Chemistry of Powder and Explosives, John Wiley & Sons, NY, 1956.
2. Encyclopedia of Explosives and Related Items, Picatinny Arsenal, Dover, NJ.
3. Private conversations with Peter Hefferan of Cartridge Activated Devices.
4. Tenney L. Davis, The Chemistry of Powder and Explosives, John Wiley & Sons, NY, 1956, p 435.

APPENDIX A

SRS questions about research efforts

&

EMRTC “out-brief” outline

Questions to Consider in Developing Report

- Discuss the completeness of the program.
- Do you recommend any additional tests?
- Do the proposed tests with silver nitride add significant value to current data?
- Should we consult with other individuals or organizations?
- Do you know literature data we overlooked or sources we should investigate?
- Have we investigated at sufficient scale to conclude safety of operations?
- Discuss the validity of the experimental work.
- Would you recommend alternate sample preparation or handling methods?
- Do any specific tests results cause concern?
- Comment on the chemistry of interest for this application.
- Would you recommend testing with any alternate energetic compound?
- Do you know of other instances of energetic materials formed in highly alkaline solutions such as our waste?
- Do you know of any industry analogies we should consider?
- Do you believe any energetic compounds likely survive these environments (i.e., caustic and radiation)?

MAIN ISSUES

- Do primary explosives exist at all in sludge
 - Are they formed
 - Do tank conditions destroy them
- Will sludge propagate detonation
 - Sensitivity to initiation
 - Energy absorption of buffer

General Impressions

- Approach
 - Two pronged simultaneously wise
- Experimentation
 - WSRC work thorough and well executed
- Vendor Validation
 - Tendency to cloud the issue

Program Completeness

- Additional Tests (Existence)
 - Higher levels of irradiation of both oxalate and fulminate
 - Irradiation of Chilworth fulminate
 - Potential irradiation of Millon's Base (to avoid getting into circular arguments about surrogates)

Program Completeness

- Additional Tests (Propagation)
 - Drophammer with surrogate (white) sludge
 - Determine if initiation occurs
 - Determine what initiation energy truly is
 - Alternative: Increase fulminate % in sludge until an observable “Go” occurs

Program Completeness

- Additional Tests (Propagation)
 - Larger scale cook-off, thermal run-away
 - Gap test
 - Ignition test
 - To be run in the event that existence of energetic materials is believed to survive irradiation

Program Completeness

- Silver Nitride
 - Tests of limited value
 - Silver in low concentration
 - Handling very problematic
 - Need cost/benefit analysis
 - Immediate impressions are against

Program Completeness

- Individuals
 - Gerald Laib (NSWC); Primary explosive expert
 - Peter Hefferen (CAD); Primary disposal specialist

Program Completeness

- Literature Sources
 - Picatinny Encyclopedia of Explosives and Related Items
 - Tenney L. Davis, The Chemistry of Powder and Explosives

Program Completeness

- Scale of testing
 - Small-scale (DSC, Impact) good for determination of existence
 - Propagation needs to be on intermediate scale

Validity of Experiments

- Alternate Sample Prep
 - Discusses surrogate sludge for impact
 - Resolve discrepancies in fulminate
- Alternate Handling
 - None immediately apparent

Validity of Experiments

- Concerns over test results
 - Carius tests did not include baseline runs for the sludge samples
 - Chilworth vs. WSRC fulminate issues
 - Uncertainty in initiation in drophammer
 - Results of more representative doses on explosives

Chemistry of Interest

- Alternate energetic compounds
 - Minimum of literature search on suspected Hg compounds
- Other instances with alkaline solutions
 - Needs further research, none currently known

Chemistry of Interest

- Industry analogies
 - None of this complexity
- Survivability of compounds
 - Initially would seem unlikely
 - Need higher dosing experiments for more definitive data

APPENDIX B

Literature Review of Explosives

Based on Mercury

Studied by SRS

ENCYCLOPEDIA OF EXPLOSIVES AND RELATED ITEMS

**PATR 2700
VOLUME 8**

BY

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1978

(Oct 1963), 45-6 7) Merck (1968), 194-L
8) CondChemDict (1971), 158-L 9) Sax
(1975), 512-L & 988-L

Lead Oxalate. PbC_2O_4 , mw 295.23; wh, heavy powd; mp, decomp 300°; d 5.28g/cc. Insol in w, sl sol in acet ac, sol in dil nitric ac & fixed alkali hydroxides. *Poisonous!*

Warren (Ref 1) evaluated Pb oxalate as a possible replacement for MF in primer compns, and concluded that it lacked the sensitivity necessary for an initiating agent. Sensitivity data obtained are given below:

<i>Drop Test.</i> (BurMines app; 2kg wt)	100+ inches
<i>Expln Temp Test, 5 sec.</i>	> 500°
<i>Sand Test</i> (200g bomb)	
Initiation by fuse, g sand crushed	0
Initiation by 0.3g MF, g sand crushed	0

There is no US Mil Spec for Pb oxalate
Refs: 1) K.S. Warren, "Properties of Possible Constituents of Primer Compositions. Metallic Salts of Chlorous and Oxalic Acids", PATR 1389 (1944) 2) Merck (1968), 613-R

Mercurous Oxalate. $\text{Hg}_2\text{C}_2\text{O}_4$, mw 489.22, wh cryst powd. Prepd by Souchay & Lenfsen (Ref 2) by treating sol mercurous salts, such as the nitrate, with oxalic acid. Insol in cold w, alc & eth; decompd by hot w; insol in dil sulfuric acid; sol in dil hydrochloric and nitric acids

Explds on impact (Ref 2); does not expld or deflagrate on heating or rubbing in a porcelain mortar (Ref 3)

There is no US Mil Spec for Mercurous oxalate
Refs: 1) Beil 2, 516 & [489] 2) A. Souchay & E. Lenfsen, Ann 103, 308 (1857) 3) A. Langhans, SS 15, 89-90 (1920)

Mercuric Oxalate. HgC_2O_4 , mw 288.61, wh cryst powd; mp, decomp. Prepd by Souchay & Lenfsen (Ref 2) by adding an aq soln of mercuric nitrate to an aq soln of oxalic acid. Insol in cold w, difficulty sol in hot w and dil sulfuric acid; sol in dil hydrochloric and nitric acids

Explds on heating or impact (Ref 2); deflagrates on rubbing in a porcelain mortar (Ref 3)

Warren (Ref 4) evaluated mercuric oxalate as a possible replacement for MF in primer compns, and concluded that it lacked the sensitivity necessary for an initiating agent. Sensitivity data obtained are given below:

<i>Drop Test</i> (BurMines app; 2kg wt)	95 inches
<i>Expln Temp Test, 5 sec</i>	170°
<i>Sand Test</i> (200g bomb)	
Initiation by fuse, g sand crushed	0
Initiation by 0.3g MF, g sand crushed	6.5

There is no US Mil Spec for Mercuric oxalate
Refs: 1) Beil 2, 516 & [489] 2) A. Souchay & E. Lenfsen, Ann 102, 42-44 (1857) 3) A. Langhans, SS 15, 89-90 (1920) 4) K.S. Warren, "Properties of Possible Constituents of Primer Compositions. Metallic Salts of Chlorous and Oxalic Acids", PATR 1389 (1944)

Note: R. Philip reported that Hg oxalates are always present as impurities in commercial MF, and that the determination of Hg is not sufficient to give the true fulminate content [R. Philip, SS 7, 110, 156, 180, 198 & 221 (1912)]

Potassium Oxalate. $\text{K}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$, mw 184.23; colorl, odorless crysts; mp, loses H_2O at about 160°, when ignited is converted into carbonate without appreciable charring; d 2.13g/cc, sol in 3p of w. Can be prepd by heating a mixt of K formate or carbonate with oxalic acid and a small amt of K hydroxide, with subsequent extraction of w. Highly toxic by inhalation and ingestion

K oxalate was used as a cooling agent in mining expls such as Oxalate Blasting Powder (see in this Vol) and Gelatine-Prosperit (see in Vol 6, G52)

There is no US Mil Spec for K oxalate
Refs: 1) Beil 2, 513, (224) & [485] 2) Daniel (1902), 592 3) Naoúm, NG (1928), 418 4) Merck (1968), 856-L 5) CondChemDict (1971), 723-R

Silver Oxalate. $\text{Ag}_2\text{C}_2\text{O}_4$, mw 303.78, wh cryst powd; mp, decomp violently between 130° & 190° (see below); d 5.03g/cc. Sol in 24000p of w, moderately concd nitric acid, and ammonia. Can be prepd by mixing cold solns of oxalic acid and Ag nitrate (Refs 1, 2 & 6)

ENCYCLOPEDIA OF EXPLOSIVES AND RELATED ITEMS

**PATR 2700
VOLUME 6**

BY

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THE FRANKLIN INSTITUTE RESEARCH LABORATORIES

**PICATINNY ARSENAL
DOVER, NEW JERSEY, USA
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of Amm iodide on SF. It is a less violent expl than SF [Ref 1, p [777]]

Cadmium Fulminate, $\text{Cd}(\text{ONC})_2$; mw 196.45, N 14.26%; wh crystals, mp - expl at 215° in 5 sec; sol in w & methanol; sl sol in ethanol. Can be prepd by shaking Cd amalgam with MF dissolved in methanol. Heat of deton 470 cal/g. It is a powerful expl resembling MF in its props. It is stable when kept dry but decomp in the presence of moisture. Smallest amts which cause detonation of: Tetryl 0.008g, PA 0.05g, TNT 0.11g, TNAnisol 0.26g & TNXylene 0.35- [Ref 1, p (376) & Ref 23, pp 407 & 411]

Copper (I) Fulminate or Cuprous Fulminate. See Vol 3 of Encycl, p C520-R and Davis (Ref 23, p 407) gives smallest amts of Copper Fulminate which cause detonation of: Tetryl 0.025g, PA 0.08g, TNT 0.15g, TNAnisole 0.32 & TNXylene 0.43g

Copper (I) Fulminate Explosive Complexes, listed below are described in Vol 3 on pp C520-R & C521-L:

Copper(I)-barium Fulminate, $\text{Ba}[\text{Cu}(\text{ONC})_3] \cdot 4\text{H}_2\text{O}$

Copper(I)-calcium Fulminate, $\text{Ca}[\text{Cu}(\text{ONC})_3] \cdot 4\text{H}_2\text{O}$

Copper(II)-dicopper(I) Fulminate, $\text{Cu}[\text{Cu}_2(\text{ONC})_4] \cdot 2\text{H}_2\text{O}$

Copper(I)-disodium Fulminate, $\text{Na}_2[\text{Cu}(\text{ONO})_3] \cdot 3\text{H}_2\text{O}$

Copper(I)-sodium Fulminate, $\text{Na}[\text{Cu}(\text{ONC})_2]$

Copper(I)-strontium Fulminate, $\text{Sr}[\text{Cu}(\text{ONC})_4] \cdot 2\text{H}_2\text{O}$

Mercuric Fulminate or Mercury Fulminate

[Fulminate de mercure in Fr; Knallquecksilber in Ger; Fulminato di mercurio in Ital; Fulminato de mercurio in Span; Gremuchaya rtut' in Russ; and Raikō or Raisan suigin (Thunder Mercury) in Japan], $\text{Hg}(\text{ONC})_2$. Structural formula not established. Pepin Lehalleur (Addnl Ref J, p 141) proposed $\text{Hg}(\text{ON} \ddot{\text{C}})_2$ and that of Scholl

$\text{Hg} \begin{array}{l} \text{ON} \ddot{\text{C}} \\ \text{ON} \ddot{\text{C}} \end{array}$; mw 284.65, N 9.85%, OB to CO_2 -17% & to CO -5.5%; hydrate $\text{Hg}(\text{ON} \ddot{\text{C}}) \cdot \frac{1}{2}\text{H}_2\text{O}$ (crystd from w) (Ref 23, p 410) has mw 293.64, N 9.55%. Anhydrous form (crystd from alc) is

white to grey crystals of density 4.42-4.43, exploding at 210° in 5 sec; its apparent density is 1.55 to 1.75; when subjected to pressures of 3, 10 20 & 50 thousand psi, densities of 3.0, 3.6, 4.0 & 4.3 are obtd. Pressures of 25 to 30 thousand psi (or more) cause the desensitization of MF to the extent of becoming *dead-pressed*. Such material merely ignites and burns when subjected to contact with flame, but it can be detonated if it is covered with a layer of loose or sl compressed MF and ignited

MF is sol in 1 liter of w to the extent of: 0.71g at 12° , 1.74 at 49° and 7.7 at 100° (Ref 23, p 410); only sl sol in cold ethanol. It decomp in the presence of aq solns, chlorides, carbonates, hydroxides etc. Due to the presence of small amts of Hg, formed by exposure of MF to light or elevated temps, it readily forms amalgams with Co, brass or bronze, thus components contg these metals must be protectively coated if used with MF. MF is also sol in pyridine and aq NH_3 or K cyanide and can be recovered from pyridine by adding w and from NH_3 & cyanide solns by adding acid

MF reacts with concd HCl to form hydroxylamine, $\text{H}_2\text{N.OH}$, & formic acid, HCOOH , and it reacts with Na thiosulfate in aq soln to form Hg tetrathionate, accdg to the equation:

This reaction can be used for detm of purity of MF

Preparation of MF

MF was first prepd in the 17th century by Swedish-German alchemist Baron Johann Kunkel von Löwenstern living from 1630 to 1703 (Hackh's Dict gives 1638 as date of birth). He obtd this dangerous expl by treating mercury with nitric acid and alcohol. The method was described in the book of Kunkel published in 1716 after his death. This book is listed and the prepn is briefly described by

Davis (Ref 23, p 404) and Pérez Ara (Ref 24, p 541). A brief biography of Kunkel is given in Ref 24, p 541 and in Hackh's (1944), p 474

As no use of Kunkel's expl was found by him and by other alchemists, the compd became forgotten until Edward Howard of England rediscovered it in 1799-1800. He described its prepn in *PhilTransRoySoc* 1800, 204, and his method of prepn is given in Davis (Ref 23, p 404). Howard examined props of MF but it does seem that he proposed its use as a *percussion initiator* of BkPdr. This honor belonged to the Scottish Clergyman Alexander Forsyth who patented in 1807 in England such a device. The history of this and of later development of MF initiators and of various types of cartridges is described in Vol 5 of *Encycl*, p D755-R & D756-L. More important application of MF was in A. Nobel's Blasting Cap invented in 1867. This cap was used for detonation of NG and Dynamite (See "Fulminate Blasting Cap" in Vol 5 of *Encycl*, p D1588-R).

Besides describing Howard's method, Davis (Ref 23) described on p 406 a laboratory method using 5g of Hg. We found that it is safer to start with 2g Hg and to proceed as follows:

Laboratory Preparation:

- 1) 2g of pure redistd Hg is added to 10ml of pure nitric acid (sp gr 1.42) in a 100-ml Erlenmeyer placed under a hood and left there without agitation until complete dissolution
- 2) The resulting soln of Hg nitrate in excess of acid is poured into 20ml of 90% alcohol contd in the 2nd 100-ml flask, which is placed in a trough of running water located under a hood and behind a safety glass or plastic. A vigorous reaction results, accompanied first by evoln of white fumes, then by brownish-red and finally again by white fumes. At the same time crystals of MF deposit on the bottom of the flask. After about 20 mins, the fuming ceases and the contents of flask are poured into a 250-ml beaker contg cold w. After the bulk of acid w has been removed by decantation, the crystals are transferred onto a Büchner connected with suction flask to be washed with w until it becomes neutral to litmus. This gives about 3.4g of crude greyish (due to presence of small amt of metallic Hg) product, which corresponds to good-grade commercial product. It can be

stored under water until a sample is required for expl purposes. Then part of product is dried in a desiccator

MF has been thoroughly investigated especially before and during WWI by Col Solonina of Russia (Addnl Ref A). Other investigators were Liebig, Chandelon, Bechmann, Tschelzof (Chel'tsoff), Wöhler, Martin, Langhans & Stettbacher (Ref 17, p 141)

Pepin Lehalleur (Ref 17, pp 143-44) described Liebig's and Chandelon's methods of manuf which have been used in France

Pérez Ara (Ref 24, p 545) briefly describes an industrial method using 1 kg of Hg, 9kg of nitric acid and 8-12kg of alcohol. He also describes on p 546 industrial methods of Bechmann, de Bruyn and of the Troisdorf Fabrik of DAG in Germany. All of these methods differ only slightly from the US method described below. The method of de Bruyn, instead of adding acidic Hg nitrate to alc, bubbles vapors of alc thru the soln of Hg in nitric acid. The reaction proceeds at 70°. In the method of the Troisdorf Fabrik, small quantities of Zn & Cu are added during dissoln of Hg in nitric acid (2g of Zn & 3g of Cu per 600g Hg and 5kg nitric acid). This method is claimed to give white MF

In all methods, except that of Troisdorf, the resulting MF is of greyish color due to the presence of small quantity of free Hg. Such MF is not suitable for loading into caps made of Cu or Cu-contg alloys such as brass or bronze. This is because free Hg attacks Cu forming a Cu amalgam, and this will react with MF to form Cuprous Fulminate which is less stable and more sensitive than MF

In order to avoid the formation during manuf of greyish MF, Solonina proposed adding 1.5g of CuCl_2 per each 50g of Hg during its dissoln in nitric acid, whereas Adler proposed dissolving in nitric acid a small quantity of Zn before adding Hg (4g Zn per 50g Hg)

Accdg to Davis (Ref 23, p 407), MF can also be prepd by replacing ethanol with acetaldehyde, paraldehyde, metaldehyde or dimethyl- and ethylacetal. Another method consists of

treating the Na salt of nitromethane with an aq soln of HgCl_2 at 0° to form a wh ppt of mercuric nitromethanate. This gradually becomes yel and when digested with warm dil HCl yields MF

MF can also be manufd by Biazzi Process. Since it is not described in Vol 3 of this Encycl, pp C501ff, under "Continuous Methods for Manufacturing Explosives" it is suggested that info be obtained directly from Dr Mario Biazzi, Ing, Vevey, Switzerland

Manufacture of MF in the USA

The following method used to be employed at Picatinny Arsenal and probably is still used in other US plants because a similar method is described in Ref 32 and Ref 35 (1967)

In order to produce MF of quality complying with requirements of US Military Specification JAN-M-219, all raw materials: mercury, nitric acid and ethanol should be of high purity
Procedure:

1) About 1 lb of pure, redistilled mercury was carefully added to an open earthenware vessel (or a 5 liter flask) contg 8 to 10 lbs nitric acid (d 1.4), which was in excess of the amount required by the equation: $3\text{Hg} + 8\text{HNO}_3 \rightarrow 3\text{Hg}(\text{NO}_3)_2 + 2\text{NO} + 4\text{H}_2\text{O}$

A large number of such charges were usually prepared and allowed to stand overnight until the Hg was completely dissolved

2) A 10 gallon Pyrex flask or balloon, contg 8-10 lbs of 95% alcohol and fitted with a reflux condenser, was placed on a rack in a trough with running cold water. This installation had to be either outside or in a building provided with an exhaust system

3) With the condenser removed, the acidic soln of mercuric nitrate was poured into the alcohol and then the condenser was replaced. After about 2-3 minutes, a violent reaction started and the liquid boiled with evoln of white fumes. Most of these fumes were recovered by the condenser, however. As the reaction approached the end point, the color of the fumes usually changed to brownish-red due to the decomposition of nitric acid by heat. As this heat might

also decompose the MF (which had just formed), a small quantity of dilute alcohol had to be added at this point to moderate the reaction. The reaction normally lasted about $1\frac{1}{2}$ hours and MF crystallized

5) After cooling the charge in the flask, it was dumped onto a cloth screen and the crystals of MF washed with cold running water to remove excess nitric acid and impurities known as "fulminate mud"

6) The washed MF was then drained and packed into cloth bags which were stored in tanks of water until required for use

For shipment, the bags were packed in barrels of wet sawdust

7) When required for use, the MF was removed from the bag and spread on a cloth in a thin layer and dried in a special building where the temp was carefully regulated to 43° (110°F)

8) The acid mother liquor and the water washings were neutralized with alkali, evaporated to recover the alcohol and treated to recover any Hg or its salts

The usual yield was about 1.25 parts of slightly greyish MF per one part of Hg. Its purity was 98-99%, which corresponded to usual commercial product (Ref 32, p 588 & Ref 35, pp 7-5 & 7-6)

The intermediate products of oxidation and nitration involved in the prepn of MF are as follows:

(Ref 35, p 7-6 & Ref 23, p 407)

Accdg to Ref 35, p 7-6, the above commercial product can be purified to 99.75% by dissolving it in concd Amm hydroxide, filtering the soln, cooling the filtrate, and reprecipitating slowly, adding concd nitric acid with rapid agitation, while keeping the temp below

35°. The pptd pure MF is washed with distd w until free of acid. The yield is 80–87%

Accdg to Ref 17, p 146, a fairly pure MF can be obt'd by rinsing the crude MF (packed on two layers of filter paper placed in a Büchner) with several portions of 80–85% ethanol, thoroughly removing by suction each rinsing and testing it by diluting with w. The completion of rinsing is indicated by absence of turbidity on addn of w

There are two other methods of purification listed in Ref 17, p 146. Steiner dissolved crude MF in concd aq soln of KCN followed by adding concd HCl and washing the resulting ppt with w. Solonina dissolved 1 part of crude MF in 7 parts of pyridine, filtered the soln and poured it into 100 parts of cold w

The size of the crystals of MF is an important factor. While very finely divided MF (consisting mostly of fragments of crystals) is undesirable because the crystals might contain large amt of impurities, thus diminishing the efficiency of MF, too large crystals are also not desirable because they are very sensitive to friction and shock. Therefore, the US Military Specifications such as JAN-M-219, provide a certain minimum and maximum size for crystals. Fig F24 reproduced from Ref 35, p 7-5, shows

FIG F24 MF Crystals

typical crystals magnified 125 times. The Fig 94 on p 409 of Ref 23 (not reproduced here) shows crystals for use in primer comps, magnified 35 times

If crystals of MF are so small that they look like colloidal particles, the material is very difficult to initiate even if it is nearly 100% pure

Explosive and Other Properties of MF (Refs 5, 7, 9, 11, 12a, 15, 16, 17, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 32, 33, 34, 35, 37 & 38) (Also Addnl Refs F, R, S, T & X):

Activation Energy. 29.81 kcal/mol; *Induction Period* 0.5–10 sec (Ref 34)

Ballistic Mortar Test – not found

Behavior Towards Flame. When a single crystal is ignited, it burns rapidly with a flash, but does not detonate; when a layer of crystals is ignited, a high order of deton takes place

Brisance by Sand Test in 200g Bomb. 0.4g MF crushes 17.9 to 23.4g sand compared with 48g for TNT, which means 27.3 to 59% of TNT. It is greater than LA and smaller than DADNPh

Compatibility with Metals. When dry – reacts rapidly with Al & Mg and slowly with Cu, Zn, brass & bronze. When wet – reacts immediately with Al & Mg and rapidly with Cu, Zn, brass & bronze. Dry or wet does not attack iron or steel (Ref 34)

Destruction of MF can be achieved by adding it, with stirring, to at least 10 times its weight of 20% Na thiosulfate. Some poisonous cyanogen gas may be evolved (Ref 34)

Deterioration of MF in Storage at 10–20, 30–35, 50 and 80°. See under Stability of MF in Storage
Detonation Rate for Pressed MF. 3500m/sec at d 2.0, 4250 at 3.0 & 5000 at 4.0 (Ref 34)

Electric Spark; Sensitivity to. MF is capable of being ignited by a spark from a person charged to less than 5000 volts, a condition that is possible in plant operations. Brown et al (Ref 27) give for Sensitivity to Electrostatic Discharge 0.025 joules (Ref 34)

Explosion (or Ignition) Temperature. 210° (in 5 sec), 237° in 1 sec & 263° in 0.1 sec (no cap used) (Ref 34)

Flammability Index – not found

Friction Pendulum Test. Expl on fiber & steel shoes (Ref 34)

Gas Volume Evolved on Explosion - 243cc/g (Ref 34)

Heat of Combustion. 938cal/g

Heat of Explosion. 427cal/g

Heat of Formation. 226cal/g

Heat Test at 100°. Explodes in 16 hrs (Ref 34)

Hygroscopicity. Gains 0.02% at 30° % 90% RH (Ref 34)

Impact Sensitivity Tests. Bur Mines App - 5cm for 2kg wt (20mg sample); Pic Arsn App - 4 inches for 1 lb wt (30mg sample) (Ref 34). It is more sensitive than LA of LStyphnate (Ref 35)

Initiating Efficiency of MF. Although MF is not as efficient an initiator as LA or DAZDNPh, it is satisfactory when used in conjunction with Tetryl, RDX or PETN boosters. During the 1st half century MF was almost the only initial detonating agent used and its efficiency was considered satisfactory (Ref 35)

Initiating Efficiency. Grams of MF Required to Give Complete Initiation: 0.25 for TNT,

0.20 for Tetryl, 0.19 for RDX and 0.17 for PETN (Ref 34). Also Expl D 0.85, TeN-Aniline 0.25 and PA 0.21. Rather different values are given by Davis (Ref 23, p 407): Tetryl 0.29, PA 0.30, TNT 0.36, TNAnisole 0.37 & TNXylene 0.40g

Initiating Sensitivity to Electrostatic Discharge. See under Electric Spark; Sensitivity to International Heat Test (75°). Loss in wt in 48 hrs 0.18% (Ref 34)

Loading Into Blasting Caps pressed at 3000 psi (Ref 23, p 410)

Plate Dent Test - not found

Power (or Strength) by Trauzl Lead Block

Test. 37 to 50% TNT (Addnl Ref T); 51% (Refs 12a & 34). It is more powerful by Trauzl Test than LA (Ref 35)

Rate of Detonation. See Detonation Rate

Rifle Bullet Impact Test - not found

Sand Test. See under Brisance

Sensitivity to Electric Spark or to Electrostatic Discharge. See under Electric Spark

Sensitivity to Initiation - not found

Sensitivity to Pressure. When pressed at pressures in excess of 25000psi, MF will

become *dead-pressed*, which means that it will not detonate either by flame, percussion or stab action. When such MF is ignited by heat or flame (as happens in electric detonators), it will burn but not detonate. However, it is possible to detonate the dead-pressed material by means of a strong Blasting Cap or by covering it with loose (or sl pressed MF) and then igniting the ensemble. In these cases the velocity of deton is even higher than for material that has not been dead-pressed (Ref 35 & Addnl-Ref T)

Specific Heat. 1.1cal/g/°C (Ref 34)

Stability. Accdg to Ref 35, p 7-7, the relatively poor stability of MF has been its most disadvantageous characteristic and the main reason for efforts to replace it with a superior substitute. The usual stability tests are only applicable to temps up to about 85° due to expln in a relatively short time at temps above 85°. When MF deteriorates, it is chiefly with the production of a

non-explosive solid rather than gaseous products of decompn. It has been found that when its purity has been reduced to approx 92%, the initiating efficiency is practically destroyed, although the material will explode when ignited. When purity has been reduced to 95%, the stability is considerably impaired. (Note: Because of the poor stability of MF, it is no longer permitted by the US Military for service use)

Stability of MF in Storage. MF of purity 99.75% has been found to require storage at 50° for 24 months to become deteriorated to 92% (Ref 35, p 7-7). Different results are given in Ref 34, p 203, where MF of 99.75% purity deteriorated in 18 mos to 94.81%, while 98.86% deteriorated at the same period to 79.99%. Still other results are given in Table 7-3 on p 7-7 of Ref 35. Here, after storage at 50° for 8 months, the purity decreased to 95% and after 11 mos to 92%. When stored at 80°, purity dropped to 95% in half a day and to 92% in one day. When stored at 30-35° purity dropped to 95% in 1.7 years and to 92% in 5.8 years. When stored at 10-20°, a purity of 95% was

obtd in 7-8 years, while 92% was obtd after 9-10 years

Stab Sensitivities at Various Densities are given in Table listed on p 202 of Ref 34

Storage. MF is stored under water and transported in a wet condition, because in the dry state it is extremely sensitive to any mechanical action. In winter it is stored in 50/50-water/methanol or water/ethanol. MF should never be stored together with any other expl(s) because the expln of even a relatively small amt of MF present in a dried state might cause the detonation of wet MF and other expls. If any of the material contg MF is spilled on the floor or table, it must be destroyed by washing with a satd soln of Na thiosulfate (Ref 35)

Thermal Conductivity. 1×10^{-4} cal/sec/cm/°C (Ref 34)

Thermal Stability. See Heat Test at 100°, International Test (75°) and Vacuum Stability Test at 100°

Toxicity of MF. Mercury and its compds are of recognized toxicity. The handling of MF is not unduly hazardous from a toxicity viewpoint, but should be done with the minimum contact with the skin. Its dust should not be inhaled and it has been recommended that, in order to avoid undue toxicity, the air in loading plant buildings should contain not more than 0.1mg of MF per cubic meter (Ref 35)

Trauzl Lead Block Test. See under Power (or Strength)

Vacuum Stability Test at 100°. Explodes (Ref 34)

Velocity of Detonation. See Detonation Rate
Volatility - not found

Uses of MF. Until the invention of LA (Lead Azide), MF was practically the only expl used both in primers, blasting caps and detonators, either by itself or in compns. When loaded alone in blasting caps [also known as "commercial (or nonmilitary) detonators"] it is subdivided into eight numbers accdg to the amt of MF contd in them: No 1 contains 0.30g, No 2 0.40, No 3 0.54, No 4 0.65, No 5 0.80, No 6 1.00, No 7 1.50 and No 8

2.00g. The Table on p 414 of Davis (Ref 23) gives also external dimensions in mm. This classification is international. Nos 6, 7 and 8 caps are the only ones manufd in the US and the No 6 is the one most commonly used (Ref 23, p 416). The fulminate in commercial and military detonators was first modified by mixing it with BkPdr, then with K nitrate, and later with K chlorate. The chlorate mixts soon attained commercial importance and by 1910 had largely displaced straight MF. These were "single component caps" which are described under "BLASTING CAP" in Vol 2 of Encycl, p B185-R. They are known in Gt Britain as "Plain Detonators" as mentioned in Vol 4, p D737, under "Non-military Detonators". Most commonly used mixts have been MF/KClO₃-90/10 and 80/10 and weight by weight they are more brisant than straight MF, when determined by Sand Test (See Table on p 417 of Ref 23). These mixts are more hygroscopic than straight MF, but are cheaper and slightly safer to handle and to load. Plain detonators have been largely (but not wholly) displaced during and after WWII by Compound Detonators, which are described as "Compound Caps" in Vol 2, p B185ff

There are in the USA two caps stronger than No 8: 1) US Army Special Blasting Cap, formerly known as "Special Army Engineer Cap" (Vol 2, p B188-R) and "Western Big Inch Cap" (Vol 2, p B186-R). They are "compound caps" but do not contain MF

When MF is mixed with inert materials and/or fuels, such as antimony sulfide (Sb₂S₃), it merely rapidly burns (deflagrates) and can be used (especially if some K chlorate is also included) for igniting propellants, etc (See "Mercuric Fulminate and Its Mixtures and Qualitative & Quantitative Analyses", described after Addnl Refs for SF)

As already mentioned, MF was largely (and now wholly) displaced since 1930 by LA (Lead Azide) and also by DAzDNPh (Diazodinitrophenol), Cyanuric Triazide and LSt (Lead Styphnate). This took place first in

Germany, than elsewhere in Europe and finally in the USA

Specification Requirements and Tests of US Armed Forces are covered by JAN-M-219(1945). It is discussed after AddnlRefs for SF (Silver Fulminate) under "Mercuric Fulminate and Its Mixtures; Qualitative and Quantitative Analyses and Specification Requirements and Tests"

Mercuric Fulminate-Sulfur Compound, $C_2H_4N_2O_2S$; mw 121.14, N 23.13%; crysts, mp - deflagrates below 100° ; sol in eth & alc; insol in water; was prepd by heating MF in abs ether & hydrogen sulfide
Refs: 1) Beil 1, 723 2) Steiner, Ber 8, 1177(1875); 9, 779(1876)

Mercuric Pyrofulminate or Pyrofulmin. An expl solid of empirical formula $Hg_6O_5C_8N_{12}$ with Hg content 77.77%; prepd by P.Y. Narayana [Current Sci 13, 313-15(1944) & CA 39, 4227(1945)] by heating MF for 64 hours or until gases CO & CO_2 ceased to evolve. The compd was stable to at least 125° . It is identical with *Pyrofulmin* previously prepd by A. Langhans [SS 17, 9-11, 18-21 & 26-28(1922) & CA 16, 2603(1922)]

Narayana presumed that 3 mols of MF polymerized in the manner characteristic of cyanogen compds and then decompd according to equations:

Potassium Fulminate, KONO, mw 81.11, N 17.27%; crysts (from alc); very hygroscopic; sp gr 1.80; mp - expl; expl also by the action of flame. Can be prepd by shaking K amalgam with MF either in methanol or abs ethanol. Expln temp in 5 secs 225° (See Ref 1, p [777] & Ref 23, p 411)

Potassium-Silver Fulminate, $KAg(ONC)_2$, mw 231.01, N 12.13%; mp - expl; sol in 8 parts of w. Can be prepd accdg to Daniel (1902), p 319 by adding KCl to a hot aq soln of SF. When treated with dil nitric acid, a ppt of Acid Potassium Fulminate is formed which is also explosive (See also Ref 1, p 722 & Ref 23, p 413)

Silver Fulminate (Fulminate d'argent in Fr; Knallsilber in Ger; Fulminato d'argento in Ital; Fulminato de plata in Span and Gremucheye Serebro in Russ), $AgONO$, mw 149.90, N 9.34%; wh crysts or amorphous aggregates; darkens on exposure to light; mp - expl at 170° in 5 sec (Ref 23, p 411); soly in w 0.0075 parts in 100ml at 13° , 0.018 at 30° and 0.25 at 100° ; insol in nitric acid and is decompd by HCl

Preparation of SF

Caution: Due to its extreme sensitivity to mechanical action, it should be prepd only in very small quantities. When working in the lab, do it under a hood behind a safety glass or plastic, while for the plant production a room with good ventilation is required; a barricade, and an arrangement for remote control

Accdg to Davis (Ref 23, p 405), E. Howard, after successfully prepg MF in 1799-1800, attempted to prep fulminates of Au, Pt, Sb, Sn, Cu, Fe, Pb, Ni, Bi, Co, As, Mn & Ag, but only with Ag had any success. In 1802, L. Brugnatelli worked out a satisfactory method, which consisted in pouring onto 100 grains of powdered Ag nitrate, first an ounce of alcohol and then an ounce of nitric acid. After the ppt was formed, the slurry was immediately diluted with water (to prevent the dissoln of SF) and immediately filtered

Because SF is extremely sensitive to friction and heat it quickly became an object of amateur interest and public wonderment; one of the standard exhibits of street fakirs, etc. J. von Liebig (1803-1873) saw, when he was a boy, a demonstration of SF in the market place at Darmstadt and learned how

exploded on a surface of a silver spoon, a blow like a musket was heard and this punched a hole thru the spoon

FG is not suitable for practical use on acct of its extreme sensitiveness to shock, friction or heat, and also to its high cost (Ref 5, p 568

(Compare this compd with *Auric Imidoamide* or *Gold Amidoimide*, described in Encycl under AMIDES, IMIDES AND DERIVATIVES on p A169-L of Vol 1. It seems that the compd there was erroneously named Fulminating Gold)
 Refs: 1) Daniel (1902), 313-14 2) A. Langhans, SS 25, Sonderdruck 70 (1930) (Explosionen, die man nicht erwarten) 3) Stettbacher (1933), 330-31 4) Davis (1943), 400-01 5) Pérez Ara (1945), 567-68

Fulminating Mercury or Mercury Nitride.

Accdg to Marshall (Ref 1), its formula is Hg_3N_2 , mw 629.85, N 4.45% and it can be prepd by treating mercury oxide with ammonia. It is very sensitive and must not be confused with Mercury Fulminate

Accdg to Davis (Ref 2), Fourcroy, by digesting red oxide of mercury (HgO) in ammonia water for 8 to 10 days, prepd a material which became white and finally assumed the form of crystalline scales. The dried product exploded loudly from fire, but underwent spontaneous decomposition when left alone. At slightly elevated temp it gave off ammonia and left a residue of mercury oxide

In the Journal de Physique for 1779 the French apothecary Bayen described a fulminating mercurial compd of a different kind. It was obtd by mixing 30 parts of precipitated Hg oxide (washed and dried) with 4 or 5 parts of sulfur. This mixt exploded violently when struck with a heavy hammer or on being heated on an iron plate

Accdg to Pérez Ara (Ref 3), there exist two *nitruros de mercurio* (Mercury Nitrides) - one is mercurous, while another is mercuric

None of the above listed expls found application in commercial or military primary or detonating compns, but they are interesting from an historical point of view

Refs: 1) Marshall 2(1917), 703 2) Davis (1943), 402 3) Pérez Ara (1945), 567

Fulminating Platinum (FP) (Platine fulminant in Fr)

Accdg to Daniel (Ref 1), when a soln of platonic oxide in sulfuric acid was treated with an excess of aq ammonia; a black ppt of platine fulminant was obtd. When dry it detonated violently by shock, friction and heat (at 160°). Some scientists consider it as being identical with the *nitride* (azoture, in Fr)

Accdg to Davis (Ref 4, p 402), FP was first prepd by Davy (Sir Humphry, 1778 to 1829) about 1825, by adding ammonia water to a soln of Pt sulfate, boiling the ppt with a soln of potash, washing, and allowing to dry. It was exploded by heat, but not easily by percussion or friction. No formula is given

Accdg to Jacobson (Refs 2 & 3), the compd of the formula $(\text{HO})_5\text{PtNH}_3\text{Pt}(\text{OH})_5$ was prepd by him by treating dichloroplatinic acid with an excess of ammonia. The soln first turned dark and then a brownish ppt appeared, which could be separated and dried. When heated, it blackened and detonated violently yielding Pt, N_2 , O_2 and H_2O vapor. Dichloroplatinic acid was obtd in 80-90% yield by boiling Ag tetrachloroplatinate in water

A compd of similar props, $(\text{HO})_5\text{PtC}_5\text{H}_5\text{NPt}(\text{OH})_5$, was obtd by the action of pyridine on dichloroplatinic acid

Refs: 1) Daniel (1902), 313 & 314 (Platine fulminant) 2) J. Jacobsen, CR 149, 574-77 (1909) & CA 4, 1002 (1910) 3) Clift & Fedoroff 2(1943), p F6 4) Davis (1943), 402

Fulminating Powder of Forsyth. Under this name Newman (Ref) lists the mixture of K chlorate, sulfur & charcoal which could be detonated by percussion. It was invented at the beginning of the 19th century by the Scotch clergyman, A. Forsyth. It was replaced later by the mixture consisting of K chlorate, MF & powdered glass

Ref: J.R. Newman, "Tools of War", Doubleday-Doran & Co, NY (1943), p 42

The Chemistry of Powder and Explosives

BY

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COMPLETE IN ONE VOLUME

NEW YORK

JOHN WILEY & SONS, INC.

LONDON: CHAPMAN & HALL, LIMITED

Cassius practically to the manufacture of ruby glass. In his posthumous *Laboratorium Chymicum* he says: *

Further evidence that mercury is gold is to be seen when you dissolve it in *aqua fortis* (nitric acid), evaporate the solution to dryness, pour highly rectified *spiritum vini* (alcohol) over the residue, and then warm it slightly so that it begins to dissolve. It commences to boil with amazing vigor. If the glass is somewhat stopped up, it bursts into a thousand pieces, and, in consequence, it must by no means be stopped up. I once dissolved silver and mercury together in *aqua fortis* and poured over it an excess of *spiritum vini*, and set the mixture to putrify in *fimum equinum* (horse manure) after having stopped up the glass with mere sealing wax only. When it happened a few days later that the manure became a little warm, it made such a thunder-crack, with the shattering of the glass, that the stable-servant imagined, since I had put it in a box, either that someone had shot at him through the window or that the Devil himself was active in the stable. As soon as I heard this news, I was able easily to see that the blame was mine, that it must have been my glass. Now this was with silver and mercury, 2 *lots* of each. Mercury does the same thing * alone, but silver not at all.

The preparation and properties of mercury fulminate were described in much detail by Edward Howard * in 1800 in a paper presented to the Royal Society of London. The method of preparation which he found to be most satisfactory was as follows: 100 grains of mercury was dissolved by heating in 1½ drams of nitric acid (specific gravity 1.3), the solution was cooled and added to 2 ounces of alcohol (specific gravity 0.849) in a glass vessel, the mixture was warmed until effervescence commenced, the reaction was allowed to proceed to completion, and the precipitate which formed was collected on a filter, washed with distilled water, and dried at a temperature not exceeding that of the water bath. Howard found that the fulminate was exploded by means of an electric spark or by concentrated sulfuric acid brought into contact with it. When a few grains were placed on a * Kunckel, "Collegium Physico-Chymicum Experimentale, oder Laboratorium Chymicum," ed. Engelstedt, Hamburg, 1716, p. 213. Cf. Davis, *Army Ordnance*, 7, 62 (1926).

* Kunckel's meaning in the last sentence is evidently that mercury nitrate reacts with alcohol on warming, and that silver nitrate does not react with alcohol under the same conditions.

Phil. Trans. Roy. Soc., 204 (1800).

cold anvil and struck with a cold hammer, a very stunning disagreeable noise was produced and the faces of the hammer and anvil were indented. A few grains floated in a tin-foil capsule on hot oil exploded at 368°F. (186.7°C.). When a mixture of fine and coarse-grain black powder was placed on top of a quantity of fulminate and the fulminate was fired, the black powder was blown about but it was not ignited and was recovered unchanged. Howard also attempted by means of alcohol to produce fulminating compounds from gold, platinum, antimony, tin, copper, iron, lead, nickel, bismuth, cobalt, arsenic, and manganese, but silver was the only one of these metals with which he had any success. Brugnatelli in 1802 worked out a satisfactory method for the preparation of silver fulminate by pouring onto 100 grains of powdered silver nitrate first an ounce of alcohol and then an ounce of nitric acid. After the fulminate had precipitated, the mixture was diluted with water to prevent it from dissolving again and immediately filtered. Silver fulminate explodes more easily from heat and from friction than mercury fulminate and is more spectacular in its behavior. It quickly became an object of amateur interest and public wonderment, one of the standard exhibits of street fakirs and of mountebanks at fairs. Lichig, who was born in 1803, saw a demonstration of silver fulminate in the market place at Darmstadt when he was a boy. He watched the process closely, recognized by its odor the alcohol which was used, went home, and succeeded in preparing the substance for himself. He retained his interest in it, and in 1823 carried out studies on the fulminates in the laboratory of Gay-Lussac at Paris.

Mercury Fulminate

The commercial preparation of mercury fulminate is carried out by a process which is essentially the same as that which Howard originally recommended. Five hundred or 600 grams of mercury is used for each batch, the operation is practically on the laboratory scale, and several batches are run at the same time. Since the reaction produces considerable frothing, capacious glass balloons are used. The fumes, which are poisonous and inflammable, are passed through condensers, and the condensate, which contains alcohol, acetaldehyde, ethyl nitrate, and ethyl nitrite, is utilized by mixing it with the alcohol for the next batch.

Pure fulminate is white, but the commercial material is often grayish in color. The color is improved if a small amount of cupric chloride is added to the nitric acid solution of mercury before it is poured into the alcohol in the balloon, but the resulting white fulminate is actually less pure than the unbleached material.

Preparation of Mercury Fulminate. Five grams of mercury is added to 35 cc. of nitric acid (specific gravity 1.42) in a 100-cc. Erlenmeyer

FIGURE 93. Fulminate Manufacture. (Courtesy Atlas Powder Company.) At left, flasks in which mercury is dissolved in nitric acid. At right, balloons in which the reaction with alcohol occurs.

flask, and the mixture is allowed to stand without shaking until the mercury has gone into solution. The acid liquid is then poured into 50 cc. of 90% alcohol in a 500-cc. beaker in the hood. The temperature of the mixture rises, a vigorous reaction commences, white fumes come off, and crystals of fulminate soon begin to precipitate. Red fumes appear and the precipitation of the fulminate becomes more rapid, then white fumes again as the reaction moderates. After about 20 minutes the reaction is over, water is added, and the crystals are washed with water repeatedly by decantation until the washings are no longer acid to litmus. The product consists of grayish-yellow crystals, and corresponds to a good grade of commercial fulminate. It may be obtained white and entirely pure by dissolving in strong ammonia

water, filtering, and reprecipitating by the addition of 30% acetic acid. The pure fulminate is filtered off, washed several times with cold water, and stored under water, or, if a very small amount is desired for experimental purposes, it is dried in a desiccator.

The chemical reactions in the preparation appear to be as follows. (1) The alcohol is oxidized to acetaldehyde, and (2) the nitrous acid which is formed attacks the acetaldehyde to form a nitroso derivative which goes over to the more stable, tautomeric, isonitroso form.

(3) The isonitrosoacetaldehyde is oxidized to isonitrosoacetic acid, and (4) this is nitrated by the nitrogen dioxide which is present to form nitroisonitrosoacetic acid.

(5) The nitroisonitrosoacetic acid loses carbon dioxide to form formonitrolic acid which (6) decomposes further into nitrous acid and fulminic acid, and (7) the fulminic acid reacts with the mercury nitrate to form the sparingly soluble mercury fulminate which precipitates.

Fulminate can be prepared from acetaldehyde instead of from alcohol, and from substances which are convertible into acetaldehyde, such as paraldehyde, metaaldehyde, dimethyl- and diethyl-acetal. Methyl alcohol, formaldehyde, propyl alcohol, butyraldehyde, glycol, and glyoxal do not yield fulminate.⁶ Fulminate can, however, be prepared from a compound which contains only one carbon atom. The sodium salt of nitromethane gives with an aqueous solution of mercuric chloride at 0° a white

⁶ Wöhler and Theodorovits, *Ber.*, 38, 1345 (1905).

precipitate of the mercuric salt of nitromethane which gradually becomes yellow and which, digested with warm dilute hydrochloric acid, yields mercury fulminate.⁷

Sodium fulminate, soluble in water, has a molecular weight which corresponds⁸ to the simple monomolecular formula, NaONC. These facts, taken together with the fact that mercury fulminate warmed with concentrated aqueous hydrochloric acid yields hydroxylamine and formic acid,⁹ prove that fulminic acid is the oxime of carbon monoxide.

Mercury fulminate dissolves readily in an aqueous solution of potassium cyanide to form a complex compound from which it is reprecipitated by the addition of strong acid. It dissolves in pyridine and precipitates again if the solution is poured into water. A sodium thiosulfate solution dissolves mercury fulminate with the formation of mercury tetrathionate and other inert compounds, and this reagent is used both for the destruction of fulminate and for its analysis.¹⁰ The first reaction appears to be as follows.

The cyanide and cyanate are salts of weak acids and are largely hydrolyzed, and the solution, if it is titrated immediately, appears to have developed four molecules of sodium hydroxide for every molecule of mercury in the sample which was taken. If the solution is allowed to stand, the alkalinity gradually decreases because of a secondary reaction whereby sulfate and thiocyanate are formed.

⁷ Nef, *Ann.*, 280, 275 (1894); Jones, *Am. Chem. J.*, 20, 33 (1898).

⁸ Wöhler, *Ber.*, 43, 754 (1910).

⁹ Carstenjen and Ehrenberg, *J. prakt. Chem.*, [2] 25, 232 (1883); Steiner, *Ber.*, 16, 1494, 2419 (1883); Divers and Kawita, *J. Chem. Soc.*, 45, 17 (1884).

¹⁰ Brownson, *Chem. News*, 89, 303 (1904); Philip, *Z. ges. Schiess- u. Sprengstoffw.*, 7, 109, 156, 180, 198, 221 (1912); Taylor and Rinkenbach, "Explosives, Their Materials, Constitution, and Analysis," *U. S. Bureau of Mines Bulletin* 219, Washington, 1923, p. 62.

This reaction is restrained by a large excess of thiosulfate, and even more effectively by potassium iodide. A moderate excess of thiosulfate is commonly used, and an amount of potassium iodide

FIGURE 94. Mercury Fulminate Crystals for Use in Primer Composition (30X).

equal to 10 times the weight of the fulminate, and the titration for acidity (methyl orange indicator) is made as rapidly as possible. After that, the same solution is titrated with iodine (starch indicator) to determine the amount of unused thiosulfate and hence, by another method, the amount of actual fulminate in the sample. Speed is not essential in the second titration, for the iodine value does not change greatly with time as does the alkalinity. Blank determinations ought to be made because of the

possibility that the iodide may contain iodate, and the apparent analytical results ought to be corrected accordingly.

Mercury fulminate has a specific gravity of 4.45, but a mass of the crystals when merely shaken down has an apparent density (gravimetric density) of about 1.75. In detonators the material is usually compressed to a density of about 2.5, but densities as high as 4.0 have been obtained by vigorous compression. Mercury fulminate crystallizes from water in crystals which contain $\frac{1}{2}\text{H}_2\text{O}$, from alcohol in crystals which are anhydrous. One liter of water at 12° dissolves 0.71 gram, at 49° 1.74 grams, and at 100° 7.7 grams.

Mercury fulminate is usually stored under water, or, where there is danger of freezing, under a mixture of water and alcohol. When wet it is not exploded by a spark or by ordinary shock, but care must be taken that no part of the individual sample is allowed to dry out, for wet fulminate is exploded by the explosion of dry fulminate. It is not appreciably affected by long storage, either wet or dry, at moderate temperatures. At the temperature of the tropics it slowly deteriorates and loses its ability to explode. At 35°C. (95°F.) it becomes completely inert after about 3 years, at 50°C. (122°F.) after about 10 months. The heavy, dark-colored product of the deterioration of fulminate is insoluble in sodium thiosulfate solution.

When loaded in commercial detonators mercury fulminate is usually compressed under a pressure of about 3000 pounds per square inch, and in that condition has a velocity of detonation of about 4000 meters per second, explodes from a spark, and, in general, has about the same sensitivity to fire and to shock as the loosely compressed material. When compressed under greater and greater pressures, it gradually loses its property of detonating from fire. After being pressed at 25,000–30,000 pounds per square inch, mercury fulminate becomes "dead pressed" and no longer explodes from fire but merely burns. Dead-pressed fulminate however is exploded by loosely pressed fulminate or other initial detonating agent, and then shows a higher velocity of detonation than when compressed at a lower density.

The temperature at which mercury fulminate explodes depends upon the rate at which it is heated and, to some extent, upon the state of subdivision of the sample. Wöhler and Matter¹¹ experimentally

¹¹ *Z. ges. Schiess- u. Sprengstoffw.*, 2, 181, 203, 244, 265 (1907).

mented with small particles of various primary explosives, heated in copper capsules in a bath of Wood's metal. If a sample did not explode within 20 seconds, the temperature of the bath was raised 10° and a new sample was tried. The temperatures at which explosions occurred were as follows.

190°	Mercury fulminate
150°	Sodium fulminate
190°	Nitrogen sulfide
90°	Benzene diazonium nitrate
130°	Chlorato trimercaptaldehyde
290°	Silver azide
160°	Basic mercury nitromethane

In a later series of experiments Wöhler and Martin¹² studied a large number of fulminates and azides. The materials were in the form of microcrystalline powders, and all were compressed under the same pressure into pellets weighing 0.02 gram. The temperatures at which explosions occurred within 5 seconds were as follows.

215°	Mercury fulminate
170°	Silver fulminate
205°	Copper fulminate
215°	Cadmium fulminate
215°	Sodium fulminate
225°	Potassium fulminate
120°	Thallium fulminate
148°	Cobalt azide
152°	Barium azide
158°	Calcium azide
169°	Strontium azide
174°	Cuprous azide
200°	Nickel azide
203°	Manganese azide
245°	Lithium azide
281°	Mercurous azide
289°	Zinc azide
291°	Cadmium azide
297°	Silver azide
327°	Lead azide

Wöhler and Martin¹³ in the same year also reported determinations of the smallest amounts of certain fulminates and

¹² *Z. angew. Chem.*, 30, 33 (1917).

¹³ *Z. ges. Schiess- u. Sprengstoffw.*, 12, 1, 18 (1917).

azides necessary to cause the detonation of various high explosives.

SMALLEST AMOUNT (GRAMS) WHICH WILL (CAUSE DETONATION OF)	Tetryl	Picric Acid	Trinitro- toluene	Trinitro- anisol	Trinitro- xylene
--	--------	----------------	----------------------	---------------------	---------------------

Cadmium azide.....	0.01	0.02	0.04	0.1	..
Silver azide.....	0.02	0.035	0.07	0.26	0.25
Lead azide.....	0.025	0.025	0.09	0.28	..
Cuprous azide.....	0.025	0.045	0.095	0.375	0.40
Mercurous azide.....	0.045	0.075	0.145	0.55	0.50
Thallium azide.....	0.07	0.115	0.335	..	..
Silver fulminate.....	0.02	0.05	0.095	0.23	0.30
Cadmium fulminate.....	0.008	0.05	0.11	0.26	0.35
Copper fulminate.....	0.025	0.08	0.15	0.32	0.43
Mercury fulminate.....	0.29	0.30	0.36	0.37	0.40
Thallium fulminate.....	0.30	0.43	..	..	..

From these data it is apparent that mercury fulminate is by no means the most efficient initiating agent among the fulminates and azides. Silver fulminate is about 15 times as efficient as mercury fulminate for exploding tetryl, but only about $\frac{1}{3}$ as efficient for exploding trinitroxylene. Mercury fulminate however will tolerate a higher temperature, and is much less sensitive to shock and friction, than silver fulminate. Lead azide, which has about the same initiating power as silver fulminate, has an explosion temperature more than 100° higher than that of mercury fulminate. Many other interesting inferences are possible from the data. Among them we ought especially to note that the order of the several fulminates and azides with respect to their efficiency in detonating one explosive is not always the same as their order with respect to their efficiency in detonating another.

Silver Fulminate

Silver fulminate is so sensitive and so dangerous to handle that it has not been used for practical purposes in blasting or in the military art. It early found use in toys, in tricks, and in such devices for entertainment as those which Christopher Grotz described in 1818 in his book on "The Art of Making Fireworks, Detonating Balls, &c."

Amusements with Fulminating Silver. . . .

Segars.

Are prepared by opening the smoking end, and inserting a little of the silver; close it carefully up, and it is done.

Spiders.

A piece of cork cut into the shape of the body of a spider, and a bit of thin wire for legs, will represent with tolerable exactness this insect. Put a small quantity of the silver underneath it; and on any female spying it, she will naturally tread on it, to crush it, when it will make a loud report.

Silver fulminate is still used for similar purposes in practical jokes, in toy torpedoes (see Vol. I, p. 106), and in the snaps or pull-crackers which supply the noise for bon-boms, joy-boms, and similar favors.

Silver fulminate is insoluble in nitric acid, and is decomposed by hydrochloric acid. It darkens on exposure to light. One liter of water at 13° dissolves 0.075 gram of the salt, and at 30° 0.18 gram. The double fulminate of silver and potassium, AGONC·KONC, is soluble in 8 parts of boiling water.

Detonators

The discovery of the phenomenon of initiation by Alfred Nobel and the invention of the blasting cap¹⁴ stand at the beginning of the development of modern explosives, perhaps the most important discovery and invention in the history of the art. The phenomenon has supplied a basis for the definition of high explosives, that is to say, of those explosives, whether sensitive or insensitive, which are incapable, without the invention, of being used safely and controllably or perhaps even of being used at all. Nobel's experiments quickly led him to the form of the blasting cap which is now in use, a cylindrical capsule, generally of copper but sometimes of aluminum or zinc, filled for about half of its length with a compressed charge of primary explosive. The charge is fired either by an electric igniter or by a fuse, crimped into place, its end held firmly against the charge in order that the chances of a misfire may be reduced. Its action depends upon the development of an intense pressure or shock. Fulminate of mercury was the only substance known at the time of Nobel's invention which could be prepared and loaded for the purpose with reasonable safety, and caps loaded with straight fulminate were the first to

¹⁴ Nobel, Brit. Pat. 1345 (1867).

APPENDIX C

Sources for Explosive Literature

CHEMISTRY OF POWDER & EXPLOSIVES

by Tenney L. Davis. Primarily for Chemists. To supply information concerning the modes of behavior of explosive substances & the phenomena, both chemical & physical, which they exhibit ISBN 0913022-00-4

CHEMISTRY OF PYROTECHNICS

by John A. Conkling. Information on the components and preparation of mixtures; ignition and propagation; heat and delay composition; color, light, smoke, and sound production. An indispensable learning aid. Hard cover, 1985, 190 pp. ISBN 0-824-77443-4

CHARACTERISTICS OF NON-MILITARY EXPLOSIVES

by R. Liepens, et. al. of Research Triangle Institute. Report on use of non-military explosives prepared for the Army Mobility Equipment Res & Dev Ctr Naval Explosive Ordnance Disposal Facility, Soft cover, 1974, 50 pp. REP04791

COMPRESSED AIR SYSTEMS

by H. Van Ormer. A practical guide includes departmental or central air systems, terminology, compressors, application, selection, and installation, oil-cooled rotary vane, screw compressor capacity controls & more. Soft cover, 1987, 142 pp. MAN07789

CONSTRUCTION VIBRATIONS

by Charles H. Dowding. This book synthesizes consulting experience and research to transfer advances in earthquake engineering, nuclear blast protective design, construction & mine blasting to the entire field of construction-induced vibrations. Basic principles are emphasized through inclusion of some 120 example questions & their answers & explanations. 598 pp. ISBN 013299108X

CONSTRUCTION DEWATERING NEW METHODS AND APPLICATIONS

by J. Patrick Powers. Explanation of the physical laws governing ground water and soils. Practical solutions to dewatering problems and information on the latest equipment and methods in the field. Hard cover 2nd Edition. 1992. 528 pp. ISBN 47165-0185-3.

CONTEMPORARY HISTORY OF INDUSTRIAL EXPLOSIVES IN AMERICA

by Joe Dannenberg. Changes in the explosives industry from one of the most recognized names in blasting, focussing on the profession. Includes info about development of ANFO, slurries, and blasthole dewatering. Great for collectors too. Paperback, 1978, 248 pp. COL08791

DRILLING AND BLASTING OF ROCKS

Geomining Tech. Inst. Of Spain, edited by Carlos L. Jimeno, Emilio L. Jimeno & Francisco J A Carcedo. This handbook which brings together practical & theoretical aspects, should be of use to all engineers who work with drilling & blasting as a rock breakage method. 1995 ISBN 9054101997

ENGINEERING GEOLOGY

by Richard E. Goodman. For student and practitioners. Emphasis on experience record and performance of different types of rocks. Includes a mix of historical projects and more recent ones. Hard Cover, 1993, 412 pp. ISBN 0-4715-44248

EXPLOSIVES AND BLASTING PROCEDURES

by R. Dick, L. Fletcher and D. D'Andrea. A guide for training programs and for experienced blasters with an update on the latest technology in blasting. Hard cover, 1986, 105 pp. IC8925

EXPLOSIVES ENGINEERING

By Paul Cooper. Details the basic technologies utilized in the engineering of explosives and explosive systems. Illustrates chemistry of explosives, energetics of explosives, shock waves, detonation, initiation & initiators, and the numerous engineering applications for explosives and explosives technology. 425 pp. ISBN 3-527-26345-4

Explosives Engineering

EXPLOSIVES: AN ENGINEERING TOOL

by Giorgio Berta. Popular text, clearly presented. Use and characteristics of explosives, energy balance and design, control blasting, environmental effects, standards, rounds, tunneling and bench blasting data, description of major civil engineering processes and demolition. Mechanism of blasting is analyzed and partition of energy between various blast effects is quantified. Hardcover, 1990, 484 pp. TXT 0991.

GREAT REFERENCE TOOLS!

DICTIONARY OF MINING, MINERAL, AND RELATED TERMS

by American Geological Institute. A collaborative project with the US Bureau of Mines providing information on minerals & mining. Second Edition, Hard Cover, 1997, 646 pp., ISBN 0922152365

ENCYCLOPEDIA OF EXPLOSIVES & RELATED ITEMS

Edited by B. Fedoroff, O. Sheffield, H. Herman, and S. Kaye. World's largest explosives encyclopedia on military and industrial explosives, analytical procedures for common explosives propellants, much more. 45 lbs. 10-Vol Set, 1960, 9,000 pp. Call for shipping & handling costs. AD257189. Some volumes may be out of print.

GUIDE TO EXPLOSIVES PRODUCTS

Published by ISEE. Updated product charts include ANFOs, Emulsions, Emulsion/ANFO Blends, Water Gels, Specialty Explosives, Dynamites, Cast Boosters, Detonators/Initiation Systems and list of Mfgs. 1998. See ISEE price list p. 15. GU04991

DICTIONARY OF BLASTING TECHNOLOGY

Includes terms from mining, chemistry and pyrotechnics that relate to explosives and blasting. 1987. 331 pp. ISBN 3-527-26345-4.

SURFACE MINE BLASTING

by Carl E. Pavetto
Training manual for MSHA Certification. Covers major types of explosives, initiation systems, and shot checking systems in surface coal mining. Tools to meet certification requirements. Soft cover, 1989, 317 pp. MAN09891

DEMOLITION SAFETY MANUAL

The bible of the demolition industry for safe work practices. Describes safety measures to be followed before the demolition work actually begins. MAN20000

RUDIMENTS OF MINING PRACTICE

by D.E. Gregory. Gives an overview of the wide spectrum of mining engineering operations. Designed primarily as a textbook, written in straightforward manner. Hard cover, 1983. 143 pp. ISBN 0-87201-783-4

TEST METHODS FOR EXPLOSIVES

Muhammed Sucasca, Treats the experimental methods used to determine the physical properties of explosives & explosions - physical principles, operating procedures and evaluation of results. 1995, 225 pp. ISBN 0387945555.

UNDERGROUND BLASTING WORKSHOP

Edited by Trevor Little
Proceedings of the Underground Blasting Workshop conducted by the Blasting Research Group of the Western Australia School of Mines, Curtin University of Technology. Softcover, 1992 PRO02911

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ATTACHMENT 2

Day 1 Agenda

- 0800 - 0830 Arrival and Badging
- 0830 - 0845 Introductions and Agenda Overview
- 0845 - 0945 Program Overview (Wilmarth)
- 0945 - 1000 Break
- 1000 - 1045 Selection of Compounds for Study (Hobbs)
- 1045 - 1130 Synthesis of Compounds (Wilmarth)
- 1130 - 1230 Lunch
- 1230 - 1300 SRTC Study 1: Impact Testing (Group Discussion)
- 1300 - 1345 SRTC Study 1: DSC/TGA Data (Fondeur)
- 1345 - 1400 Break
- 1400 - 1445 Vendor Testing (Fondeur)
- 1445 - 1545 SRTC Study 2 (Fondeur)
- 1545 - 1630 Open Discussion
- 1630 - 1700 Panel Meeting (closed session)

Day 2 Agenda

- 0800 - 0815 Arrival
- 0815 - 1000 Lab Tour
- 1000 - 1100 Discussion of Panel Questions
- 1100 - 1200 Lunch
- 1200 - 1400 Panel Working Session
- 1400 - 1500 Panel Summary (presentation on findings and recommendations)

Dry Sludge Impact Tests

- All Impact Tests were run at 6 kg weight and 50 cm height (maximum for our Impact Tester)
- Tests run on
 - Mercury Fulminate
 - Mercury Oxalate
 - Basic Sludge Simulant (1-A)
 - Basic Sludge Simulant with Organics (7-D)
 - Basic Simulant with Mercury Oxalate (~6 wt%, ~15 wt% mixed dry)
 - Basic Simulant with Mercury Oxalate (~6 wt%, ~15 wt% mixed wet)
 - Basic Simulant with Organics and Mercury Oxalate (~6 wt%, ~15 wt% mixed dry)
 - Basic Simulant with Mercury Fulminate (~ 3 wt %, ~6 wt%, ~15 wt% mixed dry)
 - Basic Simulant with Mercury Fulminate (~ 3 wt %, ~6 wt%, ~15 wt% mixed wet)
 - Basic Simulant with Organics and Mercury Fulminate (~ 3 wt %, ~6 wt%, ~15 wt% mixed dry)
 - Basic Simulant with Mercury, Silver and Organics
- Results
 - Both fulminate and oxalate standards gave positive results (smoke) at amounts of 1-3 mg
 - No sludge simulants (with or without standards) gave positive results
 - Some evidence of degradation of standards in sludge

- **Problems**

- **Impact tester not on completely stable base (some bouncing)**
- **Samples not ground to uniform particle size (sticky samples and concerns about setting off standards)**
- **Masses used not entirely uniform (sticky samples made weighing difficult)**
- **Sample material ejected from sample cup during impact**

Simultaneous test matrix provided by Mark Barnes is given
 The basic sludge simulant for these tests is given on the
 as page. The matrix for additives and drying conditions
 given below

Test Solution #																
Additive	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
Temperature or condition	all 4	all 4	all 4	all 4	all 4	all -4	all 4	all 4	air dried	air dried	air dried	air dried	all 4	all 4	orst condition of 11-14	
mercury & silver	0	1	0	0	0	0	0	1	0	0	0	0	0	0	0	0
undigested resin	0	0	1	0	0	0	2	2	0	0	0	0	0	0	1	1
digested resin	0	0	0	0	0	0	2	2	0	0	0	0	0	0	1	1
TBP/n-paraffin	0	0	0	0	0	1	0	2	0	0	0	0	0	0	1	1
oxalate	0	0	0	0	0	1	2	2	0	0	0	0	0	0	1	1
mercury oxalate	0	0	0	0	0	0	0	0	1	0	1	0	1	0	1	0
mercury fulminate	0	0	0	0	0	0	0	0	0	1	0	1	0	1	0	1
Drying Temp. Label																
0 = absent from test	50 C A															
1 = added to test	150 C B															
2 = added to test at 25% of individual (1) level	250 C C															
Additive Concentration																
mercury = 6.0 wt% <i>nickel</i> 350 C D																
silver = 0.0015 wt% <i>no base</i>																
lonac resin = 3 wt% each																
TBP/n-paraffin = 3 wt%																
oxalate = 3 wt%																
mercury oxalate = 6.0 wt%																
mercury fulminate = 6.0 wt%																

9/10/98

Evaluation of Possible Explosive Compounds in SRS Waste Tank Farm Facilities

D. T. Hobbs

- original evaluation completed in 1992 (WSRC-TR-91-444, rev. 0)
- revision 1 of the report issued in 1995
shock sensitive deposits from DWPF recycle stream
dried waste
- PISAs (1997)
dry sludge
organics

July 13, 1999

SRT-LWP-99-00094

Evaluation Methodology

- **identify waste constituents**
- **determine compounds that could possibly form**
- **compare possible compounds to those reported to be explosive in the literature**
- **assess the formation and stability against conditions in Tank Farm facilities**

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Possible Classes of Explosive Compounds

- flammable gases
- metal nitrides
- ammonia compounds & derivatives
- metal NO_x compounds
- organic compounds
- metal fulminates
- metal azides
- halogen compounds
- metal amine complexes
- nitrate - oxalate mixtures
- metal oxyhalogenates
- metal cyanides/cyanates
- peroxides

Classes of Explosive Compounds Known to Exist, But Controlled

- Flammable gases
 - hydrogen
 - methane, ethane, ethylene
 - butanol
 - benzene
- Metal nitrides
 - silver nitride (Ag_3N)
 - mercuric nitride (Hg_3N_2)
- Ammonia compounds & derivatives
 - ammonium nitrate
 - hydrazine
 - hydroxylamine

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Classes That Are Not a Hazard

- metal fulminates
- metal azides
- halogen compounds
- metal amine complexes
- nitrate/oxalate mixtures
- metal oxalates
- metal cyanides/cyanates
- peroxides

Classes That Exist and Need Additional Study

- **Organic compounds**
(DWPf Recycle and In-Tank Precipitation)
 - phenol
 - nitrated aromatics
- **Metal NO_x compounds**
 - Millon's base & derivatives

Dry Sludge Studies

- **Mercury oxalate**
 - mercury and oxalate prevalent in sludge
 - impurities such as nitrate increase reactivity
- **Mercury fulminate**
 - surrogate for Millon's base & mercuric nitride
 - high formation energy
- **Silver nitride**
 - identified in 1970 incident with dry waste

Synthesis of Energetic Materials for the High Level
Waste Dry Sludge Program

W. R. Wilmarth

Potential Energetic Material Screening

Hobbs (WSRC-TR-91-444, Rev. 1)

- Metal Fulminates
- Metal Azides
- Metal Nitrides
- Metal NO_x Compounds
- Ammonia Compounds and Derivatives
- Halogen Compounds
- Metal Amines
- Nitrate/Oxalate Mixtures
- Metal Oxalates
- Metal Halogenates
- Metal Cyanides/Cyanates
- Flammable Gases
- Peroxides

Approach to Handling Energetic Materials

- Recognized new and very different hazards existed
- Approach to safety similar to EMRTC
 - Initial approval to handle energetic materials received from Director of SRTC

- Minimized amounts of material handled
- Control provide by procedure
- Pre-job briefings for all involve personnel daily
- Minimized number of "other" personnel in lab at time of handling energetic material
- Materials were locked with surveillance or barricade to prevent inadvertent personnel from entry

Compounds used in SRTC Research

- Mercury Oxalate
 - Formed by precipitation of Hg(II) with $\text{C}_2\text{O}_4^{=}$
 - Previously shown safe by Wallace
- Mercury Fulminate
 - Formed by reaction of Hg metal with concentrated HNO_3 followed by reaction with ethanol
 - Can form in caustic solutions by reaction of NaCH_2NO_2 with HgCl_2
- Silver Nitride
 - Formed by KOH reaction with $\text{Ag(NH}_3)_2^+$

Requirements Documents

- DOE Explosives Manual
 - Quantities in use less than Explosives Limit for plastic face shields
 - Limits formulation, characterization to less than 2 grams
- Prudent Practices in the Laboratory
 - Limits reactions to 0.5 g amounts
- ANSI Standard for Impact Testing
 - 20 mg limit
- LWP Handling Requirements
 - 200 mg inventory limit
 - 100 mg/sample preparation; initially 30-50 mg
 - >> 20 mg per Impact

Technical and Safety Reviews

- Task Technical Plan and Environmental Evaluation Checklist
- USQ Process - Explosions enveloped by Safety Analysis Report
 - Approved by Facility Operations Safety Committee
- Procedure for synthesis and experiments
- Job Hazard Analysis
 - Hazards found in JHA include spills, chemical exposure, fire, splash, chemical burn, transportation, bumping
- Formal review by Senior Research Personnel

Energetic Compound Formation in Dry High Level Waste Sludge Program Review

13 July 1999

SRT-LWP-99-00

SRS Background

- Production of Nuclear Weapons materials generated millions of gallons of highly radioactive liquid and solids wastes
- At SRS, the nitric acid-based liquid wastes were neutralized to > 2 M free hydroxide and stored in carbon steel tanks
 - Transition metals precipitate and form hydrated oxides/hydroxides referred to as high level waste sludge
- SRS stores sludge and supernate in 1.3 million gallon waste tanks

High-Level Waste Flowsheet

Sludge Processing

- Currently, sludge processed into glass in the Defense Waste Processing Facility
 - Two waste tanks officially closed pre CERCLA protocol
 - Over 500 canisters produced to date
- Extended Sludge Process washes the sludge with 0.1 M NaOH to remove entrained salts
- Sludge is combined with glass formers and vitrified
- Ultimate disposal is to National Repository

Salt/Supernate Processing

- Original plans were to dissolve salt and precipitate radio-caesium with sodium tetraphenylborate and remove radio-strontium and actinides with monosodium titanate
 - ~ 430 kgal processed in 1985 demonstration
- During initial batch processing in the In-Tank Precipitation (ITP) process, benzene generation rates observed
 - Research program identified active transition metal catalyst that likely originated from sludge entrained solids
- Systems Engineering approach used to identify replacement process
 - Three candidate processes undergoing final selection
 - Tetraphenylborate process using engineered safety features
 - Crystalline silicotitanate ion exchange
 - Grout

Problem Statement

- Authorization Basis for Tank Farm assumes sludge remains wet
 - Release fraction and respirable fraction possibly higher for dry tank
- 5 tanks dry at start of program
 - 2 tanks have been re-wetted (Tank 6F and 8F)
 - Tank 15H has cracks that may preclude efforts to re-wet
 - Potential Inadequacy in Safety Analysis (PISA) declared
 - Establishes schedule to revise SAR as necessary
- Hazardous chemical formation during dry process could lead to shock sensitive compound formation
- Sludge contains ~ 4wt % Hg and ~ 1 wt% Ag

Investigation Approach

- Use DSC/TGA, Impact (ASTM) testing and Friction testing to test for energetic behavior
 - Parallels LANL's approach for ferrocyanide-bearing Hanford tanks
- Examine archive tank samples located in SRTC facilities from previous experimentation
- Prepare simulate sludge at range of worse case conditions to ensure experimental methods would detect energetic behavior
 - organic components, drying temperature, high mercury and silver content
- Test behavior at larger scale (~10 g)
- Review results with independent consultants to guide program

Program Evolution

- Initial work by WPT focused on proving safety of sampling operations
 - Performed impact tests on simulated sludges with energetic materials
 - Energetic standards selected and prepared
- Radiological safety concerns preclude safe sampling operations
 - Cracks in Tank 15 preclude wetting
- Emphasis change caused research to shift to ensuring safety of sludge containing energetic materials
 - Demonstrate low probability of compound formation
 - Demonstrate short lifetime

H-Area Evaporator Incident

- In July 1970, operators noticed “popping” sounds during work near the 2H high level waste evaporator
- Investigation by SRL suggested silver nitride
 - Limited XRD data corroborated identification
 - Large quantities of silver discharged to the tank farm prior to incident
 - Later, silver blended to limit recurrence
- Wallace previously addressed Hg and Ag oxalate safety for Tank 16H
 - Concluded oxalates safe especially if maintained wet
 - Impact and heat caused decomposition when dry

Archived Sludge

- Differential Scanning Calorimetry analysis of archived samples from Tanks 8F, 12H, and 15H showed no exothermic behavior to temperatures as high as 400 °C
- Chemical analysis of Tank 12H and 15H sludge showed materials experienced pre-treatment prior to DSC test
- Chemical analysis of Tank 8F sludge showed no evidence of pre-treatment

Impact Testing

- Impact testing (780 psi) of simulated sludge samples showed no visible reaction (i.e., smoke or spark) at conservative mercury and silver concentrations
- Tests containing pure explosives showed positive
 - Smoke and sparks observed
 - Small masses required for positive tests (3 mg HgC_2O_4 , 2mg $\text{Hg}(\text{CNO})_2$)
- Impact testing with mixtures of sludge and explosive (14.9 wt % HgC_2O_4 or 21.5 wt % $\text{Hg}(\text{CNO})_2$) showed no visible signs of reaction per standard protocol

Calorimetric Studies

- Mixtures of dry, simulated sludge and mercury oxalate (14.9 wt %) showed no net exothermic behavior
 - Oxalate decomposition occurs at temperature overlapping an endotherm in the sludge
 - Wet mixtures suggest oxalate may decompose during drying process
- Mixtures of dry, simulated sludge and mercury fulminate (21 wt % fulminate) exhibit exothermic reaction at the decomposition temperature of the fulminate
 - Across the entire temperature range, the net heat flow is endothermic
- Calorimetric studies of simulants containing oxalate/fulminate do not show signs of propagating into doped organic material

Effects of Radiation and Caustic Exposure

- Studies have shown very short lifetimes for mercury oxalate in both alkaline environments or during exposure to gamma radiation
- Lifetimes for similar exposures are lengthened for mercury fulminate
- Synergism between radiation and alkaline exposure significantly reduces fulminate lifetime

Preliminary Conclusions

- Studies do not preclude the formation of energetic compounds as High Level Waste sludge dries
 - Simulate sludge prepared in similar heat treatments do not show energetic behavior
- Mixtures of simulated sludge and energetic compounds do not exhibit a net exothermic reaction when heat to temperatures near 400 °C
 - Organic compounds within simulated sludge does not enhance behavior
- Impact studies of energetic compounds within sludge matrices do not show energetic behavior
- Vendor studies at larger scale show similar behavior for fulminate - containing sludge
- Radiation and caustic stability indicate expected lifetimes of oxalate and fulminate are sufficiently low to ensure these energetic materials will not survive under real waste conditions

RESEARCH TEAM

SRTC

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Fernando Fondeur

Mike Hay

David Hobbs

Mark Geeting

Tom Nance

Rob Swingle

Bill Wilmarth

CST

Tom Britt

Greg Hutchens

Rahn Ross

MERCURY FULMINATE STABILITY (LITERATURE REVIEW)

- DECOMPOSITION TEMPERATURE FUNCTION OF EXPOSURE AT TEMPERATURE (FIGURE 10)
 - 12 MIN AT 132 °C
 - INSTANT AT 277 °C
- DECOMPOSITION TEMPERATURE
 - DECREASES WITH INCREASING SAMPLE SIZE
 - INCREASES WITH HEATING RATE (TABLE 6)
- DETERIORATES WITH STORAGE, 10 % LOSS IN (P 9)
 - 12 MONTHS AT 50 °C
 - 2 DAYS AT 80 °C
- INTERNET: AVOID CONTACT WITH ALUMINUM, COPPER, ZINC, LEAD (*Z. ges. Schiess- u. Sprengstoffw. 1921, 16, 105*)

DIFFERENTIAL SCANNING CALORIMETRY RESULTS

- VENDOR FULMINATE DECOMPOSES AT 235 °C
 - PEAKS FUNCTION OF SAMPLE CONTAINMENT: LOSE, TIGHT, CRIMPED
 - MEASURED EXOTHERM HEAT VARIABLE, 21 TO 96 CAL/G
 - EXOTHERM HEAT MEASUREMENT IS COMPLICATED BY MERCURY VAPOR RECONDENSATION
- SRTC FULMINATE DECOMPOSES AT 175 °C
- DECOMPOSITION TEMPERATURE LOWERED IN 10 WT % MIX IN CAUSTIC SLUDGE
 - VENDOR 182 °C
 - SRTC 169 °C

CARIUS SEALED TUBE THERMAL DECOMPOSITION

- MAJOR EXOTHERM AT 123 °C, 10 WT% FULMINATE IN 10-G CAUSTIC SLUDGE SAMPLE (RUN 3)
 - NOT CONFIRMED BY RETESTING USING ORIGINAL SLUDGE AND FULMINATE
 - NOT SEEN IN 3-G CAUSTIC SLUDGE OR IN NEUTRAL SLUDGE.
- GAS GENERATION REDUCED BY 2/3 IN CAUSTIC SLUDGE, INCLUDING 3-G SAMPLES (TABLE 7)
 - PEAK PRESSURE DEVELOPED IN SEALED TUBE ALSO REDUCED IN CAUSTIC SLUDGE.
- RE-TESTED JULY 99, 10 WT% FULMINATE IN 10-G CAUSTIC SLUDGE SHOWED NO RESIDUAL GAS GENERATION.
- SUSPECT FULMINATE AGING AND FULMINATE DECOMPOSITION IN CAUSTIC SLUDGE.

VISUAL DECOMPOSITION IN CAPILLARY TUBE (MELTING POINT TECHNIQUE - VIDEO)

- STRC MERCURY OXALATE DECOMPOSES RAPIDLY, LEAVING MERCURY DEPOSITS IN THE LOWER CAPILLARY AND CRYSTALLINE DEPOSITS AT CAPILLARY END.
- SRTC MERCURY FULMINATE DETONATES, LEAVING AN ATOMIZED CLOUD OF MERCURY DEPOSITED TO THE END OF THE CAPILLARY.
- VENDOR FULMINATE DECOMPOSES SLOWLY, LEAVING A RESIDUE AND MERCURY DEPOSITS AT LOWER END OF CAPILLARY.
- MERCURY OXALATE IN DRY SLUDGE MIX DECOMPOSES AT TEMPERATURE, LEAVING MERCURY DEPOSITS ABOVE THE SLUDGE, CLEARLY INDICATING PRESENCE OF SENSITIVE MERCURY COMPOUNDS.
- A MIX OF SRTC FULMINATE WITH DRY SLUDGE HAS NOT BEEN TESTED (DETONATION?).

UNRESOLVED ISSUES

- SRTC MERCURY FULMINATE DECOMPOSITION IN DRY SLUDGE MIX (CAPILLARY TEST)
 - DETONATION VS. DECOMPOSITION
- SRTC VS. VENDOR MERCURY FULMINATE (IR, XRD)
 - XRD, DSC, VISUAL DECOMPOSITION DIFFERENCES.
- REACTIVITY OF MERCURY FULMINATE WITH DRY CAUSTIC SLUDGE (DSC)
 - AGING, EFFECT OF TEMPERATURE
- FLAME PROPAGATION IN DRY SLUDGE MIX (BURNING TEST)
 - IS DILUTE FULMINATE SAFE?
- IMPACT TEST FULMINATE/DECOMPOSITION (USE HOT PLATE)
 - DID HAMMER TESTING DECOMPOSE DILUTE FULMINATE, OR
 - IS THE FULMINATE STABILIZED BY DILUTION?

The Effect of Alkaline Media on Energetic Materials

Objective

- Determine the lifetime of HgC_2O_4 and $\text{HgC}_2\text{N}_2\text{O}_2$.
- HgC_2O_4 and $\text{HgC}_2\text{N}_2\text{O}_2$ in 1.8 M $[\text{OH}^-]$ wet sludge.
- Dose rates of 23800 Rad/hour

Figure 1. The Effect of Alkaline Media on Mercury Fulminate

Figure 2. The Effect of Alkaline Media on the Energetic of Mercury Fulminate

Figure 3. The Effect of Alkaline Media on the Energetic of Mercury Oxalate

The Effect of Radiation on Energetic Materials

Figure 4. Radiation Effects on Mercury Fulminate

Figure 5. Infrared spectra of Mercury Fulminate after Radiation Exposure

K u b e l k a - M u n k U n i t s

Figure 6. Infrared Difference Spectra of Mercury Fulminate After Radiation Exposure

Figure 7. The Effect of Radiation Dose on The Energetic of Mercury Fulminate and Oxalate

Figure 8. The Effect of Radiation Dose on The Onset of Decomposition of Mercury Fulminate and Oxalate

Figure 9. The Effect of Radiation Dose (23800 rad/hr) on the Differential Scanning Calorimetry spectrum of Mercury Oxalate

Figure 10. Infrared Spectra of Mercury Oxalate after Radiation Exposure

K u b e l i k a - M u n k U n i t s

Figure 11. Infrared Difference Spectra of Mercury Oxalate After Radiation Exposure

The Effect of Radiation and Wet Alkaline on Energetic Materials

Figure 12. The Effect of Alkaline Media and Radiation on the Mercury Oxalate

Figure 13. The Effect of Alkaline Media and Radiation on Mercury Fulminate

MAIN ISSUES

- Do primary explosives exist at all in sludge
 - Are they formed
 - Do tank conditions destroy them
- Will sludge propagate detonation
 - Sensitivity to initiation
 - Energy absorption of buffer

General Impressions

- Approach
 - Two pronged simultaneously wise
- Experimentation
 - WSRC work thorough and well executed
- Vendor Validation
 - Tendency to cloud the issue

Program Completeness

- Additional Tests (Existence)
 - Higher levels of irradiation of both oxalate and fulminate
 - Irradiation of Chilworth fulminate
 - Potential irradiation of Millon's Base (to avoid getting into circular arguments about surrogates)

Program Completeness

- Additional Tests (Propagation)
 - Drophammer with surrogate (white) sludge
 - Determine if initiation occurs
 - Determine what initiation energy truly is
 - Alternative: Increase fulminate % in sludge until an observable “Go” occurs

Program Completeness

- Additional Tests (Propagation)
 - Larger scale cook-off, thermal run-away
 - Gap test
 - Ignition test
 - To be run in the event that existence of energetic materials is believed to survive irradiation

Program Completeness

- Silver Nitride
 - Tests of limited value
 - Silver in low concentration
 - Handling very problematic
 - Need cost/benefit analysis
 - Immediate impressions are against

Program Completeness

- Individuals
 - Gerald Laib (NSWC); Primary explosive expert
 - Peter Hefferen (CAD); Primary disposal specialist

Program Completeness

- Literature Sources

- Picatinny Encyclopedia of Explosives and Related Items

- Tenney L. Davis, The Chemistry of Powder and Explosives

Program Completeness

- Scale of testing
 - Small-scale (DSC, Impact) good for determination of existence
 - Propagation needs to be on intermediate scale

Validity of Experiments

- Alternate Sample Prep
 - Discusses surrogate sludge for impact
 - Resolve discrepancies in fulminate
- Alternate Handling
 - None immediately apparent

Validity of Experiments

- Concerns over test results
 - Carius tests did not include baseline runs for the sludge samples
 - Chilworth vs. WSRC fulminate issues
 - Uncertainty in initiation in drophammer
 - Results of more representative doses on explosives

Chemistry of Interest

- Alternate energetic compounds
 - Minimum of literature search on suspected Hg compounds
- Other instances with alkaline solutions
 - Needs further research, none currently known

Chemistry of Interest

- Industry analogies
 - None of this complexity
- Survivability of compounds
 - Initially would seem unlikely
 - Need higher dosing experiments for more definitive data

APPENDIX B

Literature Review of Explosives

Based on Mercury

Studied by SRS