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PRELIMINARY PROBLEM DEFINITION STUDY OF 48 MUNITIONS-RELATED CHEMICALS

VOLUME IV PRIMER AND TRACER RELATED CHEMICALS

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FINAL REPORT

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R. S. Wentsel
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April 1978

Supported by:

U. S. ARMY MEDICAL RESEARCH AND DEVELOPMENT COMMAND
Fort Detrick, Frederick, Maryland 21701

Contract No. DAMD17-77-C-7057

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Results are presented of a preliminary problem definition study on primer and tracer related chemicals. The purpose of this study was to determine the Army's responsibility for conducting further research on these chemicals to determine toxicological and environmental hazards, so that effluent standards can be recommended. Both civilian and military uses of this chemical were evaluated.

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EXECUTIVE SUMMARY

The goal of this problem definition study was to assess the Army's responsibility for conducting further investigations into the toxicological and environmental hazards of twenty chemicals associated with the production of primers and tracers. The twenty chemicals evaluated during this study were:

- barium nitrate
- strontium nitrate
- calcium silicide
- magnesium carbonate
- zirconium
- lead dioxide
- lead thiocyanate
- potassium chlorate
- Parlon®
- poly(vinyl chloride)
- barium peroxide
- strontium peroxide
- calcium resinate
- magnesium
- antimony sulfide
- lead azide
- sodium nitrate
- TACOT
- oxamide
- acetylene black, carbon black and graphite

These chemicals are used in various primer, tracer, igniter and pyrotechnic formulations as oxidizers, initiators, coloring agents and fuels. These formulations are mixed and loaded at various currently operational Army Ammunition Plants including Lake City, Lone Star, Longhorn AAP and Pine Bluff Arsenal. Carbon black, graphite and barium nitrate are also used in propellant manufacture at Radford AAP.

The results of this preliminary problem definition study are summarized in Table S-1 and discussed briefly in the following paragraphs.

Barium Compounds

Two barium compounds were included in this study - barium nitrate and barium peroxide.

Barium nitrate is widely used in the munitions industry in a variety of products. This chemical serves as a flash supplement and barrel coolant in solid propellants and as an oxidizer and coloring agent in pyrotechnic, tracer and primer formulations. These formulations are made at several Army Ammunition Plants including Radford, Lake City, Lone Star, Longhorn AAPs and Pine Bluff Arsenal. The treatment of wastes from these plants range from discharge of untreated wastes into local waterways to disposal in holding ponds and precipitation techniques. Thus, the amount of barium nitrate or barium salts entering the environment varies from plant to plant. Significant widespread pollution of barium also results from use of the munitions and pyrotechnics produced by the Army.

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Table S-1. Summary of Recommendations for Future Work on Primer and Tracer Related Chemicals

Compound	Where Used or Produced	Toxicological	Environmental	Other Recommendations
Barium Nitrate	RAAP, LAAP, LSAAP LCAAP, PBA	Yes	Yes	The effects of barium compounds and environmental synergistic effects with other metals should be investigated.
Barium Peroxide	LCAAP, LSAAP	Yes	Yes	
Strontium Nitrate	LCAAP, LAAP, LSAAP	No	Yes	The effects of all strontium compounds and then synergistic effects with other metals should be investigated.
Strontium Peroxide	LCAAP	?	Yes	
Calcium Silicide	LCAAP,PBA	No	No	
Calcium Resinate	LCAAP	No	No	
Magnesium Carbonate	PBA, LAAP	No	No	
Magnesium	LCAAP, LSAAP, LAAP	No	No	
Zirconium	LCAAP, LAAP, PBA	No	No	
Antimony Sulfide	LCAAP, LSAAP, LAAP PBA	No	No	
Lead Dioxide	LCAAP	No	No	
Lead Azide	LCAAP, LSAAP, JAAP, KAAP, TCAAP, IAAP	Yes	?	Environmental studies should include all lead compounds used at the AAPs.
Lead Thiocyanate	LSAAP	Yes	Yes	
Sodium Nitrate	PBA, LAAP, HAAP	No	Yes	An environmental study of sodium nitrate by-product at HAAP should be undertaken.
Potassium Chlorate	PBA, LSAAP	Yes	Yes	
TACOT	AARADCOM, Dover	No	No	
Parlon®	LAAP	No	No	
Oxamide	LCAAP	No	No	
Polyvinyl Chloride	LAAP	No	No	
Carbon Black and	RAAP, PBA, LCAAP	No	No	

Civilian production capacity for barium nitrate is ∿8 million lb/year. However, this figure is based on no production of strontium nitrate. Barium nitrate uses in the civilian community include production of optical glass, ceramic glazes, rodenticides and in the electronics industry. These uses are minor when compared to military wartime needs for barium nitrate.

Barium nitrate is relatively toxic to mammals in subcutaneous or interveneous injections. It has a low toxicity to most aquatic organisms. The most sensitive aquatic organism is *Daphnia magna*. Reductive impairment in this invertebrate is observed with low concentrations of soluble barium salts.

Barium peroxide was used as a starting material for the production of hydrogen peroxide in the 1930's. However, new processes for manufacture of hydrogen peroxide were introduced in the 1940's. Since this time, barium peroxide has declined in importance in the civilian community. Current uses of this compound are as a bleaching agent, oxidizer and in fireworks.

The Army uses barium peroxide in igniter and tracer formulations manufactured at Lake City and Lone Star AAPs. The current use rate of barium peroxide is 13,000-15,000 lb/year. Under full mobilization production schedules, the amount of barium peroxide used by Lake City and Lone Star AAPs would be 58,000-60,000 lb/year.

The toxicity of barium peroxide is mainly due to that of the metal, although it can damage tissues on contact due to its strong oxidizing capability. Barium is moderately toxic to most species. Some invertebrate, such as *Daphnia magna*, are very sensitive to barium salts.

Neither barium nitrate nor barium peroxide are military unique chemicals; however, the Army usage and pollution of these compounds are significant. Therefore, it is recommended that a Phase II detail toxicological and environmental study of these two compounds be undertaken. However, to make this study of value, all barium in the effluents from the various Army Ammunition plants should be quantified. The synergistic effects of barium and other metals such as calcium, magnesium, lead and strontium in the effluents on the aquatic life of the receiving also should be investigated.

Strontium Compounds

Two stronium compounds were included in the preliminary problem definition study - strontium nitrate and strontium peroxide.

Strontium nitrate is a widely used chemical in the civilian market. Estimated annual production is ∿12 million lb. Most of strontium nitrate produced is used in the flare industry. When the flares are burned, the strontium nitrate is oxidized. The resulting oxide is unstable in water and decomposes to the hydroxide. Thus, ∿100% of the strontium in these flares enters the environment in an uncontrolled manner.

In comparison, the military use of strontium nitrate is small. Total usage of this chemical at Lake City, Longhorn and Lone Star AAPs in tracer and pyrotechnic formulations is only ∿100,000 lb/year. At full mobilization use rate of strontium, a total of 400,000 lb would be needed by these plants each year. Most of the strontium from the manufacturing processes at these AAPs ends up in ponds and does not enter the aquatic environment. As with the civilian use of flares, the military use of tracers dissiminates virtually all the strontium back into the environment.

Strontium peroxide is used by the Army as an oxidizer in primer and tracer mixes. Under current production, this compound is used only at Lake City AAP. Current use rate of strontium peroxide by the Army is ∿21,000 lb/year. This usage would increase to ∿50,000 lb/year under full mobilization schedules. Losses from the mixing and loading processes could be as high as 90 lb/month at full mobilization production. These wastes flow into an industrial wastewater treatment plant. During the treatment process, the strontium is precipitated. The sludge is disposed of in ponds. The water discharged contains a maximum of 3.5 ppm of strontium.

Civilian production of strontium peroxide is estimated at less than 200,000 lb/year. There are only limited civilian uses of strontium peroxide - as a bleaching agent and an antiseptic. No information is available on the pollution resulting from the civilian production or use of strontium peroxide.

In general, strontium salts are toxic only in large doses to most living organisms. However, they can be very toxic to plants in the absence of calcium.

These strontium salts are not military unique compounds. However, strontium in the Lake City AAP effluents from the combined use of all strontium compounds could be an Army problem. Therefore, it is recommended that a Phase II study be undertaken. This study should include the effect of strontium salts on the Little Blue River and any synergistic effects of calcium, barium, strontium, lead and magnesium.

Calcium Compounds

The two calcium compounds were studied in this program - calcium silicide and calcium resinate. Calcium silicide is refined to military specification from calcium-silicon alloy for use at Lake City AAP. As refined, it has no civilian uses. Military purchases of calcium silicide are 2,000-3,000 lb/year at current production rates. At full mobilization, ∿14,000 lb/year of calcium silicide would be needed by the Army. The calcium-silicon alloys are used in the civilian community in the production of high grade steel.

Calcium silicide is readily hydrolyzed upon contact with moisture to calcium hydroxide, silicon dioxide and hydrogen. Thus, the toxicological and environmental hazards of calcium silicide are those of calcium hydroxide. Calcium hydroxide is added to the wastewater generated at Lake City AAP in order to remove metals. Any added amount of calcium hydroxide resulting from calcium silicide is negligible compared with the quantity used in the industrial wastewater treatment process.

Calcium resinate is a flammable solid used as a fuel, binding and water proofing agent in primers and tracers. At the present time, the use of this compound by the Army is limited to 4,000-6,000 lb per year at Lake City AAP. Full mobilization production of primer and tracer mixes containing calcium resinate would require about 10,000 lb of this chemical per year. It appears that any calcium resinate lost in the processing is effectively removed as sludge by the industrial waste treatment system at Lake City AAP.

In contrast to Army use, calcium resinate is used in a wide variety of consumer products. Civilian production capacity is ∿25 million lb/year. Because of the widespread use of this chemical in paints and varnishes, significant non-point source pollution of calcium resinate is expected. However, no specific pollution statistics appear in the literature.

Calcium resinate has a low toxicity for mammals. With the exception of Chinook Salmon, this chemical does not appear to be a significant aquatic hazard. This conclusion is based on relatively little information and the aquatic toxicity of this chemical requires further evaluation.

Based on the limited Army usage and pollution from calcium resinate and calcium silicide, any further Army sponsored studies on these compounds should be a low priority.

Magnesium and Magnesium Carbonate

Magnesium is a highly reactive metal. Due to its strong reducing ability, magnesium is used in a wide variety of products. The military uses magnesium in flares and signal devices. Current military use of this element is ∿200,000 lb/year. This usage will increase to ∿8 million lb/year at full mobilization. Greater than 90% of the current military use of magnesium is for flares produced at Longhorn AAP. The environmental pollution resulting from the manufacture of these flares is negligible. However, magnesium oxide will be released into the environment when the flares are used.

The civilian production of magnesium is ∿438 million lb/year. Of this 438 million lb, ∿20 million lb is powdered magnesium. The major civilian uses of magnesium are in flares, flash photography and in steel where it acts as a desulfurization agent. The pollution resulting from civilian production and usage of magnesium has not been quantitated.

Magnesium and magnesium salts are realtively non-toxic to living organisms with effects observed only at high doses. For example, the 3-week LC50 for *Daphnia magna* exposed to magnesium chloride is 190 ppm.

The Army is a major user of magnesium powder. However, in comparison with the total amount of magnesium produced and used in the United States each year, the current military use of magnesium is small (∿0.04%). At full mobilization this use rate would only increase to 1.6% of the civilian production of this metal. In view of the small percentage of magnesium used by the Army and the low toxicity of this metal and its salts, Phase II studies on this metal should be a low priority item.

Magnesium carbonate is used in the civilian economy as a precursor of many otehr magnesium salts. These salts are used in fire retardants and in the manufacture of ceramics and glass. Magnesium carbonate is also used in many formulations for human consumption such as pharmaceuticals and antacids.

The Army uses magnesium carbonate as a burning rate regulator in pyrotechnic, primer and tracer applications. Total military use is 50,000 lb/year. At full mobilization, 500,000 lb/year of magnesium carbonate would be needed by the Army, about 0.1% of the civilian use. Total losses to the environment from military use would be less than 10,000 lb/year, even at full mobilization. This amount is negligible compared to civilian sources of entry into the environment.

Magnesium carbonate is relatively non-toxic to humans, aquatic organisms and microorganisms. However, some plant species may suffer chlorosis and growth inhibition when exposed to this chemical.

The military use of magnesium carbonate is insignificant compared to the civilian use. This fact and the low toxicity of this chemical indicate that the Phase II study of magnesium should be a low priority item.

Zirconium

Zirconium is produced by the Teledyne Wah Chang Corporation, which is the only United States producer. The major use of zirconium is as a cladding material for uranium fuel elements. Other civilian uses of zirconium are as a reducing agent and as a component of vacuum tubes, flask bulbs and lamp filaments.

Military use of zirconium is as a fuel in pyrotechnic, primer and tracer formulations. The military requirement for zirconium would be about 2% of civilian production capacity at full mobilization. The military contribution to pollution by zirconium is small compared to losses through civilian use of this metal.

The toxicity of zirconium and its compounds to mammals and aquatic organisms is relatively low. This metal is widespread in the environment and is found in the tissues of most animals. Because of the modest military use of zirconium and its low toxicity, Phase II studies on this metal should be a low priority.

Antimony Trisulfide

Antimony trisulfide is used in yellow pigments, matches, ruby glass manufacture and as a flame proofing agent. Total civilian usage of this material is estimated at 5-10 million lb/year.

The Army uses antimony trisulfide as a fuel in pyrotechnic compositions and primer mixes. Total military use even at full mobilization would represent less than 0.5% of civilian use.

Antimony compounds exhibit relatively low toxicity to mammals, aquatic organisms, microorganisms and plants. Antimony trisulfide occurs widely in nature as stibnite ore.

The military sources of pollution by antimony trisulfide are negligible compared to civilian sources. Because of the low usage and relatively low toxicity of antimony trisulfide, a Phase II study should be a low priority.

Lead Compounds

Three lead compounds were included in this preliminary problem definition study - lead dioxide, lead azide and lead thiocyanate.

Lead dioxide is used by the Army in igniter and tracer mixes compounded at Lake City AAP. The mixes calling for lead dioxide require only 2.9 to 6.5% of this compound. Thus, the use rate of lead dioxide by the Army is small - 300 lb/year under current production schedules and 700 lb/year at full mobilization. The losses of lead dioxide from the mixing and loading processes at Lake City AAP are estimated at less than 2 lb/month at full mobilization usage. The industrial waste treatment plant should remove essentially all the lead from the waste stream.

The civilian production of lead dioxide is ∿2 million lb/year. The major portion of this chemical is used as a curing agent in polysulfide elastomers. The pollution resulting from the manufacture and use of lead dioxide by the civilian community is not known.

Lead dioxide, like other lead compounds, is toxic when absorbed by the human body over long periods of time. However, due to its lower solubility in body fluids, it is not as toxic as the more common carbonate, sulfate and oxide salts of lead when injested or inhaled. Since lead dioxide is very insoluble in water, it will not present an acute toxicity problem to the aquatic environment. However, accumulation in the sediment and bioaccumulation of lower organisms could occur.

Because of the limited use of lead dioxide by the Army, this compound should be a low priority for a Phase II study.

Lead azide is used at Lake City AAP and Lone Star AAP as a component of detonators. The current use rate is about 600 lb/year at LCAAP and 2,400-3,600 lb/year at LSAAP. Total use at full mobilization would be about 16,000 lb/year at these two facilities. At full mobilization, other facilities would also use lead azide. The total military use under these circumstances would exceed 50,000 lb/year. Current losses of lead azide from production operations are 5-7 lb/month. At full mobilization, 27-54 lb/month would be lost. The lead azide is treated with strong base or with sodium nitrite and acetic acid before discharge. These lead-containing effluents are, or will be further treated in the near future, at Lake City and Lone Star AAPs.

Lead azide is currently produced by Olin Corporation and E.I. duPont. DuPont uses up to 25,000 lb/year for manufacture of civilian detonators. All other lead azide produced is sold to the Army for use in military ordnance.

Lead azide is toxic to man. No data on the toxicity of lead azide to aquatic organisms, microorganisms or plants are available. The environmental toxicity of this compound must be inferred from the available data on lead and the azide anion or hydrazoic acid.

Further studies on lead azide should be limited to its effects on workers exposed to the azide itself. Any environmental study of lead azide should be part of an overall evaluation of all lead compounds used at Army Ammunition Plants.

Lead thiocyanate is a fuel used in detonators, primers and igniters. The only Army user is Lone Star AAP. The current use rate is less than 500 lb/yr. At full mobilization, about 5,000-7,000 lb/yr would be required. The losses of lead thiocyanate from loading operations are less than 1 lb/month currently and would be in the range of 4-12 lb/month at full mobilization.

Lead thiocyanate has very limited usage in the civilian community. No reports of pollution by this material have been found.

Literature data indicate that lead thiocyanate is moderately toxic. Long term exposure will result in chronic lead poisoning. No specific data on the toxicity of lead thiocyanate to aquatic organisms or microorganisms was found. Similarly, phytotoxicity data from other lead compounds must be used to infer the effects of lead thiocyanate.

While the amount of lead thiocyanate used by the Army is small, the Army is the primary user of this chemical. A Phase II study of the toxicological and environmental hazards of lead thiocyanate is recommended. This study should be part of an overall evaluation of all lead compounds used or produced by the Army.

Sodium Nitrate

Sodium nitrate is used as an oxidizing agent in explosives, a fertilizer and as a food preservative. Civilian use of this material accounts for 98-99% of total use in the United States.

The Army uses sodium nitrate as an oxidizer in incendiary and tracer mixtures. The current use rate of this material at Longhorn AAP is 7,700 lb/month. At full mobilization, the use would increase to over 300,000 lb/month.

Sodium nitrate is a relatively non-toxic substance, as would be expected considering its use as a fertilizer and food preservative. Some toxic effects have been observed in mammals at dosages of >200 mg/kg, however.

Since civilian usage represents the vast majority of sources of entry of sodium nitrate into the environment, this chemical would not appear to be a military responsibility. However, the largest single Army source of waste sodium nitrate results from the production of RDX/HMX. This material is pumped into the holding ponds and made into fertilizer. The effects of this by-product in the environment should be further evaluated.

Potassium Chlorate

Potassium chlorate is widely used in the civilian community in the manufacture of matches. The Army's use of this salt is mainly in the production of smokes and pyrotechnics at Pine Bluff Arsenal. The current military use of potassium chlorate represents only 0.7 to 1.4% of the estimated United States civilian production capacity. This percentage would increase to 6% at full mobilization production rates. Discharges of potassium chlorate into the Arkansas River are ∿173 to 346 lb/month. This discharge should stop when the new waste water treatment facility becomes operational in 1979.

The toxicity of potassium chlorate to mammals is relatively low. However, some teratogenic effects have been observed. Chlorates are toxic to many microorganisms. Chlorates are toxic to plants in low concentrations as evidenced by the use of sodium chlorate as a herbicide. The toxicity of potassium chlorate to fish is not well established.

Based on the information evaluated during this study, it is recommended that potassium chlorate be included in the Phase II detailed toxicological and environmental evaluations.

TACOT

TACOT is a secondary explosive used in primer mixes where good temperature stability is required. This compound was developed by and is manufactured exclusively by E.I. duPont. The production capacity of and plans for future use of TACOT by duPont are unknown.

The only Army use of TACOT was for a research program at ARRADCOM, Dover. During this program, small amounts of TACOT were evaluated for use in Army primer mixes. No primer mixes containing TACOT were ever put into production. There are no plans for any future Army use of TACOT. Therefore, it is recommended that no future toxicological or environmental evaluations of this compound be carried out by the Army unless TACOT is utilized in production operations.

Parlon®

Parlon® is a chlorinated rubber that is manufactured for its chemical and thermal stability. It is used in a variety of consumer products such as

paints, coatings and inks. The amount of Parlon® entering the environment from the civilian manufacture or use is not known.

The Army used Parlon® in some pyrotechnic and tracer formulations manufactured at Longhorn AAP. This use was small and sporadic. No future use of this compound at Longhorn AAP is anticipated.

Relatively little toxicological and environmental information on Parlon® is available in the general literature. The FDA has approved Parlon® for contact with food. In the environment, Parlon® is expected to accumulate in sediments. The bioaccumulation potential of this compound is not known.

In view of the limited past use of Parlon® by the Army, this chemical should be a low priority for a Phase II study.

Oxamide

Oxamide is used by Lake City AAP in tracer formulations as a burning rate retardant and stabilizer. The use of this compound by the Army is small, ~5,000 lb/year under full mobilization schedules. The pollution potential of oxamide at Lake City AAP is also small. The maximum full mobilization estimated losses is 9 lb/month. Most of this 9 lb/month will be precipitated in the form of calcium oxalate and removed from the effluent by the industrial waste treatment facility.

Civilian production capacity for oxamide is estimated at 1 million lb per year. The main civilian uses of oxamide are as a nitrocellulose stabilizer and fertilizer. From its use as a fertilizer, widespread environemntal contamination of oxamide is anticipated.

Literature on the toxicity of oxamide is sketchy. However, it is readily degraded to oxalic acid in the environment.

Based on the low Army use and discharge of oxamide, oxamide should be a low priority for a Phase II study.

Poly(vinyl chloride)

Poly(vinyl chloride) production in the United States is nearly 7 billion lb/year. This material is used in construction, consumer goods, packaging, electrical products, home furnishings and many other applications.

The military use of poly(vinyl chloride) is as a burning rate retardant, a color intensifier and a bonding agent in pyrotechnic and tracer formulations. Total military use even at full mobilization would represent only 0.001% of civilian use.

Civilian means of entry of poly(vinyl chloride) into the environment are widespread, largely through disposal of consumer goods. Military sources of environmental contamination by poly(vinyl chloride) are negligible by comparison.

Polyvinyl chloride is relatively non-toxic. However, the monomer, vinyl chloride, is toxic and is a potent carcinogen. When combusted, poly(vinyl chloride) releases hydrogen chloride gas which is irritating and corrosive.

Because of the small military use compared to civilian requirements, pollution by poly(vinyl chloride) is primarily a civilian problem. Thus, this compound should be a low priority for a Phase II study by the Army.

Acetylene Black, Carbon Black, Graphite

Civilian use of acetylene black, carbon black and graphite centers on the production of tires and other rubber goods. Several billion lb/year are used for this purpose.

Military uses of acetylene black and carbon black are small, with only 5,000-6,000 lb/year required even at full mobilization. Graphite use is more substantial at 25,000 lb/year currently and up to 235,000 lb/year at full mobilization.

Military pollution with these carbon materials is less than 200 lb/month. At full mobilization, the potential pollution from military pollution might increase to 1,200 lb/month. This level of loss is negligible compared to civilian pollution sources.

These carbon materials are all relatively non-toxic. Thus, any further Army study of the environmental or toxicological hazards of these materials should be a low priority.

FOREWORD

This report details the results of a preliminary problem definition study on primer and tracer related chemicals. The purpose of this study was to determine the Army's responsibility for conducting further research on these chemicals in order to determine their toxicological and environmental hazards so that effluent standards can be recommended. In order to determine the Army's responsibility for further work on these primer and tracer related chemicals, the military and civilian usage and pollution of these substances were evaluated. In addition, a preliminary overview of toxicological and environmental hazards was conducted.

The primer and tracer related chemicals represent 20 of the 48 chemicals evaluated under Phase IA of Contract No. DAMD17-77-C-7057. These chemicals are grouped in four categories:

- explosives related chemicals
- propellant related chemicals
- pyrotechnics
- primers and tracers

Each category is a major report. Section I of each report is an overview of the military processes which use each chemical and the pollution resulting from the use of these chemicals. The problem definition study reports on each chemical are separable section of these four reports.

In addition, a general methodology report was also prepared. This report describes the search strategy and evaluation methodology utilized for this study.

In the preparation of this report, several reference sources have been directly quoted. Permission has been obtained from the appropriate sources for reprint of the quoted information.

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I. GENERAL OVERVIEW OF PRIMER AND TRACER MANUFACTURE, LOADING AND DISPOSAL

Primer (initiator) formulations are used to ignite explosives or propellants in munitions, pyrotechnics or rockets. Tracers are used to visually track the trajectory of a projectile. The primer and tracer formulation components of concern to this study are listed below:

Primer Chemicals	Tracer Chemicals
Barium nitrate	Magnesium
Antimony sulfide	Strontium nitrate
Potassium chlorate	Poly(vinyl chloride)
Lead thiocyanate	Strontium peroxide
Calcium silicide	Calcium resinate
Lead dioxide	Sodium nitrate
Lead azide	Parlon
TACOT*	Barium peroxide
Acetylene black	Oxamide
Zirconium	Magnesium carbonate

*Tetranitrodibenzo-1,3a,4,6a-tetraazapentalene

A. Manufacture

1. Facilities

The majority of primer and tracer formulations are currently produced at Lake City Army Ammunition Plant. Other facilities which have the capability of manufacturing these items include Joliet AAP, Twin Cities AAP, Indiana AAP, Lone Star AAP, Longhorn AAP and the Navy installations at Indian Head (NOS) and Crane (NAD). Pine Bluff Arsenal also uses some of the primer and tracer chemicals for production of pyrotechnics.

2. Formulations and Uses

a. Lake City AAP

Lake City AAP (LCAAP) produces a large variety of small caliber munitions. In addition, LCAAP provides ignitors and incendiary mixes for use at other loading and packing facilities. Some high volume production items at LCAAP include the 5.56 mm cartridge, the 7.62 mm cartridge, the 20 mm shell and 50 caliber ammunition. These items use many of the primer and tracer components of interest (USAEHA, 1970a). Table I-1 lists the pounds of each chemical used per 100,000 rounds of each munition.

A listing of specific primer and tracer mixes produced at LCAAP is given in Table I-2. Not all of these are in current (Feb. 1978) production. However, each is in present use and will be in production as needs arise, or if mobilization schedules increase.

The number of pounds of each mix type manufactured at LCAAP during 1975, 1976 and 1977 is given in Table I-3. Table I-4 shows the quantities of

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Table I-1. Pounds of Primer and Tracer Chemicals Used/100,000 Rounds of Munitions Produced.

	Barium Nitrate	Antimony Sulfide	Calcium Silicide	Magnesium	Strontium Nitrate	PVC	Strontium Peroxide	Calcium Resinate	Barium Peroxide	Oxamide	Zirconium	Lead Azide	Lead Dioxide	Acet. Black
5.56mm Primer	2.1	.9												
7.62mm Primer	2.7	1.3												
.50 Cal. Pr.	14.5	3.0	2.5											
20mm Elect.	18.4		3.9											.3
20mm Pr.	10.4	4.9												
20mm M47 Det.												27.6		
5.56mm Tracer				16.2	22.7	7.7	13.3	1.2	.7				.7	
7.62mm Tracer				32.8	63.5	20.2	15.9	2.0			25.7			
.50 Cal. M48				47.9	64.9	14.5	17.1	6.9	45.4	(Red Phosphorus - 276 lbs.)				
.50 Cal. M17				206.7	431.7	117.7	61.1	24.3	129.7					
20mm M53	189.1							13.1						
20mm M221				130.3	267.9		140	54.4		56.4				
20mm M246				157.8	330.6		140	61.0		69.6				
20mm M244				103.8	213.8		132.7	46.0		45.0				

Table I-2. Formulations of Primer and Tracer Mixes Produced at Lake City AAP.

Item	Antimony Sulfide	Barium Nitrate	Calcium Silicide	Acetylene Black	Polyvinyl Chloride	Strontium Nitrate	Magnesium	Barium Peroxide	Parlon	Strontium Peroxide	Sodium Nitrate	Calcium Resinate	Oxamide	Lead Dioxide	Magnesium Carbonate	Other	
Primer Mix 5061 (50 Cal.)	9.0	43.4	7.5													*Lead Styphnate*	37.9
																Tetracene	2.2
Primer Mix FA874 (20mm Electric)		42.8	15.5	0.5												Lead Styphnate	39.2
																Gum Arabic	1.0
																TNM	1.0
Primer Mix FA956 (5.56mm, 7.62mm, 20mm XM115, 30 Cal. Carbine)	14.8	31.5														Lead Styphnate	37.4
																Atomized Aluminum	6.9
																PETN	5.0
																Tetracene	4.4
Igniter R284 (5.56mm, 7.62mm tr. 30, 50 Cal., M206, 20mm)					17±1	55±1	28±1										
Igniter I-276 (50 cal.)							15±1	84±1								Zinc Stearate	1.0±1
Igniter I-508							14.15±1	79.2±1	5.66±1							Zinc Stearate	0.94±0.1
																Toluidine Red Toner	0.5±0.1
Igniter I-237						25.0±1		4±0.5	70±5								
Igniter I-547										76.5±2		23.5±2				Zinc Stearate	1±0.2
Igniter I-548 (20mm)							15±2			65±2		20±2					
Igniter I-560 (5.56mm)					15±1	27.5±1	27.5±1			30.0±1							
Igniter I-559 (5.56 mm)							41.5±1							6±0.5		I-136	79.5±1
Igniter I-280 (30 cal., 7.62 mm, 20mm)							15±1									I-136A	85±1
Igniter I-136 (30 cal., 7.62 mm, 20 mm)										90±1		10±1				Toluidine Red Toner	<0.1
R-200							21.6±1	27.5±1		65.5±1		6±0.5		3.4±0.5			
IM-103A (50 Cal.)												8±1				Potassium Chlorate	24±1
																Mg-Al Alloy	21±1
																Graphite	2±1
																I-136	45±1
IM-68 (20 mm)		24											1.87			Lead Styphnate	50
																Zinc Stearate	1
																Ammonium Nitrate	25
IM-136 (20 mm)																Lead Syphnate	51.26
																Graphite	46.87
IM-11		50														Mg-Al Alloy	50
IM-28		40.625														Potassium Perchlorate	9.375
																Mg-Al Alloy	50
IM-144 (50 Cal.)		49														Red Phosphorus	49
																Graphite	2
R-440 (5.56 mm, 7.62 mm tr.)								40±1		40±1		10±1			10±1		
R-10E (5.56 tr.)			5.55±0.5					4.1		79±1		7.25		4.1			
R-403 (20 mm tr.)					17.6±2	48±2	25±2						9.4±1				
R-505 (20 mm)						39.9 min	25±1					19.2 max	12.4 max			Polyethylene	3.6 max
R-322					16±1	52±1	26±1		6±1								
R-256 (50 Cal.)						33.3±1	26.7±1			26.7±1		8.3±1.1				Strontium Oxalate	5±1
R-512 (7.62 mm)						27.3	46.2				14.8					Ammonium Nitrate	8.6
																Perchlorate	3.1

Table I-3. Pounds of Mix by Type Manufactured at Lake City AAP During 1975, 1976, and 1977.

Item	1975	1976	1977
R-284, Cal. 30, 7.62 mm Cal. 0.50, 5.56 mm	68,300	91,700	50,355
I-548, 20 mm	1,755	2,310	2,890
I-276, Cal. 0.50	4,545	24,057	10,290
R-440 7.62 mm, 5.56 mm	300	-	45
IM-163, 0.50 Cal.	466	918	1,894
R-284B, 5.56 mm	16,800	7,082	-
I-136, Cal. 0.30; 7.62 mm, 20 mm	7,865	4,300	6,362
I-559, 5.56 mm	13,744	6,135	1,340
R-505, 20 mm	8,336	13,668	15,984
R-284C, 20 mm	1,050	1,455	1,095
IM-136, 20 mm	1,530	1,002	2,190
I-560, 5.56 mm	-	2,265	2,205
I-280, Cal. 0.30; 7.62 mm, 20 mm	3,240	1,025	1,727
R-256, 0.50 Cal.	5,895	30,100	13,470
R-403, 20 mm	2,547	370	-
IM-144, Cal. 0.50	2,355	6,495	13,860
IM-68, 20 mm	2,595	1,485	3,150

Table I-4. Primer and Tracer Chemicals Purchased by Lake City AAP-Calendar Years 1975, 1976, and 1977.

	Pounds		
	1975	1976	1977
Barium Nitrate	32,100	17,510	22,400
Antimony Sulfide LCC 24	6,248	8,588	8,272
Calcium Silicide	3,300	0	3,250
Magnesium Powder Gran 12	8,040	7,750	2,750
Magnesium Powder Gran 11	14,990	40,975	15,500
Magnesium Powder Type III	2,000	3,000	0
Strontium Nitrate, Grade B	66,000	59,850	55,200
Lead Azide	0	1,800	0
Lead Dioxide	600	540	0
Acetylene Black	0	0	150
PVC	17,500	25,000	5,000
Strontium Peroxide	31,200	21,300	10,500
Barium Peroxide	4,400	28,400	7,400
Calcium Resinate High Fuzed	1,125	2,225	0
Oxamide	2,000	1,100	1,600
Calcium Resinate P & P	3,060	4,350	2,180
Zirconium	200	650	951
Red Phosphorus	560	6,006	4,000

some of the chemicals of interest to this study which were purchased during 1975-1977.

LCAAP is currently operating at an overall rate of about 20% of full mobilization capacity. For the main production items, the percentage of full mobilization ranges from 2 to 40% as shown below:

Item	1977 Production No. of Rounds	Full Mobilization Production, No. of Rounds	% of Full Mobilization During 1977
5.56 mm	409,724,000	1,010,400,000	40.5
7.62	127,586,000	461,580,000	27.6
50 cal	8,372,000	358,248,000	2.3
20 mm	18,540,000	48,384,000	38.3

b. Lone Star AAP

Currently fuses and detonators as well as many primer and tracer assemblies are produced at Lone Star AAP (LSAAP). Table I-5 shows a summary of the products manufactured at LSAAP during June, 1974 (USAEHA, 1974). To manufacture these items, LSAAP processes propellants and explosives from outside sources as well as many primer and tracer chemicals. A summary of the usage of such chemicals during June, 1974, is shown in Table I-6. The chemicals under study here which were used for primers and tracers are designated with an asterisk.

c. Longhorn AAP

Longhorn AAP (LAAP) produces simulators, signal devices and some pyrotechnic items. LAAP also loads rocket motors. In operations at LAAP which involve use of primer and tracer related compounds, the following chemicals are used:

Barium nitrate	Antimony sulfide
Lead dioxide	Zirconium
Magnesium	Strontium nitrate
Poly (vinyl chloride)	Sodium nitrate
Parlon	Magnesium carbonate

These chemicals are used even though LAAP procures most of the primer devices they need as finished products from other plants.

d. Pine Bluff Arsenal

Pine Bluff Arsenal (PBA) produces smoke grenades and other pyrotechnic devices. The production of smoke grenades requires use of potassium chlorate in large quantities. Potassium chlorate forms about 25% by weight of the smoke grenade mix. Over the years 1965-1975, PBA used an average of

Table I-5. Summary of Production Activity for June 1974
Lone Star AAP
(USAEHA, 1974)

Area	Item	Total Number Produced
Load Line C	81mm Projectile w/Fuze (Loaded with Comp B, Grade A)	82,000
Load Line E	M67 Grenade w/Fuze (Loaded with Comp B, Grade A)	550,000
	105mm Projectile (Loaded with Comp B, Grade A)	80,000
Load Line F	Delay Cartridge Assy CCU-18/B	3,952
	105mm Projectile w/Fuze (Loaded with Comp B, Grade A)	18,000
	Supplementary Charge Assy	660,000
Load Line G	M9 Non-Delay Element (Loaded with Tetryl)	166,800
	M9 Delay Element (0.010 sec)	68,055
	M12 Tracer Projectile Assy	4,610
	M13 Tracer Projectile Assy	125,000
	66mm Rocket (Loaded with Octol)	20,000
	M412A1 Fuze	40,000
Load Line K	M61 Primer Assy	900,000
	M567 Fuze	35,000
Load Line O	M53A1 Burster Projectile	80,000
Load Line P	M7 Relay	1,300,000
	M24 Detonator	1,100,000
	M53 Delay Element	80,000
Load Line Q	M7 Relay	1,300,000
	M24 Detonator	1,100,000
	M2 Delay Element (0.5 sec)	1,000,000
	M17 Detonator	750,000
	M44E1 Detonator	540,000
	M47 Detonator	21,515
	M55 Stab Detonator	1,000,000
	M63 Detonator	340,000
	M76 Stab Detonator	122,000
	M80 Detonator	250,000
	M87 Detonator	200,000
	MK95 Mode Detonator	750,000
	M98 Stab Detonator	62,858
	M53 Delay Element Assy	80,000
	Lead Assy for Fuze PD M567	118,000
Load Line R	Percussion Primer (Loaded with Black Powder)	860,000
	M80A1 Electric Primer	40,000
	M83 Electric Primer	35,000

Table I-6. Summary of Explosives and Chemical Usage
For the Month of June 1974
Lone Star AAP
(USAEHA, 1974)

Item	Quantity	
	Monthly Total	Average Per Day
Comp B, Grade	116,000 lbs	5800 lbs
Comp A5	3,300	165
Octol 70/30	2,400	120
Tetryl	1,800	90
TNT	1,230	61.5
TNT Crystalline	2	0.1
RDX	220	11
Black Powder, Class 1	48,000	2400
Black Powder, Class 2	915	45.8
Black Powder, Class 5	1,430	71.5
Black Powder, Class 7	85	4.3
Propellant, M7	40,000 each	2000 each
Benite 10 inch	7,142 lbs	357 lbs
Benite 17 inch	6,214	311
*Lead Azide, Type I	600	30
Lead Styphnate, Basic	337	16.9
*Lead Thiocynate	46	2.3
*Lead Azide, Special Purpose	147	7.4
*Lead Azide, RD-1333	84	4.2
*Antimony Sulfide, Grade 1, Class 2	161	8.1
*Potassium Chlorate, Grade A, Class 2	95	4.8
Tetracene	10	0.5
*Barium Nitrate, Class 1	197	9.9
*Barium Peroxide, Grade A, Class 2	936	46.8
Barium Chromate, Grade A	24	1.2
Boron	5	0.3
Normal Butyl Acetate	135	6.8
*Strontium Nitrate	2,290	115
Vinyl Alcohol Acetate Resin (VAAR)	38	1.9
Dechlorane	338	16.9
Ethylene Chloride	2 gal	0.1 gal
Methyl Ethyl Ketone	2	0.1
Magnesium Aluminum Alloy, Type B	114 lbs	5.7 lbs
*Magnesium Powder, Type III Gran. 15	43	2.2
*Magnesium Atomized Powder, Type I, 100/200	1,015	50.8
*Magnesium Atomized Powder, Type I, 200/325	1,162	58.1

* Chemical of concern in this study.

203,000 lb/year of potassium chlorate in their smoke grenade operations (Burrows, 1977).

3. Manufacturing Processes

a. Production of Primer and Tracer Mixes

Production of primer and tracer mixes is generally a dry process. The steps involved include pulverizing and seiving some of the components. In many cases, two or more components are blended to form a pre-mix. This pre-mix is later blended with the remaining components to yield the final product. Figures I-1 to I-9 are examples of the processes used to make primer and tracer mixes. They illustrate the use of most of the primer and tracer chemicals of concern in this study.

In some cases, the composition is produced in a wet process using a solvent. Figure I-10 shows such a process. The production of igniter mix I-136 and I-280 involves the use of methyl chloroform and isopropyl alcohol as solvents. Calcium resinate is dissolved in a mixture of these solvents, then blended with strontium perioxide. The mixture is then dried by evaporating the solvents. This process yields the I-276 ignition compositions. It can then be blended with magnesium powder to form the I-280 mix.

b. Production of Lead Azide

Lead azide is used in many of the products made at LCAAP. It is produced off-site, however, and shipped to LCAAP and other use sites. It is shipped in bags, usually wetted with water or an alcohol-water mixture. The bags are placed in drums with a packing material such as sawdust.

Lead azide is not currently produced at any Army facility. However, Lake City AAP, Joliet AAP, Kansas AAP, Twin Cities AAP and Iowa AAP all have the capability to produce lead azide (DARCOM, 1977; Faurout, 1973; Eskelund, 1978). The manufacturing process is as follows:

- Sodium azide is mixed with lead nitrate or lead acetate in water.
- The lead azide precipitates and is filtered off.
- The supernatent solution is treated with nitric acid, sodium nitrate and sodium carbonate to destroy any residual lead azide. This process is illustrated in Figure I-11 (Train *et al.*, 1976).

The primary form of lead azide used by the military in the United States is dextrinated lead azide. This chemical is produced by precipitating the lead azide from a dextrin solution. The dextrin acts as a binder and reduces the shock sensitivity of the lead azide (Ottinger *et al.*, 1973).

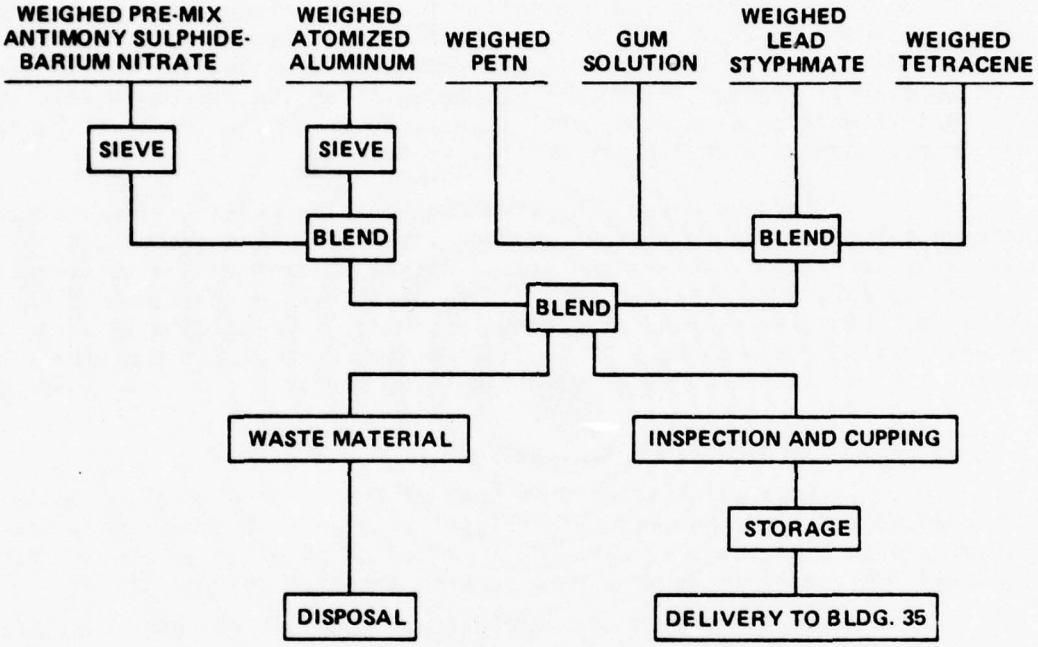


Figure I-1. Process Flow Sheet-FA 956 Primer Composition.

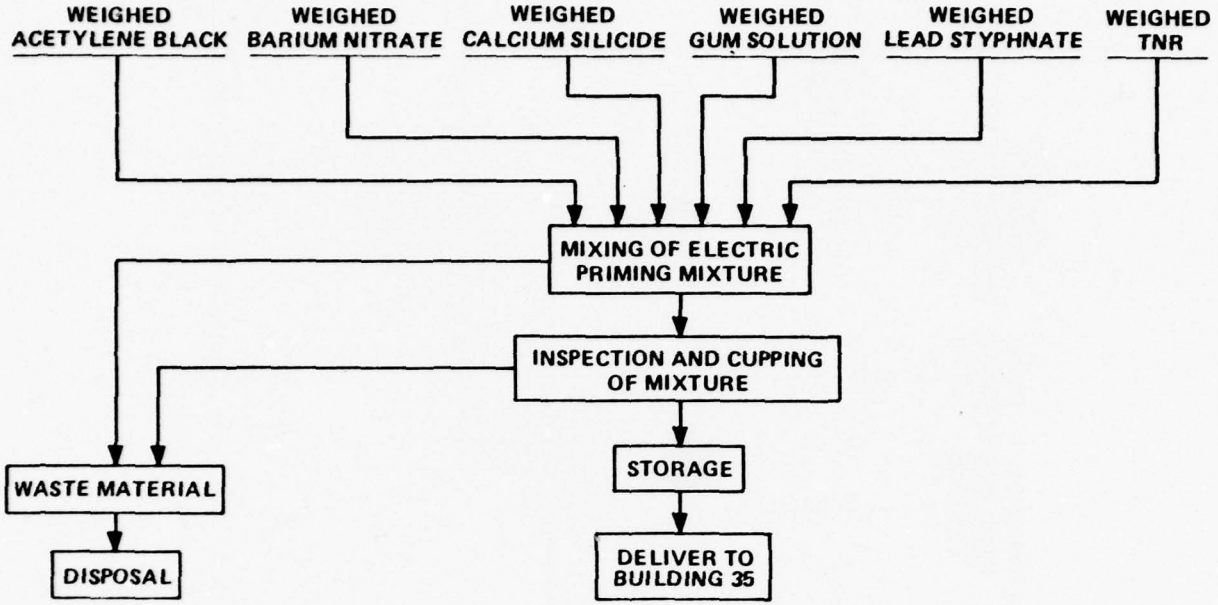


Figure I-2. Process Flow Sheet-Electric Priming Mixture.

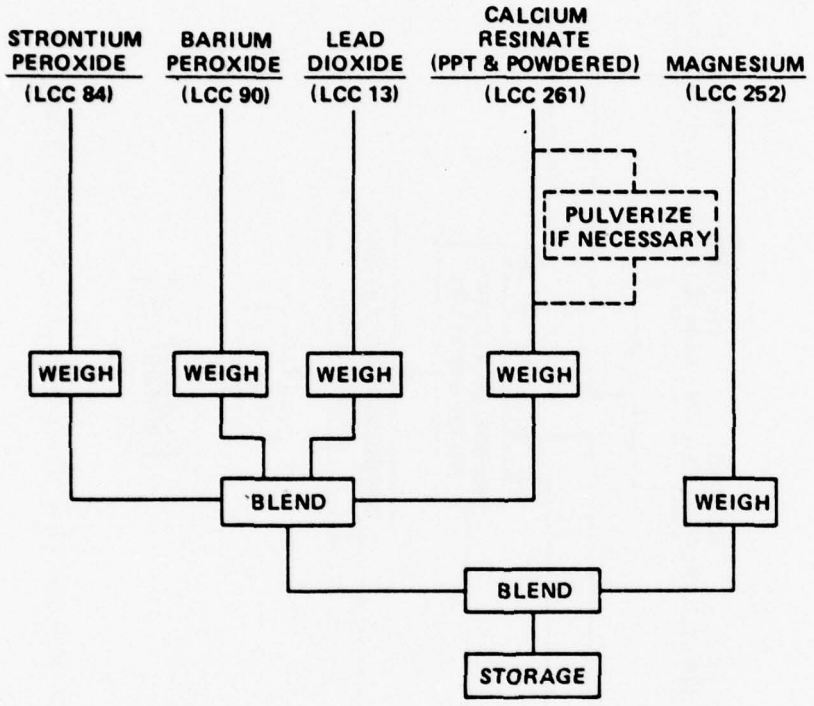


Figure I-3. Process Flow Sheet - R-20C Sub Igniter.

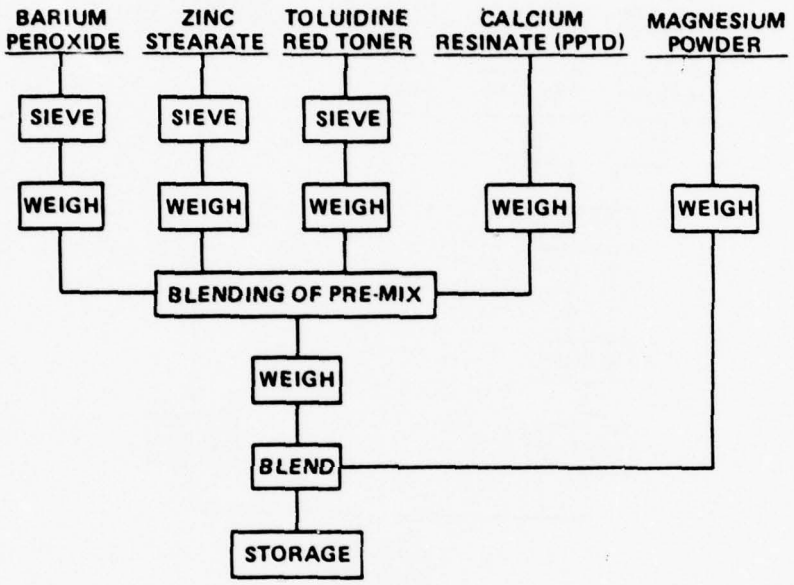


Figure I-4. Process Flow Sheet - I-276A Igniter Mixture.

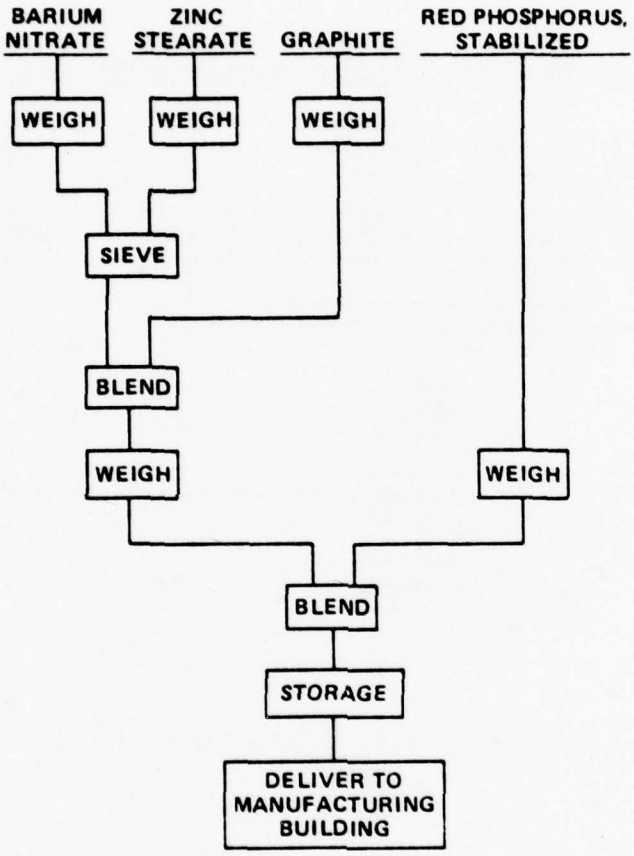


Figure I-5. Process Flow Sheet - IM-144 Incendiary Mixture.

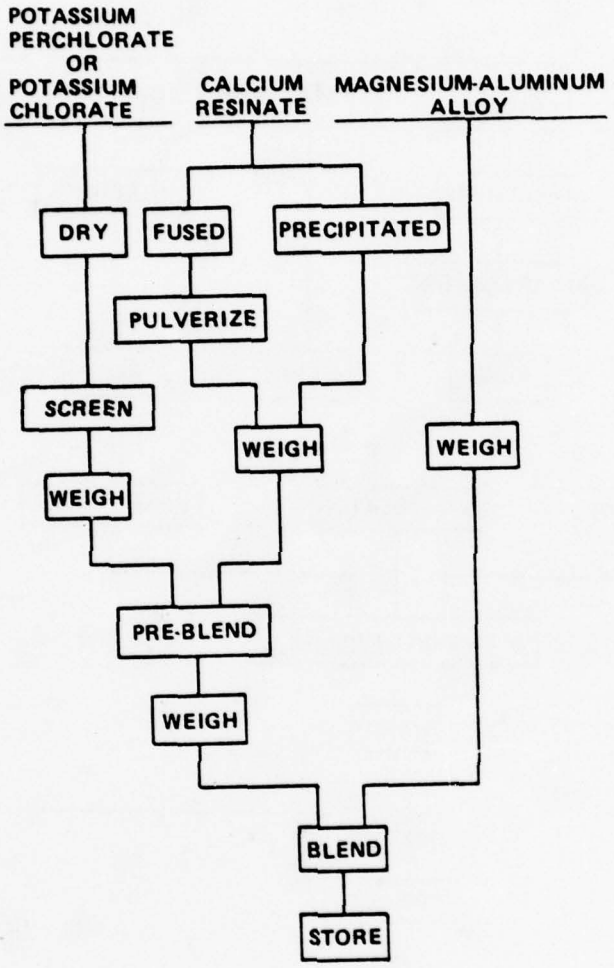


Figure I-6. Process Flow Sheet - Incendiary Mixture IM-136.

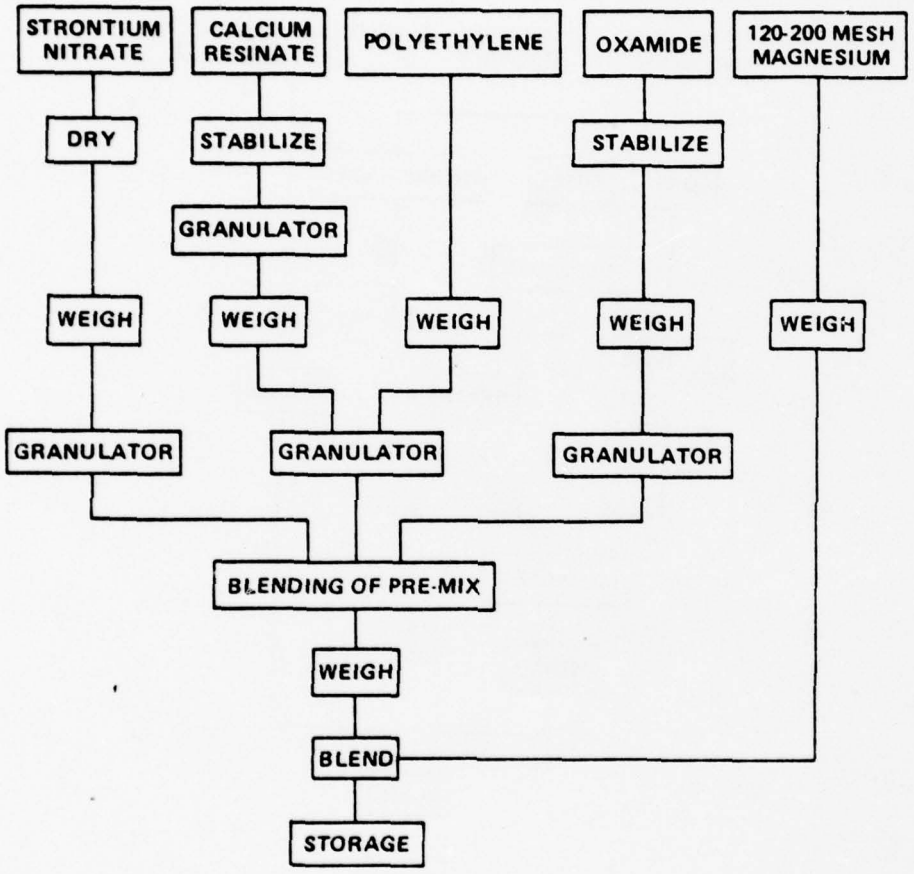


Figure I-7. Process Flow Sheet - R-505 Tracer Composition.

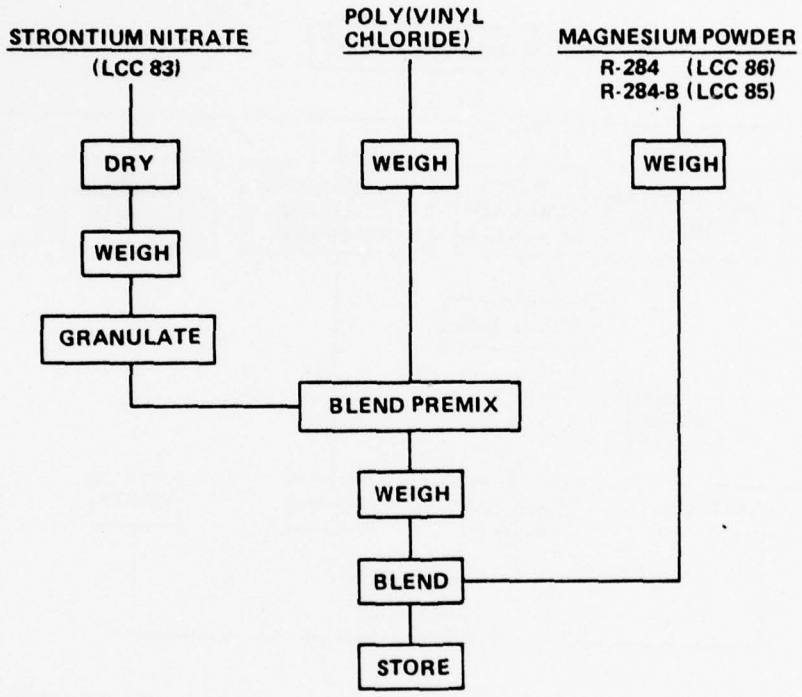


Figure I-8. Process Flow Sheet - R-284 Tracer Composition.

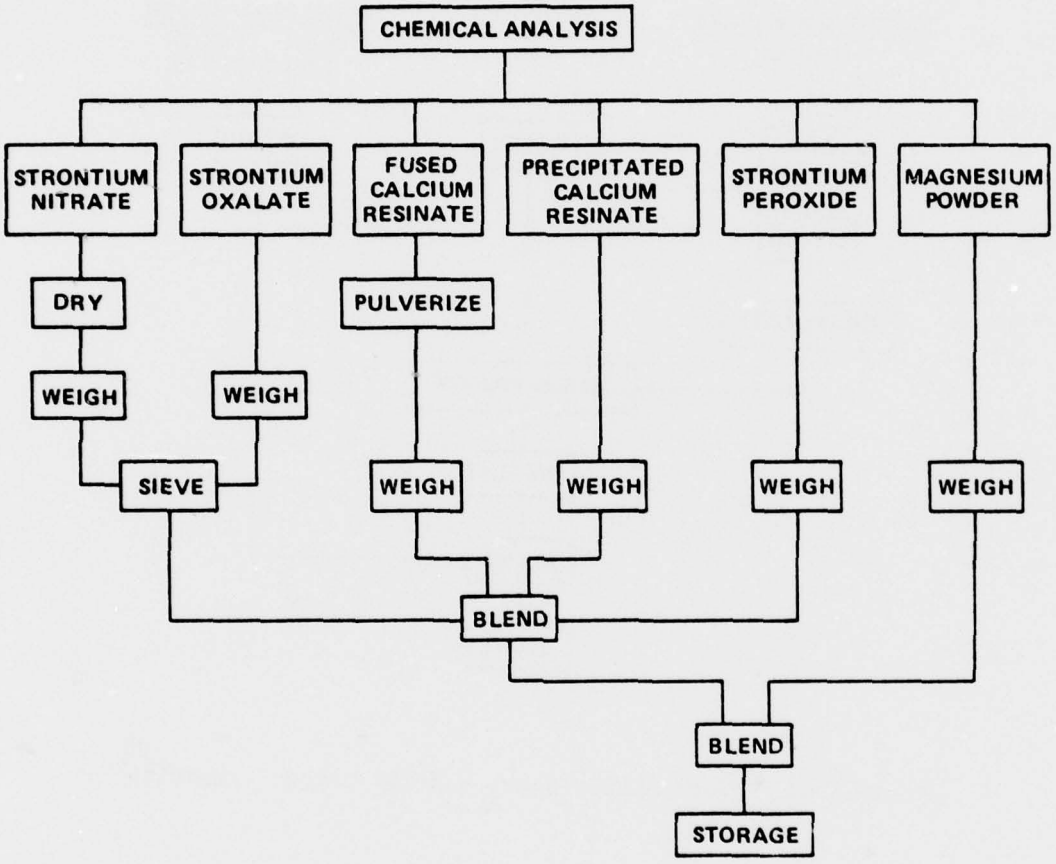


Figure I-9. Process Flow Sheet - Tracer Composition K-256.

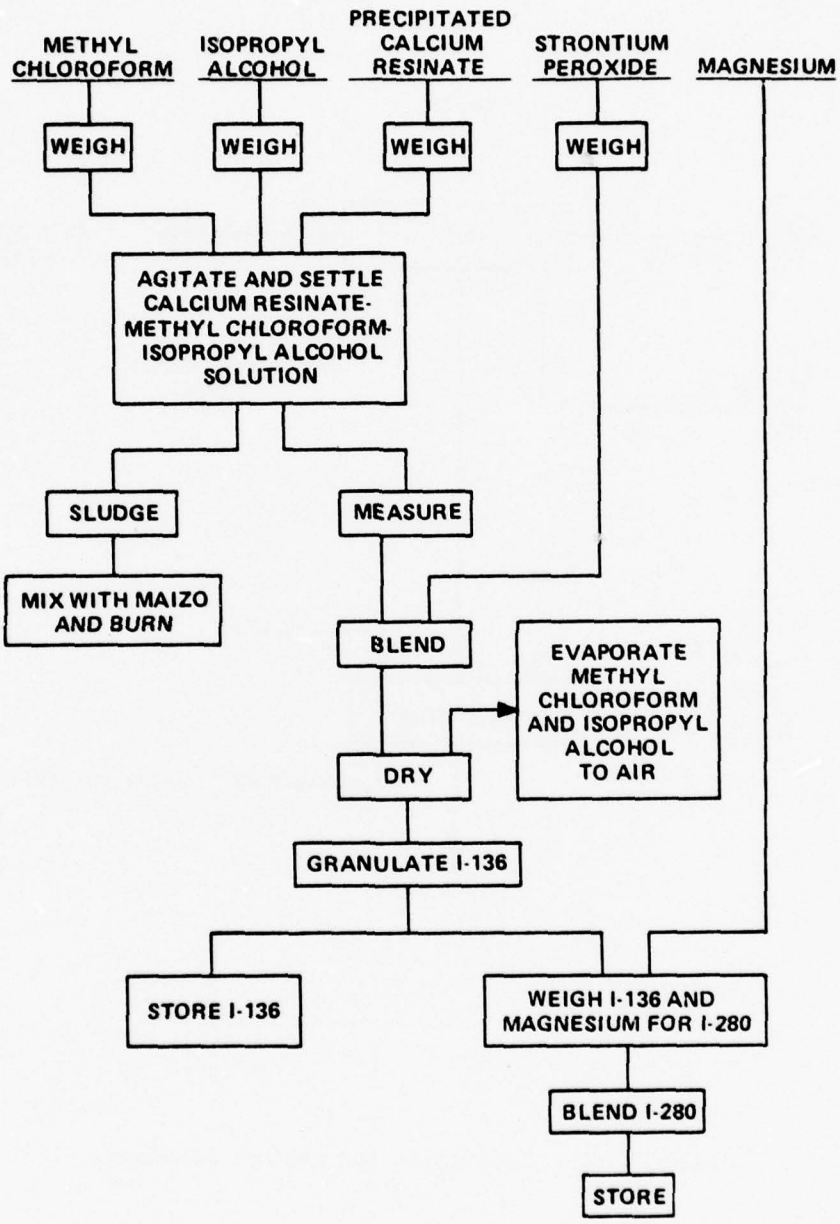


Figure I-10. Process Flow Sheet - Igniter Compositions I-136 and I-280.

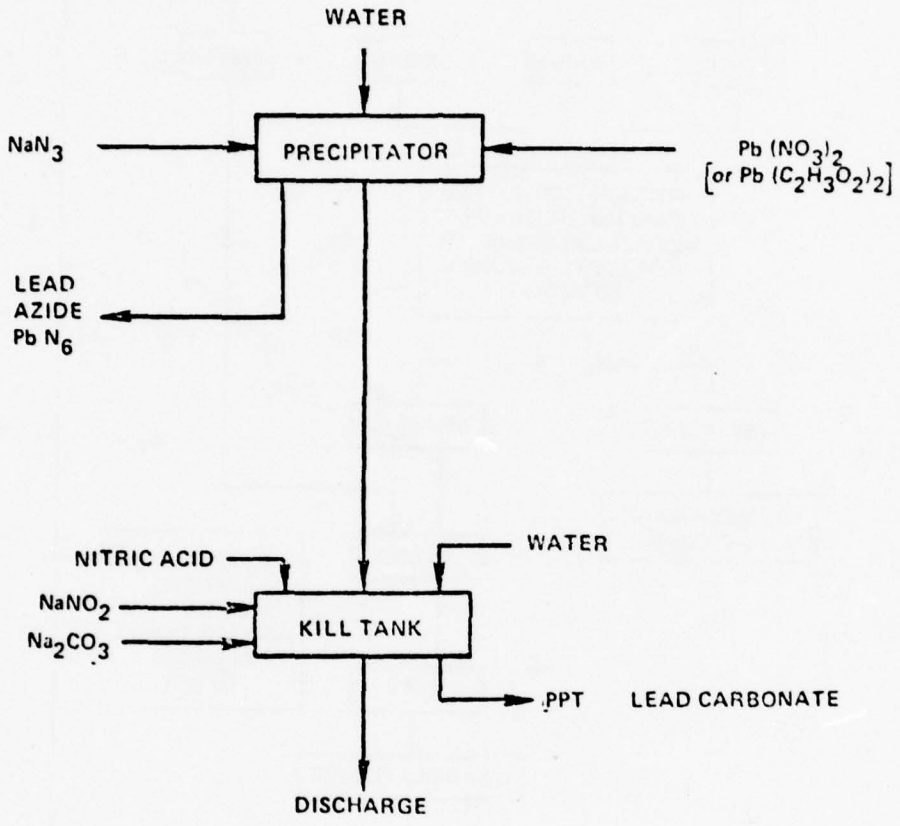


Figure I-11. Lead Azide Production Schematic.

4. Effluent Streams and Treatment

Wastes from primer and tracer manufacture average 0.5-2% of the ingredients used. In some cases losses of as high as 10% have occurred (Aikman, 1978; Melton, 1978; Alexander, 1978; Maley, 1978). Losses are relatively high because primers and similar compositions are generally produced in small batches. The extreme sensitivity of some of these compositions plus their high explosive power also requires remote controlled processing.

Wastes occur during processing due to minor spills during transfer or as dust from dry blending operations. Each blending unit is washed down daily to remove waste substances. Because of the sensitivity of many of the products, the washwater is collected and treated near the production site. This operation involves immersion in a kill tank containing sodium hydroxide or other strong base to destroy the explosives. The kill tanks contain many times the stociometric quantity of base required to destroy the waste material. After the kill step, the waste effluent can be neutralized and discharged into conventional industrial waste treatment facilities.

Wastes from primer and igniter manufacturing operations are never collected dry as are propellant or explosive wastes. The primer type compounds are so sensitive that it would be too dangerous to attempt to transport them dry to a burning site or incinerator.

a. Lake City AAP

The industrial waste treatment plant at LCAAP was constructed in 1942 (USAEHA, 1971). This facility treats wastes generated by the manufacturing process in the principal production buildings. The plant is designed to handle a maximum flow of 1,500,000 gpd. The treatment plant consists of a mixing well, a Parshall flume and two parallel series of three partitioned treatment basins (USAEHA, 1971). In the first two treatment basins, oil and grease are skimmed off the water. Lime and alum are added in the third stage to neutralize, precipitate and flocculate other wastes. The effluents are sent to lagoons, where the solid constituents settle out. The supernatent liquid after settling is discharged into the West Fire Prairie Creek. This creek flows in a northwesterly direction across the facility and drains into the Little Blue River.

b. Lone Star AAP

At LSAAP, wastewaters generated from production operations in Areas P and Q contain lead azide (USAEHA, 1972b). These wastes are collected in stainless steel vats and treated with sodium nitrite and acetic acid. The lead azide is converted to soluble lead acetate. The effluent is disposed of in gravel bottom leaching pits. There is potential for ground water contamination by percolation of lead acetate from the leaching pits.

Future plans for effluent treatment at LSAAP are primarily oriented towards reduction of the lead content of the discharges. It is anticipated that the lead content of these wastes can be reduced to 1 mg/l or

less by precipitation or flocculation processes. Current attempts to accomplish this level of lead reduction have been unsuccessful.

c. Longhorn AAP

Wastes generated from loading operations at Longhorn AAP are washed into sumps. The sumps are emptied by pumping the contents into trucks. The wastes are transported to an evaporation pond. This pond has accumulated solid residues from munition wastes for many years. The bottom of the pond is believed to have a layer of waste materials 8-12 inches thick covering it. This pond may be a source of chemical substances in the ground water. A second pond is being considered, as the ability of the existing pond to handle future wastes is uncertain.

d. Pine Bluff Arsenal

Pine Bluff Arsenal discharges wastes containing potassium chlorate, lead oxide, barium nitrate and magnesium carbonate (USAEHA, 1970b; USAEHA, 1972a). These wastes enter four surface streams which empty into the Arkansas River on the eastern boundary of the facility. These discharges are of concern, as Pine Bluff Arsenal is underlain by a water table aquifer which receives wastes from the facility (USAEHA, 1973). To overcome this problem, Pine Bluff Arsenal is installing a central waste water treatment plant. This plant is to be operational in 1979. The treatment plant will reduce all chemicals in the effluent to current permissible discharge levels.

B. Load, Assembly and Pack

With the exception of Holston, Badger, Newport, Volunteer and Indiana, all Army Ammunition Plants perform load, assembly and pack operations when in production. Most of these facilities use only end items such as fuses and detonators. They do not handle the primer or initiator chemicals as such.

Wastes from LAP operations are minimal in quantity. However, spills and dusts must be collected and treated to avoid accumulations to dangerous levels. Treatment with strong base results in solutions having a pH of 12. These wastes are sometimes discharged directly with no further treatment (Train *et al.*, 1976).

C. Disposal of Outdated Shells Containing Primer and Tracer Chemicals

Shells which have been rejected, or have exceeded storage life limitations, must be disposed of. In some cases, some of the components are reclaimed. For example, the Navy reclaims dyes from waste smoke compositions (Dinerman and Gilliam, 1976). This operation results in a filtrate containing potassium chlorate which is not recovered.

Shell washout is generally accomplished by steam cleaning. The resulting washwater is filtered. The recovered water is reused until the level of dissolved explosives becomes excessive. It is then sent to an evaporation

pond. Solids collected by filtration are burned.

A serious problem exists with aged shells containing lead azide as an initiator. The cartridge cases are usually brass. If the lead azide comes into contact with copper, it forms copper azide which is extremely shock sensitive. If this situation occurs, any movement of the shell could cause it to explode. Some old shells even explode spontaneously, although this problem is rare. Many shells, some of World War II vintage, are in storage. It would be desirable to demilitarize them, but because of potential formation of copper azide, there is great concern over moving them to disposal sites. No resolution to this problem has been devised to date.

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AD

PRELIMINARY PROBLEM DEFINITION STUDY OF 48 MUNITIONS-RELATED CHEMICALS

VOLUME IV PRIMER AND TRACER RELATED CHEMICALS

BARIUM NITRATE

FINAL REPORT

J. F. Kitchens
W. E. Harward III
D. M. Lauter
R. S. Wentsel
R. S. Valentine

April 1978

Supported by:

U. S. ARMY MEDICAL RESEARCH AND DEVELOPMENT COMMAND
Fort Detrick, Frederick, Maryland 21701

Contract No. DAMD17-77-C-7057

COTR: Clarence Wade, Ph.D.

ATLANTIC RESEARCH CORPORATION
Alexandria, Virginia 22314

Approved for Public Release
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The findings of this report are not to be construed as an official Department of the Army position unless so designnated by other authorized documents.

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SUMMARY

Barium nitrate is widely used in the munitions industry in a variety of products. This chemical serves as a flash supplement and barrell coolant in solid propellants and as an oxidizer and coloring agent in pyrotechnic, tracer and primer formulations. These formulations are made at several Army Ammunition Plants including Radford, Lake City, Lone Star, Longhorn AAPs and Pine Bluff Arsenal. The treatment of wastes from these plants range from discharge of untreated wastes into local waterways to disposal in holding ponds and precipitation techniques. Thus the amount of barium nitrate or barium salts entering the environment varies from plant to plant. Significant widespread pollution of barium also results from use of the munitions and pyrotechnics produced by the Army.

Civilian production capacity for barium nitrate is ~8 million lb/year. However, this figure is based on no production of strontium nitrate. Barium nitrate uses in the civilian community include production of optical glass, ceramic glazes, rodenticides and in the electronics industry. These uses are minor when compared to military wartime needs for barium nitrate.

Barium nitrate is relatively toxic to mammals in subcutaneous or interveneous injections. It has a low toxicity to most aquatic organisms. The most sensitive aquatic organism is *Daphnia magna*. Reductive impairment in this invertebrate is observed with low concentrations of soluble barium salts.

Barium nitrate is not a military unique chemical. However, military usage of barium nitrate and pollution of barium resulting from this use is significantly greater than that of the civilian community. Thus, barium nitrate is a chemical for which the Army should consider for further evaluation of toxicological and environmental hazards. It is recommended that a Phase II study on this chemical be conducted. However, this study should not be limited to the nitrate alone but should include all barium compounds used at the Army Ammunition Plants.

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FOREWORD

This report details the results of a preliminary problem definition study on barium nitrate. The purpose of this study was to determine the Army's responsibility for conducting further research on barium nitrate in order to determine its toxicological and environmental hazards so that effluent standards can be recommended. In order to determine the Army's responsibility for further work on barium nitrate, the military and civilian usage and pollution of this chemical were evaluated. In addition, a preliminary overview of toxicological and environmental hazards was conducted.

Barium nitrate was only one of 48 chemicals evaluated under Phase IA of contract No. DAMD17-77-C-7057. These chemicals are grouped in four categories

- explosives related chemicals
- propellant related chemicals
- pyrotechnics
- primers and tracers

Each category is a major report. Section I of each report is an overview of the military processes which use each chemical and the pollution resulting from the use of these chemicals. The problem definition study reports on each chemical are separable sections of these four reports.

In addition a general methodology report was also prepared. This report describes the search strategy and evaluation methodology utilized for this study.

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II. BARIUM NITRATE

A. Alternate Names

Barium nitrate is a chemical which has increased and declined in importance in direct correlation with the military market. Barium nitrate has a molecular formula of BaN_2O_6, a molecular weight of 261.35 g/mole and a structural formula of

$$O_3N - Ba - NO_3$$

Pertinent alternate names are presented below:

CAS Registry No.:	10022-31-8
CA Name (8CI):	Nitric acid, barium salt
Wiswesser Line Notation:	Ba N-02-Q*2
Synonyms:	Barium dinitrate; Barium nitrate; Nitrobarite

B. Physical Properties

The physical properties of barium nitrate are presented in Table II-1.

C. Chemical Properties

1. General Reactions

The primary reaction of barium nitrate is its decomposition to barium oxide, oxygen, and toxic oxides of nitrogen (Kirk and Othmer, 1964).

$$Ba(NO_3)_2 \longrightarrow BaO + 2NO_2 + 1/2\ O_2$$

The reaction is easily initiated by flame, heat, or shock. It may occur spontaneously in the presence of easily oxidizable materials (OSHA, 1972).

2. Environmental Reactions

Barium nitrate is a soluble salt which dissociates to Ba^{+2} and nitrate anions in water. In near neutral waters, nitrate is chemically stable to reduction. Depending on the availability of other ions in the environment, insoluble barium salts may precipitate. In the presence of sulfate anion, barium sulfate will be formed (Hawley, 1977).

$$Ba^{+2}(aq) + SO_4^{-2}(aq) \longrightarrow BaSO_4(s)$$

Table II-1. Physical Properties of Barium Nitrate*.

Physical Form @20°C:	solid
Color:	glossy white
M.P.:	592°C
B.P.:	decomposes
Crystal Density:	3.24 g/cm^3 @ 23°C
Solubility:	water - 5.0 g/100 g @ 0°C 7.0 g/100 g @ 10°C 9.2 g/100 g @ 20°C 17.1 g/100 g @ 50°C 34.2 g/100 g @ 100°C slightly soluble in acid hardly soluble in alcohol and acetone

*References: Kirk and Othmer, 1964; Hodgman *et al.*, 1963.

Barium oxide, the decomposition product of barium nitrate, is chemically unstable in the environment. Exposed to air, it absorbs carbon dioxide to form barium carbonate (Kirk and Othmer, 1964).

$$BaO(s) + CO_2(g) \longrightarrow BaCO_3(s)$$

Barium oxide reacts violently with water to form the hydroxide (Kirk and Othmer, 1964).

$$BaO + H_2O \longrightarrow Ba(OH)_2$$

Nitrate ion is photochemically reactive. It is reduced to nitrite by ultraviolet light, particularly at wavelengths below 265 nm and around 300 nm. Irradiation of insoluble nitrate salts on the surface at 250 nm also forms nitrite. The reaction occurs faster under alkaline conditions (Coldwell and McLean, 1959).

3. Sampling and Analysis

Determination of barium nitrate may be done by analysis of barium or nitrate. Barium can be determined using atomic absorption spectrophotometry. A nitrous oxide-acetylene flame is used and absorption is measured at 553.6 nm. The reported sensitivity is 300 mg/l of barium for 1% absorption (Franson, 1975).

Four methods for the determination of nitrate are described below. The nitrate ion electrode is applicable over the widest range of concentrations. The UV spectrophotometric method is also widely useful while the last two are limited in their effective concentration ranges (Franson, 1975).

- Determination of nitrate with a nitrate ion electrode allows analysis of concentrations from 0.2 to 1,400 mg of NO_3^-/l. The disadvantage is the numerous interferences which must be chemically removed prior to analysis. Chloride and bicarbonate at relatively high concentrations interfere with the electrode as do nitrite, sulfide, bromide, iodide, chlorate and perchlorate.

- Nitrate in solution may be determined by measurement of UV absorption at 220 nm. Beer's law is obeyed up to concentrations of 11 mg/l. Dissolved organic matter may interfere with this analysis.

- Nitrate is reduced by cadmium to nitrite which can undergo further reactions with sulfanilamide and N-(1-napthyl)-ethylenediamine to form a colored product that may be determined colorimetrically. Correction for any nitrite initially present must be made. This method is used for determinations below 0.1 mg NO_3^-/l.

- Colorimetric estimation of the yellow reaction product of brucine and nitrate allows determination of nitrate in water. This method is applicable to the narrow concentration range of 0.1 to 2 mg/l.

D. Uses in Army Munitions

1. Purposes

a. Propellant Uses

Barium nitrate is used by Radford AAP as a propellant additive. This material serves as a flash suppressant and barrell coolant. The only formulation specifying barium nitrate is the M-26 propellant. This formulation requires 0.75 ± 0.2% barium nitrate.

b. Pyrotechnic Uses

Barium nitrate is also used in various pyrotechnic compositions. The purpose of the chemical is to serve as an oxidizer. It also imparts a green color to burning compositions. Barium nitrate is used in the following compositions produced at Pine Bluff Arsenal:

	% Barium Nitrate in Composition
Starter mixture XXVI	45±0.5
Incendiary mixture TH3	29±0.4
Incendiary misture TH4	22±0.5
Coating mixture	10±0.5

Longhorn AAP utilizes barium nitrate as a constituent of first fire compositions. These compositions are used to ignite flares, candles and other pyrotechnic items.

c. Primer and Tracer Uses

Another major use of barium nitrate is as an oxidizer in primer and tracer mixes. At Lake City AAP, the following compositions are produced with barium nitrate as a constituent:

	% Barium Nitrate in Composition
Primer mix 5061	43.4
Primer mix FA874	42.8
Primer mix FA956	31.5
Igniter mix 68	25
Igniter mix 11	50
Igniter mix 28	40.6

Lone Star AAP also uses barium nitrate for primer and tracer applications.

2. Quantities Used

a. Historical Use

i. Use in Propellants

The use rate of barium nitrate for M-26 propellant at Radford AAP (RAAP) over the period 1968-1977 is given below (Watts, 1978).

Year	Quantity Purchased, lb
1968	14,400
1969	3,900
1970	0
1971	13,500
1972	750
1973	1,200
1974	22,850
1975	15,800
1976	5,400
1977	14,700

The average annual use during this period was 9,250 lb/year. Longhorn AAP used 14,651 lb of barium nitrate in 1977. Historical use rate was not available.

ii. Use in Pyrotechnics

Pine Bluff Arsenal has used barium nitrate primarily to produce thermite incendiary mixtures. Over the last ten years, about 328,000 lb of barium nitrate has been used (Aikman, 1978). The average use rate during this period was 32,800 lb/year or 2,733 lb/month.

iii. Uses in Primers and Tracers

Purchases of barium nitrate by LCAAP has been as follows during the 1975-1977 period:

Year	Quantity Purchased, lb
1975	32,100
1976	17,510
1977	22,400

Lone Star AAP has also used barium nitrate (USAEHA, 1974). During 1974, the use rate of this material was approximately 200 lb/month.

b. Current Use

During 1977, RAAP produced 2,570,800 lb of M-26 propellant. This amount of propellants required 19,280 lb of barium nitrate, or a current use rate of 1,607 lb/month.

The 1978 production schedule for Pine Bluff Arsenal calls for 18,020 TH3 grenades. Based upon 330 g of active material per grenade, this production rate will require 4,000 lb of barium nitrate or 317 lb/month. Longhorn AAP also uses barium nitrate for pyrotechnic items. The most recent use rate was 14,651 lb during the year 1977. This averages 1,221 lb/month.

The most recent use rate of barium nitrate at LCAAP was 1,867 lb/month. This quantity represents the average use rate during 1977. Lone Star AAP currently uses barium nitrate at the rate of about 220 lb/month, similar to the rate of use in June, 1974, as noted above.

c. Use at Full Mobilization

The estimated use rates of barium nitrate at full mobilization are given below:

Propellants	RAAP	12,000 lb/month	144,000 lb/year
Pyrotechnics	PBA	6,400 lb/month	76,800 lb/year
Primer and Tracers	LAAP	43,800 lb/month	525,600 lb/year
	LCAAP	6,200 lb/month	74,400 lb/year
	LSAAP	∿1,000 lb/month	12,000 lb/year

3. Documented or Speculated Occurrences in Air or Water

a. Losses from Propellant Manufacture

The M-26 propellant is a double base composition made at RAAP by the solvent process. Typically, losses from this type of propellant processing average 6-7% of the amount produced. Some of the waste is collected as solids, however, and sent to a burning ground for destruction. It is estimated that actual losses of barium nitrate to the New River from propellant processing operations ranges from 32 to 64 lb/month. In addition, 1-3% of the barium nitrate handled is lost in preparation operations such as sieving, weighing or grinding. Thus the total current loss of barium nitrate is estimated at 48-112 lb/month. At full mobilization, the expected loss rate would be 360-840 lb/month. Losses of barium nitrate from propellant operations at LAAP are estimated at 0.5-1.0% of the amount handled (Maley, 1978). Thus, losses of barium nitrate at current operating levels are ∿6-12 lb/month. At full mobilization losses of barium nitrate would reach 220-440 lb/month. These wastes are collected in sumps and discharged into an onsite evaporation pond.

b. Losses from Pyrotechnic Manufacture

Losses from pyrotechnic manufacture generally amount to 1-2% of the amount handled (Aikman, 1978). At the estimated 1978 use rate, losses of barium nitrate at PBA would be 3-6 lb/month. At full mobilization this figure would increase to 64-128 lb/month. All of this loss may be discharged into the Arkansas River. There is currently no treatment of pyrotechnic wastes at PBA.

c. Losses from Primer and Tracer Manufacture

Wastes from primer and tracer manufacture average 1-2% of the amount handled (Melton, 1978). At LCAAP, losses from current operations would be 19-38 lb/month. At full mobilization, 62-124 lb/month would be lost. This material is discharged into conventional industrial waste treatment facilities. Based on the solubility of the sulfate and carbonate salts of barium, a maximum of 5.5 mg/l of barium would be discharged from this facility. However, during a monitoring program in 1971, no barium was detected in any of the effluent streams from Lake City AAP (USAEHA, 1971). At LSAAP, losses are also estimated at 1-2% of the amount used (Alexander, 1978). The wastes at LSAAP are collected in on-site evaporation ponds and not discharged directly.

E. Uses in the Civilian Community

1. Production Methodology

Barium nitrate is manufactured by the action of nitric acid on barium carbonate (FMC Corp., 1978).

$$BaCO_3 + 2HNO_3 \longrightarrow Ba(NO_3)_2 + H_2CO_3$$

Barium carbonate is mixed with a nitric acid solution. The precipitated barium nitrate is filtered, then recrystallized.

Barium nitrate may also be produced by dissolving sodium nitrate in a saturated barium chloride solution (Kirk and Othmer, 1964).

$$BaCl_2 + NaNO_3 \longrightarrow Ba(NO_3)_2$$

2. Manufacturers, Production and Capacity

The U.S. manufacturers of barium nitrate, plant locations and capacities are listed in Table II-2.

Table II-2. Barium Nitrate Manufacturers, Locations and Capacities (S.R.I., 1977).

Manufacturer	Location	Capacity
Barium and Chems. Inc.	Steubenville, Ohio	not available
FMC Corp. Chem. Group Indust. Chem. Div.	Modesto, California	7×10^6 lb/year
Mallinckrodt, Inc. Indust. Chems. Div.	St. Louis, Missouri	not available
Richardson-Merrell, Inc. J.T. Baker Chem. Co., subsid.	Phillipsburg, New Jersey	not available
Cooper Chemical Co.	Long Valley, New Jersey	3×10^3 lb/year

Barium and Chemicals, Inc. manufactures $Ba(NO_3)_2$ to military specifications. They do not manufacture any commercial grade material (Barium and Chemicals, 1978).

The FMC Corporation produces strontium nitrate as well as barium nitrate at their Modesto facility. Their production capacity of $7x10^6$ lb/year is based on shutting down strontium nitrate production and manufacturing $Ba(NO_3)_2$ exclusively (FMC Corp., 1978).

Cooper Chemical manufactures reagent grade $Ba(NO_3)_2$ for research labs and chemical supply houses (Cooper Chemical, 1978).

The Hummel Chemical Co. purchases barium nitrate and reprocesses it in South Plainfield, NJ (Hummel Chem., 1978).

Table II-3 lists importers of barium nitrate and their source countries.

Table II-3. Barium Nitrate Importers and Sources.
(OPD Chemical Buyers Directory, 1977)
(personal communications with importers, 1978).

Aceto Chemical Co.	W. Germany
American Hoechst Corp.	W. Germany
E.M. Laboratories, Inc.	W. Germany
ICD Chemicals, Inc.	China
Pharmacie Centrale de France	France

3. Usages

Civilian uses of barium nitrate are minor compared to the quantities employed by the military in wartime. Uses of barium nitrate in the civilian sector include the production of optical glass, ceramic glazes, rodenticides and in the electronics industry (Hawley, 1977; FMC Corp., 1978).

4. Future Trends

There are no anticipated uses for $Ba(NO_3)_2$ which would increase civilian usage to the level of military use at full mobilization.

5. Documented or Speculated Occurrences in the Environment

Barium has been reported in U.S. drinking waters in concentrations from 0.7 to 900 µg/l. The mean value is 49 µg/l (Franson, 1975).

F. Comparison of Military and Civilian Uses and Pollution

Barium nitrate is widely used in the munitions industry in a variety of products. At current production rates, the five Army Ammunition Plants surveyed

uses ∿73,000 lb/year. Requirements for barium nitrate by these five plants at full mobilization production would be 833,000 lb/year. In contrast to the military use of barium, civilian uses are minor especially when compared to military wartime needs.

The amount of barium entering the environment from the military use of barium nitrate varies as a function of its end product use and the production facility which makes the product. Lone Star and Longhorn AAP's put wastes into evaporation ponds. Thus no significant amount of barium nitrate enters the aquatic environment from these facilities. Radford AAP and Pine Bluff Arsenal dump all of the wastes into the New River and the Arkansas River. Lake City AAP uses a conventional industrial waste treatment facility to remove pollutants from their effluents. The maximum concentration which could occur in Lake City's effluent is 5.5 mg/l.

Full utilization of primers, tracers and pyrotechnics releases large amounts of barium in the air and the soil. These items contribute more to barium pollution than do rocket fuels due to the higher percentage of barium nitrate in these mixes. Essentially 100% of the barium in the various military munitions devices is lost to the environment when the munitions are used. Thus, although barium nitrate is not a military unique chemical, it is a military problem chemical.

G. Toxicological and Environmental Hazards

1. Toxicity to Mammals

The available acute toxicity data of barium nitrate are shown in Table II-4. S-W mice are the most sensitive animals tested with a LD50 of 8.49 mg Ba^{++}/kg. Due to its solubility in water (9.2 g/100 g H_2O), barium nitrate is more toxic in acute doses than are the insoluble barium salts.

Table II-4. Toxicity of Barium Nitrate to Mammals

Species	Dose (mg/kg)	Route of Adminis.	Effects	References
Rats	355	Oral	LD50	NIOSH, 1977
Mice S-W	8.5 (as Ba^{2+})	i.v.	LD50	Syed & Hosain, 1972
Mice ICR	20.1 (as Ba^{2+})	i.v.	LD50	"
Mice	10	s.c.	LDLo	NIOSH, 1977

No chronic studies with barium nitrate appeared in the literature surveyed. However, the chronic effects of barium chloride were studied by

Fazekas *et al.* (1953). These researches subcutaneously injected 2, 5 and 10 mg/kg of aqueous barium chloride solution into rabbits. Deaths were observed at 98 and 193 days. In spite of its toxicity, there is some evidence that small quantities of barium are essential for proper health and growth. Beliles (1975) maintained rats on a barium-free diet. These rats failed to grow in a normal manner.

Although barium has a short biological half-life in man of 24 hours, oral doses of soluble barium salts are very toxic. An oral dose of soluble barium salt in man can produce gastroenteritis, muscular paralysis, decreased pulse rate and ventricular fibrillation (Casarett and Doull, 1975). Barium ions may substitute for sodium ions in B and C nerve fibers to produce prolonged action potentials (Greengard and Straub, 1959). Also, Douglas *et al.* (1961) found barium to have a stimulating effect on the release of acetyl choline from cholinergic nerves.

2. Aquatic Toxicity

Barium levels in natural waters range from 5-45 ppb. The toxic effects of this metal are mainly exhibited when ionic barium is present. In most natural waters, sufficient sulfate or carbonate is present to precipitate barium. The carbonate or sulfate salts would thus accumulate in the sediment. These salts have a very low toxicity. Bioaccumulation of barium by most aquatic organisms is low (Hildebrand *et al.*, 1976). However, Templeton (1958) found that barium could be concentrated in goldfish (*Carassium auratus*) up to 150 times.

In general, soluble barium salts have a relatively low toxicity to aquatic organisms. Concentrations greater than 50 mg/l are necessary for toxic effects to be observed in most aquatic organisms (EPA, 1976). The exception is *Daphnia magna*. Biesinger and Christensen (1972) determined a chronic 3-week LC50 for *Daphnia* to be 13.5 ppm of $BaCl_2$. They also found a 16% reproductive impairment at 5.8 ppm $BaCl_2$.

3. Toxicity to Microorganisms

No information was found during this literature search on the toxicity of barium nitrate to microorganisms.

4. Phytotoxicity

McHargue (1919) studied the effect of certain compounds of barium on the growth of plants. It was concluded from his investigation that barium compounds in the absence of calcium carbonate are poisonous to plants; but barium carbonate in the presence of an excess of calcium carbonate may stimulate plant growth. Growth comparison studies on corn plants treated with several barium compounds are shown in Table II-5. The effects of barium carbonate upon the growth of cowpeas is shown in Table II-6.

Robinson *et al.* (1938) surveyed several areas of infertile soil for chemical content. The infertile soils contained up to 3.74% BaO while the

Table II-5. Air-Dry Weights of the Corn Plants Treated with Barium Salts (McHargue, 1919).

Pot No. and Treatment	Air-dry Weights				Gain or loss in weight when compared with the controls			
	Roots	Stalks	Fodder	Entire Plants	Roots	Stalks	Fodder	Entire Plants
	Gm.	Gm.	Gm.	Gm.	Gm.	Gm.	Gm.	Gm.
Pot 1 (control)	11.50	13.25	17.60	42.35				
Pot 2 (control)	8.00	10.30	15.35	33.65				
Average	9.75	11.77	16.47	38.00				
Pot 3+2 gm. of barium carbonate	10.65	14.25	18.75	43.65				
Pot 4+2 gm. of barium carbonate	12.10	8.25	19.30	39.65				
Average	11.38	11.25	19.02	41.65	+1.63	-0.52	+2.55	+3.65
Pot 7+2 gm. of barium carbonate & 2 gm. of strontium carbonate	14.75	13.00	20.25	48.00	+5.00	+1.23	+3.78	+10.00
Pot 8+2 gm. of barium nitrate	11.50	13.25	18.75	43.50	+1.75	+1.48	+2.28	+ 5.50
Pot 9+5 gm. of barium sulphate	10.75	8.00	14.25	33.00	+1.00	-3.77	-2.22	- 5.00
Pot 10+2 gm. of barium chlorid	11.50	7.50	19.25	38.25	+1.75	-4.27	+2.78	+ 0.25
Pot 11+5 gm. of barium carbonate	13.5	12.00	20.00	45.50	+3.75	+ .23	+3.53	+ 7.50
Pot 12+5 gm. of strontium carbonate	13.2	14.5	20.7	48.40	+3.45	+2.73	+4.23	+10.40

Table II-6. Effect of Barium Carbonate upon the Growth of Cowpeas. (McHargue, 1919)

Pot No.	Quantity of barium carbonate added to soil	Weight of 10 Air-dried Plants	Pot No.	Quantity of barium carbonate added to soil	Weight of 10 Air-dried Plants
	Gm.	Gm.		Gm.	Gm.
1 (control)	None	9.15	7	5	11.40
2	0.5	12.00	8	6	10.90
3	1	11.20	9	8	11.15
4	2	10.15	10	10	10.80
5	3	9.50	11a	5	-
6	4	10.55	12	5	11.65

exchangeable Ca and Mg levels were low, being nearly equal to or exceeded by the exchangeable barium.

Colin and de Rufz (1900) studied the absorption of barium by peas, maize and beans in dilute (0.125 ppt) solutions of barium nitrate. Practically all the barium was found localized in the roots although there were traces in the stems of the plants.

5. Availability of Literature for Phase II

The literature on the toxicological and environmental properties of barium nitrate is sufficient for a Phase II study. Additional information can be obtained by comparison with the more common, chloride salt.

H. Regulations and Standards

1. Air and Water Regulations

EPA has listed 1 mg/l of barium as a criterion for domestic water supplies (EPA, 1976). No fresh water standard appears to be necessary for protection of aquatic life due to the low aquatic toxicity of this compound and its removal by precipitation as the carbonate or sulfate salts (EPA, 1976)

2. Human Exposure Standards

The present limit for barium in air is 0.5 mg Ba/m^3 (American Conference of Governmental Industrial Hygienists, 1971). This limit was employed at Los Alamos Laboratories for several years for control of exposure to barium nitrate. Results were found to be satisfactory using this limit. The OSHA standard for air is the same (Federal Register, 1974). This compound is not on the NCI suspected carcinogen list.

3. DOT Labeling Requirements

The Department of Transportation lists barium nitrate as an oxidizer. Labels on this material should state "Oxidizer" (Federal Register, 1976).

I. Conclusions and Recommendations

Barium nitrate, although not a military unique chemical, is a military problem chemical. The current military usage of this chemical is significant. During wartime, the military usage is greater than the civilian usage. Pollution of barium resulting from military munitions production and use is widespread. Thus, it is recommended that barium nitrate be included in a Phase II detailed toxicological and environmental evaluation. However, this evaluation should include all barium salts used by the Army. This recommendation is based on the fact that the toxicity of these salts is mainly that of the metal. Thus to get an accurate view of the environmental problems, the total load of barium being discharged must be evaluated. Toxicological and environmental interaction with other metals such as strontium and calcium as well as the type of receiving waters also requires further evaluation.

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PRELIMINARY PROBLEM DEFINITION STUDY OF 48 MUNITIONS-RELATED CHEMICALS

VOLUME IV PRIMER AND TRACER RELATED CHEMICALS

ANTIMONY SULFIDE

FINAL REPORT

J. F. Kitchens
W. E. Harward III
D. M. Lauter
R. S. Wentsel
R. S. Valentine

April 1978

Supported by:

U. S. ARMY MEDICAL RESEARCH AND DEVELOPMENT COMMAND
Fort Detrick, Frederick, Maryland 21701

Contract No. DAMD17-77-C-7057

COTR: Clarence Wade, Ph.D.

ATLANTIC RESEARCH CORPORATION
Alexandria, Virginia 22314

Approved for Public Release
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The findings of this report are not to be construed as an official Department of the Army position unless so designnated by other authorized documents.

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SUMMARY

Antimony sulfide or antimony trisulfide is used in yellow pigments, matches, ruby glass manufacture and as a flame proofing agent. Total civilian usage of this material is estimated at 5-10 million lb/year.

The Army uses antimony sulfide as a fuel in pyrotechnic compositions and primer mixes. Total military use even at full mobilization would represent less than 0.5% of civilian usage.

Antimony compounds exhibit relatively low toxicity to mammals, aquatic organisms, microorganisms and plants. Antimony trisulfide occurs widely in nature as stibnite ore.

The military sources of pollution by antimony sulfide are negligible compared to civilian sources. Because of the low usage and relatively low toxicity, further studies of the environmental or toxicological hazards of the compound by the Army should be a low priority.

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FOREWORD

This report details the results of a preliminary problem definition study on antimony trisulfide. The purpose of this study was to determine the Army's responsibility for conducting further research on antimony trisulfide in order to determine its toxicological and environmental hazards so that effluent standards can be recommended. In order to determine the Army's responsibility for further work on antimony trisulfide, the military and civilian usage and pollution of this chemical were evaluated. In addition, a preliminary overview of toxicological and environmental hazards was conducted.

Antimony trisulfide was only one of 48 chemicals evaluated under Phase IA of contract No. DAMD17-77-C-7057. These chemicals are grouped in four categories

- explosives related chemicals
- propellant related chemicals
- pyrotechnics
- primers and tracers

Each category is a major report. Section I of each report is an overview of the military processes which use each chemical and the pollution resulting from the use of these chemicals. The problem definition study reports on each chemical are separable sections of these four reports.

In addition a general methodology report was also prepared. This report describes the search strategy and evaluation methodology utilized for this study.

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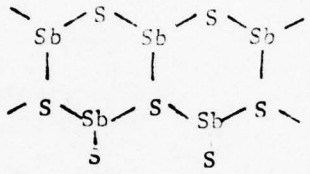
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III. ANTIMONY TRISULFIDE

A. Alternate Names

The sulfide of the lower oxidation state of antimony sulfide is used in pyrotechnic and primer formulations. This sulfide has a molecular formula of Sb_2S_3 and a molecular weight of 339.69 g/mole. Antimony trisulfide has a ribbon like polymeric structure. In this structure each antimony and each sulfur atom is bound to 3 atoms of the opposite kind, forming interlocking SbS_3 and SSb_3 pyramids as shown below (Cotton and Wilkinson, 1967):



Pertinent alternate names for antimony trisulfide are listed below:

CAS Registry No.:	1345-04-6
Replaces CAS Registry Nos.:	12138-10-2; 28767-59-1
CA Name (8CI):	Antimony sulfide (Sb_2S_3)
Wiswesser Line Notation:	
Synonyms:	Antimonous sulfide; Antimony orange; Antimony sesquisulfide; Antimony (III) sulfide; Antimony trisulfide; Antimony vermilion; C.I. 77060; C.I. Pigment Red 107; Crimson antimony sulphide; Diantimony trisulfide; Needle antimony

B. Physical Properties

The physical properties of antimony trisulfide are listed in Table III-1.

C. Chemical Properties

1. General Reactions

When antimony trisulfide is heated with iron, metallic antimony is formed (Smith, 1973).

$$Sb_2S_3 + 3Fe \longrightarrow 2Sb + 3FeS$$

This method can be employed to obtain metallic antimony from stibnite rich ores.

Table III-1. Physical Properties of Antimony Trisulfide*

Physical Form @ 20°C:	1) gray, lustrous crystals or 2) gray-black powder or 3) orange-red crystals
M.P.:	546°C
B.P.:	~1150°C
Density:	gray crystals - 4.64 g/cm^3 orange crystals - 4.12 g/cm^3
Vapor Pressure:	0.033 mmHg at 400°C 1.17 mmHg at 500°C 13.45 mmHg at 650°C 244 mmHg at 850°C
$\Delta H_f 298$	-174.9 kJ mol^{-1}
Magnetic susceptibility:	$-10.8 \times 10^{-10} m^3 mol^{-1}$
Solubilities:	1.75×10^{-4} g/100g H_2O @ 18°C soluble in conc. HCl soluble in 0.5 M NaOH

*References: Hawley, 1977; Windholz, 1976; Smith, 1973; Weast, 1970; U.S. Army Materiel Command, 1963.

Antimony sulfide halides are produced when antimony trisulfide is fused with antimony trihalides (Smith, 1973).

$$Sb_2S_3 + SbBr_3 \longrightarrow 3SbSBr$$

Antimony trisulfide is incompatible with strong oxidizing agents, representing a moderate fire and explosion hazard when mixed with them. Upon burning in the presence of oxygen, antimony trisulfide emits toxic fumes containing oxides of sulfur and antimony (Hummel Chemical, 1978).

Antimony trisulfide is soluble in concentrated hydrochloric acid. Upon dissolution it gives off hydrogen sulfide. Antimony trisulfide also dissolves in alkaline sulfide solution. In the absence of air the thioantimonate (III) ion, SbS_3^{-3}, is formed. In the presence of air the tetrathioantimonate (V) ion, SbS_4^{-3}, is formed (Grayson).

2. Environmental Reactions

Antimony trisulfide is stable in air at room temperature (Smith, 1973). It is very slightly soluble in water. Aqueous antimony will form hydroxides or complex with available ligands (Smith, 1973). Photochemical studies have not been reported.

3. Sampling and Analysis

Antimony is best determined using atomic absorption spectroscopy. Measurements may be taken at 206.8, 217.6, or 231.2 nm using an air-acetylene flame. The 217.6 line is most commonly used (Little, Incorporated, 1976). Aqueous antimony may also be determined volumetrically by titration with standardized oxidizing agents such as potassium iodate or permanganate. Sodium tartrate must be added prior to analysis to prevent precipitation of antimony salts. Small amounts of antimony may be determined colorimetrically as the rhodamine B complex at 550 nm or as SbI_4^- at 330 nm. Traces of antimony may also be estimated by emission spectrography or neutron activation analysis (Smith, 1973).

D. Uses in Army Munitions

1. Purpose

Antimony trisulfide is used as a fuel in pyrotechnic formulations. It also imparts a pale green color to burning compositions. This compound is used by Pine Bluff Arsenal to produce match head mixtures. Match Head Mixture V requires 30±0.5% antimony trisulfide and Match Head Mixture VI specifies 33±0.5% of this chemical.

Antimony trisulfide is also a constituent of primer mixes. At Lake City AAP, this chemical is used in Primer Mix 5061 and Primer Mix FA956. The amounts of antimony trisulfide used in each of these mixes are 9% and 14.8%, respectively.

2. Quantities Used

a. Historical Use

The use rate of antimony trisulfide at Pine Bluff Arsenal has been negligible over the past 10 years.

Purchases of antimony trisulfide by Lake City AAP during 1975-1977 were as follows:

1975	6,248 lb
1976	8,588 lb
1977	8,272 lb

Antimony trisulfide has also been used at Lone Star AAP. During June, 1974, 161 lb of the chemical was used (USAEHA, 1974).

Antimony trisulfide has also been used in the past at Longhorn AAP. The exact quantities used are not known, but believed to be small compared to uses by other facilities. No antimony trisulfide was used at Longhorn AAP during 1977. Only small amounts, if any, are expected to be used at this facility in the foreseeable future.

b. Current Use

The production plan for Pine Bluff Arsenal for 1978 does not call for any compositions requiring antimony trisulfide. It is not expected that there will be any uses of this chemical at Pine Bluff Arsenal in the near future.

Lake City AAP used 8,272 lb of antimony trisulfide in 1977, or 690 lb/month. This amount represents the approximate current use rate.

c. Use at Full Mobilization

The estimated use rate of antimony trisulfide at full mobilization at Lake City AAP is 2350 lb/month.

3. Documented or Speculated Occurrences in Air or Water

Typical losses from manufacture of pyrotechnics, primers and tracers average 1-2% of the amount handled (Melton, 1978). Based upon the current use rate at Lake City AAP, the estimated losses of antimony trisulfide are 7-14 lb/month. At full mobilization, this value would increase to 24-47 lb/month. This material is discharged into a conventional industrial waste treatment facility.

E. Uses in the Civilian Community

1. Production Methodology

There are two methods employed to manufacture antimony trisulfide.

- Treatment of antimony tricholoride with hydrogen sulfide or sodium thiosulfate will form orange-red crystals of antimony trisulfide (Little, 1976).

- Antimony trisulfide can be made by heating either metallic antimony or antimony trioxide with elemental sulfur (Little, 1976).

2. Manufacturers, Production, and Capacity

The U.S. producers of antimony trisulfide are listed in Table III-2.

Table III-2. U.S. Producers of Antimony Trisulfide (S.R.I., 1977a).

Barium and Chems., Inc.	Steubenville, Ohio
Hummel Chem. Co., Inc.	South Plainfield, N.J.
McGean Chem. Co., Inc.	Cleveland, Ohio
Rare Metal Products Co.	Atglen, Pa.

Antimony (III) sulfide is imported to the U.S. and reprocessed. None of the producers manufacture Sb_2S_3 from some other starting material.

3. Usages

Civilian uses of antimony trisulfide include as an intermediate for antimony trihalides, yellow pigments, in matches, the manufacture of ruby glass, gold refining, veterinary surgery, rubber pigments, flame-proofing and camouflage paints (S.R.I., 1977b; Hawley, 1977).

4. Future Trends

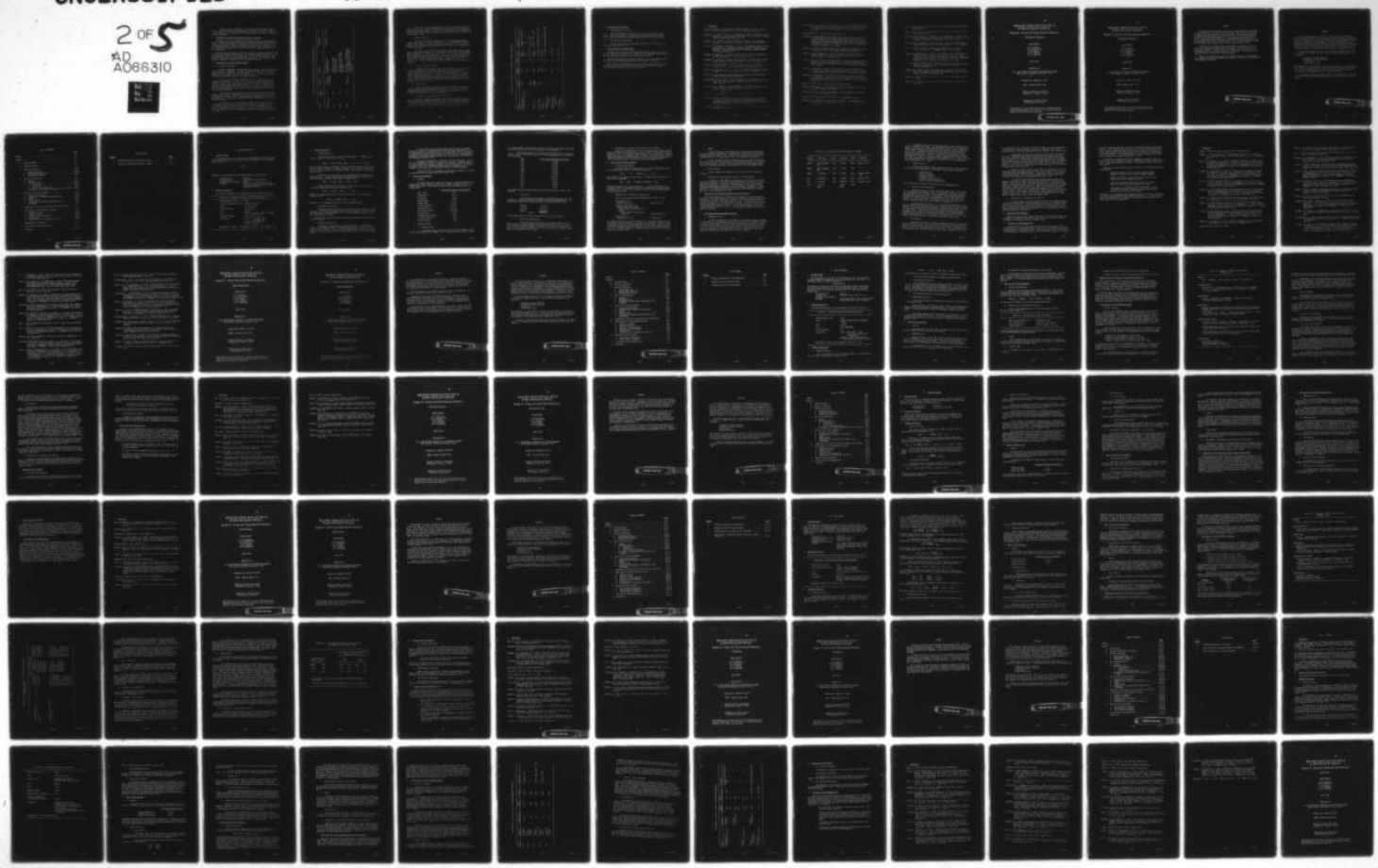
We are unaware of any anticipated changes in the civilian use or production of antimony trisulfide.

5. Documented or Speculated Occurrences in the Environment

Antimony trisulfide occurs widely in nature as stibnite ore. Deposits are found in China, South America and Europe (Smith, 1973).

AD-A066 310 ATLANTIC RESEARCH CORP ALEXANDRIA VA F/G 19/1
PRELIMINARY PROBLEM DEFINITION STUDY OF 48 MUNITION-RELATED CHE--ETC(U)
APR 78 J F KITCHENS, W E HARWARD, D M LAUTER DAMD17-77-C-7057
UNCLASSIFIED ARC-49-5730-04 NL

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The gross annual discharge of total antimony and antimony compounds to U.S. waters in 1976 has been estimated at 444 tons (EPA, 1977). There are no reports in the literature of civilian discharge of antimony trisulfide to the environment.

F. Comparison of Civilian and Military Uses and Pollution

Antimony trisulfide is produced in the United States by several manufacturers. High purity antimony trisulfide is generally produced by reprocessing imported antimony trisulfide. Total production capacity is estimated to be 5-10 million lb/year. Antimony trisulfide is used in paint formulations and as a flame-proofing agent. This type of use leads to widespread entry into the environment.

Military use of antimony trisulfide is currently less than 10,000 lb/year, or 0.1% of the estimated civilian use. At full mobilization, the military use would represent about 0.4% of civilian use. Losses to the environment from military use would be less than 600 lb/year even at full mobilization. This amount is negligible compared to civilian pollution sources.

G. Toxicological and Environmental Hazards

1. Toxicity to Mammals

Antimony compounds in general have been found to have a low acute and chronic toxicity to mammals. The LDLo for intraperitoneal injection of antimony trisulfide is 1000 mg/kg for rats (NIOSH, 1977). Gross *et al.* (1955) tested the oral toxicity of antimony trioxide on rats. No ill effects were found after oral administration of a single 16 g/kg dose.

The results of chronic inhalation toxicity of antimony trisulfide to mammals are presented in Table III-3. The most consistent effects were damage to heart tissue. Rats fed 2% antimony trioxide for 34 weeks gained weight at a slower rate than controls (Gross *et al.*, 1955). Schroeder *et al.* (1968 and 1970) exposed mice and rats to 5 ppm of antimony in their drinking water for their lifetimes. They found that this concentration reduced the life span of the animals.

No evidence of carcinogenicity was found in white Swiss mice given 1 µg/ml antimony potassium tartrate in their drinking water over a life span (Kanisawa and Schroeder, 1969). Some impairment of reproductive functions was observed in rats exposed to 250 mg/m^3 antimony trioxide dust for 2 months (Belyaeva, 1967).

Felicetti *et al.* 1974) studied the retention of trivalent aerosols in hamsters. They observed that 65% of the antimony was present after one day and estimated a biological half-life of 16 days. Erusalimskii and Suspa (1972) found that 5 mg of metallic antimony and 4 mg of 3,4-benzopyrene given intratrachially to rats potentiated benzopyrene carcinogenicity in the rat lungs.

Table III-3. Inhalation Toxicity of Antimony Trisulfide.

Animal	Dose mg/m^3	Duration	Effects	Reference
Rats Male Wistar	3.07	6 weeks 5 days/week 7 hours/day	ECG changes, some dilated hearts	Brieger *et al.* 1954
Dog	5.32	"	Slight ECG changes some swelling of myocardial fibers	"
Rabbit	5.60	"	Dilated heart, swelling myocardial fibers, slight ECG changes	"
Rabbit	27.8	5 days 7 hours/day	ECG changes, some parenchymatous changes of myocardium, slight degeneration of liver and kidney	"

The effects of antimony exposure on workers has been recently reviewed (Little, Inc., 1976). Symptoms of antimony intoxication include irritation and eczematous eruption of the skin, inflammation of mucous membranes, metallic-taste and stomatitis, gastrointestinal upset and various nervous complaints (OSHA, 1972).

2. Aquatic Toxicity

The EPA (1971) found antimony levels in drinking water samples ranging from <2 ppb to 100 ppb. Maxfield *et al.* (1974) determined antimony levels in the sediment below a mining and smelting operation. The levels ranged from 270-900 ppm. Background levels of antimony in the sediment are in the 1 ppm range.

The acute toxicity of several antimony compounds to aquatic organisms are presented in Table III-4. Their toxic levels are in the 10-20 ppm range. Bentley *et al.* (1975) tested the toxicity of a priming mixture FA956, which contains 15% antimony trisulfide. They found that this mixture had a 48 hour LC50 of 29 ppm to the *Daphnia magna*. Bringman and Kuhn (1959) observed that 9 ppm of antimony reduced the movements of *Daphnia magna*. Hildebrand *et al.* (1976) found that antimony was not a bioaccumulation threat in fish.

3. Toxicity to Microorganisms

Antimony has been found to have some inhibitory effect on bacteria. Diantimony tartrate and potassium antimony tartrate concentrations of 4.244×10^{-6} M/ml and 19.510×10^{-6} M/ml, respectively, have been shown to inhibit RNA and DNA synthesis in *Escherichia coli* B (Khafagy and El-Hawary, 1974). However, Richtarik *et al.* (1965) found that .125 ppm of antimony thioglycollamide did not affect the growth of five strains of *Staphylococcus aureus*. Also, Nishioka (1975) found that antimony chloride did not produce mutagens in *Bacillus subtillis*.

4. Phytotoxicity

The only phytotoxic information reviewed on antimony sulfide was a section in the National Academy of Sciences *Water Quality Criteria* 1972 citing Bringmann and Kuhn (1959) as reporting that antimony at 3.5 mg/l hindered the cellular division of green algae.

5. Availability of Literature for Phase II

There is a significant amount of toxicological literature on antimony trisulfide and antimony compounds. Most of this literature pertains to studies on worker exposure. Several aquatic and environmental studies on antimony compounds have been reported. Thus, there is sufficient available literature for a Phase II detailed toxicological and environmental study.

Table III-4. Acute Toxicity of Antimony to Aquatic Organisms.

Species	Compound	Water Hardness	Level in ppm	Effect	Reference
Fathead minnow (*Pimephales promelas*)	$SbCl_3$	Hard	17	LC50 96 hour	Tarzwell & Henderson, 1960
" "	"	Soft	9	"	" "
" "	Sb_2S_3	--	0.5	No effect	Kenison, 1975
Daphnia magna	Sb_2S_3 (15%)	Soft	29	LC50 48 hour	Bentley *et al.*, 1975
Rainbow trout	$SbCl_3$	Hard	5	No effect	Applegate *et al.*, 1957
Bluegill	"	Hard	5	No effect	"
Squawfish (*Ptychocheilus oregonensis*)	"	Soft	10	No effect	MacPhee and Ruelle, 1969
Chinook Salmon (*Oncorhynchus tshawytscha*)	"	Soft	10	No effect	" "
Coho Salmon (*O. kisutch*)	"	Soft	10	No effect	" "

H. Regulations and Standards

1. Human Exposure Standards

The OSHA standard for antimony in air is 0.5 mg(Sb)/m^3 (NIOSH, 1977). American Conference of Governmental Industrial Hygienists (1971) also lists this value as the accepted threshold workroom air (TWA) limit.

2. DOT Labeling Requirements

Antimony trisulfide is categorized ORM-A by DOT. No label is required for this material by DOT.

I. Conclusions and Recommendations

Military use of antimony trisulfide represents less than 0.5% of civilian use, even at full mobilization. Losses to the environment from military use are negligible compared to civilian pollution sources.

Antimony trisulfide occurs widely in nature. It is not a highly toxic compound to mammals, aquatic organisms, microorganisms or plants.

Because of the low military use of this chemical and the relatively low toxicity, further studies on the environmental or toxicological hazards of this compound by the Army should be a low priority.

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PRELIMINARY PROBLEM DEFINITION STUDY OF 48 MUNITIONS-RELATED CHEMICALS

VOLUME IV PRIMER AND TRACER RELATED CHEMICALS

POTASSIUM CHLORATE

FINAL REPORT

J. F. Kitchens
W. E. Harward III
D. M. Lauter
R. S. Wentsel
R. S. Valentine

April 1978

Supported by:

U. S. ARMY MEDICAL RESEARCH AND DEVELOPMENT COMMAND
Fort Detrick, Frederick, Maryland 21701

Contract No. DAMD17-77-C-7057

COTR: Clarence Wade, Ph.D.

ATLANTIC RESEARCH CORPORATION
Alexandria, Virginia 22314

Approved for Public Release
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The findings of this report are not to be construed as an official Department of the Army position unless so designated by other authorized documents.

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SUMMARY

Potassium chlorate is widely used in the civilian community in the manufacture of matches. The Army's use of this salt is mainly in the production of smokes and pyrotechnics at Pine Bluff Arsenal. The current military use of potassium chlorate represents only 0.7 to 1.4% of the estimated United States civilian production capacity. This percentage would increase to 6% at full mobilization production rates. Discharges of potassium chlorate into the Arkansas River are ~173 to 346 lb/month. This discharge should stop when the new waste water treatment facility becomes operational in 1979.

The toxicity of potassium chlorate to mammals is relatively low. However, some teratogenic effects have been observed. Chlorates are toxic to many microorganisms. Chlorates are toxic to plants in low concentrations as evidenced by the use of sodium chlorate as a herbicide. The toxicity of potassium chlorate to fish is not well established.

Based on the information evaluated during this study, it is recommended that potassium chlorate be included in the Phase II detailed toxicological and environmental evaluations.

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FOREWORD

This report details the results of a preliminary problem definition study on potassium chlorate. The purpose of this study was to determine the Army's responsibility for conducting further research on potassium chlorate in order to determine its toxicological and environmental hazards so that effluent standards can be recommended. In order to determine the Army's responsibility for further work on potassium chlorate, the military and civilian usage and pollution of this chemical were evaluated. In addition, a preliminary overview of toxicological and environmental hazards was conducted.

Potassium chlorate was only one of 48 chemicals evaluated under Phase IA of contract No. DAMD17-77-C-7057. These chemicals are grouped in four categories

- explosives related chemicals
- propellant related chemicals
- pyrotechnics
- primers and tracers

Each category is a major report. Section I of each report is an overview of the military processes which use each chemical and the pollution resulting from the use of these chemicals. The problem definition study reports on each chemical are separable sections of these four reports.

In addition, a general methodology report was also prepared. This report describes the search strategy and evaluation methodology utilized for this study.

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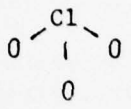
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IV. POTASSIUM CHLORATE

A. Alternate Names

Potassium chlorate is an ionic salt of the composition $ClKO_3$ and formula weight of 122.55 g/mole. The chlorate anion is pyramidal with the chlorine atom at the apex.



Pertinent alternate names for potassium chlorate are listed below:

CAS Registry No.:	3811-04-9
CA Name (8CI):	Chloric acid, potassium salt
Wiswesser Line Notation:	KA-02-Q
Synonyms:	Berthollet salt; Berthollet's salt; Fekabit; Potassium chlorate; Potassium oxymuriate; Potcrate.

B. Physical Properties

The physical properties of potassium chlorate are listed in Table IV-1.

Table IV-1. Physical Properties of Potassium Chlorate.*

Physical Form @ 20°C:	solid
Color and Crystalline Form:	colorless monoclinic
Taste:	cooling, saline
Crystal Density:	2.337 g/cm^3
M.P.:	368.4°C
B.P.:	400°C, decomposes - gives off oxygen
Refractive index:	1.409, 1.517, 1.524
Solubility:	water - 7.1 g/100g @ 20°C 57 g/100g @ 100°C alcohol - 0.83 g/100g soluble in alkali

*References: Windholz, 1976; Hawley, 1977; Sax, 1976; Hodgman, 1963.

C. Chemical Properties

1. General Reactions

Potassium chlorate is a strong oxidizing agent. At 380°C it will oxidize ammonia to nitrate (Whaley, 1973).

$$3KClO_3 + 2NH_3 \longrightarrow 2KNO_3 + KCl + Cl_2 + 3H_2O$$

When potassium chlorate is rubbed or heated with reducing agents such as phosphorous, sulfur, charcoal, or sugars, oxidation occurs violently. This reaction is the basis for use of potassium chlorate in pyrotechnics and matches (Whaley, 1973).

Dissolved in strong acids, potassium chlorate forms chloric acid, a strong oxidizer. In high concentrations, disproportionation to perchloric acid and chlorine dioxide occurs (Downs and Adams, 1973).

$$3HClO_3 \longrightarrow HClO_4 + H_2O + 2ClO_2$$

Thermal decomposition of potassium chlorate may follow two routes. At moderate temperatures disproportionation occurs.

$$4KClO_3 \longrightarrow 3KClO_4 + KCl$$

Pyrolysis at higher temperatures involves direct loss of molecular oxygen (Whaley, 1973).

$$2KClO_3 \longrightarrow 2KCl + 3O_2$$

Catalysts such as manganese dioxide accelerate oxygen evolution.

2. Environmental Reactions

Potassium chlorate dissociates to potassium cations and ClO_3^- anions in water. The chlorate ion in neutral or alkaline environments does not exhibit oxidizing ability (Kirk and Othmer, 1964). In acid solution a strong oxidizer, chloric acid, is formed.

Photochemical studies of aqueous chlorate solutions have not been reported in the literature.

3. Sampling and Analysis

Potassium can be analyzed using flame photometry. Measurements are taken at a wavelength of 768 nm. Potassium levels down to 0.1 mg/l can be determined by this method. Sodium, calcium and magnesium may interfere with the analysis when their ratios to potassium are greater than 5, 10 and 100, respectively.

A second method for potassium analysis may be used for concentrations above 10 mg/l. Potassium precipitates with sodium cobaltinitrite to form dipotassium sodium cobaltinitrite. The dipotassium sodium cobaltinitrite is oxidized with a known amount of $K_2Cr_2O_7$ in sulfuric acid. The remaining dichromate is determined colorimetrically and the potassium calculated from the difference (Franson, 1975).

Chlorate is determined by reduction with ferrous sulfate. The sample to be determined is added to a strong acid solution. A measured excess of $FeSO_4$ is added and partially oxidized. The remaining Fe(II) is determined titrametrically with a standardized permanganate or dichromate solution. Chlorate is calculated from the quantity of ferrous sulfate oxidized.

Chlorate may also be determined by quantitative reduction to chloride ion and analyzing for chloride (Kirk and Othmer, 1964).

D. Uses in Army Munitions

1. Purposes

Potassium chlorate is used as an oxidizer in primer and pyrotechnic formulations. This chemical is also used to impart a purple-red color to burning compositions. Some compositions specifying potassium chlorate are listed below:

	% Potassium Chlorate in Forumlation
White smoke	8±1
Green smokes	27-32
Red smokes	26-32.1
Yellow smokes	20-31
Violet smokes	22.2-25
Starter mixture VI	42.6±0.5
Fuel mixture VI	40.7±4
Match head mixtures	50.5-63.6
Riot mixtures	17-22
Incapacitating mixture I	23.0
Irritant mixture CS	18±2
CS pyro mixture	18±2

2. Quantities Used

a. Historical Use

Potassium chlorate was used at the rate of 95 lb/month at Lone Star AAP during June, 1974 (USAEHA, 1974). The end use is not known. LSAAP

is a Load, Assembly and Pack (LAP) facility, but does process some propellants and explosives as well as various primer and tracer chemicals.

The principal Army use of potassium chlorate has been at Pine Bluff Arsenal. During the 1965-1975 period, the following amounts of this chemical were purchased:

Year	Lb of Potassium Chlorate Purchased
1965	68,000
1966	471,000
1967	596,000
1968	287,000
1969	18,000
1970	178,000
1971	257,000
1972	168,000
1973	92,000
1974	48,000
1975	50,000

The average use rate during this period was 203,000 lb/year or about 17,000 lb/month.

b. Current Use

The 1978 production schedule for Pine Bluff Arsenal calls for production of smoke grenades, 105 mm smoke canisters and smoke markers. The approximate quantities of potassium chlorate required are listed below:

grenades	35,000 lb
canisters	20,000 lb
markers	153,000 lb
Total	208,000 lb

These items represent a current average use rate of 17,333 lb/month.

c. Use at Full Mobilization

The full mobilization use rate of potassium chlorate at Pine Bluff Arsenal is 160,000 lb/month. The maximum actual use rate in recent years was 49,667 lb/month during 1967, about 31% of the full mobilization use rate. Use of potassium chlorate by other Army facilities is considered negligible in comparison to these figures.

3. Documented or Speculated Occurrences in Air or Water

Aikman (1978) estimates that 1-2% of the potassium chlorate used at Pine Bluff Arsenal is lost as waste. Current losses of this chemical are estimated at 173 to 346 lb/month. Essentially all of this material is currently being discharged to the Arkansas River. However, PBA is installing a central waste water treatment facility which will reduce all chemical effluents to current acceptable levels. This plant will be operational in 1979.

E. Uses in the Civilian Community

1. Production Methodology

Potassium chlorate is manufactured by a double decomposition reaction between sodium chlorate and potassium chloride.

$$NaClO_3 + KCl \longrightarrow KClO_3 + NaCl$$

Sodium chlorate is formed by electrolysis of a sodium chloride solution in a cell without diaphragms.

$$NaCl + 3H_2O + 6Faraday \longrightarrow NaClO_3 + 3H_2$$

Potassium chlorate may be produced directly by a similar electrolysis of potassium chloride. The higher solubility of sodium chlorate makes primary production of the sodium salt followed by reaction with KCl more desirable (Kirk and Othmer, 1964).

2. Manufacturers, Production and Capacities

The three potassium chlorate manufacturers in the U. S. are

Mallinckrodt, Inc. Indust. Chems. Div.	Jersey City, NJ
Occidental Petroleum Corp. Hooker Chem. Corp., subsid. Hooker Chems. and Plastics Corp., subsid. Electrochemical and Specialty Chems. Div.	Niagara Falls, NY
Pennwalt Corp. Inorganic Chem. Div.	Portland, OR

The Pennwalt plant has a capacity between 10 and 12 million pounds per year. Mallinckrodt's and Occidental's capacities are unavailable. However, they are probably in the 10 to 12 million pound per year range. Thus an estimate of the total United States $KClO_3$ production capacity is 30 million pounds per year. The Hummel Chemical Co. imports $KClO_3$ from France for processing to military specifications.

3. Usages

Potassium chlorate is used primarily in the manufacture of matches. It is also used in pyrotechnics, in pharmaceutical preparations and for heating pads (Kirk and Othmer, 1964). Sodium chlorate cannot be substituted for potassium chlorate in these products due to its hygroscopic properties.

In 1964, the match industry consumed 25 million pounds of potassium chlorate; military and civilian pyrotechnic production together only accounted for 4 million pounds. Of this 4 million pounds used for pyrotechnic production, <0.5 million pounds were used by the Military (Kirk and Othmer, 1964).

4. Future Trends

No major changes are expected in the civilian uses of potassium chlorate.

5. Documented or Speculated Occurrences in the Environment

No reports of environmental contamination from $KClO_3$ were found in the recent literature. Production wastes are expected to contain NaCl, $NaClO_3$ and KCl and some $KClO_3$. The major environmental pollution of $KClO_3$ occurs from match manufacture and disposal of unused matches. The amount of $KClO_3$ entering the environment from these sources is unknown. However, it is estimated that ~1% of the 30 million pound capacity or 300,000 pounds of $KClO_3$ are lost to the environment each year.

F. Comparison of Civilian and Military Uses and Pollution

The major military use of $KClO_3$ is as an oxidizer in pyrotechnic smoke mixtures. At full mobilization, ~1.92 million pounds per year of $KClO_3$ would be needed by the Army. This need represents ~6% of the estimated United States $KClO_3$ capacity of 30 million pound per year. At smoke and pyrotechnic current production rates, only 208,000 lb of $KClO_3$ are used per year or 1% of the estimated United States capacity. Current Army discharges at Pine Bluff Arsenal represents only 0.7 to 1.4% of the estimated discharges from civilian production and use.

G. Toxicological and Environmental Hazards

1. Mammalian Toxicity

As shown in Table IV-2, the toxicity of potassium chlorate to mammals is relatively low. Potassium chlorate itself is not toxic to animals at levels of 1 g/kg, but a mixture of sodium chlorate and potassium chlorate was lethal to cats at levels between 1.35-1.94 g/kg. Ross (1925) exposed pregnant dogs to an oral dose of 0.5 g/kg of potassium chlorate. While no effects were observed in the dogs, the offspring had histological abnormalities indicating that potassium chlorate was transferred across the placenta.

Table IV-2. Toxicity of Potassium Chlorate to Mammals.

Species	Dose Level	Route	Duration	Effect	Reference
Rabbit	60-120 mg/kg/day	oral	6 weeks	none	Gajatto, 1947
Rabbit	185-738 mg/kg/day	oral	6 weeks	none	"
Rabbit	1 g/kg/day	oral	4 weeks	none	Kleiner & Dotli, 1940
Rat	1 g/kg/day	oral	4 weeks	none	Gajatto, 1947
Cat	0.5 g/kg	oral	unstated	none	Lipschitz, 1932
Cat	1.35-1.94 g/mg		single dose	death	"

Potassium chlorate at one time was used as an anti-infective drug, however, overdoses were common. One man died 10 days after he consumed 10 grams of potassium chlorate (Cochrane and Smith, 1940). Another woman died after taking 6.5 grams of potassium chlorate over 6-10 weeks (Gordon and Brown, 1947). Symptoms of potassium chlorate poisoning include nausea, vomiting, abdominal pain, diarrhea; hypertension and bradycardia; cyanosis; hepatomegaly and jaundice; oliguria, anuria, hemoglobinuria; albumin, red blood cells and casts in a dark brown urine (Plunkett, 1976). The lethal dose for humans is estimated at 80 mg/kg for children and 140 to 420 mg/kg for adults (Rosenblatt *et al.*, 1975).

2. Aquatic Toxicity

Voinescu and Voinescu (1967) evaluated the toxicity of a saturated solution of potassium chlorate (71,000 mg/l) to six aquatic organisms:

- *Cyprinus carpio*
- *Lepomis gibbosus*
- *Carassius carassius*
- *C. auratus gibelio*
- *Scardinius erythrophthalmus*
- *Rutilus rutilus carpathorossicus*

This concentration was found to be lethal for all organisms tested.

3. Toxicity to Microorganisms

Chlorate is toxic to certain fungi and algae (Cove, 1972; Goksyr, 1951; Solomonson and Vennesland, 1972). The basis for chlorate toxicity is the reduction to toxic chlorite. Chlorate reduction occurs when organisms are utilizing nitrate as a source for nitrogen. Nitrate ions induce the formation of nitrate reductase. Chlorates appear to be competitive with nitrates as a substrate for this enzyme which will also reduce chlorate to chlorite (Tromballa and Broda, 1971; Fumimoto and Nakamura, 1971).

Coliform bacteria such as *E. coli* are more susceptible to chlorate toxicity than the true lactic acid bacteria. The addition of 0.002% potassium chlorate to raw milk selectively inhibits coliform bacterial growth. One per cent solutions of chlorate are tolerated by numerous bacteria and fungi (Aslander, 1931). Bryan and Rohlich (1954) reported that 1000 ppm chlorate in sewage was not toxic to the over-all microbial flow and that chlorate served as an oxygen source to the microbes. The green alga, *Chlorella fusea*, reduces chlorates to non-toxic chloride (Tromballa and Broda, 1971).

4. Phytotoxicity

Sensitivity of plants to chlorate depends primarily upon the species of plant (Stone and Smith, 1954; Hurd-Karrer, 1940; Fron, 1934; Hanada, 1955); nitrates, arsenites, and borates in soil (Crafts and Cleary, 1936; Helgeson, 1940), type of soil (Crafts and Cleary, 1936; Crafts, 1939; Schwendiman, 1941); and concentration of chlorates (Stone and Smith, 1954; Jannson *et al.*, 1951;

Ito and Kuroski, 1957). Chlorate is absorbed through all plant surfaces and is a non-selective systemic poison which may be cumulative in plants until concentrations in cells are high enough to cause cellular death (Crafts, 1935a).

Chlorate may be moderately persistant in areas where leaching does not occur. Researchers have reported persistence from three to five years in an area treated with 800 lb/acre potassium chlorate (Sigler and Andrews, 1961). Loomis *et al.* (1933) showed that elevated temperatures or increased soil moisture hastens a decrease in chlorate phytotoxicity. Half the chlorate applied to an aerated soil was reduced in 5 months at 20°C while chlorate applied to a wet clay soil lacking sub-soil oxygen underwent only 8% reduction (Tovborg-Jensen and Larsen, 1957).

Leaching of soils to lower the chlorate ion concentration to below phytotoxic levels was demonstrated by Crafts (1935b) using 40 cm of water for a clay loam and a fine sandy loam soil. Ninety-five percent of the applied chlorate was removed by 20 cm of water or sandy soil, 40 cm on humus soil, and 30-70 cm on clay soils (Tovborg-Jensen and Larsen, 1957).

In a survey of 80 California soils, higher chlorate toxicities generally occurred in coarser soils and lower toxicities in alluvial soils (Crafts, 1939; Crafts, 1935a). Sublethal concentrations of chlorate in plants produce a characteristic mottling with chlorosis and over-all stunted growth (Owen, 1937; Crafts, 1935a; Owen, 1934. When the concentration of chlorate is lowered, plants may recover from sublethal amounts with no permanent effects (Crafts, 1935a). Toxic concentrations range from 6 ppm for witch weed (Timson, 1933) to approximately 1000 ppm for certain grasses and broadleaf plants (Isensee *et al.*, 1973). Many plants have stunted growth with treatment of 10 ppm sodium chlorate (Stone and Smith, 1954).

5. Availability of Literature for Phase II

The toxicological and environmental literature on potassium chlorate is limited. However, most of the hazards properties of this compound result from the chlorate anion. Sufficient information on sodium chlorate is available to assess the hazards of potassium chlorate. Since sodium chlorate is used as a herbicide, significant information will be available from the United States Department of Agriculture.

H. Regulations and Standards

There are no EPA or OSHA standards specific for potassium chlorate. The Department of Transportation requires that containers of potassium chlorate be labeled as an oxidizer (Federal Register, 1976).

I. Conclusions and Recommendations

The goal of this problem definition study was to determine the Army's responsibility for conducting further research on the environmental and toxicological hazards of potassium chlorate. The military use of potassium chlorate is limited mainly to pyrotechnic production at Pine Bluff Arsenal. At current

production rates the Army uses only 1% of the estimated civilian production capacity. This percentage will increase to ~6% at full mobilization production. Since the aqueous effluents at Pine Bluff Arsenal are not currently treated, discharges of potassium chlorate could be as high as 3200 lb/month at full mobilization. This problem should be alleviated when the new waste water treatment plant becomes operational in 1979.

The toxicity of potassium chlorate to mammals is relatively low. However, there is some evidence of potential teratogenic effects. Chlorates are toxic to some microorganisms and plants. The toxicity of these fish is not well defined.

Based on the data evaluated during this study, the following conclusions can be drawn:

- potassium chlorate is not a military unique chemical; however, it appears to be a military problem chemical
- further information on the aquatic toxicity and environmental fate of this compound is needed
- waste water sampling at Pine Bluff Arsenal to further detect potassium chlorate discharges are needed
- the ability of the planned pollution abatement facilities at Pine Bluff Arsenal to remove potassium chlorate from the waste waters needs to be assessed.

Therefore, it is recommended that potassium chlorate be included in the Phase II detailed toxicological and environmental evaluation. It is also recommended that sampling be undertaken to determine the amount of chlorate currently entering the Arkansas River.

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AD

PRELIMINARY PROBLEM DEFINITION STUDY OF 48 MUNITIONS-RELATED CHEMICALS

VOLUME IV PRIMER AND TRACER RELATED CHEMICALS

LEAD THIOCYANATE

FINAL REPORT

J. F. Kitchens
W. E. Harward III
D. M. Lauter
R. S. Wentsel
R. S. Valentine

April 1978

Supported by:

U. S. ARMY MEDICAL RESEARCH AND DEVELOPMENT COMMAND
Fort Detrick, Frederick, Maryland 21701

Contract No. DAMD17-77-C-7057

COTR: Clarence Wade, Ph.D.

ATLANTIC RESEARCH CORPORATION
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Approved for Public Release
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The findings of this report are not to be construed as an official Department of the Army position unless so designated by other authorized documents.

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SUMMARY

Lead thiocyanate is a fuel used in detonators, primers and igniters. The only Army user of lead thiocyanate is Lone Star AAP. The current use rate is less than 500 lb/yr. At full mobilization, about 5000-7000 lb/yr of lead thiocyanate would be required by the Army. The losses of lead thiocyanate from loading operations are less than 1 lb/month currently and would be in the range of 4-12 lb/month at full mobilization.

Lead thiocyanate has very limited usage in the civilian community. No reports of pollution by this material have been found.

Literature data indicate that lead thiocyanate is moderately toxic. Long term exposure will result in chronic lead poisoning. No specific data on the toxicity of lead thiocyanate to aquatic organisms or microorganisms was found. Similarly, phytotoxicity data from other lead compounds must be used to infer the effects of lead thiocyanate.

While the amount of lead thiocyanate used by the Army is small, the Army is the primary user of this chemical. Further study of the toxicological and environmental hazards of lead thiocyanate are recommended as part of an overall evaluation of all lead compounds used or produced by the Army.

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FOREWORD

This report details the results of a preliminary problem definition study on lead thiocyanate. The purpose of this study was to determine the Army's responsibility for conducting further research on lead thiocyanate in order to determine its toxicological and environmental hazards so that effluent standards can be recommended. In order to determine the Army's responsibility for further work on lead thiocyanate, the military and civilian usage and pollution of this chemical were evaluated. In addition, a preliminary overview of toxicological and environmental hazards was conducted.

Lead thiocyanate was only one of 48 chemicals evaluated under Phase IA of contract No. DAMD17-77-C-7057. These chemicals are grouped in four categories

- explosives related chemicals
- propellant related chemicals
- pyrotechnics
- primers and tracers

Each category is a major report. Section I of each report is an overview of the military processes which use each chemical and the pollution resulting from the use of these chemicals. The problem definition study reports on each chemical are separable sections of these four reports.

In addition a general methodology report was also prepared. This report describes the search strategy and evaluation methodology utilized for this study.

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V. LEAD THIOCYANATE

A. Alternate Names

Lead thiocyanate is the lead salt of thiocyanic acid. This salt has a molecular formula of $C_2N_2PbS_2$ and a molecular weight of 323.38 g/mole. The structural formula of lead thiocyanate is

N≡C-S-Pb-S-C≡N

The bonding is through the sulfur and the thiocyanate ligand is believed to be linear, although this fact has not been inclusively proven (Cotton and Wilkinson, 1976). The pertinent alternate names for lead thiocyanate are listed below:

CAS Registry No.:	592-87-0
CA Name (8CI):	Thiocyanic acid, lead (2+) salt
Wiswesser Line Notation:	
Synonyms:	Lead dithiocyanate; Lead isothiocyanate; Lead sulfocyanate; Lead thiocyanate

B. Physical Properties

The physical properties of lead thiocyanate are listed in Table V-1.

Table V-1. Physical Properties of Lead Thiocyanate.*

Physical Form @ 20°C:	solid
Color:	white to light yellow crystalline powder
Odor:	odorless
M.P.:	190°C decomposes
Crystal Density:	3.82
Solubility:	water: ∿0.5 g/100 g - cold ∿2.0 g/100 g @ 100°C with decomposition soluble in nitric acid, alkali, hydroxide and thiocyanate solutions

*References: Hawley, 1977; Windholz, 1976; Weast, 1970.

C. Chemical Properties

1. General Reactions

Lead thiocyanate reacts with hydrogen sulfide to form lead sulfide and thiocyanic acid (Schmidt and Siebert, 1973).

$$Pb(SCN)_2 + H_2S \longrightarrow PbS + 2HSCN$$

Thiocyanic acid is a strong acid which is completely dissociated in water.

Lead thiocyanate decomposes at temperatures around 190°C.

2. Environmental Reactions

Lead thiocyanate is slightly soluble in water to a level of 1 part in 200. It dissociates to lead(II) and thiocyanate ions. The thiocyanate ion can form highly colored coordination complexes with aqueous transition metals. Thiocyanate in water may also react with aqueous chlorine to form the highly toxic compound cyanogen chloride (Franson, 1975).

Photochemical studies have not been reported.

3. Sampling and Analysis

Lead thiocyanate may be determined by analysis for either lead(II) or thiocyanate anion.

Total lead may be determined by atomic absorption spectrophotometry, anodic dissolution polarography, gravimetrically as precipitated lead(II) sulfate, or colorimetrically a lead(II) dithizonate (Franson, 1975; Abel, 1973).

Dissolved thiocyanate may be determined in the range of 1 to 10 mg/l by treating the sample with Fe(III). Ferric ion complexes with the thiocyanate to form an intense red color which may be determined colormetrically (Franson, 1975).

D. Uses in Army Munitions

1. Purposes

Lead thiocyanate is a fuel used in detonators, primers and igniters. The only known Army user is Lone Star AAP (LSAAP).

2. Quantities Used

During the month of June, 1974, LSAAP used lead thiocyanate at the rate of 46 lb/month. Current usage rates are not known but believed to be less than the 1974 use rate (Ryan, 1978). Currently, lead thiocyanate is used to produce the M86 detonator, M26 primer and the M59 and M63 igniters.

At full mobilization, it is estimated that 400-600 lb/month of lead thiocyanate would be used in the production of these items.

3. Documented or Speculated Occurrences in Air or Water

Actual losses of lead thiocyanate have not been measured. Typically, 1-2% of the primer materials handled are lost to waste streams (Alexander, 1978). Current losses of lead thiocyanate at LSAAP are estimated to be less than 1 lb/month. At full mobilization, the loss would be in the range of 4-12 lb/month.

E. Uses in the Civilian Community

1. Production Methodology

Details of the production process are unavailable. Lead thiocyanate is manufactured by a straight-forward precipitation from a solution of a soluble lead salt and thiocyanate source. Lead nitrate and ammonium thiocyanate can be used (Kirk and Othmer, 1967).

$$Pb(NO_3)_2 + 2NH_4SCN \longrightarrow Pb(SCN)_2 + NH_4NO_3$$

The precipitated $Pb(SCN)_2$ is filtered and impurities removed.

2. Manufacturers, Production and Capacity

There are three manufacturers of lead thiocyanate in the U.S. They are listed in Table V-2.

Table V-2. Manufacturers of Lead Thiocyanate.

Barium and Chemicals, Inc.	Steubenville, Ohio
City Chemical Corp.	Jersey City, New Jersey
Hummel Chemical Co.	South Plainfield, New York

All three manufacturers process the lead thiocyanate to military specifications (communications with manufacturers).

3. Usages

Lead thiocyanate has very limited uses in the civilian community. It can be used in safety matches and as a source of cyanogen in reverse dyeing with aniline black (Kirk and Othmer, 1967).

4. Future Trends

No changes in the levels of civilian usage of lead thiocyanate are expected.

5. Documented or Speculated Occurrences in the Environment

We found no reports of lead thiocyanate pollution in the literature.

F. Comparison of Civilian and Military Use and Pollution

Lead thiocyanate is a low volume chemical in both the civilian and military sectors. Estimated United States production capacity is <100,000 lb/year. Military usage of the chemical is confined to Lone Star AAP and is ∿600 lb/year. At full mobilization production rates, this usage could increase to 48,000 to 72,000 lb/year. Thus at full mobilization, the Army would be the major user of lead thiocyanate.

Pollution resulting from the civilian manufacture and use of lead thiocyanate is not known. Wastes of lead thiocyanate and military production of primer and ignitors are estimated at 4-12 lb/month at full mobilization. These wastes are pumped into leaching ponds or treated to remove lead before discharge. Some thiocyanate could enter the environment from these operations, but the amount is expected to be small.

G. Toxicological and Environmental Hazards

1. Toxicity to Mammals

From the data available, lead thiocyanate appears to be moderately toxic. Buck and Kumro (1930) intraperitoneally injected rats with 70-100 mg/kg of lead thiocyanate. No deaths occurred. They did note acute tubular nephritis in the kidneys. Testing lead thiocyanate subcutaneously, Buck and Kumro (1930) found a toxic threshold near 150 mg/kg. However, at this level sublethal effects such as local necrosis and blood changes were noted. The EPA (1976) stated that thiocyanate ions were a detoxified form of cyanide produced by the enzyme rhodanese. Thiocyanate was observed to be slowly eliminated in the urine.

Long term exposure to lead thiocyanate will be accompanied by chronic lead poisoning. The many symptoms associated with chronic lead poisoning are listed in Table V-3. The toxicity of lead compounds is influenced by several factors:

- solubility of the compound in body fluids
- quantity of lead ingested, inhaled or absorbed
- quantity present in the circulation at one time
- length of time the lead is in contact with body fluids

Lead intake over that which can be eliminated (∿0.28 mg/kg) can be stored and accumulated by the body. It is believed that the stored lead is non-toxic. However, stored lead can be later released into the circulatory system and exhibit toxic reactions.

The biochemical mode of action of lead is to inhibit the activity of erythrocyte delta-aminolevulnic acid dehydratase. Thus heme synthesis is

Table V-3. Symptoms of Chronic Lead Poisoning
(Plunkett, 1976)

GENERAL:

Pallor · Weakness · Loss of weight · Lassitude · Malnutrition

GASTROINTESTINAL:

Metallic taste · Increased salivation · Burton's lead line on gums
Pyorrhea · Anorexia, nausea, vomiting · Constipation · Abdominal colic and tenderness

GENITOURINARY:

Nocturia · Albuminuria and hematuria · Increased bilirubinuria · Secondary hyperuricemia · Azotemia

NEUROMUSCLAR:

Numbness and tingling of extremities and associated sensory disturbance
Extensor weakness of wrists and ankles; brachial palsy has also been described
Loss of muscle tone · Tremor · Increased deep-tendon reflexes · Muscular cramps and aching · Arthralgia · Muscular atrophy

CENTRAL NERVOUS SYSTEM:

Visual disturbances · Headache · Dizziness · Nervousness or depression
Insomnia · Mental confusion and delirium · Convulsions · Coma

Encephalopathy may be acute or chronic; acute usually associated with blood levels above 120 µg Pb

Retinal hemorrhages and optic neuritis; gray stippling of lead pigment about the optic disc has also been reported

HEMOTOPOIETIC:

Erythrocyte stippling
Hypochromic normocytic anemia
Increased peripheral reticulocytes

impaired, and the life span of the red blood cell is shortened. An increase in urinary excretion of delta-aminolevulinic acid is also observed (EPA, 1976).

Epidemiological studies have shown that lead has an injurious effect on germ cells of both sexes. Development of the fetus is impaired often to the point of miscarriages. Those infants born to women lead workers are underweight and have a high incidence of nervous disorders (Lambou and Lim, 1970). No evidence has been found to link lead with human cancer (EPA, 1976). However, renal cancer in rats has been observed with >1% lead in the diet (EPA, 1976).

2. Aquatic Toxicity

No information was retrieved on the aquatic toxicity of lead thiocyanate. Thiocyanate is the detoxification product of cyanide (EPA, 1976). Thus, the toxicity of this anion is presumably low.

While specific data on the aquatic toxicity of lead thiocyanate is not available, the toxicity of lead to the aquatic environment is well documented (Lambou and Lim, 1970). Available bioassay data indicate that lead is more toxic in soft water (<50 ppm $CaCO_3$) than in hard water systems. The difference in toxicity is due to the availability of ionic lead in soft water systems.

3. Toxicity to Invertebrates

The toxicity of the soluble lead chloride to *Daphnia magna* was studied by Biesinger and Christensen (1972). They found an LC50 of 300 ppb and reproductive impairment at 30 ppb.

4. Toxicity to Microorganisms

No specific data on the toxicity of lead thiocyanate to microorganisms was retrieved. In general lead is toxic to aerobic bacteria at a concentration of 1 ppm and to flagellates and infusoria at a concentration of 0.5 ppm (Lambou and Lim, 1970). The decomposition of organic materials by bacteria is inhibited at lead concentrations of 0.1 to 0.5 ppm (Lambou and Lim, 1970).

Results of experimental work by Tornabene and Edwards (1972) indicate that microbial systems are capable of abstracting substantial quantities of lead from sources containing insoluble inorganic lead-salt precipitates. The viability of bacterial cells (*Micrococcus luteus* ATCC 533) exposed to a medium containing lead for one complete growth cycle (48 hrs.) was not seriously affected and virtually all of the lead taken up by the cells was immobilized in the cellular membrane.

The occurrence of lead in the membranes of bacterial cells does not have a significant effect until the cells of more sensitive strains have been exposed to lead over an extended period. Tornabene *et al.* (1974) reported

that lead impregnated cells were affected to the extent that an osmotically instable condition existed causing changes in the cytoplasmic membrane These changes resulted in cellular leakage and protoplast instabilities. Apparently, the lead is bound to complex lipid mixtures in the cell membrane.

5. Phytotoxicity

No phytotoxicity information on lead thiocyanate was encountered. However, phytotoxic data on other lead compounds was obtained and may be indirectly related.

The pattern of lead uptake by plants has been rarely studied and little can be concluded about the mechanism involved. The uptake of lead was reported constant with increasing levels of soil lead, until a certain point is reached when uptake becomes unrestricted and rises abruptly (Nicolls *et al.*, 1965). Only soluble lead salts and ionic lead are available to plant roots. The uptake of lead by ryegrass grown in a solution containing lead is shown in Table V-4 (Hepple, 1972). The total content of lead in roots plus shoots of perennial ryegrass increases with increasing levels in the soil. The roots take up lead readily but pass on only a small proportion to the shoots. Thus, the roots act as a barrier which restricts the movement of lead from the soil through the plant to growing animals. A similar pattern was found by Wallace *et al.* (1971) in their studies on the uptake of lead by bush-bean plants. During winter months when plant growth is low, a considerable increase in the lead content of the ryegrass shoots was observed (Hepple, 1972).

Corn was grown in the field where lead acetate had been soil-applied at eight rates ranging from 0 to 3,200 kg lead/ha. No changes in emergence, plant height, grain yield, color maturity or other growth differences were observed during the 2-year study (Baumhardt and Welch, 1972).

Five crops (cauliflower, tomatoes, cabbage, strawberries and Valencia oranges) were analyzed for their lead content by Schuck and Locke (1970). These plants revealed little inclinations to absorb lead via their root system (Schuck and Locke, 1970).

6. Availability of Literature for Phase II

Literature on the toxicological and environmental hazards of lead in general is plentiful. However, studies specifically on lead thiocyanate are few. Thus most of the toxicological and environmental properties of lead thiocyanate will have to be inferred from the studies of other lead and other thiocyanate compounds.

H. Regulations and Standards

1. Air and Water Regulations

There are no air and water standards specific for lead thiocyanate. Criteria have been set for lead in potable water and effluents, however (EPA,

1976). For potable water, the lead content cannot exceed 50 µg/1. Due to the variability of lead solubility and toxicity in different waters, the following criteria have been set for effluents (using the receiving water as a diluent):

- 0.01 times the 96-hour LC50 value expressed as dissolved lead for the most sensitive species

This criteria requires that the 96-hour LC50 tests be performed with the actual water samples and the most sensitive species in the local ecosystem.

2. Human Exposure Standards

No specific standards for lead thiocyanate have been set for occupational exposure to this chemical. The recommended TLV for worker protection is 150 µgPb/m^3 (American Conference of Government Industrial Hygienists, 1977).

I. Conclusions and Recommendations

The goal of this problem definition study is to determine the Army's responsibility for conducting further studies on the toxicological and environmental hazards of lead thiocyanate. The results of this study indicate that lead thiocyanate should be further studied by the Army. However, it should be a low priority chemical for further study. In addition, it is recommended that all lead compounds be included in this study in order to determine the effects of the total lead effluent on the environment. These recommendations are based on the following conclusions from the current study.

- At current production rates, the amount of lead thiocyanate used by the Army is small; however, during wartime the Army is the major user of lead thiocyanate.

- The toxicity of this compound is mainly that of the lead cation

- The effect of lead on the aquatic environment near Lone Star is from the total lead content of the effluent and is independent of the original lead compound.

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AD

PRELIMINARY PROBLEM DEFINITION STUDY OF 48 MUNITIONS-RELATED CHEMICALS

VOLUME IV PRIMER AND TRACER RELATED CHEMICALS

CALCIUM SILICIDE

FINAL REPORT

J. F. Kitchens
W. E. Harward III
D. M. Lauter
R. S. Wentsel
R. S. Valentine

April 1978

Supported by:

U. S. ARMY MEDICAL RESEARCH AND DEVELOPMENT COMMAND
Fort Detrick, Frederick, Maryland 21701

Contract No. DAMD17-77-C-7057

COTR: Clarence Wade, Ph.D.

ATLANTIC RESEARCH CORPORATION
Alexandria, Virginia 22314

Approved for Public Release
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SUMMARY

Calcium silicide is refined to military specification from calcium-silicon alloy for use at Lake City AAP. As refined, it has no civilian uses. Military purchase of calcium silicide are 2000-3000 lb/year at current production rates. At full mobilization ~14,000 lb/year of calcium silicide would be needed by the Army. The calcium-silicon alloys are used in the civilian community in the production of high grade steel.

Calcium silicide is readily hydrolyzed upon contact with moisture to calcium hydroxide, silicon dioxide and hydrogen. Thus, the toxicological and environmental hazards of calcium silicide are those of calcium hydroxide. Calcium hydroxide is added to the wastewater generated at Lake City AAP in order to remove metals. Any added amount of calcium hydroxide resulting from calcium silicide is negligible compared with the quantity used in the industrial wastewater treatment process.

In view of the limited use of calcium silicide and the widespread use of its hydrolysis product, calcium hydroxide, it is concluded that calcium silicide as used by the Army does not represent an environmental hazard. Therefore, any further Army-sponsored studies on this compound should be a low priority.

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FOREWORD

This report details the results of a preliminary problem definition study on calcium silicide. The purpose of this study was to determine the Army's responsibility for conducting further research on calcium silicide in order to determine its toxicological and environmental hazards so that effluent standards can be recommended. In order to determine the Army's responsibility for further work on calcium silicide, the military and civilian usage and pollution of this chemical were evaluated. In addition, a preliminary overview of toxicological and environmental hazards was conducted.

Calcium silicide was only one of 48 chemicals evaluated under Phase IA of contract No. DAMD17-77-C-7057. These chemicals are grouped in four categories

- explosives related chemicals
- propellant related chemicals
- pyrotechnics
- primers and tracers

Each category is a major report. Section I of each report is an overview of the military processes which use each chemical and the pollution resulting from the use of these chemicals. The problem definition study reports on each chemical are separable sections of these four reports.

In addition a general methodology report was also prepared. This report describes the search strategy and evaluation methodology utilized for this study.

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VI. CALCIUM SILICIDE

A. Alternate Names

Calcium silicide is a flammable compound having a molecular formula of $CaSi_2$. This compound has a molecular weight of 96.25 g/mole. The following alternate names were found for calcium silicide:

CAS Registry No.:	12013-56-8
CA Name (9CI):	Calcium silicide ($CaSi_2$)

B. Physical Properties

Very little information was retrieved on the physical properties of calcium silicide. This solid has a specific gravity of 2.5 (Hawley, 1977). It is insoluble in cold water and decomposes in hot water. It is soluble in acids and alkalies with decomposition (Hawley, 1977).

C. Chemical Properties

1. General Reactions

When calcium silicide is heated with carbon it forms calcium carbide and carborundum (Berezhnoi, 1960).

$$CaSi_2 + C \xrightarrow{\Delta} CaC_2 + SiC$$

Heating in a nitrogen atmosphere yields calcium silicocyanide, calcium silicocyanamide, elemental silicon and small amounts of silicon and calcium nitrides (Berezhnoi, 1960).

$$CaSi_2 + N_2 \xrightarrow{\Delta} Ca(SiN)_2 + CaSiN_2 + Si + Si_3N_4 + Ca_3N_2$$

Calcium silicide reacts with HCl to form a yellow silicone and Si_2H_2. It is a potent reducing agent and reacts readily with fluorine and sulfur. Calcium silicide will react with aluminum at 1000°C (Berezhnoi, 1960).

$$CaSi_2 + Al \xrightarrow{1000°C} Ca_2Al_4Si_3$$

2. Environmental Reactions

Calcium silicide is unstable in water or moist air. It decomposes to calcium hydroxide, silicon dioxide and hydrogen gas (Berezhnoi, 1960).

$$CaSi_2 + 6H_2O \longrightarrow Ca(OH)_2 + 2SiO_2 + 5H_2$$

Calcium hydroxide readily absorbs carbon dioxide from the air to form the insoluble calcium carbonate.

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3. Sampling and Analysis

Calcium silicide in environmental samples will be in the form of calcium hydroxide and silicon dioxide. Analyses may be conducted for either Ca^{+2} or SiO_2.

Calcium may be determined using atomic absorption methods. Absorption is measured at a wavelength of 422.7 nm. The sensitivity limit is reportedly 70 µg Ca^{+2}/l for 1% absorption (Franson, 1975).

Calcium may also be determined by quantitative precipitation as calcium oxalate followed by titration with a standardized permanganate solution. Direct titration with the complexing agent EDTA in the presence of an indicator allows a rapid and simple determination of calcium (Franson, 1975).

Silicon dioxide can be measured gravimetrically. The sample is treated with acid, dried, and weighted. Following weighing, the sample is ignited to volatilize the silicon. The sample is reweighed and SiO_2 content calculated from the weight loss. This determination is reliable for water samples containing at least 20 mg SiO_2/l (Franson, 1975).

For concentrations below 25 mg SiO_2/l, colorimetric methods which possess greater sensitivity are used. Silicon dioxide is reacted with ammonium molybdate to form yellow molybdosilicic acid which is measured with a spectrophotometer. For determination of concentrations below 2 mg/l, the molybdosilicic acid is reduced further to heteropoly blue which is measured spectrophotometrically. The blue color is more intense than the yellow, allowing greater sensitivity (Franson, 1975).

D. Uses in Army Munitions

1. Purpose

Calcium silicide is used as a constituent of primer and tracer mixes. It has also been used in pyrotechnic mixes. This chemical serves as a fuel and imparts a yellow-red color to burning compositions. It is used in igniter compositions for tracer projectiles.

At Lake City AAP (LCAAP), calcium silicide is used in the following compositions:

	% Calcium Silicide in Formulation
Primer Mix 5061	7.5
Primer Mix FA874	15.5
Tracer Mix R-10E	5.55±0.5

This chemical is also used in Starter Mixture I, produced at Pine Bluff Arsenal. Calcium silicide comprises 33.2±4% of this mixture.

2. Quantities Used

a. Historical Use

LCAAP purchased 3,300 lb of calcium silicide in 1975, none in 1976 and 3,250 lb in 1977. The average use rate over these three years was 2,103 lb/year or 182 lb/month.

No calicum silicide has been used at Pine Bluff Arsenal in recent years. No significant future use is currently anticipated.

b. Current Use

Based upon the 1977 purchase of calcium silicide, LCAAP is currently using this material at the rate of 270 lb/month.

c. Use at Full Mobilization

Full mobilization production of the items using calcium silicide in their formulations would require about 14,000 lb/year of this chemical. This requirement is equivalent to an average monthly use rate of 1,167 lb/month.

3. Documented or Speculated Occurrences in Air or Water

Melton (1978) estimates that losses of materials used in primer and tracer mixes are about 1-2% of the amount handled. Thus, current losses of calcium silicide at LCAAP are about 3-6 lb/month. At full mobilization, the losses would increase to 12-24 lb/month. Primer and tracer wastes are generally discharged into a kill tank where they are treated with strong base to destroy explosive constituents. The waste material is then neutralized and discharged into conventional industrial waste treatment facilities. During this treatment process calcium silicide will be decomposed to $Ca(OH)_2$, SiO_2 and hydrogen gas. Since addition of $Ca(OH)_2$ is one of the steps in the industrial waste treatment process at Lake City AAP, any additional amount added by hydrolysis of calcium silicide will be insignificant.

E. Uses in the Civilian Community

1. Production Methodology

Calcium silicide is produced by the physical reprocessing of calcium silicon alloy. The alloy is manufactured in a submerged-arc electric furnace by carbon reduction of lime and silica rock (Kirk and Othmer, 1969).

2. Manufacturers, Production and Capacity

The two U.S. manufacturers of calcium silicide are Barium and Chemicals, Inc. in Stubenville, Ohio, and Hummel Chemical in South Planfield, New Jersey (S.R.I., 1977). They produce calcium silicide to military specifications from commercial calcium silicon alloy (Hummel Chemical, 1978). Capacities are unavailable.

Union Carbide Corporation, Metals Division and Belmont Smelting and Refining produce calcium silicon alloy in Alloy, WV and Brooklyn, NY (S.R.I., 1977).

The calcium silicon alloy produced for civilian use is available in three grades. The best grade has a Ca+Si content of ≥ 90% and a Ca content of ≥ 31%. The least pure grade contains ≥ 23% Ca and ≥ 85% Ca+Si (Berezhnoi, 1960). Due to the large amount of electricity required for production of calcium silicon alloys, the costs per pound of these chemicals are high. Based on the high costs, total United States production capacities are estimated at less than 1 million lb per year.

3. Usages

The only non-military use for calcium silicide is in its calcium silicon alloy form. In this form, it is used for the deoxidation/degassification of high grade steel. The presence of this alloy prevents formulation of alumina type inclusions by reacting with oxygen to form silicate inclusions which are less damaging to the physical properties of steel. Calcium silicide also minimizes formulation of polysulfide chain inclusions (Kirk and Othmer, 1969).

4. Future Trends

There are no anticipated civilian uses for military grade $CaSi_2$. Civilian use of calicum silicon alloy should be directly related to the U.S. production of high grade steel.

5. Documented or Speculated Occurrences in the Environment

There are no reports of calcium silicide as an environmental pollutant in the literature. However, hydrolysis products such as calcium hydroxide and silicon dioxide are expected to be pollutants from both the civilian production and use of calcium-silicon alloy. Any pollution by these two chemicals from calcium-silicon alloy is expected to be small.

F. Comparision of Civilian and Military Usages and Pollution

Military grade of calcium silicide is only produced on demand by refinement of calcium-silicon alloy. The yearly production of military grade calcium silicide represents ∿0.2-0.3% of the estimated 1 million pounds of calcium-silicon alloy produced in the United States each year. At full mobilization use rate, the Army would require ∿1% of the alloy produced by the civilian community. Pollution from both the civilian manufacturing and use and military use of calcium silicide will be in the form of calcium hydroxide. Military pollution of calcium hydroxide from Lake City AAP is expected to be negligible. Likewise, pollution from the civilian production and usage of calcium-silicon alloy is expected to be small.

G. Toxicological and Environmental Hazards

1. Mammalian Toxicity

Due to the rapid hydrolysis of calcium silicide, toxicity of the compound will be that of calcium hydroxide. Calcium hydroxide is a skin and lung irritant. The oral toxicity of this compound to rats is 7.34 g/kg (LD50) (Windholz, 1976).

Russian researchers (El'pener and Voitenko, 1968) exposed male rats to 50 and 350 mg/l $Ca(OH)_2$ in drinking water. Restlessness, aggressiveness and decrease in appetite were observed after two months. By the end of three months, decreases in weight, erythrocytes and blood hemoglobin content, phagocytal index and uropepsin activity in the urine were observed.

2. Aquatic Toxicity

Calcium silicide hydrolyzes rapidly when exposed to moisture; therefore, the aquatic toxicity of this compound will be that of its hydrolysis product, calcium hydroxide. Most calcium compounds have a low aquatic toxicity. However, calcium hydroxide is relatively toxic to fish. An exposure of 92 ppm of calcium hydroxide for 7 hours was toxic to trout (Department of Transportation, 1974). The 24 hour TL_m for mosquito fish is 240 ppm.

Absorbtion of carbon dioxide from the atmosphere will precipitate calcium carbonate and reduce the toxicity of the calcium hydroxide.

3. Phytotoxicity

Laloraya (1970) reported that high concentrations of calcium in soil cause metabolic disturbances and an overall inhibitory effect on peanut and linseed plants (*Arachis hypogaea* and *Linum usitatissimum*). The effect of calcium ion on growth and metabolism may be related to its controlling effect on the membrane structure and, therefore, the uptake of water and essential ions. High levels of calcium are correlated with the inhibition of chlorophyll biosynthesis. Calcium is known to inhibit the uptake of Mg^{++}, which is a constituent of chlorophyll molecules, and to inactivate the iron present in plants which is a requirement in synthesis.

4. Toxicity to Microorganisms

No information was found on the toxicity of calcium silicide or its breakdown products to microorganisms.

5. Availability of Literature for Phase II

The toxicological and environmental hazards of calcium silicide are those of calcium hydroxide. There is sufficient literature on this compound for a Phase II study.

H. Regulations and Standards

There are no regulations or standards specific for calcium silicide. Calcium hydroxide, the hydrolysis product of calcium silicide, is listed as a hazardous substance by EPA (Federal Register, 1978). It is placed in category "D", 100 mg/l>LC50<500 mg/l. The harmful quantity is set at 5,000 lb discharged over a 24 hour period (Federal Register, 1978). A TLV of 5 mg/m^3 as calcium for calcium hydroxide is recommended by the American Conference of Governmental Industrial Hygienists (1977) to protect workers against upper respiratory tract, skin and eye irritations.

I. Conclusions and Recommendations

The purpose of this study was to assess the Army's responsibility for conducting further toxicological and environmental research on calcium silicide. Calcium silicide is refined to specifications solely for Army use. In this respect, it is a military unique compound. However, upon contact with moisture calcium silicide is readily hydrolyzed to calcium hydroxide, silicon dioxide and hydrogen. Calcium hydroxide is used in the treatment industrial waste waters at Lake City AAP to remove metals. Any additional calcium hydroxide from calcium silicide hydrolysis entering the waste water treatment plant will be insignificant. In view of this use of calcium hydroxide and the small amount of calcium silicide used by the Army, it is concluded that calcium silicide is not a toxicological or environmental problem. Therefore, .t further studies on this compound by the Army should be a low priority.

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AD

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VOLUME IV PRIMER AND TRACER RELATED CHEMICALS

LEAD DIOXIDE

FINAL REPORT

J. F. Kitchens
W. E. Harward III
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SUMMARY

Lead dioxide is used by the Army in igniter and tracer mixes compounded at Lake City AAP. The mixes calling for lead dioxide require only 2.9 to 6.5% of this compound. Thus the use rate of lead dioxide by the Army is small - 300 lb/year under current production schedules and 700 lb/year at full mobilization. The losses of lead dioxide from the mixing and loading processes at Lake City AAP are estimated at less than 2 lb/month at full mobilization usage. The industrial waste treatment plant should remove essentially all the lead from the waste stream.

The civilian production of lead dioxide is ∿2 million lb/year. The major portion of this chemical is used as a curing agent in polysulfide elastomers. The pollution resulting from the manufacture and use of lead dioxide by the civilian community is not known.

Lead dioxide, like other lead compounds, is toxic when absorbed by the human body over long periods of time. However, due to its lower solubility in body fluids, it is not as toxic as the more common carbonate, sulfate and oxide salts of lead when injested or inhaled. Due to its very limited solubility in water, lead dioxide will not present an acute toxicity problem to the aquatic environment. However, accumulation in the sediment and bioaccumulation of lower organisms could occur.

Based on the limited use of lead dioxide by the Army, any further research on lead dioxide should be a low priority.

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FOREWORD

This report details the results of a preliminary problem definition study on lead dioxide. The purpose of this study was to determine the Army's responsibility for conducting further research on lead dioxide in order to determine its toxicological and environmental hazards so that effluent standards can be recommended. In order to determine the Army's responsibility for further work on lead dioxide the military and civilian usage and pollution of this chemical were evaluated. In addition, a preliminary overview of toxicological and environmental hazards was conducted.

Lead dioxide was only one of 48 chemicals evaluated under Phase IA of contract No. DAMD17-77-C7057. These chemicals are grouped in four categories

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- propellant related chemicals
- pyrotechnics
- primers and tracers

Each category is a major report. Section I of each report is an overview of the military processes which use each chemical and the pollution resulting from the use of these chemicals. The problem definition study reports on each chemical are separable sections of these four reports.

In addition a general methodology report was also prepared. This report describes the search strategy and evaluation methodology utilized for this study.

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VII. LEAD DIOXIDE

A. Alternate Names

Lead dioxide is the highest oxidation state (+4) oxide of lead. It occurs in nature as the mineral, plattnerite. Lead dioxide has a molecular formula of PbO_2 and a corresponding molecular weight of 239.21 g/mole. This oxide exists in two crystalline forms: the orthorhombic α-PbO_2 and the more common tetragonal β-PbO_2. Pertinent alternate names for lead dioxide are listed below:

CAS Registry No.:	1309-60-0
Replaces CAS Registry Nos.:	7720-76-5; 60525-54-4
CA Names (8CI):	Lead oxide (PbO_2)
Wiswesser Line Notation:	
Synonyms:	C.I. 77580; Lead brown; Lead dioxide; Lead oxide; Lead oxide brown; Lead peroxide; Lead Peroxide (PbO_2); Lead superoxide

B. Physical Properties

The physical properties of lead dioxide are presented in Table VII-1.

Table VII-1. Physical Properties of Lead Dioxide.*

Physical Form @ 20°C:	solid
Color and Crystal Form:	α-PbO_2 - black orthorhombic β-PbO_2 - brown tetragonal
M.P.:	290°C decomposes with release of O_2
Density:	9.375g/cc
Solubility:	water - insoluble in hot and cold water; soluble in dilute HCl; slightly soluble in acetic acid; insoluble in alkali

*Reference: Hawley, 1977; Weast, 1970.

C. Chemical Properties

1. General Reactions

Solid lead dioxide can exist in two forms. The more common crystalline form possesses a tetragonal rutile structure. It is known as β-PbO_2. The other is an orthorhombic form known as α-PbO_2. The chemistry of the two forms is similar.

The thermal decomposition of PbO_2 has been closely examined. However, there remains much controversy on the subject. This controversy can be attributed to different researchers obtaining PbO_2 from different sources. Lead dioxides varying slightly in physical make-up exhibit different behavior to thermal decomposition (Gillibrand and Halliwell, 1972). Differences in specific surface areas of the lead dioxide particles also affects the thermolysis. At temperatures between 400 and 500°C, particles also affect the thermolysis. Further heating to 600°C yields PbO.

$$\beta PbO_2 \xrightarrow{400\text{-}600^\circ C} Pb_3O_4 \xrightarrow{550\text{-}600^\circ C} PbO$$

For more disperse solids, transformation to PbO occurs between 300° and 500°C without intermediate red lead formation.

At temperatures above 200°C, α-PbO_2 changes to the β form. Further heating gives the Pb_3O_4, then PbO as in the previously mentioned reaction scheme.

$$\alpha PbO_2 \xrightarrow{200\text{-}300^\circ C} \beta PbO_2$$

Very disperse α-PbO_2 is stable to 350°C. Between this temperature and 500° it is transformed to PbO.

$$\alpha PbO_2 \text{ (disperse)} \xrightarrow{350\text{-}500^\circ C} PbO$$

Thermolysis of both crystalline forms is accompanied by the evolution of oxygen and the formation of unstable PbO_x intermediates ($1< x <2$).

Lead dioxide dissolves readily in acids. Oxygen is generated and lead sulphate precipitates upon warming in sulfuric acid (Abel, 1973).

$$PbO_2 + H_2SO_4 \longrightarrow PbSO_4\ (s) + H_2O + \tfrac{1}{2}O_2$$

It is insoluble in basic solutions but will react with basic oxides upon heating. Heating with calcium oxide or potassium hydroxide yields plumbates (Abel, 1973).

$$PbO_2 + CaO \xrightarrow{\Delta} Ca_2PbO_4$$
$$PbO_2 + KOH \xrightarrow{\Delta} K_2PbO_3$$

Lead dioxide reacts with elemental lead and acid to form lead (II) salts (Kirk and Othmer, 1967).

$$Pb + PbO_2 + 2H_2SO_4 \rightleftharpoons 2PbSO_4 + 2H_2O$$

This highly reversible reaction is the basis for the lead storage battery.

2. Environmental Reactions

No photochemical studies of lead dioxide have been reported in the literature.

Lead dioxide is insoluble in neutral and near neutral pH waters. It will, however, dissolve in acidic solutions as discussed above.

3. Sampling and Analysis

Total lead may be determined by atomic absorption spectrophotometry (Franson, 1975). Lead may also be measured by anodic dissolution polarography at concentrations down to 10^{-8} molar. Lead dioxode may be determined gravimetrically by dissolution in sulfuric acid, then weighing the precipitated lead sulfate (Abel, 1973). Alternatively, lead dioxide may be determined by the reaction of lead (II) with dithizone following the reduction with sulfuric acid (Franson, 1975).

D. Uses in Army Munitions

1. Purpose

Lead dioxide is a constituent of igniter and tracer formulations. It is used at Lake City AAP (LCAAP) to produce the following compositions:

	% lead dioxide in formulations
Igniter Mix I-559	6±0.5
Tracer Mix R-20C	3.4±0.5
Tracer Mix R-10E	4.1

2. Quantities Used

a. Historical Use

LCAAP purchased 600 lb of lead dioxide in 1975 and 540 lb in 1976. None was purchased in 1977. The average use rate over the past three years was 380 lb/year or 32 lb/month.

b. Current Use

Lead dioxide is currently used to produce the 5.56 mm tracer projectile. Approximately 41,000,000 tracer rounds were produced in 1977. This production rate corresponds to a lead dioxide use rate of 287 lb/year or 24 lb/month.

c. Use at Full Mobilization

Full mobilization production of the 5.56 mm projectile at LCAAP would require approximately 708 lb/year or 59 lb/month of lead dioxide.

3. Documented or Speculated Occurrences in Air or Water

Losses of primer and tracer constituents generally represent 1-2% of the amount handled (Melton, 1978). Thus, less than 1 lb/month of lead dioxide is lost to the environment in current operations of LCAAP. Even at

full mobilization, losses of less than 2 lb/month would be the maximum amount expected. Due to the limited solubility of lead dioxide in water and basic solutions, it will be removed in the sludge from the industrial waste treatment plant. Indeed in an AEHA survey, no lead was detected in the effluents from the Lake City AAP industrial wastewater treatment plant (USAEHA, 1971).

E. Uses in the Civilian Community

1. Production Methodology

Lead dioxide is manufactured by oxidation of Pb(II) in the form of lead salt solutions, lead monoxide, or red lead. The oxidation may be accomplished electrochemically or with strong chemical oxidizing agents such as hydrogen peroxide, chlorine or bromine gas, or a hypochlorite. The preferred commercial process is reportedly oxidation of an alkaline red lead slurry with chlorine (Kirk and Othmer, 1967).

2. Manufacturers, Production and Capacity

Eagle-Picher Industries and Hummel Chemical produce lead dioxide in Joplin, MO, and South Plainfield, NJ, respectively (S.R.I., 1977). Eagle-Picher has a capacity between 1 and 2 million pounds per year. Their primary sales are to civilian manufacturers of polysulfide elastomers (Eagle-Picher, 1978). Hummel Chemical's production capacity is considered proprietary information and is unavailable.

3. Usages

Lead dioxide is widely employed as an industrial oxidizing agent. It is used in the manufacture of dyes, chemicals, matches, pyrotechnics and rubber substitutes. Lead dioxide acts as a curing agent for polysulfide polymers such as the highly inert, solvent resistant Thiokol-type rubbers. It is also used in lead-acid storage batteries, electrodes, and as an analytical reagent (S.R.I., 1977; Kirk and Othmer, 1967; Hawley, 1977).

4. Future Trends

No major changes are expected in the civilian use or manufacture of lead dioxide.

5. Documented or Speculated Occurrences in the Environment

Lead dioxide occurs in nature as the mineral plattnerite (Abel, 1973). Japanese researches (Hori *et al.*, 1973) measured lead emissions from industrial sources and found lead dioxide particulate emissions from a battery plant, a cable manufacturing plant and a steel plant.

F. Comparison of Military and Civilian Uses and Pollution

Lead dioxide is used by the civilian community as an oxidizing agent in the production of several types of end products. Civilian production capacity

of lead dioxide is estimated at slightly over 2 million pounds per year. No documentation of the lead levels entering the environment from the manufacture or use of lead dioxide was found in the literature. However, loss of one to two percent of the lead dioxide manufactured or used as various lead compounds is not unreasonable. This loss would result in 17,320-34,640 lb of lead entering the environment each year.

In contrast to the widespread civilian use of lead dioxide, the military use of this compound is limited to ∿400 to 500 lb/year at Lake City AAP under current production rates. At full mobilization, this usage would increase to ∿700 lb/year. Maximum expected pollution of lead resulting from use of lead dioxide at Lake City is less than 2 lb/month.

G. Toxicological and Environmental Hazards

1. Toxicity to Man

Lead salts are absorbed only slowly by the human body. Therefore, their acute toxicity is low (Lambou and Lim, 1970). However, chronic lead poisoning as a result of occupational exposure or ingestion of contaminated food is common. The many symptoms associated with chronic lead poisoning are listed in Table VII-2. The toxicity of lead compounds is influenced by several factors

- solubility of the compound in body fluids
- quantity of lead ingested, inhaled or absorbed
- quantity present in the circulation at one time
- length of time the lead is in contact with body fluids

Lead intake over that which can be eliminated (∿0.28 mg/kg) can be stored and accumulated by the body. It is believed that the stored lead is non-toxic. However, stored lead can be later released into the circulatory system and exhibit toxic reactions.

The toxicity of lead compounds depends on their solubility in body fluids. As shown below, solubility of lead compounds in body fluids can be very different than their water solubility (Jacobs, 1967).

Compound	Solubility in Serum at 25°C mg/l	Solubility in Water at 25 C°mg/l
Lead monoxide (PbO)	1152.0	17.1
Lead (Pb)	578.0	-
Lead sulfate ($PbSO_4$)	43.7	44.0
Lead carbonate ($PbCO_3$)	33.3	1.7

The relative toxicity of lead compounds are presented in Table VII-3. Inspection of this table indicates that lead dioxide has a lower toxicity than the more common carbonate, sulfate or monoxide compounds.

Table VII-2. Symptoms of Chronic Lead Poisoning.
(Plunkett, 1976)

GENERAL:

Pallor · Weakness · Loss of weight · Lassitude · Malnutrition

GASTROINTESTINAL:

Metallic taste · Increased salivation · Burton's lead line on gums · Pyorrhea
Anorexia, nausea, vomiting · Constipation · Abdominal colic and tenderness

GENITOURINARY:

Nocturia · Albuminuria and hematuria · Increased bilirubinuria · Secondary hyperuricemia · Azotemia

NEUROMUSCLAR:

Numbness and tingling of extremities and associated sensory disturbance
Extensor weakness of wrists and ankles; brachial palsy has also been described
Loss of muscle tone · Tremor · Increased deep-tendon reflexes · Muscular cramps and aching · Arthralgia · Muscular atrophy

CENTRAL NERVOUS SYSTEM:

Visual disturbances · Headache · Dizziness · Nervousness or depression
Insomnia · Mental confusion and delirium · Convulsions · Coma

Encephalopathy may be acute or chronic; acute usually associated with blood levels above 120 µg Pb

Retinal hemorrhages and optic neuritis; gray stippling of lead pigment about the optic disc has also been reported

HEMATOPOIETIC:

Erythrocyte stippling
Hypochromic normocytic anemia
Increased peripheral reticulocytes

Table VII-3. Relative Toxicity of Lead and Its Compounds.
(Jacobs, 1967)

Order of Toxicity	Method of Introduction		
	Injection	Ingestion	Inhalation
Most toxic	Lead arsenate	Lead arsenate	Lead carbonate
		Lead carbonate	Lead monoxide
		Lead monoxide	
		Lead sulfate	
Of similar but lower degree of toxicity	Metallic lead	Metallic lead	Metallic lead
	Lead carbonate	Lead chromate	Lead arsenate
	Lead chromate	Red lead	Lead chromate
	Lead monoxide	Lead dioxide	Red lead
	Red lead	Lead phosphate	Lead dioxide
	Lead dioxide	Lead sulfide	Lead phosphate
	Lead phosphate		Lead silicate
	Lead sulfate		Lead sulfide
	Lead sulfide		

The biochemical mode of action of lead is to inhibit the activity of erythrocyte delta-aminolevulinic acid dehydratase. Thus, heme synthesis is impaired and the life span of the red blood cell is shortened. An increase in urinary excretion of delta-aminolevulinic acid is also observed (EPA, 1976).

Epidemiological studies have shown that lead has an injurious effect on germ cells of both sexes. Development of the fetus is impaired often to the point of miscarriages. Those infants born to women lead workers are underweight and have a high incidence of nervous disorders (Lambou and Lim, 1970). No evidence has been found to link lead with human cancer (EPA, 1976). However, renal cancer in rats has been observed with 71% lead in the diet (EPA, 1976).

2. Aquatic Toxicity

The toxicity of lead to the aquatic environment is well documented (Lambou and Lim, 1970). Available bioassay data indicate that lead is more toxic in soft water (<50 ppm $CaCO_3$) than in hard water systems. This difference in toxicity is due to the availability of ionic lead in soft water systems.

Specific data on the aquatic toxicity of lead dioxide is not available. Due to the insolubility of lead dioxide in water, it is expected to have a low toxicity toward aquatic organisms. This compound will accumulate in the sediment. Microscopic aquatic organisms have shown to bioaccumulate insoluble lead compounds. The concentration factors range from 700 for benthic algae to 3,000 for zooplankton and 40,000 for phytoplankton (Lambou and Lim, 1970).

3. Toxicity to Invertebrates

The toxicity of the soluble lead chloride to *Daphnia magna* was studied by Biesinger and Christensen (1972). They found an LC50 of 300 ppb and reproductive impairment at 30 ppb.

4. Toxicity to Microorganisms

No specific data on the toxicity of lead dioxide to microorganisms was retrieved. In general lead is toxic to aerobic bacteria at a concentration of 1 ppm and to flagellates and infusoria at a concentration of 0.5 ppm (Lambou and Lim, 1970). The decomposition of organic materials by bacteria is inhibited at lead concentrations of 0.1 to 0.5 ppm (Lambou and Lim, 1970).

Results of experimental work by Tornabene and Edwards (1972) indicate that microbial systems are capable of abstracting substantial quantities of lead from sources containing insoluble inorganic lead-salt precipitates. The viability of bacterial cells (*Micrococcus luteus* ATCC 533) exposed to a medium containing lead for one complete growth cycle (48 hrs.) was not seriously affected and virtually all of the lead taken up by the cells was immobilized in the cellular membrane.

The occurrence of lead in the membranes of bacterial cells does not have a significant effect until the cells of more sensitive strains have been exposed to lead over an extended period. Tornabene *et al.*(1974) reported that lead impregnated cells were affected to the extent that an osmotically instable condition existed causing changes in the cytoplasmic membrane. These changes resulted in cellular leakage and protoplast instabilities. Apparently, the lead is bound to complex lipid mixtures in the cell membrane.

5. Phototoxicity

No phytotoxicity information on lead dioxide was encountered. However, phytotoxic data on other lead compounds was obtained and may be indirectly related.

The pattern of lead uptake by plants has been rarely studied and little can be concluded about the mechanism involved. The uptake of lead was reported constant with increasing levels of soil lead, until a certain point is reached when uptake becomes unrestricted and rises abruptly (Nicolls *et al.*, 1965). Only soluble lead salts and ionic lead are available to plant roots. The uptake of lead by ryegrass grown in a solution containing lead is shown in Table VII-4 (Hepple, 1972). The total content of lead in roots plus shoots of perennial ryegrass increases with increasing levels in the soil. The roots take up lead readily but pass on only a small proportion to the shoots. Thus, the roots act as a barrier which restricts the movement of lead from the soil through the plant to growing animals. A similar pattern was found by Wallace *et al.* (1971) in their studies on the uptake of lead by bush-bean plants. During winter months when plant growth is low, a considerable increase in the lead content of the ryegrass shoots was observed (Hepple, 1972).

Corn was grown in the field where lead acetate had been soil-applied at eight rates ranging from 0 to 3,200 kg lead/ha. No changes in emergence, plant height, grain yield, color, maturity or other growth differences were observed during the 2-year study (Baumhardt and Welch, 1972).

Five crops (cauliflower, tomatoes, cabbage, strawberries and Valencia oranges) were analyzed for their lead content by Schuck and Locke (1970). These plants revealed little inclinations to absorb lead via their root system (Schuck and Locke, 1970).

6. Availability of Literature for Phase II

Literature on the toxicological and environmental hazards of lead in general is plentiful. However, studies specifically on lead dioxide are few. Thus most of the toxicological and environmental properties of lead dioxide will have to be inferred from the studies of other lead compounds.

Table VII-4. Lead Uptake by Perennial Ryegrass Grown in Solution-Culture (Hepple, 1972).

Level of Pb added to solution		Pb content of plants at 14 days after addition of solution			
		Roots		Shoots	
(ppm)	(µg)	(ppm)	(µg)	(ppm)	(µg)
0.4*	400	98	201	3	37
1.0+	12500	3696	9610	104	1055

* In 1 liter of static solution-culture; controlled environment experiment.

+ In 12.5 liter of flowing solution-culture; glass-house experiment.

H. Regulations and Standards

1. Air and Water Regulations

There are no air and water standards specific for lead dioxide. However, criteria have been set for lead in potable water and effluents (EPA, 1976). For potable water, the lead content cannot exceed 50 µg/1. Due to the variability of lead solubility and toxicity in different waters, the following criteria have been set for effluents (using the receiving water as a diluent):

- 0.01 times the 96-hour LC50 value expressed as dissolved lead for the most sensitive species

This criteria requires that the 96-hour LC50 tests be performed with the actual water samples and the most sensitive species in the local ecosystem.

2. Human Exposure Standards

OSHA has set a standard for inorganic lead compounds in air at 200 µg Pb/m^3, The recommended TLV for worker protection is 150 µg Pb/m^3 (American Conference of Government Industrial Hygienists, 1977).

3. DOT Labeling Requirements

The Department of Transportation lists lead dioxide as an oxidizer. Labels on this material should state "Oxidizer" (Federal Register, 1976).

I. Conclusions and Recommendations

The goal of this study was to determine the Army's responsibility for conducting further toxicological and environmental studies on lead dioxide. As a result of this study, it is recommended that a low priority should be placed on any further Army supported toxicological and environmental studies on lead dioxide. This recommendation is based on the following conclusions:

- under current operations, the Army uses lead dioxide only at Lake City AAP
- the current use of lead dioxide at Lake City AAP is ~300 lb/year
- full mobilization use at Lake City AAP is only 700 lb/year
- losses of lead dioxide at full mobilization at Lake City AAP is estimated at less than 2 lb/month
- the Army uses and losses are insignificant compared to those of the civilian community
- due to its insolubility in water, lead dioxide will be unavailable to fish; however, sediment and biological accumulation could occur.

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AD

PRELIMINARY PROBLEM DEFINITION STUDY OF 48 MUNITIONS-RELATED CHEMICALS

VOLUME IV PRIMER AND TRACER RELATED CHEMICALS

ZIRCONIUM

FINAL REPORT

J. F. Kitchens
W. E. Harward III
D. M. Lauter
R. S. Wentsel
R. S. Valentine

April 1978

Supported by:

U. S. ARMY MEDICAL RESEARCH AND DEVELOPMENT COMMAND
Fort Detrick, Frederick, Maryland 21701

Contract No. DAMD17-77-C-7057

COTR: Clarence Wade, Ph.D.

ATLANTIC RESEARCH CORPORATION
Alexandria, Virginia 22314

Approved for Public Release
Distribution Unlimited

The findings of this report are not to be construed as an official Department of the Army position unless so designated by other authorized documents.

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SUMMARY

Zirconium is produced by the Teledyne Wah Chang Corporation, which is the only United States producer. The major use of zirconium is as a cladding material for uranium fuel elements. Other civilian uses of zirconium are as a reducing agent and as a component of vacuum tubes, flash bulbs and lamp filaments.

The military uses zirconium as a fuel in pyrotechnic, primer and tracer formulations. The military requirement for zirconium would be about 2% of civilian production capacity at full mobilization. The military contribution to pollution by zirconium is small compared to losses through civilian use of this metal.

The toxicity of zirconium and its compounds to mammals and aquatic organisms is relatively low. This metal is widespread in the environment and is found in the tissue of most animals. Because of the modest military use of zirconium and its low toxicity, further studies on this substance by the Army should be a low priority.

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FOREWORD

This report details the results of a preliminary problem definition study on zirconium. The purpose of this study was to determine the Army's responsibility for conducting further research on zirconium in order to determine its toxicological and environmental hazards so that effluent standards can be recommended. In order to determine the Army's responsibility for further work on zirconium, the military and civilian usage and pollution of this chemical were evaluated. In addition, a preliminary overview of toxicological and environmental hazards was conducted.

Zirconium was only one of 48 chemicals evaluated under Phase IA of contract No. DAMD17-77-C-7057. These chemicals are grouped in four categories

- explosives related chemicals
- propellant related chemicals
- pyrotechnics
- primers and tracers

Each category is a major report. Section I of each report is an overview of the military processes which use each chemical and the pollution resulting from the use of these chemicals. The problem definition study reports on each chemical are separable sections of these four reports.

In addition, a general methodology report was also prepared. This report describes the search strategy and evaluation methodology utilized for this study.

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VIII. ZIRCONIUM

A. Introduction

Elemental zirconium is a silvery grey metal having an atomic number of 40 and an atomic weight of 91.22. The CAS Registry No. for the element is 7440-67-7. The Wiswesser Line Notation is Zr. In nature, it exists as the following isotopes:

Zr^{90}, 51.5%; Zr^{91}, 11.2%; Zr^{92}, 17.1%; Zr^{94}, 17.4% and Zr^{96}, 2.8%

The electronic orbital arrangement of the ground state of the zirconium atom is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 4d^2\ 5s^2$. The ionization potentials of the $4d^2\ 5s^2$ valence electrons are 6.84, 13.13, 24 and 33.8 electron volts. The low ionization potentials of zirconium account for its high reactivity.

In nature, zirconium exists as the dioxide in such ores as zircon, $ZrO_2 \cdot SiO_2$. The element hafnium is found in all zirconium ores usually at levels of ~2 wt% of the zirconium. The α form of zirconium metal is stable at low temperatures (<863°C). This form is a hexagonal close packed lattice. The high temperature β form has a body centered cube symmetry (Kirk and Othmer, 1970).

B. Physical Properties of Zirconium

The physical properties of zirconium are listed in Table VIII-1.

C. Chemical Properties

1. General Reactions

Zirconium is a very chemically reactive element. Newly formed zirconium will react rapidly with the atmosphere to form a protective coating of nitrides and oxides. During the production of zirconium care must be taken to exclude atomospheric gases to prevent formation of impurities (Kirk and Othmer, 1970).

Zirconium metal will absorb gases upon heating. Absorption of oxygen occurs at 650°C and nitrogen at 900°C. Further heating to 1200°C gives uniform distribution of nitrogen. In the presence of oxygen, solid zirconium will ignite at temperatures around 1000°C. Powdered zirconium ignites at much lower temperatures (Kirk and Othmer, 1970).

Zirconium metal is dissolved by heating in oxidizing acids such as a 3:2 mixture of sulfuric acid and ammonium sulfate. Aqueous hydrochloric acid in the absence of an oxidizer does not dissolve the metal when heated. An aqueous solution of cupric chloride will attack zirconium and cause pitting of the metal (Kirk and Othmer, 1970).

At room temperature, zirconium metal shows little reactivity and outstanding corrosion resistance due to its protective film. In general zirconium is resistant to organic solvents, non-oxidizing aqueous salt solutions,

Table VIII-1. Physical Properties of Zirconium*

Physical Form @ 20°C:	solid
Color:	silver grey white
Crystal Form:	hexagonal below 865°C body centered cube above 865°C
M.P.:	1857°C
B.P.:	3577°C
Density, g/cm^3:	6.506
Specific Heat, cal(g)(°C):	0.67
Thermal Conductivity, $cal/(sec)(cm^2)(°C/cm)$:	0.0505
Solubility:	insoluble in cold water slightly attacked by hot water reacts with hot concentrated sulfuric acid not attacked by nitric acid attacked by fused potassium hydroxide or nitrate

*References: Kirk and Othmer, 1970

water, and 50% sulfuric acid (Kirk and Othmer, 1970).

2. Environmental Reactions

Zirconium metal will be chemically unreactive in the environment. Exposed to the atmosphere it develops a protective coating which will leave it unreactive to water, very dilute acid solutions, and sunlight.

3. Sampling and Analysis

Available analytical procedures are for the determination of Zr(IV) rather than elemental zirconium. The quantitative techniques include gravimetric methods involving precipitation with mandelic acid followed by ignition to zirconium dioxide, or precipitation with phosphate followed by ignition to ZrP_2O_7. Zirconium may be determined volumetrically with EDTA at pH 2.0 via a back titration with bismuth(III) and thiourea. Spectrophotometric methods have also been developed using alizarin Red S, pyrocatechol violet, or xylenol orange (Bradley and Thornton, 1973).

D. Uses in Army Munitions

1. Purpose

Zirconium is used as a fuel in pyrotechnic, primer and tracer formulations. Pine Bluff Arsenal uses zirconium in the following compositions:

	% Zirconium in Composition
Igniter Mixture III	17.5±0.2
Ignition Composition	48.6±1
Ignition Composition	65±2

Zirconium is used by Lake City AAP (LCAAP) to produce the 7.62 mm tracer shell. This item requires 25.7 lb zirconium per 100,000 rounds. Longhorn AAP (LAAP) also uses zirconium as a fuel in primer and tracer formulations. The specific end items using zirconium are not known.

2. Quantities Used

a. Historical Use

Pine Bluff Arsenal has not produced any formulations requiring zirconium in recent years. Thus, the use rate of zirconium at PBA has been essentially zero for at least the last three years (Aikman, 1978).

Lake City AAP procured the following amounts of zirconium during the 1975-1977 period:

1975	200 lb
1976	650 lb
1977	951 lb

The average use rate of zirconium at LCAAP was 600 lb/year or 50 lb/month during this period.

In 1977, Longhorn AAP used 3,586 lb of zirconium (Marshall, 1978). This facility also used 2,234 lb of zirconium hydride in 1977.

b. Current Use

The current use rate of zirconium at Lake City AAP is 80 lb/month, based upon 1977 data. Longhorn AAP uses about 300 lb/month also based upon 1977 operations. LAAP also used 186 lb/month of zirconium hydride. Pine Bluff Arsenal is not using any zirconium in current operations.

c. Use at Full Mobilization

At full mobilization, Lake City AAP would use about 300 lb/month of zirconium. The full mobilization use rate at Longhorn AAP would be on the order of 9500 lb/month. LAAP would also use about 7300 lb/month of zirconium hydride at full mobilization (Leander, 1978). Pine Bluff Arsenal would use about 100 lb/month of zirconium at full mobilization (Aikman, 1978).

3. Documented or Speculated Occurrences in Air or Water

According to Melton (1978), typical losses from manufacture of pyrotechnics, primers and tracers are 1-2% of the amount handled. Thus, current losses of zirconium from Lake City AAP are on the order of 1-2 lb/month. At full mobilization, losses of 3-6 lb/month may be expected.

Zirconium use at Longhorn AAP results in an estimated current loss of 3-5 lb/month, including that from use of the hydride. At full mobilization, losses of 80-170 lb/month would be expected at LAAP. These figures are based upon an estimate by Maley (1978) that 0.5 to 1.0% of the amount of primer and tracer material handled is lost to waste streams.

E. Uses in the Civilian Community

1. Production Methodology

Zirconium metal is prepared from zirconium tetrachloride by the Kroll method (Kirk and Othmer, 1970; Bradley and Thornton, 1973).

$$ZrCl_4 + 2Mg \longrightarrow Zr + MgCl_2$$

Vaporized zirconium tetrachloride is introduced into the reactor containing liquid magnesium at 800-850°C under an inert atmosphere of helium or argon. The reaction is exothermic. The magnesium chloride and unreacted magnesium are vacuum distilled at 925°C leaving behind a spongy zirconium product which is cooled and compacted by arc melting of argon. The absence of oxygen, nitrogen, or carbon throughout the process is essential to prevent contamination of the product. Impurities as small as 0.1% alter the physical properties unexceptably.

All naturally occurring zirconium contains approximately two percent hafnium as an impurity. Hafnium is similar in its chemical behavior to zirconium, making separation difficult and expensive. For most commercial uses, the hafnium impurity does not adversely affect the behavior of zirconium and is not removed. Zirconium which is used in nuclear reactors requires separation of the hafnium impurity due to the different nuclear properties. The separation may be achieved by solvent extraction, ion-exchange techniques, or partition chromatography. The separation may also be done prior to reduction of the tetrachloride.

2. Manufacturers, Production, and Capacity

The Teledyne Wah Chang Corporation in Albany, Oregon is the only U.S. manufacturer of zirconium metal. They possess a capacity between six and nine million pounds of zirconium sponge per year (Teledyne Wah Chang, 1978).

3. Usages

The major use of zirconium metal is as a protective cladding for uranium fuel elements. This use requires hafnium-free zirconium. Zirconium is also used in flash powders and bulbs, as a gas "getter" in vacuum tubes, a deoxidizer in metallurgy, in corrosion resistant alloys, as a special welding flux, in construction of rayon spinnerets, in lamp filaments, in fireworks, and in metal to glass seals (Kirk and Othmer, 1970; Hawley, 1977; and Windholz, 1976).

4. Future Trends

Teledyne Wah Chang anticipates a slight increase in the scale of zirconium use in the future. Protective nuclear fuel claddings are expected to continue as the major use of the metal (Teledyne Wah Chang, 1978).

5. Documented or Speculated Occurrences in the Environment

Exposed to the environment, elemental zirconium reacts with air to form zirconium dioxide or nitrides. There are no reports of environmental pollution from the manufacture or use of zirconium metal. Losses probably are ~1% of the metal produced or ~60,000 lb per year. However, zirconium compounds are widespread in the environment. This metal is found in trace quantities in water and animal tissues.

F. Comparison of Civilian and Military Uses and Pollution

The major civilian use of zirconium is as a cladding material for nuclear fuel elements. The only United States producer of zirconium is Teledyne Wah Chang. This company has a production capacity of about 9 million lb/year of this metal in the form of zirconium sponge. No reports of zirconium pollution in air or water from these operations were found in the literature.

The military use rate of zirconium is currently about 7,000 lb/year. This represents about 0.1% of the civilian production capacity. At full mobilization, the military use would rise to about 2% of the civilian production capacity. These figures include use of zirconium hydride as well as the metal. Even at full mobilization, losses of zirconium from munitions production operations would be less than 200 lb/year. Thus, the military contributions to pollution by zirconium would be negligible compared to anticipated losses through civilian use of this metal.

G. Toxicological and Environmental Hazards

1. Toxicity to Mammals

The acute toxicity data of several zirconium compounds to mammals are presented in Table VIII-2. As observed from the table, the toxicity of zirconium compounds to mammals is low. The compound that was found to be the most toxic in these studies was zirconium sodium glutamate with an LD50 of 247 mg/kg.

Chronic studies with zirconium compounds have been conducted. Schroeder *et al.* (1968) observed no accumulation of zirconium in tissues of rats exposed to 5 ppm of this metal in their drinking water. High concentrations of zirconium in the diet (~20%) of rats for long periods of time produced no harmful effects (Schubert, 1947). Daily injections of up to 450 mg/kg were tolerated by rats for 8 days (Schubert, 1949). Pulmonary granulomata were found in rabbits exposed to zirconium lactate mist (Prior *et al.*, 1960).

Toxicity and epidemiological studies on humans indicate a low toxic response to zirconium compounds. Barsi (1963) studied five workers exposed to zirconium dust. They found no adverse effects. Injections of humans with sodium zirconium lactate showed only the formation of fibrous papules (Shelley and Hurley, 1957). Some effects have been observed with humans exposed to zirconium from deodorant stick and poison-oak lotions (Epstein and Allen, 1964).

Zirconium is found in a wide variety of foods. The daily intake of zirconium has been estimated at 4150 µg for the average man (Schroeder and Balassa, 1966). Human and mammalian tissue samples examined were shown to contain as much as 48 µg zirconium per g of tissue. Most of the zirconium is found in the fatty tissue, liver or spleen. None was found in the urine. In general, the concentration of zirconium in mammalian tissue remains fairly constant. The main route for elimination of this element from the body is through the feces (Schroeder and Balassa, 1966).

2. Aquatic Toxicity

Some research has been conducted on the levels of zirconium in the aquatic environment. Kleinkoff (1960) found the average zirconium level in the lakes of northern Maine to be 2.6 ppb. Durum and Haffty (1961) found an

Table VIII-2. Acute Toxicity of Zirconium Compounds to Mammals.

Animal	Compound	Administered	Dose mg/kg	Effect	Reference
Rats	Zirconium nitrate	Oral	853	LD50	Browning, 1961
Rats	Sodium zirconyl sulfate	Oral	2290	LD50	"
Mice	Sodium zirconium	i.p.	2700	LD50	Indust. Hyg. Found., 1954
Rats	Zirconium sodium citrate	i.p.	1710	LD50	Schubert, 1947
Rats	Zirconium sodium glutamate	i.p.	247	LD50	"

average of 0.1 ppb of zirconium in 10 to 15 rivers in North America. Tong *et al.* (1974) found the average zirconium level in lake trout (*Salvelinus namaycush*) was 0.53 ppb.

The toxicity data of three zirconium compounds to aquatic organisms are presented in Table VIII-3. These data indicate that zirconium in soft water is much more toxic than in hard water. Hildebrand *et al.* (1976) found that zirconium had a low bioaccumulation and toxicity potential in aquatic systems.

3. Toxicity to Microorganisms

Microorganisms are known to accumulate zirconium. Engle (1970) noted several bacteria which could fix zirconium from aqueous solutions. Conner *et al.* (1964) found that ammonium carbonatozirconate was a good algicide. According to Blumenthal (1976), zirconium has the potential to increase the toxicity of bactericides. He cited the reduction of gut flora in mice after a dose of zirconium lactate. Blumenthal (1976) hypothesized that zirconium assisted in the binding of a bactericide to the surface of bacteria increasing the toxicity of the bacteriocide. Thus, while zirconium itself is not toxic to microorganisms, it can increase the toxicity of bactericides.

4. Phytotoxicity

No evidence exists that zirconium is essential for the growth of plants or is toxic in the concentrations naturally occurring in soils (~300 ppm max.). A number of researchers found no zirconium in plant materials investigated (Carrigan and Rogers, 1940; Allison and Whitehead, 1943; and Vanselow, 1946). Hodgkiss and Errington (1941) found no traces of zirconium in three hay and three grain samples. Borovik *et al.* (1943) reported that zirconium was found in the roots of plants but not in the shoots.

More recent investigative work using radioactive zirconium indicated that a small amount may be translocated to the tops of plants (Jacobson and Overstreet, 1948; and Vlamis and Pearson, 1950). Gulyakin and Yudintseva (1956) grew oats and wheat in nutrient solutions containing radioactive zirconium. The zirconium was adsorbed by or absorbed into the roots but was not translocated to the shoots.

5. Availability of Literature for Phase II

Several studies on the toxicity and environmental distribution of zirconium are reported in the literature. These studies along with contacts with the manufacturer should provide sufficient information for a detailed Phase II toxicological and environmental evaluation of zirconium.

Table VIII-3. Aquatic Toxicity of Zirconium Compounds.

Species	Compound	Water Hardness	Level in ppm	Effect	Reference
Fathead minnow *(Pimephales promelas)*	Zirconium sulfate	hard	115	LC50	Tarzwell and Henderson, 1960
" "	"	soft	14	"	" "
" "	Zirconium oxychloride	hard	240	"	" "
" "	"	soft	18	"	" "
Bluegill *(Lepomis macrochirus)*	"	hard	270	"	" "
" "	"	soft	15	"	" "
Squawfish *(Ptychocheilus oregonensis)*	Zirconium tetrafluoride	soft	10	No effect	MacPhee and Ruelle, 1969
Coho salmon *(Oncorhynchus kisutch)*	"	soft	10	No effect	" "

H. Regulations and Standards

1. Air and Water Standards

No standards for exposure to zirconium in air or water are listed.

2. Human Exposure Standards

No threshold limit values for human exposure to zirconium are listed. The substance is not on the NCI suspected carcinogen list.

3. DOT Labeling Requirements

The Department of Transportation lists zirconium as a flammable solid (Federal Register, 1976). Labels on this material should state "Flammable Solid".

I. Conclusions and Recommendations

The goal of the preliminary problem definition study was to determine the Army's responsibility for conducting further studies on the toxicological and environmental hazards of zirconium. From the information gathered and evaluated during this study, the following conclusions can be drawn. These conclusions do not indicate any need for further Army sponsored hazards evaluation of this element.

- the Army usage of zirconium is insignificant compared to that of the civilian community.
- the major Army user of zirconium is Longhorn AAP. Essentially no zirconium enters the environment in effluent streams from this plant. Some leaching into the ground water from the evaporation pond could occur, but this source is expected to be small.
- the mammalian and aquatic toxicity of zirconium and its compounds is low.
- zirconium is relatively widespread throughout the environment and is found in tissue of most mammals.

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PRELIMINARY PROBLEM DEFINITION STUDY OF 48 MUNITIONS-RELATED CHEMICALS

VOLUME IV PRIMER AND TRACER RELATED CHEMICALS

LEAD AZIDE

FINAL REPORT

J. F. Kitchens
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D. M. Lauter
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April 1978

Supported by:

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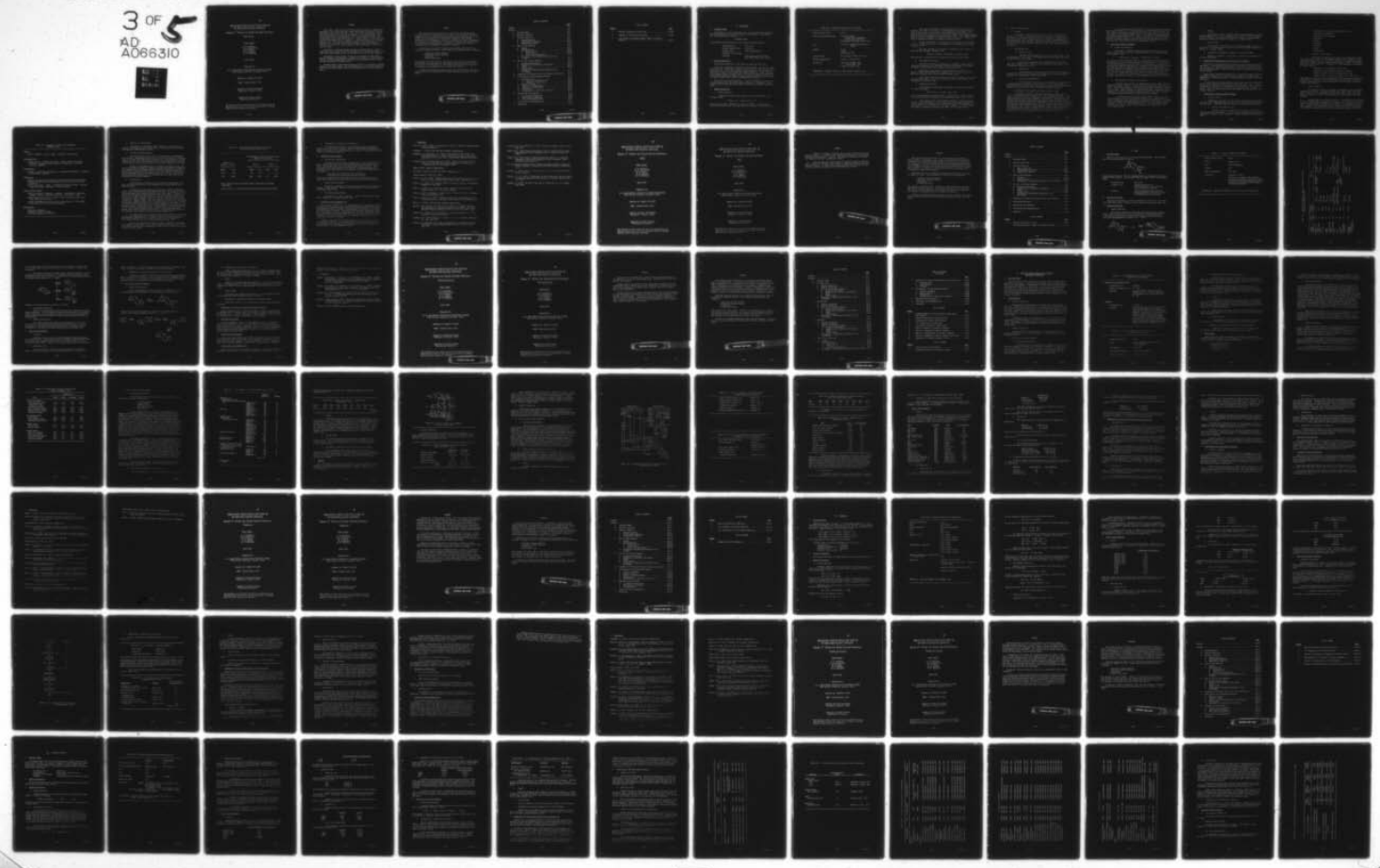
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VOLUME IV PRIMER AND TRACER RELATED CHEMICALS

LEAD AZIDE

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SUMMARY

Lead azide is used at Lake City AAP and Lone Star AAP as a component of detonators. The current use rate is about 600 lb/year at Lake City AAP and 2400-3600 lb/year at Lone Star AAP. Total use at full mobilization would be about 16,000 lb/year at these two facilities. At full mobilization, other facilities would also use lead azide. The total military use under these circumstances would exceed 50,000 lb/year. Current losses of lead azide from production operations are 5-7 lb/month. At full mobilization, 27-54 lb/month would be lost. The lead azide wastes are treated with strong base or with sodium nitrite and acetic acid before discharge. These lead-containing effluents are or will be further treated in the near future at Lake City and Lone Star AAPs.

Lead azide is currently produced by Olin Corporation and E.I. duPont. DuPont uses up to 25,000 lb/year for manufacture of civilian detonators. All other lead azide produced is sold to the Army for use in military ordnance.

Lead azide is toxic to man. No data on the toxicity of lead azide to aquatic organisms, microorganisms or plants are available. The environmental toxicity of this compound must be inferred from the available data on lead and the azide anion or hydrazoic acid.

Further studies on lead azide should be limited to its effects on workers exposed to the azide itself. Any environmental study of lead azide should be part of an overall evaluation of all lead components used at Army ammunition plants.

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FORWORD

This report details the results of a preliminary problem definition study on lead azide. The purpose of this study was to determine the Army's responsibility for conducting further research on lead azide in order to determine its toxicological and environmental hazards so that effluent standards can be recommended. In order to determine the Army's responsibility for further work on lead azide, the military and civilian usage and pollution of this chemical were evaluated. In addition, a preliminary overview of toxicological and environmental hazards was conducted.

Lead azide was only one of 48 chemicals evaluated under Phase IA of contract No. DAMD17-77-C-7057. These chemicals are grouped in four categories

- explosives related chemicals
- propellant related chemicals
- pyrotechnics
- primers and tracers

Each category is a major report. Section I of each report is an overview of the military processes which use each chemical and the pollution resulting from the use of these chemicals. The problem definition study reports on each chemical are separable sections of these four reports.

In addition, a general methodology report was also prepared. This report describes the search strategy and evaluation methodology utilized for this study.

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IX. LEAD AZIDE

A. Alternate Names

Lead azide is a salt of hydrazoic acid. It has a molecular formula of N_6Pb corresponding to a molecular weight of 291.258g/mole. Lead azide has the following structural formula:

$$N{\equiv}N{=}N\text{-}Pb\text{-}N{=}N{\equiv}N$$

The pertinent alternate names for lead azide are presented below:

CAS Registry No.:	13424-46-9
Replaces Registry Nos.:	12286-22-5
CA Name (8CI):	Lead azide($Pb(N_3)_2$)
Wiswesser Line Notation:	
Synonyms:	Lead azide; Lead (2+) azide; Lead azide (PbN_6); Lead diazide

B. Physical Properties

The physical properties of lead azide are listed in Table IX-1.

Lead azide is dimorphic, existing in an orthorhombic form (α) and a monoclinic form (β). The α form is stable relative to the β form. The β form is converted to the α form upon standing at high temperatures around 160°C, by the action of light, or by contact with either lead(II) solutions or aqueous α-lead azide crystals (Urbanski, 1965). In order to decrease its sensitivity to spontaneous explosion, dextrin is added during this manufacturing process. This type of lead azide is known as dextrinated lead azide.

Lead azide is a primary explosive. It may be detonated by contact with a metal plate at 380°C, by intense light, by impact, or by burning. Lead azide may explode spontaneously during crystallization (Urbanski, 1965; Abel, 1973).

C. Chemical Properties

1. General Reactions

Lead azide will react with copper or brass to form cupric azide (Urbanski, 1965).

$$Pb(N_3)_2 + Cu \longrightarrow Cu(N_3)_2 + Pb$$

Cupric azide is highly sensitive to friction or impact. For this reason, casings for blasting caps containing lead azide are made of aluminum or zinc.

Table IX-1. Physical Properties of Lead Azide*

Physical Form @ 20°C:	solid
Color and Crystalline Form:	colorless needles α-lead azide orthorhombic β-lead azide monoclinic dextrinated lead azide is buff color
M.P.:	245°-250°C decomposes when heated slowly
Density:	α-4.71 β-4.93 dextrinated 4.38
Specific Heat:	0.110 cal/g/°C from -50 to 50°C
Thermal Conductivity:	1.55×10^{-4} cal/sec/cm/°C
Solubility:	water 0.05 g/100g @ 20°C 0.09 g/100g @ 70°C soluble in acetic acid

*References: Windholz, 1976; U.S. Army Materiel Command, 1971.

Lead azide will decompose in boiling water with the evolution of hydrazoic acid, HN_3. Lead azide is also decomposed by the action of dilute nitric acid or acetic acid solutions containing added sodium nitrite. An aqueous solution of 15% nitric acid and 8% sodium nitrite can be used for disposal of lead acid residues and wastes (Urbanski, 1965). A 10% sodium hydroxide solution is also recommended for disposal of waste lead azide. Complete removal of explosive residue is accomplished within 16 hours.

Thermal decomposition of lead azide in the presence of light begins at 50°C. In the dark at 115°C, no decomposition is observed after 24 hours (Urbanski, 1965).

The azide nitrogen in lead azide is oxidized by ceric sulfate to give molecular nitrogen (Urbanski, 1965).

$$Pb(N_3)_2 + 2Ce(SO_4)_2 \longrightarrow PbSO_4 + Ce_2(SO_4)_3 + 3N_2$$

This reaction is utilized for the quantitative analysis of lead azide.

2. Environmental Reactions

Lead azide is partially decomposed by atmospheric oxygen with the evolution of hydrazoic acid, molecular nitrogen, and ammonia. The presence of carbon dioxide promotes the decomposition (Urbanski, 1965).

Hydrolysis of lead azide produces numerous basic salts of the general formula $nPb(N_3)_2 \cdot mPbO$ with n ranging from 1 to 3 and m from 4 to 9. Basic salt formation also occurs in base (Urbanski, 1965).

Light causes partial decomposition of solid lead azide. The exposed portions turn yellow. The yellow layers protect the covered portions from decomposition (Urbanski, 1965).

3. Sampling and Analysis

Lead azide may be determined by oxidation of azide with cerium(IV) to liberate nitrogen.

$$2Ce^{4+} + 2N_3^- \longrightarrow 3N_2 + 2Ce^{3+}$$

The nitrogen gas may be measured directly or alternatively excess cerium(IV) can be back titrated with standard ferrous ammonium sulfate (Jones, 1973).

Lead azide may also be determined as lead(II). Lead may be determined by atomic absorption; by anodic dissolution polarography; gravimetrically by addition of sulfuric acid followed by weighing of the precipitated lead sulfate; or by the reaction of lead with dithizone to form a pink complex which is measured colorimetrically (Abel, 1973; Franson, 1975).

D. Uses in Army Munitions

1. Purpose

Lead azide is used at Lake City AAP to produce the 20 mm M47 detonator. The amount required is 27.6 lb lead azide per 100,000 rounds. Lead azide is also used at Lone Star AAP as a component of detonators. At the present time, all lead azide utilized by the Army is purchased from civilian manufacturers. However, the Army has the capability of manufacturing lead azide at Lake City AAP, Kansas AAP, Joliet AAP, Iowa AAP and Twin Cities AAP.

2. Quantities Used

a. Historical Use

Lake City AAP purchased 1800 lb of lead azide in 1976. None was purchased in 1975 or 1977. The average use rate over these three years was 600 lb/year or 50 lb/month.

Lone Star AAP used 600 lb of lead azide during the month of June, 1974 (USAEHA, 1974). This use rate is believed to be typical of the requirements during the year 1974.

b. Current Use

The current use of lead azide by Lake City AAP is estimated to be about 600 lb/year or 50 lb/month. The amount used by Lone Star AAP is believed to be on the order of 200-300 lb/month.

c. Use at Full Mobilization

The full mobilization use rate of lead azide at Lake City AAP is approximately 130 lb/month. At Lone Star AAP, about 1200 lb/month of lead azide would be used at full mobilization. Other currently non-operational plants would also use lead azide, if wartime conditions prevailed.

3. Documented or Speculated Occurrences in Air or Water

According to sources at Lake City AAP (Melton, 1978), about 1-2% of the materials used in primer mixes is lost during processing. Thus, losses at Lake City of up to 1 lb/month of lead azide are expected. At full mobilization, the losses would increase to 3-6 lb/month. The effluents containing lead azide are treated with strong base in order to destroy the explosive. The resulting solution is neutralized to form free lead and sent to the industrial waste treatment plant. In this facility, the wastes are treated with alum and lime in order to precipitate the metals. Most of the lead is thus removed as the carbonate ($K_{sp}=3.3\times10^{-14}$). Based on the solubility of lead carbonate, the maximum concentration of lead (from all lead sources including the lead azide) leaving this facility should be <0.04 ppm.

At Lone Star AAP, lead azide losses of 4-6 lb/month would be expected from current operations. At full mobilization, 24-48 lb/month would be lost. These wastes are treated with sodium nitrite and acetic acid to convert the lead azide to lead acetate (USAEHA, 1972). The treated effluent is disposed of in gravel bottom leaching pits. There is a potential for contamination of ground water by percolation of lead acetate from the leaching pits. A new facility to remmove lead from the waste water has recently been installed at Lone Star AAP. This facility should be operational in 1978.

E. Uses in the Civilian Community

1. Production Methodology

Lead azide is reportedly manufactured by the reaction of a lead nitrate solution with a alkaline sodium azide solution in a continuous process (Urbanski, 1965).

$$Pb(NO_3)_2(aq) + 2NaN_3(aq) \longrightarrow Pb(N_3)_2 + 2NaNO_3$$

The process involves continuous addition of the heated reactant solutions to the upper part of a reaction column with concurrent removal of the product, a lead azide suspension, from the bottom. The suspension is transferred to a vacuum filter where the lead azide is collected and the mother liquor removed. The crude lead azide is transferred to a second vacuum filter where it is washed to remove the alkalinity. Both the mother liquor and the wash water are piped directly to a destruction vat for removal of residual lead azide. The product is transferred while still damp to a drying room followed by sifting. The purity of the final product is below 95%. If higher purity is desired, lead acetate is used as a starting material instead of lead nitrate.

2. Manufacturers, Production, and Capacity

Currently there are two U.S. manufacturers of lead azide; The Olin Corporation and E.I. duPont. The Olin Corporation produces lead azide to order in East Alton, Illinois. They possess an estimated capacity of 100,000 lb/yr. Their current production is below capacity due to the limited demand for lead azide. Recent production levels are considered proprietary and are unavailable. Olin manufactures lead azide exclusively for sale. Virtually all their production is eventually used in military ordnance.

E.I. duPont manufactures lead azide in Pompton Lakes, New Jersey. Their production capacity is estimated at 50,000 lb/yr. DuPont also has another 50,000 lb/yr lead azide facility in Parsons, Kansas which is currently not in use. DuPont uses approximately 25,000 lb of their annual production (greater than 50%) for captive manufacture of civilian detonators. Their remaining production is sold for use exclusively in military detonators (E. I. duPont, 1978).

3. Usages

Lead azide is used as a primary explosive in detonators for high explosives (Hawley, 1977). It is estimated that current use of lead azide in military detonators and civilian detonators are roughly of the same magnitude, with military use being a bit larger (E. I. duPont, 1978).

4. Future Trends

Civilian use of lead azide is not expected to change drastically in the future. Any variations in the market will be attributable to military demands (E. I. duPont, 1978).

5. Documented or Speculated Occurrences in the Environment

There are no reports of lead azide occurring as a pollutant in the civilian environment.

F. Comparison of Military and Civilian Usage and Pollution

Lead azide is used exclusively in detonators for military and civilian explosives. At the present, military use of lead azide is slightly greater than civilian use. However during wartime, the military uses virtually all the lead azide produced. Thus at full mobilization, lead azide is a military unique compound.

Under current operating procedures, all the lead azide used by the Army is purchased from the two civilian producers. However, the Army has the capability of producing lead azide at several ammunition plants should the need arise.

All lead azide containing effluents from military uses are reacted with either sodium hydroxide or sodium nitrite and acetic acid. This treatment decomposes the lead azide to non-explosive lead compounds. These compounds are treated by lagooning or in conventional industrial waste treatment plants. Thus, no lead azide enters the environment from the military usage of this compound.

G. Toxicological and Environmental Hazards

1. Toxicity to Man

Depending on the route of entry into the body, lead ions and hydrazoic acid can be liberated from lead azide. Both the lead and the hydrazoic acid are toxic. Their toxicities are discussed in the following sections.

a. Toxicity of Hydrazoic Acid

Hydrazoic acid or the azide ion acts directly on the smooth muscles producing vasodilation. It also inhibits cytochrome oxidase and phosphorylation (Plunkett, 1976). Symptoms of azide poisoning include (Plunkett, 1976):

- irritation of eyes, skin and respiratory tract
- "Nitroglycerine headache"
- decrease in blood pressure
- palpitation
- dyspnea
- dizziness
- weakness
- nausea
- joint aching

b. Toxicity of Lead to Man

Lead salts are absorbed only slowly by the human body. Therefore, their acute toxicity is low (Lambou and Lim, 1970). However, chronic lead poisoning as a result of occupational exposure or ingestion of contaminated food is common. The many symptoms associated with chronic lead poisoning are listed in Table IX-2. The toxicity of lead compounds is influenced by several factors

- solubility of the compound in body fluids
- quantity of lead ingested, inhaled or absorbed
- quantity present in the circulation at one time
- length of time the lead is in contact with body fluids

Lead intake over that which can be eliminated ($\sim$0.28 mg/kg) can be stored and accumulated by the body. It is believed that the stored lead is non-toxic. However, stored lead can be later released into the circulatory system and exhibit toxic reactions.

2. Aquatic Toxicity

The toxicity of lead to the aquatic environment is well documented (Lambou and Lim, 1970). Available bioassay data indicate that lead is more toxic in soft water (<50 ppm $CaCO_3$) than in hard water systems. This difference in toxicity is due to the availability of ionic lead in soft water systems.

Specific data on the aquatic toxicity of lead azide is not available. Due to the insolubility of lead azide in water, it is expected to have a low toxicity toward aquatic organisms. This compound will accumulate in the sediment. Microscopic aquatic organisms have shown to bioaccumulate insoluble lead compounds. The concentration factors range from 700 for benthic algae to 3,000 for zooplankton and 40,000 for phytoplankton (Lambou and Lim, 1970).

Table IX-2. Symptoms of Chronic Lead Poisoning
(Plunkett, 1976)

GENERAL:

Pallor · Weakness · Loss of weight · Lassitude · Malnutrition

GASTROINTESTINAL:

Metallic taste · Increased salivation · Burton's lead line on gums
Pyorrhea · Anorexia, nausea, vomiting · Constipation · Abdominal
colic and tenderness

GENITOURINARY:

Nocturia · Albuminuria and hematuria · Increased bilirubinuria · Secondary
hyperuricemia · Azotemia

NEUROMUSCLAR:

Numbness and tingling of extremities and associated sensory disturbance
Extensor weakness of wrists and ankles; brachial palsy has also been
described
Loss of muscle tone · Tremor · Increased deep-tendon reflexes · Muscular
cramps and aching · Arthralgia · Muscular atrophy

CENTRAL NERVOUS SYSTEM:

Visual disturbances · Headache · Dizziness · Nervousness or depression
Insomnia · Mental confusion and delirium · Convulsions · Coma

Encephalopathy may be acute or chronic; acute usually associated with
blood levels above 120 µg Pb

Retinal hemorrhages and optic neuritis; gray stippling of lead pigment
about the optic disc has also been reported

HEMATOPOIETIC:

Erythrocyte stippling
Hypochromic normocytic anemia
Increased peripheral reticulocytes

3. Toxicity to Invertebrates

The toxicity of the soluble lead chloride to *Daphnia magna* was studied by Biesinger and Christensen (1972). They found an LC50 of 300 ppb and reproductive impairment at 30 ppb.

4. Toxicity to Microorganisms

No specific data on the toxicity of lead azide to microorganisms was retrieved. In general, lead is toxic to aerobic bacteria at a concentration of 1 ppm and to flagellates and infusoria at a concentration of 0.5 ppm (Lambou and Lim, 1970). The decomposition of organic materials by bacteria is inhibited at lead concentrations of 0.1 to 0.5 ppm (Lambou and Lim, 1970).

Results of experimental work by Tornabene and Edwards (1972) indicate that microbial systems are capable of abstracting substantial quantities of lead from sources containing insoluble inorganic lead-salt precipitates. The viability of bacterial cells (*Micrococcus luteus* ATCC 533) exposed to a medium containing lead for one complete growth cycle (48 hrs.) was not seriously affected and virtually all of the lead taken up by the cells was immobilized in the cellular membrane.

5. Phytotoxicity

No phytotoxicity information on lead azide was encountered. However, phytotoxic data on other lead compounds were obtained and may be indirectly related.

The pattern of lead uptake by plants has been rarely studied and little can be concluded about the mechanism involved. The uptake of lead was reported constant with increasing levels of soil lead, until a certain point is reached when uptake becomes unrestricted and rises abruptly (Nicolls *et al.*, 1965). Only soluble lead salts and ionic lead are available to plant roots. The uptake of lead by ryegrass grown in a solution containing lead is shown in Table IX-3 (Hepple, 1972). The total content of lead in roots plus shoots of perennial ryegrass increases with increasing levels in the soil. The roots take up lead readily but pass on only a small proportion to the shoots. Thus, the roots act as a barrier which restricts the movement of lead from the soil through the plant to growing animals. A similar pattern was found by Wallace *et al.* (1971) in their studies on the uptake of lead by bush-bean plants. During winter months when plant growth is low, a considerable increase in the lead content of the ryegrass shoots was observed (Hepple, 1972).

Corn was grown in the field where lead acetate had been soil-applied at eight rates ranging from 0 to 3,200 kg lead/ha. No changes in emergence, plant height, grain yield, color, maturity or other growth differences were observed during the 2-year study (Baumhardt and Welch, 1972).

Five crops (cauliflower, tomatoes, cabbage, strawberries and Valencia oranges) were analyzed for their lead content by Schuck and Locke (1970). These plants revealed little inclinations to absorb lead via their root system (Schuck and Locke, 1970).

Table IX-3. Lead Uptake by Perennial Rygrass Grown in Solution-Culture (Hepple, 1972).

Level of Pb added to solution		Pb content of plants at 14 days after addition of solution			
		Roots		Shoots	
(ppm)	(µg)	(ppm)	(µg)	(ppm)	(µg)
0.4*	400	98	201	3	37
1.0†	12500	3696	9610	104	1055

* In 1 liter of static solution-culture; controlled environment experiment.

† In 12.5 liter of flowing solution-culture; glass-house experiment.

6. Availability of Literature for Phase II

The available literature on the toxicological and environmental properties of lead azide is limited. Most of the information necessary for Phase II will have to come from manufacturers' studies or be inferred from the studies on lead and the azide ion.

H. Regulations and Standards

1. Air and Water Regulations

There are no air and water standards specific for lead azide. However, criteria have been set for lead in potable water and effluents (EPA, 1976). For potable water, the lead content cannot exceed 50 µg/l. Due to the variability of lead solubility and toxicity in different waters, the following criteria have been set for effluents (using the receiving water as a diluent):

- 0.01 times the 96-hour LC50 value expressed as dissolved lead for the most sensitive species

This criteria requires that the 96-hour LC50 tests be performed with the actual water samples and the most sensitive species in the local ecosystem.

2. Human Exposure Standards

No specific standards for lead azide have been set for occupational exposure to this chemical. However, an air standards of 150 µg $(Pb)/m^3$ is recommended (NIOSH, 1977).

3. DOT Labeling Requirements

Lead azide is a class A explosive. Labels on this material should state "Explosive-A" (Federal Register, 1976).

I. Conclusions and Recommendations

The sole use of lead azide is in detonators in both civilian and military explosives. At the present time, civilian and military usage of lead azide is approximately equal. However, during wartime, the military uses virtually all the lead azide produced. Thus under full mobilization production schedules, lead azide is a military unique compound. However, lead azide residues are treated with either sodium hydroxide or sodium nitrite and acetic acid to eliminate the explosive hazards from this compound. Thus little, if any, lead azide enters the environment.

A Phase II study should concentrate mainly on the toxicological effects of lead azide on workers. Any environmental study on lead azide should not only encompass this compound but should include the fate of all other lead compounds used at the Army Ammunition Plants.

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AD

PRELIMINARY PROBLEM DEFINITION STUDY OF 48 MUNITIONS-RELATED CHEMICALS

VOLUME IV PRIMER AND TRACER RELATED CHEMICALS

TACOT

FINAL REPORT

J. F. Kitchens
W. E. Harward III
D. M. Lauter
R. S. Wentsel
R. S. Valentine

April 1978

Supported by:

U. S. ARMY MEDICAL RESEARCH AND DEVELOPMENT COMMAND
Fort Detrick, Frederick, Maryland 21701

Contract No. DAMD17-77-C-7057

COTR: Clarence Wade, Ph.D.

ATLANTIC RESEARCH CORPORATION
Alexandria, Virginia 22314

Approved for Public Release
Distribution Unlimited

The findings of this report are not to be construed as an official Department of the Army position unless so designated by other authorized documents.

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SUMMARY

TACOT is a secondary explosive used in primer mixes where good temperature stability is required. This compound was developed by and is manufactured exclusively by E. I. duPont. The production capacity of and plans for future use of TACOT by duPont are unknown.

The only Army use of TACOT was for a research program at ARRADCOM, Dover. During this program, small amounts of TACOT were evaluated for use in Army primer mixes. No primer mixes containing TACOT were ever put into production. There are no plans for any future Army use of TACOT.

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FOREWORD

This report details the results of a preliminary problem definition study on TACOT. The purpose of this study was to determine the Army's responsibility for conducting further research on TACOT in order to determine its toxicological and environmental hazards so that effluent standards can be recommended. In order to determine the Army's responsibility for further work on TACOT, the military and civilian usage and pollution of this chemical were evaluated. In addition, a preliminary overview of toxicological and environmental hazards was conducted.

TACOT was only one of 48 chemicals evaluated under Phase IA of contract No. DAMD17-77-C-7057. These chemicals are grouped in four categories

- explosives related chemicals
- propellant related chemicals
- pyrotechnics
- primers and tracers

Each category is a major report. Section I of each report is an overview of the military processes which use each chemical and the pollution resulting from the use of these chemicals. The problem definition study reports on each chemical are separable sections of these four reports.

In addition a general methodology report was also prepared. This report describes the search strategy and evaluation methodology utilized for this study.

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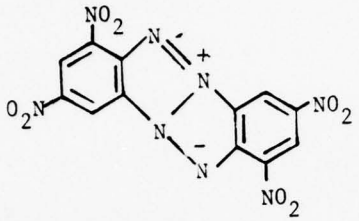
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X. TACOT

A. Alternate Names

TACOT is a nitro derivative of dibenzotetraazapentalene. This compound has the following molecular structure.



The molecular formula of TACOT is $C_{12}H_4N_8O_8$ which corresponds to a molecular weight of 388.21 g/mole. The pertinent alternate names of TACOT are presented below:

CAS Registry No.:	25243-36-1
CA Name (9 CI):	5H-benzotriazolo(2,1-A) benzotriazol-6-ium, 2,4,8,10-tetranitro, hydroxide, inner salt
Synonyms:	TACOT; tetranitrodibenzo-1,3a,4,6a-tetraazapentalene; tetranitro-1,3,5,6-tetraazadibenzocyclo-octatetrene

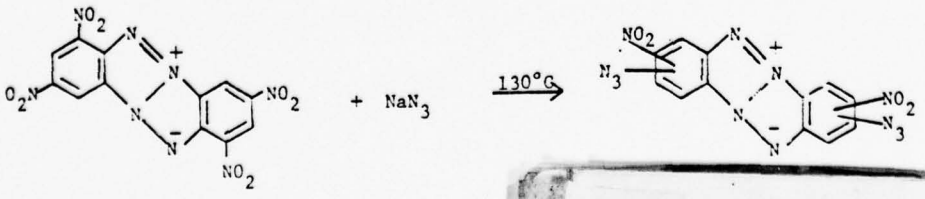
B. Physical Properties

The physical properties of TACOT are presented in Table X-1. The ultraviolet absorption bands of TACOT in various solvents are given in Table X-2.

C. Chemical Properties

1. General Reactions

The reaction chemistry of TACOT has not been extensively investigated. The only reaction that has been reported for TACOT specifically is a nucleophilic substitution by azide anion to yield diazidinitrodibenzo-1,3a,4,6a-tetraazapentalene (Carboni *et al.*, 1967b).



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Table X-1. Physical Properties of TACOT.*

Physical Form @ 20°C:	solid
Color:	orange to red
M.P.:	378°C (decomposes)
Density:	1.84
Heat of Combustion:	3575 cal/g
Solubility:	insoluble in water
	soluble in: sulfuric acid; perchloric acid; glycerin (50°C); dimethylsulfoxide; 20% sodium hydroxide; ammonium hydroxide; morpholine; piperidine; triethanolamine; N,N-dimethylformamide.

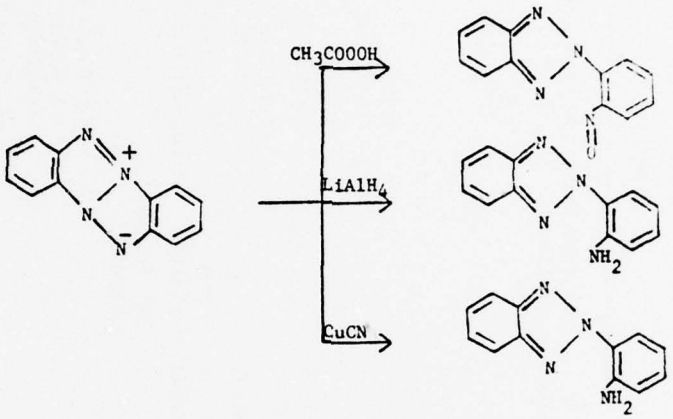
* References: Federoff and Sheffield, 1972; Norwitz and Gordon, 1975.

Table X-2. Ultraviolet Spectra of TACOT in Different Solvents.
(Norwitz and Gordon, 1975)

Solvent & Color	Cut-off Point (nm)	Concentration of TACOT (mg/ml)	Peaks (nm)				
Sulfuric acid orange	200	0.01	475 (ε=7570)	416 (ε=22500)	403 (shoulder) (ε=19800)	345 (shoulder) (ε=6990)	281 (ε=24100)
Perchloric acid orange	205	0.01	486 (ε=32300)			318 (ε=22100)	281 (ε=17900)
Nitric acid	340	0.005	487 (ε=52000)				
Glycerin orange	250	0.0125	496 (ε=15400)			322 (ε=10300)	
Dimethylsulfoxide orange	270	0.005	506 (ε=43500)			324 (ε=25200)	
Ammonium hydroxide amber	220	0.01	~450 (plateau) (peak not clearly defined)			350 (very broad) (ε=23700)	248 (ε=9710)
Morpholine amber	290	0.01	~490 (plateau) (peak not clearly defined)		308 (ε=27400)	340 (plateau) (peak not clearly defined)	
Piperidine amber	330	0.005			395 (broad) (ε=28000)		
Triethanolamine brownish red	280	0.015	479 (ε=16600)			330 (very broad, possibly 2 peaks) (ε=19400)	
N,N-Dimethyl-formamide yellowish with olive green tint	380	0.005	499 (ε=31100)			325 (ε=18600)	

The exact positions of the substitution were not established. Similar reactions between TACOT and other nucleophiles such as cyanide or chloride might be expected.

The reaction chemistry of TACOT's parent compound, dibenzo-1,3a,4,6a-tetraazapentalene has been examined. It undergoes ring opening of the tetraazapentalene system when treated with peracetic acid, lithium aluminum hydride, or cuprous cyanide (Carboni *et al.*, 1967b).



Analogous ring openings might be expected with TACOT.

2. Environmental Reactions

There is no information on possible reactions of TACOT under environmental conditions. TACOT is insoluble in water and, therefore, has no aqueous solution chemistry. No photochemical studies on TACOT have been reported, although spectral shifts as a function of time have been reported (Norwitz and Gordon, 1975).

3. Sampling and Analysis

No reliable methods for quantitative determination of TACOT have been reported. The UV and visible spectra have been recorded in a variety of solvents but the absorption changes slightly with time making spectrophotometric or colorimetric analyses useless (Norwitz and Gordon, 1975).

D. Uses in Army Munitions

1. Purposes

TACOT has not been used in any Army munitions formulations except on a research basis. The only known use was at ARRADCOM, Dover (Seeger, 1978). This use was for a research program in which TACOT was evaluated as a constituent of primer mixes. However, no mix using TACOT was put into production.

2. Quantities Used

A total of 80 lb of TACOT was procured from duPont by ARRADCOM, Dover. Little of the material was used, and essentially the entire 80 lb

remains available. It has been declared surplus by the Army, and duPont plans to buy it back from the Army. No future use of TACOT is planned.

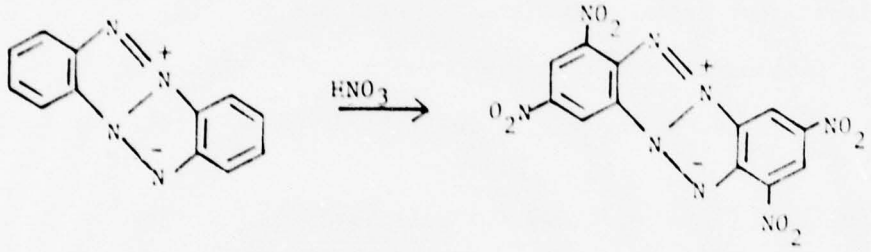
3. Documented or Speculated Occurrences in Air or Water

No significant amount of TACOT has ever been released to the environment as a result of any Army use. The total quantity used at ARRADCOM, Dover, was on the order of a few grams for research purposes. No pollution resulted from this use; no future Army pollution by TACOT is anticipated.

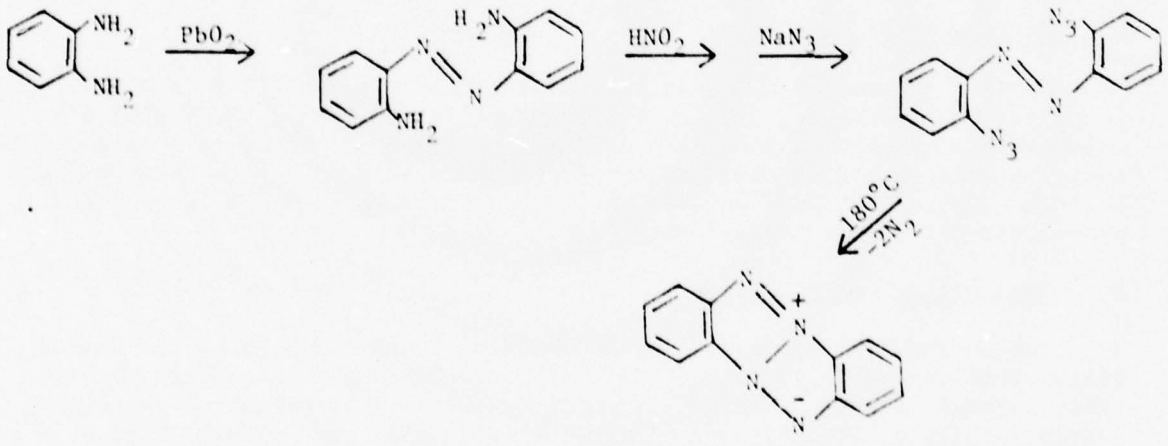
E. Uses in the Civilian Community

1. Production Methodology

TACOT is manufactured by direct nitration of dibenzo-1,3a,4,6a-tetraazapentalene with fuming nitric acid (Norwitz and Gordon, 1975).



Dibenzo-1,3a,4,6a-tetraazapentalene is made by the following reaction sequence from o-phenylenediamine (Carboni *et al*, 1967a).



2. Manufacturers, Production, and Capacity

TACOT is manufactured exclusively by E. I. duPont in Pompton Lakes, New Jersey. Their production figures and capacities are not available. From the data available, it appears that TACOT is a small production item. Quantities produced are estimated to be <1000 lb annually.

3. Usages

TACOT is a secondary high energy explosive. It is used in situations where a high-temperature, heat resistant explosive is needed. The use of this compound is probably limited to high temperature situations such as oil well fires.

4. Future Trends

The future uses of TACOT are uncertain. It is not known if duPont is developing new primer formulations which use TACOT.

5. Documented or Speculated Occurrences in the Environment

There are no reports in the literature on TACOT as an environmental pollutant.

F. Comparison of Civilian and Military Uses and Pollution

The past military uses of TACOT were limited to primer research studies at AARADCOM, Dover. No future Army use of TACOT is planned. TACOT is used and produced by E. I. duPont. Quantities of TACOT produced and used by duPont are uncertain as are future civilian uses of this compound.

G. Environmental Hazards

No data on mammalian, aquatic or microorganism toxicity of TACOT was found in the literature. Due to its insolubility in water, TACOT should be relatively non-toxic to aquatic organisms. Build up of TACOT in aquatic sediment could occur. Microorganism breakdown could lead to a slow disappearance of this compound from the environment. However, fate of TACOT in the ecosystem has not been established.

H. Regulations and Standards

Due to the limited quantities of TACOT produced and used in the United States each year, there are no OSHA or EPA regulations or standards specifically related to this compound. TACOT is a secondary explosive. Therefore, labels for interstate shipment of TACOT should be marked "Class B Explosive".

I. Conclusions and Recommendations

TACOT is not an explosive of military importance. Its use by the military has been for research only. There are no plans for any future use of this

compound by the military. Therefore, no future toxicological or environmental studies on this compound by the Army is warranted

J. References

Carboni, R.A.; Kauer, J.C.; Castle, J.E. and Simmons, H.E. (1967a), "Aromatic Azapentalenes I. Dibenzo-1,3a,4,6a-tetraazapentalene and Dibenzo-1, 3a,6,6a-tetraazapenalene. New Heteroaromatic Systems," *J. Amer. Chem. Soc.*, 89, 2618.

Carboni, R.A.; Kauer, J.C.; Hatchard, W.R. and Harder, R.J. (1967b), "Aromatic Azapentalenes II. Reactions of Monobenzo- and Dibenzo-1,3a,4,6a-tetraazapentalenes," *J. Amer. Chem. Soc.*, 89, 2626.

Federoff, B.T. and Sheffield, D.E. (1972), *Picatinny Arsenal Explosive Handbook Vol. V*, "Dibenzotetraazapentalene and Derivatives," D1185, Picatinny Arsenal TR 2700.

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Seeger, D. (1978), ARRADCOM, Dover, personal communication.

AD

PRELIMINARY PROBLEM DEFINITION STUDY OF 48 MUNITIONS-RELATED CHEMICALS

VOLUME IV PRIMER AND TRACER RELATED CHEMICALS

ACETYLENE BLACK

FINAL REPORT

J. F. Kitchens
W. E. Harward III
D. M. Lauter
R. S. Wentsel
R. S. Valentine

April 1978

Supported by:

U. S. ARMY MEDICAL RESEARCH AND DEVELOPMENT COMMAND
Fort Detrick, Frederick, Maryland 21701

Contract No. DAMD17-77-C-7057

COTR: Clarence Wade, Ph.D.

ATLANTIC RESEARCH CORPORATION
Alexandria, Virginia 22314

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SUMMARY

Civilian use of acetylene black, carbon black and graphite centers on the production of tires and other rubber goods. Several billion lb/year are used for this purpose.

Military uses of acetylene black and carbon black are small, with only 5,000-6,000 lb/year required even at full mobilization. Graphite use by the Army is more substantial at 25,000 lb/year currently and up to 235,000 lb/year at full mobilization.

Military pollution with these carbon materials is less than 200 lb/month. At full mobilization, the potential pollution from military utilization might increase to 1200 lb/month. This level of loss is negligible compared to civilian pollution sources. These carbon materials are all relatively non-toxic. Thus, any further Army study of the environmental or toxic hazards of these materials should be a low priority.

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FOREWORD

This report details the results of a preliminary problem definition study on acetylene black. The purpose of this study was to determine the Army's responsibility for conducting further research on acetylene black in order to determine its toxicological and environmental hazards so that effluent standards can be recommended. In order to determine the Army's responsibility for further work on acetylene black, the military and civilian usage and pollution of this chemical were evaluated. In addition, a preliminary overview of toxicological and environmental hazards was conducted.

Acetylene black was only one of 48 chemicals evaluated under Phase IA of contract No. DAMD17-77-C-7057. These chemicals are grouped in four categories

- explosives related chemicals
- propellant related chemicals
- pyrotechnics
- primers and tracers

Each category is a major report. Section I of each report is an overview of the military processes which use each chemical and the pollution resulting from the use of these chemicals. The problem definition study reports on each chemical are separable sections of these four reports.

In addition, a general methodology report was also prepared. This report describes the search strategy and evaluation methodology utilized for this study.

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XI. ACETYLENE BLACK, CARBON BLACK, GRAPHITE AND RELATED SUBSTANCES

A. Alternate Names

This report covers the various forms of carbon used by the Army in the manufacture of munitions. Included in this document are acetylene black, carbon black and graphite. The pertinent alternate names for these substances are presented in Table XI-1. Sections B, C, and D of this report discuss the physical and chemical properties and civilian manufacture and use of acetylene black, carbon black and graphite, respectively. The military usage and pollution resulting from these substances are discussed in Section E. The toxicological and environmental hazards of these substances are detailed in Section G.

B. Acetylene Black

1. Physical Properties

Relevant physical properties of acetylene black are listed in Table XI-2. Thermal acetylene black is a very high purity carbon black made up of over 99.5% carbon. Impurities include magnesium and silicon at levels of 10 ppm. Acetylene black is composed of carbon particles ranging in size from 50 to 2000 Å. The particles are joined in a chainlike fashion to give acetylene black a microscopic three-dimensional fishnet structure (Kirk and Othmer, 1964).

Acetylene black has an apparent density of 1.2 lb/ft^3 and can be compressed to a maximum density of 20 lb/ft^3. Its high resiliency prevents further compression. Acetylene black also exhibits low electrical resistivity, high conductivity, and resistance to wetting with water (Kirk and Othmer, 1964).

2. Chemical Properties

Acetylene black is chemically inert. It possesses low surface activity and does not act as a gas absorbent or a decolorizing agent (Kirk and Othmer, 1964).

3. Uses in the Civilian Community

a. Production Methodology

Acetylene black is manufactured on a commercial scale by the continuous thermal decomposition of acetylene. Thermolysis is carried out in a retort at 800°C. The reaction is exothermic and the heat generated is used to maintain the reaction. Acetylene black is removed from the bottom and separated from hydrogen without combustion. The separated black is then compressed to the desired degree (Kirk and Othmer, 1964).

Table XI-1. Alternate Names for Acetylene Black, Carbon Black and Graphite.

Carbon Black (Acetylene Black)	
CAS Registry No.:	1333-86-4
Replaces CAS Registry No.:	17375-05-2
Synonyms:	Activated carbon; Carbon activated; Channel black; CI 77266; Columbia carbon; Pigment Black 7; TM-30; Witcoblak No. 100
Graphite	
CAS Registry No.:	7782-42-5
Synonyms:	AG 1500; Aqua dag; ATJ-S graphite; Black lead; Ceylon black lead; CI Pigment Black 10; CI 77265; DC 2; EG 0; Electrographite; E patscalist; EGO; Fortatil 54; Gratdil; Graphite (9CI); Graphitite; GY-70; Hitco HMC 50; Kordeon; Mineral carbon; Plumbago; Plumbago (Graphite); Pyro-Cari 406; Seast 50; Silver graphite; SKLN 1; Stove black; Swedish black lead; Thornel; Thornel 40; Toxline; Vcar 38

Table XI-2. Physical Properties of Acetylene Black (Kirk and Othmer, 1964)

Physical Form @ 20°C:	solid
Color:	black, nigrometer value of 91-95, blue undertone
True density:	1.95 g/cm^3
Electrical Resistivity:	0.135 Ω cm at 1500 psi
Thermal Conductivity:	0.35 BTU at 1040°C

b. Manufacturers, Production, and Capacity

Acetylene black accounts for less than 1% of the total U.S. carbon black production (Serth and Hughes, 1977). The only manufacturer of acetylene black in the United States is the Union Carbide Corp. They operate a plant of unknown capacity in Ashtabula, Ohio.

The Shawinigan Products Corp., a subsidiary of Gulf Oil, currently imports acetylene black from Canada. They are currently constructing an acetylene black plant in Cedar Bayou, Texas which is scheduled to begin operation in 1979. The capacity will be in excess of 10 million pounds per year (Shawinigan, 1978).

c. Usages

There are two major uses of acetylene black. The principal use is in the manufacture of dry cells as a filler material. The second major use is in rubber compounding to produce conductive, non-static rubbers found in tires, hospital materials and antistatic equipment for use in potentially explosive atmospheres.

Minor uses of acetylene black include the production of conductive and antistatic plastics, tapes, greases, and inks (Kirk and Othmer, 1964; Shawinigan, 1978).

d. Future Trends

Acetylene black will continue to be an extremely minor part of the total U.S. carbon black production in the foreseeable future.

4. Documented or Speculated Occurrences in the Environment

There are no reports of acetylene black (differentiated from general carbon blacks) as a pollutant in the air or water.

C. Carbon Black

Carbon blacks are important industrial compounds used primarily as rubber strengthening agents and black pigments. There are five major types of carbon black. In order of importance they are:

- oil furnace carbon black
- thermal carbon black
- channel carbon black
- gas furnace carbon black
- lampblack

All are produced by various thermal decompositions of liquid or gaseous hydrocarbons. Currently only oil furnace black and thermal black are manufactured in the U.S. with oil furnace black accounting for 90% of production.

1. Physical Properties

The physical properties of carbon black varies depending on the specific manufacturing process and conditions used for its formation. All carbon blacks are particulates composed of spherical particles with quasi-graphitic structure. The two physical parameters which determine other characteristics of a particular black are particle size and structure. Oil furnace blacks range from 18 to 60 nm in diameter. Channel blacks are formed in the range of 10 to 30 nm while gas furnace blacks range from 40 to 80 nm. Thermal blacks are the coarsest, ranging from 140 nm to 400 nm. The structure of carbon black is a measurement of the particles tendency to aggregate in a chain-like manner. High structure blacks possess well developed chain structure at the microscopic level. Acetylene black is a specialty carbon black which possesses high structure while channel and thermal blacks are generally low in structure. Oil furnace, blacks which account for most of the domestic carbon black produced, can be made to vary over wide ranges of structure.

Other physical properties such as electrical conductivity, jetness, and compressibility are functions of particle size and structure. High structure carbon blacks are used widely in conductive rubbers while a low structure black will show a high electrical resistivity. Jetness (darkness) increases with decreasing particle size (Kirk and Othmer, 1964; Serth and Hughes, 1977).

2. Chemical Properties

Carbon blacks are composed of between 90% and 99% elemental carbon. Oxygen, hydrogen, and sulfur account for the remaining material. Some organic functional surface groups can be determined chemically including phenolic, quinonic, carboxylic, and lactonic functions. The sulfur may occur as free sulfur or chemically combined. Elemental compositions of various carbon blacks are listed in Table XI-3.

The chemistry of carbon black resembles the chemistry of large polynuclear aromatic hydrocarbons. Carbon black will participate in complexing reactions and reduce weak Lewis acids (Ag^+, Au^{3+}, I_2). It will even undergo electrophilic aromatic substitution (Kirk and Othmer, 1964).

Upon heating carbon black from 600°C to 1500°C, CO_2, CO, and H_2 are evolved. The carbon oxides predominate at lower temperatures but above 1000°C, hydrogen is the predominant product (Kirk and Othmer, 1964).

Table XI-3. Composition of Typical Carbon Blacks
(Serth and Hughes, 1977)

Type	Composition, %			
	Carbon	Oxygen	Hydrogen	Sulfur
Oil furnace blacks				
Super abrasion furnace	97.6	1.01	0.47	0.64
Intermediate super abrasion furnace	97.6	1.17	0.32	0.51
High abrasion furnace	97.9	0.79	0.34	0.59
Fast extruding furnace	98.4	0.58	0.38	0.67
General purpose furnace	98.6	0.21	0.37	0.55
Conductive furnace	97.4	1.18	0.21	0.60
Gas furnace blacks				
Fine furnace	98.2	0.40	0.4	0.01
High modulus furnace	98.8	0.23	0.4	0.23
Semireinforcing furnace	99.2	0.22	0.4	0.00
Thermal blacks				
Fine thermal	99.3	0.10	0.49	0.01
Medium thermal	99.4	0.00	0.36	0.01
Channel blacks				
High color channel	88.0	10.5	0.9	0.57
Low color channel	95.2	3.6	0.6	0.50
Easy processing channel	95.6	3.5	0.6	0.19
Medium flow channel	94.5	4.9	0.5	0.10
Long flow channel	91.6	7.7	0.6	0.12

3. Uses in the Civilian Community

a. Production Methodology

The commercial processes for manufacture of carbon black are listed below in order of importance:

- oil furnace process
- thermal process
- channel process
- gas furnace process
- lamp process

The oil furnace process accounts for approximately 90% of domestic carbon black production. It is a continuous process involving combustion of a vaporized hydrocarbon feed in a natural gas-fired furnace. Preferred feedstock materials are highly aromatic oils which are free of ash, carbon, and water and low in sulfur, asphaltenes, and high molecular weight resins. A basic oil furnace plant consists of the burner, furnace, quench, and collector. Pre-heated air and natural gas are burned to produce a combustion zone with temperatures from 1300°C to 1550°C. The pre-heated (200°C to 370°C) oil feed is injected into this zone to form carbon black. Maximum efficiency is obtained when the heat forming gas-air reaction is as physically far as possible from the carbon forming reaction. The gas stream carries the carbon black in suspension to the quench where it is cooled to ~200°C by direct water sprays. The black is then collected with cyclone collectors and bag filters. Yields are between 35% and 65% depending on the final particle size.

The thermal process is a cyclic process involving cracking of natural gas in a preheated furnace. The furnace (typical dimensions are outer diameter 4.25m, height 7.5m) is filled with a checkerwork pattern of silica brick. The bricks are heated above 870°C and natural gas is passed into the furnace where it is cracked to carbon and hydrogen. Approximately 50% of the carbon formed stays on the brickwork while the remainder is removed from the furnace by the gas stream. The product is passed through a water cooler and collected with bag filters. After a period of time the natural gas flow is replaced with a natural gas/air/hydrogen mixture. This mixture is used to ignite the residual carbon on the bricks to reheat them. After the bricks have again reached a temperature above 870°C, natural gas is reintroduced to begin the cycle again (Lowenheim and Moran, 1975; Kirk and Othmer, 1964).

The lamp process, channel process, and gas furnace process are no longer used in the United States. Reviews on these processes are available (Kirk and Othmer, 1964).

b. Manufacturers, Production, and Capacity

Domestic manufacturers of carbon black are listed in Table XI-4

Table XI-4. U.S. Manufacture of Carbon Black (S.R.I., 1977).

		Capacity (10^6 lb/yr)	Process
Ashland Oil, Inc.			
Ashland Chem. Co., div.			
Carbon Black and Synthetic Rubber Div.	Aransas Pass, TX	150	F
	Belpre, OH	100	F
	Iberia, LA	255	F
	Mojave, CA	60	F
	Shamrock, TX	105	F
Cabot Corp.	Big Spring, TX	238	F
	Franklin, LA	215	F
	Pampa, TX	53	F
	Villa Platte, LA	243	F
	Waverly, WV	163	F
Cities Service Co.			
Chems. Group			
Columbian Chems., div.	Conroe, TX	97	F
	El Dorado, AR	82	F
	Eola, LA	70	F
	Mojave, CA	53	F
	Moundsville, WV	157	F
	North Bend, LA	157	F
	North Bend, LA	55	T
	Seagraves, TX	90	F
	Ulysses, KS	50	F
Continental Carbon Co.	Bakersfield, CA	77	F
	Ponca City, OK	135	F
	Sunray, TX	95	F
	Westlake, LA	120	F
Harmon Colors Corp.	Haledon, NJ	n.a.	
J.M. Huber Corp.	Baytown, TX	258	F
	Borger, TX	139	F
	Borger, TX	40	T
Internat'l Minerals & Chem. Corp.			
IMC Chem. Group, Inc., subsid.			
Thermatomic Carbon Co. Div.	Sterlington, LA	130	T
Phillips Petroleum Co.			
Rubber Chems. Div.	Borger, TX	287	F
	Orange, TX	115	F
	Toledo, OH	70	F
Sid Richardson Carbon Co.	Addis, LA	102	F
	Big Spring, TX	110	F
	TOTAL	4071	

F = Oil furnace
T = Thermal

with their plant sites and capacities. Domestic production since 1970 is listed in Table XI-5.

Table XI-5. Historical Production of Carbon Black (Predicasts, 1977).

Year	1970	1971	1972	1973	1974	1975	1976	1977
10^6 lbs	2,931	3,017	3,201	3,500	3,355	2,742	3,004	Not available

c. Usages

The rubber industry accounts for 91% of the domestically produced carbon black. An estimated sixty percent of this product is used in tires. The remainder is used in a variety of rubber products including inner tubes, conveyor belts, fan belts, electrical insulation, hoses, and gaskets. Paint and printing ink manufacture uses approximately 3% of the domestic production. The remaining 6% is equally divided between export and miscellaneous applications including plastics, specialty papers, dry cells, insulation, carbon brushes and electrodes, and as a grinding agent (S.R.I., 1977; Kirk and Othmer, 1964).

d. Future Trends

The carbon black market is determined by demand from the rubber industry. Serth and Hughes (1977) predicted a growth rate between 2% and 2.5% for carbon black through 1980 with a projected 1980 production of 4.15 billion pounds.

e. Documented or Speculated Occurrences in the Environment

Serth and Hughes (1977) estimated the total carbon black emission from U.S. production at 4.5 million pounds per year. These emissions are as particulate matter vented to the air. Due to the geographical locations of U.S. carbon black plants, carbon black emissions occur primarily in Texas and Louisiana.

D. Graphite

The term graphite is used for both naturally occurring graphite (natural graphite) and manufactured graphite (synthetic graphite). Both possess a crystal structure composed of layered planes of polynuclear aromatic bonds as in Figure XI-1.

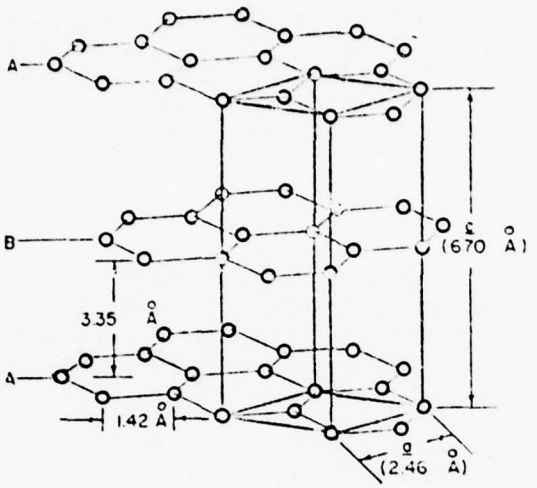


Figure XI-1. Crystal Structure of Graphite
(Kirk and Othmer, 1964).

1. Physical Properties

Representative physical properties for two common grades of synthetic graphite are given in Table XI-6. Mold stock is a medium to fine-grained grade used in crucibles and molds. The electrode grade graphite is used for a large electrothermic electrode.

Table XI-6. Typical Properties of Synthetic Graphite
(Kirk and Othmer, 1964).

	Mold Stock	Electrode
Particle size range	<0.02 in	<0.25 in
Apparent density	1.70 g/cm^3	1.55 g/cm^3
Total porosity	26%	31%
Rockwell hardness	R-12	R-15
Specific heat at 1500°C	0.45 cal/g	0.45 cal/g
at 2500°C	0.16 cal/g	0.16 cal/g

Natural graphite is a relatively soft, steel gray to black colored solid. It has a soft greasy feel. The specific gravity of natural graphite ranges from 2.0 to 2.5 g/cm^3 (Hawley, 1977). Other properties of natural graphite are its electrical conductivity, lubricity, solubility in molten iron, thermal conductivity, and resistance to thermal fatigue. Graphite is also hydrophobic, forms emulsions, carries a negative charge, and is diamagnetic (Kirk and Othmer, 1964).

2. Chemical Properties

Both natural and synthetic graphite are very unreactive and are chemically inert under environmental conditions. At high temperatures graphite will react with a number of chemicals. Above 800°C, graphite reacts with water vapor and carbon oxides. Many metals and their oxides will form carbides with graphite at 1500°C (Kirk and Othmer, 1964).

3. Uses in the Civilian Community

a. Production Methodology

Figure XI-2 is an outline of a generalized process for producing graphite of large dimensions for structural or furnace electrode applications. The raw materials are classified as product or process materials. Product raw materials, which include filters, binders, and additives, are incorporated into the graphite while process materials are essential to the process although they don't enter the product. The process begins with the mixing of the raw carbon filler, binders, and additives in a heated mixer. The mix is shaped using large mechanical or hydraulic presses to form what is called green carbon bodies. The green bodies are inspected and then baked. Most furnaces are either gas-fired or oil-fired. Following baking the product is inspected electrically and physically. The baked carbon is then placed in an electrically heated furnace, heated to between 2200°C and 3200°C, and cooled over a period of days to yield graphite.

b. Manufacturers, Production and Capacity

The major domestic producers of synthetic and natural graphite are listed with their locations in Tables XI-7 and XI-8. Exact figures for current production or capacities for graphite production were not available. The current domestic production of natural graphite is on a scale of hundreds of millions of pounds per year (Predicasts, 1977) while synthetic graphite is produced on a scale of millions of pounds per year (Carborundum Corp., 1978).

c. Usages

Domestic consumption of natural graphite in the past is listed in Table XI-9.

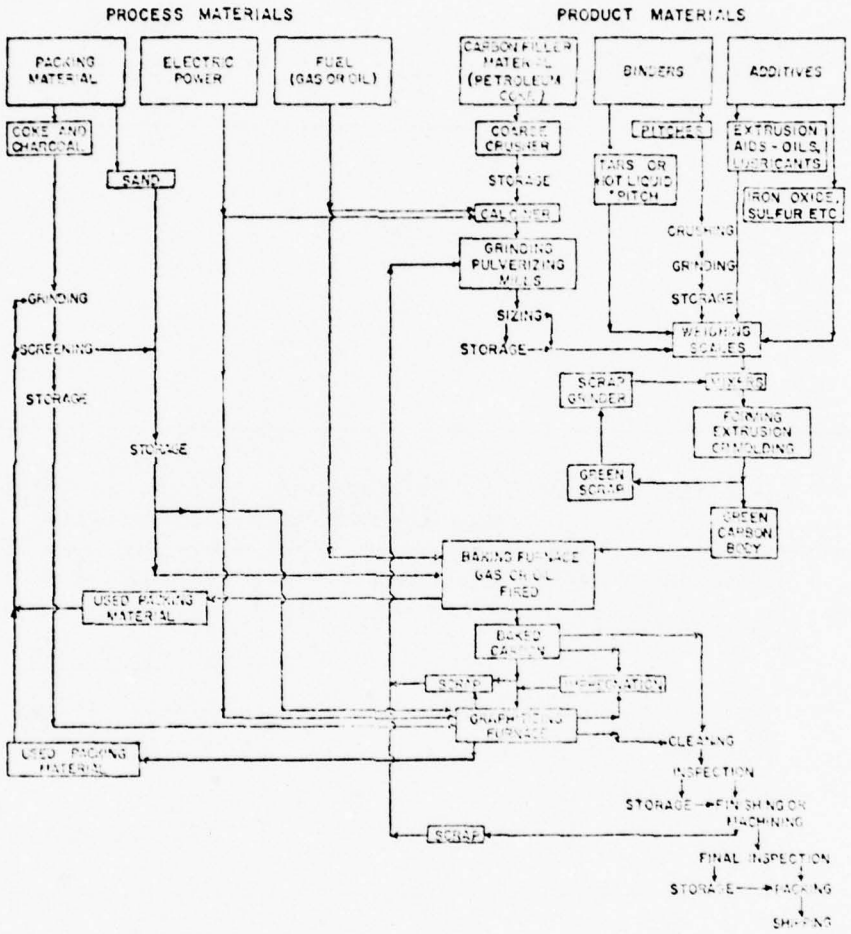


Figure XI-2. Generalized Process for Synthetic Graphite (Kirk and Othmer, 1964)

Table XI-7. Major U.S. Producers of Natural Graphite
(communications with producers)

Asbury Graphite Mills, Inc.	Asbury, NJ
Cummings-Moore Graphite Co.	Detroit, MI
Joseph Dixon Crucible Corp.	Jersey City, NJ
Southwestern Graphite	Burnett, TX
Superior Graphite	Chicago, IL
Wickes Engineered Materials Div.	Saginaw, MI

Table XI-8. Major U.S. Manufacturers of Synthetic Graphite
(communications with manufacturers)

AirCo Speer Carbon-Graphite	St. Marys, PA
The Carborundum Co.	Solon, OH
	Niagara Falls, NY
Great Lakes Carbon Corp.	Niagara Falls, NY
Stackpole Carbon Co.	St. Marys, PA
Union Carbide Corp.	
Carbon Products Div.	Niagara Falls, NY

Table XI-9. Domestic Consumption of Natural Graphite Since 1970 (Predicasts, 1977).

Year	1970	1971	1972	1973	1974	1975	1976	1977
10^6 lbs	66	78	96	125	130	108	--	--

A breakdown of the various uses of natural graphite is presented in Table XI-10.

Table XI-10. Domestic Use of Natural Graphite in 1975 (Predicasts, 1977).

Use	Tons	% of Total Use
Primary iron and steel industry	17,970	33%
Iron and steel foundries	9,710	18%
Nonclay refractories	9,038	17%
Laboratory and scientific instruments	4,215	7.8%
Lubricants	3,138	5.8%
Brake linings	1,553	2.9%
Carbon products	989	1.8%
Pencils	878	1.6%
Storage batteries	691	1.3%
Rubber products	228	0.4%
Miscellaneous	5,690	10.5%

Synthetic graphite is used mainly in electrical applications. Other uses are found in the chemical, metallurgical, nuclear, and aerospace industries. These applications include baked carbon electrodes for the aluminum industry, graphite electrodes used in the manufacture of stainless steel, ferroalloys, and phosphorus, in calcium carbide and ferroalloy production, in electrolytic anodes, for molds, crucibles, other metallurgic uses, and nuclear reactor applications, arc carbons, structural carbons, specialty carbons, and electrical brushes (Kirk and Othmer, 1964).

d. Future Trends

The market for graphite is strong and no decline is expected. Use of natural graphite is expected to continue to exceed that of synthetic

graphite due to its lower cost (Joseph Dixon Crucible Comp., 1978).

4. Documented or Speculated Occurrences in the Environment

Natural graphite is found throughout the world in Ceylon, Korea, Europe and North America. No information on the artificial introduction of graphite to the environment was retrieved.

E. Uses in Army Munitions

1. Purpose

Acetylene black and other forms of carbon black as well as graphite are used as minor constituents of propellants, pyrotechnic and primer mixes. The function of these materials is to act as a pigment and/or to provide a protective coating or glaze to the surface of these items. Formulations specifying graphite or carbon blacks are listed below:

Item	Facility	Form	% in Formulation
CBI Powder	RAAP	Graphite	0.5
HES 6706-1	RAAP	Graphite	0.03
IMR 1050	RAAP	Graphite	0.4
M-10	RAAP	Graphite	0.25
AAH Casting Powder	RAAP	Graphite	0.03±0.06
ARP Casting Powder	RAAP	Graphite	0.04±0.01
M7	RAAP	Carbon Black	0.6
M7 for TOW	RAAP	Carbon Black	1.2
M26	RAAP	Graphite	0.3±0.1
M26E1	RAAP	Graphite	0.3±0.1
PNJ Casting Powder	RAAP	Graphite	0.34
NOSIH-AA-6	RAAP	Carbon Black	0.05
M30	RAAP	Graphite	0.2
M30A2	RAAP	Graphite	0.15
PNJ for TOW	RAAP	Graphite	0.03
Bermite grain	RAAP	Carbon Black	0.03
Starter Mix XXVI	PBA	Carbon Black	13.5±0.2
Ignition Mix, Sustainer I	PBA	Carbon Black	2±0.2
Ignition Mix, Sustainer II	PBA	Carbon Black	2±0.2
Fuel Mix (Smoke Pot)	PBA	Carbon Black	2±0.2
Primer Mix FA874	LCAAP	Acetylene Black	0.5

2. Quantities Used

a. Historical Use

Based upon the production history at Radford AAP (Watts, 1978), the amount of carbon materials used over the period 1968-1977 is as follows:

	lb/year used
Graphite	8,000-45,000
Carbon Black	430-2,600
Acetylene Black	150-172*

*1975-1977 only

Pine Bluff arsenal has not produced formulations requiring carbon black in recent years (Aikman, 1978).

Lake City AAP procured 150 lb of acetylene black in 1977. None was purchased in either 1975 or 1976.

b. Current Use

The current use rate of carbon materials at Radford AAP is given below:

Graphite	35.000 lb/year
Carbon Black	430 lb/year
Acetylene Balck	150 lb/year

These values are based upon 1977 production data.

The most recent use of acetylene black at Lake City AAP was 150 lb in 1977.

c. Use at Full Mobilization

The estimated mobilization use rates of graphite, carbon black and acetylene black are given below:

Graphite (RAAP)	235,000 lb/year
Carbon Black (RAAP)	4,300 lb/year
Acetylene Black (RAAP)	1,000 lb/year
Acetylene Black (LCAAP)	400 lb/year

3. Documented or Speculated Occurrences in Air and Water

The major losses of carbon materials are associated with operations at Radford AAP. At current use rates, the anticipated losses at Radford AAP are given below:

Material	Loss, lb/year	loss, lb/month
Graphite	2100	175
Carbon Black	26	2.2
Acetylene Black	9	0.8

Losses of acetylene black at Lake City AAP are estimated at 0.1 lb/month, which is negligible compared to losses at Radford AAP.

At full mobilization at Radford AAP, the process losses would increase as follows:

Graphite	1175 lb/month
Carbon Black	22 lb/month
Acetylene Black	5 lb/month

Since carbon is not water soluble, only 1/3 to 1/2 of this material would enter the environment. The remainder would be collected in filters and destroyed by combustion at the Radford AAP burning grounds.

F. Comparison of Civilian and Military Uses and Pollution

1. Acetylene Black

Acetylene black is produced in the United States by Union Carbide Corp. Their production capacity is not know, but is probably in excess of 10 million lb/year. Another company, Shawinigan Products Corp. expects to put a new plant for manufacture of acetylene black into operation in 1979. This plant will have a capacity in excess of 10 million lb/year.

Acetylene black is used primarily in dry cells and the production of rubber materials. Domestic production plus imports result in current use rates of about 15 million lb/year in the civilian economy. The use of acetylene black represents only about 1% of the total use of carbon blacks in the United States.

Military use of acetylene black is currently on the order of 300 lb/year. Use of this material at full mobilization would rise to about 1400 lb/year, less than 0.1% of the civilian uses. As in the civilian sector, military uses of acetylene black represent less than 1% of total use of carbon blacks and graphites.

Losses of acetylene black to the environment through military operations are only about 10 lb/year currently. Losses would rise to about 60 lb/year at full mobilization. These amounts are negligible compared to civilian pollution through disposal of dry cells, tires and other rubber goods.

2. Carbon Blacks

Carbon blacks are produced by numerous manufacturers in the United States. Total production exceeds 4 billion lb/year. About 80% of this is produced by the oil furnace process.

The rubber industry uses over 90% of the carbon black produced. About 60% of this amount goes into tires, the remainder into other rubber

goods. The other 10% is used in paint and printing inks and specialty uses.

Military use of carbon blacks is currently about 430 lb/year. At full mobilization, usage would rise to over 4000 lb/year. Losses of carbon black to the environment are about 22 lb/year at current use rates. At full mobilization, these losses would increase to 260 lb/year. This loss is negligible compared to civilian sources of pollution with carbon black through normal disposal of tires and other rubber goods.

3. Graphite

Graphite is manufactured either from natural sources or synthetically. A dozen plants produce over 100 million lb/year of this material. Production of natural graphite exceeds production of synthetic graphite by a factor of 10 or more.

The major uses of graphite in the civilian economy are in the primary iron and steel industry, foundries, and in production of refractory materials. There are numerous smaller civilian uses.

Military use of graphite is in a glaze or protective coating on propellant particles. The use of graphite is substantially higher than that of other carbons at 38,000 lb/year. At full mobilization, 235,000 lb/year would be required.

Losses of graphite to the environment from military operations is on the order of 2100 lb/year. At full mobilization, losses of 14,000 lb/year would be expected. As with the other carbons, this amount is negligible compared to civilian losses.

G. Toxicological and Environmental Hazards

1. Toxicity to Mammals

Carbon black has a very low oral toxicity to mammals and is used as a food coloring (Nau *et al.*, 1960). Nau *et al.* (1976) found that skin applications of carbon black and ingestion of 10% carbon black in the food produced no toxic effects in mice. However, Nau *et al.* (1976) did observe that the inhalation of carbon black did produce moderate to severe perifocal emphysema in monkeys. An intravenous LD50 for carbon black in mice was established at 440 mg/kg (NIOSH, 1977).

Studies on the toxic effects of carbon black to workers have shown a low toxicity. Ingalls and Risquez-Irabarren (1961) found employees in the carbon black industry had a low rate of cancer. Of workers exposed to carbon black dust for an average of 19 years, 20% had pneumoconiotic lesions (Cocarla *et al.*, 1976).

2. Aquatic Toxicity

The aquatic toxicity of carbon black should be similar to suspended soil particles in water. Suspended particles may clog fish gills and harm other aquatic organisms. In high levels, particles can cut down on light penetration, temperature and soluble products. Thus, they can have a drastic impact on aquatic systems. The Water Quality Criteria 1972 (EPA, 1973) reported that 25 ppm of suspended solids do not have harmful effects on fish, and they recommended a moderate level of protection at 80 ppm.

3. Phytotoxicity

Heavy discharges of carbon black into the environment may act as an aerological agent directly upon the foliage of susceptible plants causing disease. Dochinger (1968) reported that gaseous dispersoids having a particle size of 0.3μ or less cause chlorotic dwarf disease to eastern white pine (*Pinus strobus* L.) with characteristic stunted growth and mottled foliage.

4. Availability of Literature for Phase II

Carbon blacks and graphite are widely used throughout the civilian community. A large number of studies have been conducted on the health and environmental effects of carbon blacks and graphite. Thus, there is a large amount of literature available for a Phase II study.

H. Regulations and Standards

The threshold limit value for air exposure to carbon black is 3.5 mg (C)/m^3 (Federal Register, 1974). A study of incidence of all forms of cancer on employees of a carbon black plant showed the death rate from cancer to be comparatively low (American Conference of Governmental Industrial Hygienists, 1977). The activity of some carcinogens may be inhibited by carbon black (American Conference of Governmental Industrial Hygienists, 1977).

I. Conclusions and Recommendations

Military use of acetylene black, carbon blacks and graphite represents only a fraction of 1% of civilian use of these materials. Military pollution sources are even smaller relative to civilian sources. Civilian disposal of tires and rubber goods leads to widespread dispersal of large quantities of carbon blacks.

These carbon materials exhibit low toxicity to all forms of life. They are inert, thus their toxic affects tend to be physical rather than chemical.

The very low military use rate and low toxicity of carbon materials leads to the conclusion that no further Army study of environmental or toxic hazards is warranted at this time.

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AD

PRELIMINARY PROBLEM DEFINITION STUDY OF 48 MUNITIONS-RELATED CHEMICALS

VOLUME IV PRIMER AND TRACER RELATED CHEMICALS

MAGNESIUM

FINAL REPORT

J. F. Kitchens
W. E. Harward III
D. M. Lauter
R. S. Wentsel
R. S. Valentine

April 1978

Supported by:

U. S. ARMY MEDICAL RESEARCH AND DEVELOPMENT COMMAND
Fort Detrick, Frederick, Maryland 21701

Contract No. DAMD17-77-C-7057

COTR: Clarence Wade, Ph.D.

ATLANTIC RESEARCH CORPORATION
Alexandria, Virginia 22314

Approved for Public Release
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The findings of this report are not to be construed as an official Department of the Army position unless so designated by other authorized documents.

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SUMMARY

Magnesium is a highly reactive metal. Due to its stong reducing ability, magnesium is used in a wide variety of products. The military uses magnesium in flares and signal devices. Current military use of this element is ∿200,000 lb/year. This usage will increase to ∿8 million lb/year at full mobilization. Greater than 90% of the current military use of magnesium is in flares produced at Longhorn AAP. The environmental pollution resulting from the manufacture of these flares is negligible. However, magnesium oxide will be released into the environment as the result of use of these flares.

The civilian production of magnesium is ∿438 million lb/year. Of this 438 million lb, ∿20 million lbs is powdered magnesium. The major civilian uses of magnesium are in flares, flash photography and in steel where it acts as a desulfurization agent. The pollution resulting from civilian production and usage of magnesium has not been quantitated.

Magnesium and magnesium salts are relatively non-toxic to living organisms with effects observed only at high doses. For example, the 3 week LC50 for *Daphnia magna* exposed to magnesium chloride is 190 ppm.

The Army is a major user of magnesium powder. However, in comparison with the total amount of magnesium produced and used in the United States each year, the current military use of magnesium is small (∿0.04%). At full mobilization this use rate would only increase to 1.6% of the civilian production of this metal. In view of the small percentage of magnesium used by the Army and the low toxicity of this metal and its salts, magnesium should be a low priority chemical for inclusion in the Phase II detailed toxicological and environmental study.

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FOREWORD

This report details the results of a preliminary problem definition study on magnesium. The purpose of this study was to determine the Army's responsibility for conducting further research on magnesium in order to determine its toxicological and environmental hazards so that effluent standards can be recommended. In order to determine the Army's responsibility for further work on magnesium, the military and civilian usage and pollution of this chemical were evaluated. In addition, a preliminary overview of toxicological and environmental hazards was conducted.

Magnesium was only one of 48 chemicals evaluated under Phase IA of contract No. DAMD17-77-C-7057. These chemicals are grouped in four categories

- explosives related chemicals
- propellant related chemicals
- pyrotechnics
- primers and tracers

Each category is a major report. Section I of each report is an overview of the military processes which use each chemical and the pollution resulting from the use of these chemicals. The problem definition study reports on each chemical are separable sections of these four reports.

In addition a general methodology report was also prepared. This report describes the search strategy and evaluation methodology utilized for this study.

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XII. MAGNESIUM

A. Alternate Names

Magnesium is a group IIA metal. It has an atomic number of 12. The electronic arrangement in the free atom is $1s^2\ 2s^2\ 2p^6\ 3s^2$. This configuration results in a valency of 2 which explains the chemical reactivity of the free metal. Magnesium exists in three isotopic forms

- mass number of 24; relative abundance of 77%
- mass number of 25; relative abundance of 11.5%
- mass number of 26; relative abundance of 11.1%

The average mass of this element is 24.312 g/mole.

Alternate names for metallic magnesium are listed below:

CAS Registry No.:	7439-95-4
Replaces CAS Registry No:	14147-08-1
CA Name (8 CI):	Magnesium
Wiswesser Line Notation:	Mg

B. Physical Properties

The physical properties of magnesium metal are presented in Table XII-1.

C. Chemical Properties

1. General Reactions

Elemental magnesium is an exceptionally strong reducing agent. Its reactivity is held in check by a protective film of oxide or nitride which forms spontaneously in air.

$$2Mg + O_2 \longrightarrow 2MgO$$
$$3Mg + N_2 \longrightarrow Mg_3N_2$$

The high ratio of surface area to mass of powdered Mg maintains its high reactivity. Magnesium powder will ignite easily. If the concentration of powder is above the lower explosive unit, a violent explosion occurs.

Magnesium metal reacts readily with water to form the insoluble hydroxide and hydrogen gas.

$$Mg + 2H_2O \longrightarrow Mg(OH)_2 + H_2\uparrow$$

Hydrogen halides attack magnesium rapidly.

$$Mg + 2HX \longrightarrow MgX_2 + H_2$$

Table XII-1. Physical Properties of Magnesium.*

Physical Form @ 20°C:	solid
Color:	silver white
Crystal structure:	close packed hexagonal
M.P.:	650°C
B.P.:	1110 ± 10°C
Density, g/cm^3:	1.74 @ 20°C
	1.64 @ 650°C (solid)
	1.57 @ 650°C (liquid)
	1.54 @ 700°C
Specific Heat, cal/g-°C:	0.245 @ 20°C
	0.275 @ 300°C
	0.325 @ 650°C (solid)
	0.316 @ 650°C (liquid)
Thermal Conductivity, cal/(sec)(cm^2) (C/cm) @ 20°C:	0.37
Solubility:	insoluble in cold water
	slightly soluble in hot water - decomposes to $Mg(OH)_2$
	soluble in mineral acids except CrO_3
	insoluble in alkali

*Reference: Kirk and Othmer, 1967; Hodgman, 1963.

Metallic magnesium combines directly with the free halogens.

$$Mg + Cl_2 \longrightarrow MgCl_2$$

It also reacts with elemental phosphorous and sulfur at elevated temperatures.

$$Mg + P \longrightarrow Mg\ P$$
$$Mg + S \longrightarrow Mg\ S$$

The reduction of other metals including Fe, Ti and U can be achieved with metallic magnesium leading to a number of industrial applications.

$$Mg + FeS \longrightarrow MgS + Fe$$
$$2Mg + TiCl_4 \longrightarrow 2MgCl_2 + Ti$$
$$2Mg + UF_4 \longrightarrow U + 2MgF_2$$

Magnesium metal reacts with alkyl halides to form Grignard reagents which are stable in ethyl ether.

$$Mg + RCl \longrightarrow RMgCl$$

Grignard reagents are widely used in synthetic chemistry as alkylating agents. They decompose in water and other protic solvents to the corresponding hydrocarbons. Grignard reagents also react spontaneously with electrophiles.

2. Environmental Reactions

Magnesium powder spontaneously forms the oxide and nitride when exposed to the atmosphere.

$$Mg + air \longrightarrow MgO + Mg_3N_2$$

If there is appreciable moisture in the air the oxide is hydrated and the nitride decomposes to ammonia and hydroxide.

$$MgO + H_2O \longrightarrow Mg(OH)_2$$
$$Mg_3N_2 + 6H_2O \longrightarrow 3Mg(OH)_2 + 2NH_3$$

Magnesium hydroxide is formed directly when the metal is placed in water.

$$Mg + 2H_2O \longrightarrow Mg(OH)_2 + H_2$$

3. Sampling and Analysis

Magnesium may be determined in a number of ways:

- Atomic absorption spectrophotometry. Magnesium is measured at a wavelength of 285.2 nm with a reported sensitivity of 7 µg Mg/l giving 1% absorption (Franson, 1975).

- Gravimetric analysis. Magnesium is quantitatively precipitated by treatment with diammonium hydrogen phosphate to give magnesium ammonium phosphate. This material is ignited to magnesium pyrophosphate which is weighted (Franson, 1975).

- Total magnesium and calcium in a sample may be determined by EDTA complexiometric titration. Calcium may then be determined separately and the magnesium calculated as the difference (Franson, 1975).

D. Uses in Army Munitions

1. Purpose

Magnesium is used as a fuel in tracer, igniter, signal flare and pyrotechnic compositions. At Lake City AAP, magnesium is a component of the following formulations:

	% Magnesium in Formulation
Igniter R284	28±1
Igniter I-276	15±1
Igniter I-508	14.2±1
Igniter I-548	15±2
Igniter I-560	27.5±1
Igniter I-559	41.5±1
Igniter I-280	15±1
R-20C	21.6±1
R-403	25±2
R-505	25±1
R-321	26±1
R-256	26.7±1
R-512	46.2

Magnesium is also used at Lone Star AAP to make tracer projectiles. At Longhorn AAP, magnesium is used to make tracers as well as flares and signal devices.

2. Quantities Used

a. Historical Use

Magnesium powder is used in relatively large quantities in munitions manufacture. The quantities of this material procured by LCAAP during the period 1975-1977 are listed below:

1975	25,030 lb
1976	51,725 lb
1977	18,250 lb

This corresponds to an average use rate of 31,700 lb/year or 2640 lb/month.

Based upon June, 1974 usage, LSAAP used magnesium in 1974 at the rate of 26,640 lb/year or 2,220 lb/month (USAEHA, 1974).

Longhorn AAP used 169,818 lb of magnesium in 1977 (Marshall, 1978). They currently have in stock some 450,000 lb of magnesium for future use.

b. Current Use

The current rate of usage of magnesium at the various AAP's is listed below:

	Magnesium currently used	
LCAAP	1,521 lb/month	18,252 lb/year
LSAAP	1,110 "	13,320 "
LAAP	14,152 "	169,824 "

Longhorn AAP is the major current user of magnesium. The use figure for LSAAP is an estimate based upon the current operating factor compared to that of 1974.

c. Use at Full Mobilization

At full mobilization, the approximate usage of magnesium would be as follows:

	Full Mobilization Use Rate of Magnesium	
LCAAP	7,500 lb/month	90,000 lb/year
LSAAP	5,500 "	66,000 "
LAAP	632,500 "	7,590,000 "

3. Documented or Speculated Occurrences in Air or Water

The losses associated with pyrotechnic, primer and tracer manufacture are generally about 0.5-2% of the amount handled (Melton, 1978; Alexander, 1978; Maley, 1978). On this basis, current losses of magnesium would be as listed below:

	Current Losses of Magnesium lb/month
LCAAP	15-30
LSAAP	11-22
LAAP	71-142

At full mobilization, the losses would increase to the following levels:

	Full Mobilization Losses of Magnesium, lb/month
LCAAP	75-100
LSAAP	55-110
LAAP	3000-6000

The major contributor to magnesium loss is LAAP. Wastes at LAAP are collected in sumps and transported to an evaporation pond. The pond bottom is heavily contaminated with munitions ingredients. Some leaching into groundwater is suspected, but has not been detected (USAEHA, 1972).

E. Uses in the Civilian Community

1. Production Methodology

Powdered magnesium is produced by mechanical grinding of magnesium ingots (Reade Manufacturing Co., 1978). Magnesium may be manufactured either by electrolytic or thermal reduction of magnesium salts (Kirk and Othmer, 1968).

The electrolytic reduction, known as the Dow process, begins with precipitation of magnesium hydroxide from seawater by the addition of lime. The hydroxide is treated with hydrochloric acid to form magnesium chloride which is isolated as the hydrate $MgCl_2 \cdot 1.5H_2O$. This hydrate is added to a bath of fused chlorides, the residual water is removed, and the electrolysis is carried out producing elemental magnesium and chlorine. The chlorine is chemically recycled to hydrochloric acid used in the earlier stages of the process.

The second commercial process, known as the Pidgeon process, involves reduction of calcined dolomite with ferrosilicon.

$$2MgO \cdot CaO + Si(Fe) \longrightarrow 2Mg + (CaO)_2 \cdot SiO_2(Fe)$$

A flowchart of the Pidgeon process is shown in Figure XII-1.

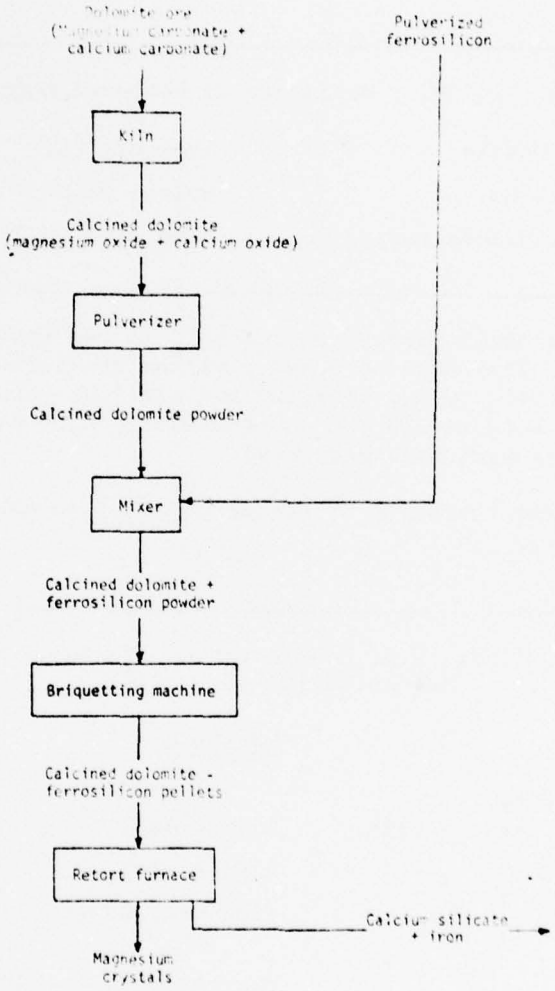


Figure XII-1. Pidgeon Process for Magnesium. (Kirk and Othmer, 1968)

2. Manufacturers, Production, and Capacity

The U.S. producers of powdered magnesium metal are listed in Table XII-2.

Table XII-2. U.S. Producers of Powdered Magnesium

Hart Metals	Tamaqua, Pa.
Pesses Co.	Solon, Ohio
Reade Manufacturing Co.	Lakehurst, N.J.

The Pesses Co. sells their product exclusively to the steel industry for use in desulfurization. They have no other civilian or military outlet. Reade Manufacturing sells both to the military and civilian market. They have a production capacity between 300 and 400 thousand pounds of powdered Mg per month (communications with manufacturers).

The U.S. manufacturers of magnesium metal in non-powder form are listed in Table XII-3.

Table XII-3. U.S. Manufacturers of Non-powdered Magnesium (S.R.I., 1977)

Manufacturer	Location	Annual Capacity in Thousand Tons
Aluminum Co. of America Northwest Alloys, Inc., subsid.	Addy, Wash.	24
American Magnesium Co.	Snyder, Tex.	30
Dow Chem. U.S.A.	Freeport, Tex.	125
N L Indust., Inc. Magnesium Div.	Rowley, Utah	25
Oregon Metallurgical Corp.	Albany, Ore.	<3
Titanium Metals Corp. of America TIMET Div.	Henderson, Nev.	12
	TOTAL	~219

3. Usages

Powdered magnesium is used in pyrotechnics, flash photography, and in the steel industry for desulfurization. Other uses for magnesium (not necessarily powdered) included in the production of other metals; for organomagnesium compounds, particularly Grignard reagents; for cathodic protection; as a general reducing agent; in precision instruments; optical mirrors; and dry and wet batteries. Magnesium alloys are used in structural materials, die-cast auto parts, missiles, and the aerospace industry (Hawley, 1977).

4. Future Trends

We are not aware of any major changes expected in the magnesium industry.

5. Documented or Speculated Occurrences in the Environment

There are no reports in the literature of powdered magnesium as an environmental contaminant.

F. Comparison of Civilian and Military Uses and Pollution

Magnesium is produced in the United States by nine manufacturers. Total production capacity is in excess of 400 million lb/year. The U.S. production capacity for powdered magnesium is estimated at >20 million lb/year. Magnesium is used as a structural material in weight-sensitive applications. It is also a component of civilian pyrotechnic formulations and chemical reagents. Entry into the environment is common through disposal of metal parts containing magnesium.

Magnesium is used by the military in the production of flares and signal devices. Current use rates are about 200,000 lb/year, or 0.04% of civilian use. At full mobilization, this military use would rise to 8 million lb/year, representing 1.6% of the civilian use. However, full mobilization use rate of powdered magnesium would probably tax civilian production capacity for this material. Losses of magnesium in the environment through military use are about 2,500 lb/year currently. At full mobilization this would rise to as much as 75,000 lb/year. The primary collection point for magnesium pollution by military munitions production is the evaporation pond at LAAP. However, widespread pollution of magnesium oxide will occur from the use of the flares and signal devices.

G. Toxicological and Environmental Hazards

1. Toxicity to Mammals

The only data on the toxicity of magnesium found in this brief literature search was for oral administration to dogs. The lowest effective dose was found to be 230 mg/kg for dogs (NIOSH, 1977).

If magnesium is burned, the oxide is formed. This compound can irritate mucous membranes. Reactions were observed after exposure of human

subjects to 400-600 mg/m^3 of magnesium oxide for 10 minutes.

2. Aquatic Toxicity

Due to its insolubility, magnesium powder will have limited availability to aquatic organisms. However upon prolonged contact with water, magnesium hydroxide will form. This compound is also insoluble. Therefore, any magnesium powder entering the aquatic environment will accumulate in the sediment either as the metal or the hydroxide.

Most magnesium compounds are toxic to aquatic organisms only in high concentrations. For example, the 3 week LC50 of magnesium chloride on *Daphnia magna* is 190 ppm. A concentration of 82 ppm is required before 16% reproductive impairment is observed (Biesinger and Christensen, 1976).

3. Toxicity to Microorganisms

Specific reports of magnesium toxicity to microorganisms were not found. Kelley (1948) reported that a heavy clay soil from Napa, California, in which more than 90 percent of the cation exchange capacity was saturated with magnesium, was almost completely unproductive indicating a depressive effect on the microbial population. Lisanti (1958) suggested that the toxic effect of high magnesium levels may be inhibited by increasing the sulfate ion concentration. Magnesium applications to soils that are low in calcium may produce magnesium toxicity unless supplemental calcium is applied (Garner *et al.*, 1930).

A number of microorganisms are known to metabolize or accumulate magnesium compounds. *Aspergillus niger* is used in a test to determine the exchangeable magnesium content of soils (Smith and Mulder, 1942).

4. Phytotoxicity

Magnesium, when present in soils beyond certain amounts, produce injurious effects on many higher plants. Sievers (1924) described the phytotoxic effect of magnesium oxide discharges from a furnace stack on surrounding vegetation. Soils with a magnesium content ranging from approximately 10,000 to 56,000 lb per acre foot (14 times that of the normal surface soil) produced chlorosis and stunted growth in oats.

The toxic action of magnesium is both physical and chemical. Soils may accumulate a thick and slightly impervious crust which restricts many plants from surviving germination. When magnesium oxide comes in contact with the soil and is exposed to CO_2 in air and to moisture, it is soon converted to magnesium carbonate. The magnesium carbonate is not readily soluble in water but forms a soluble bicarbonate in soil solutions containing carbon dioxide. This reaction is partly responsible for the toxic effect of magnesium. This effect is being more pronounced in soil high in organic matter or where there is an opportunity for large amounts of carbon dioxide to be evolved.

Various types of soybeans (*Glycine max. L.*) were grown in soil which had been treated with $MgCO_3$. The resulting high soil pH and low phosphorous-high magnesium content caused growth inhibition and chlorosis due to iron deficiency from low iron uptake (Wallace *et al.*, 1976).

Boischot and Drouineau (1941) reported that Hydrangea and bean cultures were damaged (stunted growth) by an excessive amount of magnesium. The tissue of these plants showed a considerable increase in magnesium and reduced potassium content. Coupin (1918) stated that the injurious effects of magnesium carbonate on plants include reduction in length of main root and rootlets, a black or brown coloration of the branches and rootlets and stunted aerial growth.

5. Availability of Literature for Phase II

The toxicological literature on magnesium powder consists mainly of occupational exposure studies. The availability of literature on the environmental hazards of magnesium is limited to that of the more commonly used magnesium compounds such as the chloride and carbonate salts.

H. Regulations and Standards

1. Air and Water Regulations

There are no EPA effluent regulations for magnesium.

2. Human Exposure Standards

No specific standards are listed for human exposure to magnesium. However, a limit of 10 mg/m^3 has been recommended for exposure to magnesium oxide fumes (American Conference of Governmental Industrial Hygienists, 1977).

3. DOT Regulations

The Department of Transportation requires the following label on magnesium: "Flammable Solid and Dangerous When Wet" (Federal Register, 1976).

I. Conclusions and Recommendations

This problem definition study has as its goal an assessment of the Army's responsibility for conducting further studies on powdered magnesium. Powdered magnesium is used by the Army to make flares and other signal devices. Longhorn AAP uses >90% of the magnesium purchased by the Army. At current production rates, Longhorn AAP uses ~14,000 lb of powdered magnesium per month. This usage rate would increase to 632,500 lb/month or 7,590,000 lb/year at full mobilization production rates. Production losses could run as high as 1% of the quantity used. These wastes are disposed of in an evaporation pond. Loss of magnesium salts to the ground water from this pond is possible, however, no leaching into the ground water has been documented.

Although large quantities of magnesium powder are used by the Army, the Army's needs for this metal are small compared to the civilian production and use. The toxicological and environmental hazards from the metal are low. Based upon these findings, a Phase II detailed toxicological and environmental study of this metal by the Army should be a low priority item.

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PRELIMINARY PROBLEM DEFINITION STUDY OF 48 MUNITIONS-RELATED CHEMICALS

VOLUME IV PRIMER AND TRACER RELATED CHEMICALS

STRONTIUM NITRATE

FINAL REPORT

J. F. Kitchens
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Supported by:

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Fort Detrick, Frederick, Maryland 21701

Contract No. DAMD17-77-C-7057

COTR: Clarence Wade, Ph.D.

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Alexandria, Virginia 22314

Approved for Public Release
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The findings of this report are not to be construed as an official Department of the Army position unless so designated by other authorized documents.

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SUMMARY

Strontium nitrate is a widely used chemical in the civilian market. Estimated annual production is ~12 million lb. Most of strontium nitrate produced is used in the flare industry. When the flares are burned, most of the strontium nitrate is oxidized. The resulting oxide is unstable in water and decomposes to the hydroxide. Thus, ~100% of the strontium in these flares enters the environment in an uncontrolled manner.

In comparison, the military use of strontium nitrate is small. Total usage of this chemical at Lake City, Longhorn and Lone Star AAPs in tracer and pyrotechnic formulations is only ~100,000 lb/year. At full mobilization use rate of strontium, a total of 400,000 lb would be needed by these plants each year. Most of the strontium from the manufacturing processes at these AAPs ends up in ponds and does not enter the aquatic environment. As with the civilian use of flares, the military use of tracers dissiminates virtually all the strontium back into the environment.

In general, strontiun nitrate is toxic only in large doses to most living organisms.

In view of the large civilian production and usage of strontium nitrate and the widespread uncontrollable pollution resulting from consumer products using this chemical, strontium nitrate is not a military problem. However, strontium in the LCAAP effluents from the combined use of all strontium compounds could be an Army problem. Therefore, it is recommended that further studies on the effects of strontium salts and the interactions of strontium with other metals in the Little Blue River be underdaken.

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FOREWORD

This report details the results of a preliminary problem definition study on strontium nitrate. The purpose of this study was to determine the Army's responsibility for conducting further research on strontium nitrate in order to determine its toxicological and environmental hazards so that effluent standards can be recommended. In order to determine the Army's responsibility for further work on strontium nitrate, the military and civilian usage and pollution of this chemical were evaluated. In addition, a preliminary overview of toxicological and environmental hazards was conducted.

Strontium nitrate was only one of 48 chemicals evaluated under Phase IA of contract No. DAMD17-77-C-7057. These chemicals are grouped in four categories

- explosives related chemicals
- propellant related chemicals
- pyrotechnics
- primers and tracers

Each category is a major report. Section I of each report is an overview of the military processes which use each chemical and the pollution resulting from the use of these chemicals. The problem definition study reports on each chemical are separable sections of these four reports.

In addition, a general methodology report was also prepared. This report describes the search strategy and evaluation methodology utilized for this study.

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XIII. STRONTIUM NITRATE

A. Alternate Names

Strontium nitrate exists as the anhydrous form, $Sr(NO_3)_2$ and the tetrahydrate, $Sr(NO_3)_2 \cdot 4H_2O$. The anhydrous compound is the most important commercial product. The molecular weight of $Sr(NO_3)_2$ is 211.65 g/mole; that of $Sr(NO_3)_2 \cdot 4H_2O$ is 283.71 g/mole. The pertinent alternate names for strontium nitrate are listed below:

CAS Registry No.:	10042-76-9
CA Name (8CI):	Nitric acid, strontium salt
Wiswesser Line Notation:	Sr N-02-Q*2
Synonyms:	Strontium dinitrate; Strontium nitrate

B. Physical Properties

The physical properties of strontium nitrate and strontium nitrate tetrahydrate are presented in Table XIII-1.

C. Chemical Properties

1. General Reactions

Thermal decomposition of strontium nitrate yields strontium oxide, oxygen, and oxides of nitrogen.

$$Sr(NO_3)_2 \longrightarrow SrO + 2NO_2 + 1/2\ O_2$$

The reaction is easily initiated by flame, heat, or shock in the presence of reducing agents.

2. Environmental Reactions

Strontium nitrate is a soluble salt which dissociates to Sr^{+2} cation and the nitrate anion in water. Depending on the availability of other cations and anions in the surroundings, insoluble strontium salts or nitrate salts may precipitate. At near neutral pH's, nitrate is chemically stable. Nitrate, however, is photochemically reduced by UV light at wavelengths below 265 nm and at 300 nm. Nitrite is also formed by irradiation of insoluble nitrate salts on water surfaces at 250 nm. Reduction occurs faster under alkaline conditions (Coldwell and McLean, 1959).

Strontium oxide, the thermolysis product of strontium nitrate, is unstable in water. It undergoes a highly exothermic reaction to yield strontium hydroxide (Windholz, 1976).

$$SrO + H_2O \longrightarrow Sr(OH)_2$$

Table XIII-1. Physical Properties of Strontium Nitrate.*

	$Sr(NO_3)_2$	$Sr(NO_3)_2 \cdot 4H_2O$
Physical Form @ 20°C:	solid	solid
Color and Crystalline Form:	colorless cubic	white monoclinic
M.P.:	570°C	
B.P.:	645°C	
Crystal Density:	2.986 g/cm^3	2.2 g/cm^3
Refractive Index:	1.567	
Solubility: water -	39.5 g/100 g @ 0°C	60.43 g/100 g @ 0°C
	68.9 g/100 g @ 20°C	
	94.0 g/100 g @ 60°C	
	101 g/100 g @ 100°C	206.5 g/100 g @ 100°C
absolute alcohol -	0.012 g/100 g	very slightly soluble
acetone -	slightly soluble	

* References: Windholz, 1976; Sax, 1976; Hawley, 1977; Kirk and Othmer, 1968; Hodgman, 1963

3. Sampling and Analysis

Strontium nitrate may be determined either as strontium or as nitrate. Analysis for strontium is best done using flame photometry. This technique can determine strontium at concentrations of 12.0 mg/l with an accuracy of ±1 or 2 mg/l (Franson, 1975).

Four methods for the determination of nitrate are described below. The nitrate ion electrode is applicable over the widest range of concentrations. The UV spectrophotometric method is also widely useful while the last two are limited in their concentration ranges (Franson, 1975).

- Determination of nitrate with a nitrate ion electrode allows analysis of concentrations from 0.2 to 1,400 mg of NO_3^-/l. The disadvantage of this method is the numerous interferences which must be chemically removed prior to analysis. Chloride and bicarbonate at relatively high concentrations interfere with the electrode as do nitrite, sulfide, bromide, iodide, chlorate and perchlorate.

- Nitrate in solution may be determined by measurement of UV absorption at 220 nm. Beer's law is obeyed up to concentrations of 11 mg/l. Dissolved organic matter may interfere with this analysis.

- Nitrate is reduced by cadmium to nitrite which can undergo further reactions with sulfanilamide and N-(1-napthyl)-ethylenediamine to form a colored product that may be determined colorimetrically. Correction for any nitrite initially present must be made. This method is used for determinations below 0.1 mg NO_3^-/l.

- Colorimetric estimation of the yellow reaction product of brucine and nitrate allows determination of nitrate in water. This method is applicable to the narrow concentration range of 0.1 to 2 mg/l.

D. Uses in Army Munitions

1. Purpose

Strontium nitrate is used as a fuel in tracer and pyrotechnic formulations. This material imparts a crimson color to burning compositions. The following formulations produced at Lake City AAP specify strontium nitrate:

	% Strontium Nitrate in Formulation
Igniter R284	55±1
Igniter I-237	25±1
Igniter I-560	27.5±1
R-403	48±2
R-505	39.8 min
R-321	52±1

	% Strontium Nitrate in Formulation
R-256	33.3±1
R-512	27.3

Strontium nitrate is also used by Lone Star AAP and Longhorn AAP as a constituent of tracer mixes.

2. Quantities Used

a. Historical Use

During the 1975-1977 period, Lake City AAP was a major Army user of strontium nitrate. The amounts of this chemical procured in each of these years are given below:

1975	66,000 lb
1976	59,850 lb
1977	55,200 lb

The average use rate during this period was 60,350 lb/year or 5,030 lb/month.

Lone Star AAP used 2,290 lb of strontium nitrate during June, 1974 (USAEHA, 1974). This amount is equivalent to an annual use rate of 27,500 lb/year.

Longhorn AAP used a total of 5,403 lb of strontium nitrate in 1977 or an average of 450 lb/month.

b. Current Use

The most recent use rate of strontium nitrate at the various AAP's is as follows:

	lb/month	lb/year
LCAAP	4,600	55,200
LSAAP	1,150	13,800
LAAP	450	5,400

c. Use at Full Mobilization

The estimated requirements for strontium nitrate at full mobilization are given below:

	lb/month	lb/year
LCAAP	23,000	276,000
LSAAP	5,750	69,000
LAAP	3,400	40,800

3. Documented or Speculated Occurrences in Air or Water

About 0.5-2% of the amounts handled are normally lost to waste streams during processing of pyrotechnic and tracer formulations (Melton, 1978; Aikman, 1978; Maley, 1978; Alexander, 1978). This loss rate would result in the following losses at current and full mobilization use rates:

	Losses of Strontium Nitrate, lb/month	
	Current	Full Mobilization
LCAAP	46-92	230-460
LSAAP	12-23	58-115
LAAP	2-5	17-34

At LCAAP, the waste streams are treated with strong base, neutralized, then sent to conventional industrial waste treatment facilities. Any strontium salts entering the industrial waste treatment plant will be precipitated as strontium carbonate. Based on the solubility of this salt (K_{sp}= 1.6×10^{-9}), the maximum concentration of strontium leaving Lake City AAP is 3.52 ppm.

At LSAAP and LAAP, wastes are discharged into evaporation ponds. Some contamination of ground water is likely from percolation of wastes into the soil. The actual degree of contamination from this source has not been determined.

E. Uses in the Civilian Community

1. Production Methodology

Strontium nitrate is manufactured by the action of nitric acid on strontium carbonate (FMC Corp., 1978).

$$SrCO_3 + 2HNO_3 \longrightarrow Sr(NO_3)_2 + H_2CO_3$$

The carbonate is added to a nitric acid solution and the precipitated strontium nitrate is filtered, then recrystallized.

2. Manufacturers, Production and Capacity

The U.S. manufacturers of strontium nitrate are listed in Table XIII-2. The FMC Corp. produces barium nitrate as well as strontium nitrate at their Modesto facility. Their capacity of 20 million pounds per year is based on shutting down $Ba(NO_3)_2$ production and manufacturing $Sr(NO_3)_2$ exclusively (FMC Corp., 1978).

Barium and Chemicals manufacture strontium nitrate to military specifications. They do not manufacture any commercial grades. Hummel Chemical Co. purchases strontium nitrate and reprocesses it to military specifications in South Plainfield, NJ (Hummel Chemical, 1978).

Table XIII-2. U.S. Manufacturers of Strontium Nitrate (S.R.I., 1977).

Manufacturer	Location	Capacity
Barium and Chemicals, Inc.	Steubenville, OH	not available
FMC Corp., Chem. Group, Ind. Chem. Division	Modesto, DA	20×10^6 lbs/yr
Richardson-Merrell, Inc. J.T. Baker Chem. Co., Subsid.	Philispsburg, NJ	not available

Strontium nitrate is also manufactured abroad and imported. Importers include the American Hoechst Corp. and E.M. Laboratories, Inc., from West Germany and Pharmacie Centrale de France from France (OPD Chemical Buyers Guide, 1977).

3. Usages

Strontium nitrate is used primarily in the flare industry. It emits a bright red fire upon combustion. Strontium nitrate is used in highway flares, pyrotechnics, and matches. Minor uses are found in medicine and electron tubes (S.R.I., 1977; Hawley, 1977).

4. Future Trends

No major changes in the strontium nitrate industry are anticipated.

5. Documented or Speculated Occurrences in the Environment

Strontium has been measured in concentrations ranging from 8 to 10 mg/l in seawater. The freshwater concentration usually falls in the range of 0.05 to 0.5 mg/l (Burrows and Dacre, 1975).

F. Comparison of Military and Civilian Uses and Pollution

Military use of strontium nitrate at the facilities for which data is available is less than 100,000 lb/year at current production levels. Under full mobilization schedules, ~400,000 lb/year of strontium nitrate would be used by the Army in tracer and pyrotechnic formulations.

Current civilian production of strontium nitrate is estimated at ~12 million lb/year. However, significantly greater capacity to produce this chemical is available if needed. Most of the strontium nitrate produced each year is used in the production of flares for civilian use. Thus the Military use of strontium nitrate is very small in comparison with civilian flares.

Due to the nature of the use of flares, the strontium pollution in the form of strontium oxide or hydroxide resulting from the use of these items will be widespread. It is estimated that ~100% of the strontium in the

products will enter the environment in an uncontrollable manner. Thus if 10 million lb/year of strontium nitrate go into the manufacture of flare type materials, ~5.9 million lb of strontium will re-enter the environment. Therefore, any strontium pollution resulting from the Military use of strontium nitrate is insignificant when compared to the pollution resulting from the civilian use of flares.

G. Toxicological and Environmental Hazards

1. Mammalian Toxicity

Much of the toxicological research on strontium has concerned the radioactive isotope strontium Sr-90. Chemically the toxicity of Sr is very low (Casarett and Doull, 1975). No adverse effects from industrial use have been reported. Experimentally electrocardiograph changes and death due to respiratory paralysis have been produced by the injection of high doses of strontium (Beliles, 1975).

2. Toxicity to Fish

Strontium levels in natural waters range from 50-500 ppb (Templeton and Brown, 1964). Burrows and Dacre (1975) observed that waters high in calcium contained high levels of strontium. Strontium nitrate is very soluble in water (68 g/100g); therefore, it is available to the organisms.

The acute toxicity of strontium nitrate to aquatic organisms (Table XIII-3) is low. Table XIII-4 shows the biocencentration of strontium in aquatic organisms. Considering the low toxicity and the lack of bioaccumulation of strontium nitrate, the release of this substance into aquatic systems should not pose any treat to the aquatic organisms.

3. Toxicity to Invertebrates and Microorganisms

Several studies have shown that the microcrustacean, *Daphnia magna*, is substantially more sensitive to strontium salts than fish. Anderson (1948) reported that the 64-hour immobilization threshold for strontium chloride to be 63 mg/l as strontium. Bringman and Kuhn (1959) found the 48-hour toxic threshold to be 210 mg/l.

The planarian, *Polycelis nigra*, was found to have a 48 hr threshold survival rate in concentrations of 6600 mg/l as Sr for strontium chloride and 3500 mg/l as Sr for strontium nitrate (Jones, 1940).

Yarbrough and O'Kelley (1962) demonstrated that the complete substitution of strontium for calcium levels of 18 mg Sr/l in the nutrient medium of the protozoan, *Paramecium multimicronucleatum*, had no effect on the rate of growth.

For a wide range of bacterial species, strontium salts have been found to be toxic only at very high concentrations (refer to Table XIII-5). The resistance of many fungi to strontium is the same or greater than for bacteria.

Table XIII-3. Toxicity of Strontium to Freshwater and Marine Fishes.

Fish	Salt	Sr Concn. mg/l	Reported Effect	Reference
Goldfish (*Carassius carassius*)	$Sr(NO_3)_2$	3,980	Lethal in 32-146 hr	Powers, 1917
Goldfish			Depression of movement and respiration	Okuda, 1932
Stickleback (*Gasterosteus aculeatus*)	$Sr(NO_3)_2$	1,200	Min. lethal conc.	Jones, 1939
Stickleback (*Gasterosteus aculeatus*)	$Sr(NO_3)_2$	3,000	Av. survival 96 hr	Jones, 1939
Stickleback (*Gasterosteus aculeatus*)	$Sr(NO_3)_2$	7,000	Av. survival 48 hr	Jones, 1939
Stickleback (*Gasterosteus aculeatus*	$Sr(NO_3)_2$	10,000	Av. survival 24 hr	Jones, 1939

Table XIII-4. Bioaccumulation of Strontium in Aquatic Organisms.

Organism	Bioaccumulation factor	Reference
Brown trout *(Salmo trutta)*		
bone	.45-56	Templeton & Brown, 1964
muse	.53-1.00	Templeton & Brown, 1964
Rainbow Trout *(S. gairdneri)*	.37	Ichikawa, 1960
Snail *(Lymnaea stagnalis)*	.5	Van der Borght, 1962
Water flea *(Daphnia magna)*	.58	Marshall *et al.*, 1967

Table XIII-5. Effects of Strontium Salts on Microorganisms.

Microorganism	Salt	Sr Concn. mg/l	Reported Effect	Reference
Protozoa				
Microregma heterostoma	$SrCl_2$	329	28 hr toxic threshold for feeding	Bringmann and Kuhn, 1959
Paramecium	$SrCl_2$	8000	All dead in 4.5 hr	Dale, 1913
Bacteria				
Bacillus anthracis	$SrCl_2$	23×10^3	Growth inhibition threshold	Eisenberg, 1919
Bacillus anthracis	$SrCl_2$	26×10^3	Growth inhibition	Eisenberg, 1919
Sarcina tetragena	$SrCl_2$	17×10^3	Growth inhibition threshold	Koulumies, 1946
Micrococcus phogenes	$SrCl_2$	17×10^3	Growth inhibition threshold	Eisenberg, 1919
Micrococcus candicans	$SrCl_2$	13×10^3	Growth inhibition threshold	Eisenberg, 1919
Corynebacterium diphtheriae	$SrCl_2$	6700	Growth inhibition threshold	Eisenberg, 1919
Corynebacterium diphtheriae	$SrCl_2$	10×10^3	Growth inhibition	Koulumies, 1946
Corynebacterium pseudodiphtheriae	$SrCl_2$	10×10^3	Growth inhibition threshold	Eisenberg, 1919
Corynebacterium pseudodiphtheriae	$SrCl_2$	4×10^3	Growth inhibition	Koulumies, 1946
Bacillus typhi	$SrCl_2$	30×10^3	Growth inhibition threshold	Eisenberg, 1919
Bacillus pneumoniae	$SrCl_2$	13×10^3	Growth inhibition threshold	Eisenberg, 1919
Bacillus pyrocyaneus	$SrCl_2$	10×10^3	Growth inhibition threshold	Eisenberg, 1919
Bacillus vulgare	$SrCl_2$	27×10^3	Growth inhibition threshold	Eisenberg, 1919
Vibrio cholerae	$SrCl_2$	1700	Growth inhibition threshold	Eisenberg, 1919
Escherichia coli	$SrCl_2$	27×10^3	Growth inhibition threshold	Eisenberg, 1919

Table XIII-5 (continued)

Escherichia coli	$SrCl_2$	22×10^3	Growth inhibition threshold	Hotchkiss, 1923
Escherichia coli	$SrCl_2$	18×10^3	Growth inhibition	Koulumies, 1946
Salmonella paratyphi B	$SrCl_2$	10×10^3	Growth inhibition	Koulumies, 1946
Salmonella paratyphi A	$SrCl_2$	10×10^3	Growth inhibition	Koulumies, 1946
Eberthella typhosa	$SrCl_2$	18×10^3	Growth inhibition	Koulumies, 1946
Proteus vulgaris	$SrCl_2$	18×10^3	Growth inhibition	Koulumies, 1946
Shigella paradysenteriae	$SrCl_2$	7×10^3	Growth inhibition	Koulumies, 1946
Brucella abortus	$SrCl_2$	7×10^3	Growth inhibition	Koulumies, 1946
Pasteurella pestis (Tjevidei)	$SrCl_2$	7×10^3	Growth inhibition	Koulumies, 1946
Pasteurella pestis (Soemedang)	$SrCl_2$	22×10^3	Growth inhibition	Koulumies, 1946
Hemophilus pertussis	$SrCl_2$	10×10^3	Growth inhibition	Koulumies, 1946
Hemophilus influenza	$SrCl_2$	10×10^3	Growth inhibition	Koulumies, 1946
Neisseria catarrhalis	$SrCl_2$	18×10^3	Growth inhibition	Koulumies, 1946
Neisseria gonorrhoeae	$SrCl_2$	10×10^3	Growth inhibition	Koulumies, 1946
Staphylococcus aureus	$SrCl_2$	10×10^3	Growth inhibition	Koulumies, 1946
Staphylococcus albus	$SrCl_2$	10×10^3	Growth inhibition	Koulumies, 1946
Streptococcus pyrogenes	$SrCl_2$	10×10^3	Growth inhibition	Koulumies, 1946
Streptococcus viridans	$SrCl_2$	10×10^3	Growth inhibition	Koulumies, 1946
Diplococcus pneumoniae	$SrCl_2$	10×10^3	Growth inhibition	Koulumies, 1946
Actinomyces graninis	$SrCl_2$	44×10^3	Growth inhibition	Koulumies, 1946
Mycobacterium tuberculosis hominis	$SrCl_2$	7×10^3	Growth inhibition	Koulumies, 1946

Table XIII-5 (continued)

Mycobacterium tuberculosis bovis	$SrCl_2$	7×10^3	Growth inhibition	Koulumies, 1946
Clostridium (7 species)	$SrCl_2$	7 to 10×10^3	Growth inhibition	Koulumies, 1946
Leptospira icterohaemorrhagiae (3 strains)	$SrCl_2$	7 to 10×10^3	Growth inhibition	Koulumies, 1946
Fungi				
Epidermophyton Kaufmann-Wolff	$SrCl_2$	26×10^3	Growth inhibition	Koulumies, 1946
Trichophyton (3 species)	$SrCl_2$	26 to 52×10^3	Growth inhibition	Koulumies, 1946
Penicillium (Orion)	$SrCl_2$	70×10^3	Growth inhibition	Koulumies, 1946
Mucor corymbifer	$SrCl_2$	26×10^3	Growth inhibition	Koulumies, 1946
Cladisporium mansoni	$SrCl_2$	44×10^3	Growth inhibition	Koulumies, 1946
Scopularia brevicaulis	$SrCl_2$	66×10^3	Growth inhibition	Koulumies, 1946
Aspergillus fumigatus	$SrCl_2$	70×10^3	Growth inhibition	Koulumies, 1946
Altenaria	$SrCl_2$	66×10^3	Growth inhibition	Koulumies, 1946
Altenaria tenuis	$Sr(NO_3)_2$	30×10^3	ED50, germination inhibition	Somers, 1959; 1961
Botrytis fabae	$Sr(NO_3)_2$	13×10^3	ED50, germination inhibition	Somers, 1961
Algae				
Coccomyxa pringsheimii	----	5 - 10	Inhibition of growth and calcium utilization	Walker, 1956
Chlorella vulgaris	$SrCl_2$-$6H_2O$	$>13 \times 10^3$	Lowest inhibitory conc.	den Dooren de Jong, 1965

4. Phytotoxicity

Strontium compounds may be highly toxic to plants under certain conditions such as in the absence of calcium carbonate. McHargue (1919) studied the effects of strontium nitrate on the growth of winter wheat (*Triticum aestivum*). He reported that increasing the amount of strontium nitrate gave a corresponding increase in the nitrogen content of the wheat. The yields and average weight of the wheat produced in each experiment are presented in Table XIII-6. The results obtained are probably due to the large amounts of nitrate radical present rather than to the strontium ion since strontium carbonate experiments didn't show marked increase in yields. Other investigations proved that strontium carbonate is less toxic than barium carbonate in the absence of calcium carbonate.

Scharrer and Schropp (1937) reported that concentrations of strontium higher than 10^{-1} milliequivalents/ml were toxic to peas. Plants less sensitive to strontium include wheat, maize, oats, barley and rye.

Walsh (1945) studied the effect of strontium (various salts) on the growth of mustard, oats, barley and wheat. He concluded that strontium is capable of substantially replacing calcium in the vegetative growth of these plants but not in the formation of grain in the cereals. The toxicity of strontium seems to be directly related to the amount absorbed.

5. Availability of Literature for Phase II

Strontium nitrate is a widely used chemical. Numerous studies have been conducted in order to evaluate its toxicological and environmental properties. Thus there is a large amount of literature available for Phase II.

H. Regulations and Standards

1. Air and Water Regulations

No standards are listed for exposure to strontium nitrate in air or water.

2. Human Exposure Standards

No human exposure standards are listed. This chemical is not entered on the NCI list of suspected carcinogens.

3. DOT Labeling Requirements

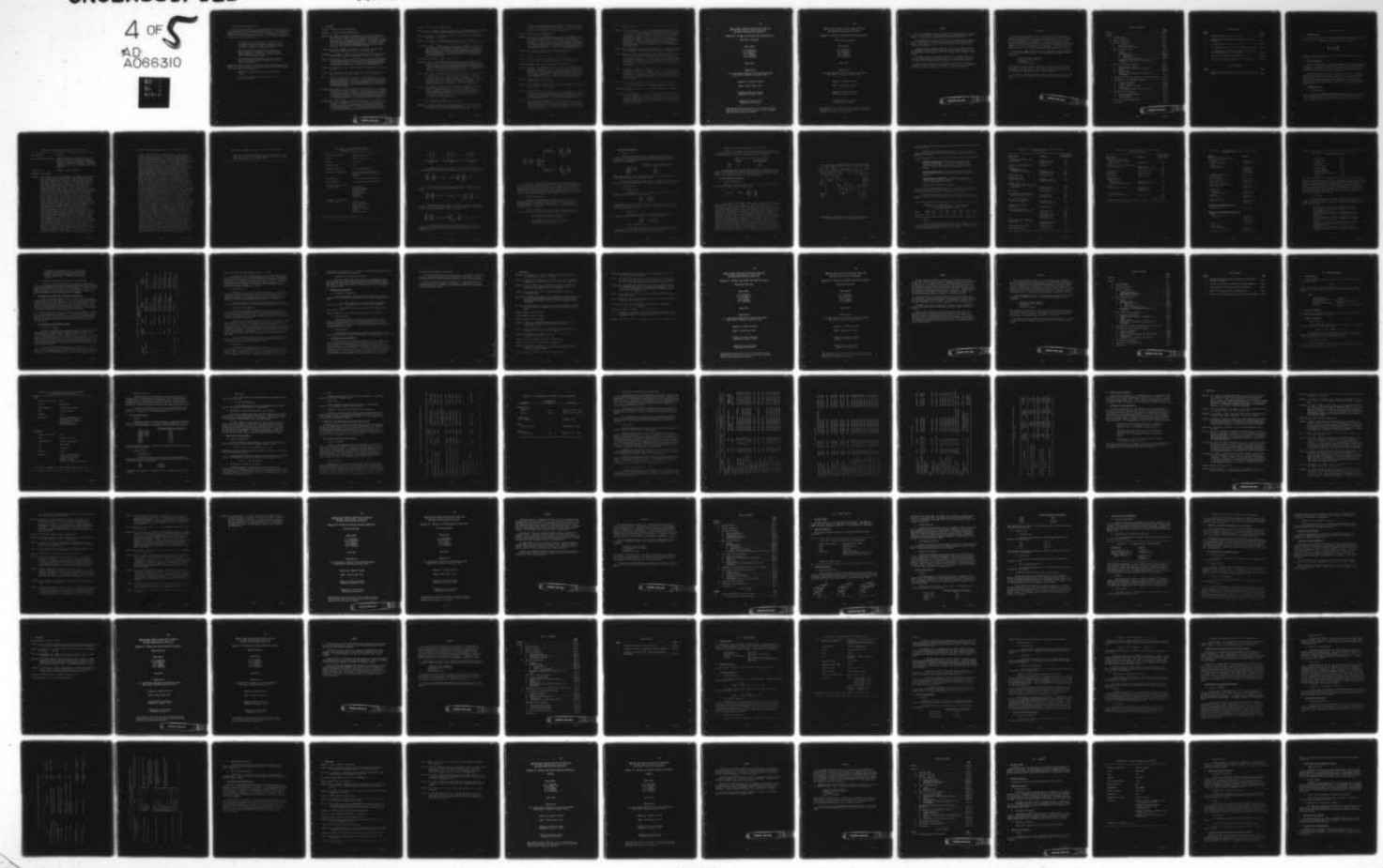
The Department of Transportation classifies strontium nitrate as an oxidizer. Labels on this material should bear the word "Oxidizer."

Table XIII-6. Effects of Strontium Nitrate on the Growth of Winter Wheat (McHargue, 1919).

Pot No. and treatment	Number of grains per pot.	Weight of grain per pot.	Average weight per grain.	Weight of straw.
		Gm.	Gm.	Gm.
Pot 1 (control), no strontium nitrate	372	8.8872	0.0239	34.50
Pot 2 (control), no strontium nitrate	292	7.7650	.0266	27.50
Average	332	8.3261	.0252	31.00
Pot 3+5 gm. of strontium nitrate	369	11.9065	.0323	44.50
Pot 4+5 gm. of strontium nitrate	555	19.6108	.0353	52.00
Average	462	15.7586	.0338	48.25
Pot 5+10 gm. of strontium nitrate	561	17.6505	.03146	62.00

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UNCLASSIFIED ARC-49-5730-04 NL

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I. Conclusions and Recommendations

The goal of this preliminary problem definition study was to assess the Army's responsibility for conducting further research on toxicological and environmental properties of strontium nitrate. Based on the information gathered and evaluated during this study, it is recommended that strontium nitrate, itself, not be included in a Phase II study. This recommendation is based on the following conclusions:

- the current civilian production of strontium nitrate is ~15 million lb/year with addition capacity available if needed. In contrast, the full mobilization military use of this chemical is <0.5 million lb/year.

- the civilian use of strontium nitrate is mainly in flares. Because of the nature of the use of flares, large quantities of strontium will enter the environment in an uncontrollable manner.

- the environmental and mammalian toxicity of strontium nitrate is low when high doses required before any effects are observed.

However, the effects of the total combined strontium in the Lake City AAP effluent on the water quality of the Little Blue River need further evaluation. This study should include the

- analysis of strontium and other metals in the LCAAP effluent

- the effect of strontium and combined metals on the aquatic environment.

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PRELIMINARY PROBLEM DEFINITION STUDY OF 48 MUNITIONS-RELATED CHEMICALS

VOLUME IV PRIMER AND TRACER RELATED CHEMICALS

POLYVINYL CHLORIDE

FINAL REPORT

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SUMMARY

Poly(vinyl chloride) production in the United States is nearly 7 billion lb/year. This material is used in construction, consumer goods, packaging, electrical products, home furnishings and many other applications.

The military use of poly(vinyl chloride) is as a burning rate retardant, a color intensifier and a bonding agent in pyrotechnic and tracer formulations. Total military use even at full mobilization would represent only 0.001% of civilian use.

Civilian sources of entry of poly(vinyl chloride) into the environment are widespread, largely through disposal of consumer goods. Military sources of environmental contamination of (polyvinyl chloride) are negligible by comparison.

Poly(vinyl chloride) is relatively non-toxic. The monomer, vinyl chloride, does exhibit some toxic effects however. When combusted, poly(vinyl chloride) releases hydrogen chloride gas which is irritating and corrosive.

Because of the small military use compared to civilian requirements, pollution by poly(vinyl chloride) is primarily a civilian problem. Thus, this compound should be a low priority for a Phase II study by the Army.

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FOREWORD

This report details the results of a preliminary problem definition study on polyvinyl chloride. The purpose of this study was to determine the Army's responsibility for conducting further research on polyvinyl chloride in order to determine its toxicological and environmental hazards so that effluent standards can be recommended. In order to determine the Army's responsibility for further work on polyvinyl chloride, the military and civilian usage and pollution of this chemical were evaluated. In addition, a preliminary overview of toxicological and environmental hazards was conducted.

Poly(vinyl chloride) was only one of 48 chemicals evaluated under Phase IA of contract No. DAMD17-77-C-7057. These chemicals are grouped in four categories

- explosives related chemicals
- propellant related chemicals
- pyrotechnics
- primers and tracers

Each category is a major report. Section I of each report is an overview of the military processes which use each chemical and the pollution resulting from the use of these chemicals. The problem definition study reports on each chemical are separable sections of these four reports.

In addition a general methodology report was also prepared. This report describes the search strategy and evaluation methodology utilized for this study.

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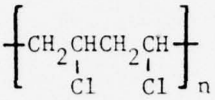
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XIV. POLY(VINYL CHLORIDE)

A. Alternate Names

Poly (vinyl chloride) is a synthetic thermoplastic polymer. Due to its excellent physical properties, this polymer is used in a wide variety of consumer products. Poly(vinyl chloride) has the general formula:



There are numerous alternate names for poly(vinyl chloride). These alternate names are listed in Table XIV-1.

B. Physical Properties

The physical properties of poly(vinyl chloride) vary widely depending on the details of polymerization and treatment. Various methods of processing and addition of stabilizers, modifiers, or pigments also radically affect the physical properties. The general physical structure and properties of unmodified poly(vinyl chloride) are discussed below.

The basic structure of poly(vinyl chloride) is a chain of monochloro ethylene units attached head to tail. Long chain branching occurs during polymerization resulting in an average number of 0.2 to 2 branches per 100 carbon atoms. The average molecular weight of a polymer chain is usually between 60,000 and 150,000 or between 960 and 2,400 monomer units. Other physical properties are listed in Table XIV-2 (Kirk and Othmer, 1970; Windholz, 1977).

C. Chemical Properties

1. General Reactions

Poly(vinyl chloride) will react with molecular chlorine in carbon tetrachloride at moderate temperatures under UV irradiation to form more highly chlorinated polymers. These polymers contain 1,1-dichloro and 1,2-dichloro ethylenic units as well as the 1-chloroethylenic units of poly(vinyl chloride) (Kirk and Othmer, 1970).

Table XIV-1. Alternate Names for Poly(vinyl chloride).

CAS Registry No.: 9002-86-2

Replaces CAS Registry No.(s): 8063-94-3; 9006-09-1; 9036-81-1; 9043047-4; 9043-48-5; 9072-17-7; 11097-91-9; 11111-94-7; 11119-27-0; 37357-61-2; 39287-89-3; 39296-17-8; 39387-43-4; 39389-56-5; 50642-89-2; 51540-75-1; 51569-45-0; 53112-41-7; 54328-28-8; 55465-75-3; 59678-57-8

CA Name (8 CI): Ethylene, chloro-, polymer

Wiswesser Line Notation:

Synonyms: AD 254; Airex; AL 30; AL 31; Armodour; Aron 1100; Aron Compound HW; Aron NS 1100; Astralon; Atactic Poly (Vinyl Chloride); Bakelite OYNV: Bakelite QSAH 7; Bakelite QSAN 7: Bakelite QYAC 10; Bakelite QYJV: Bakelite QYJV 1; Bakelite QYOH-1; Bakelite QYSJ: Bakelite QYSL 7; Bakelite QYTO 7; Bakelite UCA 3310; Benvic; Blacor 1716; Bolatron 6200; Bonloid; Breon; Breon 107; Breon 111EP; Breon 112EP; Breon 113; Breon 121; Breon 125/10; Breon 151; Breon 4121; Breon P 130/1; Breon S 110/10; Breon S 125/12; C 65; Caliplast; Carina S 70-01; Carina S 70-71; Chemosol; Chloroethylene Polymer; Chlorostop; Cobex; COBEX(polymer); Contizell; Corvic 55/9; Corvic 65/50; Corvic 206573; Corvic 20460600; Corvic 20650600; Corvic C 65/02; Corvic D 55/9; Corvic D 57/15; Corvic D 57/17; Corvic D 60/11; Corvic D 65; Corvic D 65/02; Corvic D 65/8; Corvic D 6518; Corvic D 75/10; Corvic H 55/34; Corvic P 65/50; Corvic P 65/54; Corvic P 65/55; Corvic R 65/81; Corvic S 46/70; Dacovin; Dacovin 2082; Danvil 70; Darvic 110; Darvis Clear 025; Daycell; Decatone; Decelith H; Denka Vinyl SS-Y; Denka VInyl SS-80; Denka Vinyl SS 110; Diamond Shamrock 40; Diamond Shamrock 71; Diamond Shamrock 450; Diamond Shamrock 7602; DN 4; Dorlyl; Durofol P; Dynadur; E 62; E 66; E 66P; E-PVC; Ekavyl SD 2; Ekavyl SDF 58; Ekaryl SK 55; Ekaryl SK 60; Ekavyl SK 64; Ekaryl SK 66; 103 EP8; Escambia 2160; Escambia 2200; Europhan; Exon 640; Exon 654; Exon 965; Exon 9269; Exon 9269A; Exon 9290; FC 4648; Flocor; FPC-XR 6379; Genotherm; Genotherm G; Genotherm N; Genothern UG 200; Geon 51; Geon 59; Geon 72; Geon 101; Geon 101EP; Geon 102EP-FS: Geon 103; Geon 103EP; Geon 103EPF7; Geon 103FP8; Geon 110X233; Geon 120X241; Geon 121; Geon 121L; Geon 124; Geon 126; Geon 128; Geon 131; Geon 135J; Geon 151; Geon 300X6; Geon 440X110A; Geon 85542; Geon 85851; Geon G 25; Geon Latex 151; Guttagena; Halvic 223; Halvic 229; Halvic 336; HC 825; Hi-S Film No. 111L; Hishirex 502; Hishirex 5022; Hishirex 502Z; Hispavic 229; Hostalit; Hostalit E; Hostalit P 7078; Hostalit PVP 3475; Hostalit PVP 5470; Hostalit S; Hostalit S 4070; HX-M; Igelite F; Igelite P; Improved Wilt Pruf; Kanevinyl P 1050; Kanevinyl P 2300; Kanevinyl PSH 10;

Table XIV-1. Alternate Names for Poly(vinyl chloride) (Cont.)

Kanevinyl PSL 81; Kanevinyl S 100; Kanevinyl S 1001; Kanevinyl S 1007; Kanevinyl S 2300; KhS 010; KhSe 3; Klegecell; Kohiner R 687; KR 800; Kureha S 901; L 5; Lak Kh SL; Lonza 380ES; Lonza G; Lucoflex; Lucovyl BB 800; Lucovyl BB 8010; Lucoyvl GB 1150; Lucoyvl GB 9550; Lucobyl GS 1200; Lucovyl GS 8001; Lucovyl PB 1302; Lucovyl PE; Lucovyl PE 1100; Lucovyl PE 1290; Lucovyl PE 1311; Lucovyl PE 1355; Lucovyl RB 8010; Lucovyl RS 8000; Lutofan; Marvinal; Marvinol; Marvinol 14; Marvinol 23; Marvinol 53; Marvinol 57; Marvinol 2002; Marvinol 7000; Marvinol VR 50; Marvinol VR 53; Mirrex MCFD 1025; Movinyl 100; Mowilith F: Myraform; NIKA-TEMP; Nikavinyl SG 700; Nipeon A 21; Nipol 151; Nipol 576; Nipolit CM 081; Nipolit SK; Nipolit SK 081; Nipolit SL 082; Nipolit SM 092; Nipolit SV 1308i; Norvinyl; Norvinyl P 2; Norvinyl P 10; Norvinyl S 1-70; Norvinyl S 1-80; Norvinyl S 3-68; Novon 712; Ongrovil S 165; Ongrovil S 470; Opalon; Opalon 300; Opalon 410; Opalon 440; Opalon 610; Opalon 630; Opalon 650; Opalon 660; Opalon R 7611; Ortodur; P 400; P 400 (Vinyl Polymer); Pantasote R 873; Patina V 82; Pevikon D 61; Pevikon KL2; Pevikon PE 709; Pevikon PS 690; Pevikon PE712; Pevikon R 23; Pevikon R 25; Pevikon R 45; Pevikon R 341; Pevikon S 602; Pliovic D 100X; Pliovic DB 80V; Pliovic K 90E; Pliovic K 906; Pliovic S 50; POK 60; Polivinit; Polwinit; Poly(chloroethylene); Polyco 2622; Poly(vinyl chloride; Polytherm; Porodur; Prototype III Soft; PVC; PVKh-S 63Zh; PVKh-S 65; PVKhS 60; PX11; QSAH 7; QSAN 7; Quirvil; Quirvil 170; Quirvil 278; QYSA; Ravinil R 100/65D; Resinite 90; Rucon; Rucon B 20; Ryurene S 800B; S 61; S 63M; S 65; S 65(Polymer); S 70; S 901; Scon 5300; Scon S 5300; Sicron; Sicron 530; Sicron 540; Sicron 548; Sicron 548FM; SG 1100; SKhV 7; SKhV 71; S-Low; SM 200; Solvic; Solvic 223; Solvic 229; Solvic 334; Solvic 340; Solvic 406; SP 60; SP 60(chlorocarbon); Sulvic 239; SR 11; Sumikathene SX 800; Sumilit EXA 13; Sumilit PX-A; Sumilit PX-N; Sumilit PXNH; PX-NL; Sumilit PXA 13; Sumilit S X-D; Sumilit SX7G; Sumilit SX 11; SX 7G; Sumilit SX 13; Sumilit VS 9200; Sumitomo PX 11; SV-55; SX 8T; SX 11; SV-55; SX FG; SX 11; Takilon; Tarwinyl S 64; Technopor; Tenneco 1742; TK 1000; Tocryl C 440; Trovidur; Trovidur N; Trovithern HTL:; TS 1100; U 1; Ultron; VA 15; VC 100; VC 410; Veron P 130/1; Vestolit B 7021; Vestolit GH; Vestolit S 60; Vestolit S 6554; Vestolit S 6857; Vestolit S 7554; Vestolit S 7054; Vinika 35R; Vinika 37M; Vinika KR 600; Vinika KR 800; Vinikulon; Viniplast; Viniplen P 73; Viniplen P 73A; Viniplen P 73EM; Viniplen P 74; Vinnol E 75; Vinnol E 100/75; Vinnol H 60D; Vinnol H 70D; Vinnol H 75F; Vinnol H 100/65; Vinnol H 100/70; Vinnol H 100/70D; Vinnol P 70; Vinnol P 70E; Vinnol P 100/70E; Vinnol Y; Vinoflex; Vinoflex P 313; Vinyl Chloride Homopolymer; Vinyl Chloride Polymer; Vinylchlon 4000LL; Vinylite QYJV; Viplast RA/F; Vixir 2170; Volgovinyl E 62; Volgovinyl E 62P; Volgovinyl E 66P; VSKh-S; Vygen 85; Vygen 110; Vygen 120; Vygen 313; Welvic G 2/5;

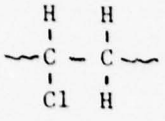
Table XIV-1. Alternate Names for Poly(vinyl chloride) (Cont.)

Welvic PRIO 953; Welvic PRO 686; Welvic R 7/622; Welvic RI 7/316; Welvic RIO 715; Wilt Pruf; Winidur; X-AB; Yugovinyl 121; 1 (Polymer); 90; 103EP8; 110A; 238; 195J; 309M

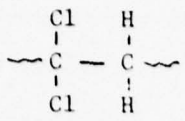
Table XIV-2. Average Physical Properties of Unmodified Poly(vinyl chloride).*

Physical form @ 20°C:	solid, powder or film
Color:	white to colorless
Density:	1.406 g/cm^3
Refractive index:	1.54
Dielectric constant:	3.54 at 60 Hz and 30°C
Water vapor transmission:	0.03 g/(24 hr)(100 in^2)(Torr/mil) at 23°C from 50 to 100% relative humidity
O_2 permeability:	6.2 cm^3/(24 hr)(100 in^2)(torr/mil)
CO_2 permeability:	28.5 cm^3/(24 hr)(100 in^2)(torr/mil)
Solvents for high molecular weight polymer:	cyclohexanone methylcyclohexanone dimethylformamide nitrobenzene tetrahydrofuran isophorone mesityl oxide
Solvents for low molecular weight polymer:	dipropyl ketone methyl amyl ketone methyl isobutyl ketone acetonylacetone methyl ethyl ketone dioxane methylene chloride

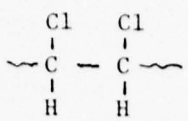
*Reference: Kirk and Othmer, 1970; Windholz, 1977



1-chloroethylenic unit

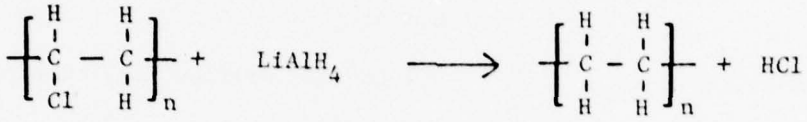


1,1-dichloroethylenic unit

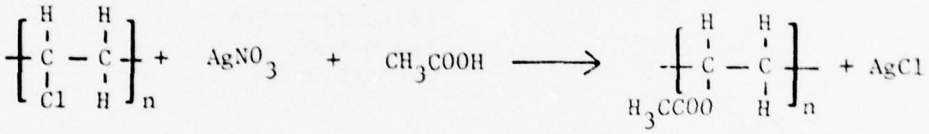


1,2-dichloroethylenic unit

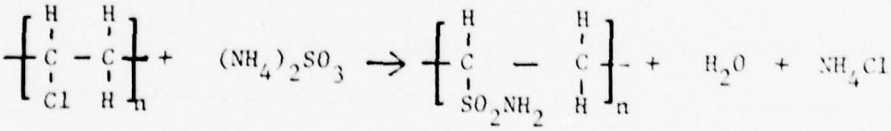
Treatment of poly(vinyl chloride) with lithium aluminum hydride causes reductive hydrogenation with chlorine removal (Kirk and Othmer, 1970).



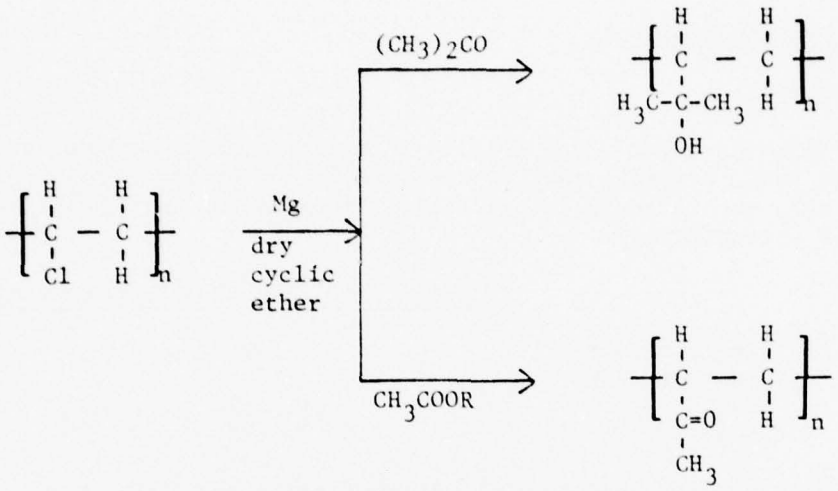
Poly(vinyl acetate) is formed from poly(vinyl chloride) in the presence of silver nitrate in glacial acetic acid at 65°C (Kirk and Othmer, 1970).



Sulfonamide groups may also be exchanged for the chlorine substituents by reacting poly(vinyl chloride) in aqueous suspension with ammonium sulfate followed by dehydration (Kirk and Othmer, 1970).



Poly(vinyl chloride) can react with magnesium in cyclic ether solvents to form grignard-type compounds. These compounds will react with ketones and esters to yield alcoholic and ketonic substituents (Kirk and Othmer, 1970).



Close *et al.* (1977) recently reviewed the thermal degradation of poly(vinyl chloride). Hydrogen chloride is the major product of thermolysis. The literature is divided as to whether vinyl chloride monomer is produced although recent studies indicate that varying amounts are emitted. Other products include aromatic hydrocarbons such as benzene, toluene, ethylbenzene, xylene, stryene, and napthalene and chlorobenzenes. Various additives are available to increase heat stability of poly(vinyl chloride).

2. Environmental Reactions

Ultraviolet radiation degrades unstabilized poly(vinyl chloride) causing HCl emissions and significantly altering the physical properties. Effected properties include tensile strength, loss of light transmission, and embrittlement. Various additives are available which improve UV light stability (Close *et al.*, 1977).

It has been reported that various air pollutants in contact with poly(vinyl chloride) accelerate the photodegradation. Specific examples are

- the reaction of ozone with unsaturated sites in the polymer, promoting degradation,
- the formation of photochemically active sites with sulfur dioxide which increase chain cleavage (Close *et al.*, 1977).

D. Uses in Army Munitions

1. Purpose

Poly(vinyl chloride) acts as a burning rate retardant, a color intensifier and a bonding agent in pyrotechnic and tracer formulations. At Lake City AAP, the following compositions are produced using poly(vinyl chloride) as a constituent:

	% Poly(vinyl chloride) in Composition
Ignitor R-284	17±1
Ignitor I-560	15±1
R-403	17.6±2
R-321	16±1

These compositions are used in the 5.56 mm tracer, the 6.62 mm tracer, the .50 caliber M48 and the .50 caliber M17 shells.

Poly(vinyl chloride) is also used as a component of tracer mixes and pyrotechnic items by Longhorn AAP. The specific end items are not known.

2. Quantities Used

a. Historical Use

The amounts of poly(vinyl chloride) procured by Lake City AAP during the 1975-1977 period are listed below:

1975	17,500 lb
1976	25,000 lb
1977	5,00 lb

The average use rate of poly(vinyl chloride) during this 3-year period was 15,833 lb/year or 1320 lb/month. In addition, Longhorn AAP used 1904 lb of poly(vinyl chloride) in 1977.

b. Current Use

Based upon 1977 data, Lake City AAP and Longhorn AAP are currently using poly(vinyl chloride) at the following rates:

LCAAP	417 lb/month
LAAP	159 lb/month

c. Use at Full Mobilization

At full mobilization, Lake City AAP would use approximately 1400 lb/month of poly(vinyl chloride). The full mobilization use rate at Longhorn AAP would be about 4,800 lb/month (Leander, 1978).

3. Documented or Speculated Occurrences in Air or Water

Production of pyrotechnic and tracer formulations generally results in losses of 0.5-2% of the amount handled (Melton, 1978; Maley, 1978). Thus, the expected losses of poly(vinyl chloride) would be as follows:

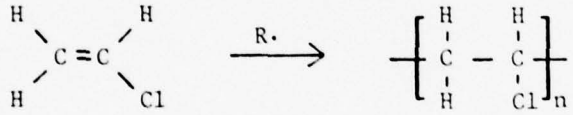
	Losses of Poly(vinyl chloride), lb/month	
	Current	Full Mobilization
LCAAP	4-8	14-28
LAAP	1-2	24-48

At Lake City AAP, the wastes are treated with strong base, neutralized, then discharged to conventional industrial waste treatment facilities. Any poly(vinyl chloride) which enters this treatment will be removed in the sludge. This sludge is removed to an evaporation pond.

E. Uses in the Civilian Community

1. Production Methodology

Poly(vinyl chloride) is manufactured by free radical polymerization of vinylchloride monomer (Kirk and Othmer, 1970).



Most poly(vinyl chloride) in this country is manufactured by suspension polymerization. A flow diagram for a typical batch process is shown in Figure XIV-1. Vinyl chloride monomer and water are charged to the reactor in ratios ranging from 1.5:1 to 4:1. A monomer-soluble free radical initiator and a water-soluble suspension stabilizer are charged to the reactor via the charge bomb. The suspension stabilizer is added to minimize coalescence of the growing polymer chains. Vigorous agitation is initiated, dispersing the monomer in the water. The reactor is brought to temperature, generally around 50°C (the average poly(vinyl chloride) particle molecular weight is inversely related to the polymerization temperature). The reaction rate speeds up as the extent of polymerization increases. The reaction is carried to 90% conversion. The crude product is transferred to the dump tank and unreacted monomer is removed by vacuum. This vinyl chloride monomer is dried and recycled. The poly(vinyl chloride) is transferred to the blend tank and mixed with several previous batches to improve product uniformity. When the blend tank is full, the poly(vinyl chloride is centrifuged to remove bulk water and then hot air dried in a rotary drier. The wet air stream is removed in the

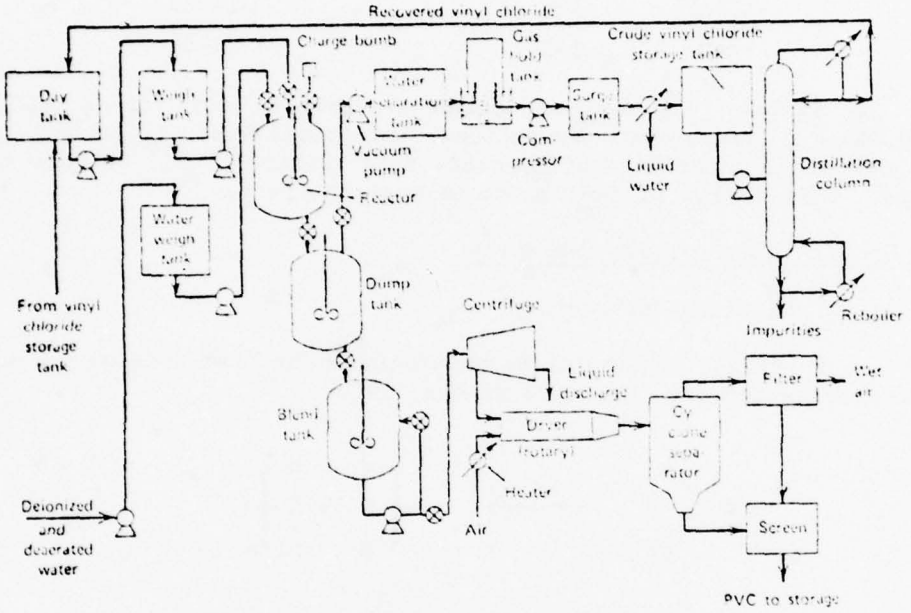


Figure XIV-1. Simplified Flow Diagram of Batch Suspension Polymerization Plant (Kirk and Othmer, 1970).

cyclone separator and the final product is screened and sent to storage (Kirk and Othmer, 1970).

Depending on the intended end product uses, poly(vinyl chloride) can be stabilized, plasticized, dispersed in water or organics, solubilized, pigmented, or blended.

Other methods of vinyl chloride polymerization include (Kirk and Othmer, 1970):

- emulsion polymerization - This technique involves radical initiated polymerization of vinyl chloride monomer emulsified in water by means of surfactants. Emulsion polymerization is employed when small particle size (0.5-2μ) is desired.

- solution polymerization - Polymerization occurs in a medium which stabilizes both the vinyl chloride monomer and poly(vinyl chloride).

- precipitation polymerization - Polymerization occurs in a reaction medium in which the monomer is soluble but poly(vinyl chloride) precipitates as it forms.

2. Manufacturers, Production, and Capacity

The U.S. manufacturers of poly(vinyl chloride), their locations and production capacities are listed in Table XIV-3. U.S. manufacturers of poly(vinyl chloride) copolymers are listed in Table XIV-4.

Historical figures for the total U.S. production of poly(vinyl chloride) and poly(vinyl chloride) copolymers since 1969 are listed in Table XIV-5.

Table XIV-5. U.S. Production of Poly(vinyl chloride) and Poly(vinyl chloride) Copolymers in Million Pounds (U.S. Tariff Commission, 1978).

Year	1969	1970	1971	1972	1973	1974	1975	1976
Production	3,032	3,115	3,437	4,322	4,594	4,744	3,695	4,545

3. Usages

Poly(vinyl chloride) polymers are widely used in the U.S. In 1975, poly(vinyl chloride) resins were ranked fourth in quantity produced and production value for organic end chemicals (S.R.I., 1977a). Table XIV-6 shows the U.S. consumption patterns for poly(vinyl chloride).

Table XIV-3. U.S. Manufacturers of Poly(vinyl chloride)
(S.R.I., 1977a)

Manufacturer	Location	Annual Capacity (10^6 lbs)
Air Products and Chems., Inc.		
Plastics Div.	Calvert City, Ky.	120
	Pensacola, Fla.	150
Atlantic Tubing & Rubber Co.	Cranston, R.I.	50
Borden Inc.		
Borden Chem. Div.		
Thermoplastic Products	Illiopolis, Ill	340
	Leominster, Mass.	180
Certain-Teed Corp.	Lake Charles, La.	385
Continental Oil Co.		
Conoco Chems. Div.	Aberdeen, Miss.	380
	Oklahoma City, Okla.	
Diamond Shamrock Corp.		
Indust. Chems. and Plastics Unit		
Plastics Div.	Deer Park, Tex.	470
	Delaware City, Del.	100
Ethyl Corp.	Baton Rouge, La.	180
The Firestone Tire & Rubber Co.		
Firestone Plastics Co. div.	Perryville, Md.	290
	Pottstown, Pa.	160
The Gen. Tire & Rubber Co.		
Chemical/Plastics Div.	Ashtabula, Ohio	125
	Point Pleasant, W.Va.	55
Georgia-Pacific Corp.		
Chem. Div.	Plaquemine, La.	220
The B.F. Goodrich Co.		
B.F. Goodrich Chem. Co., div.	Avon Lake, Ohio	260
	Henry, Ill	190
	Long Beach, Calif.	140
	Louisville, Ky.	340
	Pedricktown, N.J.	120
The Goodyear Tire & Rubber Co.		
Chem. Div.	Niagara Falls, N.Y.	75
	Piaquemine, La.	200
Great American Chem. Corp.	Fitchburg, Mass.	40
Keysor-Century Corp.	Saugus, Calif.	50

Table XIV-3. U.S. Manufacturers of Poly(vinyl chloride) (S.R.I., 1977a) (Cont.).

Manufacturer	Location	Annual Capacity (10^6 lbs)
Occidental Petroleum Corp.		
Hooker Chem. Corp. subsid.		
RUCO, subsid.	Burlington, N.J.	180
The Pantasote Co. of New York, Inc.		
Eleonora Chem. Div.	Passaic, N.J.	60
	Point Pleasant, W.Va.	60
Rico Chem. Corp.	Guayanilla, P.R.	160
ROBINTECH Inc.	Painesville, Ohio	300
SHINTECH Inc.	Freeport, Tex.	330*
Stauffer Chem. Co.		
Plastics Div.		
Polymers East	Delaware City, Del.	270
Resins and Compounds West	Carson, Calif.	145
Tenneco Inc.		
Tenneco Chems., Inc.	Burlington, N.J.	165
	Flemington, N.J.	90
	Pasadena, Tex.	265
Union Carbide Corp.		
Chems. and Plastics div.	Texas City, Tex.	300
	TOTAL	6,945

*SHINTECH manufactures their Poly(vinyl chloride) for captive use only.

Table XIV-4. U.S. Manufacturers of Poly(vinyl chloride) Copolymers (S.R.I., 1977a).

Manufacturer	Location
Poly(vinyl chloride)-acetate copolymers	
Air Products and Chems., Inc.	
Plastics Div.	Calvert City, Ky.
Atlantic Tubing & Rubber Co.	Cranston, R.I.
Borden Inc.	
Borden Chem. Div.	
Thermoplastic Products	Bainbridge, N.Y.
	Compton, Calif.
	Demopolis, Ala.
	Illiopolis, Ill
	Leominster, Mass.
The Firestone Tire & Rubber Co.	
Firestone Plastics	Pottstown, Pa.
The B. F. Goodrich Co.	
B.F. Goodrich Chem. Co., div.	Avon Lake, Ohio
Keysor-Century Corp.	Saugus, Calif.
National Starch and Chem. Corp.	Meredosia, Ill.
The Pantasote Co. of New York, Inc.	
Eleonora Chem. Div.	Passaic, N.J.
	Point Pleasant, W.Va.
Stauffer Chem. Co.	
Plastics Div.	
Polymers East	Deleware City, Del.
Resins and Compounds West	Carson, Calif.
Tenneco Inc.	
Tenneco Chems., Inc.	Burlington, N.J.
	Flemington, N.J.
Union Carbide Corp.	
Chems. and Plastics, div.	Institute and South Charleston, W.Va.
	Texas City, Tex.
Poly(vinyl chloride)-propylene copolymers	
Air Products and Chems., Inc.	
Plastics Div.	Calvert City, Ky.
Poly(vinyl chloride)-vinylidene chloride copolymers	
Borden Inc.	
Borden Chem. Div.	
Thermoplastic Products	Bainbridge, N.Y.
	Compton, Calif.
	Demopolis, Ala.
	Illiopolis, Ill
	Leominster, Mass.
Dow Chem. U.S.A.	Midland, Mich.
W.R. Grace & Co.	
Indust. Chems. Group	
Dewey and Almy Chem. Div.	Owensboro, Ky.
	South Acton, Mass.
National Starch and Chem. Corp.	Meredosia, Ill.

Table XIV-6. Poly(vinyl chloride) Consumption Patterns (S.R.I., 1977b).

Construction	45.9%
Consumer Goods	15.0%
Packaging	8.4%
Electrical Uses	8.4%
Transportation	6.0%
Home Furnishings	5.7%
Miscellaneous Applications	6.3%
Exports	4.3%

Poly(vinyl chloride) uses in construction include piping and conduits, siding, gutters, window and door frames, interior and exterior plumbing, and flooring. Other uses include in raincoats, leather substitutes, film and sheeting, electrical insulation, artificial athletic playing surfaces, phonograph records, magnetic tape, toys, adhesives and bonding agents, sealants, containers for cosmetics, household chemicals, and toiletries, flexible food wraps, wire and cable protection, paper and textile coatings, upholstery, shoe soles, plastisols, and organosols.

4. Future Trends

Poly(vinyl chloride) will continue to be one of the major organic end chemicals produced and used in the U.S. Several manufacturers are currently increasing production capacities to meet future demands (S.R.I., 1977a). They include;

- Air Products and Chemicals is expanding its Calvert City capacity by 90 million pounds per year. Completion is scheduled in 1978.
- Conoco Chemicals is expanding its Aberdeen capacity by 165 million pounds per year. Completion is scheduled in 1978.
- Diamond Shamrock is expanding its Delaware City capacity by 32 million pounds per year. Completion is scheduled in 1978.
- Firestone is constructing a 200 million pound per year plant at an unspecified location. Completion is scheduled in 1979.
- Georgia-Pacific is expanding its capacity from 220 to 700 million pounds per year. Completion is scheduled in 1979.

- ROBINTECH is expanding its capacity to 500 million pounds per year. Completion is scheduled in 1979.
- Tenneco is expanding its Pasadena capacity by 235 million pounds per year. Completion is scheduled in 1978.

5. Documented or Speculated Occurrences in the Environment

The use of poly(vinyl chloride) is so widespread in the present world that its ubiquitous occurrence through man made waste cannot be avoided. It has been estimated that poly(vinyl chloride) makes up 0.2 percent of the annual solid waste in the U.S. (EPA, 1974). When burned, poly(vinyl chloride) releases hydrogen chloride gas which can cause irritation to humans and animals and damage to structures and mechanical equipment.

F. Comparison of Civilian and Military Uses and Pollution

The civilian production capacity for poly(vinyl chloride) is nearly 7 billion lb/year. Poly(vinyl chloride) is the fourth largest quantity organic chemical produced in the United States. It is used in construction and in a variety of consumer goods. Use of poly(vinyl chloride) in the civilian sector is common throughout the United States. The types of products used are such that waste poly(vinyl chloride) would be expected to occur ubiquitously and in substantial quantities throughout the country.

Military use of poly(vinyl chloride) is very modest compared to civilian use. At full mobilization, only about 75,000 lb/year would be used, representing only 0.001% of the civilian use. Losses to the environment through all munitions manufacture uses of poly(vinyl chloride) would be less than 1000 lb/year at full mobilization. This amount is negligible compared to civilian losses.

G. Toxicological and Environmental Hazards

1. Toxicity to Mammals

The acute oral LD50 for poly(vinyl chloride) to mammals is difficult to determine due to large amounts of material necessary to cause toxic effects (Eckardt and Hindin, 1973). According to Patty (1963), poly(vinyl chloride) is physiologically inert. However, poly(vinyl chloride) in the presence of a surfactive agent can have a high haemolytic potential. Some neoplasms have been observed, however, it is not known whether these were caused by the polymer or the presence of a small amount of unreacted monomer. The vinyl chloride monomer has been shown to be carcinogenic to humans and other mammals (see Table XIV-7).

Most of the human toxicological data on poly(vinyl chloride) is the result of worker exposure to vinyl chloride monomer fumes. There have been reports of liver damage (Gedigk *et al.*, 1975; EPA, 1974), capillary abnormalities (Maricq *et al.*, 1976), angiosarcoma of the liver and other forms of

Table XIV-7. Toxicity of Vinyl Chloride and Poly(vinyl chloride) (NIOSH, 1977).

Compound	Species	Route	Dosage	Effect
Vinyl chloride	Man	Inhalation	500 ppm, intermittent for 4 yrs.	toxic effect carcinogenic effects
" "	Rat	Oral	500 mg/kg	LD50
" "	Rat	Inhalation	6000 ppm/4 hours/ 12-18 day of pregnancy	toxic effects neoplastic effects
" "	Rat	Inhalation	250 ppm/4 hours/ 130 weeks intermittent	toxic effects carcinogenic effects
" "	Mouse	Inhalation	250 ppm for 35 weeks intermittent	toxic effects carcinogenic effects
" "	Hamster	Inhalation	500 ppm/4 hours/ 30 weeks intermittent	toxic effects carcinogenic effects
Poly(vinyl chloride)	Rat	Implant	100 mg/kg	toxic effects neoplastic effects

cancer (EPA, 1976) and other symptoms (Vale *et al.*, 1976).

Although the vinyl chloride monomer is toxic, the polymer appears to be relatively non-toxic. However, acroosteolysis has been reported among workers who scrape poly(vinyl chloride) polymerization vessels. Symptoms of this affliction are tegmental thickening and nodules on hands and forearms, rheumatic pain and clubbing and shortening of distal phalanges. Workers in other phases of vinyl chloride or poly(vinyl chloride) manufacture do not develop the affliction (Dinman *et al.*, 1971).

2. Aquatic Toxicity

The aquatic toxicity of poly(vinyl chloride) is low due to the low solubility of this polymer in water. However, toxic additives in poly(vinyl chloride) can leach out of the polymer into the water (EPA, 1974). For example, an increase in eye abnormalities in fish receiving water through poly(vinyl chloride) pipes has been observed (Poston *et al.*, 1973).

Due to its limited solubility and high volatilization rate from water, the aquatic toxicity of the vinyl chloride monomer is low (EPA, 1974).

3. Toxicity to Microorganisms

A survey of environmental literature concerning poly(vinyl chloride indicates that it is decomposed by certain bacteria and other microorganisms but only over extended periods of time. Schweitzer (1975) reported that poly(vinyl chloride) materials may be more susceptible to bacterial degradation in humid areas such as the tropics.

Hueck (1974) tested plastic poly(vinyl chloride) for residual strength after incubation in soil. After 16 weeks microbial growth was observed on the poly(vinyl chloride) and its residual strength was increased 78%. The poly(vinyl chloride) plastic became less flexible over time when exposed to microorganisms in the soil. Hueck also noted that the main problem with the degradation of plastics is that they contain many impurities, which make the degradation a more complex problem. For example, poly(vinyl chloride) is known to contain 5-20 ppm of unreacted monomer as well as plasticizers and other additives (EPA, 1974).

The vinyl chloride monomer was shown to cause mutations in several strains of *Salmonella typhimurium* when they were exposed to 0.2 to 20% of this chemical in air (Bartsch and Montesano, 1975).

4. Phytotoxicity

No literature concerning the phytotoxicity of poly(vinyl chloride) was encountered. It is most probable that poly(vinyl chloride) poses no serious threat to vegetation due to its relative insolubility and environmentally stable characteristics. One document suggested that since poly(vinyl chloride) degrades very slowly in a landfill environment, it should not add

significantly to the production of leachate or decomposition gases (EPA, 1974) which could be detrimental to vegetation.

5. Availability of Literature for Phase II

Due to the higher than normal incidences of angiosarcomas among poly(vinyl chloride) workers, many toxicological and environmental studies have been conducted on poly(vinyl chloride) and the vinyl chloride monomer. Thus, there is a significant amount of literature that would be available for a Phase II study.

H. Regulations and Standards

1. Air and Water Regulations

EPA has proposed the following emission standard for ethylene dichloride, vinyl chloride and poly(vinyl chloride) plants (Federal Register, 1977):

- For those plants for which construction had commenced before June 2, 1977 - 10 ppm until June 2, 1980 and 5 ppm thereafter.

- For those plants for which construction commenced after June 2, 1977 - 5 ppm.

Emission standards for the various process steps were also proposed.

2. Health Standards

The OSHA air standard for exposure to vinyl chloride monomer is 1 ppm. This concentration is the ceiling concentration for a 15 minute exposure (Federal Register, 1975). No exposure limits have been set for poly(vinyl chloride). A study of the carcinogenic potential of this polymer yielded undetermined results.

3. DOT Regulations

The Department of Transportation requires that shipments of the vinyl chloride monomer be labelled "Flammable Gas" (Federal Register, 1976).

I. Conclusions and Recommendations

Poly(vinyl chloride) is the fourth highest volume organic chemical produced in the United States, with production capacity nearing 7 billion lb/year. Military use of this material are insignificant in comparison to civilian usage. At full mobilization the military use rate would be 75,000 lb/year, or 0.001% of the civilian use. Civilian uses include construction, packaging and home furnishings. Disposal of consumer items containing poly(vinyl chloride) leads to widespread environmental dispersion of extremely large quantities of this material. Military sources of entry into the

environment are negligible by comparison.

Poly(vinyl chloride) is physiologically inert. The polymer is relatively non-toxic, although the monomer, vinyl chloride, has been shown to cause angiosarcomas of the liver in humans and mutagenic effects in microorganisms.

Because of the low military use compared to civilian requirements, this chemical is clearly not a military responsibility. Therefore, poly(vinyl chloride) should be a low priority for an Army sponsored Phase II toxicological and environmental study.

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AD

PRELIMINARY PROBLEM DEFINITION STUDY OF 48 MUNITIONS-RELATED CHEMICALS

VOLUME IV PRIMER AND TRACER RELATED CHEMICALS

STRONTIUM PEROXIDE

FINAL REPORT

J. F. Kitchens
W. E. Harward III
D. M. Lauter
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R. S. Valentine

April 1978

Supported by:

U. S. ARMY MEDICAL RESEARCH AND DEVELOPMENT COMMAND
Fort Detrick, Frederick, Maryland 21701

Contract No. DAMD17-77-C-7057

COTR: Clarence Wade, Ph.D.

ATLANTIC RESEARCH CORPORATION
Alexandria, Virginia 22314

Approved for Public Release
Distribution Unlimited

The findings of this report are not to be construed as an official Department of the Army position unless so designated by other authorized documents.

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SUMMARY

Strontium peroxide is used by the Army as an oxidizer in primer and tracer mixes. Under current production schedules, this compound is used only at Lake City AAP. Current use rate of strontium peroxide by the Army is ∿21,000 lb/year. This usage would increase to ∿50,000 lb/year under full mobilization schedules. Losses from the mixing and loading processes could be as high as 90 lb/month at full mobilization production. These wastes flow into an industrial wastewater treatment plant. During the treatment process, the strontium is precipitated. The sludge is disposed of in ponds. The water discharges could contain a maximum of 3.5 ppm of strontium.

Civilian production of strontium peroxide is estimated at less than 200,000 lb/year. There are only limited civilian uses of strontium peroxide - as a bleaching agent and an antiseptic. No information is available on the pollution resulting from the civilian production or use of this chemical.

Strontium salts have a low toxicity to mammals, aquatic organisms and plants, being toxic only when administered in doses of several grams per kilogram.

Based on the information gathered and evaluated during this study, strontium peroxide or strontium salts resulting from this chemical are probably present in significant quantities in the Lake City AAP effluent. Thus, this compound could present an environmental problem. Further Army sponsored work on strontium peroxide should include the combined effects of all strontium compounds and their interaction with other cations present in the Little Blue River.

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FOREWORD

This report details the results of a preliminary problem definition study on strontium peroxide. The purpose of this study was to determine the Army's responsibility for conducting further research on strontium peroxide in order to determine its toxicological and environmental hazards so that effluent standards can be recommended. In order to determine the Army's responsibility for further work on strontium peroxide, the military and civilian usage and pollution of this chemical were evaluated. In addition, a preliminary overview of toxicological and environmental hazards was conducted.

Strontium peroxide was only one of 48 chemicals evaluated under Phase IA of contract No. DAMD17-77-C-7057. These chemicals are grouped in four categories

- explosives related chemicals
- propellant related chemicals
- pyrotechnics
- primers and tracers

Each category is a major report. Section I of each report is an overview of the military processes which use each chemical and the pollution resulting from the use of these chemicals. The problem definition study reports on each chemical are separable sections of these four reports.

In addition a general methodology report was also prepared. This report describes the search strategy and evaluation methodology utilized for this study.

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XV. STRONTIUM PEROXIDE

A. Alternate Names

Strontium peroxide, SrO_2, has a molecular weight of 119.62 g/mole and a structural formula:

Sr-O-O

It also exists as the octahydrate, $SrO_2 \cdot 8H_2O$, of molecular weight 263.74 g/mole. The pertinent alternate names for strontium peroxide are listed below:

SrO_2

CAS Registry No.:	1314-18-7
Replaces CAS Registry No.:	45335-79-3
CA Name (8CI):	Strontium peroxide ($Sr(O_2)$)
Wiswesser Line Notation:	Sr Q*2
Synonyms:	Strontium peroxide; Strontium dioxide

B. Physical Properties

The physical properties of strontium peroxide and strontium peroxide octahydrate are presented in Table XV-1.

C. Chemical Properties

1. General Reactions

Strontium peroxide reacts with dilute or strong acid to generate hydrogen peroxide (Kirk and Othmer, 1968).

$$SrO_2 + 2H^+ \longrightarrow Sr^{++} + H_2O_2$$

Strontium peroxide is a strong oxidizing agent. It will readily react with combustibles or easily oxidizable materials. Such mixtures are explosive and ignite easily with friction (OSHA, 1972).

2. Environmental Reactions

Strontium peroxide is almost insoluble in water but will slowly decompose with O_2 evolution in contact with it (Windholz, 1977). There are no reports of photochemical instability.

Table XV-1. Physical Properties of Strontium Peroxide and Strontium Peroxide Octahydrate*.

SrO_2	
Physical Form @ 20°C:	solid
Color:	white powder
Taste and Odor:	odorless and tasteless
M.P.:	2.5°C decomposes
Density:	4.56
Solubility:	water - 0.008 g/100g @ 20°C decomposes in hot water very soluble in alcohol and ammonium chloride insoluble in acetone
$SrO_2 \cdot 8H_2O$	
Physical Form @ 20°C:	solid
Color:	colorless crystals
Taste and Odor:	odorless and tasteless
M.P.:	100°C $-8H_2O$
B.P.:	decomposes
Density:	1.951
Solubility:	water - 0.018 g/100g @ 20°C decomposes in hot water soluble in alcohol and ammonium chloride insoluble in ammonium hydroxide

* References: Hodgman *et al.*, 1963; Windholz, 1976; Hawley, 1977.

3. Sampling and Analysis

Strontium peroxide may be determined titrametrically using permanganate, ceric sulfate, potassium iodide, thiosulfate, titanous chloride, or sodium nitrite; eudiometrically by measurement of O_2 generation upon decomposition; and various spectrophotometric methods. A spectrophotometric determination using a titanium-peroxide complex has been reported for the measurement of strontium peroxide in tracer bullets (Norwitz and Galan, 1976).

Analysis for dissolved strontium is best accomplished using flame photometry. This technique can determine strontium at concentrations of 12.0 mg/l with an accuracy of ± 1 or 2 mg/l (Franson, 1975).

D. Uses in Army Munitions

1. Purpose

Strontium peroxide is used as an oxidizer in primer and tracer mixtures. This material imparts a red color to burning compositions. At Lake City AAP, strontium peroxide is a component of the following formulations:

	% Strontium Peroxide in Formulation
Igniter I-547	76.5±2
Igniter I-548	65±2
Igniter I-560	30.0±1
Igniter I-136	90±1
R-20C	65.5±1
R-440	40±1
R-10E	79±1
R256	26.7±1

These formulations are used to produce the 5.62 mm and 7.62 mm tracers as well as .50 cal. and 20 mm shells.

2. Quantities Used

a. Historical Use

Strontium peroxide is used in relatively large quantities in munitions manufacture. The amounts of this material procured by LCAAP during the 1975-1977 period are listed below:

1975	31,200 lb
1976	21,300 lb
1977	10,500 lb

The purchases correspond to an average use rate of 21,000 lb/year or 1,750 lb/month.

b. Current Use

The current use rate of strontium peroxide at LCAAP is 875 lb/month or 10,500 lb/year.

c. Use at Full Mobilization

At full mobilization the use of strontium peroxide at LCAAP would be approximately 4,400 lb/month or 52,000 lb/year.

3. Documented or Speculated Occurrences in Air or Water

The losses associated with primer and tracer manufacture are generally about 1-2% of the amount handled (Melton, 1978). Based on this estimate, current losses of strontium peroxide at LCAAP would be 9-18 lb/month. At full mobilization, losses would increase to 45-90 lb/month.

At LCAAP, primer and tracer wastes are treated with strong base to destroy explosive components. These wastes are then neutralized and discharged into conventional industrial waste treatment facilities. Treatment of strontium peroxide waste with alum and calcium hydroxide in this plant will result in the precipitation of strontium sulfate ($K_{sp} = 3.81 \times 10^{-7}$) or calcium carbonate ($K_{sp} = 1.6 \times 10^{-9}$). The maximum concentration of strontium which could occur in the effluent from this treatment plant is 3.5 mg/l.

E. Uses in the Civilian Community

1. Production Methodology

Strontium peroxide is manufactured by the action of alkaline hydrogen peroxide on a soluble strontium salt (Hummel Chemical, 1978).

$$Sr^{++} + 2OH^{-} + H_2O_2 \longrightarrow SrO_2 + 2H_2O$$

During the process, strontium hydroxide is formed and it reacts with the H_2O_2. Strontium peroxide precipitates.

Strontium peroxide may also be made by direct oxidation of strontium oxide at 200 atmospheres of pressure and 350°C (Kirk and Othmer, 1968).

$$SrO + \tfrac{1}{2}O_2 \longrightarrow SrO_2$$

2. Manufacturers, Production and Capacity

Strontium peroxide is manufactured by Barium and Chemicals in Steubenville, Ohio, and Hummel Chemical in South Plainfield, New Jersey. Their plant capacities and past production figures are not available (S.R.I., 1977). Strontium peroxide is a minor chemical; total United States production capacity is estimated at <200,000 lb/year.

3. Usages

Strontium peroxide is used in the civilian community as a bleaching agent and an antiseptic (Windholz, 1977).

4. Future Trends

No major changes are anticipated in civilian use of strontium peroxide. It is expected to remain a minor chemical.

5. Documented or Speculated Occurrences in the Environment

There are no reports in the literature of strontium peroxide as an environmental pollutant. Strontium has been measured in seawater at levels of 8 to 10 mg/l. Freshwater concentrations usually fall in the range of 0.05 to 0.5 mg/l (Burrows and Dacre, 1975).

F. Comparison of Military and Civilian Usage and Pollution

Strontium peroxide is a small production chemical which finds limited use as a bleaching agent and an antiseptic in the civilian community. Estimated production of this compound is less than 200,000 lb/year. Military use of strontium peroxide averages ∿21,000 lb/year at current production rates. At full mobilization rates ∿52,800 lb/year would be needed for primer and tracer mixes manufactured at Lake City AAP. This need represents a significant portion of the civilian production of strontium peroxide.

G. Toxicological and Environmental Hazards

1. Toxicity to Mammals

Much of the toxicological research on strontium has concerned the radioactive isotope strontium Sr-90. Chemically the toxicity of Sr is very low (Casarett and Doull, 1975). No adverse effects from industrial use have been reported. Experimentally electrocardiograph changes and death due to respiratory paralysis have been produced by the injection of high doses of strontium (Beliles, 1975). However, due to its strong oxidizing ability, strontium peroxide will cause irritation to skin and lung tissue similar to that observed with contact with hydrogen peroxide (OSHA, 1972).

2. Aquatic Toxicity

Normal levels of strontium in natural water range from 50-500 ppb (Templeton and Brown, 1964). Most of the strontium aquatic toxicity studies have examined $SrCl_2$ or $Sr(NO_3)_2$; both of these compounds are soluble in water. As shown in Table XV-2, these salts are not highly toxic to fish. Strontium peroxide is insoluble in water; therefore, it will be less available to fish and will have a lower toxicity than the more soluble nitrate and chloride salts. As shown in Table XV-3, strontium is not bioaccumulated by aquatic organisms.

Table XV-2. Toxicity of Strontium to Freshwater and Marine Fishes.

Fish	Salt	Sr Concn. mg/l	Reported Effect	Reference
Goldfish (*Carassius carassius*)	$SrCl_2$	8,500	Lethal in 17-31 hr.	Powers, 1917
Goldfish (*Carassius carassius*)	$Sr(NO_3)_2$	3,980	Lethal in 32-146 hr.	Powers, 1917
Goldfish			Depression of movement and respiration	Okuda, 1932
Stickleback (*Gasterosteus aculeatus*)	$Sr(NO_3)_2$	1,200	Min. lethal conc.	Jones, 1939
Stickleback (*Gasterosteus aculeatus*)	$Sr(NO_3)_2$	3,000	Av. survival 96 hr.	Jones, 1939
Stickleback (*Gasterosteus aculeatus*)	$Sr(NO_3)_2$	7,000	Av. survival 48 hr.	Jones, 1939
Stickleback (*Gasterosteus aculeatus*)	$Sr(NO_3)_2$	10,000	Av. survival 24 hr.	Jones, 1939
Orizias latipes	$SrCl_2$	11,000	Lethal in 24 hr.	Iwao, 1936
Mediterranean Fishes				
Serranus cabrilla				
Crenolabrus Mediterraneus	$SrCl_2$	2,200	Survive > 48 hr.	Richet, 1881
Julius vulgaris				
Julius giofredi				

Table XV-3. Bioaccumulation of Strontium in Aquatic Organisms.

Organism	Bioaccumulation factor	Reference
Brown trout *(Salmo trutta)*		
bone	.45-56	Templeton & Brown, 1964
muscle	.53-1.00	Templeton & Brown, 1964
Rainbow Trout *(S. gairdneri)*	.37	Ichikawa, 1960
Snail *(Lymnaea stagnalis)*	.5	Van der Borght, 1962
Water flea *(Daphnia magna)*	.58	Marshall *et al.*, 1962

3. Toxicity to Microorganisms and Invertebrates

Several studies have shown that the microcrustacean, *Daphnia magna*, is substantially more sensitive to strontium salts than fish. Anderson (1948) reported that the 64-hour immobilization threshold for strontium chloride to be 63 mg/l as Sr. The 48-hour toxic threshold is 210 mg/l (Bringman and Kuhn, 1959). The 48-hour threshold survival concentration of the planarian, *Polycelis nigra*, is 6600 mg/l as Sr for strontium chloride and 3500 mg/l as Sr for strontium nitrate (Jones, 1940).

Yarbrough and O'Kelley (1965) demonstrated that the complete substitution of strontium for calcium at 18 mg Sr/l in the nutrient medium of the protozoan, *Paramecium multimicronucleatum*, had no effect on the rate of growth.

For a wide range of bacterial species, strontium salts have been found to be toxic only at very high concentrations (refer to Table XV-4). The resistance of many fungi to strontium is the same or greater than for bacteria.

4. Phytotoxicity

Strontium compounds may be highly toxic to plants under certain conditions such as in the absence of calcium carbonate.

McHargue (1919) studied the effects of strontium nitrate on the growth of winter wheat (*Triticum aestivum*). He reported that increasing the amount of strontium nitrate gave a corresponding increase in the nitrogen content of the wheat. The yields and average weight of the wheat produced in each experiment are presented in Table XV-5. The results obtained are probably due to the large amounts of nitrate radical present rather than to the strontium ion since strontium carbonate experiments didn't show marked increase in yields. Other investigations proved that strontium carbonate is less toxic than barium carbonate in the absence of calcium carbonate.

Scharrer and Schropp (1937) reported that concentrations of strontium higher than 10^{-1} milliequivalents were toxic to peas. Plants less sensitive to strontium include wheat, maize, oats, barley and rye.

Walsh (1945) studied the effect of strontium (various salts) on the growth of mustard, oats, barley and wheat. He concluded that strontium is capable of substantially replacing calcium in the vegetative growth of these plants but not in the formation of grain in the cereals. The toxicity of strontium seems to be directly related to the amount absorbed.

5. Availability of Literature for Phase II

Although the availability of environmental and toxicological literature specifically for strontium peroxide is limited, a large number of studies on strontium salts have been reported. Thus, sufficient information is available for a Phase II study.

Table XV-4. Effects of Strontium Salts on Microorganisms.

Microorganism	Salt	Sr Concn. mg/l	Reported Effect	Reference
Protozoa				
Microregma heterostoma	$SrCl_2$	329	28 hr toxic threshold for feeding	Bringmann and Kuhn, 1959
Paramecium	$SrCl_2$	8000	All dead in 4.5 hr	Dale, 1913
Bacteria				
Bacillus anthracis	$SrCl_2$	23×10^3	Growth inhibition threshold	Eisenberg, 1919
Bacillus anthracis	$SrCl_2$	26×10^3	Growth inhibition	Eisenberg, 1919
Sarcina tetragena	$SrCl_2$	17×10^3	Growth inhibition threshold	Koulumies, 1946
Micrococcus phogenes	$SrCl_2$	17×10^3	Growth inhibition threshold	Eisenberg, 1919
Micrococcus candicans	$SrCl_2$	13×10^3	Growth inhibition threshold	Eisenberg, 1919
Corynebacterium diphtheriae	$SrCl_2$	6700	Growth inhibition threshold	Eisenberg, 1919
Corynebacterium diphtheriae	$SrCl_2$	10×10^3	Growth inhibition	Koulumies, 1946
Corynebacterium pseudodiphtheriae	$SrCl_2$	10×10^3	Growth inhibition threshold	Eisenberg, 1919
Corynebacterium pseudodiphtheriae	$SrCl_2$	4×10^3	Growth inhibition	Koulumies, 1946
Bacillus typhi	$SrCl_2$	30×10^3	Growth inhibition threshold	Eisenberg, 1919
Bacillus pneumoniae	$SrCl_2$	13×10^3	Growth inhibition threshold	Eisenberg, 1919
Bacillus pyrocyaneus	$SrCl_2$	10×10^3	Growth inhibition threshold	Eisenberg, 1919
Bacillus vulgare	$SrCl_2$	27×10^3	Growth inhibition threshold	Eisenberg, 1919
Vibrio cholerae	$SrCl_2$	1700	Growth inhibition threshold	Eisenberg, 1919
Escherichia coli	$SrCl_2$	27×10^3	Growth inhibition threshold	Eisenberg, 1919

Table XV-4 (continued)

Escherichia coli	$SrCl_2$	22×10^3	Growth inhibition threshold	Hotchkiss, 1923
Escherichia coli	$SrCl_2$	18×10^3	Growth inhibition	Koulumies, 1946
Salmonella paratyphi B	$SrCl_2$	10×10^3	Growth inhibition	Koulumies, 1946
Salmonella paratyphi A	$SrCl_2$	10×10^3	Growth inhibition	Koulumies, 1946
Eberthella typhosa	$SrCl_2$	18×10^3	Growth inhibition	Koulumies, 1946
Proteus vulgaris	$SrCl_2$	18×10^3	Growth inhibition	Koulumies, 1946
Shigella paradysenteriae	$SrCl_2$	7×10^3	Growth inhibition	Koulumies, 1946
Brucella abortus	$SrCl_2$	7×10^3	Growth inhibition	Koulumies, 1946
Pasteurella pestis (Tjevidei)	$SrCl_2$	7×10^3	Growth inhibition	Koulumies, 1946
Pasteurella pestis (Soemsdang)	$SrCl_2$	22×10^3	Growth inhibition	Koulumies, 1946
Hemophilus pertussis	$SrCl_2$	10×10^3	Growth inhibition	Koulumies, 1946
Hemophilus influenza	$SrCl_2$	10×10^3	Growth inhibition	Koulumies, 1946
Neisseria catarrhalis	$SrCl_2$	18×10^3	Growth inhibition	Koulumies, 1946
Neisseria gonorrhoeae	$SrCl_2$	10×10^3	Growth inhibition	Koulumies, 1946
Staphylococcus aureus	$SrCl_2$	10×10^3	Growth inhibition	Koulumies, 1946
Staphylococcus albus	$SrCl_2$	10×10^3	Growth inhibition	Koulumies, 1946
Streptococcus pyrogenes	$SrCl_2$	10×10^3	Growth inhibition	Koulumies, 1946
Streptococcus viridans	$SrCl_2$	10×10^3	Growth inhibition	Koulumies, 1946
Diplococcus pneumoniae	$SrCl_2$	10×10^3	Growth inhibition	Koulumies, 1946
Actinomyces israelis	$SrCl_2$	44×10^3	Growth inhibition	Koulumies, 1946
Mycobacterium tuberculosis hominis	$SrCl_2$	7×10^3	Growth inhibition	Koulumies, 1946

(SI-AA)

Table XV-4 (continued)

Mycobacterium tuberculosis bovis	$SrCl_2$	7×10^3	Growth inhibition	Koulumies, 1946
Clostridium (7 species)	$SrCl_2$	7 to 10 $\times 10^3$	Growth inhibition	Koulumies, 1946
Leptospira icterohaemorrhagiae (3 strains)	$SrCl_2$	7 to 10 $\times 10^3$	Growth inhibition	Koulumies, 1946
Fungi				
Epidermophyton Kaufmann-Wolff	$SrCl_2$	26×10^3	Growth inhibition	Koulumies, 1946
Trichophyton (3 species)	$SrCl_2$	26 to 52 $\times 10^3$	Growth inhibition	Koulumies, 1946
Penicillium (Orion)	$SrCl_2$	70×10^3	Growth inhibition	Koulumies, 1946
Mucor corymbifer	$SrCl_2$	26×10^3	Growth inhibition	Koulumies, 1946
Cladisporium mansoni	$SrCl_2$	44×10^3	Growth inhibition	Koulumies, 1946
Scopularia brevicaulis	$SrCl_2$	66×10^3	Growth inhibition	Koulumies, 1946
Aspergillus fumigatus	$SrCl_2$	70×10^3	Growth inhibition	Koulumies, 1946
Altenaria	$SrCl_2$	66×10^3	Growth inhibition	Koulumies, 1946
Altenaria tenuis	$Sr(NO_3)_2$	30×10^3	ED50, germination inhibition	Somers, 1959; 1961
Botrytis fabae	$Sr(NO_3)_2$	13×10^3	ED50, germination inhibition	Somers, 1961
Algae				
Coccomyxa pringsheimii	----	5 - 10	Inhibition of growth and calcium utilization	Walker, 1956
Chlorella vulgaris	$SrCl_2$-$6H_2O$	$>13 \times 10^3$	Lowest inhibitory conc.	den Dooren de Jong, 1965

Table XV-5. Effects of Strontium Nitrate on the Growth of Winter Wheat.
(McHargue, 1919)

Pot No. and treatment	Number of grains per pot.	Weight of grain per pot.	Average weight per grain.	Weight of straw.
		Gm.	Gm.	Gm.
Pot 1 (control), no strontium nitrate	372	8.8872	0.0239	34.50
Pot 2 (control), no strontium nitrate	292	7.7650	.0266	27.50
Average	332	8.3261	.0252	31.00
Pot 3+5 gm. of strontium nitrate	369	11.9065	.0323	44.50
Pot 4+5 gm. of strontium nitrate	555	19.6108	.0353	52.00
Average	462	15.7586	.0338	48.25
Pot 5+10 gm. of strontium nitrate	561	17.6505	.03146	62.00

H. Regulations and Standards

There are no EPA regulations or standards specific to strontium peroxide. As a health hazard, strontium peroxide is classified as a nuisance dust. The respirable fraction should be held below 5 mg/m^3 and the total dust concentration below 15 mg/m^3 (OSHA, 1972). The Department of Transportation requires an "oxidizer" label for shipment of strontium peroxide (Federal Register, 1974).

I. Conclusions and Recommendations

In order to assess the Army's responsibility for conducting further research on strontium peroxide, the Army and civilian usage and pollution of this compound have been reviewed and evaluated. A preliminary overview of the toxicological and environmental properties of strontium peroxide was undertaken. In view of the data evaluated during this search, it is recommended that the Army sponsor Phase II research on the toxicological and environmental properties of this compound. However, strontium peroxide should be a low priority chemical. This recommendation is based on the following conclusions:

- The military use of strontium peroxide is a significant portion of the civilian production capacity for this chemical; thus, it is a military problem chemical.
- The wastes generated from the Lake City AAP industrial treatment plant could contain as much as 3.5 mg/l of strontium. This concentration is above that of natural waters.
- Strontium has a low toxicity for most aquatic species, microorganisms, mammals and plants.

This study should include an evaluation of the effects of all strontium salts released from LCAAP on the Little Blue River with particular attention to the interaction of strontium with other metals in the river.

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AD

PRELIMINARY PROBLEM DEFINITION STUDY OF 48 MUNITIONS-RELATED CHEMICALS

VOLUME IV PRIMER AND TRACER RELATED CHEMICALS

CALCIUM RESINATE

FINAL REPORT

J. F. Kitchens
W. E. Harward III
D. M. Lauter
R. S. Wentsel
R. S. Valentine

April 1978

Supported by:

U. S. ARMY MEDICAL RESEARCH AND DEVELOPMENT COMMAND
Fort Detrick, Frederick, Maryland 21701

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COTR: Clarence Wade, Ph.D.

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Alexandria, Virginia 22314

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SUMMARY

Calcium resinate is a flammable solid used as a fuel, binding and water proofing agent in primers and tracers. At the present time, the use of this compound by the Army is limited to 4,000-6,000 lb per year at Lake City AAP. Full mobilization production of primer and tracer mixes containing calcium resinate would require about 10,000 lb of this chemical per year. It appears that any calcium resinate lost in the processing is effectively removed as sludge by the industrial waste treatment system at Lake City AAP.

In contrast to Army use, calcium resinate is used in a wide variety of consumer products. Civilian production capacity is ∿25 million lb/year. Because of the widespread use of this chemical in paints and varnishes, significant non-point source pollution of calcium resinate is expected. However, no specific pollution statistics appear in the literature.

Calcium resinate has a low toxicity for mammals. With the exception of Chinook Salmon, this chemical does not appear to be a significant aquatic hazard. This conclusion is based on relatively little information and the aquatic toxicity of this chemical requires further evaluation.

Based on the information gathered during this study, calcium resinate is a civilian problem. Further studies to evaluate these studies should be carried out by the civilian community.

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FOREWORD

This report details the results of a preliminary problem definition study on calcium resinate. The purpose of this study was to determine the Army's responsibility for conducting further research on calcium resinate in order to determine its toxicological and environmental hazards so that effluent standards can be recommended. In order to determine the Army's responsibility for further work on calcium resinate, the military and civilian usage and pollution of this chemical were evaluated. In addition, a preliminary overview of toxicological and environmental hazards was conducted.

Calcium resinate was only one of 48 chemicals evaluated under Phase IA of contract No. DAMD17-77-C-7057. These chemicals are grouped in four categories

- explosives related chemicals
- propellant related chemicals
- pyrotechnics
- primers and tracers

Each category is a major report. Section I of each report is an overview of the military processes which use each chemical and the pollution resulting from the use of these chemicals. The problem definition study reports on each chemical are separable sections of these four reports.

In addition, a general methodology report was also prepared. This report describes the search strategy and evaluation methodology utilized for this study.

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XVI. CALCIUM RESINATE

A. Alternate Names

Calcium resinate is the calcium salt of resin acids. The molecular formula and exact structure of this compound are unknown. The CAS Registry Number for calcium resinate is 9007-13-0. It is also known as limed rosin.

B. Physical Properties

The available physical properties of calcium resinate are listed in Table XVI-1.

Table XVI-1. Physical Properties of Calcium Resinate

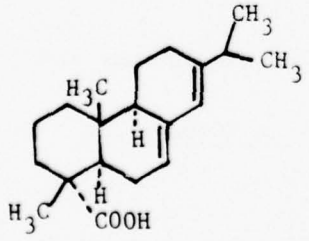
Physical form @ 20°C:	amorphous solid or lumps
Color:	yellowish-white
Odor:	rosin-like
Solubility:	insoluble in water soluble in acid, amyl acetate, butyl acetate, ether and amyl alcohol

Reference: Hawley, 1977.

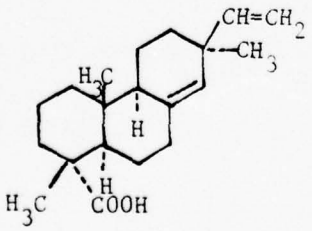
C. Chemical Properties

1. Chemical Composition

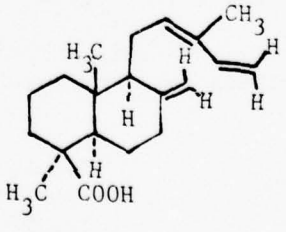
Calcium resinate is primarily the normal calcium salt of resin acids. Most gum and wood rosins are made up of about 90% resin acids and 10% nonacidic components. Resin acids include the abietic-type acids, the pimaric-type acids, and other resin acids such as elliotinoic acid (Kirk and Othmer, 1968).



Abietic Acid



Pimaric Acid



Elliotinoic Acid

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The abietic-type acids differ from abietic acid in degree of saturation and placement of the double bond. The pimaric-type acids differ from pimaric acid in the placement of the double bond and the stereochemistry of the vinyl ($-CH=CH_2$) substituent.

2. General Reactions

Calcium resinate dissolves in acids, presumably to free calcium ions and the component resin acids. The resin acids possess two reactive sites, the carboxylate function and the double bonds. The carboxyl group may be esterified, reduced, aminated or cleaved in a decarboxylation. Established reactions at the double bond include isomerization, additions, Diels-Alder addition of maleic anhydride, oxidation, hydrogenation, dehydrogenation, and polymerization (Kirk and Othmer, 1968).

3. Environmental Reactions

Little can be said on the environmental chemistry of calcium resinate. It is insoluble in water preventing its introduction to the aquatic environment. Photochemical studies have not been reported.

4. Sampling and Analysis

There are no reported analytical techniques for calcium resinate. It can be determined as calcium with standard techniques following acidification and separation of the organic components. Calcium may be determined by atomic absorption methods. Reported sensitivity limits are 70 mg calcium/l giving 1% absorption. Calcium may also be determined by quantitative precipitation as calcium oxalate followed by titration with a standard permanganate solution. Direct titration with EDTA in the presence of an indicator allows a rapid and simple determination (Franson, 1975).

D. Uses in Army Munitions

1. Purpose

Calcium resinate is used in pyrotechnics and in primer and tracer compositions. This material is a fuel, and also acts as a burning rate retardant. It imparts a yellow-red color to burning compositions. Other functions of calcium resinate are to serve as a binding agent and in some cases as a waterproofing agent.

Calcium resinate is used at Lake City AAP. The formulations requiring this substance are listed below:

	% Calcium Resinate in Formulation
Igniter I-547	23.5±2
Igniter I-548	20±2
Igniter I-136	10±1
R-20C	6±0.5
IM-163A	8±1

	% Calcium Resinate in Formulation
R-440	10±1
R-10E	7.25
R-505	19.2 max
R-256	8.3±1.1

These formulations are used in the 5.62 mm tracer, the 7.62 mm tracer and the .50 caliber and 20 mm shells.

2. Quantities Used

a. Historical Use

During the 1975-1977 period, LCAAP purchased the following amounts of calcium resinate:

1975	4,185 lb
1976	6,575 lb
1977	2,180 lb

These purchases represent an average use rate over the three year period of 4,313 lb/year or 360 lb/month.

b. Current Use

The use rate of calcium resinate during 1977 averaged 182 lb/month at LCAAP.

c. Use at Full Mobilization

The full mobilization use rate of calcium resinate at LCAAP is approximately 900 lb/month.

3. Documented or Speculated Occurrences in Air or Water

The actual losses of calcium resinate have not been measured. However, according to Melton (1978) losses of material during primer and tracer processing operations average 1-2% of the amount handled. Thus, losses of calcium resinate at LCAAP are currently in the range of 2-4 lb/month. At full mobilization, the loss would increase to 9-11 lb/month.

Waste effluents at LCAAP are treated with strong base to destroy explosive components. The waste is then neutralized and sent to conventional industrial waste treatment facilities. The fate of calcium resinate in this process has not been determined. Some free calcium and resin acids could be formed. However, it is expected that the majority of the calcium resinate remains in the sludge.

E. Uses in the Civilian Community

1. Production Methodology

Calcium resinate may be prepared by two methods. Addition of calcium hydroxide to a rosin solution at 40-70°C causes calcium resinate to precipitate. The precipitate is filtered, dried and pulverized. Calcium hydroxide may also be fused with a rosin melt at 285°C to form calcium resinate. Calcium acetate can act as a catalyst for the fusion (Kirk and Othmer, 1968; Hawley, 1977).

2. Manufacturers, Production and Capacities

The U.S. manufacturers of calcium resinate and their plant locations are listed in Table XVI-2.

Table XVI-2. U.S. Manufacturers of Calcium Resinate

Manufacturer	Location
Crosby Chemicals, Inc.	Picayune, MS
Barium and Chemicals, Inc.	Steubenville, OH
Reichhold Chemicals, Inc.	
Newport Division	Bay Minetta, AL
	Oakdale, LA
	Pensacola, FL

Crosby Chemicals manufactures calcium resinate which does not meet military specifications. They have a capacity on the order of 4 million pounds per year and are currently expanding their facilities. Barium and Chemicals manufactures calcium resinate to military specifications. They produce 5 to 10 thousand pounds per year. Reichhold Chemicals has a capacity on the order of 20 million pounds per year (communications with manufacturers).

3. Usages

Calcium resinate is used as a drier and hardener in varnishes, paints, adhesives and inks. Other uses include in protective coatings for exported fruit, waterproofing, manufacturing porcelains, perfumes, cosmetics, and enamels, as a coating for fabrics and paper, and in leather tanning. (Kirk and Othmer, 1968; Hawley, 1977; communications with manufacturers).

4. Future Trends

Only minor increases are expected in the civilian use of calcium resinate (Reichhold Chemicals, 1978).

5. Documented or Speculated Occurrences in the Environment

There are no reports in the literature of calcium resinate as an environmental pollutant. However, due to the wide variety of uses, significant non-point source pollution from consumer use and disposal of unwanted materials would be expected.

F. Comparison of Civilian and Military Uses and Pollution

The civilian production capacity of calcium resinate is ∿25 million lb/year. This compound is used in a wide variety of consumer products as a drier and hardener. Current military use of calcium resinate is less than 0.02% of the civilian production capacity. At full mobilization, the Army's needs would increase to only ∿0.04% of civilian production capacity.

The widespread use of calcium resinate in many consumer products will lead to significant non-point source pollution by this compound from disposal of these consumer products. This non-point source pollution as well as that from manufacturing facilities will be the major source of calcium resinate entering the environment. Due to its limited water solubility, little, if any, calcium resinate is expected to leave the Lake City AAP Industrial Waste Water Treatment Plant.

G. Toxicological and Environmental Hazards

1. Mammalian Toxicity

No information was found in the literature on the mammalian toxicity of calcium resinate.

2. Aquatic Toxicity

The toxic effects of calcium resinate to three species of fish was studied by MacPhee and Ruelle (1969). They found no effect on exposure of Squawfish (*Ptychocheilus oregonensis*) or Coho salmon (*Oncorhynchus kisutch*) to 10 ppm of calcium resinate for 24 hours. However, 10 ppm exposure to Chinook salmon (*Oncorhynchus shawytscha*) proved lethal in 2-4 hours.

3. Toxicity to Microorganisms

No references were found on the toxicity of calcium resinate to microorganisms.

4. Phytotoxicity

No specific references to calcium resinate phytotoxicity were found in the literature. Under acidic conditions, free calcium could be formed. Laloraya (1970) reported that high concentrations of calcium in soil cause metabolic disturbances and on overall inhibitory effect on peanut and linseed plants (*Arachis hypogaea* and *Linum usitatissimum*). The effect of calcium ion on growth and metabolism may be related to its controlling effect on the membrane structure and, therefore, the uptake of water and essential ions. High levels of calcium are correlated with the inhibition of chlorophyll biosynthesis.

Calcium is known to inhibit the uptake of Mg^{++}, which is a constituent of chlorophyll molecules, and to inactivate the iron present in plants which is a requirement in synthesis of chlorophyll.

5. Availability of Literature for Phase II

Limited information on the toxicological and environmental properties of calcium resinate are available in the literature. Any further information would have to come from the manufacturers.

H. Regulations and Standards

No EPA or OSHA regulations specific for calcium resinate exist. The Department of Transportation requires that this compound be labeled as a flammable solid (Federal Register, 1976).

I. Conclusions and Recommendations

The purpose of this study was to determine the Army's responsibility for conducting further environmental and toxicological investigations on calcium resinate. The Army's use of this compound is negligible when compared to the civilian use, being less than 1% of civilian production capacity. The industrial treatment process at Lake City AAP will remove the insoluble calcium resinate as sludge. This sludge is disposed of in ponds. Therefore, the amount entering the environment will be negligible. Civilian use of calcium resinate results in widespread discharged to the environment from landfills and sewage.

From the limited reports available, calcium resinate appears to have a low toxicity to most aquatic organisms, the exception being Chinook salmon.

Based on the data evaluated during this study, calcium resinate is not a military problem chemical. Thus, a Phase II study on calcium resinate should be a low priority.

J. References

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PRELIMINARY PROBLEM DEFINITION STUDY OF 48 MUNITIONS-RELATED CHEMICALS

VOLUME IV PRIMER AND TRACER RELATED CHEMICALS

SODIUM NITRATE

FINAL REPORT

J. F. Kitchens
W. E. Harward III
D. M. Lauter
R. S. Wentsel
R. S. Valentine

April 1978

Supported by:

U. S. ARMY MEDICAL RESEARCH AND DEVELOPMENT COMMAND
Fort Detrick, Frederick, Maryland 21701

Contract No. DAMD17-77-C-7057

COTR: Clarence Wade, Ph.D.

ATLANTIC RESEARCH CORPORATION
Alexandria, Virginia 22314

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SUMMARY

Sodium nitrate is used as an oxidizing agent in explosives, a fertilizer and as a food preservative. Civilian use of this material accounts for 98-99% of total use in the United States.

The Army uses sodium nitrate as an oxidizer in incendiary and tracer mixtures. The current use rate of this material at Longhorn AAP is 7,700 lb/month. At full mobilization, the use could increase to over 300,000 lb/month.

Sodium nitrate is a relatively non-toxic substance, as would be expected considering its use as a fertilizer and food preservative. Some toxic effects have been observed in mammals at dosages of >200 mg/kg, however.

Since civilian usage represents the vast majority of sources of entry of sodium nitrate into the environment, this chemical would not appear to be a military responsibility. However, sodium nitrate is a major by-product of RDX/HMX manufacture with 30-80 million lb/year produced. This material is placed in holding ponds. The material is pumped from the ponds and made into fertilizer. The effects of this by-product on the environment should be further evaluated.

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FOREWORD

This report details the results of a preliminary problem definition study on sodium nitrate. The purpose of this study was to determine the Army's responsibility for conducting further research on sodium nitrate in order to determine its toxicological and environmental hazards so that effluent standards can be recommended. In order to determine the Army's responsibility for further work on sodium nitrate, the military and civilian usage and pollution of this chemical were evaluated. In addition, a preliminary overview of toxicological and environmental hazards was conducted.

Sodium nitrate was only one of 48 chemicals evaluated under Phase IA of contract No. DAMD17-77-C-7057. These chemicals are grouped in four categories

- explosives related chemicals
- propellant related chemicals
- pyrotechnics
- primers and tracers

Each category is a major report. Section I of each report is an overview of the military processes which use each chemical and the pollution resulting from the use of these chemicals. The problem definition study reports on each chemical are separable sections of these four reports.

In addition, a general methodology report was also prepared. This report describes the search strategy and evaluation methodology utilized for this study.

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XVII. SODIUM NITRATE

A. Alternate Names

Sodium nitrate is a naturally occurring mineral. As crystallized from water it forms a trigonal or rhombic system with a body-centered lattice containing two $NaNO_3$ molecules per unit cell. Sodium nitrate has a molecular weight of 85.01 g/mole. Alternate names for sodium nitrate are given below:

CAS Registry No.:	7631-99-4
CA Name (8CI):	Nitric acid, sodium salt
Wiswesser Line Notation:	Na N-02-Q
Synonyms:	Chile saltpeter; Cubic niter; Natratine; Niter; Saltpeter (Chile); Soda niter

B. Physical Properties

The physical properties of sodium nitrate are presented in Table XVII-1.

C. Chemical Properties

1. General Reactions

Sodium nitrate decomposes to the oxide and gases at temperatures above 800°C (Whaley, 1973).

$$4NaNO_3 \xrightarrow{800°C} 2Na_2O + 2N_2 + 5O_2$$

The oxide is also formed by the reaction of sodium nitrate with sodium azide (Whaley, 1974).

$$5NaN_3 + NaNO_3 \xrightarrow{290°C} 3Na_2O + 8N_2$$

2. Environmental Reactions

Sodium nitrate is a soluble salt which dissociates to Na^+ and NO_3^- in water. In near neutral waters, nitrate is stable to chemical reduction. Nitrate is however photochemically reactive and can be reduced to nitrite by UV radiation, particularly at wavelengths below 265 nm and around 300 nm. Irradiation of insoluble nitrate salts on water surfaces at 250 nm will also lead to nitrite formation. This reaction occurs faster under alkaline conditions (Coldwell and McLean, 1959).

3. Sampling and Analysis

Sodium nitrate may be determined by analysis for sodium or for

Table XVII-1. Physical Properties of Sodium Nitrate*.

Physical Form @ 20°C:	Transparent crystals or white powder; deliquescent in moist air
Crystal Form:	Trigonal, rhombohedral
Taste:	Saline, slightly bitter
M.P.:	306.3°C
B.P.:	Decomposes at 380°C; explodes at 538°C
Specific Gravity:	2.257 @ 20°C
Refractive Index, n_D^{20}:	1.5874
Specific Heat:	0.262 cal/g @ 25°C
Heat of Fusion:	-5355 cal/mole @ 310°C
Heat of Solution (Water):	-4889 cal/mole @ 25°C
Solubility:	water - 38.07 g/100g @ -18.1°C 42.23 g/100g @ 0°C 46.80 g/100g @ 20°C 51.20 g/100g @ 40°C 63.77 g/100g @ 100°C soluble in glycerine ethanol - 1g/125ml @ 20°C methanol - 1g/300ml @ 20°C

* References: Kirk and Othmer, 1969; Windholz, 1976; Hawley, 1977

nitrate.

Sodium may be determined by flame photometry (Franson, 1975). This method is accurate for sodium concentrations below 10 mg/l. Sodium can also be determined gravimetrically by precipitation as sodium zinc uranyl acetate hexahydrate (Franson, 1975).

Four methods for the determination of nitrate are described below. The nitrate ion electrode is applicable over the widest range of concentrations. The UV spectrophotometric method is also widely useful while the last two methods are limited in their effective concentration ranges (Franson, 1975).

- Determination of nitrate with a nitrate ion electrode allows analysis of concentrations from 0.2 to 1,400 mg of NO_3^-/l. The disadvantage of this method is the numerous interferences which must be chemically removed prior to analysis. Chloride and bicarbonate at relatively high concentrations interfere with the electrode as do nitrite, sulfide, bromide, iodide, chlorate and perchlorate.

- Nitrate in solution may be determined by measurement of UV absorption at 220 nm. Beer's law is obeyed up to concentrations of 11 mg/l. Dissolved organic matter may interfere with this analysis.

- Nitrate is reduced by cadmium to nitrite which can undergo further reactions with sulfanilamide and N-(1-napthyl)-ethylenediamine to form a colored product that may be determined colorimetrically. Correction for any nitrite initially present must be made. This method is used for determinations below 0.1 mg NO_3^-/l.

- Colorimetric estimation of the yellow reaction product of brucine and nitrate allows determination of nitrate in water. This method is applicable to the narrow concentration range of 0.1 to 2 mg/l.

D. Uses in Army Munitions

1. Purpose

Sodium nitrate is used as an oxidizer in incendiary and tracer mixtures. This material imparts a yellow color to burning compositions.

At Pine Bluff Arsenal, sodium nitrate is used in the following compositions:

	% Sodium Nitrate in Formulations
Igniter Charge	47±1.5
Igniter Mixture	80±1.5
Oxidizing Agent	99.6±0.05

Longhorn AAP also uses sodium nitrate as a component of tracer mixes.

2. Quantities Used

a. Historical Use

Little, if any, sodium nitrate has been used at PBA during the last 10 years (Aikman, 1978). During 1977, LAAP used 92,479 lb of this material.

b. Current Use

There are no current plans for use of sodium nitrate at PBA in the foreseeable future. The use rate of sodium nitrate at LAAP during 1977 was 7700 lb/month.

c. Use at Full Mobilization

The full mobilization use rate of sodium nitrate at LAAP would be 327,000 lb/month (Leander, 1978).

3. Documented or Speculated Occurrences in Air or Water

No quantitative information is available on actual losses of sodium nitrate from tracer manufacture to the environment. However, it is estimated that losses of tracer materials during processing at LAAP are 0.5-1.0% of the amount handled (Maley, 1978). Losses of sodium nitrate at LAAP are thus on the order of 40-80 lb/month. At full mobilization, the losses would increase to 1600-3300 lb/month.

The waste materials at LAAP are discharged into sumps and transported by truck to an evaporation pond. Materials from this pond may percolate into the soil and enter the ground water. Since sodium nitrate is soluble in water, it is probable that virtually all the waste material enters the ground water soon after discharge into the pond.

Sodium nitrate is also formed as a byproduct of RDX/HMX manufacture. This material is generated during distillation of the contaminated weak acid stream. The sludge from the stripping column is treated with NaOH, converting ammonium nitrate into sodium nitrate. This material currently is discharged into storage lagoons. In the future, it will be recovered and converted into fertilizer. The estimated rate of generation of sodium nitrate from this source is 60,000-80,000 lb/day. At full mobilization, production of 200,000-220,000 lb/day of sodium nitrate would be expected (Hoard, 1978).

E. Uses in the Civilian Community

1. Production Methodology

Sodium nitrate is manufactured by the action of nitric acid on soda ash (Kirk and Othmer, 1969).

$$Na_2CO_3 + 2HNO3 \longrightarrow 2NaNO_3 + H_2O + CO_2$$

Alternatively a sodium nitrate/nitrite solution may be prepared by absorption of nitrogen dioxide by an aqueous sodium carbonate solution (Kirk and Othmer, 1969).

$$Na_2CO_3 + 2NO_2 \longrightarrow NaNO3 + NaNO_2 + CO_2$$

The nitrate/nitrite mixture is oxidized to sodium nitrate by heating with nitric acid.

The major world source of sodium nitrate is Chile saltpeter. Large deposits of sodium nitrate are found in Chile associated with sodium chloride, sodium sulfate, and other salts. Two grades of ore are found in these deposits; caliche, the high grade, and costra, the low grade. Sodium nitrate is extracted from the ore with water by a series of leachings and recovered by crystallization (Kirk and Othmer, 1969).

World production of sodium nitrate by synthetic methods is very small compared to production from natural deposits. All sodium nitrate produced in the U.S. is synthetic.

2. Manufacturers, Production, and Capacity

Sodium nitrate is manufactured by Mallinckrodt, Inc. in St. Louis, Mo. and the Olin Corporation in Lake Charles, La. Their plant capacities are unavailable (S.R.I., 1977a).

The major importer of sodium nitrate is the Chilean Nitrate Sales Corporation in New York City, N.Y. (Mallinckrodt, Inc., 1978; Olin Corporation, 1978).

3. Usages

Sodium nitrate is used as an oxidizing agent, a propellant oxidizer, a fertilizer, a metallurgical flux, in refrigerants, pyrotechnics, explosives, as an intermediate for sodium antimonate and arsenate, as a food preservative, in dyes, pottery enamels, and as an anaphrodisiac (S.R.I., 1977b; Hawley, 1977). In 1976 two hundred and six million pounds of sodium nitrate were imported for use as a fertilizer (Predicasts Basebook, 1977).

4. Future Trends

Civilian use of sodium nitrate has declined in recent years primarily because of increased use of urea fertilizers as a nitrogen source. Sodium nitrate use as a food preservative may be limited due to current concern over chemical precursors of N-nitrosamines in foodstuffs.

5. Documented or Speculated Occurrences in the Environment

Sodium nitrate occurs naturally in large deposits with other salts found primarily in Chile. Its widespread use as a fertilizer makes it readily available to the soil and environmental water from runoff.

F. Comparison of Civilian and Military Uses and Pollution

Sodium nitrate is produced in the United States by Mallinckrodt, Inc. and Olin Corporation. Their combined production capacity is probably in excess of 100 million lb/year. In addition, in 1976 over 200 million lb of sodium nitrate was imported. This material is used primarily as a fertilizer. Thus, essentially all of the material used enters the environment through land applications.

Military use of sodium nitrate is currently less than 100,000 lb/year, or less than 1% of civilian use. At full mobilization the use rate would rise to about 4 million lb/year or about 2% of civilian use. Pollution from use of sodium nitrate as a component of munitions formulations is negligible compared to civilian sources. However, sodium nitrate formed as a byproduct of RDX/HMX manufacture represents a large volume, highly concentrated source of potential entry of this material into the environment. Currently, as much as 30 million lb/year of sodium nitrate is formed and collected in storage lagoons. At full mobilization, up to 80 million lb/year would be formed. This quantity represents about 30% of the amount used annually in the United States.

G. Toxicological and Environmental Hazards

1. Toxicity to Mammals

In acute doses, sodium nitrate has a low toxicity to mammals. The LC50 of sodium nitrate to rats ranges from 4.0 to 6.1 g/kg depending on the experimental conditions (S.R.I., 1972). For rabbits, the LD50 is 1.955 g NO_3^-/kg (Dollahite and Rowe, 1974). The lowest dosage for which any effects were observed (LDLo) was 200 mg/kg. For humans, the LDLo is 500 mg/kg (NIOSH, 1977).

No evidence of any mutagenic effects were found in the dominant lethal gene test (S.R.I., 1972). However, adverse effects of sodium nitrate were observed on human embryonic lung cells in tissue culture (S.R.I., 1972). Zaldivar and Wetterstrand (1975) correlated exposure to nitrate fertilizers (sodium and potassium nitrate) and the incidence of gastric cancer deaths. They found a significant correlation coefficient of 0.745. Under certain conditions, nitrate can be reduced to nitrite in the gastrointestinal tract. Nitrites can react with the methylamines to form highly carcinogenic nitrosoamines. Once in the blood stream, nitrite reacts with hemoglobin to produce methemoglobin (EPA, 1976).

2. Aquatic Toxicity

Sodium nitrate exhibits toxic effects in fish only at high concentrations as shown in Table XVII-2. Knepp and Arkin (1973) concluded that levels of nitrate nitrogen at or below 90 mg/l would have no adverse effects on warm water fish.

3. Toxicity to Microorganisms

The Stanford Research Institute (1972) conducted a study on the mutagenic effects of sodium nitrate. They found that sodium nitrate did not produce any significant mutagenic effects in *Salmonella typhimurium*. No effects for sodium nitrate on the recombination frequency of *Saccharomyces cerevisiae* in either host-mediated assay or the associated *in vitro* tests were observed (S.R.I., 1972).

4. Phytotoxicity

Sodium nitrate is used as a fertilizer and is not toxic to plants unless present in large excess. When excess sodium nitrate is present, a condition called sodic soil occurs. This condition is due to excessive exchangeable sodium. Exchangeable sodium is that fraction of sodium that is absorbed by the soil and may be exchanged with other salt constituents such as calcium or magnesium. Sodic salts usually take water slowly, crust when dry, are sticky when wet, and have a black surface. Some crops are more sensitive to inadequate moisture and hindrance to normal root development caused by sodic soil besides being sensitive to exchangeable sodium. The tree crops that are highly sensitive to sodium may concentrate enough to cause leaf burn and abscission. Table XVII-3 lists various crops and their relative sensitivity to exchangeable sodium (Pearson, 1960).

5. Availability of Literature for Phase II

A large number of toxicological and environmental studies on sodium nitrate have been conducted as a result of its use as a fertilizer and in food. Thus, there is sufficient literature available for a detailed toxicological and environmental study of this compound.

H. Regulations and Standards

1. Air and Water Regulations

No limits of nitrate are necessary for protection of aquatic life. Levels of 90 mg/l nitrate nitrogen have been shown to have no adverse effects on warm water fish. This level would not occur in natural waters (EPA, 1976). The limit of nitrate nitrogen for domestic water supplies is 10 mg/l (EPA, 1976).

Table XVII-2. Toxicity of Nitrate to Fresh Water Aquatic Organisms.

Species	Test Conditions	Results	References
Chinook salmon			
Oncorhynchus tshawytscha	1310 mg/l nitrate N_2 for 96 hours	LC50	Westin, 1974
Oncorhynchus tshawytscha	1080 mg/l nitrate N_2 for 7 days	LC50	"
Fingerling rainbow trout			
Salmo gairdneri	1360 mg/l nitrate N_2 for 96 hours	LC50	"
Salmo gairdneri	1080 mg/l nitrate N_2 for 7 days	LC50	"
Bluegill			
Lepomis macrochirus	2000 mg/l nitrate N_2 as sodium nitrate for 96 hours	LC50	Trama, 1954
Lepomis macrochirus	420 mg/l nitrate N_2 as potassium nitrate for 96 hours	LC50	"
Large mouth bass			
Micropterus salmoides	90 mg/l nitrate N_2	No significant effects	Knepp and Arkin, 1973
Channel catfish			
Ictalurus punctatus	90 mg/l nitrate N_2	No significant effects	Knepp and Arkin, 1973

Table XVII-3. Tolerance of Various Crops to Exchangeable-Sodium-Percentage. (Pearson, 1960)

Tolerance to ESP[1] and range at which affected	Crop	Growth Response Under Field Conditions
Extremely sensitive (ESP=2-10). . .	Deciduous fruits . . . . . Nuts . . . . . . Citrus . . . . . . Avocado.	Sodium toxicity symptoms even at low ESP values.
Sensitive (ESP=10-20)	Beans	Stunted growth at low ESP values even though the physical condition of the soil may be good.
Moderately tolerant (ESP=20-40) . .	Clover . . . . . . Oats . . . . . . Tall fescue . . . . . . Rice . . . . . . Dallisgrass.	Stunted growth due to both nutritional factors and adverse soil conditions.
Tolerant (ESP=40-60).	Wheat. . . . . . Cotton . . . . . . Alfalfa . . . . . . Barley . . . . . . Tomatoes . . . . . . Beets	Stunted growth usually due to adverse physical condition of soil.
Most tolerant (ESP=more than 60) . .	Crested and Fairway wheatgrass . . . . . . Tall wheatgrass. . . . . . Rhodes grass	

[1]ESP=exchangeable-sodium-percentage.

2. Human Exposure Standards

No standards are listed for human exposure to sodium nitrate. However, an LDLo of 500 mg/kg has been determined for sodium nitrate in humans (NIOSH, 1977).

3. DOT Labeling Requirements

Sodium nitrate is classified as an oxidizer by the Department of Transportation. Labels on this material should bear the notation "Oxidizer" (Federal Register, 1976).

I. Conclusions and Recommendations

The goal of this problem definition study is to assess the Army's responsibility for conducting further evaluations of the environmental and toxicological properties of sodium nitrate. Military use of sodium nitrate represents only 1-2% of civilian use. Consequently, pollution arising from use of this chemical is primarily a civilian problem. However, the production of RDX/HMX results in formation of sodium nitrate as a byproduct. This represents a large (30-80 million lb/year) source of entry of this material into the environment.

Sodium nitrate is not highly toxic to mammals, aquatic organisms, microorganisms or plants. Thus, losses to the environment from munitions production operations does not warrant further study. However, the large amounts of sodium nitrate produced as a by-product from RDX/HMX manufacture is of greater concern. This material could leach into ground water from the holding ponds. Thus, it is recommended that sampling and analysis of water sources near the ponds be undertaken to determine if sodium nitrate is a pollution problem.

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AD

PRELIMINARY PROBLEM DEFINITION STUDY OF 48 MUNITIONS-RELATED CHEMICALS

VOLUME IV PRIMER AND TRACER RELATED CHEMICALS

PARLON

FINAL REPORT

J. F. Kitchens
W. E. Harward III
D. M. Lauter
R. S. Wentsel
R. S. Valentine

April 1978

Supported by:

U. S. ARMY MEDICAL RESEARCH AND DEVELOPMENT COMMAND
Fort Detrick, Frederick, Maryland 21701

Contract No. DAMD17-77-C-7057

COTR: Clarence Wade, Ph.D.

ATLANTIC RESEARCH CORPORATION
Alexandria, Virginia 22314

Approved for Public Release
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SUMMARY

Parlon® is a chlorinated rubber that is manufactured for its chemical and thermal stability. It is used in a variety of consumer products such as paints, coatings and inks. The amount of Parlon® entering the environment from the civilian manufacture or use is not known.

The Army used Parlon® in some pyrotechnics and tracer formulations manufactured at Longhorn AAP. This use was small and sporadic. No future use of this compound at Longhorn AAP is anticipated.

Relatively little toxicological and environmental information on Parlon® is available in the general literature. The FDA has approved Parlon® for contact with food. In the environment Parlon® is expected to accumulate in sediments. The bioaccumulation potential of this compound is not known.

In view of the limited past use of Parlon® by the Army, this chemical should be a low priority for a Phase II study.

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FOREWORD

This report details the results of a preliminary problem definition study on Parlon®. The purpose of this study was to determine the Army's responsibility for conducting further research on Parlon® in order to determine its toxicological and environmental hazards so that effluent standards can be recommended. In order to determine the Army's responsibility for further work on Parlon®, the military and civilian usage and pollution of this chemical were evaluated. In addition, a preliminary overview of toxicological and environmental hazards was conducted.

Parlon® was only one of 48 chemicals evaluated under Phase IA of contract No. DAMD17-77-C-7057. These chemicals are grouped in four categories

- explosives related chemicals
- propellant related chemicals
- pyrotechnics
- primers and tracers

Each category is a major report. Section I of each report is an overview of the military processes which use each chemical and the pollution resulting from the use of these chemicals. The problem definition study reports on each chemical are separable sections of these four reports.

In addition, a general methodology report was also prepared. This report describes the search strategy and evaluation methodology utilized for this study.

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XVIII. PARLON®

A. Alternate Names

Parlon® is the registered tradename for certain chlorinated polymers manufactured by Hercules® . The exact molecular formulas of these polymers is unknown. Chemical Abstracts has assigned Registry No. 58206-43-2 to Parlon®. The 9th Chemical Abstracts Centennial Index name for this chemical is Parlon P.

B. Physical Properties

The physical properties of Parlon® are listed in Table XVIII-1.

C. Chemical Properties

1. General Reactions

Parlon® was specifically developed for its durability and chemical inertness. It is unchanged by treatment with acids, bases or salt solutions. It will dissolve in ketones, esters, and aromatic hydrocarbons and will soften slightly when treated with aliphatic hydrocarbons. Parlon® is resistant to mineral oils but is softened by animal or vegetable oils (Hercules® , 1971).

Parlon® is thermally stable to prolonged exposure at temperatures to 125°C. At temperatures above 135°C, decomposition occurs rapidly. Addition of epoxy-type stabilizers can greatly increase the thermal stability of Parlon® (Hercules® , 1971).

2. Environmental Reactions

Unpigmented Parlon® coatings possess poor light stability. Direct sunlight causes discoloration and embrittlement. Parlon® may be stabilized against photodecomposition with dibasic lead phosphite or barium-cadmium laurate (Hercules® , 1971). Parlon® is insoluble in fresh or salt water.

3. Sampling and Analysis

Analytical techniques for Parlon® have not been developed.

D. Uses in Army Munitions

1. Purpose

Parlon® is used as a color intensifier and a binder in pyrotechnic and tracer formulations. It is also used as a component of rapid drying coatings.

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Table XVIII-1. Physical Properties of Parlon®*

Physical Form at 20°C:	grannular powder
Color:	water-white
Odor:	none
Density:	1.63 g/ml
Index of Refraction:	1.554
Softening Point:	140°C
Flammability:	nonflammable
Tensile Strength:	5200 lb/in^2
Elongation:	1.6%
Hardness, Sward Index:	79-80% of glass
Solubility:	generally soluble in ketones, esters, and aromatic hydrocarbons
	soluble in methylene chloride, ethylene dichloride, and 2-nitropropane
	generally insoluble in aliphatic hydrocarbons and alcohols
	insoluble in water, nitromethane, and nitroethane

*Reference: Hercules® Inc., 1971.

2. Quantities Used

The only known user of Parlon® is Longhorn AAP. This material has been used at LAAP in the past, but was not used in 1977. Parlon® is not called for in the mobilization schedule for LAAP. No future use is currently anticipated (Leander, 1978).

E. Uses in the Civilian Community

1. Production Methodology

Parlon® is manufactured by direct chlorination of polyisoprenoid rubber. Process details are unavailable due to their proprietary nature. Chlorination is stopped when the product is 64-65% chlorine by weight, slightly less then the theoretical maximum chlorine content (68.25%). The process is designed to minimize carbon-carbon crosslinking between polymer chains. One percent of an epoxy compound is added to Parlon® during manufacture for chemical stability (Hercules®, 1971).

2. Manufacturers, Production, and Capacity

Parlon® is the tradename for chlorinated rubber manufactured by Hercules®, Incorporated. They manufacture Parlon® in Parlin, N.J. The plant capacity is not available.

3. Usages

Parlon® is used as an additive to paints, paper lacquers, inks, and adhesives to promote fast drying, chemical inertness, flame resistance, and general durability. It is used in outdoor maintenance paints, industrial alkyd finishes, traffic paints, marine paints, swimming pool paints, wood floor finishes and sealers, fire.retardant paints, flameproof textile coatings, water-vaporproof papers, and rotogravure printing inks (Hercules®, 1978).

4. Future Trends

We are unaware of any anticipated major changes in the Parlon® market.

5. Documented and Speculated Occurrences in the Environment

There are no reports in the literature of Parlon® as an air or water pollutant.

F. Comparison of Military and Civilian Uses and Pollution

Parlon® is widely used throughout the civilian market in a variety of products including many paints and inks. In contrast, military use of Parlon® was limited to Longhorn AAP. This chemical was used in the past as a color intensifier and binder in pyrotechnic and tracer formulations.

However, no Parlon® is currently being used or are there any anticipated future uses.

G. Toxicological and Environmental Hazards

1. Mammalian Toxicity

Parlon® is a relatively non-reactive substance. The FDA cleared Parlon® for contact with foods (Hercules® , 1978). Toxicological problems with Parlon® occur in its production when workers can be exposed to CCl_4 levels above the recommended TLV (Hercules®, 1978). When Parlon® is heated, HCl may be released; but there is no data on levels (Hercules®, 1976).

2. Aquatic Toxicity

Parlon® is not soluble in water and is relatively inert to degradation by acids and bases (Hercules®, 1971). If this substance was released into an aquatic system, it would build up in the sediment. Since Parlon® is difficult to degrade chemically, it is likely that Parlon® is non-biodegradable. Thus, if levels were high enough, biomagnification in the food chain could occur.

3. Toxicity to Microorganisms, Invertebrates and Plants

No data was uncovered which related the effects of Parlon® on microorganisms, invertebrates or plants.

4. Availability of Literature for Phase II

The major references specifically related to Parlon® were from the manufacturer. Additional information for Phase II will have to come from direct contact with the manufacturer and available literature on similar chlorinated rubbers.

H. Regulations and Standards

No specific standards are listed for Parlon® exposure in air or water. No limits for human exposure have been recommended. This material is not on the NCI suspected carcinogen list.

I. Conclusions and Recommendations

Parlon® is not a compound of military significance. Its use by the Army has been small and sporadic. In contrast, Parlon® is used in a variety of consumer products. Therefore, a Phase II study on this compound should be a low priority.

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PRELIMINARY PROBLEM DEFINITION STUDY OF 48 MUNITIONS-RELATED CHEMICALS

VOLUME IV PRIMER AND TRACER RELATED CHEMICALS

BARIUM PEROXIDE

FINAL REPORT

J. F. Kitchens
W. E. Harward III
D. M. Lauter
R. S. Wentsel
R. S. Valentine

April 1978

Supported by:

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SUMMARY

Barium peroxide was used as a starting material for the production of hydrogen peroxide in the 1930's. However, new processes for manufacture of hydrogen peroxide were introduced in the 1940's. Since this time, barium peroxide has declined in importance in the civilian community. Current uses of this compound are as a bleaching agent, oxidizer and in fireworks.

The Army uses barium peroxide in igniter and tracer formulations manufactured at Lake City and Lone Star AAPs. The current use rate of barium peroxide is 13,000-15,000 lb/year. Under full mobilization production schedules, the amount of barium peroxide used by Lake City and Lone Star AAPs would be 58,000-60,000 lb/year.

The toxicity of barium peroxide is mainly due to that of the metal, although it can damage tissues on contact due to its strong oxidizing capability. Barium is moderately toxic to most species. Some invertebrate, such as *Daphnia magna*, are very sensitive to barium salts.

While limited data is available on historical civilian production and military use of barium peroxide, there is no question that the military use represents a significant fraction of the total use of this chemical in the United States. Thus, barium peroxide *is a military problem chemical and* further toxicological and environmental evaluation on this compound should be sponsored by the Army. However, in order to be of value, this study should include the total barium in effluents not just that from barium peroxide. The interaction of barium with calcium and strontium in the aquatic environment also needs further study.

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FOREWORD

This report details the results of a preliminary problem definition study on barium peroxide. The purpose of this study was to determine the Army's responsibility for conducting further research on barium peroxide in order to determine its toxicological and environmental hazards so that effluent standards can be recommended. In order to determine the Army's responsibility for further work on barium peroxide, the military and civilian usage and pollution of this chemical were evaluated. In addition, a preliminary overview of toxicological and environmental hazards was conducted.

Barium peroxide was only one of 48 chemicals evaluated under Phase IA of contract No. DAMD17-77-C-7057. These chemicals are grouped in four categories

- explosives related chemicals
- propellant related chemicals
- pyrotechnics
- primers and tracers

Each category is a major report. Section I of each report is an overview of the military processes which use each chemical and the pollution resulting from the use of these chemicals. The problem definition study reports on each chemical are separable sections of these four reports.

In addition a general methodology report was also prepared. This report describes the search strategy and evaluation methodology utilized for this study.

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XIX. BARIUM PEROXIDE

A. Alternate Names

Barium peroxide is an alkaline earth peroxide of molecular formula BaO_2 and structural formula Ba-O-O. It has a molecular weight of 169.34 g/mole.[2] Barium peroxide can also exist as the octahydrate, $BaO_2 \cdot 8H_2O$ (molecular weight, 313.46 g/mole). The pertinent alternate names for barium peroxide are listed below:

CAS Registry No.:	1304-29-6
Alternate CAS Registry No.:	16678-58-3
Replaces CAS Registry No(s):	55396-27-5; 61233-09-8
CA Name (8CI):	Barium peroxide
Wiswesser Line Notation:	
Synonyms:	Barium dioxide; Barium oxide; Barium peroxide

B. Physical Properties

The physical properties of barium peroxide are listed in Table XIX-1.

Table XIX-1. Physical Properties of Barium Peroxide.*

Physical Form @ 20°C:	powder
Color:	grayish-white
M.P.:	450°C
B.P.:	loses oxygen at 800°C
Specific Gravity:	4.96
Solubility:	water - very slightly soluble; slowly decomposes
	soluble in dilute acid
	insoluble in acetone

*References: Hawley, 1977; Weast, 1975; Sax, 1975; Windholz, 1976.

C. Chemical Properties

1. General Reactions

Barium peroxide reacts with dilute or strong acid to generate hydrogen peroxide (Kirk and Othmer, 1968).

$$BaO_2 + 2H^+ \longrightarrow Ba^{++} + H_2O_2$$

Prior to 1940 hydrogen peroxide was commercially prepared exclusively by treatment of barium peroxide with sulfuric acid.

$$BaO_2 + H_2SO_4 \longrightarrow BaSO_4 + H_2O_2$$

Barium peroxide undergoes thermal decomposition at 800°C (Hawley, 1977)

$$BaO_2 \xrightarrow{800°C} BaO + \tfrac{1}{2} O_2$$

Barium peroxide is an effective oxidizing agent. It will react with organics or reducing agents. Mixtures with oxidizable material are explosive and ignite easily by friction (OSHA, 1972).

2. Environmental Reactions

Barium peroxide is negligibly soluble in water but will slowly decompose when in contact with it (Windholz, 1977). There are no reports of photolytic instability.

3. Sampling and Analysis

Barium peroxide may be determined titrimetrically using parmanganate, ceric sulfate, potassium iodide, thiosulfate, titanous chloride or sodium nitrite. A spectrophotometric determination using a titanium-peroxide complex has been used for the measurement of barium peroxide in tracer bullets (Norwitz and Calan, 1976).

Analysis for aqueous barium is best accomplished using atomic absorption spectrophotometry. Barium absorption is measured at 553.6 nm with a reported sensitivity of 300 mg/l for 1% absorption (Franson, 1975).

D. Uses in the Army Munitions

1. Purpose

Barium peroxide is used as an oxidizer in ignitor and tracer formulations. This material also imparts a green color to burning compositions. At Lake City AAP, barium peroxide is used to produce the following formulations:

	% Barium peroxide in formulations
Ignitor I-276	84±1
Ignitor I-508	7.92±1
Ignitor I-237	4±0.5
R-20C	27.5±1
R-440	40±1
R-10E	4.1

Lone Star AAP also uses barium peroxide in the manufacture of tracer projectiles.

2. Quantities Used

a. Historical Use

During the years 1975-1977, Lake City AAP procured the following amounts of barium peroxide:

1975	4,400 lb
1976	28,400 lb
1977	7,400 lb

These purchases represent an average use rate of 13,400 lb/year of 1117 lb/month. No historical barium peroxide use rate at Lone Star AAP was available.

b. Current Use

The estimated levels of current use of barium peroxide are

LCAAP	617 lb/month
LSAAP	470 lb/month

c. Use at Full Mobilization

At full mobilization, the use of barium peroxide at LCAAP would increase to about 30,000 lb/year or 2,500 lb/month. The anticipated full mobilization use rate at LSAAP would be about 2,350 lb/month.

3. Documented or Speculated Occurrences in Air or Water

No quantitative data is available on specific losses of barium peroxide. However, losses in the production of primers and tracers are generally in the range of 1-2% of the amount handled (Melton, 1978). Thus, current losses of barium peroxide from LCAAP are 6-12 lb/month and losses from LSAAP are 5-9 lb/month. At full mobilization, these values would increase to 25-50 and 24-47 lb/month, respectively.

At LCAAP, waste effluents are treated with strong base to destroy explosive components. The wastes are then neutralized and sent to conventional industrial waste treatment facilities. Barium peroxide could undergo a variety of reactions during this treatment process depending on the other compounds present. However, the end result of this treatment will be the precipitation of most of the barium as barium sulfate or carbonate. These compounds have a solubility product constant of 1.6×10^{-9} (Hogness and Johnson, 1957). Therefore, if the discharge is saturated with barium carbonate or barium sultate, the maximum concentration of barium leaving the Industrial Treatment Plant could be 5.5 mg/l. In reality this number will be significantly smaller depending on the sulfate and carbonate concentrations and influent barium concentration.

At LSAAP, waste streams are discharged into leaching pits. Ultimately, some of the constituents may percolate into the soil and into the ground water. The extent of such contamination by barium peroxide is not known.

E. Uses in the Civilian Community

1. Production Methodology

Barium peroxide is manufactured by the action of alkaline hydrogen peroxide on a soluble barium salt (Kirk and Othmer, 1968).

$$Ba^{++} + 2OH^{-} + H_2O_2 \longrightarrow BaO_2 + 2H_2O$$

During the process, barium peroxide forms *in situ* and reacts with the hydrogen peroxide. Barium peroxide precipitates.

Barium peroxide can also be made by a dry technique involving roasting barium oxide in air (Kirk and Othmer, 1968).

$$BaO + \tfrac{1}{2}O_2 \xrightarrow{\Delta} BaO_2$$

2. Manufacturers, Production and Capacity

Barium peroxide is manufactured by Barium and Chemicals in Steubenville, Ohio; Hummel Chemical in South Plainfield, N.J.; and J.T. Baker Chemical in Philipsburg, N.J. (S.R.I., 1977). Their plant capacities and past production figures are not available.

3. Usages

Barium peroxide is used as a bleaching agent for animal substances, vegetable fibers, and straws, as a glass decolorizer, in dyeing and textile printing, in cathodes, as an oxidizer in welding and as a general oxidizing agent (Windholz, 1977).

4. Future Trends

There have been no large scale uses of barium peroxide since the production of hydrogen peroxide via barium peroxide ceased in the 1940's

(Kirk and Othmer, 1968). No major changes are anticipated in civilian use of barium peroxide. It is expected to remain a minor chemical.

5. Documented or Speculated Occurrences in the Environment

There are no reports in the literature of barium peroxide as an environmental pollutant. Barium is found in U.S. drinking waters at levels between 0.7 and 900 µg/l with a mean level of 49 µg/l (Franscon, 1975).

F. Comparison of Civilian and Military Use and Pollution

Although there are some minor uses of barium peroxide, the major use of this compound is as an oxidizing agent in pyrotechnic and ordnance devices. The distribution of this compound between military and non-military (fireworks) uses is not known. Based on the limited data on military purchases, the United States production capacity for barium peroxide is estimated at 100-200 thousand lb/year. Army purchases probably amount to ½ of the barium peroxide produced in the United States each year.

No estimates of the pollution resulting from the civilian manufacturing or use of barium peroxide are available. Any barium peroxide wastes generated at Lake City AAP are treated in the industrial waste treatment plant. This treatment will result in the removal of most of the barium in the sludge. However, depending on the losses of barium from other chemicals used, effluent concentrations of barium could be as high as 5.5 mg/l.

G. Toxicological and Environmental Hazards

1. Mammalian Toxicity

Due to its oxidizing ability, barium peroxide is an irritant and can cause local tissue damage. The LDLo from barium peroxide in a subcutaneous dose to mice was 100 mg/kg (NIOSH, 1977).

The pharmacological action of barium salts is documented in the industrial hygiene literature. The chief effect of barium is an increase in the excitability of the muscles, particularly the cardiac muscle. Effects have also been noted on the hematopoietic system and the cerebral cortex (American Conference of Governmental Industrial Hygienists, 1977). In general, the more soluble the barium compound, the more injurious it is in the acute dose. Beliles (1975) stated that barium may be an essential element because rats and guinea pigs maintained on a barium free diet failed to grow normally.

2. Aquatic Toxicity

Barium levels in natural waters range from 5-45 ppb. The toxic effects of this metal are mainly exhibited when ionic barium is present. In most natural waters, sufficient sulfate or carbonate is present to precipitate barium. The carbonate or sulfate salts would thus accumulate in the sediment. These salts have a very low toxicity. Bioaccumulation of barium by most

aquatic organisms is low (Hildebrand *et al.*, 1976). However, Templeton (1958) found that barium could be concentrated in goldfish (*Carassium curatas*) up to 150 times.

In general, soluble barium salts have a relatively low toxicity to aquatic organisms. Concentrations greater than 50 mg/l are necessary for toxic effects to be observed in most aquatic organisms (EPA, 1976). The exception is *Daphnia magna*. Biesinger and Christensen (1972) determined a chronic 3-week LC50 for *Daphnia* to be 13.5 ppm of $BaCl_2$. They also found a 16% reproductive impairment at 5.8 ppm $BaCl_2$.

3. Toxicity to Microorganisms

No information was retrieved in the limited literature search on the toxicity of barium peroxide to microorganisms.

4. Phytotoxicity

McHargue (1919) studied the effect of certain compounds of barium on the growth of plants. It was concluded from his investigation that barium compounds in the absence of calcium carbonate are poisonous to plants, but .. barium carbonate in the presence of an excess of calcium carbonate may stimulate plant growth. Growth comparison studies of corn plants treated with several barium compounds are shown in Table XIX-2. The effect of barium carbonate upon the growth of cowpeas (*Vigna sinensis*) is shown in Table XIX-3.

Robinson *et al.* (1938) surveyed several areas of infertile soil for chemical content. The infertile soils contained up to 3.74% BaO while the exchangeable Ca and Mg levels were low, being nearly equal to or exceeded by the exchangeable barium.

Colin and de Rufz (1900) studied the absorption of barium by peas, maize and beans in dilute (0.125 ppt) solutions of barium nitrate. Practically all the barium was found localized in the roots although there was traces in the stems of the plants.

5. Availability of Literature for Phase II

The toxicological and environmental literature on barium peroxide is limited. However, toxicological properties of this compound can be inferred from literature on other barium compounds.

H. Regulations and Standards

No EPA or OSHA standards or regulations specific for barium peroxide currently exist. OSHA limit for soluble barium in air is 0.5 mg/m^3 (Federal Register, 1976). The yellow oxidizer warning label is required for shipment of barium peroxide.

EPA has listed 1 mg/l of barium as a criterion for domestic water supplies (EPA, 1976). No fresh water standard appears to be necessary for protection of aquatic life due to the low aquatic toxicity of this compound and its removal by precipitation as the carbonate or sulfate salts (EPA, 1976).

Table XIX-2. Air-Dry Weights of the Corn Plants Treated with Barium Salts (McHargue, 1919)

Pot No. and Treatment	Air-dry Weights				Gain or loss in weight when compared with the controls			
	Roots	Stalks	Fodder	Entire Plants	Roots	Stalks	Fodder	Entire Plants
	Gm.	Gm.	Gm.	Gm.	Gm.	Gm.	Gm.	Gm.
Pot 1 (control)	11.50	13.25	17.60	42.35				
Pot 2 (control)	8.00	10.30	15.35	33.65				
Average	9.75	11.77	16.47	38.00				
Pot 3+2 gm. of barium carbonate	10.65	14.25	18.75	43.65				
Pot 4+2 gm. of barium carbonate	12.10	8.25	19.30	39.65				
Average	11.38	11.25	19.02	41.65	+1.63	-0.52	+2.55	+3.65
Pot 7+2 gm. of barium carbonate & 2 gm. of strontium carbonate	14.75	13.00	20.25	48.00	+5.00	+1.23	+3.78	+10.00
Pot 8+2 gm. of barium nitrate	11.50	13.25	18.75	43.50	+1.75	+1.48	+2.28	+ 5.50
Pot 9+5 gm. of barium sulphate	10.75	8.00	14.25	33.00	+1.00	-3.77	-2.22	- 5.00
Pot 10+2 gm. of barium chlorid	11.50	7.50	19.25	38.25	+1.75	-4.27	+2.78	+ 0.25
Pot 11+5 gm. of barium carbonate	13.5	12.00	20.00	45.50	+3.75	+ .23	+3.53	+ 7.50
Pot 12+5 gm. of strontium carbonate	13.2	14.5	20.7	48.40	+3.45	+2.73	+4.23	+10.40

Table XIX-3. Effect of Barium Carbonate upon the Growth of Cowpeas. (McHargue, 1919)

Pot No.	Quantity of barium carbonate added to soil	Weight of 10 Air-dried Plants	Pot No.	Quantity of barium carbonate added to soil	Weight of 10 Air-dried Plants
	Gm.	Gm.		Gm.	Gm.
1 (control)	None	9.15	7	5	11.40
2	0.5	12.00	8	6	10.90
3	1	11.20	9	8	11.15
4	2	10.15	10	10	10.80
5	3	9.50	11a	5	-
6	4	10.55	12	5	11.65

I. Conclusions and Recommendations

The objective of this study was to determine the Army's responsibility for conducting further research on the toxicological and environmental hazards of barium peroxide. This assessment is difficult due to the limited information available on the historical civilian production and the historical military uses. Complicating the problem is the fact that the toxicity of this compound is mainly that of the metal. Thus, other barium compounds used at the Army Ammunition Plant must be taken into account in estimating the environmental hazards of barium from munitions production.

Based on the limited production and use information available and the relatively high toxicity of barium salts to organisms such as *Daphnia magna*, it is recommended that the Army sponsor a Phase II study on barium salts. This study should include all barium salts used at the Army Ammunition Plants and should investigate the following parameters:

- amount of barium salts leaving Lake City AAP in their effluent
- amount of barium in the settling ponds at Lone Star AAP
- the toxicity of barium in the presence of other metals such as Ca, Sr, Pb, etc.
- the effect of these combined metals on the aquatic environment.

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PRELIMINARY PROBLEM DEFINITION STUDY OF 48 MUNITIONS-RELATED CHEMICALS

VOLUME IV PRIMER AND TRACER RELATED CHEMICALS

OXAMIDE

FINAL REPORT

J. F. Kitchens
W. E. Harward III
D. M. Lauter
R. S. Wentsel
R. S. Valentine

April 1978

Supported by:

U. S. ARMY MEDICAL RESEARCH AND DEVELOPMENT COMMAND
Fort Detrick, Frederick, Maryland 21701

Contract No. DAMD17-77-C-7057

COTR: Clarence Wade, Ph.D.

ATLANTIC RESEARCH CORPORATION
Alexandria, Virginia 22314

Approved for Public Release
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The findings of this report are not to be construed as an official Department of the Army position unless so designated by other authorized documents.

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SUMMARY

Oxamide is used by Lake City AAP in tracer formulations as a burning rate retardant and stabilizer. The use of this compound by the Army is small, ~5000 lb/year at full mobilization schedules. The pollution potential of oxamide at Lake City AAP is also small. The maximum full mobilization estimated losses are 9 lb/month. Most of this 9 lb/month will be precipitated in the form of calcium oxalate and removed from the effluent by the industrial waste treatment facility.

Civilian production capacity for oxamide is estimated at 1 million lb per year. The main civilian uses of oxamide are as a nitrocellulose stabilizer and fertilizer. From its use as a fertilizer, widespread environmental contamination of oxamide is anticipated.

Literature on the toxicity of oxamide is sketchy. However, it is readily degraded to oxalic acid in the environment.

Based on the low Army use and discharge of oxamide, oxamide should be a low priority for a Phase *II* study.

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FOREWORD

This report details the results of a preliminary problem definition study on oxamide. The purpose of this study was to determine the Army's responsibility for conducting further research on oxamide in order to determine its toxicological and environmental hazards so that effluent standards can be recommended. In order to determine the Army's responsibility for further work on oxamide, the military and civilian usage and pollution of this chemical were evaluated. In addition, a preliminary overview of toxicological and environmental hazards was conducted.

Oxamide was only one of 48 chemicals evaluated under Phase IA of contract No. DAMD17-77-C-7057. These chemicals are grouped in four categories

- explosives related chemicals
- propellant related chemicals
- pyrotechnics
- primers and tracers

Each category is a major report. Section I of each report is an overview of the military processes which use each chemical and the pollution resulting from the use of these chemicals. The problem definition study reports on each chemical are separable sections of these four reports.

In addition, a general methodology report was also prepared. This report describes the search strategy and evaluation methodology utilized for this study.

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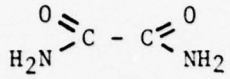
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XX. OXAMIDE

A. Alternate Names

Oxamide is the diamide of oxalic acid. It has a molecular formula of $C_2H_4N_2O_2$ and a corresponding molecular weight of 88.07 g/mole. The structural formula of oxamide is



Alternate names for oxamide are listed below:

CAS Registry No.:	471-46-5
Replaces CAS Registry No.:	4745-68-0
CA Name (9CI):	Ethanediamide
CA Name (8CI):	Oxamide
Wiswesser Line Notation:	
Synonyms:	Ethanedioic acid diamide; Oxalamide; Oxalic acid diamide; Oxamimidic acid.

B. Physical Properties

Oxamide is a nonhydroscopic white crystalline solid. Relevant physical properties are in Table XX-1. Oxamide is not known to exist in a liquid form although reports of its behavior at high temperatures vary. Terman and Fleming (1968) state that oxamide sublimes at 265°C and decomposes at temperatures above 290°C. Decomposition temperatures listed by Hawley (1977) and Windholz (1976) are 419°C and 350°C, respectively. The infrared spectrum of oxamide is presented in Figure XX-1.

Table XX-1. Physical Properties of Oxamide.*

Physical Form @ 20°C:	solid
Color and Crystalline Form:	white monoclinic
M.P.:	419°C decomposes
Specific Gravity:	1.667
Solubility:	water - 0.04 g/100g @ 7.3°C very slightly soluble in alcohol and ether

*Reference: Hawley, 1977; Hodgman *et al.*, 1963.

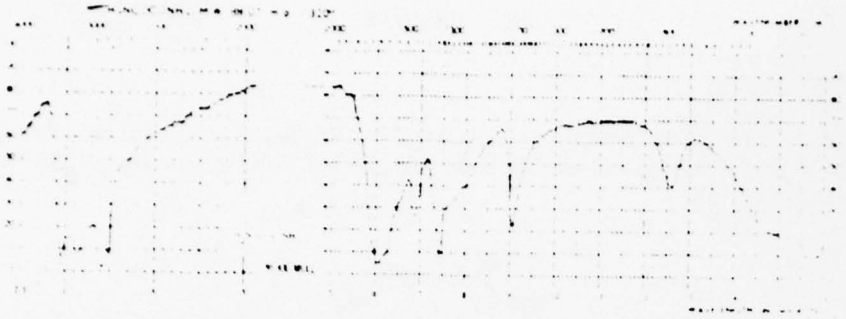
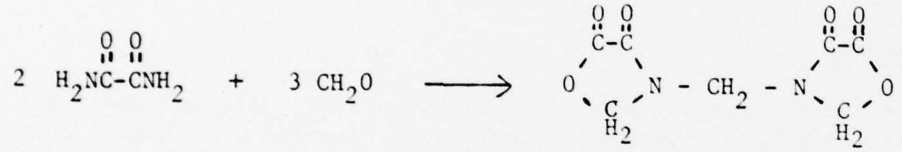


Figure XX-1. Infrared Spectrum of Oxamide (Pouchert, 1970).

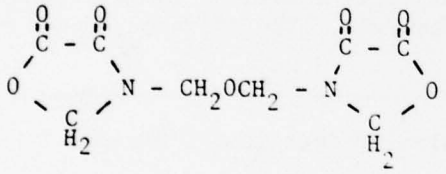
C. Chemical Properties

1. General Reactions

Oxamide reacts with paraformaldehyde in concentrated sulfuric acid to form N,N-methylene-bis[4,5-oxazolidinedione] (Gilbert, 1971).

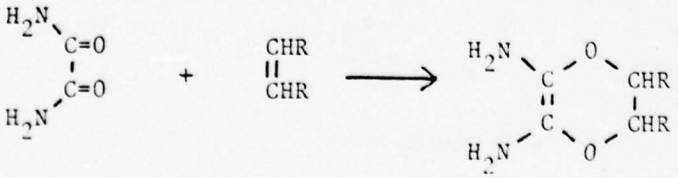


If excess paraformaldehyde is present, bis[(4,5-oxazolidinedion-3-yl)methyl] oxide is formed.



Thermal decomposition has been reported to begin at temperatures ranging from 290°C to 413°C (Hawley, 1977; Windholz, 1976; Terman and Fleming, 1968). Decomposition yields ammonia, carbon dioxide, and highly toxic cyanogen.

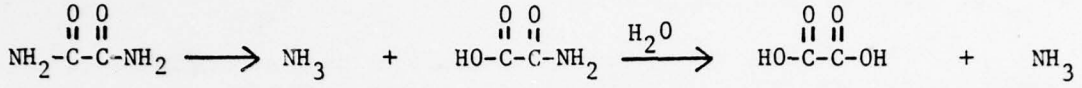
Oxamide may behave as a diene in a Diels-Alder addition.



A similar addition has been reported between the α,β-diketone tetrachloro-o-benzoquinone and stilbene (Needleman and Kuo, 1962).

2. Environmental Reactions

Oxamide undergoes stepwise hydrolysis to oxamic acid and then oxalic acid in moist soil (Terman and Fleming, 1968).



The rate of hydrolysis is greatly enhanced by the presence of microorganisms. Although oxamide is practically insoluble in water, any small amounts which may be solubilized would undergo hydrolysis very slowly.

Photolytic studies on oxamide have not been reported.

3. Sampling and Analysis

Analytical techniques specific for oxamide were not found in the literature surveyed. However, infrared spectroscopy is a possible method for quantitative analysis of oxamide.

D. Uses in Army Munitions

1. Purpose

Oxamide is used as a component of tracer formulations where it functions as a burning rate retardant and stabilizer. The only Army user of oxamide is Lake City AAP, where it is used in the following formulations:

	% Oxamide in Formulation
IM-68	1.87
R-403	9.4±1
R-505	12.4 max

2. Quantities Used

a. Historical Use

The use rate of oxamide at LCAAP during 1975-1977 is listed below:

1975	1,322 lb
1976	1,758 lb
1977	2,041 lb

The average use rate during this period was 1,707 lb/year or 142 lb/month.

b. Current Use

The most recent use rate of oxamide at LCAAP was 2,041 lb in 1977 or 170 lb/month.

c. Use at Full Mobilization

The quantity of oxamide which would be used at LCAAP under full mobilization operations would be 5,330 lb/year or 444 lb/month.

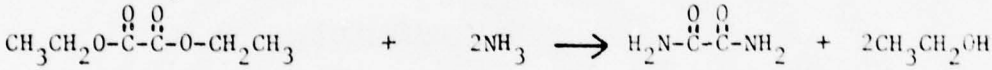
3. Documented or Speculated Occurrences in Air or Water

Actual losses of oxamide have not been determined quantitatively. However, according to Melton (1978), the production of tracers generally results in losses of 1-2% of the amount handled. Thus, oxamide losses at LCAAP should be about 2-3 lb/month. At full mobilization, losses would increase to 4-9 lb/month. Waste effluents at LCAAP are treated with strong base to destroy explosive components. The wastes are then neutralized and sent to conventional industrial waste treatment facilities. Under these conditions, hydrolysis to oxalate would be expected. Precipitation of calcium oxalate would occur thus removing most of the oxalate from the effluent.

E. Uses in the Civilian Community

1. Production Methodology

Hummel Chemical manufactures oxamide by reacting a solution of diethyl oxalate with ammonia and collecting the precipitated oxamide (Hummel Chemical, 1978).



Oxamide can also be manufactured by glow-discharge electrolysis of formaldehyde, pyrolysis of ammonium oxalate, or hydrolysis of cyanogen in concentrated hydrochloric acid (Terman and Fleming, 1968; Windholz, 1976).

2. Manufacturers, Production and Capacity

The three U.S. manufacturers of oxamide are listed in Table XX-2.

Table XX-2. U.S. Manufacturers of Oxamide (S.R.I, 1977).

Allied Chemical Corp.	Marcus Hook, PA
Guardian Chemical Corp.	Hauppauge, NY
Hummel Chemical Co.	South Plainfield, NJ

The individual plant capacities and past production figures are unavailable.

Oxamide is also imported to the U.S. from England by the Spectrum Chemical Manufacturing Corporation (Spectrum Chemical, 1978).

3. Current Usages and Future Trends

The main use of oxamide is as a stabilizer in nitrocellulose preparations. It is also used as a substitute for urea as a fertilizer. Future growth of this chemical is dependent on its increased application in fertilizers. The use of oxamide in fertilizers depends on the ability of the manufacturers to reduce production costs (Araten, 1968).

4. Documented or Speculated Occurrences in the Environment

Oxamide is used as a surface applied fertilizer. From this use, it can reach streams, ponds and major waterways in storm run-off. The amount of oxamide reaching the waterways from this use has not been documented. However, oxamide containing fertilizer is expected to be the major environmental source of this chemical.

F. Comparison of Civilian and Military Uses and Pollution

The civilian production statistics on oxamide are not available. However, with three companies possessing oxamide production facilities, the United States capacity is estimated at >1 million pounds per year. Most of this chemical is used by the civilian community as a stabilizer in nitrocellulose formulations and potentially as a fertilizer. Widespread environmental distribution of oxamide is expected from its use as a fertilizer.

The military use of oxamide is limited to 1000 to 2000 lb per year at Lake City AAP at current production rates. This use rate would increase to 5300 lb per year at full mobilization. Even at full mobilization, the Army usage of oxamide is less than 1% of the estimated civilian production capacity. Army discharges from Lake City AAP would amount to a maximum of 9 lb/month. However, most of this quantity will be removed by the industrial waste treatment facility. Thus any environmental pollution due to the use of oxamide in tracer formulations at Lake City AAP is negligible compared to the pollution of this compound from civilian production and uses.

G. Toxicological and Environmental Hazards

1. Mammalian Toxicity

Oxamide has a LDLo for intraperitoneal injections in mice of 128 mg/kg (NIOSH, 1977). In the body it is metabolized to oxalic acid (Windholz, 1977). Oxalic acid is toxic. This toxicity is believed to be due to the ability of oxalic acid to bind calcium and thus upset the calcium-potassium water in the tissues (American Conference of Governmental Industrial Hygienists, 1977).

2. Aquatic Toxicity

No aquatic toxicity data on oxamide was found in the literature.

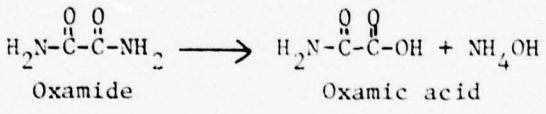
3. Toxicity to Microorganisms

Only a small number of references on the toxicity of oxamide to microorganisms was found. Most information encountered indicates that oxamide is relatively non-toxic and provides a nitrogen source for microbial growth. Immobilized nitrogen is initially incorporated into proteins and other cellular constituents of microorganisms.

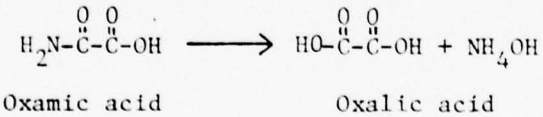
Oxamide releases ammonium nitrogen to the environment in most soil. Dissolution of oxamide in soil is greatly influenced by microorganisms (Terman and Fleming, 1968). Allen *et al.* (1973) reported that with low application rates of oxamide (~56 lg N/ha), most of the applied nitrogen was assimilated by microorganisms and incorporated into the biomass. When application rates exceed the minimum requirements of microorganisms, more of the oxamide nitrogen was available to plants. At rates exceeding the requirements of both microorganisms and plants, NO_3^- can temporarily accumulate and eventually be lost by leaching and/or denitrification.

4. Phytotoxicity

No literature was encountered that suggested any phytotoxic properties for oxamide. In fact, many researchers have studied the effects of oxamide when applied to vegetation as a fertilizer. Oxamide undergoes stepwise hydrolysis in moist soil to liberate ammonium nitrogen as follows:



Oxamide → Oxamic acid



Oxamic acid → Oxalic acid

The rate of dissolution and hydrolysis of oxamide in soil is considerably affected by the granule size. Dement *et al.* (1961) reported that fine oxamide and ammonium nitrate were equally available to maize (*Zea mays*), but that 3.3 mm to 4.7 mm granules of oxamide supplied much less nitrogen to the first crop. Total recovery of nitrogen by three successive maize crops was similar to that from ammonium nitrate and higher than from urea-formaldehyde fertilizers. Engelstad *et al.* (1964) also reported decreased availability of nitrogen from oxamide to a single corn crop with increasing granule size. Terman and Fleming (1968) suggest that large applications of granular oxamide can be surface applied to grass turf without apparent injury. Allen *et al.* (1973) reported that much of the fertilizer nitrogen that is not absorbed the first season becomes immobilized and is only slowly available to succeeding crops.

5. Availability of Literature for Phase II

Only limited literature was found on toxicity of oxamide to various organisms. Due to the use of this compound as a fertilizer, unpublished toxicological studies are probably available from manufacturers, fertilizer companies and the Agriculture Department.

H. Regulations and Standards

There are no EPA, OSHA or DOT standards or regulations specific for oxamide. Oxalic acid, the hydrolysis product of oxamide, has an OSHA standard of 1 mg/m^3 (Federal Register, 1974). It has also been selected for carcinogenesis testing by NCI (NIOSH, 1977).

I. Conclusions and Recommendations

The goal of this study was to assess the Army's responsibility for further toxicological and environmental evaluation of oxamide. After evaluation of the data gathered during this study, oxamide should be a low priority for a Phase II study. This conclusion was based on the low usage rate and pollution of oxamide at the Lake City AAP facility; the widespread pollution resulting from civilian use; and the ease with which this compound is degraded in the environment.

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PRELIMINARY PROBLEM DEFINITION STUDY OF 48 MUNITIONS-RELATED CHEMICALS

VOLUME IV PRIMER AND TRACER RELATED CHEMICALS

MAGNESIUM CARBONATE

FINAL REPORT

J. F. Kitchens
W. E. Harward III
D. M. Lauter
R. S. Wentsel
R. S. Valentine

April 1978

Supported by:

U. S. ARMY MEDICAL RESEARCH AND DEVELOPMENT COMMAND
Fort Detrick, Frederick, Maryland 21701

Contract No. DAMD17-77-C-7057

COTR: Clarence Wade, Ph.D.

ATLANTIC RESEARCH CORPORATION
Alexandria, Virginia 22314

Approved for Public Release
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The findings of this report are not to be construed as an official Department of the Army position unless so designated by other authorized documents.

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SUMMARY

Magnesium carbonate is used in the civilian economy as a precursor of many other magnesium salts. These salts are used in fire retardants and in the manufacture of ceramics and glass. Magnesium carbonate is also used in many formulations for human consumption such as pharmaceuticals and antacids.

The Army uses magnesium carbonate as a burning rate regulator in pyrotechnic, primer and tracer applications. Total military use is 50,000 lb/year. At full mobilization, quantities of 500,000 lb/year would be required, about 0.1% of the civilian use. Total losses to the environment from military uses would be less than 10,000 lb/year, even at full mobilization. This amount is negligible compared to civilian source of entry into the environment.

Magnesium carbonate is relatively non-toxic to humans, aquatic organisms and microorganisms. Some plant species may suffer chlorosis and growth inhibition when exposed to this chemical.

The military use of magnesium carbonate is insignificant compared to civilian use. This fact and the low toxicity of this chemical indicate that a Phase II study on this chemical should be a low priority.

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FOREWORD

This report details the results of a preliminary problem definition study on magnesium carbonate. The purpose of this study was to determine the Army's responsibility for conducting further research on magnesium carbonate in order to determine its toxicological and environmental hazards so that effluent standards can be recommended. In order to determine the Army's responsibility for further work on magnesium carbonate, the military and civilian usage and pollution of this chemical were evaluated. In addition, a preliminary overview of toxicological and environmental hazards was conducted.

Magnesium carbonate was only one of 48 chemicals evaluated under Phase IA of contract No. DAMD17-77-C-7057. These chemicals are grouped in four categories

- explosives related chemicals
- propellant related chemicals
- pyrotechnics
- primers and tracers

Each category is a major report. Section I of each report is an overview of the military processes which use each chemical and the pollution resulting from the use of these chemicals. The problem definition study reports on each chemical are separable sections of these four reports.

In addition, a general methodology report was also prepared. This report describes the search strategy and evaluation methodology utilized for this study.

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XXI. MAGNESIUM CARBONATE

A. Alternate Names

Magnesium carbonate, $MgCO_3$, is one of the commercially important magnesium compounds. The alternate names for magnesium carbonate are presented below:

Molecular Weight:	84.32g/mole
CAS Registry No.:	546-93-0
Replaces CAS Registry No.(s):	18976-97-1; 19078-16-1
CA Names (8 CI):	Carbonic acid, magnesium salt (1:1)
Wiswesser Line Notation:	Mg C-O-Q2
Synonyms:	C.I. 77713; Carbonate magnesium; DCI Light magnesium carbonate; Magnesium carbonate; Magnesium carbonate (1:1); Magnesium carbonate ($MgCO_3$); Stan- Mag

B. Physical Properties

The physical properties of magnesium carbonate, the hydrates and basic carbonates are presented in Table XXI-1.

C. Chemical Properties

1. General Reactions

Magnesium carbonate forms three hydrates: $MgCO_3 \cdot 5H_2O$, $MgCO_3 \cdot 3H_2O$ and $MgCO_3 \cdot H_2O$. These solid hydrates are stable only in a carbon dioxide atmosphere. Exposed to air, they slowly form the basic carbonate $5MgO \cdot 4CO_2 \cdot xH_2O$ (x is approximately 5 or 6). The trihydrate can exist in solution at temperatures between 13 and 50°C. Its solubility at 25°C is 0.129 grams per 100 grams H_2O. Upon heating of a $MgCO_3 \cdot 3H_2O$ solution above 50°C, basic magnesium carbonate, $5MgO \cdot 4CO_2 \cdot xH_2O$, precipitates.

Magnesium carbonate forms double salts with magnesium halides. It also forms alkali double salts such as $MgCO_3 \cdot K_2CO_3 \cdot 8H_2O$ and $MgCO_3 \cdot Na_2CO_3$.

Thermal decomposition occurs between 500 and 600°C. Carbon dioxide is given off and magnesium oxide forms.

$$MgCO_3 \xrightarrow{\Delta} MgO + CO_2$$

Table XXI-1. Physical Properties of the Magnesium Carbonates.*

	$MgCO_3$	$MgCO_3 \cdot 3H_2O$	$MgCO_3 \cdot 5H_2O$	$MgCO_3 \cdot Mg(OH)_2 \cdot 3H_2O$	$3MgCO_3 \cdot Mg(OH)_2 \cdot 3H_2O$	$4MgCO_3 \cdot MgO \cdot 5(or\ 6)H_2O$
Physical Form @ 20°C:	solid	solid	solid	solid	solid	solid
Crystal Form:	trigonal	rhombic	monoclinic	rhombic	rhombic	thin flakes
Color:	white	colorless	colorless	colorless	white	
Index of Refraction:	1.717, 1.515	1.495, 1.501 1.526	1.456, 1.468 1.507	1.489, 1.534 1.557	1.527, 1.530 1.540	
Density, g/cm^3:	3.037	1.850	1.69 - 1.73	2.02	2.16	0.08 - 0.13
M.P.:	decomp. 350°C	165°C			decomp.	
B.P.:	$-CO_2$, 900°C					
Thermal Conductivity:	0.00023 cal/(sec)(cm^2)(°C/cm) @ 100°C 0.00625 cal/(sec)(cm^2)(°C/cm) @ 300°C					
Solubility, g/100g H_2O:	0.0034 @ 25°C Soluble in acid Insoluble in acetone, NH_3	0.129 @ 25°C Soluble in acid				

*References: Kirk and Othmer, 1967; Hodgman *et al.*, 1963.

Magnesium carbonate reacts with many anions leading to replacement of the carbonate by the anion. Some of these reactions are discussed below:

- Formic acid reacts with $MgCO_3$ to yield magnesium formate.

$$HCOOH + MgCO_3 \longrightarrow Mg(HCO_2)_2$$

- Magnesium nitrate is formed by the reaction of nitric acid with magnesium carbonate.

$$HNO_3 + MgCO_3 \longrightarrow Mg(NO_3)_2$$

- Magnesium carbonate will react with calcium sulfate in a reversible equilibrium forming calcium carbonate and magnesium sulfate.

$$MgCO_3 + CaSO_4 \longrightarrow MgSO_4 + CaCO_3$$

- Basic magnesium carbonate will react with excess sulfur dioxide to form magnesium sulfite hexahydrate.

$$5MgO \cdot 4CO_2 \cdot xH_2O + SO_2 \longrightarrow MgSO_3 \cdot 6H_2O$$

- Magnesium acetate tetrahydrate is produced by addition of glacial acetic acid to a heated aqueous suspension of magnesium carbonate (Kirk, 1977).

$$MgCO_3 + CH_3COOH \longrightarrow Mg(CH_3CO_2) \cdot H_2O$$

- A solution of magnesium carbonate and ammonium phosphate will form magnesium ammonium phosphate hexahydrate.

$$MgCO_3 + (NH_4)_2HPO_4 \longrightarrow MgNH_4PO_4 \cdot 6H_2O$$

- Magnesium carbonate reacts with arsenic acid to give magnesium arsenate.

$$MgCO_3 + As_2O_5 \longrightarrow Mg_3(AsO_4)_2 \cdot xH_2O$$

- Magnesium carbonate dissolved in gluconic acid yields magnesium gluconate (Hawley, 1977).

2. Environmental Chemistry

Magnesium carbonate is found in the environment. Its naturally occurring form is magnesite. It is also found in large deposits of dolomite as the double salt. Hydrates are found in small infrequent deposits.

3. Sampling and Analysis

Magnesium carbonate may be determined by dissolving the sample with acid and then analyzing for magnesium. Magnesium may be determined by a number of methods including:

- Atomic absorption spectrometry. Magnesium is measured at a wavelength of 285.2 nm with a reported sensitivity of 7 ug/l giving 1% absorption (Franson, 1975)

- Gravimetric analysis. Magnesium is quantitatively precipitated by treatment with diammonium hydrogen phosphate to form magnesium ammonium phosphate. This compound is ignited to magnesium pyrophosphate which is weighed (Franson, 1975).

- Total magnesium and calcium in the sample may be determined by EDTA complexiometric titration. Calcium may then be determined separately and the magnesium content calculated as the difference (Franson, 1975).

D. Uses in Army Munitions

1. Purpose

Magnesium carbonate is used as a burning rate regulator in pyrotechnic, primer and tracer formulations. The predominant use of this material is at Pine Bluff Arsenal. Formulations produced at PBA using magnesium carbonate are listed below:

	% Magnesium carbonate in Formulation
Green smoke, 105 canister	3±1
Green smoke	3.5±1
Red smoke VIII	5±2
Red smoke, 105 canister	4±1
Red smoke	5±1
Yellow smoke, 105 canister	11±2
Yellow smoke	7.1±1
Fuel mixture VI	29±4
Riot mixture CSI	12±1
Irritant mixture, CS II	12±1
Riot mixture, CS II	12±2.5
CS Pyro mixture	9±2

Magnesium carbonate is also used at Lake City AAP for the manufacture of R-440 tracer mix. This formulation specifies use of 10% magnesium carbonate.

Longhorn AAP uses magnesium carbonate in some tracer formulations as well. As at LCAAP, use of magnesium carbonate at LAAP is in relatively low volumes.

2. Quantities Used

a. Historical Use

The approximate quantities of magnesium carbonate used at PBA during the 1965-1975 period are given below:

	Magnesium Carbonate Used, lb
1965	17,000
1966	118,000
1967	149,000
1968	72,000
1969	4,500
1970	44,500
1971	64,000
1972	42,000
1973	23,000
1974	12,000
1975	12,500

The average annual use rate was 50,750 lb/year or 4,230 lb/month.

b. Current Use

The 1978 production schedule at PBA calls for manufacture of smoke grenades, smoke canisters and smoke markers, requiring a total of 52,000 lb of magnesium carbonate. This quantity represents a current average use rate of 4,333 lb/month.

Longhorn AAP used a total of 680 lb of magnesium carbonate during 1977. This amounts to an average rate of 57 lb/month.

c. Use at Full Mobilization

The full mobilization use rate of magnesium carbonate at PBA is 39,500 lb/month. At full mobilization, LAAP would use about 2400 lb/month of this material (Leander, 1978), a minor amount compared to PBA.

3. Documented or Speculated Occurrences in Air or Water

The production of pyrotechnic and tracer formulations generally results in loss of 0.5-2% of the materials handled (Aikman, 1978; Maley, 1978). Losses of magnesium carbonate at PBA thus would amount to 43-87 lb/month. At full mobilization, losses at PBA would rise to 400-800 lb/month. In the past, essentially all of the magnesium carbonate lost at PBA was discharged into the Arkansas River. There was no treatment of pyrotechnic wastes at PBA in the past. However, a central waste treatment facility will be operational in 1979. This treatment facility will reduce all discharges down to currently acceptable levels.

Current losses of magnesium carbonate at LAAP are less than 1 lb/month, and would be in the range of 12-24 lb/month at full mobilization. This material is collected in sumps and discharged into an evaporation pond. The pond bottom is heavily contaminated with munitions ingredients. Some leaching into ground water is suspected, but has not been confirmed (USAEHA, 1972).

E. Uses in the Civilian Community

1. Production Methodology

Magnesium carbonate is prepared industrially either from slurries of magnesium hydroxide from brines and seawater or directly from magnesite and dolomite ores (Kirk and Othmer, 1967; S.R.I., 1977a).

Direct carbonation of magnesium hydroxide slurries yield magnesium carbonate trihydrate. If high purity is a concern, the magnesium hydroxide is first converted to the bicarbonate.

Magnesium carbonate may be isolated from magnesite by mechanical beneficiation such as screening or hydraulic separation of impurities, froth flotation, or heavy media separation techniques. Magnesium carbonate is obtained from dolomite by calcining the ore followed by carbonation of the resulting slurry to give magnesium bicarbonate in solution with calcium carbonate and other impurities in suspension. This slurry is clarified and filtered and the pure filtrate is heat treated to precipitate magnesium carbonate.

Magnesium carbonate may also be manufactured from magnesium sulfate and calcium carbonate (Hawley, 1977). A magnesium sulfate solution and calcium carbonate solution are mixed and the precipitated magnesium carbonate is filtered and dried.

2. Manufacturers, Production and Capacity

The U.S. manufacturers of magnesium carbonate are listed with their plant locations in Table XXI-2. Individual plant capacities are unavailable.

3. Usages

Magnesium carbonate is used as a chemical precursor for numerous magnesium salts including:

- magnesium acetate which is used in disinfectants, deodorants, textiles and calico printing

Table XXI-2. U.S. Manufacture of Magnesium Carbonate (S.R.I., 1977a).

Combustion Engineering, Inc. C-E Minerals Div.	Camden, NJ
Gen. Telephone & Electronics Corp. GTE Sylvania Inc., subsid. Chem. and Metallurgical Div.	Towanda, PA
Kaiser Aluminum & Chem. Corp. Kaiser Refractories Div.	Moss Landing, CA
Mallinckrodt, Inc. Indust. Chems. Div.	St. Louis, MO
Merck & Co., Inc. Merck Chem. Mfg. Div.	South San Francisco, CA
Morton-Norwich Products, Inc. Morton Chem. Co., div.	Manistee, MI
Northwest Indust., Inc. Velsicol Chem. Corp., subsid.	St. Louis, MO
Richardson-Merrell, Inc. J.T. Baker Chem. Co., subsid.	Phillipsburg, NJ
Smith Chem. & Color Co., Inc.	Jamaica, NY
Tamms Indust. Co. Western Div.	Itasca, IL Bellflower, CA

- magnesium ammonium phosphate which is used as a fire retardant for fabrics and a fertilizer
- basic magnesium carbonate
- magnesium citrate which is used as a supplemental dietary source of citric acid
- magnesium fluoride which is used in ceramics, glass and polarizing prisms
- magnesium fluosilicate which is used in ceramics, concrete, mothproofing and magnesium castings
- magnesium gluconate

Magnesium carbonate is also used in refractories, polishing agents, rubber pigments, inks, glass, dentifrices, mineral water, as a filler for paper, paint, pharmaceuticals, plastics, rubber, and varnishes, and as a stomach antacid (S.R.I., 1977b).

4. Future Trends

We are unaware of any anticipated major changes in civilian production or use of magnesium carbonate.

5. Documented or Speculated Occurrences in the Environment

Magnesium carbonate is found widely in nature in the form of magnesite ore and in dolomite ($MgCO_3 \cdot CaCO_3$). There are no reports in the literature of magnesium carbonate as a man-made environmental pollutant.

F. Comparison of Civilian and Military Uses and Pollution

Magnesium carbonate is produced by numerous manufacturers in the United States. Total production capacity is estimated to be in excess of 500 million lb/year. This chemical is used widely as an additive in various formulations and as a precursor for making other magnesium salts. It is used as a stomach antacid, which is indicative of the harmless nature of this chemical.

Military use of this chemical is currently about 50,000 lb/year or about .01% of the civilian production capacity. Even at full mobilization, the use rate would represent only about 0.1% of civilian use. Losses of magnesium carbonate to the environment without the treatment plant at PBA would not exceed 12,000 lb/year even at full mobilization. Thus, military sources of magnesium carbonate as a pollutant are negligible compared to civilian sources.

G. Toxicological and Environmental Hazards

1. Aquatic Toxicity

Magnesium carbonate ($MgCO_3$) is relatively insoluble in water (.0034 g/100g water). Upon release into an aquatic system, $MgCO_3$ would build up in the sediment and would be almost completely unavailable to aquatic organisms.

NIOSH (1977) found a 96 hour TLM rating aquatic toxicity over 1,000 ppm for $MgCO_3$. Biesinger and Christensen (1972) tested *Daphnia magna* and found a chronic 3 week LC50 for $MgCl_2$ to be 190 ppm and a 16% reproductive impairment of 82 ppm. From this data, $MgCO_3$ has a very low toxicity to aquatic organisms.

2. Mammalian Toxicity

Magnesium carbonate ($MgCO_3$) has a very low toxicity to mammals. $MgCO_3$ is used in antacids, and magnesium is an essential nutrient.

3. Toxicity to Microorganisms

Thompson *et al.* (1972) developed a process using $MgCO_3$ in water treatment. $MgCO_3$ levels in the 100 ppm range were used with no toxic effects noted to the microorganisms present in the floc.

4. Phytotoxicity

Magnesium, when present in soils beyond cartain amounts, produce injurious effects on many higher plants. Sievers (1924) described the phytotoxic effect of magnesium oxide discharges from a furnace stack on surrounding vegetation. Soils with a magnesium content ranging from approximately 10,000 to 56,000 lb per acre foot (14 x the normal surface soil) produced chlorosis and stunted growth in oats.

The toxic action of magnesium is both physical and chemical. Soils may accumulate a thick and slightly impervious crust which restricts many plants from surviving germination. When magnesium oxide comes in contact with the soil and is exposed to CO_2 in air and to moisture, it is soon converted to magnesium carbonate. The magnesium carbonate is not readily soluble in water but forms a soluble bicarbonate in soil solutions containing carbon dioxide. This reaction is partly responsible for the toxic effect of magnesium. The effect is more pronounced in soil high in organic matter or where there is an opportunity for large amounts of carbon dioxide to be evolved.

Various types of soybean (*Glycine max.* L.) were grown in soil which had been treated with $MgCO_3$. The resulting high soil pH and low phosphorous-high magnesium content caused growth inhibition and chlorosis due to iron deficiency from low iron uptake (Wallace *et al.*, 1976).

Boischot and Drouineau (1941) reported that Hydrangea and bean cultures were damaged (stunted growth) by an excessive amount of Mg. The composition of such plants showed a considerable increase in Mg and reduced K content. Coupin (1918) stated that the injurious effects of magnesium carbonate on plants include reduction in length of main root and rootlets, a black or brown coloration of the branches and rootlets and stunted aerial growth.

H. Regulations and Standards

1. Air and Water Regulations

No limits are listed for exposure to magnesium carbonate in air or water.

2. Human Exposure Standards

No specific standards are listed for human exposure to magnesium carbonate. However, a limit of 10 mg/m^3 has been recommended for exposure to magnesium oxide fumes (American Conference of Governmental Industrial Hygienists, 1971).

I. Conclusions and Recommendations

Military use of magnesium carbonate is currently about 50,000 lb/year, or 0.01% of the civilian production capacity. At full mobilization, the military use rate would increase to 0.1% of civilian use.

Magnesium carbonate is non-toxic to mammals, aquatic organisms and micro-organisms. Phytotoxic effects have been noted in thy presence of excessive quantities of magnesium.

Magnesium carbonate is used commonly in the civilian economy. The low military use and the non-toxic nature of this chemical indicate that this chemical should be a low priority for a Phase II study.

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LIST OF ABBREVIATIONS

$\mathring{A}$	Angstom Unit
@	At
AAP	Army Ammunition Plant
Ag	Silver
Aq	Aqueous
Au	Gold
Av	Average
B.P.	Boiling Point
BTU	British Thermal Unit
°C	Degree Centigrade
CA	Chemical Abstracts
cal	Calories
CAS	Chemical Abstracts Services
cm.	Centimeter
cm^3	Cubic Centimeters
CO	Carbon Monoxide
CO_2	Carbon Dioxide
conc.	Concentration
Δ	Heat
ECG	Electrocardiogram
EDTA	Ethylenediaminetetra acetic acid
F	Oil Furnace Process
g	Grams
(g)	Gas
gpd	Gallons Per Day
H_2	Hydrogen Gas
ha	Hectare
ΔHf	Latent Heat of Fusion
Hz	Hertz
I_2	Iodine
in	Inch
i.v.	Intravenous
kg	Kilograms

LIST OF ABBREVIATIONS
(continued)

kJ	Kilojoule
ℓ	Liter
LAAP	Longhorn Army Ammunition Plant
LCAAP	Lake City Army Ammunition Plant
lb	Pound
LC50	Concentration Required to Kill 50% of the Exposed Population
LD50	Dose Required to Kill 50% of the Exposed Population
LDLo	Lowest Dose Required to Affect any of the Exposed Population
LSAAP	Lone Star Army Ammunition Plant
m	Meter
M	Molar
m^3	Cubic Meter
mg	Milligram
µg	Microgram
λ	Wavelength
mm	Millimeter
mol	Mole
M.P.	Melting Point
n	Number
n_D	Refractive Index
$NaCO_3$	Sodium Carbonate
NAD	Naval Ammunition Depot
NaN_3	Sodium Azide
$NaNO_2$	Sodium Nitrite
ng	Nanogram
nm	Nanometer
NO_3^-	Nitrate Anion
NOS	Naval Ordance Station
Ω	Ohms
PBA	Pine Bluff Arsenal
$Pb(NO_3)_2$	Lead Nitrate

LIST OF ABBREVIATIONS
(continued)

$Pb(C_2H_3O_2)_2$	Lead Acetate
PETN	Pentaerythritol tetranitrate
pH	Negative Log of Hydrogen Ion Concentration
PbN_6	Lead Azide
ppb	Parts Per Billion
ppm	Parts Per Million
ppt	Parts Per Trillion
PPT	Precipitate
psi	Pounds Per Square Inch
PVC	Polyvinyl Chloride
R	Alkyl Radical
s.c.	Subcutaneous
sec	Second
T	Thermal Process
TLm	*Median Tolerance Limit*
TLV	Threshold Limit Value
TNR	Trinitroresorcinol

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