

## Possible Explosive Compounds In The Savannah River Site Waste Tank Farm Facilities <sup>(U)</sup>

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# Possible Explosive Compounds In The Savannah River Site Waste Tank Farm Facilities

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## Summary

Based on a comparison of the known constituents in high-level nuclear waste stored at the Savannah River Site (SRS) and explosive compounds reported in the literature, only two classes of explosive compounds (metal  $\text{NO}_2$  compounds and organic compounds) were identified as requiring further work to determine if they exist in the waste, and if so, in what quantities. Of the fourteen classes of explosive compounds identified as conceivably being present in tank farm operations, nine classes (metal fulminates, metal azides, halogen compounds, metal-amine complexes, nitrate/oxalate mixtures, metal oxalates, metal oxohalogenates, metal cyanides/cyanates, and peroxides) are not a hazard because these classes of compounds cannot be formed or accumulated in sufficient quantity, or they are not reactive at the conditions which exist in the tank farm facilities. Three of the classes (flammable gases, metal nitrides, and ammonia compounds and derivatives) are known to have the potential to build up to concentrations at which an observable reaction might occur. Controls have been in place for some time to limit the formation or control the concentration of these classes of compounds. A comprehensive list of conceivable explosive compounds is provided in Appendix 3.

## Introduction

Since 1970, many studies have been conducted concerning the potential for explosive compounds in tank farm operations including ammonium nitrate, metal oxalates, and silver and mercury compounds. The study currently in progress is the most comprehensive to date, encompassing all previous studies and extending the scope to include all compounds that could be formed from the known species in SRS wastes. In addition to waste storage, the study also considers waste removal and waste processing operations.

The total number of explosive compounds is so large that it would not be useful to list them all here. Instead, the only compounds which are listed are those which are known to be present or could conceivably be formed from material that is known to be present in the waste. The general approach to the problem is: (1) identify all of the constituents that are known to be present in the waste together with those that might be present from possible chemical and radiolytic reactions, (2) determine the compounds that could be formed from these constituents, (3) compare these compounds with those listed in the literature, and (4) assess the

formation and stability of these compounds against the conditions existing in the tank farm facilities.

## Discussion

### General Description of Waste Storage and Processing

The Savannah River Site has two high-level nuclear waste storage areas. These areas are located in F Area and H Area adjacent to the separations canyons. The storage facilities consist of 51 underground carbon steel storage tanks, 4 waste evaporators, and underground transfer lines. The transfer lines allow waste to be transported from the waste generator to the tanks, from tank to tank, from tanks to evaporators, between the two tank farms, and to the Defense Waste Processing Facility (DWPF) and the Saltstone Facility.

High-level waste (HLW) generators include chemical separations, reactors, decontamination facilities, the Effluent Treatment Facility (ETF), the Receiving Basin for Off site Fuel (RBOF), analytical laboratories, and research and development laboratories. Chemical separations produces the majority of the HLW at the SRS.

Before waste is transferred into a tank, the waste generator is required to neutralize the waste to prevent general corrosion of the tank. The degree of alkalinity is determined by the chemical composition of the waste. For separations waste, the hydroxide concentration in fresh waste must be greater than 1.0 molar.

Fresh waste is placed in fresh-waste receipt tanks and allowed to stand to enable the insoluble metal oxides and hydroxides to settle. The supernatant liquid is decanted and sent to an evaporator for concentration. After evaporation, the concentrated liquid is transferred to a concentrate receipt tank and cooled. Upon cooling, salts crystallize from the concentrated supernatant liquid. The salts are allowed to settle and the cooled concentrated supernatant liquid is decanted and returned to the evaporator feed tank.

Operating practices prevent the waste from drying at any stage of the storage and handling operations. A layer of supernatant liquid is maintained on top of the sludge or salt in each tank. After each transfer, all transfer lines are flushed to prevent the accumulation of solids. Evaporators are also flushed when shutdown to remove as much waste as possible. Small amounts of dried waste can be produced when waste has leaked into a secondary enclosure and evaporates. Examples of leaked waste which possibly have

formed dried deposits include (1) leaks from the primary tank into the tank annulus, (2) leaks into the waste feed-jet enclosure, and (3) leaks into the evaporator cell.

Two additional processes, In-Tank Precipitation (ITP) and Sludge Processing (SP) are being developed to prepare the high-level waste for disposal. These processes will be carried out in waste tanks which have been modified for chemical processing. Salt waste will be redissolved with water and transferred to the ITP tank for removal of radionuclides. Sludge wastes will be slurried with water and transferred from storage tanks into the SP tanks.

In ITP, supernatant liquid is treated with sodium tetraphenylborate and monosodium titanate to remove radioactive cesium and strontium. The solids are separated from the liquid by filtration and washed with water to reduce the soluble salt content. The washed solids are stored in a waste tank until transferred to the DWPF for processing into a borosilicate glass wasteform. The decontaminated supernatant liquid is stored in a separate tank until it is transferred to the Saltstone Facility for processing into a cement wasteform. Wash waters are recycled in the process to dilute fresh concentrated supernatant liquid.

In SP, the soluble salts in sludge waste are removed by diluting the waste with water, mixing, allowing the slurry to settle and decanting the supernatant liquid. This method of washing is continued until the soluble salt content meets the requirement for processing in the DWPF. For sludge waste containing high levels of aluminum, sodium hydroxide is added to dissolve the alumina, and then the sludge is washed to remove the soluble salts. Wash waters are recycled back into waste removal operations.

### Waste Constituents

High-level nuclear waste is stored at the SRS in a highly alkaline form in underground carbon steel tanks. Because of the high pH, the waste consists of two phases, a liquid phase or supernate, comprised of water soluble salts, and a solid phase or sludge, comprised of hydrous oxides of various metal ions. Appendixes 1 and 2 list the compounds assumed to be present in the supernate and the sludge on a dry weight basis. The compositions are based on analyses of samples taken from waste tanks, essential material records, and process knowledge; a perfect blend of all waste is assumed.<sup>1</sup>

Table 1 gives a list of other species and compounds which may be present in radioactive waste as a result of reactions occurring during chemical processing, miscellaneous additions to waste tanks and new waste processing operations in support of the DWPF. There are two sources of ammonia/

**Table I. Miscellaneous Added Chemicals and Chemical Processing Reaction Products**

Ammonia/ammonium ion  
 Hydrazine  
 Hydroxylamine  
 n-Paraffin  
 Tributyl phosphate  
 Dibutyl phosphate  
 Monobutyl phosphate  
 n-Butanol  
 Gluconic acid  
 Ion-exchange resins  
 Sodium tetraphenylborate  
 Phenol

ammonium ion in the waste: (1) impurities in the process chemicals and (2) reaction of nitrogen-containing chemicals such as sulfamic acid and hydrazine during chemical processing. It has been estimated that >90% of the ammonia/ammonium ion comes from the second source.<sup>2</sup>

Hydrazine and hydroxylamine are chemical reductants which have been used in the chemical separations processes. n-Paraffin, tributyl phosphate, and the ion-exchange resins are also used in the separations processes for the recovery and purification of uranium and plutonium. Gluconic acid was used briefly in chemical separations during the late 1950's, but it has not been used since that time.

Sodium tetraphenylborate will be used to remove radiocesium from salt solution in the ITP process. Phenol is one of the hydrolysis products of tetraphenylborate. Phenol will be produced in the DWPF and it will be returned to the tank farm in a process overheads recycle stream.

During separations processing, excess hydrazine and hydroxylamine are destroyed by chemical reactions with nitrate and nitrite. n-Paraffin is volatile and effectively removed from the waste by evaporation. Thus, the concentration of hydrazine, hydroxylamine, and n-paraffin in evaporated waste would be expected to be extremely low.

Through 1984, it has been estimated that 871,000 pounds of tributyl phosphate had been added to the tank farm.<sup>3</sup> Radiolytic decomposition of the tributyl phosphate will produce n-butanol, dibutyl and monobutyl phosphates, and carbon dioxide.

Ion-exchange resins which have been used at SRS in production facilities include: polystyrene, styrene-divinylbenzene macroporous, and polyvinylpyridine. An estimated 124,000 pounds of ion-exchange resin had been sent to the tank farms through 1984. Approximately two-thirds of the resin was digested with potassium permanganate

before transfer. The digestion process would serve to chemically break the resin into smaller molecular weight fragments and solubilize the resin by formation of hydroxyl and carboxylate groups.

## Possible Classes of Explosive Compounds

Fourteen classes of explosive compounds were identified as conceivably being present by comparing the list of known elements and species in current or planned chemical processing operations with explosive compounds and reactions listed in the literature.<sup>4</sup> A list of the fourteen classes of compounds is given in Table II. A comprehensive list of conceivable explosive compounds is provided in Appendix 3.

Based on a review of the formation and stability of individual compounds at the conditions which exist in storage and processing operations, nine of the fourteen classes were eliminated as possible hazards. The nine classes are metal fulminates, metal azides, halogen compounds, metal-amine complexes, nitrate/oxalate mixtures, metal oxalates, metal oxohalogenates, metal cyanides/cyanates, and peroxides. Three classes (flammable gases, metal nitrides, and ammonia compounds and derivatives) are known to have the potential to build up to concentrations at which an observable reaction might occur. Specific compounds of these three classes include hydrogen, benzene, silver nitride, ammonium nitrate, and ammonium nitrite. Administrative and engineering controls have been in place for some time to limit the formation or control the concentration of these compounds in tank farm facilities.

Two classes (metal NO<sub>2</sub> compounds and organic compounds) may exist, but would be present in such low concentrations that they would not pose a hazard. Further work is underway to determine if these classes exist, and if sufficient quantities can accumulate to present a hazard. Specific compounds of these classes are given in Table III.

## Classes Known to Exist but Controlled

### Flammable Gases

Hydrogen is produced in the waste storage tanks as a result of the radiolysis of water. Based on experimentally measured hydrogen concentrations in the tank vapor space, the hydrogen generation rate in SRS waste tanks is ≤6.0 ft<sup>3</sup>/million Btu of fission product heat.<sup>5</sup> The hydrogen generation rate is also dependent on the nitrate concentra-

**Table II.** Conceivable Explosive Compound Classes in SRS Waste Tanks

Known To Exist But Controlled	
•	Flammable gases
•	Metal nitrides
•	Ammonia compounds and derivatives
Possible And Need Additional Study	
•	Metal NO <sub>x</sub> compounds
•	Organics
Not Possible	
•	Metal fulminates
•	Metal azides
•	Halogen compounds
•	Metal-amine complexes
•	Nitrate/oxalate mixtures
•	Metal oxalates
•	Metal oxohalogenates
•	Metal cyanides/cyanates
•	Peroxides

**Table III.** Compounds Which May Exist And Require Additional Study

Compound	Formula
Mercury NO <sub>x</sub> compounds	
Millon's base (anhydrous)	Hg <sub>2</sub> (NOH)
Nitrate salt of Millon's base	Hg <sub>2</sub> (NHOH)NO <sub>3</sub>
<b>Organic compounds</b>	
Nitrobenzene	C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub>
1,3,5-trinitrobenzene	C <sub>6</sub> H <sub>3</sub> N <sub>3</sub> O <sub>6</sub>
2-nitrophenol	C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub>
4-nitrophenol	C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub>
2,4-dinitrophenol	C <sub>6</sub> H <sub>3</sub> N <sub>2</sub> O <sub>7</sub>
2,4,6-trinitrophenol	C <sub>6</sub> H <sub>3</sub> N <sub>3</sub> O <sub>7</sub>
1,2-dinitrobenzene	C <sub>6</sub> H <sub>4</sub> N <sub>2</sub> O <sub>4</sub>
1,3-dinitrobenzene	C <sub>6</sub> H <sub>4</sub> N <sub>2</sub> O <sub>4</sub>
2-nitroaniline	C <sub>6</sub> H <sub>6</sub> N <sub>2</sub> O <sub>2</sub>
3-nitroaniline	C <sub>6</sub> H <sub>6</sub> N <sub>2</sub> O <sub>2</sub>
4-nitroaniline	C <sub>6</sub> H <sub>6</sub> N <sub>2</sub> O <sub>2</sub>

tion in solution.<sup>6</sup> An increase in the nitrate concentration decreases the rate of hydrogen generation. Since nitrate is the predominant anionic constituent in high-level nuclear waste, hydrogen generation is suppressed relative to that of pure water.

To prevent the accumulation of explosive mixtures of hydrogen in the vapor space of the waste tanks, all of the tanks are equipped with active ventilation system. Air is pulled through the tank to maintain a slight negative

pressure. Typically, the flow rate of air in the tanks ranges from 100-350 cfm.

Hydrogen monitors are installed on the waste tanks. These monitors are set to alarm when the hydrogen concentration reaches 10% of the lower flammability limit (LFL) in air (4%).<sup>7</sup> In the event that the ventilation system is shut down, administrative procedures require that the system be returned to operating condition within a period of time determined by the decay heat load of the tank.<sup>5</sup>

Other flammable gases that conceivably could be produced in the waste tanks include methane, ethane, ethylene, and n-butanol. The amount of organics in fresh waste is limited to reduce the possible formation of flammable organic vapor mixtures. Recent analyses of fresh-waste receipt tanks indicate that the total organic content is less than 350 ppm. Because of the very low organic content and the active ventilation system on each tank, the generation of flammable vapor mixtures is not possible. Even in the event of a loss of the ventilation system, flammable organic vapor mixtures could not be accumulated because of the very low organic content in the waste. Thus, these flammable gases do not present an explosion hazard in tank farm facilities.

Benzene is a volatile organic compound that can form flammable vapor mixtures with air. The LFL for benzene in air is 1.7%. Benzene will be produced during the ITP process and this hazard has been identified. The ITP processing and storage tanks, the filtrate hold tanks, and the cold chemical storage tank will be purged with nitrogen. This will reduce the oxygen concentration in these facilities to a level below that which is required to support combustion. Recommended operational safety requirements limit the oxygen concentration in these facilities to less than 6.3% by volume.<sup>8</sup>

#### Metal Nitrides

In 1970, popping noises were heard when personnel stepped on dried waste deposits, when equipment bumped into surfaces contaminated with dried waste, and when a sampling tool was intentionally scraped against dried waste in separate incidents at the Tank 21H feed-jet enclosure and the Building 242-H evaporator cell. An investigation of the incident implicated silver nitride as the cause of the explosive deposits.<sup>9</sup>

Silver nitride is formed by the decomposition of silver diammine solutions. Since silver and ammonia were known to be present in the waste sent to the evaporator, conditions existed in which silver nitride could have formed. Although



the dried waste deposits exhibited an observable reaction, the reaction was not a propagating reaction. Dried waste adjacent to the waste which was contacted did not undergo any observable reaction.

To prevent the formation of explosive silver compounds, the introduction of silver into waste tanks was discontinued in 1970. Since this administrative control has been in place, no other incidents of this type have been observed in tank farm operations.

Silver-containing waste will be removed and processed for disposal during the ITP and SP operations. However, the hazard of handling this waste will be very low because of the hydrolysis of nitrite, the dilution of the silver-containing waste, and the lack of a propagating reaction for the dried waste. Nitride ion is reported to slowly hydrolyze in aqueous solutions. Thus, any nitride which may have formed initially would have decomposed during storage. Silver-containing waste will have been diluted with other waste over the years by transfers among tanks such that the concentration would be much lower than that sent to the evaporator in 1970. Also, if small amounts of the silver-containing waste were to be dried and contacted, propagation of the reaction to other waste would not be expected to occur based on the behavior exhibited in the 1970 incidents.

#### Ammonia Compounds and Derivatives

Ammonium nitrate, ammonium nitrite, and ammonia/air mixtures are well documented explosive hazards.<sup>4</sup> Impure ammonium nitrate and ammonium nitrite are reported to be much more explosive than chemically pure compounds. The presence of organic material not only increases the sensitivity of the ammonium nitrate to decomposition, but also increases the energy released by reacting with the oxygen present in the air.<sup>10</sup>

Ammonium nitrate has been transferred from the chemical separations operations to the waste tanks. The first reported transfer of a large quantity of ammonium nitrate occurred in 1976, when approximately 3,100 kg of ammonium nitrate was discharged to two waste tanks. Radiolysis converts nitrate to nitrite. Therefore, some of the ammonium nitrate is converted to ammonium nitrite during storage.

An investigation determined that the source of the ammonium nitrate was the vessel vent filters of the F canyons.<sup>2</sup> The filters were flushed with water to remove the ammonium nitrate and the solution was transferred to the tank farm. Infrequent transfers of ammonium nitrate from the

separations canyons continue today when the vessel vent filters are flushed.

To prevent the formation of explosive ammonia/air vapor mixtures, transfers of ammonium nitrate into the tank farm are carefully controlled under written procedure. The procedure limits the concentration of ammonium nitrate to  $\leq 2.5$  wt % and the quantity of ammonium nitrate which can be received in any 12-hour period to  $\leq 1,000$  kilograms. During transfers, the vapor space is monitored for ammonia. Transfers are stopped if the ammonia concentration exceeds 1.5%, which is an order of magnitude less than the LEL of 16% for ammonia/air vapor mixtures.

Because of the high pH, most of the ammonia present in fresh waste is removed during storage and evaporation. The limit of  $\leq 2.5$  wt % ammonium nitrate in fresh waste maintains a safe concentration of ammonia in tank vapor space and in the evaporator overheads. Nitrite is produced by the radiolysis of nitrate. Thus during storage, any ammonia in the waste may be present as either ammonium nitrate or ammonium nitrite.

Ammonium nitrate is more soluble than sodium nitrate. Any ammonium nitrate remaining in the evaporator concentrate would probably remain in solution upon cooling and either be volatilized and removed in the tank ventilation system or would be returned to the evaporator and removed in the overheads. Thus, there is no identified mechanism for concentrating ammonium nitrate or ammonium nitrite in any of the tank farm facilities.

Two other ammonia derivatives, hydrazine and hydroxylamine, are used as reductants in the chemical separations processes, and could conceivably be in the high-level waste. Both compounds are explosive under certain conditions. However, because of the chemical instability of each compound at the conditions present in the separations processes and the tank farm handling facilities, neither would be present in stored waste.

Hydrazine reacts rapidly with nitrous acid to produce nitrogen, nitrous oxide, and water.<sup>2</sup> This reaction is used in the separations canyons to destroy excess hydrazine without forming ammonia. Hydrazine is a powerful reductant in basic solutions.<sup>11</sup> Known species that it could react with in the waste include nitrate, nitrite, and hydroxide. If an insufficient amount of nitrite were added to destroy the hydrazine during chemical separations, the hydrazine would rapidly react with oxidants or metal ions in solution when the waste is neutralized. Thus, hydrazine would not be expected to be present in neutralized SRS waste.

Alkaline solutions of hydroxylamine are unstable and decompose to give a mixture of nitrous oxide and ammonia. The rate of reaction is dependent on the concentrations of hydroxide and hydroxylamine and the temperature. Because of the high hydroxide concentration and moderate temperatures in the waste tanks, the decomposition of hydroxylamine would be fairly rapid. Thus, significant amounts of hydroxylamine would not be expected to be present in SRS waste.

## Classes Which May Exist and Require Further Study

### Metal NO<sub>x</sub> Compounds

Reported explosive compounds of this type include the anhydrous form and salts of Millon's base, lead hyponitrite, and silver hyponitrite. Sodium nitrate is a strong oxidizer, and explosions have been reported with mixtures containing cellulose. Cellulosic materials (wood, paper, etc.) have not been mixed with high-level waste, and thus, this type of explosion hazard would not exist in tank farm facilities.

Hyponitrite is generally formed by the reduction of nitrate by sodium amalgam. The necessary conditions are not present in SRS waste. However, nitrate is reduced by radiolysis to nitrite and lower oxidation state nitrogen-oxygen compounds such as hyponitrite may be produced radiolytically. Mercury, lead, and silver are all present in SRS waste so hyponitrite salts with these metals are conceivable.

Lead and mercuric hyponitrite are reported to decompose in the presence of sodium hydroxide. Because of the high hydroxide concentration in SRS waste, both of these compounds would not be stable and sufficient quantities would not exist to present a hazard. The introduction of silver-containing waste into the tank farms was stopped in 1970. As a result, the concentration of silver in SRS waste is very low and silver is not concentrated by the ITP or SP operations. Thus, the formation of silver hyponitrite would be very unlikely.

In 1988, shock-sensitive deposits were detected on laboratory corrosion test specimens immersed in solutions simulating the DWPF offgas condensate stream, which will be recycled to the H-Area tank farm. This stream is a relatively dilute aqueous solution containing nitrate, mercury, phenoxide, and halides. Nitrite and hydroxide will be added to the waste stream to inhibit possible pitting corrosion of the carbon steel waste tanks.

Conclusive identification of the deposits was not possible due to the small quantity of material isolated. Based on the analytical results obtained, the deposits contained mercury and nitrogen. The solid deposits may be a salt of Millon's base or some other mercury NO<sub>x</sub> compound.<sup>12</sup> Millon's base, Hg<sub>2</sub>NOH·2H<sub>2</sub>O, may exist in waste, but is not an explosive compound. The monohydrate is feebly explosive and the anhydrous compound, Hg<sub>2</sub>NOH, is explosive. The monohydrate and anhydrous compound are generally prepared by dehydrating Millon's base in an atmosphere of anhydrous ammonia or by heating in the presence of desiccants.

The shock-sensitive deposits were observed to be formed at high temperatures (>70°C) and high nitrite concentrations. Since this initial work, changes in DWPF processing have been recommended which will significantly decrease the amount of nitrite in the recycle stream. Tests are continuing to complete characterization of the shock-sensitive deposits and to determine if the deposits are formed at the new flowsheet concentrations and at conditions which will be encountered in the tank farm facilities.

### Organic Compounds

High-level waste stored at the SRS contains small amounts of organic compounds. Based on receipts of organic compounds in the tank farms through 1984, a total organic carbon concentration in the waste assuming a perfect blend is calculated to be 2,200 ppm.<sup>13</sup> The actual concentration would be much lower than this due to radiolytic and chemical decomposition. Recent analysis of two high activity waste receiver tanks indicated a total organic carbon content of 86 ppm and 220 ppm,<sup>14</sup> well below that estimated based on organic compound receipts to the tank farm.

Organic compounds which have been used in chemical processing and are present in SRS waste include n-paraffin (primarily dodecane), tributyl-phosphate, and ion-exchange resins. Significant quantities of organic compounds will be processed in the H-Area tank farm upon startup of the ITP process. Sodium tetraphenylborate will be used to remove radiocesium from salt solution. Phenoxide will be returned to the tank farm as a constituent of the DWPF offgas recycle stream.

Waste temperature and active ventilation systems on waste tanks are used to maintain the the vapor concentration of the volatile organic compounds below the LFL. Whenever possible, the temperature near the liquid surface is kept below 70°C, which is lower than the reported flash point of 74°C for dodecane, the organic diluent having the lowest

flash point. For tanks warmer than 70°C, the active ventilation system on each tank keeps the concentration below the LFL, just as in the case of hydrogen. The minimum airflow requirements increase as the temperature of the supernatant liquid increases.<sup>15</sup>

Organic solvent is entrained and dissolved to some extent in the waste streams that enter the tank farm from chemical separations. The organic solvent consists of tributylphosphate in organic diluents which are primarily dodecane. The LFL for dodecane in air is 0.6 vol %. The flash point of tributylphosphate is 146°C, which is well above temperatures at which waste is stored.<sup>16</sup> Temperatures as high as 155°C can be achieved during the evaporation of waste. However, the high water content in the evaporator vapor space would prevent the accumulation of a flammable vapor mixture during evaporation.

Tributylphosphate is known to hydrolyze in alkaline solution producing monobutylphosphate, dibutylphosphate, phosphate, and n-butanol. n-Butanol has a LFL in air of 1.7%.<sup>16</sup> Flammable vapor mixtures of n-butanol are prevented from accumulating by the active ventilation system on each tank, just as in the case of hydrogen.

Slurries produced during normal ITP operations are not ignitable due to the high water content. However, the presence of solid deposits of tetraphenylborate and nitrate are conceivably explosive. No evidence has been obtained that indicates that the dried deposits of tetraphenylborate salts are explosive; however, the deposits are combustible and produce dense black smoke when burned.<sup>17</sup> Confined heating, mechanical impact, and hot wire or flame contact of dry solids containing the maximum and minimum limits for tetraphenylborate and nitrate mixtures did not produce hazardous responses. Because of the possibility that more energetic mixtures could be formed at levels between the limits tested, additional testing is recommended.

To reduce the possibility of ignition of tetraphenylborate solids, the ITP processing and storage tanks, the filtrate hold tanks, and the cold chemical storage tank will be purged with nitrogen. This will reduce the oxygen concentration to a level below that which is required to support combustion. Recommended operational safety requirements limit the oxygen concentration in these facilities to less than 6.3 vol %.<sup>3</sup>

Sodium tetraphenylborate is known to undergo radiolytic-induced decomposition reactions which produce a variety of compounds including phenol, nitrophenol, biphenyls, terphenyls, and phenylamine. The DWPF will return a liquid waste stream which contains phenol to the tank farm. The recycle stream will be mixed with other low activity waste.

Based on a review of the reported literature, phenol (phenoxide in high pH solutions) is relatively stable. If the phenoxide were to react, the major products are predicted to be di- and tri-hydroxy benzene compounds.<sup>18</sup> However, there does exist the potential for the formation of nitro-substituted compounds, which are known explosives (Table III). Experimental studies have been planned to determine if, and in what quantity, explosive compounds can be produced from the radiolytic decomposition of waste tank organics.<sup>19</sup>

## Classes Which are Not a Hazard

### Metal Fulminates

Silver and mercury fulminates are prepared by the addition of silver or mercury nitrate solutions to an alcohol and allowing the mixture to stand.<sup>20</sup> The resulting solids are extremely shock sensitive. Because of the very high hydroxide concentration, the concentrations of silver and mercury in solution are very low. Also, very little alcohol is present in SRS waste. Thus, the chemistry present in tank farm operations is very unfavorable for the formation of metal fulminates.

During the investigation of an incident in 1970, metal fulminates were identified as possibly being formed. Laboratory tests were conducted to determine if silver and mercury fulminates could be prepared under conditions present in the waste tanks. The tests indicated that fulminates are not produced at the conditions existing in the waste tanks.<sup>9</sup>

Since 1970, the introduction of silver into the tank farm has been stopped. Mercury has been used and continues to be used in separations as a catalyst in the dissolution of aluminum. Most of the mercury is precipitated upon neutralization of the high-level waste. However, some of the mercury is soluble at the high pH and would be present in the ITP process. The average concentrations of silver, as  $\text{NaAg}(\text{OH})_2$ , and mercury, as  $\text{NaHgO}(\text{OH})$ , in the ITP salt solution are calculated to be  $4.6 \times 10^{-6}\text{M}$  and  $2.2 \times 10^{-6}\text{M}$ , respectively.<sup>21</sup>

Alcohols have not been used as process chemicals at SRS and would only be present in trace amounts as a result of laboratory operations and decomposition of tributylphosphate and other organics. Methanol and isopropanol are two impurities which may be present in the monosodium titanate (MST) slurry, which will be used in the ITP process. To reduce the quantity of alcohol which will be introduced into the tank farm, the total amount of alcohol in the MST

slurry is limited to less than vol %.<sup>22</sup> MST slurries recently prepared and submitted to WSRC by possible vendors have been analyzed to contain <0.1 vol % alcohol.

Assuming that the alcohol concentration of the MST slurry is vol %, the maximum possible concentration in the ITP processing tank is estimated to be 160 ppm.<sup>13</sup> The concentration of alcohol will be further reduced upon filtering and washing of the slurry in subsequent processing steps. Also, some of the alcohol will be removed from the decontaminated supernate during benzene stripping. Because of the very low concentrations of silver, mercury, and alcohol, the formation of silver and mercury fulminates is extremely unfavorable in tank farm facilities.

### Metal Azides

Hydrazoic acid,  $\text{HN}_3$ , is reported to be dangerously explosive.<sup>4</sup> The minimum explosive concentration of  $\text{HN}_3$  is reported to be 4.7M (17%) in aqueous solutions. Heavy metal azides such as silver, mercury, lead, cadmium, and barium are also reported to be explosive and have been used in detonation assemblies.<sup>23</sup> Electropositive metal azides such as sodium azide are not explosive, and decompose smoothly at temperatures above 300°C.<sup>11a</sup>

Azide ion is reported to react with nitrite to produce nitrous oxide and nitrogen as given in equation 1.<sup>20a</sup> Reaction rates have not been reported under alkaline conditions.



Because of the high nitrite concentration in high-level nuclear waste and the low solubility of heavy metals at high pH, there is no conceivable mechanism by which hydrazoic acid and/or metal azides could be produced during storage or during DWPF feed preparation processes. As a result, the formation of explosive azides is not a hazard in tank farm operations.

Hydrazoic acid is known to be one of the products from the reaction of hydrazine with nitrite in nitric acid solutions.<sup>24</sup> From a consideration of the accumulation of explosive solutions by distillation or the formation of explosive mixtures of  $\text{HN}_3$  in air by vaporization, it was established that a concentration of 0.05M  $\text{HN}_3$  in process solutions is a safe limit for the separations canyons. Based on laboratory studies and actual measurements of process solutions, the maximum concentration of hydrazoic acid in unneutralized waste solutions is 0.012M.

Metal azides could be produced during separations processing. Mercuric ion is the only heavy metal ion present in

significant quantities during the generation of  $\text{HN}_3$ . Thus, mercuric azide would be the only metal nitride which could be formed at this stage. Explosive or spontaneous-detonating mercury azide is reported to be formed only under conditions of slow diffusional growth.<sup>25</sup>

Laboratory tests indicated no spontaneous detonations in aqueous mercuric solutions containing less than 0.02M azide. In tests with both ferric and mercuric ions present (which would more accurately represent actual process conditions), the precipitated solids could not be detonated at mercury concentrations up to 0.08M and azide concentrations up to 0.16M. These concentrations greatly exceed the concentration of mercury in neutralized stored waste.

### Halogen Compounds

Halo-nitrogen compounds such as nitrogen triiodide and nitrogen chloride and halo-oxygen compounds such as chlorine dioxide and dichlorine heptaoxide are known to be explosive under certain conditions. All of the necessary elements are present in SRS for each of these compounds. However, the conditions necessary to produce these compounds are not present in the SRS separations and waste handling facilities. Also, these compounds are not stable in highly alkaline aqueous solutions. Consequently, none of these compounds would be present in sufficiently large enough quantities to be an explosion hazard.

Nitrogen trichloride and nitrogen triiodide are formed by reacting the ammonium halide with the appropriate hypohalous acid or halogen gas.<sup>26</sup> Traces of hypohalous acid or halogen could be present during chemical separations, and thus, these compounds could be formed in the separations canyon. However, under alkaline conditions, neither hypohalous acid nor halogen gas would be present in tank farm operations. Nitrogen trichloride and nitrogen triiodide are readily hydrolyzed in alkaline solution to reform ammonium halide and nitrogen. Since SRS waste has a high water content, any nitrogen halide formed during separations processing would be rapidly hydrolyzed to nonexplosive compounds. Dried deposits of waste containing these compounds would be very unlikely since these compounds, if formed, would have hydrolyzed before the waste could have leaked and dried.

Chlorine dioxide can be produced by one of four reactions: (1) disproportionation of chloric acid, (2) oxidation of chlorite with chlorine, (3) reduction of chlorate with oxalic acid.<sup>26</sup> Since chlorine and acid conditions do not exist during normal waste processing and storage operations, chlorine dioxide would not be expected to be generated. During cleaning of a waste tank with oxalic acid, there

would exist the possibility of generating chlorine oxide if chlorate were present. Chlorate is not a process chemical, but conceivably could be produced by the oxidation of chloride. However, from the enthalpy of formation, the concentration of chlorate in the highly alkaline waste is estimated to be  $<1.2 \times 10^{-30} \text{ M}$ . Thus, the amount of chlorine dioxide which could be produced would be extremely small and would not be an explosion hazard.

Dichlorine heptaoxide is produced by the dehydration of perchloric acid. Perchlorates are not used as process chemicals at SRS and the formation of appreciable amounts of perchlorates is not expected based on thermodynamics (see Metal Halogenates). Since the waste is stored as a highly alkaline aqueous slurry, formation of dichlorine heptaoxide is not possible. If dried waste deposits were produced, the formation of sufficient quantities of dichlorine heptaoxide to present a hazard would not be possible because of the extremely low equilibrium concentration of perchloric ( $2.3 \times 10^{-30} \text{ M}$ ) in SRS waste.

### Metal-Amine Complexes

Amine complexes of metals containing oxyanion ligands have been reported to be explosive and exhibit moderate to strong shock sensitivity. These compounds are particularly hazardous because of the presence of both fuel (amine) and oxidant (oxyanion ligand) in the same compound. SRS waste contains all three species for forming complexes of this type: ammonia, metal ions, and oxyanions (e.g., nitrate, nitrite, and sulfate). Metals ions which are present in SRS waste and which could conceivably form amine complexes include copper, chromium, cobalt, mercury, palladium, platinum, silver, and zinc.

The chemistry existing in SRS tank farm operations is extremely unfavorable for the formation of these complexes. Also, any metal amine complexes which might be introduced into the tank farm would rapidly decompose because of the high pH and produce nonexplosive compounds. Thus, metal amine complexes are not an explosion hazard in SRS tank farm facilities.

Preparation of metal-amine complexes is generally carried out in concentrated ammonium hydroxide solution or liquid ammonia. Syntheses of metal amine complexes have also been reported in which metal salts are treated with ammonia gas at elevated temperature.<sup>20b</sup> None of these conditions exist in any tank farm facility or operation.

Metal-amine complexes are known to hydrolyze in aqueous solutions. The reactivity of a particular complex varies for metal and the specific chemical conditions (e.g., concentra-

tion, pH and temperature).<sup>20b</sup> At the pH which is maintained in the waste tanks ( $\text{pH} > 12$ ), the metal-amine complexes would rapidly undergo hydrolysis to give metal hydroxide and hydrous oxide species. Thus, metal-amine complexes would not be present in sufficient quantities in SRS wastes to present an explosion hazard.

### Nitrate/Oxalate Mixtures

Based on the heats of formation, the reaction of sodium nitrate and sodium oxalate is extremely exothermic and would generate large amounts of gas that could exceed the capacity of the HEPA filters on the waste tanks. From the chemical reaction in equation 2, the heat of reaction is calculated to be  $-203.4 \text{ kcal/mole}$ .



No references to explosive hazards of mixtures of sodium nitrate and sodium oxalate have been found in the literature. Differential thermal analyses of mixtures of sodium nitrate, sodium nitrite, and sodium oxalate indicate that both endothermic and exothermic reactions are initiated upon heating to about  $150^\circ\text{C}$ . Endothermic reactions are observed to be initiated from about  $160^\circ\text{C}$  to  $315^\circ\text{C}$ . A single exothermic reaction is initiated in the range from  $375^\circ\text{C}$  to  $450^\circ\text{C}$ .<sup>27</sup> The observed reactions appeared to be well behaved.

Since SRS waste is evaporated, stored, and processed at temperatures of  $\leq 155^\circ\text{C}$ , which is well below the temperatures necessary to initiate exothermic reactions, exothermic reactions of sodium nitrate and oxalate would be very unlikely during storage and processing operations. Thus, SRS waste mixtures containing mixtures of nitrate and oxalate are not a hazard under existing operating conditions.

### Metal Oxalates

During sludge removal from Tank 16, a special procedure using oxalic acid was used to assist in slurring the final 15% of the sludge. Under acid conditions, mercury and silver oxides can react with oxalic acid to produce insoluble mercury and silver oxalates.<sup>28</sup> Since Silver and mercury oxalates are reported to be weakly explosive, an experimental study was undertaken to determine the explosive hazards of this procedure.

Based on the amount of mercury in the waste, it was estimated that the maximum amount of mercury oxalate that could be produced in the waste tank would be 900 kg. The concentration of silver was not known, but based on analysis

of similar waste in other tanks, the amount of silver was far less, and thus the amount of silver oxalate in this tank would be insignificant compared to the amount of mercury oxalate. For other waste tanks, the amount of silver may be significantly higher and therefore the amount of silver oxalate could be significant.

Experimental testing indicated that neither compound could be ignited by an electric arc when dispersed in air.<sup>29</sup> Explosions well below detonation conditions were observed only when the materials were confined or dry and in a pure form, which is not likely to occur in tank farm facilities. Testing also indicated that both mercury and silver oxalates undergo metathesis reactions under alkaline conditions to give the insoluble metal hydroxides. Thus, during typical tank farm processing and storage operations, mercury and silver oxalates would not be expected to be present. It was therefore concluded that silver and mercury oxalates do not represent an explosion hazard.

#### Metal Halogenates

Halogenates such as perchlorates, periodates, chlorates and chlorites form a well known class of explosive compounds. Acids or metal salts of the halogenates have never been used in separations operations, although very small amounts of halogenates have probably been introduced into the waste tanks from use in laboratory studies. Since chloride and iodide are known constituents of SRS waste, there exists the possibility of generating these species by oxidation of the halides in the waste.

Possible oxidants include oxygen, nitrate, nitrite, mercury(I), mercury (II), and chromate. In the highly alkaline wastes, oxygen is the strongest oxidant of those listed. Based on the redox potentials<sup>11b</sup> for the oxidation of chloride to perchlorate and reduction of oxygen to hydroxide, a chloride concentration of 0.022M in solution and an oxygen concentration of 0.01708 mL/mL of solution, the equilibrium concentration of perchlorate is calculated to be  $2.3 \times 10^{-30}$  M.<sup>13a</sup> Inspection of the redox potentials for the other oxychlorides indicates that the formation of each would be less favored thermodynamically than perchlorate. As a result, the concentration of each at equilibrium would be less than that calculated for perchlorate.

Of all the halogenates, iodate would be the most thermodynamically favored species. Assuming an iodide concentration of  $2.1 \times 10^{-6}$  M and an oxygen concentration of 0.01708 mL/mL of solution, the equilibrium concentration for iodate would be  $1.1 \times 10^{-11}$  M. This concentration is equivalent to about 10 mg of iodate in a waste tank completely filled with supernate. Because of the extremely small amounts of

halogenates which are estimated to be present in liquid waste, this class of compounds is not an explosion hazard in SRS tank farm facilities.

#### Metal Cyanides/Cyanates

This class of compounds is often endothermic and can undergo violent oxidation under certain conditions which releases significant amounts of energy. For example, mixtures of solid potassium and mercury(II) cyanides and sodium nitrite are reported to be explosive when heated. Mercury cyanate is reported to explode when crushed and endothermic compounds such as cadmium cyanide and nickel cyanide can decompose explosively under certain conditions.

Potassium, nickel, and mercury are known components of SRS high level waste. Cyanide has been detected at a very low level in one of the SRS waste tanks. However, based on the absence of an identified source of significant amounts of cyanide and cyanate and the instability of both species to the physical and chemical conditions at which waste is stored and processed in the tank farms, the accumulation of metal cyanides and metal cyanates in quantities that would be sufficient to be an explosion hazard appears unlikely.

Cyanide and cyanate compounds have not been used in processes at the SRS, although very small amounts of cyanide and cyanate could have been introduced in the waste from use at site laboratories or as impurities in process chemicals. The only documented analysis of waste in which cyanide was detected occurred in 1986 for a sample taken from Tank 50H. A cyanide concentration of 3.6 ppm was determined.<sup>30</sup> In 1986, Tank 50H contained a low-level salt solution produced by the 1983 full-scale demonstration of the ITP process. Since 1989, concentrated salt solution from the ETF process has been added to this tank.

A review of the radiation chemistry literature revealed no reports of cyanide being formed by radiolytic sources.<sup>31</sup> However, there were no reports of radiolysis of alkaline solutions containing carbonate and nitrite/nitrate levels characteristic of high-level waste at SRS. Therefore, the radiolytic generation of cyanide appears doubtful, but cannot be ruled out. The most likely source of cyanide is as an impurity in other chemicals such as sodium hydroxide or sodium tetraphenylborate.

Cyanides are easily oxidized to cyanates in solution.<sup>32</sup> Cyanide is also reported to decompose in the presence of ionizing radiation.<sup>33,34</sup>

Cyanates are reported to undergo radiolytic decomposition<sup>35</sup> and hydrolysis in strongly alkaline solutions.<sup>36</sup> Hydrolysis of the cyanate produces carbonate, carbon dioxide, and ammonia. Based on the absence of an identified source of significant amounts of cyanide and cyanate and the instability of both species to the physical and chemical conditions at which waste is stored and processed in the tank farms, the accumulation of metal cyanides and metal cyanates in quantities that would be sufficient to be an explosion hazard appears unlikely.

### Peroxides

There are three possible types of peroxide explosion hazards: (1) peroxide/organic mixtures, (2) organic peroxides, and (3) metal peroxides. Hydrogen peroxide/organic mixtures are reported to be explosive when the ratio of peroxide to water is  $>1$  and the overall fuel/peroxide composition is close to the stoichiometric value. Metal peroxides are reported to be explosive when heated above 100°C. Metal peroxides that could conceivably be present in the waste are those of silver, barium, calcium, cadmium, mercury, potassium, sodium, strontium, and zinc.

Hydrogen peroxide is not used at SRS in chemical processing operations. Very small amounts of peroxide may have been added to the tank farm from use at SRL. Radiolytic generation of peroxide is well known in aqueous solutions.<sup>37</sup> The yield or G value (molecules per 100 eV) for peroxide varies slightly with pH, decreasing slightly in alkaline solutions as compared to acidic solutions.

The G value for peroxide formation is decreased by hydroxyl radical scavengers such as chloride, bromide, iodide, and nitrite. Since nitrite and chloride are present in relatively high concentration, the formation of peroxide would be expected to be suppressed in the highly alkaline, high salt containing waste. Consequently, there is no plausible mechanism by which peroxide concentration would begin to approach that of water present in the waste. Thus, the possibility of forming an explosive peroxide/organic mixture would be unlikely.

Because of the low organic content of the waste and the instability of organic peroxides in highly alkaline solutions, organic peroxides do not present a safety hazard in tank farm operations. Organic peroxides are conceivably produced in waste by the reaction of organics with oxygen-containing radicals and/or the combination of two alkoxide radicals. These types of radicals are well known products produced by the radiolysis of water and alcohol solutions. However, the concentration of organics in the waste is very low, and as

a result, the concentration of organic peroxides generated by either of these pathways would also be very low.

One of the preferred methods for the disposal of organic peroxides is to treat the peroxide with sodium hydroxide solution.<sup>38,39</sup> Because of the high hydroxide concentration in SRS waste, organic peroxides would not be stable, and the accumulation of hazardous quantities of organic peroxide is not possible.

Because of the chemical and physical conditions at which waste is stored and processed in the tank farms, accumulation of metal peroxides in quantities that would be sufficient to be an explosion hazard appears unlikely.<sup>20c</sup> Heavy metal peroxides (e.g., Ag, Cd, Hg, and Zn) are not stable in water. Because of the high water content of SRS waste, the heavy metal peroxides would not be stable and significant quantities would not be produced. Potassium peroxide is reported to be stable only in cold ( $<10^{\circ}\text{C}$ ) aqueous solutions. Since SRS wastes are stored at much higher temperatures, potassium peroxide would not be stable and would immediately decompose. Dried deposits of waste containing metal peroxides would be very unlikely since these compounds would have decomposed before the waste could have leaked and dried.

The alkaline earth peroxides (e.g., Ca, Sr, and Ba) are reported to react with sodium carbonates and sulfates precipitating the alkaline earth carbonate or sulfate and liberating oxygen. Since appreciable quantities of carbonate and sulfate are present in SRS waste, any alkaline earth peroxides which might be formed would immediately react with carbonate and/or sulfate. Sodium peroxide is fairly stable in aqueous solutions and will crystallize from aqueous solution. However, transition metal ions (e.g., Fe, Mn, Cu, Co, and Ni) are known to catalyze the decomposition of sodium peroxide. Since all of these metals are known to be present in SRS waste, it would appear unlikely that appreciable quantities of sodium peroxide could form and crystallize from waste stored in the tank farms.

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## Appendix 1. Average Composition of Supernate (page 1 of 1)

Compound	Wt %
NaNO <sub>3</sub>	45.7
NaOH	7.30
NaNO <sub>2</sub>	18.5
NaAlO <sub>2</sub>	10.0
Na <sub>2</sub> CO <sub>3</sub>	7.70
Na <sub>2</sub> SO <sub>4</sub>	10.4
NaCl	0.313
NaF	$2.03 \times 10^{-2}$
Na[HgO(OH)]	$6.27 \times 10^{-2}$
Group A	$1.31 \times 10^{-3}$
Group B	$3.74 \times 10^{-4}$
Na <sub>2</sub> PuO <sub>2</sub> (OH) <sub>4</sub>	$2.54 \times 10^{-6}$
UO <sub>2</sub> (OH) <sub>2</sub>	$1.66 \times 10^{-4}$
Na <sub>2</sub> RuO <sub>4</sub>	$5.11 \times 10^{-3}$
Na <sub>2</sub> RhO <sub>4</sub>	$5.24 \times 10^{-4}$
CsNO <sub>3</sub>	$9.76 \times 10^{-3}$
Ba(NO <sub>3</sub> ) <sub>2</sub>	$1.64 \times 10^{-3}$
Sr(NO <sub>3</sub> ) <sub>2</sub>	$1.47 \times 10^{-3}$
Y(NO <sub>3</sub> ) <sub>3</sub>	$1.04 \times 10^{-3}$
NaI	$2.95 \times 10^{-3}$
Total organic carbon <sup>a</sup>	$7.30 \times 10^{-2}$

Group A: Tc, Se, Te, Rb, and Mo

Group B: Ag, Cd, Cr, Pd, Tl, La, Ce, Pr, Pm, Nd, Sm, Tb, Sn, Sb, Co, Zr, Nb, Eu, Np, Am, and Cm

<sup>a</sup> Based on highest measured value for fresh waste receipt tank supernate samples (D. T. Hobbs, "Organic Content of Tank 33 and Tank 34 Supernate Samples", IWT-LWP-91-033, March 7, 1991).

## Appendix 2. Average Composition of Sludge (page 1 of 1)

Compound	Wt %	Compound	Wt %
Fe(OH) <sub>3</sub>	30.1	Al(OH) <sub>3</sub>	32.9
MnO <sub>2</sub>	5.10	Ni(OH) <sub>2</sub>	1.94
CaCO <sub>3</sub>	4.00	Zeolite	3.65
SiO <sub>2</sub>	5.87	NaOH	3.28
NaNO <sub>3</sub>	2.83	HgO	1.60
CaSO <sub>4</sub>	0.475	CaC <sub>2</sub> O <sub>4</sub>	0.404
Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	0.373	CaF <sub>2</sub>	0.101
NaCl	0.101	ThO <sub>2</sub>	0.576
PbSO <sub>4</sub>	0.141	Cr(OH) <sub>3</sub>	0.384
AgOH	2.03 x 10 <sup>-2</sup>	Cu(OH) <sub>2</sub>	0.112
Co(OH) <sub>2</sub>	6.06 x 10 <sup>-2</sup>	Zn(OH) <sub>2</sub>	0.293
Mg(OH) <sub>2</sub>	0.505	Carbon	9.81 x 10 <sup>-2</sup>
Group A	0.274	Group B	0.902
PuO <sub>2</sub>	3.68 x 10 <sup>-2</sup>	SrCO <sub>3</sub>	0.105
Y <sub>2</sub> (CO <sub>3</sub> ) <sub>3</sub>	6.91 x 10 <sup>-2</sup>	RuO <sub>2</sub>	6.62 x 10 <sup>-2</sup>
RhO <sub>2</sub>	1.40 x 10 <sup>-2</sup>	CsNO <sub>3</sub>	1.06 x 10 <sup>-2</sup>
BaSO <sub>4</sub>	0.151	UO <sub>2</sub> (OH) <sub>2</sub>	3.40
NaI	1.01 x 10 <sup>-2</sup>		

Zeolite: 48.0 wt % SiO<sub>2</sub>, 19.1 wt % H<sub>2</sub>O, 18.6 wt % Al<sub>2</sub>O<sub>3</sub>, 4.1 wt % Na<sub>2</sub>O, 10.2 wt % CaO.

Group A: Tc, Se, Te, Rb, and Mo

Group B: Ag, Cd, Cr, Pd, Ti, La, Ce, Pr, Pm, Nd, Sm, Tb, Sn, Sb, Co, Zr, Nb, Eu, Np, Am, and Cm

## Appendix 3. Comprehensive Listing of Conceivable Explosive Compounds (page 1 of 3)

Compound	Formula
Barium hexanitride	$\text{BaN}_6$
Barium peroxide	$\text{BaO}_2$
Calcium peroxide	$\text{CaO}_2$
Chlorine heptaoxide	$\text{Cl}_2\text{O}_7$
Chlorine oxide	$\text{ClO}_2$
Hexaamminechromium(III) nitrate	$[(\text{H}_3\text{N})_6\text{Cr}](\text{NO}_3)_3$
Pentamminenitratochromium(III) nitrate	$[(\text{H}_3\text{N})_5\text{Cr}(\text{NO}_3)](\text{NO}_3)_2$
Diamminenitratocobalt(II) nitrate	$[(\text{H}_3\text{N})_2\text{Co}(\text{NO}_3)](\text{NO}_3)$
Tramminetrinitrocobalt	$(\text{H}_3\text{N})_3\text{Co}(\text{NO}_2)_3$
Trihydrazinecobalt(II) nitrate	$[(\text{H}_4\text{N}_2)_3\text{Co}](\text{NO}_3)_3$
Ammonium hexanitocobaltate	$(\text{H}_4\text{N}^+)_3[\text{Co}(\text{NO}_2)_6]^{3-}$
Pentaamminenitratocobalt(III) nitrate	$[(\text{H}_3\text{N})_5\text{Co}(\text{NO}_3)](\text{NO}_3)_2$
Hexamminecobalt(III) permanganate	$[(\text{H}_3\text{N})_6\text{Co}](\text{MnO}_4)_3$
Hexamminecobalt(III) nitrate	$[(\text{H}_3\text{N})_6\text{Co}](\text{NO}_3)_3$
Hexahydroxyamminecobalt(III) nitrate	$[(\text{HONH}_2)_6\text{Co}](\text{NO}_3)_3$
Hexamminecobalt(III) hexanitratocobaltate(III)	$[(\text{H}_3\text{N})_6\text{Co}][\text{Co}(\text{NO}_3)_6]$
Tetraammine copper(II) nitrite	$(\text{H}_3\text{N})_4\text{Cu}(\text{NO}_2)_2$
Tetraammine copper(II) nitrate	$(\text{H}_3\text{N})_4\text{Cu}(\text{NO}_3)_2$
Tetraammine copper(II) sulfate	$(\text{H}_3\text{N})_4\text{CuSO}_4$
Cuprous azide	$\text{CuN}_3$
Cupric azide	$\text{Cu}(\text{N}_3)_2$
Tetraammine copper(II) azide	$(\text{H}_3\text{N})_4\text{Cu}(\text{N}_3)_2$
Lead Chlorite	$\text{PbClO}_2$
Lead Tetrachloride	$\text{PbCl}_4$
Lead hyponitrite	$\text{PbN}_2\text{O}_2$
Manganese oxide	$\text{MnO}_2$
Potassium permanganate	$\text{K}_2\text{Mn}_2\text{O}_7$
Potassium peroxide	$\text{K}_2\text{O}_2$

## Appendix 3. Comprehensive Listing of Conceivable Explosive Compounds (page 2 of 3)

Compound	Formula
Mercuric fulminate	$\text{Hg}(\text{CNO})_2$
Mercuric nitride	$\text{Hg}_3\text{N}_2$
Mercuric oxalate	$\text{Hg}_2\text{C}_2\text{O}_4$
Mercuric oxycyanide	$\text{Hg}(\text{CN})_2 \cdot \text{HgO}$
Mercurous chlorate	$\text{HgClO}_3$
Mercurous nitrate	$\text{HgNO}_3$
Mercurous nitride	$\text{HgN}_2$
Mercury peroxide	$\text{HgO}_2$
Nitrobenzene	$\text{C}_6\text{H}_5\text{NO}_2$
1,3,5-trinitrobenzene	$\text{C}_6\text{H}_3\text{N}_3\text{O}_6$
2-nitrophenol	$\text{C}_6\text{H}_5\text{NO}_3$
4-nitrophenol	$\text{C}_6\text{H}_5\text{NO}_3$
2,4-dinitrophenol	$\text{C}_6\text{H}_3\text{N}_2\text{O}_7$
2,4,6-trinitrophenol	$\text{C}_6\text{H}_2\text{N}_3\text{O}_7$
1,2-dinitrobenzene	$\text{C}_6\text{H}_4\text{N}_2\text{O}_4$
1,3-dinitrobenzene	$\text{C}_6\text{H}_4\text{N}_2\text{O}_4$
2-nitroaniline	$\text{C}_6\text{H}_4\text{N}_2\text{O}_2$
3-nitroaniline	$\text{C}_6\text{H}_4\text{N}_2\text{O}_2$
4-nitroaniline	$\text{C}_6\text{H}_4\text{N}_2\text{O}_2$
Diamminepalladium(II) nitrite	$(\text{H}_3\text{N})_2\text{Pd}(\text{NO}_2)_2$
Diamminepalladium(II) nitrate	$(\text{H}_3\text{N})_2\text{Pd}(\text{NO}_3)_2$
<i>cis</i> -Diammineplatinum(II) nitrate	$(\text{H}_3\text{N})_2\text{Pt}(\text{NO}_3)_2$
Selenium nitride	$\text{SeN}_4$
Silicon diiodide	$\text{SiI}_2$
Sodium peroxide	$\text{Na}_2\text{O}_2$
Strontium peroxide	$\text{SrO}_2$
Didydrazine tin chloride	$(\text{H}_4\text{N}_2)_2\text{SnCl}_2$

## Appendix 3. Comprehensive Listing of Conceivable Explosive Compounds (page 3 of 3)

Compound	Formula
Zinc peroxide	$\text{ZnO}_2$
Dihydroxyamine zinc chloride	$(\text{HONH}_2)_2\text{ZnCl}_2$
Nitrogen trichloride	$\text{NCl}_3$
Nitrogen triiodide	$\text{NI}_3$
Ammonia nitrogen triiodide	$\text{NH}_3\text{NI}_3$
Hydroxylamine	$\text{HONH}_2$
Hydroxylamine nitrate	$\text{NH}_2\text{OH} \cdot \text{HNO}_3$
Ammonium nitrite	$\text{NH}_4\text{NO}_2$
Ammonium nitrate	$\text{NH}_4\text{NO}_3$
Ammonium iodate	$\text{NH}_4\text{IO}_3$
Ammonium chlorate	$\text{NH}_4\text{ClO}_3$
Ammonum perchlorate	$\text{NH}_4\text{ClO}_4$
Hydrazine	$\text{N}_2\text{H}_4$
Hydrazinium nitrate	$\text{N}_2\text{H}_4 \cdot \text{HNO}_3$
Hydrogen Azide (Hydrozoic Acid)	$\text{HN}_3$
Hyponitrous Acid	$\text{H}_2\text{N}_2\text{O}_2$
Hydrogen Peroxide	$\text{H}_2\text{O}_2$
Silver oxalate	$\text{Ag}_2\text{C}_2\text{O}_4$
Silver azide	$\text{AgN}_3$
Silver nitride	$\text{Ag}_3\text{N}$
Silver amide	$\text{AgNH}_2$
Silver azide chloride	$\text{AgClN}_3$
Silver perchlorate	$\text{AgClO}_4$
Silver chlorate	$\text{AgClO}_3$
Silver chlorite	$\text{AgClO}_2$
Hydrazine silver nitrate	$(\text{H}_4\text{N}_2)\text{AgNO}_3$
Silver iodate	$\text{AgIO}_3$
Silver peroxide	$\text{Ag}_2\text{O}_2$
Silver fulminate	$\text{Ag}(\text{CNO})$
Silver hyponitrite	$\text{Ag}_2\text{N}_2\text{O}_2$
Diammine silver permanaganate	$(\text{H}_3\text{N})_2\text{AgMnO}_4$

**END**

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