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COMPLEXITIES OF LEAD AZIDE

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1. GENERAL.

a. Lead azide, $Pb(N_3)_2$, is an explosive salt of hydrazoic acid, HN_3 , having a molecular weight of 291.258. It is very sensitive to impact, friction, heat, and electrical discharge. Its solubility is less than 1% in cold water and nearly zero in ammonium hydroxide solution, ether, acetone, or ethanol, but it is quite soluble in heated, strongly acid or strongly alkaline solutions. When dry, it does not corrode most metals, however, in the presence of moisture, gold, silver, copper, mercury, tin, and zinc, all form extremely sensitive and dangerous azides.

b. Pure lead azide occurs as colorless needle-like crystals. Breaking these crystals is believed to initiate detonation. Military-use lead azide is white to tan with crystals less than 0.1mm long to minimize sensitivity. It is approximately 92% pure, having about 4% lead hydroxide (a manufacturing by-product), 3% dextrin (a binder), and 1% trace impurities.

2. ACCUMULATION. Vietnam-era jungle warfare fostered the development of munitions using relatively enormous quantities of lead azide. Their sensitivity to detonation caused a reluctance among many users to deploy them, resulting in a stockpile of both munitions and bulk lead azide. The winding down of hostilities left a vast supply and an extremely small demand. Mounting environmental regulations limited most open-air detonations to emergency destruction of immediately hazardous munitions. All munitions were eventually destroyed, leaving the stockpile of bulk lead azide in deteriorating 55-gallon drums.

3. STORAGE. Long-term storage of lead azide presents some problems. Primarily, its extreme sensitivity when dry necessitates under water storage. Next, if the water freezes, spontaneous detonation occurs, presumably due to ice crystal formation breaking lead azide crystals. Addition of ethanol to the water is therefore necessary to make a non-freezing mixture. Periodic surveillance is then required both visually to assure adequate liquid level and testing to determine if ethanol evaporation has reduced antifreeze properties. Finally, the steel 55-gallon packing and storage drum has a limited life due to rust-through, which eventually results in leakage of the ethanol-water mix.

4. DISPOSAL RESEARCH. Early attempts to sell the stockpiled lead azide were fruitless, so the search for the best nonpolluting disposal method began. Lead azide can be converted to less sensitive or nonexplosive substances in many ways. There are also problems with each method. Some of the better known disposal methods are:

a. Lead azide can be dissolved in 10% sodium hydroxide forming toxic lead hydroxide and the extremely insensitive but highly toxic sodium azide. This is very time consuming and produces large quantities of hazardous chemically active waste residues which can later react to form sensitive explosive compounds.

b. Dissolving lead azide in a solution of ammonium acetate and potassium or sodium bichromate forms toxic lead chromate. A sensitive explosive sludge may also form. Again, hazardous waste residues are a problem.

c. Lead azide dissolved in a solution of sodium nitrite is destroyed by adding 36% nitric acid or glacial acetic acid while stirring. This is an extremely bulky method resulting in approximately 65 gallons of hazardous waste per pound of lead azide destroyed. Rapid heat production by this complete reaction can be hazardous, so addition of acid must be slow. The added severe hazard of hydrazoic acid also exists. Hydrazoic acid is both a highly sensitive explosive and extremely toxic. Since its boiling point is about 37° C (99° F), hydrazoic acid is also very volatile, creating additional serious containment problems.

d. Lead azide dissolved in ammonium acetate solution receives sodium nitrite, is stirred, and then receives glacial acetic acid while stirring. This also forms large quantities of hazardous wastes. It can only be done in small quantities, is slow, and risks forming hydrazoic acid.

e. Often preferred, a solution of 20-25% ceric ammonium nitrate decomposes lead azide, producing a gas in the reaction, a good indicator of reaction completion when the bubbling stops. Only small quantities may be reacted at one time due to possibility of a violent reaction. Chemicals for the process are expensive.

NOTE: The first five methods were devised for destruction of small quantities of lead azide.

f. Heating lead azide to 240-250° C (464-482° F) results in escape of nitrogen and deposit of metallic lead residue. Since the reaction is exothermic (releases heat), it is difficult to avoid reaching temperatures of 340-350° C (644-662° F) at which explosion occurs. This method was never even documented as an alternative, presumably due to its obvious hazards.

g. In the late 1960s, electrolytic decomposition of lead azide dissolved in sodium hydroxide was developed. This appeared to be a very attractive alternative due to its low chemical cost, nonpolluting nature, and production of marketable chemical lead.

5. PRODUCTION.

a. The electrolytic process was experimentally pursued and scaled up to approach production capacity. Many hazards of the process (electrical, fire, explosion, chemical, toxicity, heat, handling, etc.) were recognized and countermeasures established during the initial process development. An in-depth 163-page hazards analysis was produced, including 64 pages of risk-tree analysis, with a major effort necessarily devoted to fire and explosion hazards.

b. An industrial hygiene study by USAEHA recognized hydrazoic acid as a matter of grave concern in the process. In an acid solution, azide

ions combine with acidic hydrogen ions to form hydrazoic acid, a sensitive explosive and also being a potentially toxic vapor, immediately permeates its surroundings with its hazards when evolved. To abate the hydrazoic acid problem, airline respirators were put into service, except for certain intermittent operations which required the mobility afforded by a cartridge respirator. An exhaust hood with shrouds was installed to contain all possible air contaminants. Physiological monitoring of workers provided a positive indicator of any exposure. Despite the protective measures, physiological monitoring indicated significant over exposure to azides. Sorbent filter air monitoring in the work bay tested positive for azides beyond acceptable limits. To specifically isolate hydrazoic acid as a problem, an industrial hygiene survey of the air was taken again using a sorbent filter to capture the gaseous hydrazoic acid vapor, however, this time, a prefilter was used to capture particulates. No hydrazoic acid was found, proving that it was sodium azide in particulate form that had been transferred due to inadequate housekeeping and poor personal hygiene to insides of masks, hands, faces, and personal articles where it was absorbed and ingested by workers. A vigorous program of housekeeping, personal hygiene, and mask cleaning eliminated the problem. This is just one example of many serious problems which can occur when details are overlooked. Emphasis placed on hydrazoic acid overshadowed other problems. In reality, since hydrazoic acid can only be produced in an acid solution, the strongly alkaline electrolytic solution could not have produced it. This resulted in time and effort wasted attempting to "kill an already dead rat" while the real problem ran unchecked.

c. Sludge formation was noted early in the development of the process, but received little attention. Not until early in the production phase when electrical arcing occurred as sludge buildup on the tank bottom reached the plating electrodes did it become a concern. Consisting primarily of lead hydroxide, it was then generally considered a nuisance which must be periodically removed. Gradually, the sludge, being stored in 55-gallon drums, accumulated. Attempts to dispose of the sludge as normal hazardous waste met with problems. It could not be certified free of explosives without being incinerated. Incineration was out of the question because of pollution, cost, and other technical considerations. Without certification, it could not be accepted by hazardous waste sites. To complicate matters, the caustic nature of the sludge accelerated aging of the storage drums. Occasional leakers fostered visions of famous photographs showing rusted-out drums leaking toxic wastes into our waterways. Such fears prompted moving the sludge from open storage to inside storage. Later, it was all repacked into new steel 55-gallon drums with polyethylene liners to await final disposal. Again, this is an example of a minor nuisance which became a major problem.

d. One other problem was never considered and in fact did not surface until a few months ago. Over the years, pieces of iron pipe, wood, gloves, nails, and various other trash accumulated under the electrolysis building ramps. Among them were a few items with brass or copper parts lying partly buried in the damp, sandy soil over the years. This apparently resulted in a reaction between the brass and the sodium azide which had been hosed out of work bays by the daily washdowns during production. Extremely sensitive

copper azide was thus produced. A loud, though not extremely dangerous, explosion occurred when encountered by personnel, prompting an intense investigation revealing more explosive items (chromed brassbuckle, one-inch hose with brass coupling, and a three-inch piece of copper cable). The area was cleaned up, debris flashed, and the building permanently marked not to be used for high explosives operations. The important point is, any place that has ever been used for processing initiating explosives should be investigated to assure that a similar problem does not exist. Such a precaution may prevent some future investigating team from coming to a wrong conclusion after they sift through the remains around some big smoking hole.

6. CONCLUSION. A plethora of problems were overcome, such as implementation of respiratory program requirements, OSHA lead standard requirements, personnel monitoring requirements, hazards of hydrogen gas generated, grounding and bonding requirements, work area humidity tolerances, conductive and nonstatic work clothes, and many others covered in hazard analyses, SOPs, other studies, and actual operation countermeasures. The future value of the lead azide electrolysis project lies in its example which should reawaken us to problems which can so easily occur. It should inspire us to avoid oversights when implementing new technology, but not needlessly thwarting progress when problems can be solved.

7. UPDATE.

a. The electrolysis project was halted after approximately half the stockpile was destroyed. The remaining drums in storage began leaking more frequently due to corrosion and were finally repacked, giving them another 10 to 15 years before they will need repacking again. A commercial concern is currently interested in procuring the remaining stockpile of bulk lead azide from the Army.

b. The sludge remains stored in polyethylene lined drums. Processes are underway to contract for its disposal.

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