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PRELIMINARY PROBLEM DEFINITION STUDY ON MUNITIONS-RELATED CHEMI--ETC(U)

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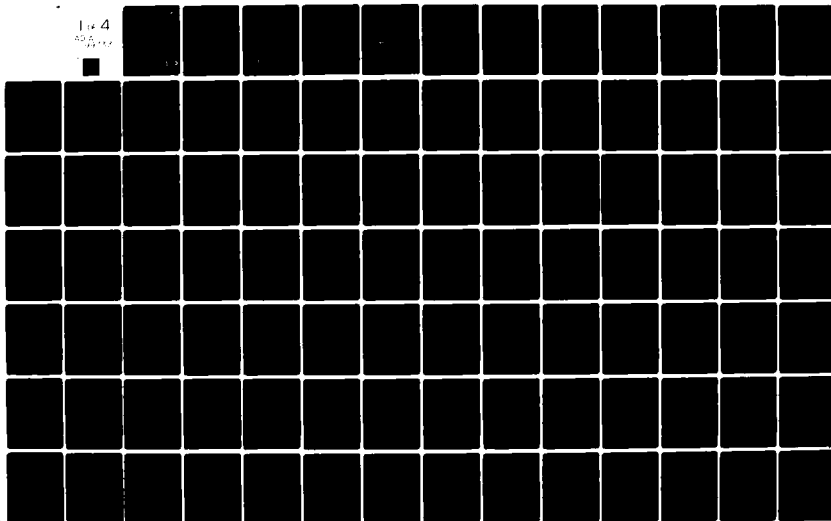
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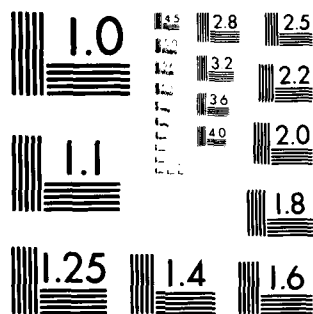
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PRELIMINARY PROBLEM DEFINITION STUDY ON
MUNITIONS-RELATED CHEMICALS

Final Report

by

J.F. Kitchens	W.E. Jones, III
S.G. Brownlee	D.A. Price
W.E. Harward, III	R.S. Wentzel
R.G. Hyde	R.S. Valentine

April 1979

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

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Solvents	Hazards	Di(2-ethylhexyl)sebacate	
Plasticizers	Toxicology	Octahydro-1,3,5,7-tetranitro-	
Uses	Triaminotrinitrobenzene	1,3,5,7-tetrazocine	
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This document presents the results of a preliminary problem definition study on munitions-related chemicals. The purpose of this study was to determine the Army's responsibility for conducting further research on the toxicological and environmental hazards of these chemicals, so that effluent criteria can be recommended. Both civilian and military uses of the chemicals were evaluated.			

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Di-n-butyl Sebacate

Octogen

Tris(Chloroethyl)phosphate

Fyrol CEF

Bis (2,2-dinitropropyl)acetal

Bis(2,2-dinitropropyl)formal

BDNPA

BDNPF

BDNPA/F

Polyethylene Emulsion AC-656

Stearic Acid

Morpholine

Acintol

Tall oil

N-Nitrosomorpholine

Tetranitrocarbazole

n-Propyl Adipate

Strontium Oxalate

Lead 2-ethylhexanoate

H101

Methyl Centralite

Toluidine Red

Dechlorane

Mirex

Ethylene Glycol Dinitrate

Triethylene Glycol Dinitrate

1,2-propylene Glycol Dinitrate

1,3-propylene Glycol Dinitrate

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EXECUTIVE SUMMARY

The goal of this preliminary problem definition study was to assess the Army's responsibility for further study on the sixteen (16) chemicals associated with munitions production. The chemicals included in this study were:

Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX)	Lead 2-ethylhexanoate (H101)
Triaminotrinitrobenzene (TATB)	Di-n-butyl Sebacate
Tris(2-chloroethyl)phosphate (CEF)	Di-n-propyl Adipate
Bis(2,2-dinitropropyl)acetal/Bis(2,2-dinitropropyl)formal (BDNPA/F)	Methyl Centralite
Polyethylene Emulsion AC-656	Glycol Dinitrates
Di(2-ethylhexyl)sebacate	Toluidine Red Toner
n-Butyl Acetate	Strontium Oxalate
Tetranitrocarbazole	Dechlorane

The recommendations resulting from this study are summarized in Table S-1 and discussed below:

HMX

HMX (octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine) is a nitramine explosive produced exclusively by Holston AAP in Kingsport, Tenn. HMX is compounded into plastic bonded explosives and other explosive formulations at Holston AAP. Approximately 28% of the HMX produced at Holston AAP is sold to civilian rocket manufacturers. These manufacturers produce solid rocket motors which use HMX in the propellant formulations. The civilian manufacturers sell most of the rocket motors they produce to the U.S. Government. Thus, HMX is a military unique compound.

The toxicity of HMX in various solvents has been studied. HMX does not penetrate the skin to any significant extent even when dissolved in DMSO. The LD50 for intravenous administration of HMX in DMSO to guinea pigs is 28.8 mg/kg.

The toxicity of HMX to aquatic life is low. The most sensitive species tested was the 7-days post hatched fathead minnows with a 96 hr LC50 of 15 ppm. The environmental fate of HMX has not been adequately studied.

In view of the military uniqueness of HMX, a Phase II detailed toxicological and environmental study should be undertaken. Further experimental studies may be warranted if a Phase II study reveals gaps in the available information.

Table S-1. Summary of Recommendations for Future Work
on Munitions Related Chemicals

Compound	Priority for Phase II Study			Basis
	Low	High	Questionable	
HMX		X		High Army use; limited environmental toxicological data
TATB		X		Expected increase in Army use; limited environmental and toxicological data
CEF	X			Limited Army use
BDNPA/F	X			Low sporadic use in Army munitions production
Polyethylene Emulsions		X		Expected increase in Army use; potential environmental formation of N-nitrosomorpholine
Di-2-ethylhexyl Sebacate	X			Discontinued use in Army munitions production
n-Butyl acetate	X			Discontinued use in Army munitions production
Tetranitrocarbazole		X		Military unique chemical; limited environmental and toxicological information
H101	X			Low use in Army munitions compared to civilian uses
Di-n-butyl sebacate	X			Discontinued use in Army munitions
Di-n-propyl adipate		X		Military unique plasticizer, possibly teratogenic
Methyl centralite	X			Low use in Army munitions
Glycol dinitrates	X			Low or discontinued use in Army munitions
Toluidine red toner	X			Low use in Army munitions compared to civilian uses
Strontium oxalate		X		High use of this strontium compound and other strontium salts in Army munitions
Dechlorane	X			Toxicology and environmental evaluation have already been conducted by EPA; Limited Army use

TATB

TATB (triaminotrinitrobenzene) is a thermally stable, relatively impact insensitive explosive. Because of these properties, TATB is expected to find increased uses in both the civilian and military communities. It is currently being manufactured in a pilot plant by Mason and Hangar and compounded into plastic bonded explosives at Holston AAP. This compounding process is probably the major source of entry of TATB into the environment.

TATB has a low toxicity to mammals (g/kg). No aquatic or environmental data on TATB were found in the literature.

In view of the expected increase in use of TATB, it is recommended that TATB be included in a Phase II study.

CEF

CEF (tris(chloroethyl)phosphate) is a chloroorganic phosphate used as a fireproofing agent in urethane foam. This chemical is produced by Stauffer Chemical Co. Production in 1975 was 29.4 million lb. Of this amount, it is estimated that 0.4 million lb/year are lost to the environment. In contrast to the high civilian production and use of this flame retardant, the Army's use of CEF in munitions production is sporadic and relatively small (0-7200 lb/year). CEF is used by the Army at Holston AAP in the formulation of plastic bonded explosive PBX-9404. Pollution of CEF resulting from this use is estimated at 6-12 lb per month at the 7200 lb/year use rate.

CEF is toxic to mammals only when administered in high doses (g/kg). The Ames test showed CEF to be non-mutagenic.

Due to the limited use of CEF in Army munitions production, any further Army sponsored studies on the toxicological or environmental hazards of CEF should be a low priority.

BDNPA/F

BDNPA/F is a 50/50 mixture of bis(2,2-dinitropropyl)acetal (BDNPA) and bis(2,2-dinitropropyl)formal (BDNPF). This mixture is used as a plasticizer in solid rocket propellants and in plastic bonded explosives formulation PBX-9501. Army use of BDNPA/F is limited to Holston AAP in Kingsport, Tenn. This use is small and sporadic (0-500 lb/year).

BDNPA/F is manufactured by Cordova Chemical Co. and the Navy for use in solid rocket propellant formulations containing polyurethane binders. However, there is no current production of BDNPA/F due to over supply.

Very little data on the toxicological or environmental hazards of BDNPA/F are available in the general literature. The only study found which pertains to the toxicological properties of this plasticizer was an acute oral study with rats. No effect was observed when rats were fed doses of 100 mg/kg.

Based on the low use of BDNPA/F in Army munitions production, any further Army sponsored studies on this plasticizer should be a low priority.

Polyethylene Emulsion AC-656

Polyethylene emulsion AC-656 is currently being piloted by Holston AAP as a desensitizer for A-3 explosives. If the A-3 product formulated with the polyethylene emulsion is put into full scale production, the Army's requirements for the AC-656 emulsion would be 400,000 lb/year at current production levels. At full mobilization, 2 million lb/year of AC-656 would be required by Holston AAP.

Polyethylene emulsion AC-656 is formulated solely for the Army by Chemical Corporation of America. this company buys the raw materials and formulates the emulsion at their Rutherford, N.J. facility. The emulsion is composed of the following ingredients:

- Polyethylene AC-656	20.38%
- Acintol	3.57%
- Morpholine	3.57%
- Stearic Acid	1.13%
- Ammonia	0.50%
- Water	70.85%

All of the ingredients are common materials for which there is widespread use and pollution.

The polyethylene emulsion AC-656 ingredients all have relatively low to moderate toxicities to mammals and aquatic life. However, the formation of N-nitrosomorpholine (a potent carcinogen) has been shown to occur from morpholine and nitrite *in vivo* and in the environment. The effluents from Holston AAP present a unique situation in which this nitrosation reaction could occur. High nitrite/nitrate concentrations are present along with suitable catalysts to promote the nitrosation reaction.

Based on the potential for the formation of N-nitrosomorpholine in the Holston AAP effluents, a Phase II study on the polyethylene emulsion AC-656 is recommended. This study should concentrate mainly on morpholine and its environmental reactions.

Di(2-ethylhexyl)sebacate

Di(2-ethylhexyl)sebacate is a plasticizer that was used by Holston AAP in C-4 products. Due to the rising prices of this plasticizer, it has been replaced by dioctyl adipate. Thus, there are no current uses of di(2-ethylhexyl)sebacate in Army munitions production.

The civilian community is also phasing out the use of di(2-ethylhexyl)sebacate. Production of this ester has dropped from 3.22 million lb in 1973 to 1.88 million lb in 1977. Future uses of di(2-ethylhexyl)sebacate by the civilian community are dependent on the price of this plasticizer in comparison with other available low temperature PVC plasticizers.

Di(2-ethylhexyl)sebacate is toxic to mammals only when given in higher doses (g/kg). In the environment, it is readily degraded and thus poses no long term environmental hazards.

In view of the discontinued use of di(2-ethylhexyl)sebacate in Army munitions production, no further Army sponsored studies on this compound by the Army are recommended.

n-Butyl Acetate

n-Butyl acetate is an ester which is used in lacquer coatings and as a solvent. The civilian production of n-butyl acetate is ~100 million lb/year. In the past, n-butyl acetate has been used as a solvent in explosives formulations and as an azeo entrainer at Holston AAP. Holston AAP no longer uses n-butyl acetate for these purposes. Other Army Ammunitions Plants use paints which contain n-butyl acetate. However, none of the raw chemical is purchased by these plants.

n-Butyl acetate exhibits a low toxicity to mammals. The main effects of exposure are irritation of the eyes and respiratory passages and narcosis. The toxicity of n-butyl acetate to aquatic organisms is moderate with LD50's in the 100 ppm range. In the environment, n-butyl acetate is readily degraded by chemical, photochemical and microbial mechanisms. Thus, this chemical does not pose a long term environmental hazard.

Based on the limited amount of n-butyl acetate now used by the Army, any further Army sponsored studies on this compound should be a low priority.

Tetranitrocarbazole

Tetranitrocarbazole is a component of the yellow first-fire mixture formulated at Longhorn AAP. This mixture is used in almost every round produced at Longhorn AAP. The tetranitrocarbazole is produced by Sodyeco for military use. Less than 25 lb of this chemical per year are used by the civilian community. Thus, tetranitrocarbazole is a military unique compound.

Only limited toxicological information on tetranitrocarbazole was found in the literature. The information suggests that tetranitrocarbazole is moderately toxic to mammals.

A phase II detailed toxicological and environmental hazards study is recommended in order to fill in the information gaps on this military unique compound.

H101

Lead 2-ethylhexanoate (H101) is widely used in the civilian community as a drier in paints and inks. Civilian production of this compound is ~2 million lb/year. Pollution of lead 2-ethylhexanoate from civilian production and formulation, use and disposal of paints and inks is expected to be high and widespread.

In contrast, Army use of lead 2-ethylhexanoate is ~22,000 lb/year under current operating conditions. This figure would increase to only 30,000 lb at full mobilization. This chemical is used in the N-5 propellant and AAH casting powder produced at Radford AAP. Pollution resulting from the use of lead 2-ethylhexanoate at Radford AAP is estimated at less than 1000 lb/year under full mobilization operating schedules.

Lead 2-ethylhexanoate is a chronic toxicity hazard to mammals. Long term exposure of this chemical leads to the symptoms of chronic lead poisoning.

In view of the limited Army use and pollution of lead 2-ethylhexanoate in munitions production, further Army sponsored toxicological or environmental studies on this compound should be a low priority.

Di-n-butyl Sebacate

Di-n-butyl sebacate is a plasticizer for PVC used when low temperature flexibility of the plastic is necessary. Only one civilian manufacturer, Union Carbide Corporation, currently produces di-n-butyl sebacate. However, other manufacturers have facilities which could be used to produce di-n-butyl sebacate if the demand for this plasticizer increases. Currently civilian production of di-n-butyl sebacate is in a decline because of high prices of starting materials.

The Army utilizes di-n-butyl sebacate in Otto II torpedo fuel produced at Radford AAP. Significant quantities of Otto II fuel have been produced at Radford in the years 1972-1977. However, no current production is scheduled nor is any production of this fuel anticipated in the near future.

Di-n-butyl sebacate is an ester of low toxicity. The LD50's for this compound are ~18 g/kg. In the environment, di-n-butyl sebacate is readily degraded by microorganisms. Thus it does not pose a long term threat to the environment.

Due to the curtailed use of di-n-butyl sebacate by Radford AAP, no immediate Army sponsored studies on this compound are recommended.

Di-n-propyl Adipate

Di-n-propyl adipate is a plasticizer that is used almost exclusively in solid propellant formulations produced at Radford AAP. There are no civilian

uses of this compound. Radford AAP buys di-n-propyl adipate from Hatco Chemical. This company produces the compound on special order. Thus Radford AAP is the main source of environmental pollution by di-n-propyl adipate.

Di-n-propyl adipate has a low acute toxicity to mammals (g/kg). However, it has been shown to be teratogenic in pregnant rats receiving an acute dose. No aquatic toxicity information on di-n-propyl adipate was found in this literature search.

In view of the military uniqueness of this compound and its potential teratogenicity, a Phase II study of the environmental and toxicological hazards of di-n-propyl adipate is recommended.

Methyl Centralite

Methyl centralite is an N,N'-disubstituted urea used as a coating for IMR propellants. These propellants are currently manufactured only at Radford AAP. The use of methyl centralite by the Army for this purpose is less than 400 lb per year. Pollution resulting from this use is negligible.

There are no civilian manufacturers or users of methyl centralite in the United States. All methyl centralite purchased by the Army is obtained from foreign manufacturers.

Based on the limited information available, the toxicological and environmental hazards of methyl centralite appear to be similar to the more widely used ethyl centralite.

Thus, even though methyl centralite is a military unique chemical, due to its low use rate methyl centralite is not a military problem chemical. Any further Army sponsored studies on this compound should be a low priority.

Glycol Dinitrates

The glycol dinitrates are manufactured for their explosive and plasticizer properties. The most commonly used of these compounds include:

- ethylene glycol dinitrate
- diethylene glycol dinitrate
- triethylene glycol dinitrate
- 1,2-propylene glycol dinitrate
- 1,3-propylene glycol dinitrate

Diethylene glycol dinitrate was evaluated in a previous problem definition study. This study completes the evaluation of the Army use of the remaining glycol dinitrates.

Of the four remaining glycol dinitrates, only 1,2-propylene glycol dinitrate is used to any extent in Army munitions production. This compound is used as a component of Otto II torpedo fuel produced at Radford AAP. Historical use of 1,2-propylene glycol dinitrate is ~137,000 lb/year. However there is no current or anticipated near future production of Otto II fuel.

In contrast, the civilian community produces glycol dinitrate for use in dynamite as a freezing point depressant. The quantities of ethylene glycol dinitrate produced in the U.S. each year is estimated at ~10 million lb.

The glycol dinitrates are moderately toxic by all routes of administration. Humans exhibit adverse responses such as headache, visual and balance impairment at concentrations as low as 0.1 - 0.2 ppm in air. The environmental fates of these compounds have not been studied. However, hydrolysis and photochemical decomposition are expected to be the major environmental reactions.

In spite of the effects of the glycol dinitrates on humans, a Phase II study of these compounds by the Army should be a low priority unless Otto II fuel production is resumed in high volume.

Toluidine Red Toner

Toluidine red toner is an azonaphthol derivative used as a red colorant. In the civilian community, the main use of this pigment is in paints for industrial and agricultural equipment. The Army uses toluidine red toner in igniter mixes formulated at Lake City AAP. Toluidine red toner is a minor constituent of these mixes and is used as a colorant. Only 75 lb/year of toluidine red toner are currently used by the Army at Lake City AAP. Under full mobilization schedules this usage would increase to 400 lb/year.

Only one study was found on the toxicological hazards of toluidine red toner. In this subacute study, no effects were observed with rats fed doses up to 2% of their diet. However, other closely related compounds are proven carcinogens in animals.

Based on the limited use of toluidine red toner, any further Army sponsored studies on this compound should be a low priority.

Strontium Oxalate

Strontium oxalate is used as a constituent of R-256 tracer mix formulated at Lake City AAP. At current production levels, Lake City AAP uses ~700 lb of strontium oxalate per year. This quantity represents ~10% of the current civilian production which is ~7000 lb/year. However, under full mobilization conditions, Lake City AAP would require 30,000 lb of strontium oxalate per year in order to meet production schedules. Thus under full mobilization schedules, all the strontium oxalate manufactured in the U.S. would be used in Army munitions production. The only civilian use of strontium oxalate is in radiator cleaners.

No toxicological or environmental hazards data specifically for strontium oxalate were found in the literature search. Information on other strontium salts indicates that they generally have a low toxicity to mammals and aquatic organisms. However, strontium salts are toxic to plants if sufficient calcium is not available.

In view of the high Army use of strontium oxalate and other strontium compounds at full mobilization and the limited information found on the toxicological and environmental hazards of strontium oxalate, a Phase II study is recommended. This study should include all strontium salts used in Army munitions production and the interaction of these salts with other metals in the environment.

Dechlorane

Dechlorane is an organochlorine compound which has been used as a pesticide and a flame retardant for plastics. The use of dechlorane (or mirex as it is called when formulated into pesticides) as a pesticide has received widespread attention. This attention is due to the persistence and mobility of dechlorane in the environment and its bioconcentration and biomagnification through the food chain. In mammals, dechlorane has been shown to be teratogenic and there is appreciable evidence that it is also carcinogenic. Based on the toxicological and environmental hazards associated with dechlorane, EPA has restricted the use of this chemical in pesticide formulations. As a result of the litigations, Allied Chemical ceased manufacture of dechlorane and sold the patent rights to the Mississippi Authority. Thus this chemical is no longer manufactured in the U.S.

The Army's main use of dechlorane is tracer mixes manufactured at Lone Star AAP. Approximately 1500 lb/year are currently procured by Lone Star AAP from importers. At full mobilization, ~5000 lb of dechlorane per year would be required in munitions production. The dechlorane wastes from tracer mixes are currently ~4 lb/month. These wastes are placed in holding ponds. However, due to the mobility of dechlorane in the environment, these ponds could be a significant source of contamination by dechlorane.

Sufficient literature summaries on the toxicological and environmental properties of dechlorane already exist. The Army could reference these summaries in their evaluations. Therefore, a Phase II study is not recommended at this time.

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FOREWORD

This report details the results of a preliminary problem definition study on 16 munitions 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 criteria can be recommended. In order to determine the Army's responsibility for further work on these munitions 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.

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PRELIMINARY PROBLEM DEFINITION STUDY ON
MUNITIONS-RELATED CHEMICALS
OCTAHYDRO-1,3,5,7-TETRANITRO-1,3,5,7-
TETRAZOCINE (HMX)

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SUMMARY

Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) is a nitramine explosive produced exclusively by Holston AAP in Kingsport, Tenn. HMX is compounded into plastic bonded explosives and other explosive formulations at Holston AAP. Approximately 28% of the HMX produced at Holston AAP is sold to civilian rocket manufacturers. These manufacturers produce solid rocket motors which use HMX in the propellant formulations. The civilian manufacturers sell most of the rocket motors they produce to the U.S. Government. Thus, HMX is a military unique compound.

The toxicity of HMX in various solvents has been studied. HMX does not penetrate the skin to any significant extent even when dissolved in DMSO. The LD50 for intravenous administration of HMX in DMSO to guinea pigs is 28.8 mg/kg.

The toxicity of HMX to aquatic life is low. The most sensitive species tested was the 7-days post hatched fathead minnows with a 96-hr LC50 of 15 ppm. Although several studies have been or are being conducted on the environmental fate of RDX, only limited information on HMX is available.

In view of the military uniqueness of HMX, a Phase II detailed toxicological and environmental study should be undertaken. Further experimental studies may be warranted if a Phase II study reveals gaps in the available information.

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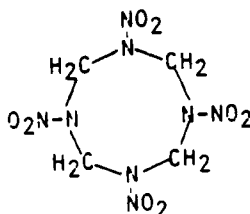
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OCTAHYDRO-1,3,5,7-TETRANITRO-1,3,5,7-
TETRAZOCINE (HMX)

A. Alternate Names

HMX is a symmetrically N-nitro substituted tetrazine with a molecular formula of $C_4H_8N_8O_8$ and corresponding molecular weight of 296.2. It has the following structural formula:



Other pertinent alternate names for HMX are listed below:

Military Specification:	Mil-H-4544
CAS Registry No.:	2691-41-0
CA Name (9 CI):	1,3,5,7-tetrazocine, octahydro- 1,3,5,7-tetranitro-
Synonyms:	cyclotetramethylenetetranitramine; C-HMX; octogen; 1,3,5,7-tetranitro- 1,3,5,7-tetrazacyclooctane; tetramethylene tetranitromine; 1,3,5,7-tetraza-1,3,5,7-tetranitro- cyclooctane; oktogen.

B. Physical Properties

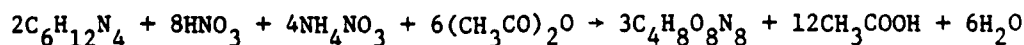
The physical properties of HMX are listed in Table I-1. The ultraviolet and mass spectra of this compound are presented in Figures I-1 and I-2. The vapor pressure of HMX as a function of temperature is shown in Figure I-3.

C. Chemical Properties

1. General Reactions

HMX has been synthesized by various modifications (Epstein and Winkler, 1952; Picard, 1967) of the Bachmann reaction (Bachmann and Sheehan, 1949). The production of HMX is maximized by using the following ratio of materials:

HMX



Hexamine	Nitric	Ammonium	Acetic	HMX	Acetic Acid
	Acid	Nitrate	Anhydride		

Table I-1. Physical Properties of HMX.*

Physical form @ 20°C:	crystalline
Color:	white
M.P.:	285-287°C
Vapor Pressure:	3×10^{-9} mm Hg @ 100°C
Density:	1.900 g/cm ³
ΔH_f°	+17.93 kcal/g
$\Delta H_{\text{detonation}}$:	1.48 kcal/g @ 25°C
C_p :	0.265 cal/g °C @ 20°C
Coefficient of Thermal Expansion:	22×10^{-6} in/in °F from -65 to 165°F
Thermal Stability:	0.07 cm ³ gas evolved from 1 g HMX @ 120°C for 48 hours.

Detonation Properties

Speed (D)	9.11 mm/μsec
Pressure (P_{cv})	387 kbar

Crystal Data

	I. Monoclinic P2 ₁ /c	II. Orthorhombic F dd2	III. Monoclinic Pc, P2/c	IV. Hexagonal P6 ₃ /22
a	6.54	15.14	10.95	7.66
b	11.05	23.89	7.93	
c	8.70	5.91	14.61	32.49

Molecular Refraction

R_{cal}	58	58	58	58
R_{obs}	56.1	55.7	55.4	55.9

Solubility

Water (mg/l)	1.14 @ 5°C	4.42 @ 10°C
	11.56 @ 30°C	6.63 @ 20°C
	17.43 @ 35°C	140 @ 83°C
	Solubility = $4.04355 + 1.42502T - 0.0727T^2 + 0.00142T^3$	

Table I-1. (continued)

Solubility (continued)

2% acetone/water (mg/l)	Solubility = $-1.54 + 0.70007T - 0.00005T^2 + 0.00031T^3$
Acetone	2.2 g/100 ml @ 30°C
Cyclohexanone	5.3 g/100 ml @ 30°C
Acetic anhydride	1.3 g/100 ml @ 30°C
DMSO	soluble
Hot 70% HNO ₃	soluble
DMF	slightly soluble
Pyridine	slightly soluble

X-Ray Diffraction Data

6.01 m	3.26 m	2.12 f-	1.66 vf
5.52 m	3.02 m	2.08 f-	1.61 vf
4.85 f	2.79 vs	2.00 f	1.57 vf
4.31 vs	2.68 vf	1.99 vv+	1.54 vf
4.05 vf-	2.53 f-	1.86 f-	1.52 vf
3.86 s-	2.41 m-	1.80 f+	1.46 vv+
3.40 m	2.18 m-	1.70 vf	1.42 vvf-
1.39 vf	1.26 f	1.16 f-	1.06 vv+
1.34 vf-	1.20 f-	1.10 vvf-	1.01 vf
1.30 vvf	1.17 vvf	1.08 vv+	

v = very

f = faint

m = medium

s = strong

* Reference: Dobratz, 1974; Barkley, 1977; Sullivan *et al.* 1979

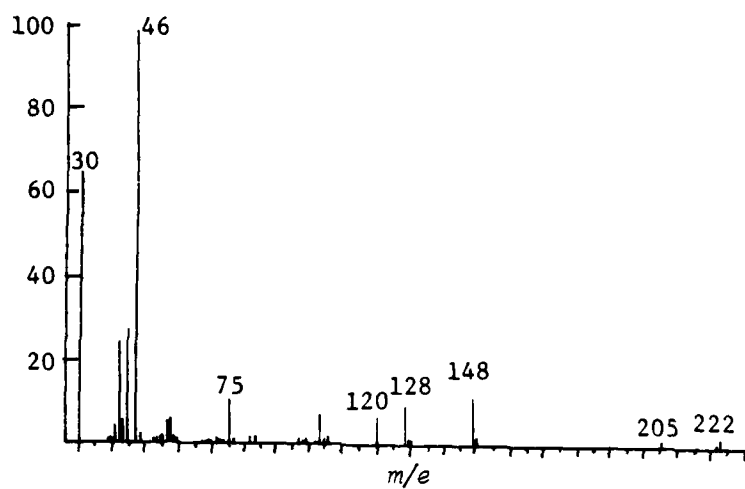


Figure I-1. Mass Spectrum of HMX
(Bulusu *et al.*, 1970)

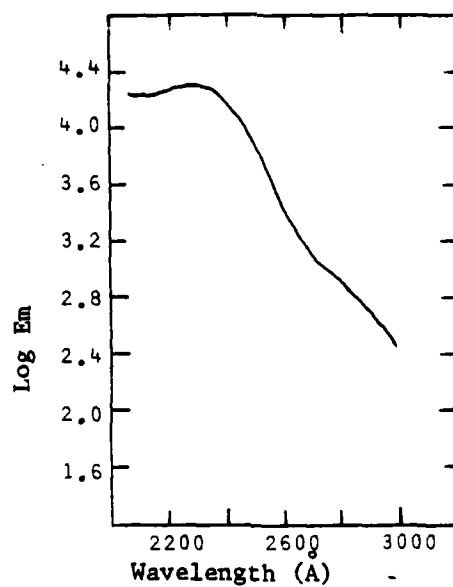


Figure I-2. Ultraviolet Spectrum of HMX in
Methanol (Jones and Thorn, 1949)

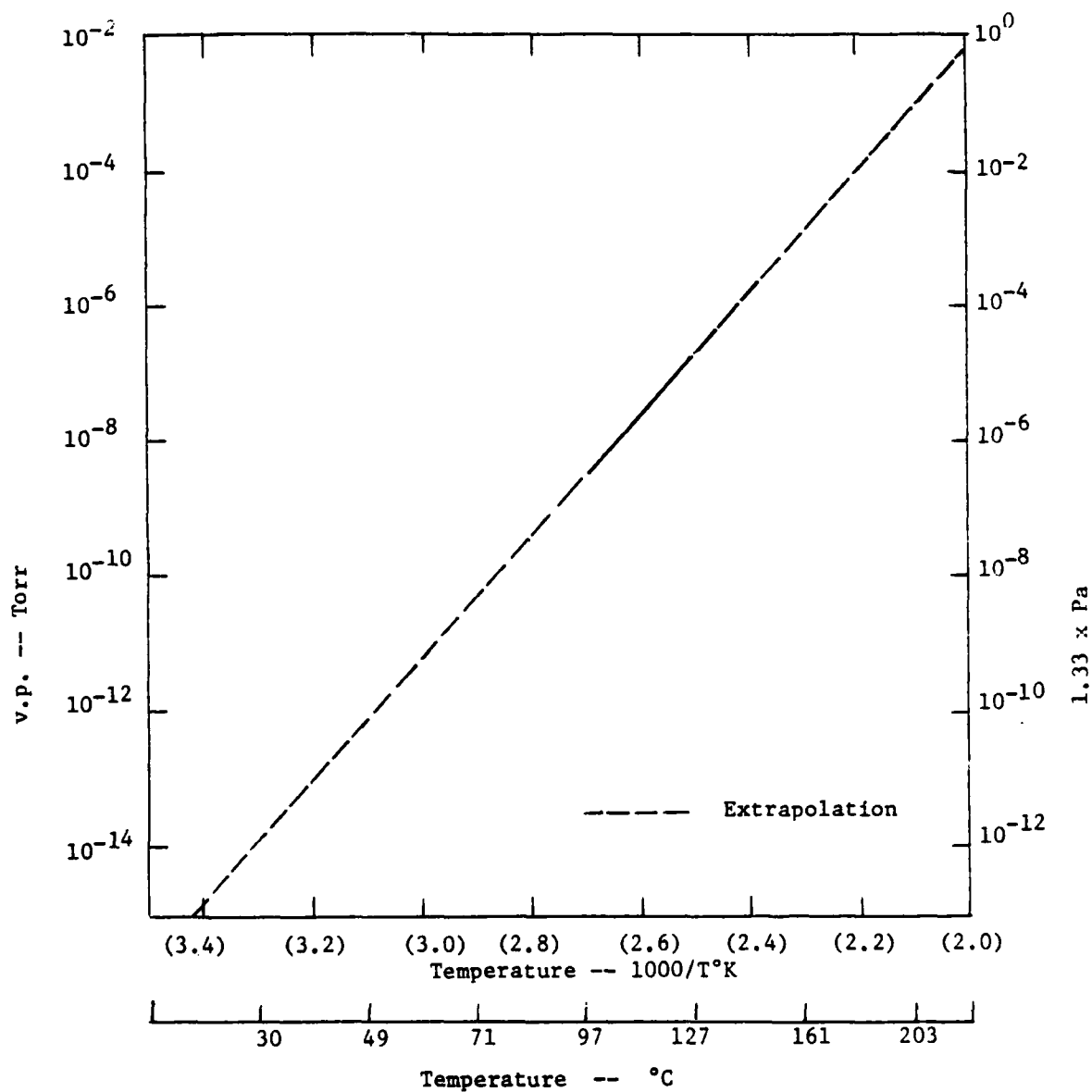
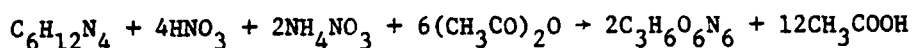


Figure I-3. Vapor Pressure of HMX as a Function of Temperature (Dobratz, 1974)

RDX, hexahydro-1,3,5-trinitro-1,3,5-triazine, is also manufactured by the Bachmann process. RDX production can be maximized by using the following materials ratio:

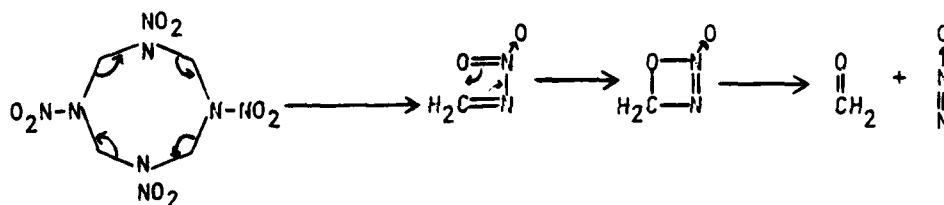
RDX



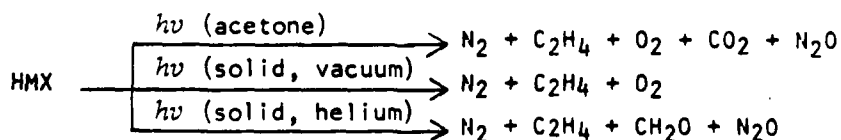
Hexamine	Nitric	Ammonium	Acetic		RDX	Acetic Acid
	Acid	Nitrate	Anhydride			

HMX is a by-product in RDX synthesis being present at concentrations up to 5% in the final RDX products. HMX can also be produced by treating SEX (another by-product of RDX preparation) with nitric acid (Aristoff *et al.*, 1949).

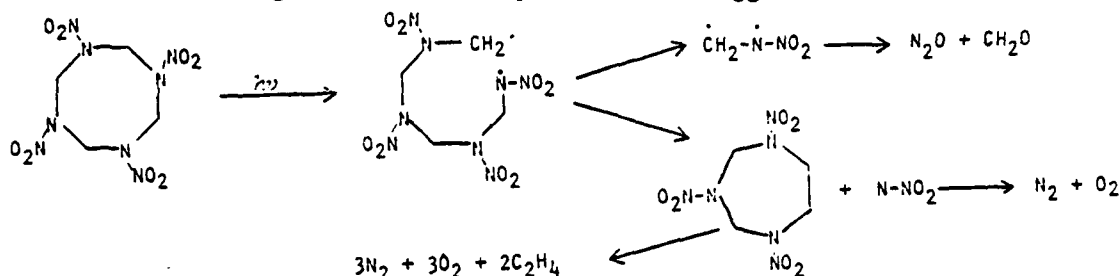
HMX is thermally unstable, decomposing to form predominantly nitrous oxide and formaldehyde. A mechanism for this reaction has been proposed by (Suryanarayana *et al.*, 1967; Suryanarayana *et al.*, 1968; Suryanarayana and Graybush, 1967):



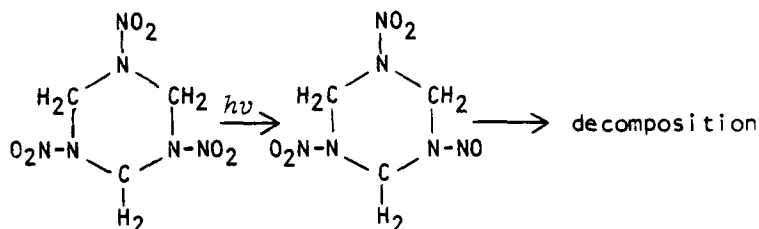
Other products such as N_2 , NO , HCN , CO and CO_2 were also observed but in less significant quantities. The mechanism of the thermal decomposition has been shown to be related to the electronic excited states of HMX. This conclusion is based on the observation that the $\beta - \delta$ phase transformation which precedes decomposition occurs at a lower temperature on exposure to light (Suryanarayana *et al.*, 1967). Thus, it is suggested that the photo-decomposition should parallel the thermal decomposition. More recent results have demonstrated that the photoproducts obtained are dependent upon the reaction conditions as described below (Torbit, 1970):



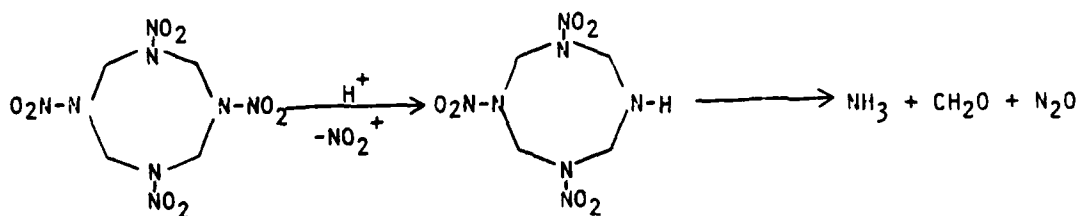
A mechanism leading to the various products was suggested:



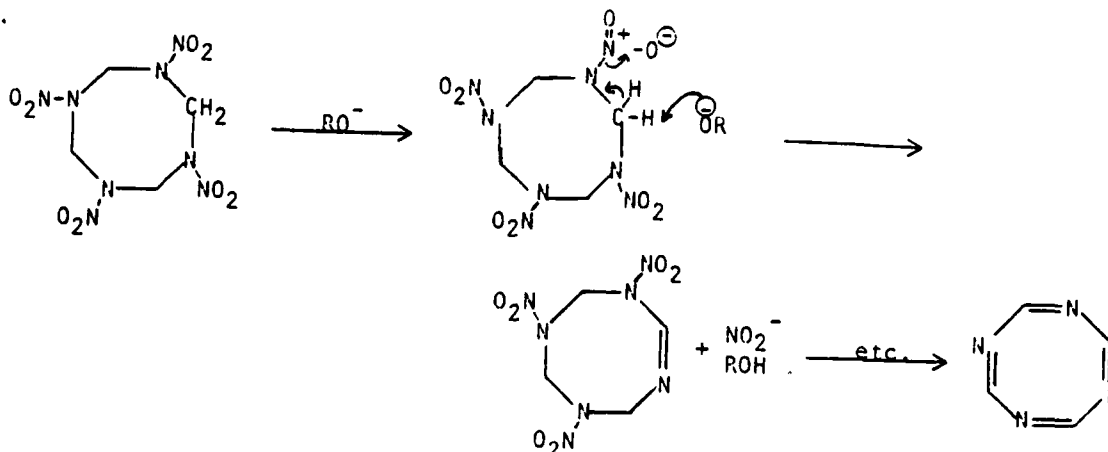
An N-nitroso intermediate has been detected in the photolytic decomposition of RDX suggesting the possibility of a similar intermediate for HMX (Sullivan *et al.*, 1979).



HMX is likely to be subject to electrophilic substitution and acid hydrolysis reactions similar to those reported for RDX (Simecek, 1957; Stals, 1969). In sulfuric acid, RDX is protonated with the expulsion of NO_2^+ and the subsequent decomposition to N_2O , NH_3 and CH_2O . The analogous reaction for HMX would lead to the same products:



Secondary nitramines are attacked by strong base resulting in elimination reactions; RDX, for example, reacts with alkoxides yielding triazines (Stals, 1969). This reaction has been shown to be initiated by extraction of a proton from the methylene carbon (Hoffsommer and Kubose, 1977). HMX should undergo an analogous reaction leading to tetrazocine.



Ring rupture follows conversion to the tetrazocine as heating in 5% NaOH results in complete decomposition of NH_3 , CH_2O , NO_2^- and NO_3^- (Sullivan *et al.*, 1979). HMX is also destroyed by chemical oxidation with potassium dichromate, potassium permanganate or calcium hypochlorite (Sullivan *et al.*, 1979). Ozone alone is not effective for oxidation of HMX, however UV-ozonolysis results in decomposition (Jain, 1976).

2. Environmental Reactions

Sullivan *et al.* (1979) conducted studies on the hydrolysis of HMX. They found that hydrolysis does not appear to be an important factor in the degradation of HMX. Only 12% hydrolysis was found after 112 days exposure to sea water and less than 10% after 12 days exposure to tap water (Sullivan *et al.*, 1979).

3. Sampling and Analysis

Analysis of HMX in environmental and explosive samples has been accomplished by a variety of techniques including thin-layer chromatography (TLC), column chromatography, volumetric analysis, gravimetric analysis, polarography, high performance liquid chromatography (HPLC). For accurate analysis with any of these methods, samples should be collected in amber bottles with Teflon lined stoppers to prevent degradation of the HMX by photolysis. The sample bottles should be stored at $4^\circ C$ until analysis. For many analysis methods concentration of the sample may be necessary. Two techniques have been used to concentrate HMX for analysis:

- vacuum evaporation at $40-50^\circ C$ and extraction of the residue into acetone (Jain, 1976)
- direct extraction with 15% acetonitrile in methyl chloride (Hash *et al.*, 1977)

HMX in RDX has been determined by semiquantitative column chromatography (Malmberg *et al.*, 1953). Silicic acid/Celite 533 (2:1) was employed as a solid support. Nitromethane in benzene was found to be the most suitable mobile phase. Fractions were removed from the extruded columns by extraction with acetone-benzene (1:1). Recovery of HMX was less than 100%, however, the recovery was repeatable within 0.2 to 0.3%. Sensitivity of the method was 0.07 mg HMX.

Separation of nitramine mixtures has also been attempted by thin layer chromatography on Silica gel G plate (Bell and Dunstan, 1966). Solvents used to develop the chromatograms included benzene-nitromethane (2:1), chloroform-nitromethane (10:1), petroleum ether-acetone (1:2), and ether-acetone (10:1). The nitramines were applied to the plate in an acetone solvent (5 µl of 1% solution). Visualization of the plates was accomplished by spraying with a 1% diphenylamine in ethanol solution followed by UV irradiation. Sullivan *et al.* (1977) chromatographed HMX using ethyl acetate as the developer. Detection was accomplished by UV light (254 nm). The lower detection limit of this method was 1 ppm for water or sediment samples.

A variety of wet analysis methods for HMX have been reported. These methods include conversion of HMX to its 1:1 dimethylformamide complex and gravimetric determination of this complex. This method can detect as little as 3% of HMX in RDX with an error of -0.2 to -0.9% (Schubert *et al.*, 1966). HMX has also been determined colorimetrically. The nitramine was decomposed with sulfuric acid and the resulting nitrate ion formed was reacted with ferric to produce the colored $[\text{Fe}(\text{NO})]^{++}$. Detection was accomplished at 515 nm. Volumetric methods for HMX determination were reviewed by Sullivan *et al.* (1979). These methods are outlined in Table I-2.

Table I-2. Volumetric Methods for Analysis of HMX
(Sullivan *et al.*, 1979)

<u>Method</u>	<u>Solvent</u>	<u>Reagent</u>	<u>Titrant</u>	<u>Sensitivity</u>
Reduction	dimethylformamide	chromous chloride	ferric ammonium sulfate	± 0.02 mg
Hydrolysis	sulfuric acid		ferrous ammonium sulfate	± 2.0 mg
Acid-Base	methylisobutyl ketone-isonopropanol, 4:1		sodium methoxide	± 0.2 mg
Acid-Base	methyl isobutyl ketone		tetrabutyl ammonium hydroxide	± 0.2 mg
Acid-Base	dimethylformamide		sodium methoxide	± 0.4 mg

Single sweep polarography (Whitnack, 1976) has been used to detect HMX in water. The current was measured over a potential range from -0.1 to -0.8 volts. HMX has a unique peak at -0.58 volts. Detection limits for this method was 0.05 mg/l.

The most suitable method of quantitative analysis of HMX is high performance liquid chromatography (HPLC). Conditions for the analysis are listed in Table I-3.

D. Uses in Army Munitions Production.

1. Purposes

HMX is manufactured exclusively at the Holston Army Ammunition Plant (Holston AAP) located in Kingsport, Tennessee. HMX is used in a variety of explosive mixtures and in solid rocket propellants. The explosive formulations produced at Holston AAP which use HMX are listed below:

Table I-3. High Performance Liquid Chromatography of HMX

<u>Phase</u>	<u>Column</u>	<u>Solvent</u>	<u>Detector</u>	<u>Sensitivity of Reproducibility</u>	<u>References</u>
Reverse	Partisil 10-ODS	40% Methanol	UV @ 230 nm	~0.05 ppm	Stillwell <i>et al.</i> , 1977
Normal	Corasil II	35% Dioxane/cyclohexane	UV @ 243 nm	not specified	Doali and Juhász, 1974; Juhász and Doali, 1973
Normal	LiChrosorb Si60	Methanol, acetonitrile, chloroform, iso-octane 5/10/15/70	UV @ 245 nm	0.005 ppm (before extraction)	Holston Defense Corporation, 1979
Reverse	RP8 LiChrosorb	Methanol, acetonitrile, water (40:10:50)	not specified	not specified	Holston Defense Corporation, 1979
Normal	Perkin-Elmer Siliccon A	Acetonitrile, Chloroform, Hexane (10:54:36)	UV @ 250 nm	<0.5 ppm	Unpublished Results, Atlantic Research Laboratory
Reverse	ODS-HC-Sil-X-1	20% Methanol 80% Water	UV @ 230 nm	<0.1 ppm	Unpublished Results, Atlantic Research Laboratory
Normal	LiChrosorb Si60 or Microporasil	55% Cyclohexane 45% Dioxane	UV @ 254 nm	<.01%	Poyet <i>et al.</i> , 1976
Reverse	ETH on Zipax	10% Methanol 90% Water	UV @ 220 nm	<1 ppm	Barkley, 1977)

<u>Formulation</u>	<u>% HMX in Formulation</u>
HMX grade A	93
HMX grade B	98
CMX-1 or -2	92.2±0.5
HMX/KEL-F	95 ±0.4
LX-04-1	94.5±0.5
LX-14-0	95.5±0.5
Octol, Type I	75 ±2
Octol, Type II	70 ±2
PBX 9404	94 ±0.5
PBX 9501	95 ±0.5
PBXN-3	86 ±0.5
PBXN-6	95.5±0.5

No solid rocket propellants containing HMX are produced at the Army Ammunition Plants. HMX is sold to private industry for use in solid rocket propellants.

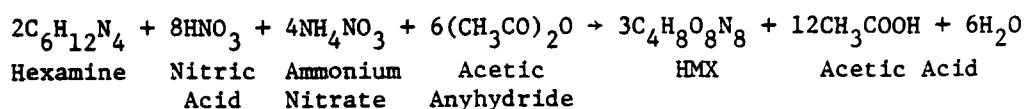
2. HMX Production Process Description

HMX and RDX are produced in the Area B Buildings at Holston AAP by the Bachmann process (Bachmann and Sheehan, 1949). In this process, hexamine is nitrated with ammonium nitrate/nitric acid mixture in an acetic acid/acetic anhydride solvent. The processing steps and the starting chemicals used in both HMX and RDX manufacture are the same. However, the proportions of materials differ as shown in Table I-4.

Table I-4. Reactants for HMX and RDX Manufacture Based on 100 lb Reactor Charge (Small and Rosenblatt, 1974).

<u>Reactant</u>	<u>Lb of Reactant for HMX Manufacture</u>	<u>Lb of Reactant for RDX Manufacture</u>
Ammonium nitrate	11.0	17.2
98% Nitric acid		13.6
Hexamine	17.0	9.2
Acetic acid	18.0	15.0
Acetic anhydride	54.0	45.0

The nominal stoichiometric reaction for the formation of HMX is:



Holston has ten HMX/RDX lines capable of producing 1.5×10^7 lb/yr HMX and 2.5×10^8 lb/yr RDX at full mobilization. Currently, Holston AAP is only operating at ~8% capacity (less than full capacity on one line). A process flow diagram of the HMX/RDX manufacture is presented in Figure I-4. This process involves six steps. These steps were described in detail in an earlier report (Kitchens *et al.*, 1978). Material balances on these processes have been attempted. For further information, the reader is referred to Heidelberg (1971).

3. Quantities Used

a. Historical Use

The historical production figures for explosives containing HMX are given in Table I-5. Data for the years 1967-1977 are included.

b. Use at Full Mobilization

A use summary of HMX in explosives production is given in Table I-6. Projected full mobilization usage estimates are also provided.

4. Documented or Speculated Losses to the Environment

a. Effluent Characterization

The surface runoff and cooling water from the Area B production facilities are discharged into ditches which lead directly to the Holston River. Process effluents from the HMX/RDX manufacture itself are discharged through catch basins into industrial sewer lines which empty directly into the Holston River or Arnett Branch. Holston Defense Corporation routinely monitors the industrial sewer effluents as well as the Area B water inlet and two stations on the Holston River downstream from Area B.

The locations of the sampling stations for Holston AAP Area B industrial effluents are shown in Figure I-5.

- Station B01A is located at the Area B pumping station and monitors the quality of the inlet water.
- Station B02B is located at Manhole No. 300 where the underground industrial sewer line emerges into an open ditch. This line carries process effluents from Buildings C through N on lines 6 and 7. The flow rate at this station was estimated to be between 0.5 and 1.5 MGD in 1976 and 1977 (Hash, 1978)

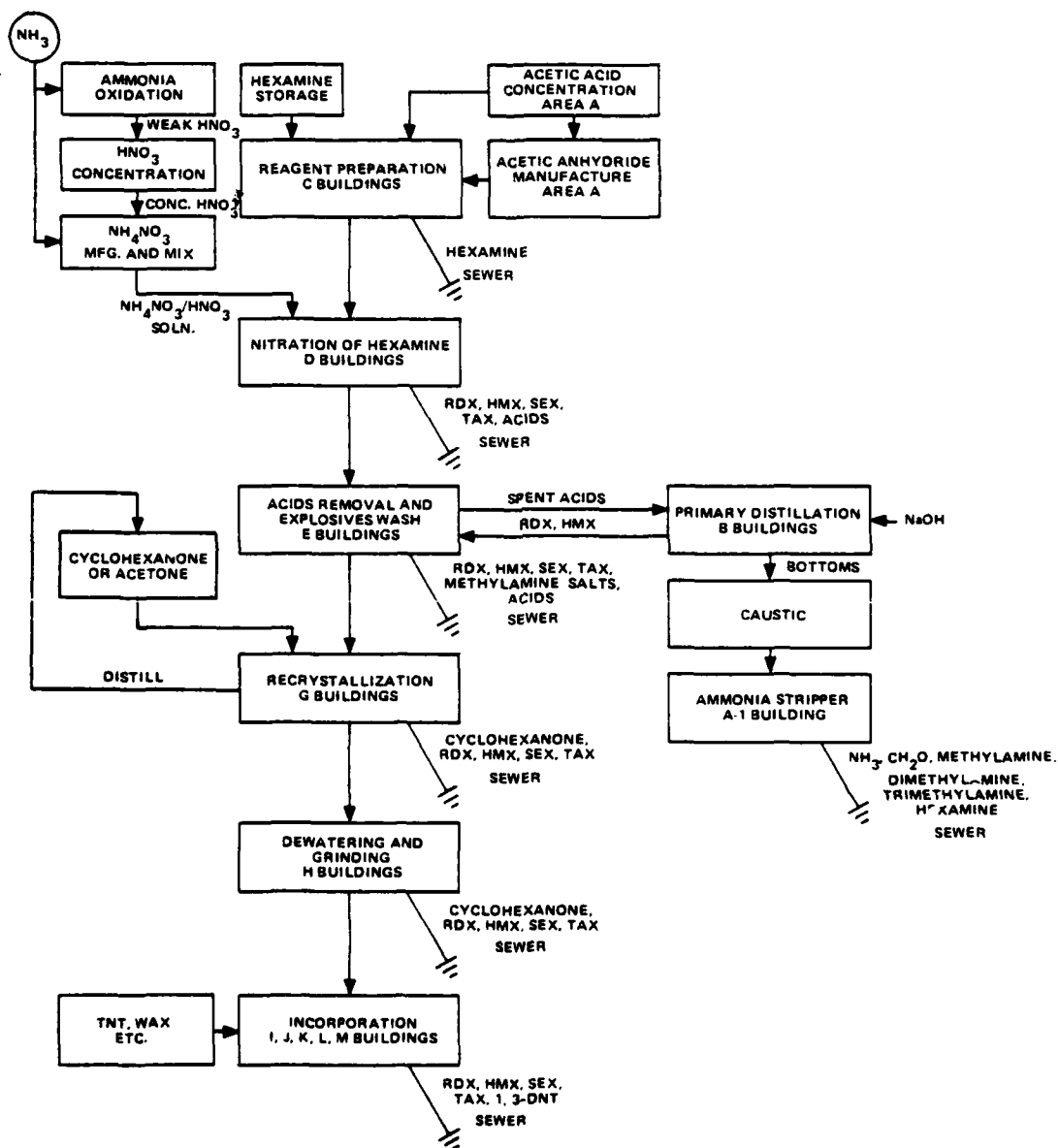


Figure I- 4. Flow Diagram of the RDX/HMX Manufacture at Holston AAP.

Table I-5. Historical Production of Explosives Containing HMX in 1000 lb.
(Holston Defense Corporation, 1978)

<u>Formulation</u>	<u>1967</u>	<u>1968</u>	<u>1969</u>	<u>1970</u>	<u>1971</u>	<u>1972</u>	<u>1973</u>	<u>1974</u>	<u>1975</u>	<u>1976</u>	<u>1977</u>
HMX, all classes	522	133	414	473	597	685	655	91	21	23	34
CXM-1	401	421	101	3	-	46	74	-	-	22	18
LX-04-1	52	-	-	11	10	125	83	131	78	-	-
PBX 9404	315	40	114	92	67	63	85	22	73	-	-
Misc. HMX's	40	22	620	70	128	516	276	787	857	1101	1906
Misc. PBX's	14	130	43	58	42	34	54	264	220	169	85



Figure I-5. Detailed Map of Area B, Holston AAP.

Table I-6. Use Summary and Projected Mobilization Use of HMX in Explosives in 1000 lb.
(Holston Defense Corporation, 1978)

Formulation	HMX Content, %	10 Year Total Production	10 Year Total HMX Used	10 Year High	10 Year Low	Production at Full Mobilization	HMX to Be Used
HMX Grade II	100	3648	3648	685	21	1908	1908
CXM-1	92	1086	999	42	0		
LX-04-1	95	490	417	131	0	240	204
PBX 9404	94	871	819	315	0		
Misc. HMX	~95	6323	6007	1906	22		
Misc. PBX	85-95	1113	946	264	14		

- Station B02A is located directly on the Holston River at the end of industrial sewer line No. 302. This line serves Buildings G through N on lines 1 through 5. Flow rates from sewer line No. 302 were estimated to be between 0.5 and 1.0 MGD in 1976 and 1977 (Hash, 1978).
- Station B03B is located on Arnott Branch. The industrial effluents from the C and D Buildings of lines 1 through 5, the B Buildings, the A-1 ammonia recovery still and the nitric acid facilities flow directly into Arnott Branch. The flow at the B03B station is ~20-22 MGD (Hash, 1978). This number represents a total combined flow rate of the process effluents and Arnott Branch. The upstream Branch flow is 12 MGD. Process effluent flow rate averages between 8 and 10 MGD.
- Station B01B is at Igloo Bridge on the Holston River downstream from the entry of Arnott Branch.
- Station B01C is at Churchill Bridge, downstream from Holston AAP Area B.

The flow of the Holston River varies considerably within a twenty-four hour period due to the intermittent releases from Ft. Patrick Henry Dam (Sullivan *et al.*, 1977). This intermittent variation in river flow condition influences the ability of the river to dilute Holston AAP Area B wastes. The capacity of the Holston River to dilute Holston AAP wastes may vary by a factor of 12 within a 2 hour period (Sullivan *et al.*, 1977). In addition to the flow variation, dye tracer studies have shown that the mixing of the North and South Forks is not complete until mile 137 (~1 mile downstream from Arnott Branch). Thus, the North and South Forks behave as two contiguous streams occupying the same river bed from the point of convergence to mile 137 (Sullivan *et al.*, 1977). The result is widely differing water qualities on the North and South banks of the River and relatively little dilution of Holston AAP Area B wastes for at least one mile downstream.

Many studies have been conducted to determine the various levels of discharges from Holston AAP and their effects on the Holston River (Sullivan *et al.*, 1977; Bender *et al.*, 1977; Patterson *et al.*, 1976; Huff *et al.*, 1975; USAEHA, 1972; USAEHA, 1971; Heidelberger, 1971). The reader is referred to the original documents for earlier sampling data. Analyses for 1976 and 1977 are presented in Table I-7.

Estimates of the amount of explosives and related compounds discharged from Holston AAP at production levels of 275 tons/day of Composition B have been made by Patterson *et al.* (1976). These estimated discharges are:

HMX	-	45.2 lb/day	0.164 lb/ton of product
RDX	-	124 lb/day	0.451 lb/ton of product

Table I-7. Water Quality Data Summary for Explosives (1976-1977)
Area B Holston AAP (Holston Defense Corporation, 1978)

	Sampling Point	1976		1977	
		HMX	RDX	HMX	RDX
Mean (mg/l)	B01A	0	0	0	0
S.D. (mg/l)		0	0	0	0
High (mg/l)		0	0	0	0
Low (mg/l)		0	0	0	0
No. of observations		5	5	9	9
Mean (mg/l)	B02A	4.6	7.4	2.9	3.0
S.D. (mg/l)		11.89	7.43	2.51	2.55
High (mg/l)		59.3	33.9	8.4	7.6
Low (mg/l)		0	0	0.9	0.6
No. of observations		25	25	9	9
Mean (mg/l)	B02B	2.6	5.5	1.4	1.3
S.D. (mg/l)		3.48	10.63	1.3	1.41
High (mg/l)		15.9	43.2	4.1	4.0
Low (mg/l)		0	0	0	0.1
No. of observations		25	25	9	9
Mean (mg/l)	B03B	0	0	0	0
S.D. (mg/l)		0.09	0.09	0	0.9
High (mg/l)		0.04	0.3	0.1	0.3
Low (mg/l)		0	0	0	0
No. of observations		25	25	9	9
Mean (mg/l)	B01B	0.2	0.0	0	0
S.D. (mg/l)		0.19	0	0	0
High (mg/l)		0.5	0.1	0	0
Low (mg/l)		0	0	0	0
No. of observations		8	8	9	9

From these numbers, discharges at full mobilization (~750 tons of product/day) can be estimated as follows:

HMX - ~123 lb/day
RDX - ~340 lb/day

b. Wastewater Treatment Facility

Plans are currently underway to build a biological treatment facility at Holston AAP. The site of the facility is shown in Figure I-5. A pipeline which will take the process effluents to the treatment facility is already under construction. The biotreatment facility will be capable of handling the 12.5 MGD of process effluents which would result during full mobilization (Hash *et al.*, 1977). However, from previous studies, it appears that a single biotreatment facility will not effectively remove HMX from the process streams. However, the tertiary carbon adsorption treatment should remove the HMX from the wastestream.

E. Uses in the Civilian Community

1. Production Methodology

HMX is produced by the Bachmann process (Bachmann and Sheehan, 1949). In this process, hexamine is nitrated with an ammonium nitrate/nitric acid mixture in an acetic acid/acetic anhydride solvent. The processing steps in HMX production are the same as for the manufacture of RDX, but the proportions of reactants differ.

2. Manufacturers, Production and Capacity

The only HMX producer in the United States is the Holston Army Ammunition Plant, operated by the Holston Defense Corporation, a subsidiary of Eastman Kodak. There are no civilian producers of HMX.

3. Usages

Civilian usage of HMX is limited to rocket propellants produced mainly by Hercules, Thiokol and Aerojet-General. During the 1967-1977 period, approximately 28% of the HMX produced by Holston AAP was sold to these companies for use in propellants. The average amount of HMX used in propellants over this period was about 360,000 lb/year.

4. Future Trends

Use of HMX in propellants dropped sharply in 1974 when production of Polaris and Poseidon missiles subsided. The average use rate during the 1974-1977 period was only about 42,000 lb/year compared to over 600,000 lb/year in preceding years. The lower use rate is expected to continue until

the Trident missile system becomes operational in the mid 1980's. The use rate will then increase to about 500,000 lb/year again.

5. Documented or Speculated Occurrences in the Environment

Losses to the environment from propellant manufacture are generally from 0.5 to 1.0% of the amount of materials handled. Thus, current HMX losses resulting from civilian manufacture of propellants are estimated to be about 17-35 lb/month; when Trident production commences, these losses may increase to 200-400 lb/month.

F. Comparison of Civilian and Military Uses and Pollution of HMX

The Army is the only manufacturer of HMX in the United States. Approximately 72% of the HMX produced is used by the Army in explosives. Civilian rocket manufacturers purchase the other 28% of the HMX. These manufacturers use HMX in solid propellant formulations for various missiles which are sold to the military. Thus, essentially all the end uses of HMX are in military applications. Therefore, HMX is a military unique compound. Environmental pollution of HMX results from the military manufacturing process and explosives loading, and civilian propellant formulations. However, the major source of entry of HMX into the environment is the manufacturing process at Holston AAP.

G. Toxicological and Environmental Hazards

1. Effects of HMX on Man

Only one occupational exposure study on HMX was reported in the literature (Hathaway and Buck, 1977). This study attempted to evaluate the effects of exposures of RDX on workers at an Army munitions plant. RDX concentrations measured were as high as 1.5 mg/m³ in the air. HMX was presumably also present in the air; however, levels were not measured. No difference in the number of abnormalities in the hematologic, hepatic or renal systems or the presence of autoimmune disease were found among these workers as compared to unexposed controls.

2. Toxicity of HMX to Mammals

a. Acute Toxicity

When administered by i.v. injection to guinea pigs, the LD50 of HMX in dimethylsulfoxide (DMSO) was found to be 28.2 mg/kg. Death occurred within 5 minutes after injection (McNamara *et al.*, 1974).

b. Subacute Toxicity

In subacute studies in which HMX in DMSO or acetone were applied topically to dogs, the doses used were 289.0 and 17.5 mg/kg, respectively. These doses were administered daily 5 days a week for 4 weeks. Results showed that no changes occurred in blood pressure, heart rate, or

respiratory rate during this exposure. All animals responded normally to the lid, corneal, and visual tests at all times (McNamara *et al.*, 1974). No toxic signs or deaths in rabbits, guinea pigs, or dogs were observed from a single or repeated topical application of HMX in acetone or in cyclohexanone.

After repeated 1.0 ml doses of 33% HMX in DMSO, 6 rabbits died; three died after the 2nd dose, one after the 5th dose, one after the 6th dose, and one after the 20th dose. After topical exposure to 33% HMX in DMSO, 5 of 12 guinea pigs died in 24 to 48 hours; 4 died after single doses of 405, 477, 507, and 546 mg/kg, and one after two doses of 1126 mg/kg (McNamara *et al.*, 1974).

Massive subacute toxicity studies were conducted to determine the effects of percutaneous application of HMX to dogs. HMX was applied, 480 mg HMX in DMSO/kg body weight, daily for 3 consecutive days. Results showed that this exposure produced no consistent gross noticeable changes in the animals. The animals were held for 2 weeks after exposure; all appeared normal.

c. Chronic Toxicity

The cutaneous or intradermal administration of HMX in the three solvents to guinea pigs 3 times a week for 6 weeks failed to produce any more cataracts in these animals than did the solvents alone (McNamara *et al.*, 1974).

d. Teratogenicity and Mutagenicity

No studies have been conducted to determine the teratogenic effects of HMX.

The Ames bacterial mutagenicity test was performed on the effluent from a pilot wastewater treatment facility (Stilwell *et al.*, 1977). Area A and B wastewaters were used in the test and mixed to a 1 to 9 ratio by volume to approximate actual discharge. To simulate higher production levels, acetic acid, cyclohexanone, acetone, n-butanol and hexamine were added to bring the COD value to 400 ppm. In addition, nitrates were added to levels of 150 ppm. The wastewaters analyzed before treatment had HMX and RDX levels ranging from approximately 0.1-5.0 ppm. The treated munition wastewater had HMX and RDX levels ranging from less than 0.05 to 0.7 ppm. A set of five *Salmonella typhimurium* strains, TA-1535, TA-1537, TA-1538, TA-98 and TA-100 were used in the mutagenicity testing. The histidine deficient variant strains were used to detect frame shift reverse mutations (TA-1537, 1538, and 98) or base pair substitutions (TA-1535 and 100). A dose response curve ranging from 5 ml to 100 ml of test water was used for each strain. An index of relative mutagenicity which was test reversions/control reversions was used. The value of 1.0 indicated no mutagenic activity with 10 clearly indicating mutagenic activity. The highest wastewater index was 2.07 and was attributed to chance variation.

e. Carcinogenicity

McNamara *et al.* (1974) carried out subacute percutaneous administrations of HMX in various solvents with rabbits. Administration of HMX was 5 days per week for 4 weeks. Pathological examination of sacrificed animals showed no tumors except at application site.

f. Behavior-Symptomology

The immediate symptom of high doses of HMX is cardiovascular depression or collapse depending on the dose. If the subject recovers from the cardiovascular depression, hyperactivity and convulsions occur. Increased sensitivities to light, vibratory and pain stimuli are also observed.

3. Aquatic Toxicity

The aquatic toxicity data presented in Table I-8 indicate that HMX has a low acute toxicity to fish and invertebrates. In a more detailed study on the acute effects of HMX on the life stages of fathead minnows, Bentley *et al.* (1977) found the 7-days post hatched fry to be the most sensitive. As shown in Table I-9, this lifestage had a 96-hr LC50 of 15 ppm.

HMX levels in the Holston AAP effluents and the Holston River were presented in Table I-7. These levels were measured when the Holston AAP was operating at ~10% capacity. Thus, under current product levels, HMX is not a toxic threat to aquatic organisms. However, the situation is further complicated by large fluctuations in water flow due to the Ft. Patrick Henry Dam. Thus, at low flow locally high levels of HMX could be a toxic threat to the aquatic organisms in the Holston River.

4. Toxicity to Microorganisms

No information is available in the literature on the toxicity of HMX to microorganisms. However, Holston AAP pilot plant effluents containing RDX, HMX, and presumably SEX and TAX were not mutagenic to the *Salmonella* strains in the Ames test (Stilwell *et al.*, 1977). (See Sections I, G, 2d).

5. Phytotoxicity

Bentley *et al.* (1977) tested the toxicity of HMX to four algae, *Microcystis aeruginosa*, *Anabaena flos-aquae*, *Selenastrum capricornutum* and *Navicula pelliculosa*. Cell density and chlorophyll *a* were used as criteria to determine the effects of HMX. HMX increased the number of cells/ml and chlorophyll *a* content over the controls.

Sullivan *et al.* (1979) found fault with the transformation procedure used by Bentley *et al.* (1977). Upon recalculation using a one-way analysis of variance (ANOVA), Sullivan *et al.* (1979) determined that HMX concentrations of 10 ppm produced a significant (95% level) increase in the growth of all the algae except *M. aeruginosa*.

Table I-8. Toxicity of HMX to Aquatic Organisms
(Bentley *et al.*, 1977)

Organisms	pH	Hardness (ppm as CaCO ₃)	Hours	LC50 ppm
<i>Daphnia magna</i> (water flea)	7.1	35	48	>32
<i>Gammarus fasciatus</i> (scud)	7.1	35	48	>32
<i>Asellus militaris</i> (sowbug)	7.1	35	48	>32
<i>Chironomus tentans</i> (midge)	7.1	35	48	>32
<i>Lepomis macrochirus</i> (bluegill)	7.1	35	96	>32
<i>Salmo gairdneri</i> (rainbow trout)	7.1	35	96	>32
<i>Ictalurus punctatus</i> (channel catfish)	7.1	35	96	>32
<i>Pimephales promelas</i> (fathead minnow)	7.1	35	96	>32

Table I-9. Toxicity of HMX to Selected Life Stages of the
Fathead Minnow (*Pimephales promelas*)
(Bentley *et al.*, 1977)

Life Stage	LC50 (mg/l)			
	24-hour	48-hour	96-hour	144-hour
eggs	>32	>32	>32	>32
1-hour post hatch	>32	>32	>32	-
7-days post hatch	>32	25 (7.6-8.1)	15 (8.8-26)*	-
30-days post hatch	>32	>32	>32	-
60-days post hatch	>32	>32	>32	-

*95% confidence interval

6. Environmental Fate of HMX

As discussed in the environmental chemistry section, hydrolysis is not expected to play an important role in the environmental fate of HMX. Photochemical decomposition could occur, however, photochemical reactions in the Holston River are not expected to be important. Preliminary evidence indicates that HMX is slowly biodegraded. Pilot studies using an activated sludge reactor (mainly *Pseudomonas* spp. and *Alcaligenes* spp.) showed a 55% HMX reduction (Green, 1972). The biological degradation of RDX is currently being evaluated by Sikka *et al.* (1978) and by Kaplan (1979). Sikka *et al.* (1978) are studying the aerobic degradation of RDX in Holston River water samples. Kaplan is studying anaerobic digestion. No studies on the biodegradability of HMX are in progress.

7. Availability of Literature for Phase II

Only limited studies on the toxicity and environmental hazards of HMX are reported in the literature. Therefore, the majority of material for a Phase II study would have to be obtained through personal contacts with manufacturers and researchers.

H. Regulations and Standards

There are no industrial hygiene standards for HMX. HMX is not listed in EPA's *Candidate List of Chemical Substances* (1977).

HMX is a Class A explosive and must bear the label, Explosive A, when shipped.

I. Conclusions and Recommendations

HMX is an explosive used in various plastic bonded formulations and in solid rocket motors. HMX is produced only at Holston AAP in Kingsport, Tenn. Explosive formulations are also made at Holston AAP. Approximately 28% of the HMX produced at Holston AAP is sold to the civilian industry for formulation into solid rocket motors. These motors are usually sold back to the U.S. Government. The main source of pollution of HMX is the production process at Holston AAP. Thus HMX is a military unique chemical.

The toxicity of HMX in various solvents has been studied. The LD50 for i.v. injection in guinea pigs is 28.2 mg/kg. HMX has a low acute toxicity to aquatic organisms. The fate of HMX in the aquatic environment is not well understood.

Based on the military uniqueness of HMX and the high localized pollution in the Kingsport, Tenn. area, it is recommended that a Phase II detailed evaluation of the toxicological and environmental literature be undertaken. If sufficient information is not available from the literature, additional toxicological and/or environmental studies may be warranted.

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PRELIMINARY PROBLEM DEFINITION STUDY ON
MUNITIONS-RELATED CHEMICALS
TRIAMINOTRINITROBENZENE (TATB)

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SUMMARY

Triaminotrinitrobenzene (TATB) is a thermally stable, relatively impact insensitive explosive. Because of these properties, TATB is expected to find increased uses in both the civilian and military communities. It is currently being manufactured in a pilot plant by Mason and Hangar and compounded into plastic bonded explosives at Holston AAP. This compounding process is probably the major source of entry of TATB into the environment.

TATB has a low toxicity to mammals (g/kg). No aquatic or environmental data on TATB were found in the literature.

In view of the expected increase in use of TATB, it is recommended that TATB be included in a Phase II study.

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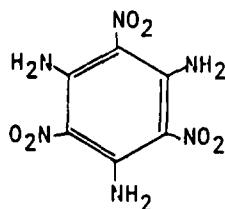
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II. TRIAMINOTRINITROBENZENE (TATB)

A. Alternate Names

Triaminotrinitrobenzene (TATB) is a fully substituted cyclic aromatic with a molecular formula of $C_6H_3N_6O_6$ and corresponding molecular weight of 258.15. Its structural formula is



Other pertinent alternate names are listed below:

CAS Registry No.:	3058-38-6
CA Name:	1,3,5-benzenetriamine, 2,4,6-trinitro-
Wiswesser Line Notation:	WNR CWN EWN BZ DZ FZ
Synonyms:	Sym-triaminotrinitrobenzene; 2,4,6-trinitro-1,3,5-benzenetriamine; 1,3,5-triamino-2,4,6-trinitrobenzene; TATB

B. Physical Properties

The physical properties of TATB are presented in Table II-1. The ultra-violet spectrum of TATB, presented in Figure II-1, is characteristic throughout a wide range of solvents. Absorption maxima occur between 270-280 and 350-360 nm.

Table II-1. Physical Properties of TATB*

Physical State @ 20°C :	crystals or powder
Color :	yellow
Melting Point:	300°C (Coffey, 1974) 450°C (Hallam, 1976)
Density :	1.938 g/cm ³
Heat of Combustion ΔH_c° :	-735.0 Kcal/mol
Heat of Formation ΔH_f° :	-36.9 Kcal/mol
Picatinny Impact Test :	2 Kg @ 85 cm
Heat of Sublimation :	40.2 Kcal/mol @ 426°K
Solubilities :	
Insoluble:	water, ethyl ether, ethyl acetate, ethanol, chloroform, carbon tetrachloride, carbon disulfide, benzene and acetone
Methanesulfonic acid :	820 ppm
DMSO:	70 ppm
Tetramethyl urea :	26 ppm
Pyridine :	12 ppm
Acetic acid :	1 ppm
Tetramethyl guanidine :	485 ppm
Tetrabutylammonium hydroxide :	390 ppm
N,N,N',N'-tetramethylglycinimide :	67 ppm

* Benzinger, 1977; Coffey, 1974; Hallam, 1976; Selig, 1977a; Yasuda, 1972; Dobratz, 1974

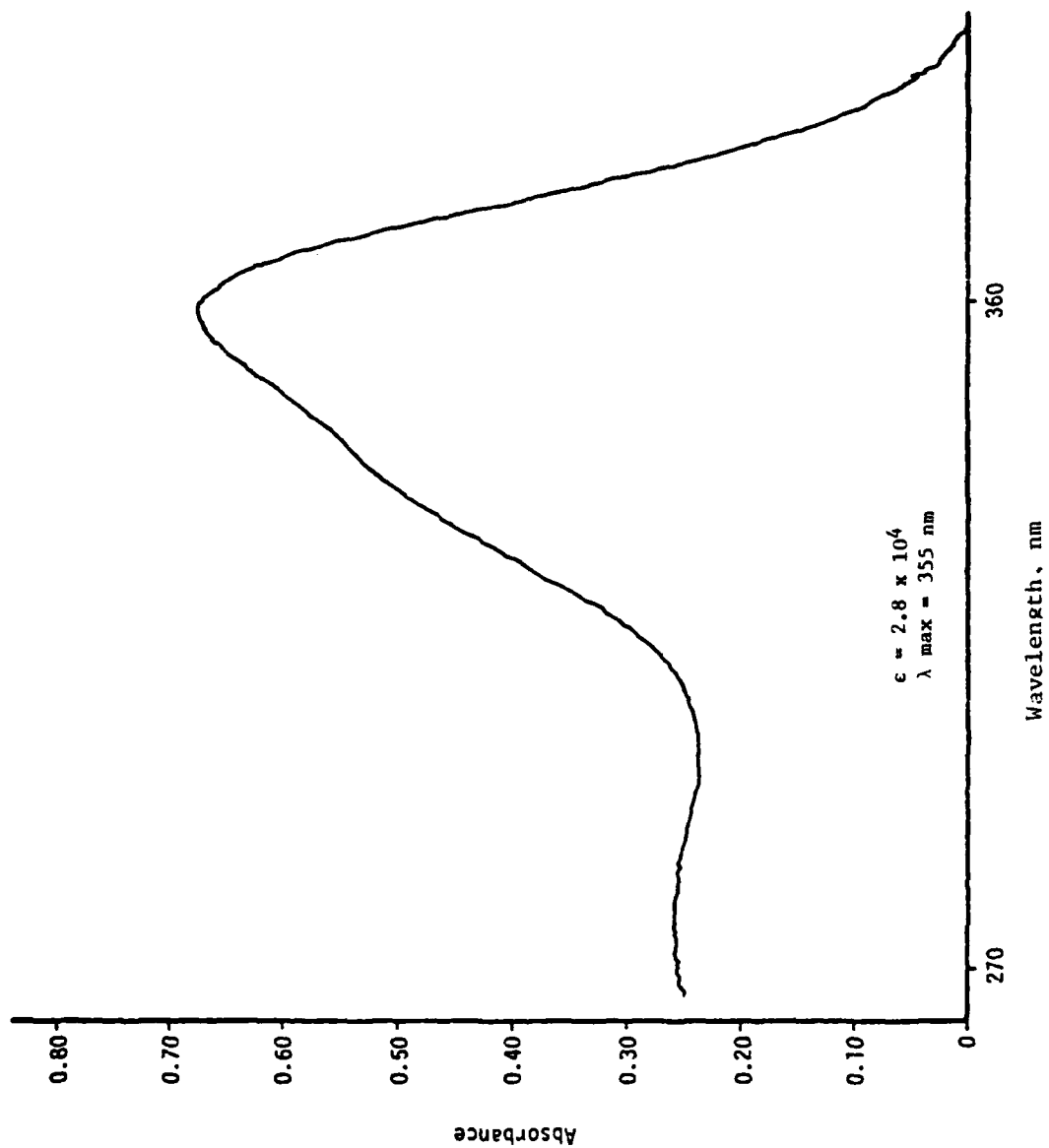
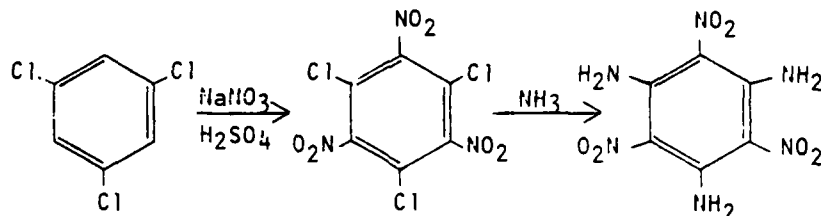


Figure II-1. Absorption Spectrum of TATB in DMSO (Saturated Solution) (Selig, 1977 a,b)

C. Chemical Properties

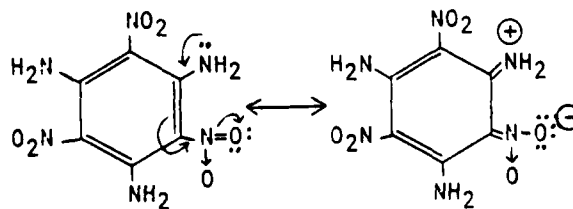
1. General Reactions

TATB is produced by the treatment of trichlorotrinitrobenzene (TCTNB) with ammonia in toluene. The TCTNB is in turn produced by nitration of 1,3,5-trichlorobenzene with sodium nitrate in sulphuric acid.

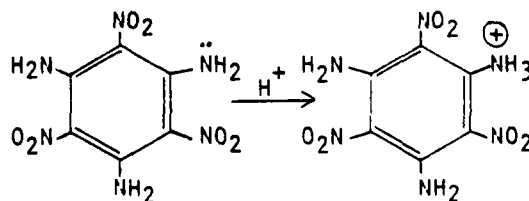


Numerous references to this process, and modifications thereof have appeared in the literature (Estes, 1977a; Evans, 1977; O'Keefe and Gurule, 1977; Kaplan and Taylor, 1959; Benzinger, 1977). Alternative synthetic routes involving nitration of 2,4-dinitro-1,3,5-trichlorobenzene (DNTCB) (O'Keefe and Gurule, 1977) and 2,4,6-trichloronitrosobenzene (Estes, 1977b) have also been discussed. The former was an unsuccessful attempt to reduce the amounts of the major impurities, DNTCB and dinitrotetrachlorobenzene. The latter demonstrated the feasibility of using trichloroaniline as a starting material rather than the more difficultly obtained TCB.

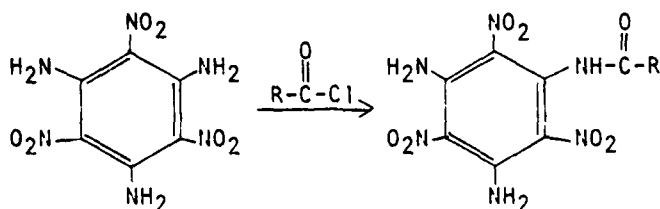
The reactions of TATB have not been reported. TATB is a very weak base. The basicity of the amino groups is significantly less than aniline or nitroaniline due to delocalization of electrons by nitro groups:



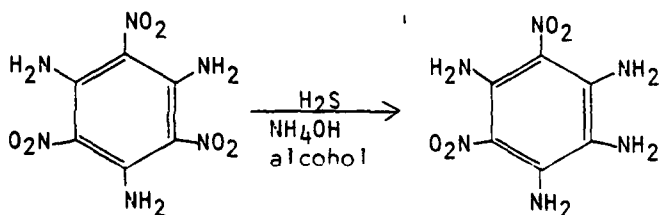
However, in strong acid, protonation is expected:



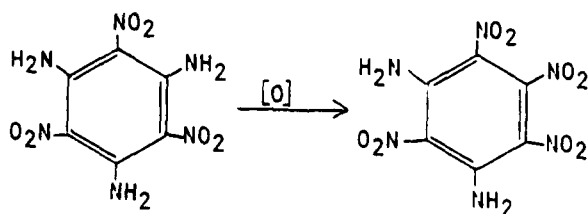
TATB would also be expected to form amides on treatment with acid chloride, although the steric interaction of the nitro groups may make this reaction extremely slow.



2,4-Dinitroaniline is easily reduced to 1,2-diamino-4 nitrobenzene (Streitwieser and Heathrock, 1976). TATB may undergo similar reductions at one or more nitro groups.



Oxidation of aromatic amines is also facile and can yield a variety of products including hydroxylamine, nitroso compounds, nitro compounds, phenols and quinones (Roberts and Caserio, 1964). Oxidation of TATB could lead to a variety of derivatives such as 1,3-diamino-2,4,5,6-tetranitrobenzene.



2. Environmental Reactions

The environmental chemistry of TATB has not been reported. Due to the thermodynamic instability of the molecule, it can be assumed that degradation due to oxidation and/or exposure to sunlight should be rapid. Due to the numerous possibilities existing, however, speculation as to specific products would be fruitless.

3. Sampling and Analysis

TATB has been analyzed by thin layer chromatography or Silica gel G-Zn dust utilizing 2-dimensional development with 1,2-dichloroethane and 11% acetone/petroleum ether (Yasuda, 1972). Photometric monitoring at 355 nm has also been employed to determine the solubility of TATB in various solvents (Selig, 1977a). Lowest reported detection was 1 ppm. The most useful technique would seem to be liquid chromatography. MacDougall (1977) developed a liquid chromatographic method for determining TATB. She used a Corasil II column and a mobile phase of DMSO. Ultraviolet detection at 350 nm was employed. Less than 0.3 μ g of TATB can be detected by this method.

D. Uses in Army Munitions

1. Purpose

TATB is used at Holston AAP in the production of explosive formulation PBX-9502. This formulation consists of $95\pm 0.3\%$ TATB and $5\pm 0.3\%$ Kel-F. PBX-9502 is a new formulation. Experimental batches were produced at Holston AAP starting in 1976. Production was initiated in 1978. The process used for production of PBX-9502 is shown in Figure II-2. In this process, a weighed quantity of TATB is charged to the charging tank with a measured amount of filtered water. The TATB/water slurry is agitated in the charging tank and transferred to the vacuum still with additional water. The slurry is heated in the vacuum still. Prepared lacquer (Kel-F 800 dissolved in ethyl acetate) is added to the heated slurry. The slurry is aged for 10 minutes. Granulation is accomplished by quenching the slurry with additional water through the charging tank. The slurry is aged for 1 hour. The solvent is distilled from the slurry at atmospheric pressure. After distillation, the material is cooled, transferred to a nutsche, dewatered and subsequently transferred to a drying building for drying and sampling (Holston Defense Corporation, 1976).

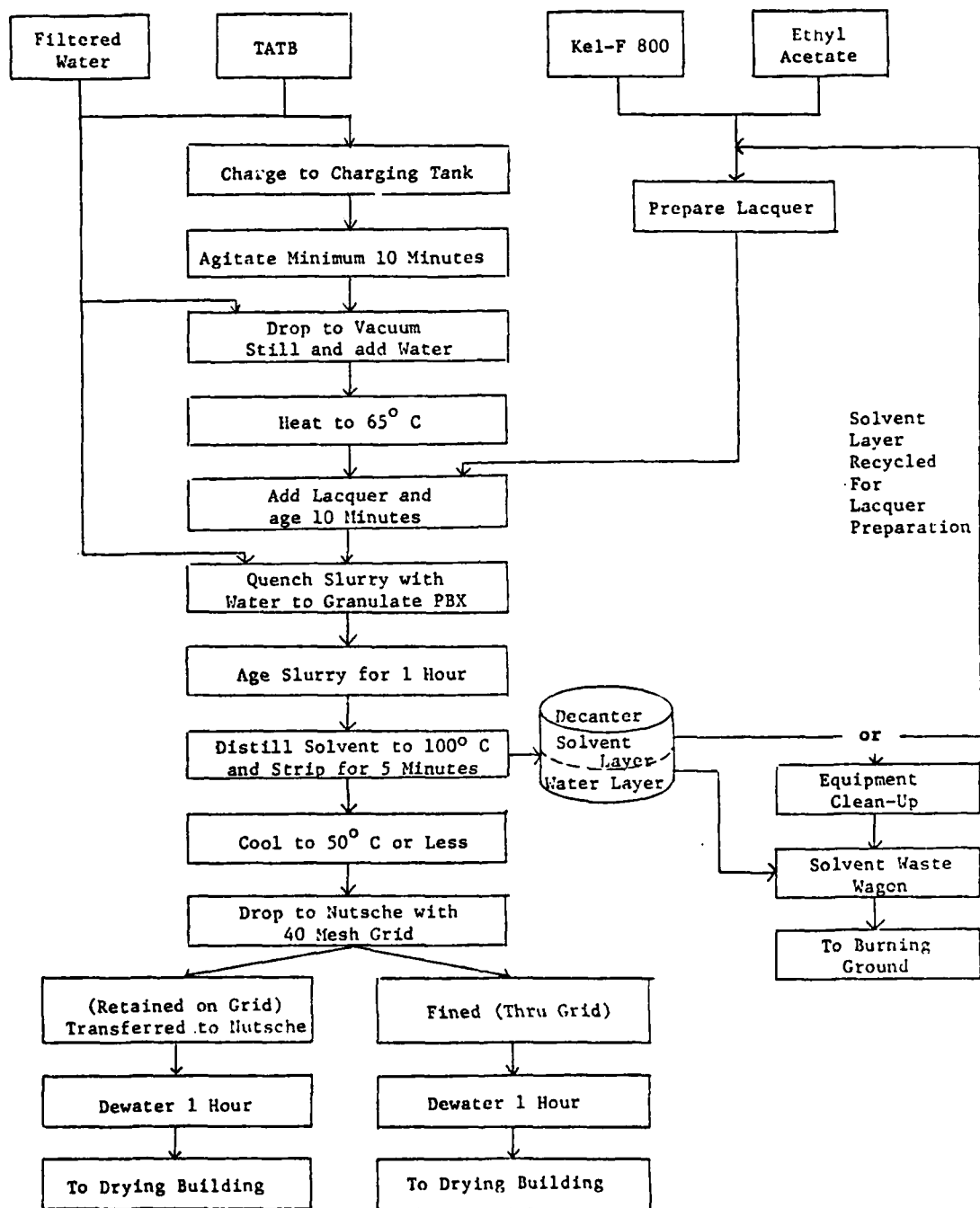


Figure II-2. Production of PBX-9502 at Holston AAP
(Holston Defense Corporation, 1976)

2. Quantities Used

Prior to 1978, only developmental quantities of TATB were used at Holston AAP. In 1978, production was initiated with 54,000 lb of TATB used to produce 60,000 lb of PBX-9502 explosive. Production of PBX-9502 is expected to increase in 1979. The total production level has not yet been determined. No PBX-9502 is called for in the mobilization schedule.

3. Documented or Speculated Occurrences in Air or Water

PBX-9502 is produced in Buildings G-5 and G-6 at Holston AAP. These buildings are used for formulation of special products. Losses of TATB from production of PBX-9502 in 1978 are estimated to be in the 540 - 1,080 lb/year range. These losses occurred during production of 3 batches of PBX-9502, therefore were not continuous. The maximum rate of loss is estimated to be 180 - 360 lb/month. In 1979, losses may increase to the level of 900 - 1,800 lb/year. The rate of loss will probably not exceed 180 - 360 lb/month. Losses in future years will probably equal or exceed the 1979 level.

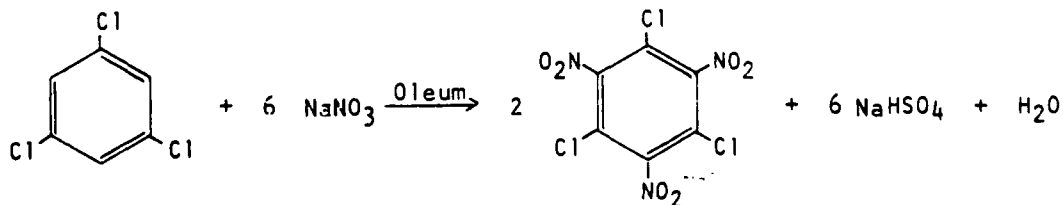
Currently, all Holston AAP Area wastes enter the Holston River with no treatment. However, a three-stage biological treatment facility is under construction which will treat future wastes in an anaerobic tower, trickling filter and with activated sludge. This facility is designed to handle 12.5 MGD of process effluents, the amount expected at full mobilization. It is expected that TATB will not be readily degraded in this treatment facility.

E. Uses in the Civilian Community

1. Production Methodology

Mason and Hanger have developed a pilot scale production process for the manufacture of TATB from trichlorobenzene. The development took place at the Pantex Plant Development Pilot Plant. The synthesis route, described below and shown schematically in Figure II-3 was based on work by Kaplan and Taylor (1959) and Benzinger (1977).

The Pantex Pilot Plant uses s-trichlorobenzene as the starting product (Quinlin *et al.*, 1976). Large excesses of raw materials are required. The efficiency of the process is determined partially by the required particle sizes. The process involves the nitration of trichlorobenzene with sodium nitrate or nitric acid.



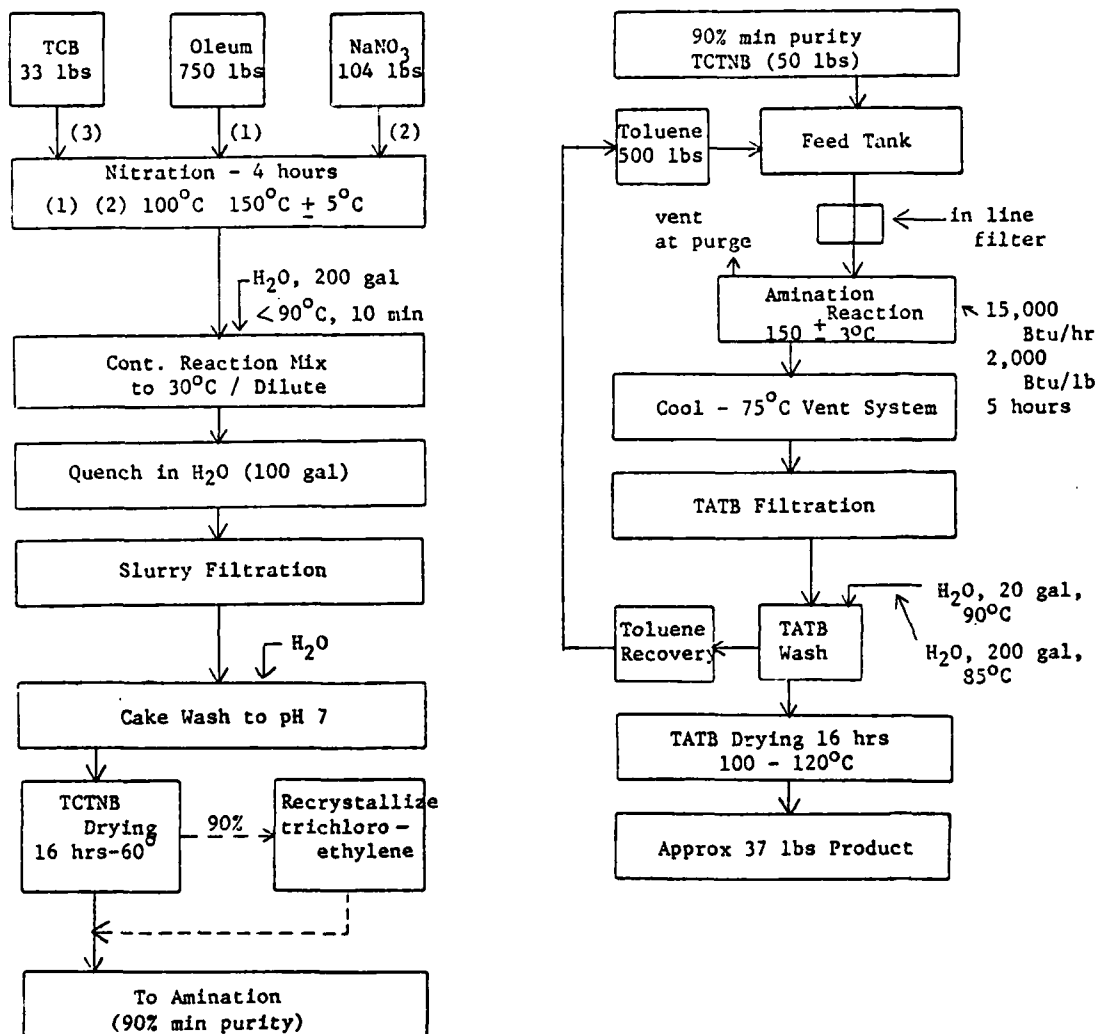
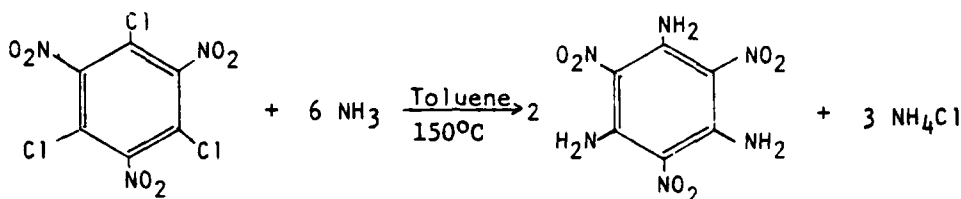


Figure II-3. Process Flow Sheet for the Manufacture of TATB
(Holston Defense Corporation, 1976)

Following nitration, amination is carried out with ammonia at 150°C and 35-40 psig:



Trichlorobenzene and trichloronitrobenzene are not available in large quantities due to environmental concerns; however, Eastman Chemical Company, Kingsport, Tenn., has indicated willingness to supply 1,3,5-trichloro-2-nitrosobenzene by conversion from their normal production of 2,4,5-trichloroaniline. 1,3,5-trichloro-2-nitrosobenzene can be oxidized to trichloronitrobenzene with fuming nitric acid. This product can then be used in place of TCB in the synthesis of TATB (Estes, 1977b).

2. Manufacturers, Production and Capacity

Mason and Hanger are the only U.S. producers of TATB. Their Pantex Pilot Plant is capable of producing 545 kg of TATB/month (Quinlin *et al.*, 1976).

3. Usages

TATB is produced exclusively for formulation into plastics bonded explosive, PBX-9502. This explosive is currently being put into production at Holston AAP. TATB explosives have been developed for their high thermal stability and insensitivity to initiation by impact and friction. Once in adequate supply, TATB explosives should find many uses in the civilian community.

4. Documented or Speculated Occurrences in the Environment

The amount of TATB lost to the environment during its production at the Pantex Pilot Plant is expected to be minor. The major pollutants from this process are expected to be nitric acid, ammonia, NO_x, ammonium nitrate, toluene, SO₂ and possibly some TCTNB.

F. Comparison of Military and Civilian Uses and Pollution

TATB is currently manufactured by one U.S. company on a pilot scale level. It is compounded at Holston AAP into PBX-9502. The PBX end product is expected to have a wide variety of civilian and military end uses. The major source of environmental pollution from TATB is the compounding process at Holston AAP. Some environmental pollution is also expected from the Pantex Pilot Plant. Thus although TATB is not a military unique chemical, it is a military problem chemical.

G. Toxicological and Environmental Hazards

1. Mammalian Toxicity

Jorgenson *et al.* (1976) studied the toxicological effects of TATB on mammals. They found that TATB was not toxic to rats or mice at levels of 5 g/kg. TATB was shown not to be a skin sensitizer in guinea pig sensitization studies. However, TATB did produce conjunctival and iris tissue irritation in unwashed rabbit eyes receiving 0.1 g of TATB.

The precursors of TATB, trichlorobenzene (TCB) and trichlorotri-nitrobenzene (TCTNB), were also tested by Jorgenson *et al.* (1976). TCTNB was relatively non-toxic, similar to TATB. TCB had an oral LD50 for rats of 1.8 - 2.8 g/kg. The oral LD50 of TCB for mice was between 3.35 - 3.40 g/kg.

2. Aquatic Toxicity

No information was found on the toxicity of TATB or related compounds to aquatic organisms.

3. Toxicity to Microorganisms

TATB was not mutagenic to five strains of *Salmonella typhimurium* and *Escherichia coli* NP2 when tested by the Ames Test (Jorgenson *et al.*, 1976). Mitotic recombination in the yeast, *Saccharomyces cerevisiae* D3 was not increased by TATB (Jorgenson *et al.*, 1976).

4. Phytotoxicity

No information on the phytotoxicity of TATB was found in the literature search.

5. Fate in the Environment

No information is available on the environmental fate of TATB. If released into the Holston River, it will be associated with the sediment due to its low water solubility. Due to its low lipid solubility, TATB will probably not bioaccumulate to any great extent. Microbial action on TATB will probably result in the formation of nitroso groups under both aerobic or anaerobic conditions.

6. Availability of Literature for Phase II

Only limited toxicological and environmental data on TATB are available in the literature. Further information will have to come from personal contacts with researchers and the manufacturer or by analogy to related compounds.

H. Regulations and Standards

There are no NIOSH or EPA regulations or standards specific for TATB. TATB is an explosive. DOT requires an Explosive A label for interstate shipment of this compound.

I. Conclusions and Recommendations

TATB is produced by Mason and Hangar and compounded into plastic explosives at Holston AAP. These explosives are expected to find a wide variety of uses in both the civilian and military communities when it becomes readily available. The compounding of TATB into PBX-9502 is expected to be the major source of entry of this compound into the environment. Thus, TATB is a military problem chemical. Therefore, a Phase II study on this compound is recommended.

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PRELIMINARY PROBLEM DEFINITION STUDY ON
MUNITIONS-RELATED CHEMICALS
TRIS(2-CHLOROETHYL)PHOSPHATE (CEF)

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SUMMARY

Tris(2-chloroethyl)phosphate (CEF) is a chloroorganic phosphate used as a fireproofing agent in urethane foam. This chemical is produced by Stauffer Chemical Co. Production in 1975 was 29.4 million lb. Of this amount, it is estimated that 0.4 million lb/year are lost to the environment. In contrast to the high civilian production and use of this flame retardant, the Army's use of CEF in munitions production is sporadic and relatively small (0-7200 lb/year). CEF is used by the Army at Holston AAP in the formulation of plastic bonded explosive PBX 9404. Pollution of CEF resulting from this use is estimated at 6-12 lb per month at the 7200 lb/year projected mobilization use rate.

CEF is toxic to mammals only when administered in high doses (g/kg). The Ames Test showed CEF to be non-mutagenic.

Due to the limited use of CEF in Army munitions production, it is recommended that further Army sponsored studies on the toxicological or environmental hazards of CEF should be a low priority.

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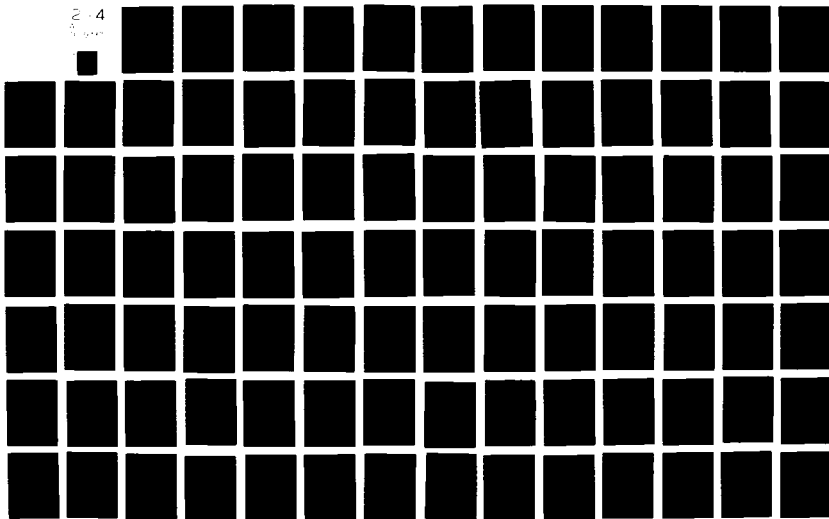
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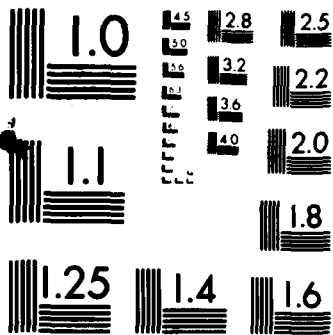
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5. Environmental Fate

No data are available on the environmental fate of CEF. Hydrolysis is expected to occur; however, this reaction should be slow.

6. Availability of Literature for Phase II

The literature on the toxicological and environmental hazards of CEF is very limited. Information for a Phase II detailed toxicological and environmental evaluation would have to come from current research and U.S. and foreign manufacturers' files.

H. Regulations and Standards

There are no current U.S. effluent guidelines or industrial hygiene standards for CEF. CEF is listed in EPA's "*Toxic Substances Control Act List of Candidate Chemical Substances*" (1977).

I. Conclusions and Recommendations

The goal of this problem definition study was to assess the Army's responsibility for conducting further studies on the toxicological and environmental hazards of CEF. CEF is widely used in the civilian community as a flame retardant in urethane foams. Civilian production of this chemical is ~29.4 million lb/year. Pollution from civilian sources is estimated at 0.4 million lb/year. In contrast to the large civilian usage of CEF, the Army uses CEF sporadically and in relatively small quantities (0-7200 lb/year). Losses of CEF from munitions production are estimated at only 6-12 lb/month at full mobilization. Thus, the use and pollution of CEF resulting from Army munitions production is negligible in comparison with civilian sources.

CEF is toxic to mammals in high doses (g/kg). Ames mutagenicity testing on CEF was negative.

In view of the limited Army usage and pollution of CEF, it is recommended that any further Army sponsored toxicological and environmental studies on this compound should be a low priority.

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**PRELIMINARY PROBLEM DEFINITION STUDY ON
MUNITIONS-RELATED CHEMICALS
BIS(2,2-DINITROPROPYL)ACETAL/FORMAL (BNDPA/F)**

SUMMARY

BDNPA/F is a 50/50 mixture of bis(2,2-dinitropropyl)acetal (BDNPA) and bis(2,2-dinitropropyl)formal (BDNPF). This mixture is used as a plasticizer in solid rocket propellants and in plastic bonded explosive formulation PBX-9501. Army use of BDNPA/F is limited to Holston AAP in Kingsport, Tenn. This use is small and sporadic (0-500 lb/year).

BDNPA/F is manufactured by Cordova Chemical Co. and the Navy for use in solid rocket propellant formulations containing polyurethane binders. However, there is no current production of BDNPA/F due to over supply.

Very little data on the toxicological or environmental hazards of BDNPA/F are available in the general literature. The only study found which pertains to the toxicological properties of this plasticizer was an acute oral study with rats. No effect was observed when rats were fed doses of 100 mg/kg.

Based on the low use of BDNPA/F in Army munitions production, it is recommended that any further Army sponsored studies on this plasticizer should be a low priority.

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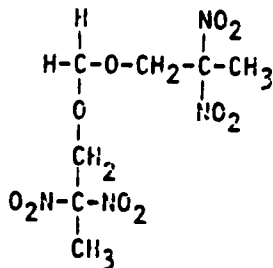
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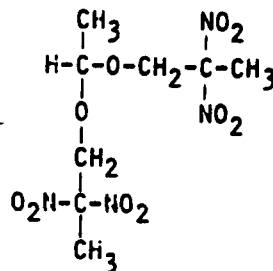
IV. BIS(2,2-DINITROPROPYL)ACETAL/FORMAL (BDNPA/F)

A. Alternate Names

BDNPA/F is an eutectic mixture of the acetals bis(2,2-dinitropropyl)acetal (BDNPA) and bis(2,2-dinitropropyl)formal (BDNPF) in a 50/50 weight ratio. The molecular weight of BDNPA is 326 and its formula is $C_8H_{14}N_4O_{10}$. BDNPF has the formula $C_7H_{12}N_4O_{10}$ and a molecular weight of 312. Their structures are:



BDNPF



BDNPA

Other names for BDNPA/F are listed below:

CAS Registry No.:	5917-61-3 - bis(2,2-dinitropropyl)formal 5108-69-0 - bis(2,2-dinitropropyl)acetal
CA Name (8CI):	Methane, bis(2,2-dinitropropoxy)-
CA Name (9CI):	Ethane, bis(2,2-dinitropropoxy)- Propane, 1,1'-(methylenebis(oxy))bis-(2,2-dinitro-) Propane, 1,1'-(ethylenebis(oxy))bis-(2,2-dinitro-)
Synonyms:	Bis(2,2-dinitropropyl)acetal/formal Bis(2,2-dinitropropyl)acetal-dehyde/formaldehyde Bis(dinitropropyl)acetal/formal

B. Physical Properties

The physical properties are listed in Table IV-1.

C. Chemical Properties

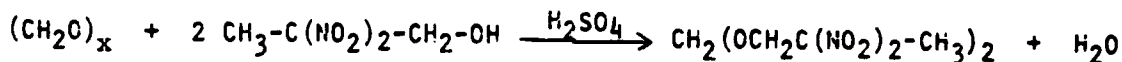
1. General Reactions

Bis-2,2-dinitropropylacetals of formaldehyde (BDNPF) and acetaldehyde (BDNPA) are stable acetals formed by the acid catalyzed reaction of 2,2-dinitropropanol and either paraformaldehyde (Shipp and Hill, 1966; Gold and Marcus, 1966

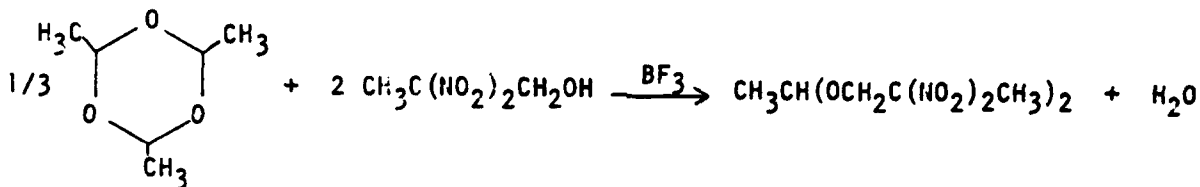
Table IV-1. Physical Properties of BDNPA/F*

Physical Form @ 20°C:	liquid
Color:	straw
Freezing Point:	below -5°C, has the tendency to supercool
Boiling Point:	150° @ 0.01 mmHg
Density:	1.383-1.397 g/cm ³
Refractive Index n_D^{25} :	1.462-1.474
Viscosity:-	20 cP @ 66°C 40 cP @ 54°C 65 cP @ 43°C 130 cP @ 32°C 260 cP @ 21°C 1135 cP @ 10°C
ΔH_f° (liquid):	BDNPF -45.72 Kcal/100g BDNPA -47.03 Kcal/100g
ΔH^{298} (fusion):	BDNPF 5.6 ± 1.2 Kcal/mole BDNPA 4.6 ± 0.6 Kcal/mole
Solubility:	insoluble in water sparingly soluble in aliphatic hydrocarbons soluble in benzene and toluene completely miscible with methanol, acetone, ethylacetate, methylene-chloride and ethylenechloride

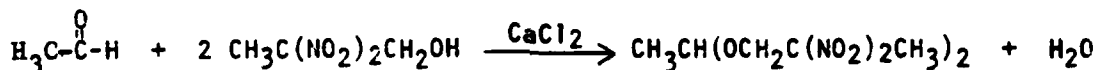
* Finger, 1972



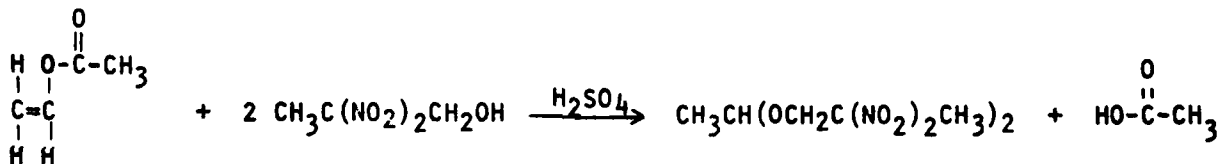
or paraldehyde (Maenosono *et al.*, 1966):



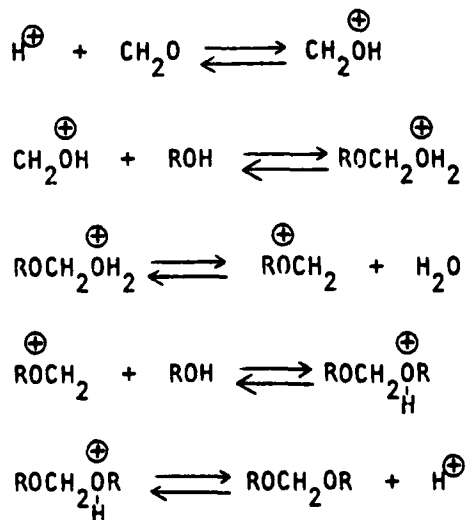
Alternatively, a dehydrating agent can be used in place of the acid catalyst (Gold and Marcus, 1966)



The acid catalyzed reaction of vinyl acetate and 2,2-dinitropropanol has also been used to prepare BDNPA (Marcus, 1963)

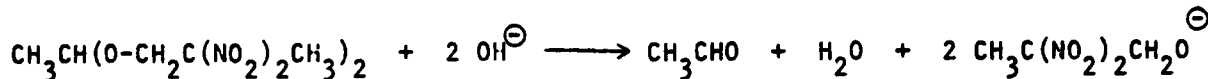


BDNPF and BDNPA exhibit a greater stability than most acetals due to the electron withdrawing nature of the nitro groups. The following equilibrium would be established for the formation of BDNPF or the reverse for the hydrolysis (Shipp and Hill, 1966)



where $\text{R} = \text{CH}_3\text{C}(\text{NO}_2)_2\text{CH}_2\text{-}$

The product acetal in this case is stable relative to its protonated analog due to the destabilizing influence of the nitro groups on the oxonium ion. Thus a more powerful acid medium is required for hydrolysis of nitro acetals than is necessary for the unnitrated analogs (Shipp and Hill, 1966). Although the acid hydrolysis is slow, one might expect base catalyzed hydrolysis to occur. However no literature references were found to confirm this reaction.



In this reaction, the ionic species would be stabilized by the nitro substituents.

2. Environmental Reactions

The environmental chemistry of BDNPA/F has not been reported. Hydrolysis to 2,2-dinitropropanol and the respective aldehydes is expected to be the major reaction despite the inhibition due to the nitro substitution.

3. Sampling and Analysis

The only reference to the analysis of BDNPA/F pertains to its extraction from explosive mixtures with chloroform (Selig, 1965) or with methyl-, ethyl- or isopropyl alcohol (Selig, 1969). The amount of BDNPA/F was determined by the weight loss of the explosive.

D. Use in Army Munitions

1. Purpose

BDNPA/F is used at Holston AAP as a binder in explosive formulation PBX 9501. This explosive consists of 2.75% BNDPA/F, 2.25% Estane 5703 F-1 and 95 ± 0.5% HMX.

PBX 9501 is produced in the special products formulation buildings, G-4 and G-6. The following process is used:

- a. The explosive component is slurried with water. If particle size control is desired, a surfactant such as gelatin or polyvinyl alcohol is added to the slurry.
- b. The binder, plasticizer and any other additives are dissolved in a water-immiscible solvent such as butyl acetate, ethyl acetate, isobutyl acetate, toluene or methyl ethyl ketone to form a lacquer.
- c. The lacquer is added to the slurry and mixed.
- d. The organic solvent is stripped off causing the explosive to form granules.

e. The granules are cooled and the water filtered off.

f. The explosive granules are dried and packed.

BDNPA/F was also used in the past to produce explosive formulation LX-09-1 at Holston AAP. This formulation is no longer in production, and no future requirements are anticipated.

2. Quantities Used

During 1978, Holston AAP used about 500 lb of BDNPA/F for production of 20,000 lb of PBX 9501 explosive. During the 1967-1977 period, total production of the 13 miscellaneous PBX's averaged 101,000 lb/year. The quantity of PBX 9501 produced was typically less than 5% of the total (Wright, 1979). Thus, the quantity of BDNPA/F used averaged only about 140 lb/year. PBX 9501 is not on the mobilization schedule and will probably be produced in very limited quantities, if any, in future years.

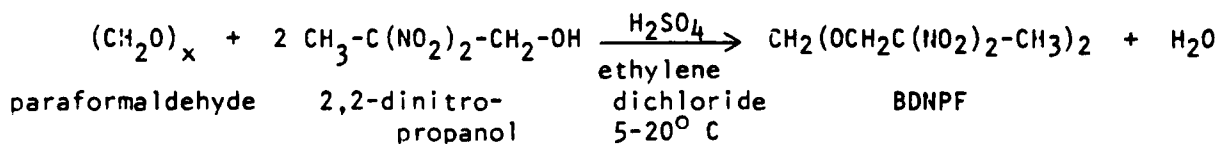
3. Documented or Speculated Occurrences in Air or Water

During the 1967-1978 period, the quantity of BDNPA/F used ranged from zero to 500 lb/year. The maximum rate of loss of BDNPA/F to the environment is estimated to have been 3 lb/month. Losses at this rate occurred only during the infrequent periods in which PBX 9501 explosive was produced. The PBX 9501 explosive is not expected to be produced in large quantities in the future, so this source of BDNPA/F pollution will be negligible.

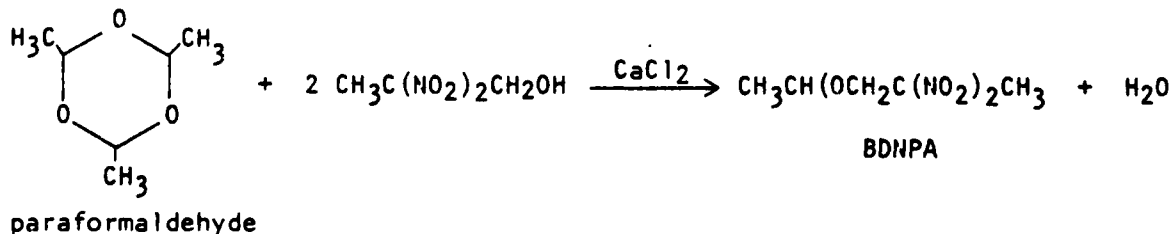
E. Uses in the Civilian Community

1. Production Methodology

The nitroacetals, BDNPA and BDNPF, are made by reacting the appropriate aldehyde with the nitroalcohol in the presence of an acidic catalyst. For BDNPF the following conditions are used (Gold and Marcus, 1966)



BDNPA is prepared by the following reaction



2. Manufacturers, Production and Capacity

Cordova Chemical Co., a division of Aerojet General Corp., and the Naval Ordnance Station at Indian Head have the capabilities for manufacturing BDNPA/F. However due to over supply and low demand, these plasticizers are not currently being produced. Production capacities for BDNPA/F are unavailable.

3. Usage

BDNPA/F are plasticizers used in the preparation of polyurethane binders for solid rocket fuels. They are compatible with polyurethane systems containing gem-dinitro or nitroaza groups. The primary users of BDNPA/F are the Navy and civilian rocket manufacturing companies engaged in the production of Polaris missiles.

4. Future Trends

No major changes in the demand for BDNPA/F are anticipated.

5. Documented or Speculated Occurrences in the Environment

No information on civilian pollution of BDNPA/F was found in the literature. Some losses are expected from manufacture of these compounds and motor castings. However, the quantities discharged into the environment are unknown.

F. Comparison of Civilian and Military Uses and Pollution

BDNPA/F are used mainly as plasticizers in solid rocket motors. These motors are made by civilian manufacturers such as Cordova Chemical Co. under Government contract and the Navy. The amount of BDNPA/F used in the production of PBX explosives at Holston AAP is small compared to the amount needed when Polaris missiles are in full production. The pollution resulting from civilian and Navy manufacture and use of BDNPA/F is not known. However, pollution of BDNPA/F from PBX explosive formulation at Holston AAP is probably less than 10% of the pollution resulting from civilian manufacture and use.

G. Toxicological and Environmental Hazards

1. Toxicity to Mammals

Finger (1977) conducted the only available toxicity study on BDNPA/F. He found an oral dose of 100 mg/kg to rats produced no effects.

2. Toxicity to Aquatic Organisms

No aquatic toxicity studies were found in the literature for BDNPA/F.

3. Toxicity to Microorganisms and Plants

No data were retrieved on the toxicity of BDNPA/F to microorganisms or plants.

4. Environmental Fate of BDNPA/F

No data are available on the environmental fate of BDNPA/F. The main reaction of these compounds in the environment is expected to be hydrolysis. Microbial degradation may also play an important role in the environmental fate of these compounds.

5. Availability of Literature for Phase II

The available literature on BDNPA/F is very limited. Any information on the toxicological or environmental properties of these plasticizers will have to come from the U.S. or possibly foreign manufacturers and current research.

H. Regulations and Standards

There are no U.S. effluent or industrial hygiene regulations or standards for BDNPA/F. BDNPA/F is listed in EPA's *"Toxic Substances Control Act Candidate List of Chemical Substances."* However, no immediate action on these chemicals is planned by EPA.

I. Conclusions and Recommendations

The goal of this study was to assess the Army's responsibility for further evaluation of the toxicological and environmental hazards of BDNPA/F plasticizers. In a sense these plasticizers are military unique compounds since all the uses of these plasticizers are in military munitions manufacture or in the manufacture of solid rocket motors for the military. However, the use of BDNPA/F in Army munitions manufacture at Holston AAP is low and sporadic. Therefore, it is recommended that any Army sponsored toxicologic or environmental studies on BDNPA/F should be a low priority. However if use of BDNPA/F by the Army increases, additional toxicological and environmental data should be sought in order to expand the very limited amount of information on these compounds.

J. References

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PRELIMINARY PROBLEM DEFINITION STUDY ON
MUNITIONS-RELATED CHEMICALS
POLYETHYLENE EMULSION AC-656

SUMMARY

Polyethylene emulsion AC-656 is currently being piloted by Holston AAP as a desensitizer for A-3 explosives. If the A-3 product formulated with the polyethylene emulsion is put into full scale production, the Army's requirements for the AC-656 emulsion would be 400,000 lb/year at current production levels. At full mobilization, 2 million lb/year of AC-656 would be required by Holston AAP.

Polyethylene emulsion AC-656 is formulated solely for the Army by Chemical Corporation of America. This company buys the raw materials and formulates the emulsion at their Rutherford, N.J. facility. The emulsion is composed of the following ingredients:

- Polyethylene AC-656	20.38%
- Acintol	3.57%
- Morpholine	3.57%
- Stearic Acid	1.13%
- Ammonia	0.50%
- Water	70.85%

All of the ingredients are common materials for which there is widespread use and pollution.

The polyethylene emulsion AC-656 ingredients all have relatively low to moderate toxicities to mammals and aquatic life. However, the formation of N-nitrosomorpholine (a potent carcinogen) has been shown to occur from morpholine and nitrite *in vivo* and in the environment. The effluents from Holston AAP present a unique situation in which this nitrosation reaction could occur. High nitrite/nitrate concentrations are present along with suitable catalysts to promote the nitrosation reaction.

Based on the potential for the formation of N-nitrosomorpholine in the Holston AAP effluents, a Phase II study on the polyethylene emulsion AC-656 is recommended. This study should concentrate mainly on morpholine and its environmental reactions.

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V. POLYETHYLENE EMULSION

A. Introduction

A polyethylene emulsion is used by Holston AAP in the formulation of A-3 explosives. This emulsion contains the following ingredients:

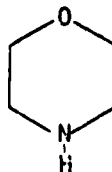
- Polyethylene
- Acintol FA-2 (Tall Oil Fatty Acid)
- Morpholine
- Stearic Acid
- Ammonia
- Water

The environmentally important individual components of this emulsion and the use of the emulsion are detailed in this report.

B. Alternate Names

1. Morpholine

Morpholine is a secondary amine with the empirical formula C_4H_9NO and a molecular weight of 87. Its structural formula is:

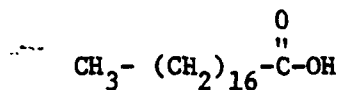


Other names for morpholine are:

CAS Registry No: 110-91-8
CA Name (8CI, 9CI): Morpholine
Wiswesser Line Notation: TGN DOTJ
Synonyms: Diethylene imidoxide; Diethylene oximide;
Diethylenimide oxide; p-Isoxazine, tetrahydro-;
1-Oxa-4-azacyclohexane; 2H-1,4-Oxazine, tetrahydro-;
4H-1,4-Oxazine, tetrahydro-; Tetrahydro-1,4-oxazine;
Tetrahydro-2H-1,4-oxazine; BASF 238

2. Stearic Acid

Stearic acid is a carboxylic acid with a molecular weight of 284.5 and the empirical formula $C_{18}H_{36}O_2$. Its structural formula is:



Other names for stearic acid are:

CAS Registry No.:	57-11-4
Replaces Registry Nos.:	8013-28-3; 8023-06-1; 8037-83-0
CA Name (8CI);	Stearic Acid
CA Name (9CI):	Octadecanoic Acid
Synonyms:	KAM 1000; KAM 2000; KAM 3000; 1-Heptadecane-carboxylic acid; Neo-Fat 18-59; Neo-Fat 18-55; Neo-Fat 18-54; Neo-Fat 18-53; Stearex beads; Stearophanic acid; Hydrofol acid 150; PD 185; Hystrene S-97; Hystrene T-70; Hystrene 80; Humko Industrene R; NAA 173; Neo-Fat 18; n-Octadecanoic acid; Industrene R.

3. Acintol (Tall Oil)

Tall oil is a by-product of the wood pulp industry ("Tall" is Swedish for "pine"). The CAS Registry No. for Acintol is 8002-26-4. Other alternate names for this product are: Tall Oil, Acintol c, Liquid Rosin, Talleol, Tallol.

4. Polyethylene

Polyethylene is a polymer formed by polymerization of ethylene. It has a molecular formula of $(\text{C}_2\text{H}_4)_x$. The molecular weights of the polymer vary from 2000 up. The CAS Registry No. for polyethylene is 9002-88-4. There are numerous other registry numbers which have been assigned to polyethylene. Alternate names for this polymer number are in the hundreds, depending on the properties of the material and the manufacturer.

C. Physical Properties

1. Morpholine

The physical properties of morpholine are listed in Table V-1. The infrared and NMR spectra of this compound are shown in Figures V-1 and V-2, respectively.

Table V-1. Physical Properties of Morpholine*

Physical Form at 20°C:	hygroscopic liquid
Color:	colorless
Odor:	amine-like
Freezing Point:	-4.9°C
Boiling Point:	128.9°C @ 760 mmHg 20.0°C @ 6 mmHg
Specific Gravity (20/20°C):	1.002
Vapor Pressure (20°C):	6.6 mm
Viscosity (20°C):	1.23 cP
Flash Point:	100°F
Autoignition Temperature:	590°F
Refractive Index n_D^{20} :	1.4540
Surface Tension (at 20°C):	37.5 dynes/cm
pK_b	5.6
Solubility:	miscible with water with evolution of heat acetone, benzene, ether, castor oil, methanol, ethanol, ethylene glycol, 2-hexanone, linseed oil, turpentine, pine oil
Will Dissolve:	109% dimethylamine; 34% trimethylamine; 35% methylamine; >5% naphtha, <1% paraffin oil; <5% sulfur by weight

*Hawley, 1977; Windholz, 1976; Weast, 1970

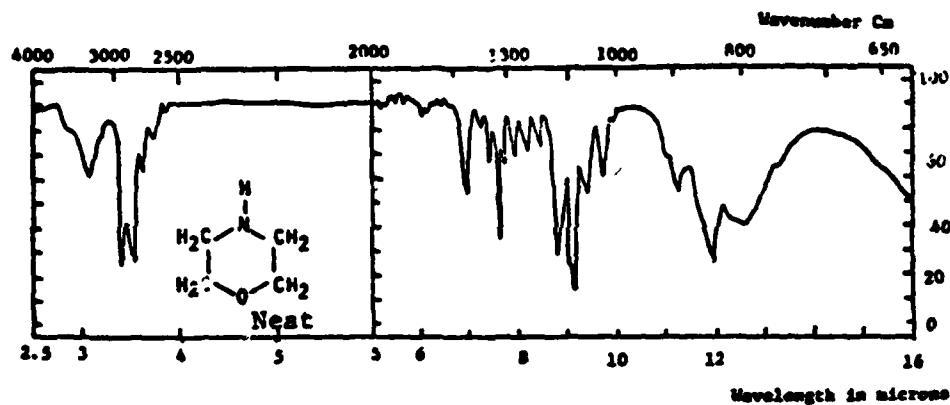
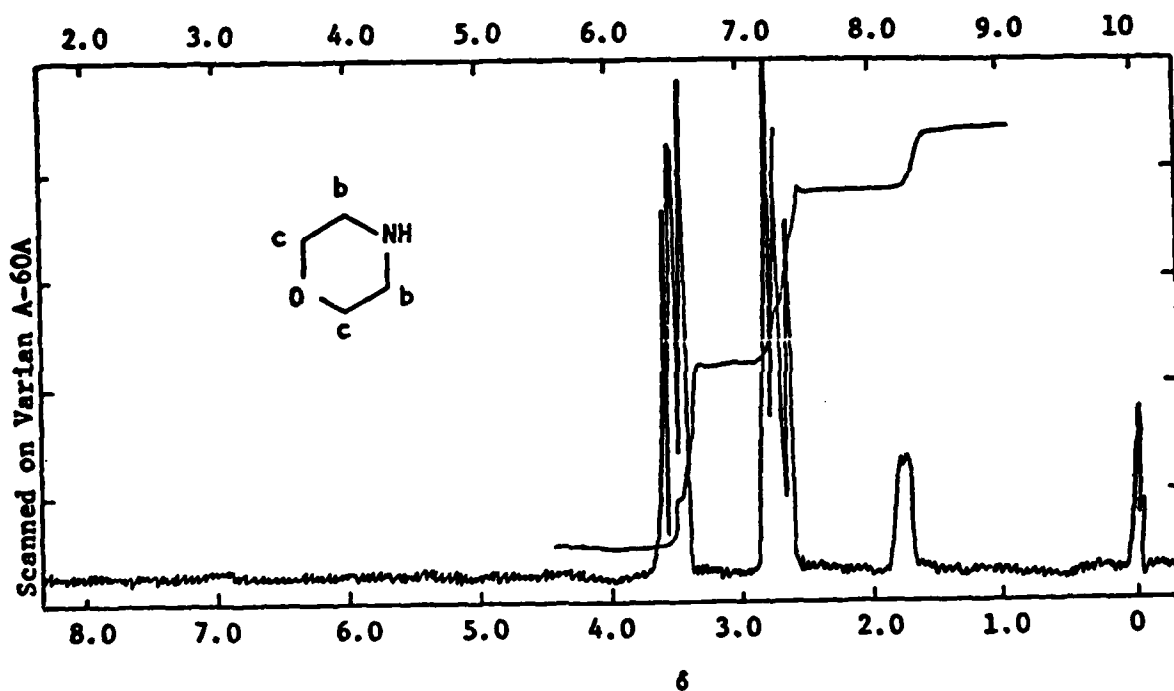


Figure V-1. Infrared Spectrum of Morpholine (Pouchert, 1970)



MORPHOLINE

C_4H_9NO

Mol. Wt. 87.12

B.P. 128.6°C

IR 100

n_D^{20} 1.4553

Source: Fluka AG,
Buchs, Switzerland

ASSIGNMENTS

Filter bandwidth: 4 Hz
 Sweep time: 250 sec
 Sweep width: 500 Hz
 Sweep offset: - Hz
 Spectrum amp: 20
 Integral amp: 80 (spec. amp. 3.2)
 Solvent: CCl_4

a	_____	b	_____
b	_____	c	_____
c	_____	d	_____
d	_____	e	_____
e	_____	f	_____
f	_____	g	_____
g	_____		_____

Figure V-2. NMR Spectrum of Morpholine © Sadtler Research Laboratories, Inc. (1967)

V-10

2. Stearic Acid

The physical properties of stearic acid are presented in Table V-2. The infrared and NMR spectra of this acid are shown in Figures V-3 and V-4, respectively.

Table V-2. Physical Properties of Stearic Acid*

Physical form at 20°C:	waxlike solid in crystal masses or powder
Color:	colorless to slightly yellow
Odor:	tallow-like
Melting Point:	69.6°C
Boiling Point:	360°C (decomposes)
Density (20/4°C):	0.9408
Refractive Index n_D^{20} :	1.4299
Flash Point:	385°F
Autoignition Temperature:	743°F
Solubility:	very slightly soluble in water; soluble in alcohol (1g/21ml), benzene (1g/5ml), chloroform (1g/2ml), acetone (1g/26ml), carbon tetrachloride (1g/6ml), carbon disulfide (1g/3.4ml), amyl acetate, toluene

*Hawley, 1977; Windholz, 1976; Weast, 1970

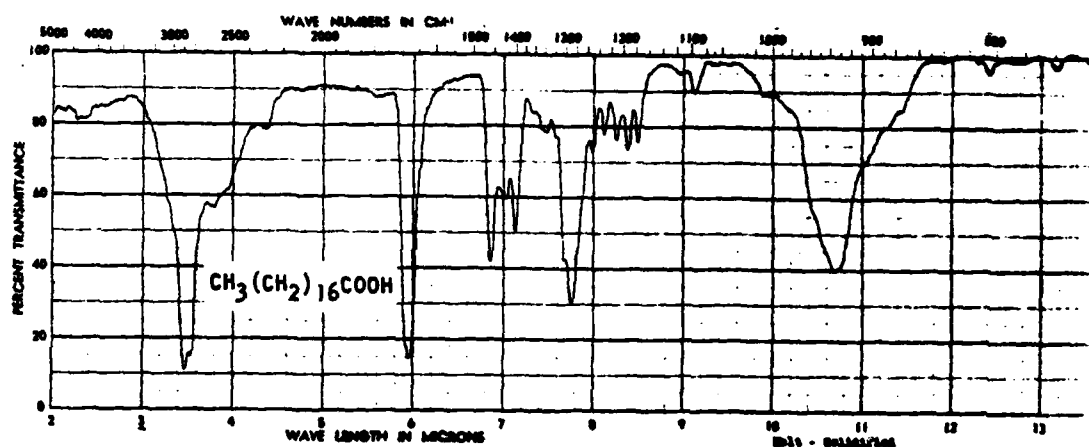
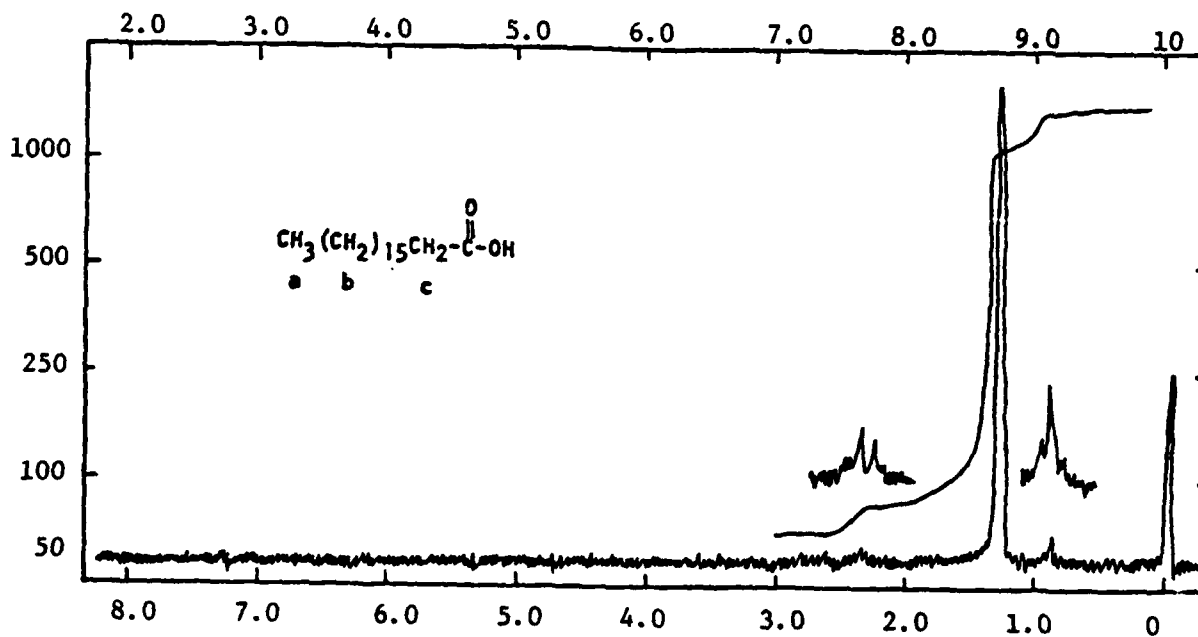


Figure V-3. Infrared Spectrum of Stearic Acid
© Sadtler Research Laboratories, Inc. (1969)



STEARIC ACID

$\text{C}_{18}\text{H}_{36}\text{O}_2$

Mol. Wt. 284.49

δ
M.P. 69-70.5°C

IR 50; 11183

Source: Fluka AG,
Buchs, Switzerland

Filter bandwidth: 4/1 Hz
Sweep time: 250 sec
Sweep width: 500 Hz
Sweep offset: - Hz
Spectrum amp: 20/100
Integral amp: 80 (apex amp. 12.5)
Solvent: CDCl_3

ASSIGNMENTS

a	0.89	h	
b	1.29	i	
c	2.35	j	
d		k	
e		l	
f		m	
g		n	
OH unobserved			

Figure V-4. NMR Spectrum of Stearic Acid © Sadtler Research Laboratories, Inc. (1967)

3. Acintol (Tall Oil)

The physical properties of Acintol are presented in Table V-3.

Table V-3. Physical Properties of Acintol*

Physical Form at 20°C:	liquid
Color:	dark brown
Odor:	acid, similar to burnt rosin
Density:	0.95-1.0
Refractive Index n_D^{20} :	approx. 1.5
Acid Number:	170-180
Saponification No.:	172-185
Iodine No.:	120-188
Flash Point:	360°F

*Hawley, 1977; Windholz, 1976

4. Polyethylene

The physical properties of polyethylene vary depending on the type and the amount of cross-linking. The polyethylene used in the emulsion is AC 656. AC 656 is an oxidized emulsifiable homopolymer with a softening point of 100°C, a density of 0.92. The hardness of this polymer is 9.0 dmm and its viscosity is 185 cP at 140°C.

D. Chemical Properties

1. Morpholine

a. General Reactions

Morpholine is generally produced by treatment of diethanolamine with sulfuric acid (Acheson, 1967). However, as shown in Figure V-5, it can also be prepared by treatment of diethanolamine with alumina (Matsuda *et al.*, 1975), by treatment of bis(2-chloroethyl) ether with ammonia; or by treatment of ethylene glycol with ammonia in the presence of hydrogen and a catalyst (Kirk and Othmer, 1967).

Morpholine is resistant to attack by either concentrated hydrochloric acid or 10% sodium hydroxide at 160°C and is an extremely powerful solvent (Acheson, 1967). Morpholine has a chemistry typical of secondary

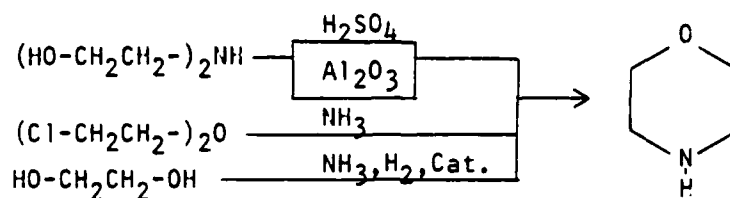


Figure V-5. Preparation of Morpholine

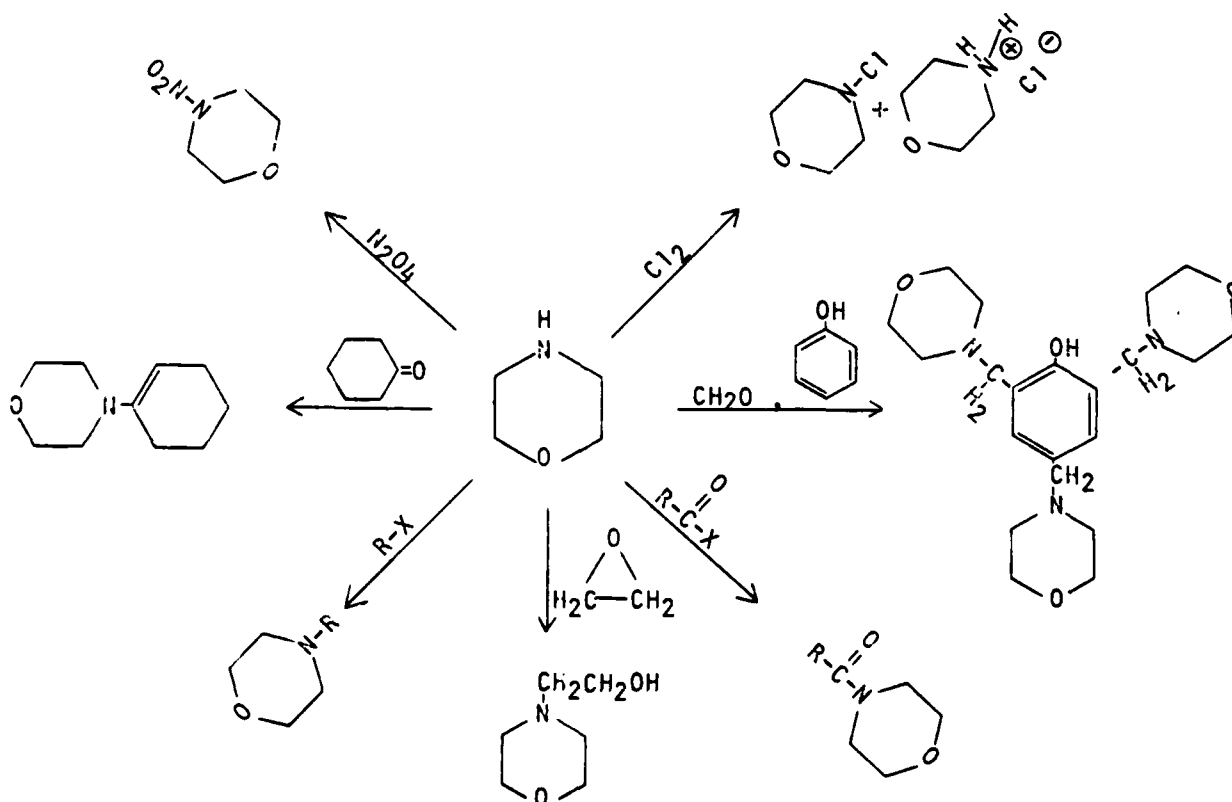
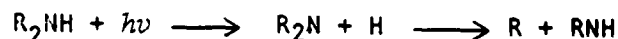


Figure V-6. Reactions of Morpholine

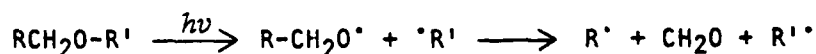
amines as shown in Figure V-6. Morpholine can be nitrated with N_2O_4 (Challis and Kyrtopoulos, 1976) and will form amides on treatment with carboxylic acids, anhydrides or acid chlorides (Kirk and Othmer, 1967). Reaction with alkyl halides yields N-alkyl-morpholines, and reaction with ethylene oxide gives N-(β -hydroxyethyl) morpholine (Kirk and Othmer, 1967). Morpholine will form enamines with ketones such as cyclohexanone and will undergo Mannich-type reactions with a wide variety of carboxyl and aromatic compounds, for example, formaldehyde and phenol (Kirk and Othmer, 1967). Chlorination of morpholine gives an equal mixture of the N-chloro derivative and morpholine hydrochloride.

b. Environmental Chemistry

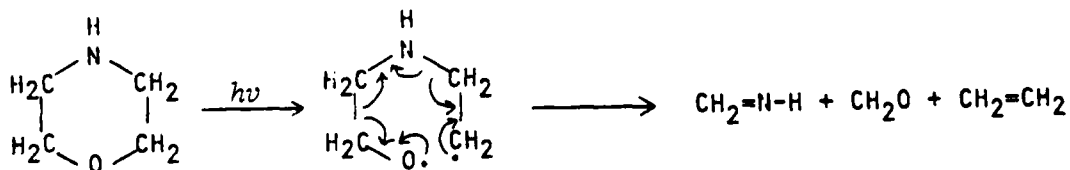
Due to the resistance of morpholine to acid or base hydrolysis, the major environmental reactions are likely to be of a photochemical nature. The primary photochemical processes of secondary amines generally involve cleavage of nitrogen-carbon bonds (Calvert and Pitts, 1966).



Similarly, ethers initially give carbon-oxygen cleavage followed by loss of formaldehyde:



Analogous reactions in morpholine could lead to formaldehyde, ethylene and ammonia.



c. Sampling and Analysis

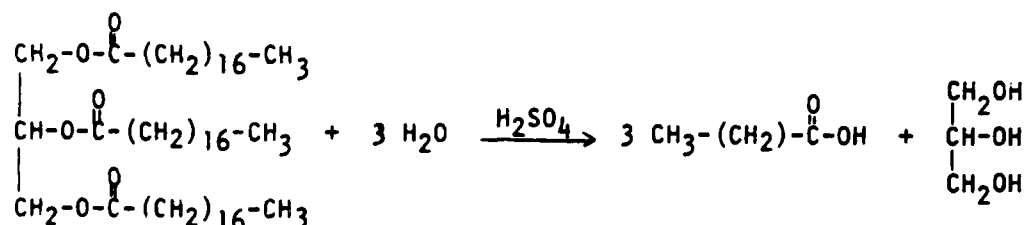
Morpholine complexes and salts have been determined by oxidation to N-chloromorpholine by treatment with sodium hypochlorite. Following reduction of the N-chloromorpholine with iodide, the free iodine liberated is titrated with standard thiosulfate (Venkappayya and Aravamudan, 1969). Potentiometric titration with fluorosulfuric acid in methanol has also been employed (Paul and Pahil, 1964). More recently morpholine has been analyzed by gas chromatography using a 10% carbowax 20M and 190 KOH on Chromosorb P column at 130°C (Lukacovic and Vanko, 1973). Morpholine has also been converted to N-tosylmorpholine. Recovery of morpholine from food or beverages by this method

were 45-67%. This derivative can be analyzed by gas chromatography/mass spectroscopy following steam distillation (Singer and Lijinsky, 1976). Minimum detectable limits of the N-tosylmorpholine were ~0.1 ppm.

2. Stearic Acid

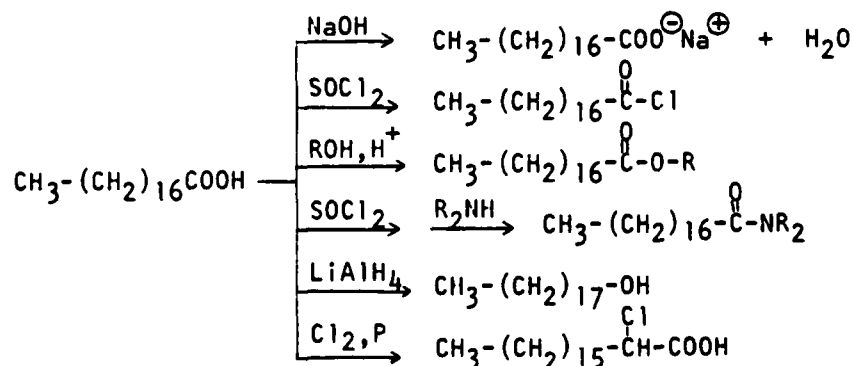
a. General Reactions

Stearic acid is produced by the acid hydrolysis of tallow and other animal fats where it exists as triglycerides (Windholz, 1968; Ralston, 1948).



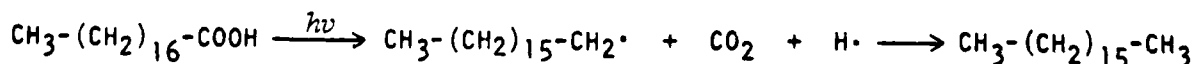
The liquid mixtures of acids thus obtained contain mainly stearic and palmitic acids which precipitate on cooling. Triple pressed (thrice precipitated and pressed free of liquid) stearic acid often contains more palmitic acid than stearic acid.

Stearic acid will undergo those reactions typical of carboxylic acids (Morrison and Boyd, 1973), such as salt formation, conversion into acid chlorides, conversion into esters, conversion into amides, reduction, and halogenation.

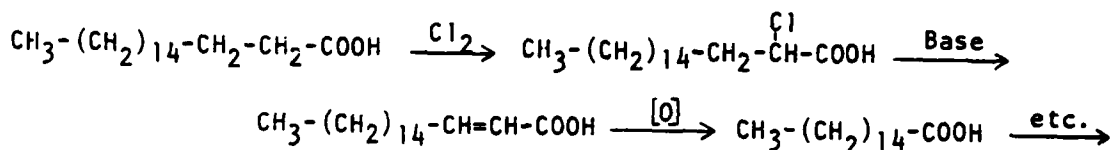


b. Environmental Chemistry

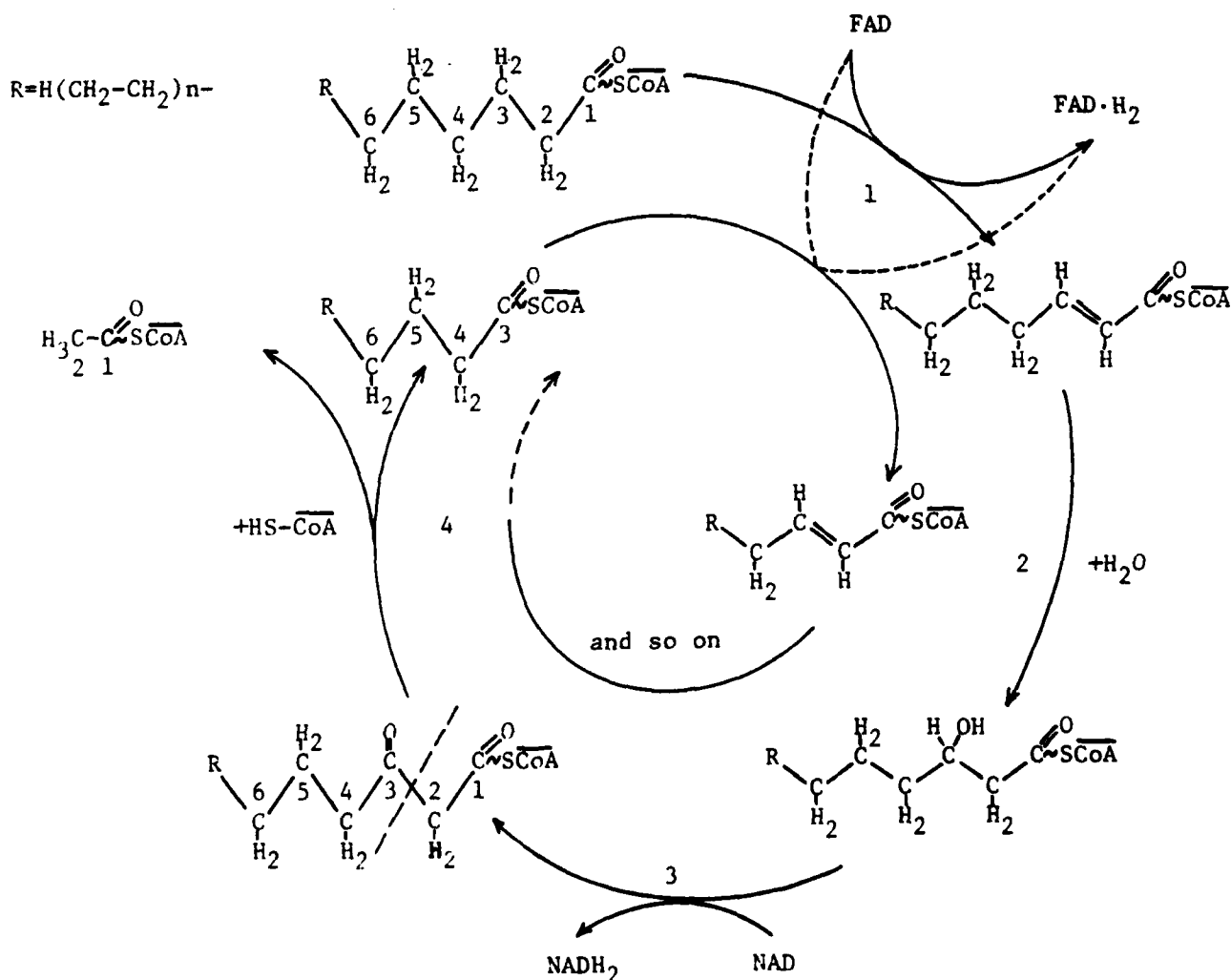
The environmental chemistry of stearic acid has not been reported. Carboxylic acids have been reported to decarboxylate in aqueous solutions upon irradiation with 254 nm UV light yielding carbon dioxide and alkyl radicals which can combine with hydrogen or other available radical scavengers.



Oxidation is also a possibility. Carboxylate anionic acids have been electrolytically oxidized leading to alkyl radicals which then dimerize (Cram and Hammond, 1964). Similar oxidations could occur in nature; metal ions acting as the oxidizing agent. If stearic acid is exposed to chlorine, such as might be found in water treatment facilities, chlorination, dehydrochlorination and oxidation might occur leading to shortening of the chain length.



Biodegradation of fatty acids such as stearic acid generally involve a β -oxidation mechanism (Karlson, 1965). The β -oxidation mechanism is initiated by the formation of a thio ester with coenzyme A followed by a series of enzymatic reactions resulting in dehydrogenation to an $\alpha\beta$ unsaturated analog, hydrations to a β -hydroxy species and oxidation to the β -keto compound which then loses a two carbon fragment. This cycle can be repeated several times for the complete degradation of the acid (Karlson, 1965).



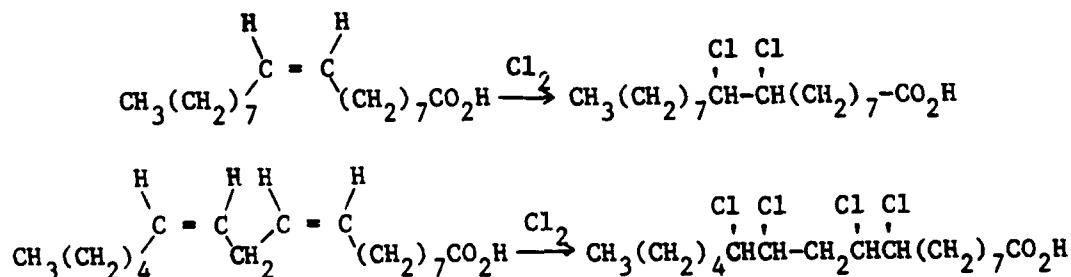
c. Sampling and Analysis

Stearic acid can be identified by conversion to derivatives such as its anilide, amide and 4-bromophenacyl ester (Shriner *et al.*, 1964). Isolation is generally accomplished by basic extraction followed by precipitation by acid. Carboxylic acids have been analyzed by gas chromatography following conversion to their methyl esters by treatment with boron trifluoride and methanol, methanol and hydrochloric acid, or diazomethane (Metcalf and Schmitz, 1961). Samples containing 1 mg-5 g can be prepared for analysis by these methods. Percentage recovery of the ester made with boron trifluoride was 86.3%.

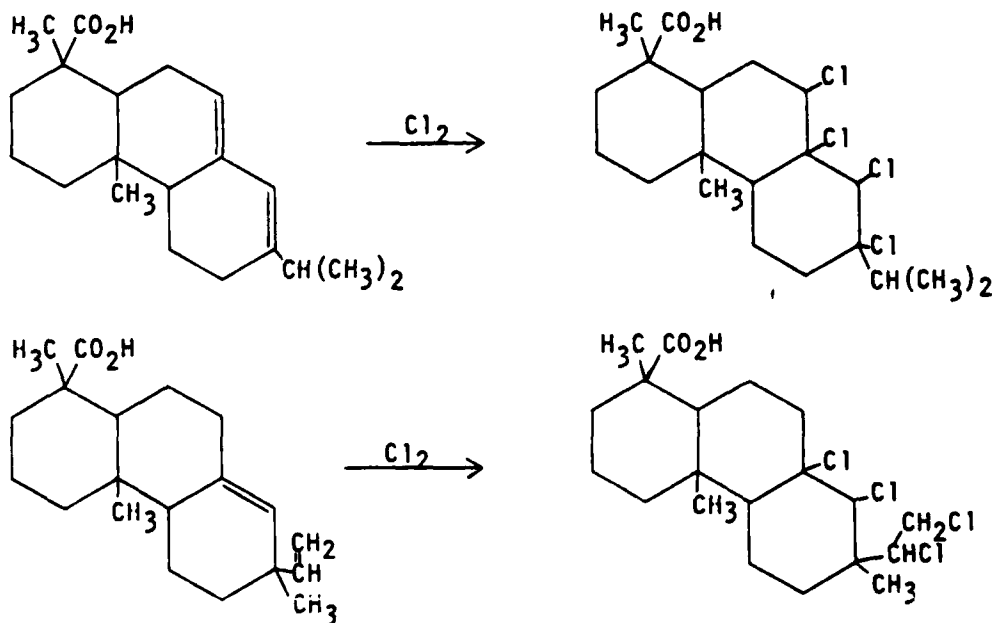
3. Acintol (Tall Oil)

a. General Reactions

Acintol FA2 or tall oil is obtained as a by-product of the sulfate paper process (Windholz, 1968; Kent, 1962). Refined tall oil contains about 97.6% fatty acids such as oleic (51%), linoleic (45%) and palmitic acid (2%) and 1.0% rosin acids such as abietic, pyroabietic and pimaric acid. The fatty acids should behave very much like stearic acid undergoing salt formation, acid chloride formation esterification, reclusion and/or halogenation. Oleic and linoleic acids, being unsaturated will undergo additional reactions at the double bonds as well:

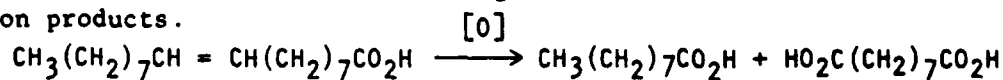


The rosin acids would likewise undergo all of these reactions except for the α C-halogenation. The rosin acids can also undergo addition at the sites of unsaturation.



b. Environmental Reactions

The environmental reactions suggested above for stearic acid are also likely for the major components of acintol. For the unsaturated acids, degradation could take place at the sites of unsaturation by oxidation. The carbon carbon double bonds should be oxidized readily by the action of air and sunlight or with the aid of metallic catalysts giving diols initially and eventually leading to bond cleavage yielding new carboxyl groups. For example, oleic acid would be expected to give nonanodic and nonanoic acid as oxidation products.



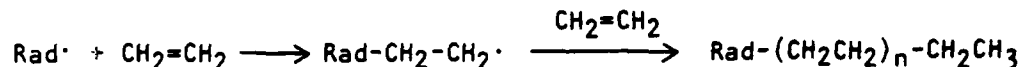
c. Sampling and analysis

Palmitic, oleic and linoleic acids can be analyzed by the same procedures as outlined for stearic acid by preparation of derivatives (Shriner *et al.*, 1964) or by gas chromatography of their methyl esters (Metcalf and Schmitz, 1961).

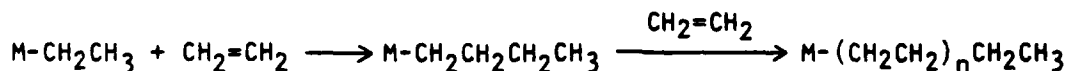
4. Polyethylene

a. General Reactions

Polyethylene is produced by the polymerization of ethylene. There are two main techniques employed, namely the high pressure process employing free radical catalysts such as oxygen or benzoyl peroxide;

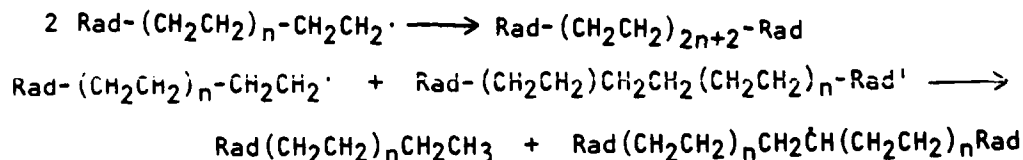


and the low pressure process employing an ionic catalyst (Kent, 1962; Morrison and Boyd, 1973):

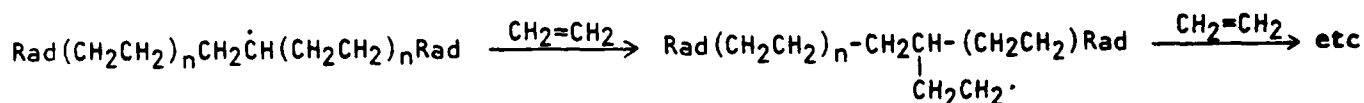


The low pressure process employs either alkyl aluminum (Zeigler process) or related catalysts to produce linear, high density polymers ($d=0.940$ to 0.965).

The high pressure process on the other hand terminates either by radical dimerization or abstraction.



The mid chain radicals generated can react with ethylene generating non-linear low density ($d=0.915$ to 0.935) polyethylene.



AC-656 (density=0.92) is a conventional high pressure polyethylene.

Polyethylene can be heat and photo-oxidized (Haslam and Willis, 1965). Heat oxidation involves the formation and decomposition of hydroperoxide groups leading to a variety of hydroxy, aldehydic, acidic and ketonic groups:

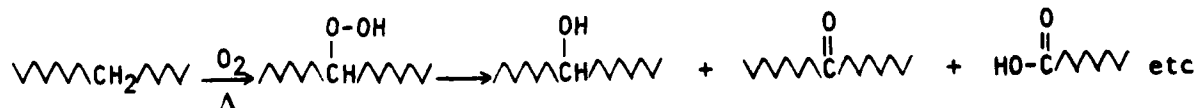
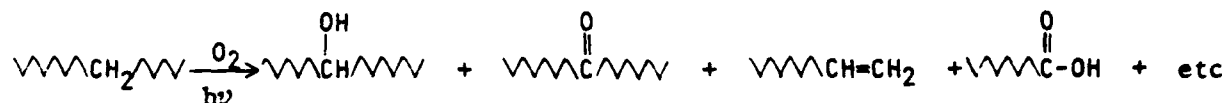
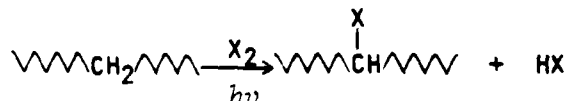


Photo-oxidation leads to a similar variety of oxidized species in addition to terminal unsaturation.



The unsaturation is thought to result from chain scission.

Polyethylene, being a long chain hydrocarbon, would be expected to be reactive toward free radical halogenation:



The most prominent feature of the chemistry of polyethylene, however, is its unreactivity. Polyethylene is one of the most inert polymers having excellent resistance to attack by acids, bases, oils and most organic solvents.

b. Environmental Reactions

The only reaction expected for polyethylene in the environment would be photo-oxidation, and even this reaction should be quite slow. Polyethylene is quite persistent in the environment. However, it is also a harmless substance and should not be an environmental hazard.

c. Sampling and Analysis

Due to the insolubility of polyethylene and its low vapor pressure, little attention has been devoted to its analysis. Gas chromatographic analysis has been employed, but requires pyrolysis in a specially designed inlet system. Hydrocarbon fingerprints of the pyrolyzate are reproducible to 1% and are specific to the various polymers (Swann and Dux, 1961). Approximately 50 mg of the polymer was pyrolyzed for analysis.

E. Uses in the Army Munitions

1. Purpose

Polyethylene emulsion AC-656 is used by Holston AAP in the production of the A-3 explosive formulation. The polyethylene emulsion is a desensitizing agent comprising 9.0±0.7% of the mix. The remainder of the formulation is RDX. The composition of the polyethylene emulsion is shown below.

Polyethylene Emulsion Formulation
(Military Specification,
MIL-E-63218, 1978)

<u>Component</u>	<u>% by Weight</u>
Polyethylene (AC-656)	20.38
Tall Oil Fatty Acid (Acintol FA-2)	3.57
Morpholine	3.57
Stearic Acid	1.13
Ammonia	0.50
Water	70.85

The production of A-3 explosive using polyethylene emulsion as the desensitizing agent has been under development since 1977. Previously, petroleum wax was used as the desensitizing agent. Composition A-3 made with polyethylene emulsions exhibits better desensitization characteristics than A-3 made with petroleum waxes (Brumley, 1977). It is also more uniformly coated and will not exude or flow at storage temperatures of 160°F, as will the petroleum wax based product.

2. Quantities Used

During 1977 and 1978, 35,000 lb of the A-3 formulation were produced using polyethylene emulsion. Total production of A-3 explosive was 2,430,000 lb in 1977, therefore the new process accounted for less than 1% of the total production.

A-3 explosive is a high volume production item at Holston AAP. The average production rate over the last 10 years has been about 4,500,000 lb/year. In 1969, over 10,000,000 lb of A-3 explosive were produced. At full mobilization, requirements for A-3 would be 21,732,000 lb/year.

If the entire production of A-3 explosive were converted to use of the polyethylene emulsion desensitizer, current requirements for the emulsion would be about 400,000 lb/year. At full mobilization, the amount of the emulsion used would increase to nearly 2,000,000 lb/year.

3. Documented or Speculated Occurrences in Air or Water

A material balance for production of A-3 explosive using polyethylene emulsion is shown in Figure V-7 (Rogers, 1979). This balance is based upon a 4,000 lb batch of A-3 explosive. The quantities of chemicals in the effluent from A-3 processing as a function of the production rate are presented in Table V-4. Barium chloride is used in the process to break the emulsion. Magnesium sulfate is added to the effluent to precipitate barium as barium sulfate.

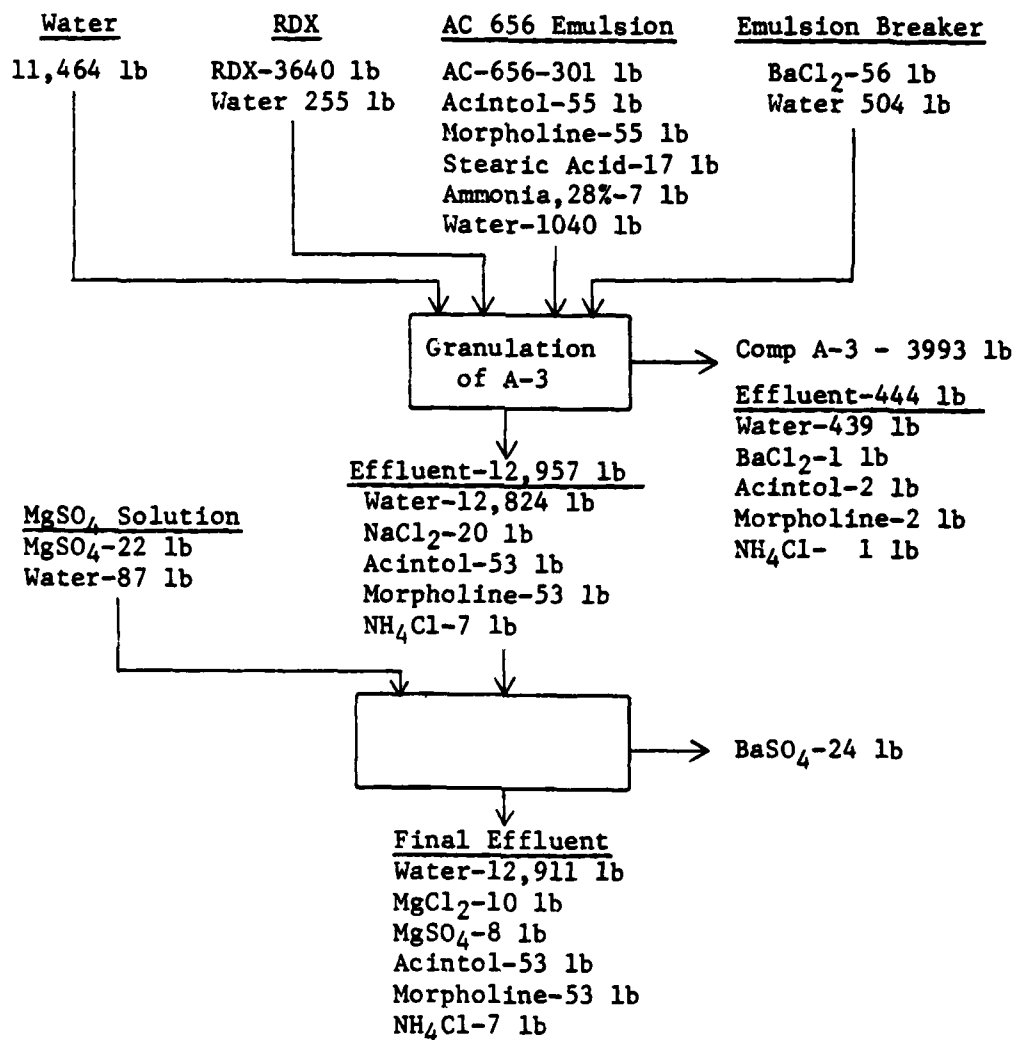


Figure V-7. Material Balance for 4000 lb Batch of A-3
Made with Polyethylene Emulsion

Table V-4. Chemicals in Total Effluents from A-3 Production

	<u>4,000 lb batch</u>	<u>Typical Production 4,500,000 lb/year</u>	<u>Full Mobilization 21,732,000 lb/year</u>
BaCl ₂	1	1,125	5,433
BaSO ₄ *	24	27,000	130,392
MgCl ₂	10	11,250	54,330
MgSO ₄	8	9,000	43,464
Acintol	55	61,875	298,815
Morpholine	55	61,874	298,815
NH ₄ Cl precipitated	8	9,000	43,464
* precipitated out			

Currently, all Holston AAP Area B wastes enter the Holston River with no treatment. However, a three-stage biological treatment facility is under construction which will treat future wastes in an anaerobic tower, trickling filter and with activated sludge. This facility is designed to handle 12.5 MGD of process effluent, the amount expected at full mobilization. It is expected that the acintol and morpholine will be degraded at least partially in this treatment facility.

F. Uses in the Civilian Community

1. Production Methodology

The polyethylene emulsion is made by emulsifying AC-656 polyethylene, ammonium stearate, acintol, and morpholine in a water solvent.

2. Manufacturers, Production and Capacity

The polyethylene emulsion AC-656 used by the Army in munitions production was developed by Chemical Corporation of America located in East Rutherford, N.J. Chemical Corporation purchases the ingredients for the emulsion from various suppliers and mixes the emulsion (Chemical Corporation, 1979). According to the Military Specification (MIL-E-63218), the polyethylene used in the emulsion must meet the following specifications:

<u>Property</u>	<u>Requirement</u>
Acid number	14-17
Penetration, mm	0.8-1.4
Viscosity @ 140°C, cP, max.	200
Softening Point, °C	95-100
Density, g/cc	0.90-0.94

Polyethylene AC-656 available from Allied Chemical meets these specifications. Many other companies also make polyethylene with a variety of properties. It is anticipated that many of these companies could also make polyethylene that meets these specifications.

Acintol (tall oil fatty acid) is supplied to the Chemical Corporation. However, there are several producers which make this chemical. These producers, their locations and production capacities are listed in Table V-5. Tall oil is used in the manufacture of a variety of products including soap pastes, flotation agents, greases, paints, alkyd resins, linoleum, soaps, fungicides, asphalt emulsions, rubber formulations, cutting oils, etc.

The morpholine for the emulsion is supplied by Jefferson Chem. Co. Inc., Conroe, Texas. The company is the only current U.S. producer of morpholine. Sales of morpholine were reported as 25,963,000 million lb in 1973 and 20,210,000 million lb in 1974. Sales or production of morpholine are not reported after 1974. Morpholine is used as a cheap solvent for resins, waxes, casein and dyes. Morpholine derivatives are used for surfactive agents, corrosion inhibitors, plasticizers, insecticides, fungicides, herbicides and local anesthetics and antiseptics.

Stearic acid is supplied to Chemical Corporation by Humko Sheffield Chem. Division of Kraft Inc. in Memphis, Tenn. As in the case of tall oil, several producers make stearic acid which would probably meet military Specifications. Other producers of stearic acid are listed in Table V-6. Stearic acid is used in the pharmaceutical industry for the manufacture of metallic soaps and in cosmetics.

3. Usages

All the ingredients in the polyethylene emulsion have a wide variety of civilian uses. Other polyethylene emulsions are used in the formulation of printing inks and xerox powders. However, when the emulsion contains ammonium stearate and AC-656, it is only used by the Army in munitions production.

4. Future Trends

The polyethylene emulsion industry is stable. No drastic changes are expected in the near future. However, the AC-656 emulsion is currently

Table 5. Producers of Tall Oil Fatty Acid
(SRI International, 1978)

		<u>Annual Capacity (Thousands of Tons)</u>
Arizona Chem. Co.	Panama City, Fla.	105
	Springhill, La.	45
Crosby Chems., Inc.	*Picayune, Miss.	90
Emery Indust., Inc.	Nitro, W. Va.	65
Hercules Inc.		
Organics Dept.	Franklin, Va.	65
	Hattiesburg, Miss	60
	Portland, Ore.	30
	Savannah, Ga.	65
Reichhold Chems., Inc.		
Newport Div.	Bay Minette, Ala.	36
	Oakdale, La.	60
Sylvachem Corp.	Port St. Joe, Fla.	150
Union Camp Corp.		
Chem. Products Div.	Savannah, Ga.	105
Westvaco Corp.		
Chem. Div.		
Custom Chems. Dept.	Charleston Heights, S.C.	<u>85</u>
TOTAL		961

*On stand-by

Table V-6. Producers of Stearic Acid
(SRI International, 1978)

Acme-Hardesty Co., Inc.	Jenkintown, Pa.
Akzona Inc.	
Armak Co., subsid.	
Armak Indust. Chems. Div.	McCook, Ill.
Ashland Oil, Inc.	
Ashland Chem. Co., div.	
Chem. Products Div.	Mapleton, Ill.
Chattem Drug & Chem. Co.	
Petrochems. Co. Inc., subsid.	Fort Worth, Tex.
Darling & Co.	Chicago, Ill.
Emery Indust., Inc.	Cincinnati, Ohio
Western Operations	City of Commerce, Calif.
Glyco Chems., Inc.	Painesville, Ohio
Gulf Oil Corp.	
Kewanee Indust., Inc., subsid.	
Millmaster Onyx Group	
A. Gross and Co., div.	Newark, N.J.
Kraft, Inc.	
Humko Sheffield Chem., Div.	Memphis, Tenn.
Murro Chem. Co.	Portsmouth, Va.
PVO Internat'l, Inc.	Boonton, N.J.
Stokely-Van Camp, Inc.	
Capital City Products Co., div.	Columbus, Ohio
Union Camp Corp.	
Chem. Products Div.	Dover, Ohio
Woburn Chem. Co.	Paterson, N.J.

only being produced in small lots. If the Army completely replaces the wax with AC-656 emulsion in A-3 explosives, then the amount of this emulsion formulated each year will increase sharply.

5. Documented or Speculated Occurrences in the Environment

No information was obtained on the entry of AC-656 emulsion into the environment from civilian formulation. However, the ingredients of this emulsion and other similar emulsions are widely used in the civilian community. Entry of tall oil, stearic acid, morpholine, ammonia and polyethylene into the environment is widespread as a result of the manufacture, use and disposal of materials containing these compounds.

G. Comparison of Military Usage and Pollution

Polyethylene emulsion AC-656 is a military unique emulsion. This emulsion is formulated according to military specifications from common materials by one company. However, many similar polyethylene emulsions are used by the printing industry. Civilian pollution resulting from the emulsion constituents is widespread due to the variety of uses. Military pollution resulting from use of emulsion AC-656 at Holston AAP is currently small. However, if this emulsion is used for A-3 production at full mobilization production rates, significant pollution would result. The major chemicals of concern in the effluent stream are barium and magnesium salts and morpholine.

H. Toxicological and Environment Hazards

1. Mammalian Toxicity

a. Morpholine

Many studies have been conducted to determine the toxicological hazards of morpholine to mammals. When this compound is administered in acute doses, it is moderately toxic to mammals. The oral LD50 of morpholine to rats is 1050 mg/kg (NIOSH, 1977). Morpholine is absorbed through the skin. The LD50 of this compound when applied percutaneously to rabbits is 500 mg/kg.

The major toxicological hazard of morpholine is the potential formation of N-nitrosomorpholine. N-nitrosomorpholine has been demonstrated to be a potent carcinogen in mammals. The feeding of certain amines, the N-nitroso derivatives of which are known carcinogens, and nitrite to laboratory animals has been shown to lead to the development of tumors. Several studies have been conducted to determine if morpholine is N-nitrosoated *in vivo*.

Garcia and Lijinsky (1973) conducted a study in which MRC rats were fed mixtures of sodium nitrite (0.05%) and morpholine (0.025%). Their results are presented in Table V-7. The formation of N-nitrosomorpholine

Table V-7. Tumors in Rats Treated with Morpholine and Nitrite
(Garcia and Liljinsky, 1973)

Treatment	Total dose (g)	No. of animals at week							No. a TBA	No. TF ^a	Animals with tumors of							
		0	20	40	60	80	100	Pituitary			Breast	Testis	Uterus/Vagina	Adrenal	Pancreas	Skin	Other	
Morpholine (0.025%) + Sodium nitrite (0.05%)	1.8	15	15	15	14	14	11	5	10	4	0	1	0	0	0	1	1 spleen	
	3.7	15	15	15	14	14	10	13	2	12	3	0	1	1	0	1	1 thyroid	
Sodium nitrite (0.2%)	15.0	15	15	15	15	15	13	9	6	1	0	2	0	1	1	3	3 soft tissue	
		15	15	15	14	13	12	10	5	6	2	0	1	0	0	1	1 stomach, 1 thymus	
Untreated Control	15	15	14	14	14	14	11	5	10	0	0	3	0	0	1	0	1 soft tissue	
	15	15	15	15	14	13	4	11		3	1	0	1	0	0	0		

^aTBA = Tumor bearing animals, TF = Tumor free.

in vivo under those particular conditions was insufficient to give rise to tumors.

However, other experimental data suggest that the induction of hepatocarcinomas and lung adenomas in animals treated with secondary amines (i.e. morpholine) and nitrite is due to *in vivo* nitrosation forming carcinogenic nitrosamines (Greenblatt *et al.*, 1971; Sander and Burkle, 1969; Sander *et al.*, 1975a). As shown in Table V-8, morpholine (6.33 g/kg of food) plus sodium nitrite (1 g/l in drinking water) fed to Swiss mice resulted in a highly significant increase in lung adenomas. Newberne and Shank (1973) reported liver and lung tumors in Sprague-Dawley rats fed various concentrations of nitrite plus morpholine or N-nitrosomorpholine. These data are presented in Table V-9. Apparently the nitrosation of morpholine occurs in the acidic gastric environment of the rat.

Shank and Newberne (1976) conducted long-term feeding studies with Sprague-Dawley rats and Syrian golden hamsters using various concentrations of nitrite plus morpholine or N-nitrosomorpholine. Nitrite plus morpholine induced a higher incidence of hepatocellular carcinoma in rats and a lower incidence in hamsters. Nitrite plus morpholine also induced angiosarcoma in both species, most frequently in the liver, with the lung as the next most common site. Data from these studies are presented in Tables V-10 and V-11.

The formation of N-nitrosomorpholine in the mouse stomach from equimolar doses of sodium nitrite and morpholine given simultaneously by a stomach tube was estimated by Braun *et al.* (1977). This estimation was made using a host-mediated assay. The mutagenic activity of the compounds (following i.p. injection of the compounds) was assayed using *Salmonella typhimurium* RA 1950 as the genetic indicator system. Estimates of N-nitrosomorpholine ranged from 1 to 3%. N-nitrosomorpholine was detected in the stomach of Syrian golden hamsters given sodium nitrite and morpholine simultaneously by stomach tube (Inui *et al.*, 1978).

Akin and Wasserman (1975) reported that guinea-pigs fed morpholine plus sodium nitrite with ascorbic acid lacked signs of the toxic responses seen with diets containing N-nitrosomorpholine. A combination of sodium ascorbate (11.5 or 23 g/kg food) and morpholine plus sodium nitrite fed to strain A mice caused an 89-98% inhibition of lung adenoma induction (Mirvish *et al.*, 1975). Adenomas induced by morpholine plus sodium nitrite were strongly inhibited by gallic acid, moderately inhibited by caffeine and unaffected by thiocyanate.

b. Stearic Acid

A single oral dose of 5 g/kg of stearic acid was administered to rats and mice. The animals were observed for a three week period following the acute dose. These animals exhibited no toxic response to the stearic acid (Komarova, 1976). In a chronic study, Komarova (1976) administered stearic acid orally to white rats at levels of 1.0 and 0.25 g/kg. No

Table V-8. Lung Adenoma Induction in Swiss Mice
(Greenblatt et al., 1971)

Compound	Dose*	Initial No. of mice (females/males)	Effective No. of mice† (females/males)	Total adenoma- bearing mice		Total No. of lung adenomas	Adenomas per adenoma- bearing mouse	Adenomas per mouse‡
				Number	Percent			
None	-	80/80	71/73	20	14	26	1.3	0.18 ± 0.43
NaNO ₂	1.0 g/liter (14.5)	40/40	38/36	14	19	16	1.1	0.2 ± 0.5
		40/40	38/36	14	19	16	1.1	0.2 ± 0.5
Morpholine	6.33 g/kg (72.5)	20/20	19/19	5	13	5	1.0	0.1 ± 0.3
Morpholine + NaNO ₂	6.33 g/kg	20/20	16/19	20	57‡	41	2.0	1.4 ± 1.4‡
	1.0 g/liter							
Nitrosomorpholine	0.080 g/liter (0.69)	20/20	14/8	16	73‡	106	6.6	4.5 ± 4.3‡

*g/kg food or g/liter water: parentheses show concentration in mmoles/kg or mmoles/liter.

†Mice surviving more than 16 weeks from beginning of experiment.

‡Mean ± standard deviation.

§ Significantly greater than control group (P<0.001).

Table V-9. Tumors in Rats Exposed to Continuous Dietary N-nitrosomorpholine or Nitrite and Morpholine (Shank and Neuberne, 1976)

Additions to diet (ppm)		Tumour incidence*				
		Liver		Lung		
		Hepatocellular carcinomas	Angiosarcoma	Metastatic hepatocellular carcinoma	Angiosarcoma	
NaNO ₂	Morpholine	N-nitrosomorpholine				
0	0	0	0/169	0/169	0/169	0/169
1000	1000	0	156/159	38/159	109/159	37/159
1000	50	0	24/122	11/122	10/122	2/122
1000	5	0	3/160	0/160	0/160	0/160
50	1000	0	4/120	0/120	0/120	0/120
0	0	5	17/132	1/132	1/132	0/132
0	0	50	77/97	10/97	21/97	4/97

*No. of rats affected/no. observed.

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Table V-10. Incidence of Hepatocellular Carcinoma and Angiosarcoma Among Rats Fed Experimental Diets (Shank and Newberne, 1976)

Test group and diet no.	Dietary level (ppm) of		No. of rats†	Incidence (%) of					Age at death with liver carcinoma	
	NaNO ₂	Morpholine		Liver- cell carcinoma	Liver- angio- sarcoma	Lung angio- sarcoma	Other angio- sarcoma	Metastases from liver to lung	First death	Median‡
1	0	0	0	0	0	0	0	-	-	-
2	1000	0	96	1	0	0	1	0	123	-
3	0	1000	104	3	0	2	1	0	68	-
4	1000	1000	159	97	14	23	1	49	19	38
5	1000	50	117	59	5	6	0	17	47	111
6	1000	5	154	28	12	8	1	7	24	-
7	50	1000	109	3	2	1	0	0	89	-
8	5	1000	172	1	2	1	1	0	64	-
9	50	50	152	2	1	1	1	0	63	-
10	5	5	125	1	2	2	1	0	88	-
11	0	0	128	58	15	9	1	22	53	106
12	0	0	94	93	21	20	1	58	30	56

†F₁ and F₂ generations combined.

‡Age (in wk) by which 50% of the population had died with hepatocellular carcinoma

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Table V-11. Incidence of Hepatocellular Carcinoma, Angiosarcoma and Other Tumours Among Hamsters Fed Experimental Diets (Shank and Neuberne, 1976)

Test Group and diet no.	Dietary level (ppm) of		No. of animals	Liver-cell carcinomas		No. of angiosarcomas	No. and type of other tumours
	NaNO ₂	Morpholine		No.	%		
1	0	0	23	1	4	4	0
2	1000	0	30	0	0	1(ac)	0
3	0	1000	22	0	0	0	0
4	1000	1000	16	5	31	0	1 lung cyst adenoma
5	1000	50	32	0	0	0	1 malignant lymphoma 1 keratinizing acanthoma of stomach 1 adrenal adenoma
6	1000	5	40	0	0	0	1 liver cyst adenoma
7	50	1000	22	0	0	1(spleen)	1 tumour of adrenal glomerulosa
8	5	1000	19	0	0	0	0
9	50	50	30	0	0	1(spleen)	1 malignant lymphoma
10	5	5	40	0	0	0	1 malignant lymphoma with leukaemia 1 ovarian adenocarcinoma 1 cyst adenoma of bile duct
11	0	0	35	0	0	0	0
12	0	0	18	1	6	1(liver)	0

animals died during the study. An increase in the weight of the liver was observed as compared to the controls. This author concluded that stearic acid was practically non-toxic by the oral route and lacked any cumulative effects. In contrast to oral dosing, stearic acid is highly toxic to mammals when administered intravenously. The intravenous LD50 for stearic acid to rats and mice are 22 and 23 mg/kg, respectively (NIOSH, 1977). Cats are affected by an intravenous dose as low as 5 mg/kg (NIOSH, 1977).

c. Acintol (Tall Oil)

No mammalian toxicological data for acintol was found in the literature search. The components of acintol, abietic acid, linoleic and oleic acid, primaric acid have a low systemic toxicity to mammals. However, they are irritating to the skin and mucous membranes (Hawley, 1977; Windholz, 1976).

d. Polyethylene

Polyethylene is normally considered an inert material. However, implants of polyethylene have been shown to cause neoplasms probably due to unreacted monomer or small amounts of catalysts. In rats, neoplasms were observed at 2120 mg/kg and at 330 mg/kg in mice (NIOSH, 1977).

2. Environmental Fate of AC-656 Polyethylene Emulsion Components

A review of the available literature yielded many research experiments which demonstrated that N-nitrosomorpholine can be synthesized from morpholine in the environment or *in vivo*. This potential reaction is of major importance to this study due to the unusual characteristics of the Holston AAP effluents. These effluents contain high nitrite/nitrate levels along with potential nitrosation catalysts such as formaldehyde. Therefore, information on N-nitrosomorpholine and its effect on the environment is essential.

Fan and Tannenbaum (1973) studied the factors influencing the rate of formation of N-nitrosomorpholine from morpholine and sodium nitrite. The factors studied included temperature, pH and the composition of the reaction medium. The results of their studies are shown in Figures V-8, V-9 and V-10. As evidenced from the figures, the nitrosation reaction proceeds most rapidly at pH 3.5. The presence of potassium thiocyanate (KSCN) has an effect of increasing the rate of nitrosation at lower pH values. Increasing the temperature also increases the rate of formation of N-nitrosomorpholine. These results are confirmed by other investigators. Ziebarth (1974) reported a 100% yield of N-nitrosomorpholine when 0.02 mole/l morpholine and 0.04 mole/l sodium nitrite were combined at 37°C, pH ~3.0 for 6 hours. In the presence of ascorbic acid or phenolic compounds, the nitrosation of morpholine is prevented for the most part. Table V-12 lists the effectiveness of five compounds against morpholine nitrosation (Mirvish, 1975).

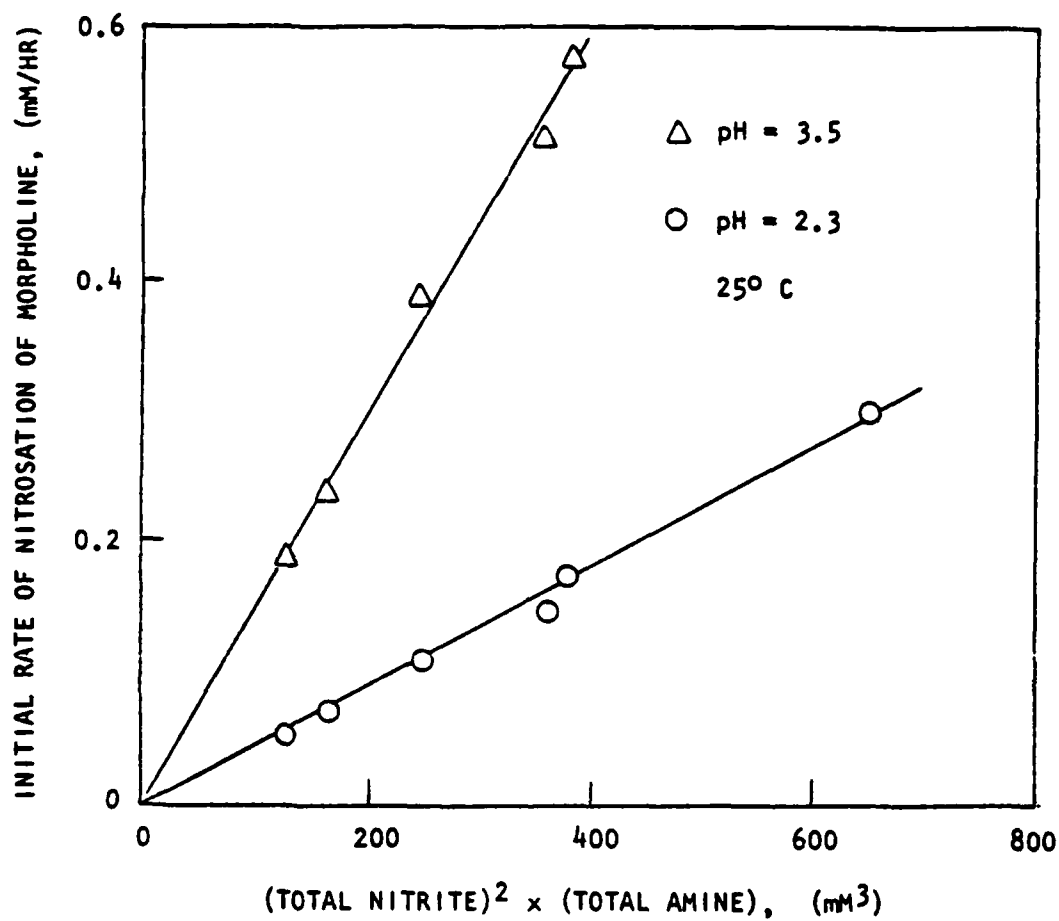


Figure V-8. Third-Order Rate Plot for Nitrosation of Morpholine
(Fan and Tannenbaum, 1973)

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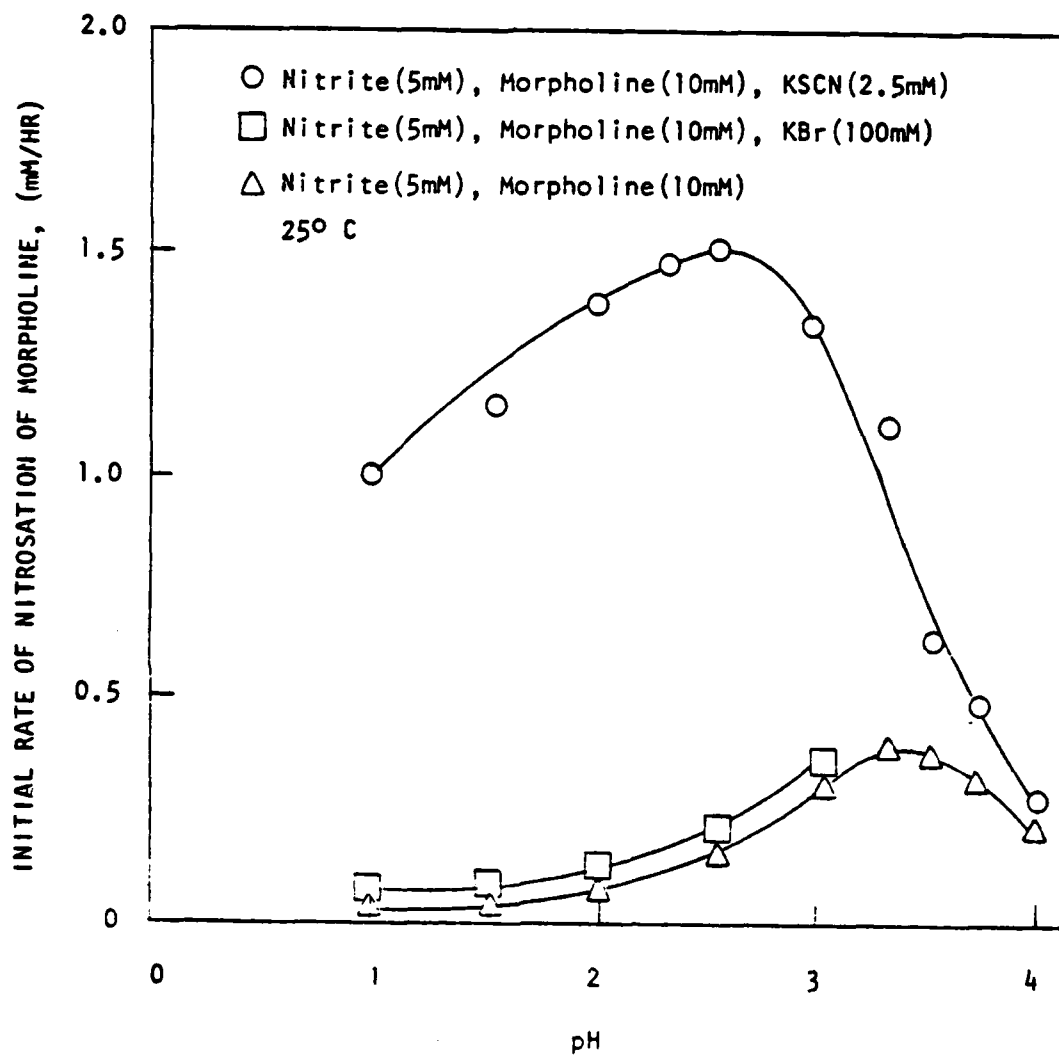


Figure V-9. Initial Rate of Nitrosation of Morpholine with Nitrite, pH Dependency, and Influence of Certain Ions (Fan and Tannenbaum, 1973)

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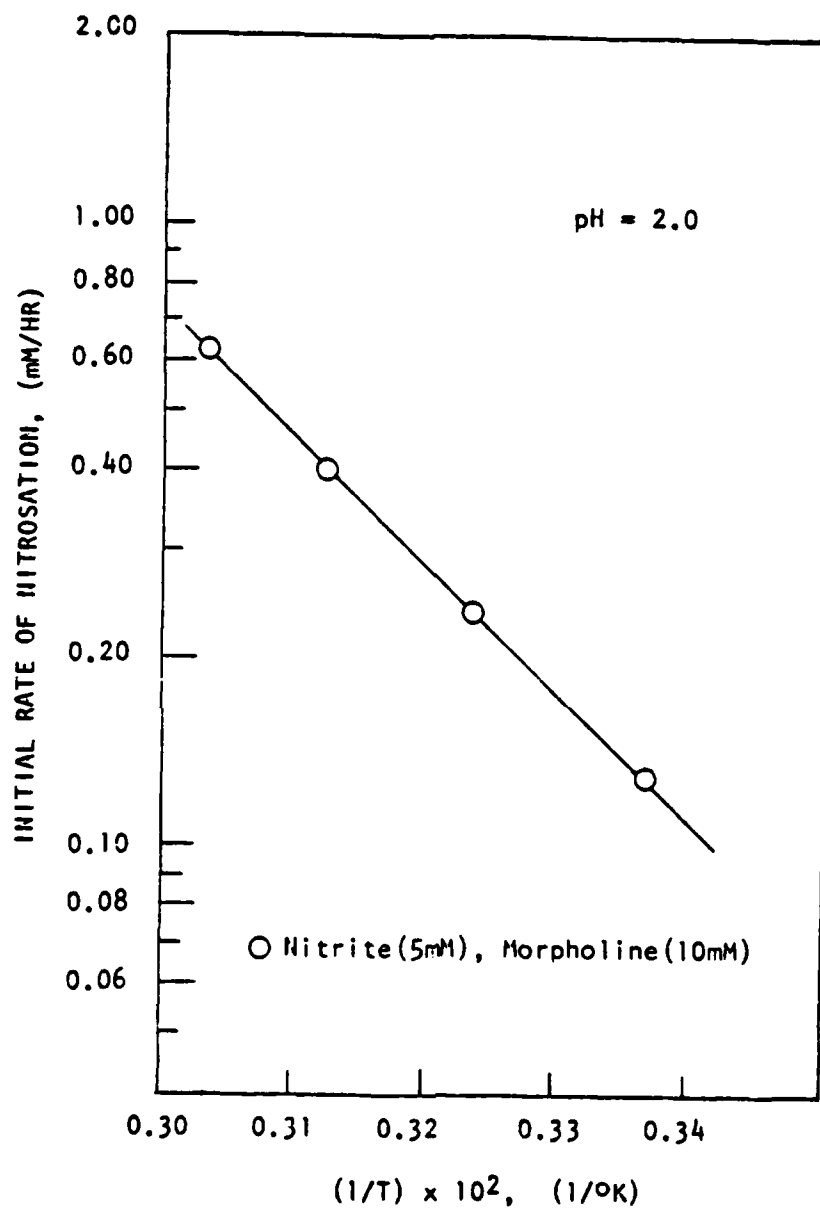


Figure V-10. The Effect of Temperature on the Nitrosation of Morpholine (Fan and Tannenbaum, 1973)

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Table V-12. Blocking Morpholine Nitrosation by Five Compounds
(Mirish, 1975)

pH	Yield in controls (%) ^b	Conc. of blocking agent (mM) ^c	Percentage of blocking			Tannic acid		
			Sodium ascorbate	Gallic acid	Sodium sulfite	Cysteine	Conc (g/liter)	Percent blocking
Morpholine nitrosation ^d								
1	2	20	89	99	100	77	4 ^e	42
2	13	20	90	96	96	93	4	78
3	43	20	97	97	86	95	4	66
3	39	10	61	95	65	56	2	49
3	41	5	28	75	41	27	1	29
4	31	20	100	96	100	100	4	80

^b Nitrosamine yield as percentage of amine in runs without blocking agent.

^c Except for tannic acid.

^d Conditions: 10 mM morpholine, 20 mM nitrite, 25 C. 90 min.

^e [Tannic acid] approximately = [gallic acid] in g/liter.

3. Toxicity to Aquatic Organisms

The formulation of A-3 explosives at Holston AAP will result in losses to the environment of several of the emulsion components and associated salts. Expected losses at full mobilization production of A-3 were discussed in Section E and Figure V-7. Estimated full mobilization production effluent concentrations of morpholine, acintol and magnesium and barium salts in the Holston River are presented in Table V-13.

The toxicity of the individual components of the AC-656 emulsion to aquatic organisms are presented in Table V-14. No aquatic toxicity data on N-nitrosomorpholine were found in this literature search.

All of these compounds have a low toxicity to aquatic organisms. Barium chloride is the most toxic with a concentration of 8 ppm causing a 16% reproduction impairment in *Daphnia magna*. No aquatic toxicity data were available for acintol.

In the effluent ditch, all the emulsion components will be toxic to aquatic organisms. However, once the chemicals are mixed with 10% of the Holston River flow, they pose only a minor toxic threat to aquatic organisms.

4. Toxicity to Microorganisms

Bringmann and Kuehn (1976) reported that inhibition of cell multiplication for *Pseudomonas putida* started at exposure to 310 mg/l morpholine. Inhibition of cell multiplication in algae (*Microcystis aeruginosa*) started at exposure to 1.7 mg/l morpholine.

Morpholine was found to be non-mutagenic to *Salmonella typhimurium* TA 1950 in the host-mediated assay in doses ranging from 1,450 to 2,900 μ moles/kg. However, N-nitrosomorpholine was mutagenic at doses of 8.62 μ moles/kg (Braun *et al.*, 1977).

No specific references to the toxicity of stearic acid to microorganisms was encountered. Mascherpa and Secchi (1969), while studying the oxygen uptake by different bacterial suspensions in the presence of long-chain fatty acids, reported that oxygen consumption *in vitro* increased with the addition of sodium salts of stearic acid to four strains of *Micrococcaceae* under aerobic conditions. A high oxygen consumption was noted with stearic acids by *Micrococcus* D10 (about 30% more than controls).

5. Phytotoxicity

No phytotoxic data on morpholine was found in the literature; however, Sander *et al.* (1975a, b) studied the effect of N-nitrosomorpholine in a series of experiments with cress plants (*Lepidium sativum*). N-nitrosomorpholine was supplied in an aqueous solution (20 mg/5l) to the roots for

Table V-13. Estimates of Levels of Emulsion Components in the Final Effluent and the Holston River at Full Mobilization

Source	MgCl ₂ , MgSO ₄ (ppm as Mg ⁺⁺)	Acintol (ppm)	Morpholine (ppm)	BaCl ₂ (ppm as Ba ⁺⁺)
Final Effluent	318	4100	4100	49
Holston River (2070 mgd)				
10% mixing	.031	.40	.4	.005
100% mixing	.0035	.047	.047	.0006

Table V-14. Toxicity of Morpholine, Magnesium Chloride and Barium Chloride to Aquatic Organisms

Chemical	Concentration (ppm)	Organism	Effect	Reference
Morpholine	10	Bluegill Sunfish	96 hr LC ₅₀	Dawson et al., 1975/77
"	350	" "	96 hr LC ₅₀	" "
"	560	" "	48 hr LC ₁₀₀	" "
Magnesium Chloride	140 as Mg ⁺⁺	<i>Daphnia magna</i>	48 acute LC ₅₀ (without food)	Biesinger and Christensen, 1972
"	322 as Mg ⁺⁺	" "	48 hr acute LC ₅₀ (with food)	" "
"	190 as Mg ⁺⁺	" "	3 week chronic LC ₅₀	" "
"	125 as Mg ⁺⁺	" "	50% reproductive impairment	" "
"	82 as Mg ⁺⁺	" "	16% reproductive impairment	" "
Barium Chloride	14.5 as Ba ⁺⁺	<i>Daphnia magna</i>	48 hr acute LC ₅₀	" "
"	13.5 as Ba ⁺⁺	" "	3 week chronic LC ₅₀	" "
"	8.9 as Ba ⁺⁺	" "	50% reproductive impairment	" "
"	5.8 as Ba ⁺⁺	" "	16% reproductive impairment	" "

17-20 hours. Upon analysis of the green plant material, 0.5-13% of the nitrosoamine was detected. These concentrations fell rapidly (within 3-4 days) to trace levels when the nitrosoamine supply was removed and replaced by fresh water.

Absorbed nitrosamines apparently do not accumulate in green plant material but very little is known about the breakdown in plants or of the toxicological significance of the metabolites (Sander *et al.*, 1975a,b).

I. Regulations and Standards

There are no U.S. effluent or industrial hygiene regulations or standards for polyethylene emulsion AC-656. However, there is a standard for morpholine in air of 20 ppm (Federal Register, 1974).

J. Conclusions and Recommendations

Polyethylene emulsion AC-656 is a new product that is being tested for use as a desensitizer for A-3 explosives produced at Holston AAP. Currently, this emulsion is used in pilot quantities, however, at full mobilization, Holston AAP would require 2,000,000 lb of the AC-656 emulsion per year. AC-656 polyethylene emulsion is specially formulated for the Army by Chemical Corporation from commonly used chemicals. Thus, the civilian pollution resulting from the manufacture and use of the emulsion components is widespread.

At first glance, pollution resulting from the use of AC-656 emulsion at Holston AAP would appear to be of little significance. However, the effluents from Holston AAP are unique in that they contain large quantities of nitrites and nitrates, acid pH, as well as materials (e.g. formaldehyde, salts) which can act as nitrosation catalysts for the formation of N-nitrosomorpholine. Thus, there exists a high probability that N-nitrosomorpholine (a potent carcinogen) is formed in significant quantities in these wastes. Therefore, a Phase II study on the toxicological and environmental hazards of polyethylene emulsion AC-656 should be undertaken. This study should concentrate on the morpholine constituent of the emulsion.

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PRELIMINARY PROBLEM DEFINITION STUDY ON
MUNITIONS-RELATED CHEMICALS
DI(2-ETHYLHEXYL)SEBACATE

SUMMARY

Di(2-ethylhexyl)sebacate is a plasticizer that was used by Holston AAP in C-4 products. Due to the rising prices of this plasticizer, it has been replaced by dioctyl adipate. Thus, there are no current uses of di(2-ethylhexyl)sebacate in Army munitions production.

The civilian community is also phasing out the use of di(2-ethylhexyl)sebacate. Production of this ester has dropped from 3.22 million lb in 1973 to 1.88 million lb in 1977. Future uses of di(2-ethylhexyl)sebacate by the civilian community are dependent on the price of this plasticizer in comparison with other available low temperature PVC plasticizers.

Di(2-ethylhexyl)sebacate is toxic to mammals only when given in high doses (g/kg). In the environment, it is readily degraded and thus poses no long term environmental hazards.

In view of the discontinued use of di(2-ethylhexyl)sebacate in Army munitions production, no further Army sponsored studies on this compound are recommended.

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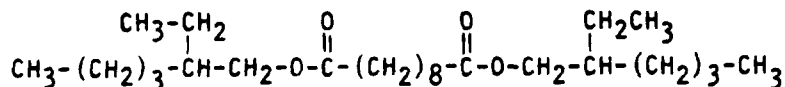
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VI. DI(2-ETHYLHEXYL)SEBACATE

A. Alternate Names

Di(2-ethylhexyl)sebacate is a long chain dicarboxylic acid ester with the molecular formula $C_{26}H_{50}O_4$ and the corresponding molecular weight of 426.69 g/mole. Its structural formula is:



Other pertinent alternate names for di(2-ethylhexyl)sebacate are listed below:

CAS Registry No.:	122-62-3
Replaces CAS Reg.:	28986-40-5
CA Name (8CI):	Sebacic Acid, bis(2-ethylhexyl)ester
CA Name (9CI):	Decanedioic acid, bis(2-ethylhexyl)-ester
Wiswesser Line Notation:	4Y2&10V8VOY4&2
Synonyms:	Bis(2-ethylhexyl)sebacate; Dioctyl sebacate; Bis(2-ethylhexyl)decanedioate; Bis(ethylhexyl)sebacate; Di-(2-ethylhexyl)sebacate; Decanedioic acid; Bis-(2-ethylhexyl)ester; Bisoflex DOS; Monoflex DOS; Octoil S; Staflex DOS; Plexol; Bisoflex Reolube DOS; Plexol 201J; Plexol 201

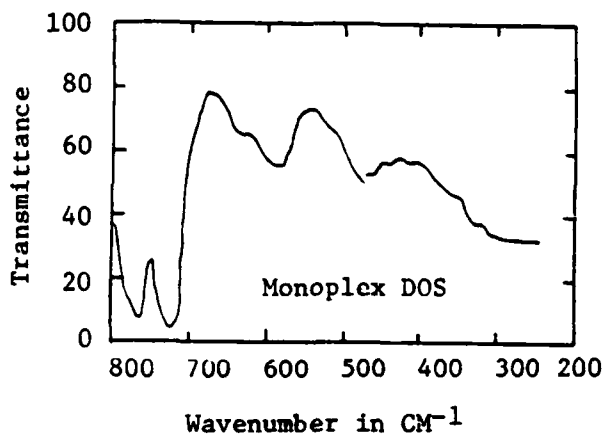
B. Physical Properties

The physical properties of di(2-ethylhexyl)sebacate are listed in Table VI-1. The infrared spectrum of di(2-ethylhexyl)sebacate is presented in Figure VI-1.

Table VI-1. Physical Properties of Di(2-ethylhexyl)sebacate*

Physical Form at 20°C:	liquid
Color:	pale yellow-brown
Refractive Index at 28°C:	1.447
Boiling Point:	248°C @ 4 mm Hg
Freezing Point:	-55°C
Flash Point (COC):	410°F
Autoignition Point (COC):	468°F
Saponification No.:	263
Weight:	7.57 lb/gal
Specific Gravity:	0.91 at 25°C
Viscosity:	25 centipoise
Solubility:	Soluble in acetone, isopropanol n-butanol, vegetable oil, mineral oil, toluol. Insoluble in water.

* Union Camp Corp, 1976



Preparation: MIR : film
FIR : 0.21 mm cell

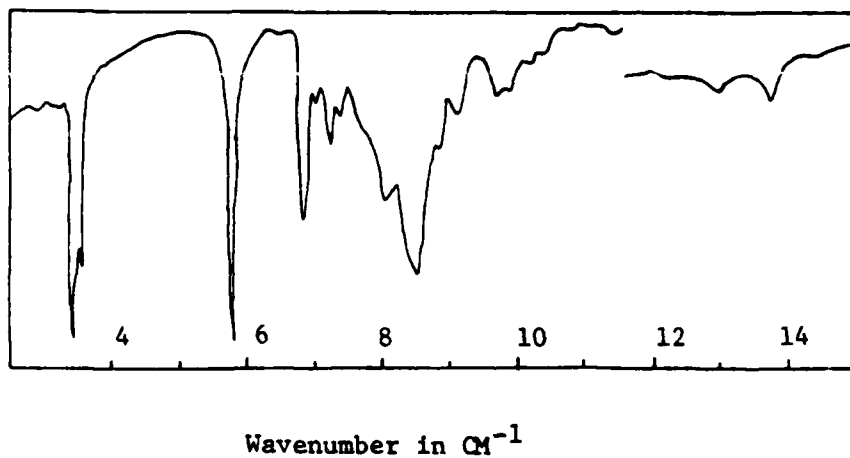


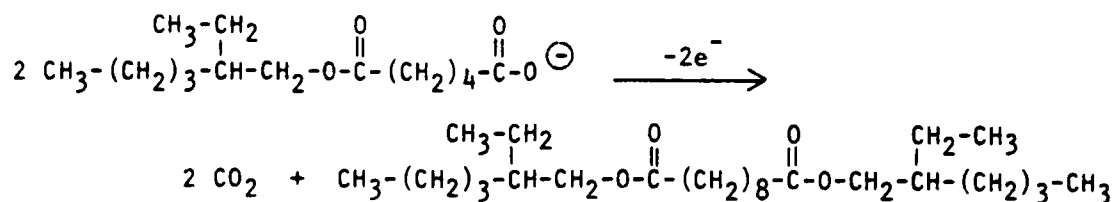
Figure VI-1. Infrared Spectrum of Di(2-ethylhexyl) sebacate
(Hummel, 1966)

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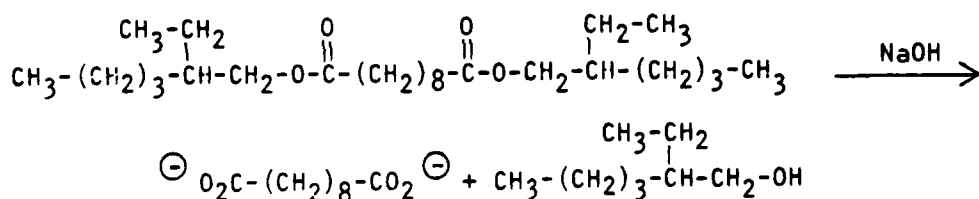
C. Chemical Properties

1. General Chemistry

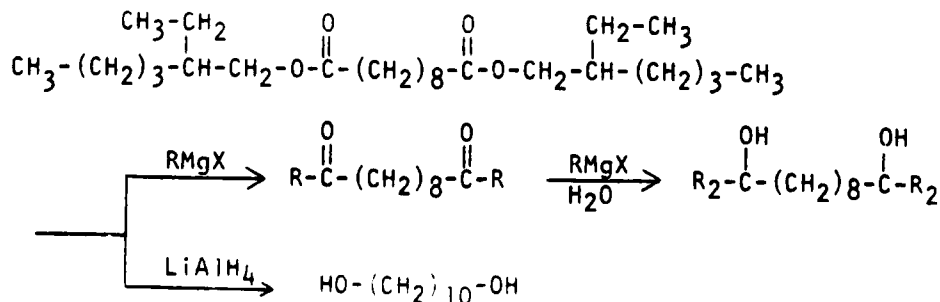
Di(2-ethylhexyl)sebacate can be synthesized by treating sebacic acid with 2-ethylhexanol and an acid catalyst (Kirk and Othmer, 1965). Di(2-ethylhexyl)sebacate can also be produced by the electrolysis of the mono-2-ethylhexyl ester of adipic acid.



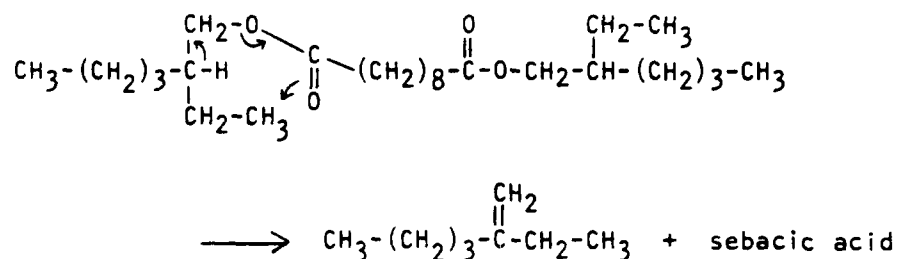
Although little has been published regarding the chemistry of di (2-ethyl)sebacate, it is expected to behave as a typical ester. As the main functionality is its ester carbonyl, nucleophilic substitution reactions should occur. Saponification of di(2-ethylhexyl)sebacate has been reported (Braun, 1965) and



acid catalyzed hydrolysis should likewise occur. With strong nucleophiles such as Grignard reagents or metal hydrides, both nucleophilic substitution and addition should occur.



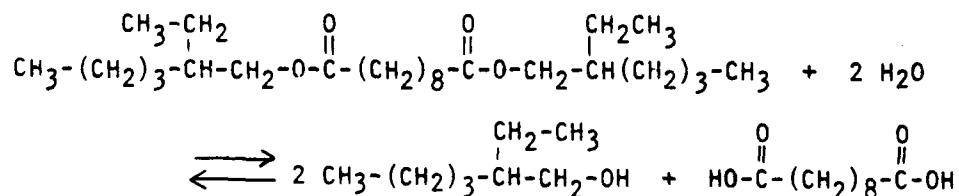
Thermal decomposition of di(2-ethylhexyl)sebacate gives sebacic acid and 3-methylene heptane (Zil'berman *et al.*, 1965; Klaus *et al.*, 1970):



Oxidation of either the ester or the resultant acid is likely to give a homologous series of dicarboxylic acids. Oxidation at elevated temperatures up to 190°C also results in decomposition of the alcohol function yielding 3-heptanone as the major product (Malmberg and Weinstein, 1959).

2. Environmental Chemistry

Acid and base catalyzed hydrolysis is expected to be the predominant environmental reaction:



The alcohol and acid produced should be readily degraded in the environment either chemically or microbially.

3. Sampling and Analysis

Di(2-ethylhexyl)sebacate has been analyzed by gas chromatography. A 20% silicone grease/chromsorb W column was employed by Esposito (1963). An oven temperature of 210°C and a thermal conductivity detector was used. Krishen (1971) employed a 10% UCW-98/Diaport S column programmed between 100 and 330°C with a flame ionization detector. No lower detection was given in either of these studies.

D. Uses in Army Munitions

1. Purpose

Di(2-ethylhexyl)sebacate is used at Holston AAP as a plasticizer in the manufacture of the C-4 explosive formulation. C-4 products consist of 89.9 - 91.0% RDX, 0.2% dye (90% lead chromate and 10% lamp black) and the remainder a binder material. The binder used in the C-4 formulation in the past was a mixture of polyisobutylene and di-2-ethylhexyl sebacate or di(2-ethyl)adipate. In recent years, dioctyl adipate has replaced these materials as it is less expensive and provides a satisfactory product.

2. Quantities Used

a. Historical Use

The quantities of C-4 explosive produced during the 1967-1977 period are given below, in 1000 lb.

<u>1967</u>	<u>1968</u>	<u>1969</u>	<u>1970</u>	<u>1971</u>	<u>1972</u>	<u>1973</u>	<u>1974</u>	<u>1975</u>	<u>1976</u>	<u>1977</u>
6,373	11,184	6,860	4,650	4,661	2,475	2,579	1,978	1,670	-	137

The di(2-ethylhexyl)sebacate component comprised about 5.3% of the C-4 mix (Dobratz, 1974). Thus, the amount of di(2-ethylhexyl)sebacate used ranged from zero in 1976 to 593,000 lb in 1968.

b. Current Use

No di(2-ethylhexyl)sebacate is currently in use, as it has been replaced by dioctyl adipate in the C-4 formulation.

c. Use at Full Mobilization

The mobilization rate of production of C-4 explosives is 6,060,000 lb/yr. This amount would require about 300,000 lb/year of dioctyl adipate as a plasticizer in the binder component of the formulation.

3. Documented or Speculated Occurrences in Air and Water

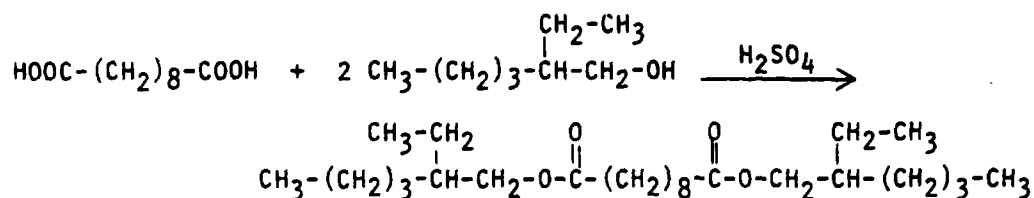
At the highest production rates of C-4 explosives in 1968, losses of di(2-ethylhexyl)sebacate from production operations were estimated to be in the 250-500 lb/month range. The average loss during the 1967-1979 period is estimated at 100-200 lb/month. Since 1975, there has been no use or loss of di(2-ethylhexyl)sebacate at Holston AAP. No future use is currently anticipated. Losses of dioctyl adipate are expected, however. Based upon the 1977 production rate of C-4 explosives, dioctyl adipate losses of 3-6 lb/month were probable. At full mobilization, dioctyl adipate losses would increase to 120-240 lb/month.

Currently all Holston AAP area B wastes enter the Holston River with no treatment. However, a three-stage biological treatment facility is under construction which will treat future wastes in an anaerobic tower, trickling filter and with activated sludge. This facility is designed to handle 12.5 MGD process effluent, the amount expected at full mobilization. Dioctyl adipate should be degraded in this treatment plant.

E. Uses in Civilian Community

1. Production Methodology

Di(2-ethylhexyl)sebacate is manufactured by esterification of decanedioic (sebacic) acid with 2-ethylhexyl alcohol in the presence of an acid catalyst (Union Camp Corp., 1979).



2. Manufacturers, Production and Capacity

Six United States manufacturers have facilities to manufacture di(2-ethylhexyl)sebacate. The manufacturers and their plant locations are given in Table VI-2.

Table VI-2. U.S. Manufacturers of Di(2-ethylhexyl)sebacate
(SRI International, 1978)

The C.P. Hall Co.*	Chicago, Ill.
Pitzer Inc., Chems. Div.*	Greensboro, N.C.
Reichhold Chems., Inc.	Carteret, N.J.
Rohm and Haas Co.*	Philadelphia, Pa.
Union Camp Corp. Chem. Products Div.	Dover, Ohio
United States Steel Corp.* USS Chems. Div.	Neville Island, Pa.

* Not currently producing di(2-ethylhexyl)sebacate

However, only two of the manufacturers are currently producing di(2-ethylhexyl)sebacate, Reichhold Chemicals, Inc. and Union Camp Corporation.

The U.S. production and sales of di(2-ethylhexyl)sebacate are presented in Table VI-3.

Table VI-3. Production and Sales of Di(2-ethylhexyl)sebacate
(U.S. Tarriff Commission, 1973-1977).

	1973	1974	1975-	1976	1977
Production (1000 lbs)	2860 (actual)	3220 (est.)	2358 (est.)	716 (est.)	1882 (est.)
Sales (1000 lbs)	2541 (actual)	-	-	365 (est.)	1761 (est.)

3. Usages

Di(2-ethylhexyl)sebacate is a plasticizer used with poly(vinyl chloride) (PVC) compounds requiring extreme low temperature flexibility. Due to its low toxicity, di(2-ethylhexyl)sebacate has been approved for food packaging films in combination with PVC polymers (Union Camp Corp, 1976). Other uses of di(2-ethylhexyl)sebacate as a plasticizer are in film and sheeting for low temperature use, low viscosity plastisols, electric insulation and strip coating compounds (Rohm and Haas, 1978). Di(2-ethylhexyl)sebacate is also used for jet turbine engine lubrication, high pressure lubricant and as a thinner for castor oil lubricants.

4. Future Trends

Production of di(2-ethylhexyl)sebacate has been reduced because of increased prices which has led many users to change plasticizers. If the high prices persist, production and use of this plasticizer are expected to remain depressed.

5. Documented or Speculated Occurrences in the Environment

No information on the release of di(2-ethylhexyl)sebacate into the environment was found in the literature search. Based on usual production and use losses, it is estimated that 1% of the di(2-ethylhexyl)sebacate produced is lost to the environment during manufacture and formulation. Thus at the 1977 production levels, ~18,820 lb/year of di(2-ethylhexyl)sebacate would enter the environment. Additional environmental contamination is expected from disposal of PVC polymers containing this material as a plasticizer.

F. Comparison of Civilian and Military Uses of Di(2-ethylhexyl)sebacate

The military and civilian community are both replacing di(2-ethylhexyl)sebacate with other plasticizers such as di(2-ethylhexyl) adipate. The declining use of this plasticizer is a result of high prices. Due to the phasing out of this compound from use in military explosives, di(2-ethylhexyl)sebacate is not an Army problem pollutant.

G. Toxicological and Environmental Hazards

1. Toxicity to Mammals

The data on the acute toxicity of di(2-ethylhexyl)sebacate to mammals and presented in Table VI-4. The data indicate a low toxicity of the compound to mammals.

Table VI-4. Acute Mammalian Toxicity of Di(2-ethylhexyl)sebacate

<u>Animal</u>	<u>Administration</u>	<u>Dose</u> g/kg	<u>Effect</u>	<u>Reference</u>
Rat	Oral	5.0	No effect	Wallace (1976)
Rat	Oral	1.28	LD50	NIOSH (1977)
Rat	Intravenous	0.90	LD50	"
Rabbit	Intravenous	0.54	LD50	"

Carson *et al.* (1961) found that heated decomposition products of di(2-ethylhexyl)sebacate were toxic to rats and dogs when the oils were pyrolyzed at 1020°F. The products were found to be eye and lung irritants.

2. Aquatic Toxicity

No information was found on the toxicity of di(2-ethylhexyl)sebacate.

3. Toxicity to Microorganisms

Hitz *et al.* (1967) studied the resistance of plasticized PVC to decomposition by fungi and bacteria. It was reported that di(2-ethylhexyl)sebacate was easily biodegradable, with deterioration by bacteria proceeding more quickly than by fungi. Weight-loss determinations showed 70 - 80% loss of the degradable plasticizer. Evidence was presented by Hoet and Stanier (1970) that *Pseudomonas fluorescens* metabolizes the higher homologs of the saturated dicarboxylic acids by β -oxidation, mediated by a specific series of inducible enzymes. The initial step in sebacic acid metabolism is the formation of the corresponding CoA-ester which is mediated by a single inducible thiokinase.

4. Phytotoxicity

No specific information on di(2-ethylhexyl)sebacate phytotoxicity was found. Goris and Bouriquet (1969) investigated the effects of sebacic acid on the growth and carbohydrate composition of carrot tissues *in vitro*. Carrot tissue grown for 60 days on a basic nutrient medium with .01 - 100 mg/l sebacic acid was not significantly influenced when compared to controls. Carbohydrate metabolism appeared unaffected.

5. Environmental Fate of Di(2-ethylhexyl)sebacate

Upon release into the environment di(2-ethylhexyl)sebacate should undergo chemical and microbial hydrolysis. The hydrolysis products, sebacic acid and 2-ethylhexyl alcohol, should be readily degradable.

6. Availability of Literature for Phase II

Several studies have been undertaken to determine the toxicity of di(2-ethylhexyl)sebacate to mammals. Thus, there is sufficient information on the mammalian toxicity of di(2-ethylhexyl)sebacate. A limited amount of literature on the environmental hazards of di(2-ethylhexyl)sebacate is available.

II. Regulations and Standards

There are no OSHA or EPA regulations specific for di(2-ethylhexyl)sebacate.

I. Conclusions and Recommendations

Di(2-ethylhexyl)sebacate poses very little toxicological or environmental hazards. This compound is toxic only in large doses (g/kg). Evidence shows that it is readily degraded in the environment and therefore poses only a short-lived environmental hazard.

The use of di(2-ethylhexyl)sebacate has declined in recent years due to high prices and the availability of cheaper substitute plasticizers. Holston AAP has joined many of the civilian users of di(2-ethylhexyl)sebacate and has changed its C-4 formulation to dioctyl adipate instead of di(2-ethylhexyl)sebacate. Thus, the Army no longer uses di(2-ethylhexyl)sebacate in its munitions. Only drastic reversal of prices would bring di(2-ethylhexyl)sebacate back into use in Army munitions. Therefore, di(2-ethylhexyl)sebacate is not a military problem chemical. It is recommended that no further Army sponsored studies on this chemical should be conducted unless it returns to high usage in munitions.

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PRELIMINARY PROBLEM DEFINITION STUDY ON
MUNITIONS-RELATED CHEMICALS
N-BUTYL ACETATE

SUMMARY

n-Butyl acetate is an ester which is used in lacquer coatings and as a solvent. The civilian production of n-butyl acetate is ~100 million lb/year. In the past, n-butyl acetate has been used as a solvent in explosives formulations and as an azeo-entrainer at Holston AAP. Holston AAP no longer uses n-butyl acetate for these purposes. Other Army Ammunitions Plants use paints which contain n-butyl acetate. However, none of the raw chemical is purchased by these plants.

n-Butyl acetate exhibits a low toxicity to mammals. The main effects of exposure are irritation of the eyes and respiratory passages and narcosis. The toxicity of n-butyl acetate to aquatic organisms is moderate with LD50's in the 100 ppm range. In the environment, n-butyl acetate is readily degraded by chemical, photochemical and microbial mechanisms. Thus, this chemical does not pose a long term environmental hazard.

Based on the limited amount of n-butyl acetate now used by the Army, any further Army sponsored studies on this compound should be a low priority.

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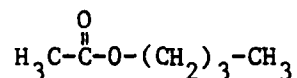
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VII. n-BUTYL ACETATE

A. Alternate Names

n-Butyl acetate is a sweet smelling, colorless ester with a molecular formula of $C_6H_{12}O_2$ and corresponding molecular weight of 116.16. The structural formula of n-butyl acetate is:



Other alternate names for n-butyl acetate are listed below:

CAS Registry:	123-86-4
CA Name (8CI);	Acetic acid, butyl ester
Wiswesser Line Notation:	40 V 1
Synonyms:	Butyl acetate; n-Butyl acetate; 1-Butyl acetate; Butyl ester; Butyl ethanoate

B. Physical Properties

The physical properties of n-butyl acetate are listed in Table VII-1. The infrared spectrum and NMR Spectra of n-butyl acetate are shown in Figures VII-1 and VII-2, respectively.

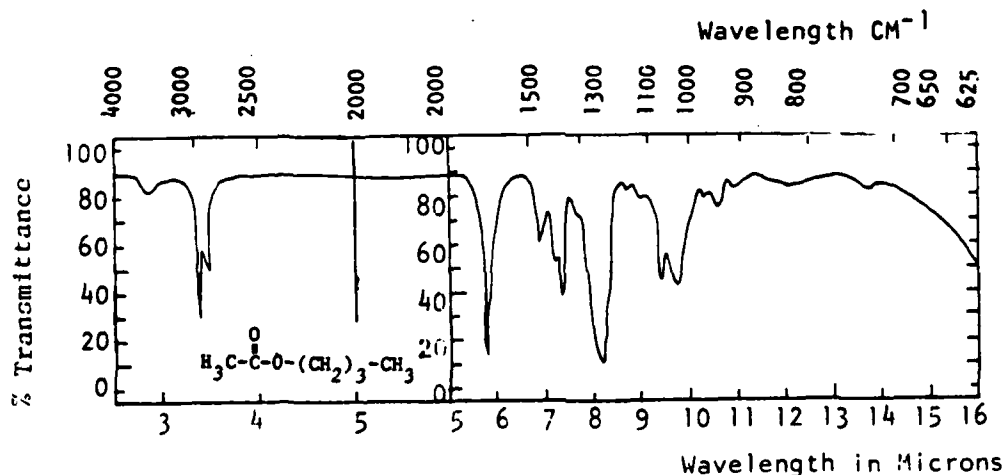


Figure VII-1. Infrared Spectrum of n-Butyl Acetate
(Pouchert, 1970)

Table VII-1. Physical Properties of n-Butyl Acetate*

Physical form @ 20°C:	liquid
Color:	colorless
Odor:	sweet, fruity
Melting Point:	-75°C
Freezing Point:	-76.8°C
Boiling Point:	126.3°C @ 760 mmHg
Vapor Pressure:	8.7 mmHg @ 20°C
Vapor Density (Air=1):	4
Flash Point:	24.4°C closed cup
Flash Point:	36.6°C open cup
Autoignition Temperature:	421.1°C
Lower Flammability Limit:	1.7 vol %
Upper Flammability Limit:	7.6 vol %
Heat of Combustion:	-3.054 X10 ⁷ J/kg
Heat of Formation:	-5.7 kcal/mole
Heat of Vaporization:	139 btu/lb
Heat Capacity:	1992.0 J/kg
Critical Temperature:	579.1°C
Critical Pressure:	3.1 X10 ⁶ N/m ²
Density of Liquid:	0.870 g/ml
Viscosity of Liquid:	0.75 cP
Refractive Index n_D^{20} :	1.3951
Surface Tension in Air:	24.0 dynes/cm
Coefficient of Cubic Expansion:	1.13 X10 ⁻³ /C° @ 20°
Solubility in Water:	0.70 wt %
Weight:	7.35 lb/gal @ 68°F

*Hawley, 1977; Celanese Chemical Co., Inc.; Kirk and Othmer, 1965; Windholz, 1976

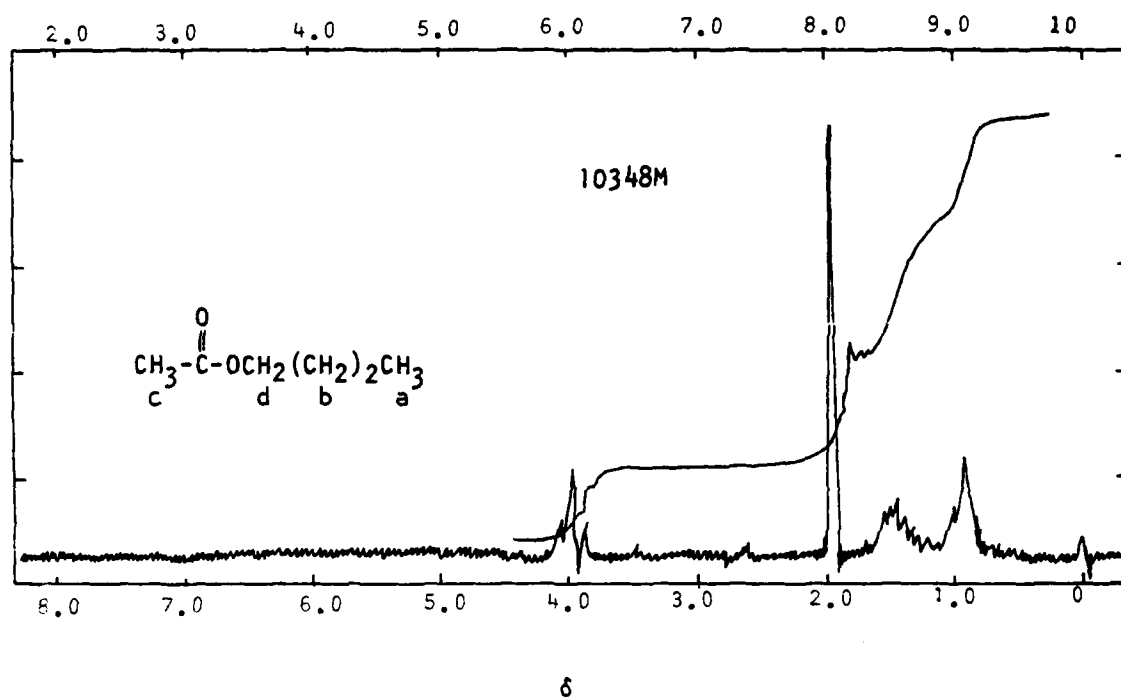
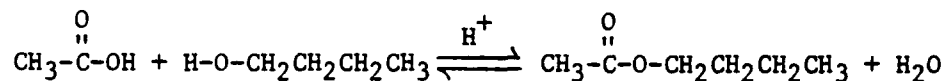


Figure VII-2. NMR Spectrum of n-Butyl Acetate
© Sadtler Research Laboratories, Inc. (1967)

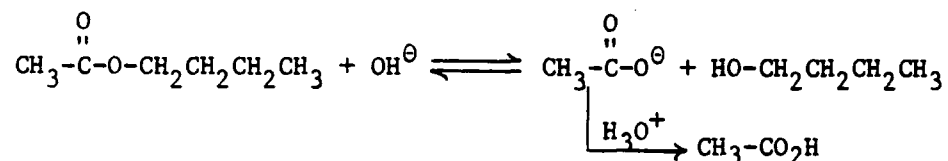
C. Chemical Properties

1. General Reactions

n-Butyl acetate is an ester produced by the acid catalyzed condensation of acetic acid and n-butanol (Lowenheim and Moran, 1975):

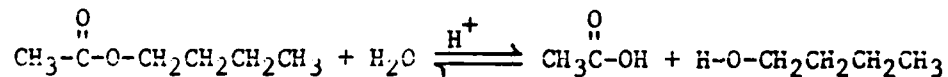


As an ester, n-butyl acetate is prone to nucleophilic substitution reactions. For example, alkaline hydrolysis or saponification has been reported (Pan *et al.*, 1962):

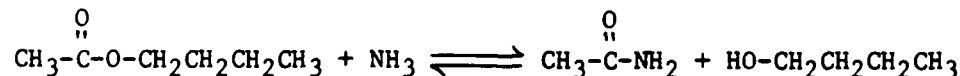


Other nucleophilic reactions typical of aliphatic esters (Morrison and Boyd, 1973) which expected for n-butyl acetate include:

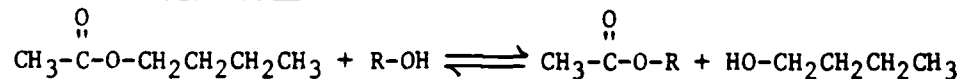
acid hydrolysis:



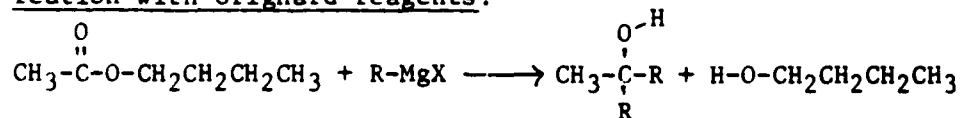
ammonolysis:



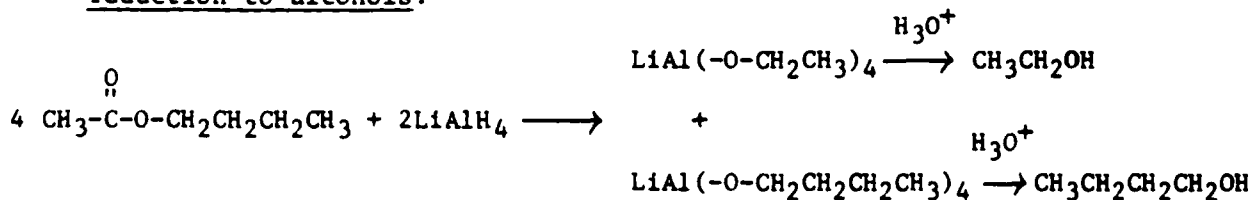
transesterification:



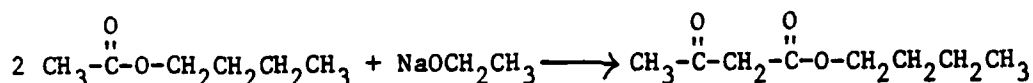
reaction with Grignard reagents:



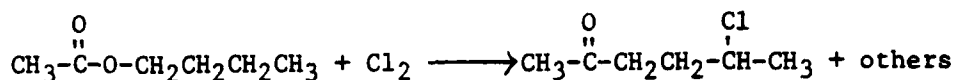
reduction to alcohols:



and the Claisen condensation:

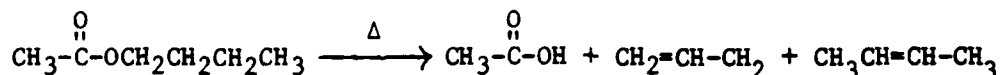


Chlorination of n-butyl acetate leads to a mixture of the 4 possible (chlorobutyl) acetates

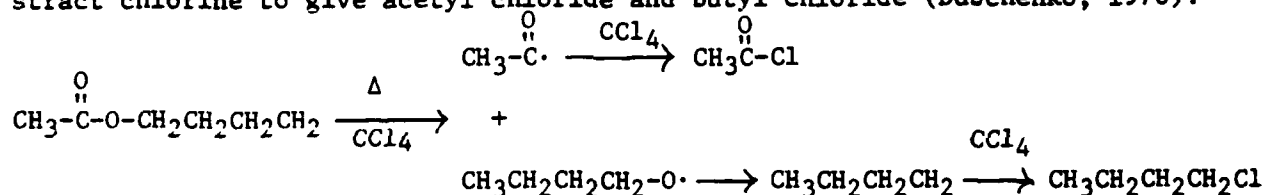


(Soumillion and Bruylants, 1969).

Pyrolysis of n-butyl acetate results in acetic acid and a mixture of 1- and 2-butenes (Scheer *et al.*, 1963; Lachowicz and Taniewski, 1969).

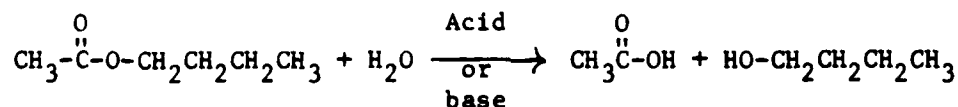


Pyrolysis with CCl_4 over carbon yields acetyl and butyl radicals which abstract chlorine to give acetyl chloride and butyl chloride (Dubchenko, 1970):

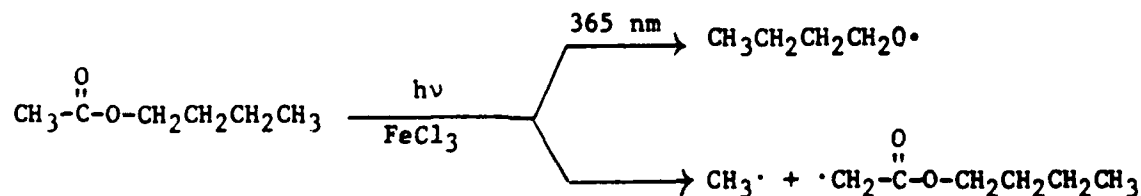


2. Environmental Reactions

In the aqueous environment the most likely reaction for n-butyl acetate would be hydrolysis:



The photochemistry of n-butyl acetate has been reported by Ivanitskaya and Kryubov (1973). With irradiation at 365 nm at 77°K, butoxy radicals were observed by E.S.R. while with visible light, methyl and carbobutoxymethyl radicals were observed:



These radicals would probably react with water yielding butanol, methanol, acetic acid and other lower alcohols and carbonyl compounds.

3. Sampling and Analysis

There have been numerous reports concerning analysis for n-butyl acetate. Gas chromatography or gas chromatography/mass spectroscopy seem to be most applicable. n-Butyl acetate has been detected in atmospheric samples by adsorption on activated carbon followed by desorption with carbon disulfide. Analysis was performed by gas chromatography using a flame ionization detector. A 10% FFAP on Chromosorb W column was employed with a column temperature of 100-150°C (Fraust and Hermann, 1966). Atmospheric n-butyl acetate has also been sampled by adsorption on Polysorbimide-1 and Carbochrom K-5 (Ioffi *et al.*, 1977) and Tenax GC and Carbopack BHT (Holzer *et al.*, 1977). In the former, organics were thermally desorbed onto a cooled copper capillary column treated with dinonyl phthalate and analyzed by gas chromatography/mass spectrometry. In the latter case, the n-butyl acetate was thermally desorbed onto a glass capillary column treated with OV-101. Oven temperatures were programmed between 20 and 200°C and mass spectral detection was employed as in the previous case. No lower detection limits were given in these papers of analysis of n-butyl acetate.

Other more traditional methods include determination of saponification equivalents and use of the infrared carbonyl bands in the 1750-1735 and 1300-1100 cm^{-1} regions (Kirk and Othmer, 1965).

D. Uses in Army Munitions

1. Purpose

n-Butyl acetate is not used as a component of any munitions formulations. Longhorn AAP and Lake City AAP use paints, lacquers and thinners which contain n-butyl acetate as a constituent. Neither facility purchases n-butyl acetate as a pure chemical.

In the past, n-butyl acetate was used at Holston AAP in the production of explosives. The n-butyl acetate served as a solvent for the binder materials. The explosive formulations which used n-butyl acetate were LX-10-2, LX-04-1 and PBX -N6. Recently, the n-butyl acetate has been replaced by isobutyl acetate. No n-butyl acetate is currently used at Holston AAP in explosives formulations.

Holston AAP also used n-butyl acetate as an azeotropic entrainer for dewatering acetic acid. n-Butyl acetate was used in the Area A azeo stills for ~1 year as a replacement for n-propyl acetate. n-Propyl acetate has been the azeo entrainer traditionally used for dewatering spent acetic acid from the RDX/HMX production at Holston AAP. n-Propyl acetate has several drawbacks which reduce its efficiency as an azeo entrainer and increase costs. Therefore, n-butyl acetate was evaluated as the azeo entrainer. However, contamination of the acetic acid with n-butyl acetate became a problem and the use of this solvent in the Area A azeo stills was discontinued.

2. Quantities Used

The quantities of paints containing n-butyl acetate used by Longhorn AAP and Lake City AAP are not known. The concentration of n-butyl acetate varies with the paint formulation and is also not known.

As noted, Holston AAP is no longer using n-butyl acetate in their explosives formulations. However, 6,800 lb of isobutyl acetate were used in 1978 as a replacement for n-butyl acetate.

When Holston AAP used n-butyl acetate in the Area A azeo stills, approximately ~500 lb/day were purchased as make-up solvent.

3. Documented or Speculated Occurrences in Air or Water

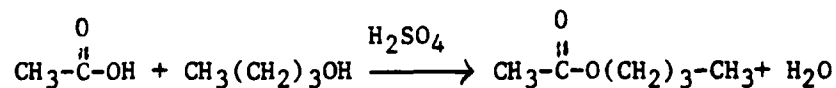
The primary source of n-butyl acetate in the environment at Longhorn AAP and Lake City AAP would be volatilization from freshly painted surfaces. It is estimated that total losses of n-butyl acetate to air in each facility would be less than 100 lb/year. Minor amounts (<10 lb/year) might also be lost to plant effluent streams through clean-up of painting materials.

No n-butyl acetate is lost at Holston AAP, as it is no longer used. During the previous use of this chemical in explosives formulation, it is estimated that about 6-12 lb/month were lost to the environment. During the period when n-butyl acetate was used in the Area A azeo stills, losses were approximately equal to the amount of make up solvent needed. Water effluent from the Area A azeo stills is pumped into an aerobic biotreatment pond. The microorganisms in the pond should have effectively removed any n-butyl acetate or its hydrolysis products, n-butanol and acetic acid, from the effluent. Thus, there were no significant amounts of n-butyl acetate entering the Holston River from the Area A azeo stills.

E. Uses in the Civilian Community

1. Production Methodology

n-Butyl acetate is formed by the esterification of acetic acid with n-butanol. The reaction is catalyzed by 0.1% sulfuric acid. The processing steps are shown schematically in Figure VII-3. The reaction proceeds according to the following equation:



The yield is reported to be 95%.

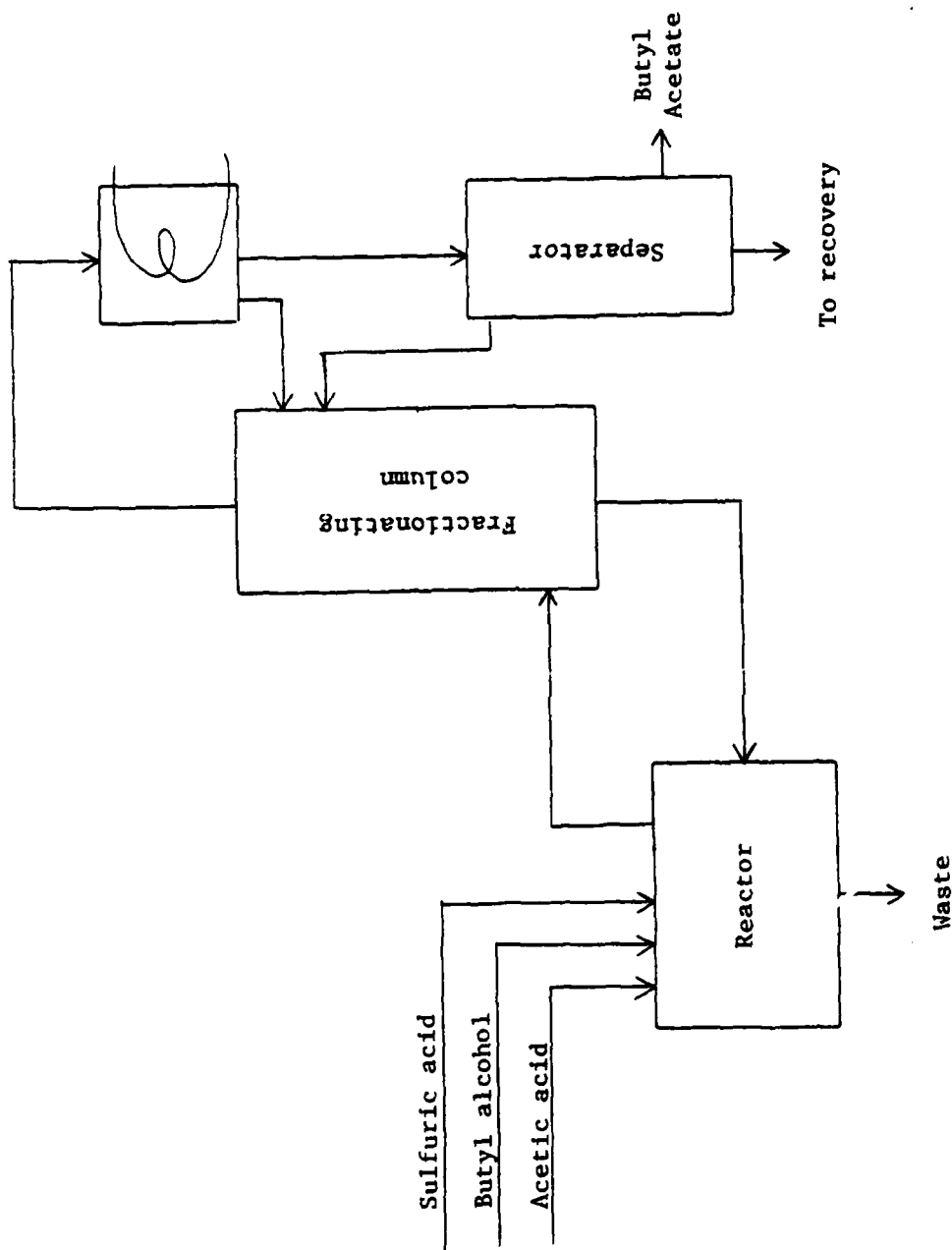


Figure VII-3. Production of n-Butyl Acetate
(Lowenheim and Moran, 1975)

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2. Manufacturers, Production and Capacity

The U.S. producers of n-butyl acetate and their capacities are listed in Table VII-2. The historical U.S. production and sales are presented in Table VII-3.

3. Usages

The primary uses of n-butyl acetate are in lacquer-type coatings, mainly nitrocellulose. Sixty percent of the n-butyl acetate produced in the United States are used in these coatings. The remaining 40% of the n-butyl acetate is used as a solvent.

4. Future Trends

n-Butyl acetate sales were in a slight decline over the years, 1965-1975. Production and sales in 1976 and 1977 have increased substantially. This growth is expected to continue for the next several years.

5. Documented or Speculated Occurrences in the Environment

n-Butyl acetate is a volatile solvent. Evaporation rates for this solvent have been determined experimentally. From a 44.15 cm^2 surface the rate of evaporation of n-butyl acetate was $1.75 \times 10^{-5} \text{ g/cm}^2\text{-sec}$ (RH=24%, P=750 mmHg) (Gilbert, 1971). Thus, significant quantities of n-butyl acetate are expected to enter the atmosphere each year from use of this compound as a solvent. Losses of n-butyl acetate to the atmosphere could be as large as 45 million lb/year.

F. Comparison of Civilian and Military Uses and Pollution

Civilian uses of n-butyl acetate are mainly in lacquer-type coatings and as a solvent. These uses consume over 110 million lb/year of this chemical. Pollution from civilian uses of n-butyl acetate occurs mainly through evaporation into the atmosphere. In contrast current military uses of n-butyl acetate are insignificant. Only minor quantities of this chemical are used. Pollution of n-butyl acetate from military uses is only a few lb/year.

G. Toxicological and Environmental Hazards

1. Toxicity to Mammals

Several studies have been conducted to determine the effects of acute exposure of n-butyl acetate to mammals. The results of these studies are summarized in Table VII-4.

Table VII-2. Manufacturers of n-Butyl Acetate and Their Capacities (SRI International, 1978)

			Annual Capacity (Millions of Pounds)
Celanese Corp.			
Celanese Chem. Co., div.	Bishop, Tex.		50
Eastman Kodak Co.			
Eastman Chem. Products, Inc. subsid.			
Tennessee Eastman Co.	Kingsport, Tenn.		45
Publicker Indust. Inc.	Philadelphia, Pa.*		15
Union Carbide Corp.			
Chems. and Plastics, div.	Institute and South Charleston, WV Texas City, Tex.		50
TOTAL			160

*Not currently producing

Table VII-3. Production and Sales of n-Butyl Acetate (U.S. Tarriff Commission, 1973-1977)

	<u>1973</u>	<u>1974</u>	<u>1975</u>	<u>1976</u>	<u>1977</u>
Production (1000 lbs)	81,050	77,218	80,341	112,508	114,291
Sales (1000 lbs)	90,746	68,994	77,570	98,409	109,797

Table VII-4. Acute Toxic Effects of n-Butyl Acetate to Mammals

Subject	Route of Administration	Dosage	Effect	Reference
Humans	Oral	500 mg/kg	LDLo	NIOSH, 1977
Humans	Inhalation	200 ppm	TCLo	Nelson <i>et al.</i> , 1943
Rat	Oral	14 g/kg	LD50	Smyth <i>et al.</i> , 1954
Mouse	Intraperitoneal	1230 mg/kg	LD50	NIOSH, 1977
Guinea Pig	Intraperitoneal	1500 mg/kg	LDLo	NIOSH, 1977

Smyth *et al.* (1954) investigated the acute skin toxicity of n-butyl acetate and other solvents to rabbits (New Zealand giant albino). Groups of four male rabbits were closely clipped over the entire trunk so that approximately one-tenth of the body surface could be contacted with chemical solution to determine primary skin irritation effects. n-Butyl acetate was reported to be one of the least irritating of the chemicals studied. The LD50 for skin penetration was >20 ml/kg. An application of 0.005 ml of undiluted n-butyl acetate to the eyes of rabbits resulted in corneal necrosis and severe burn.

The acute response of guinea pigs to n-butyl acetate vapor was reported by Sayers *et al.* (1936). Exposure to 10,000 to 14,000 ppm n-butyl acetate vapor was potentially fatal to guinea pigs after several hours; 7,000 ppm was the threshold value for a 1 hour exposure without serious injury other than eye and nasal irritation; and 3,300 ppm vapor was the maximum concentration which produced little or no toxic reaction after several hours exposure. The gross pathological findings in animals that died during exposure were moderate congestion of the brain, lungs, liver and kidneys. No gross pathology was observed in animals exposed to 3,300 ppm vapor for 13-1/2 hours.

n-Butyl acetate has narcotic and irritative effects on exposed humans. Throat irritation was reported at 200 ppm. Irritation becomes severe at concentrations of 300 ppm (Nelson *et al.*, 1943).

2. Toxicity to Birds

McLaughlin *et al.* (1964) investigated the toxicity of 14 volatile chemicals including n-butyl acetate on chicken eggs. They injected various dosages of the chemicals into the yolk sac of fresh fertile eggs before incubation. Toxicity was judged by the percentage of hatch as compared to control eggs; a study of the embryonic development of eggs which failed to hatch; and a study of the appearance and development of chicks that did

hatch. n-Butyl acetate at a dosage of 9 mg/egg yielded 60% hatchability while a dosage of 27 mg/egg and 45 mg/egg gave 45% and 0% hatchability, respectively. Kidney damage and corneal lesions were reported in affected chick embryos.

3. Aquatic Toxicity

The data in Table VII-5 indicates that n-butyl acetate has a low toxicity to aquatic organisms. Using the LC50 to *Daphnia magna* of 44 ppm, a safe level estimate would be between .4-4.4 ppm.

Table VII-5. Aquatic Toxicity of n-Butyl Acetate

Organism	Level (ppm)	Effect	Reference
Water flea (<i>Daphnia magna</i>)	44	48 hr. LC50	CHRIS (1974)
Bluegill sunfish (<i>Lepomis macrochirus</i>)	180	96 hr. LC100	Dawson <i>et al.</i> (1975/77)
	100	96 hr. LC50	"
	79	96 hr. LC20	"

4. Toxicity to Microorganisms

The effects of various solvents and volatile chemicals on the respiration of activated sludge at a biochemical sewage treatment facility was investigated by Karpukhin *et al.*, 1973. n-Butyl acetate in a concentration present in the sewage was reported to have no significant inhibitory effect on the activated sludge respiration. Table VII-6 lists the various concentrations and observed results.

5. Phytotoxicity

No information specific to the phytotoxic action of n-butyl acetate was encountered in the literature search. A reference citing the phytotoxicity of acetic acid which is chemically related to n-butyl acetate, an ester, was encountered. Lynch (1977) studied the effects of acetic acid concentrations on root growth in barley, (*Hordeum vulgare*), wheat (*Triticum aestivum*), maize (*Zea mays*), oil-seed rape (*Brassica napus*) and clover (*Trifolium repens*). Seeds from each specie were grown in glass Petri dishes containing a sand (200 g) and solution (45 ml) mixture. After incubation in darkness at 20°C for five days, the mean of the total root lengths were compared with controls. A dose-response curve for acetic acid and barley seedlings is presented in Figure VII-4.

Table VII-6. The Effect of Organic Solutions and Formaldehyde
on the Respiration of Active Sludge (Karpukhin *et al.*, 1973)

Solution	Separate Occurrence in Sewer Waters			Joint Occurrence in Sewer Waters		
	Inducing Concentrations	Maximum Stimulation (in g/l)	Maximum Stimulation (in %)	Toxic Concentrations (in g/l)	Inducing Concentrations	Toxic Concentrations (in g/l)
Butyl alcohol	0.006-0.03		146	3.2	0.01	0.11
Ethyl alcohol	0.01-0.1		135	4.0	0.01	0.12
Butyl acetate	0.02-0.32		135	2.5	0.011	0.2
Acetone	0.01-0.05		150	10.0	0.001	0.2
Formaldehyde	<0.001		100	>0.001	<0.0001	0.011

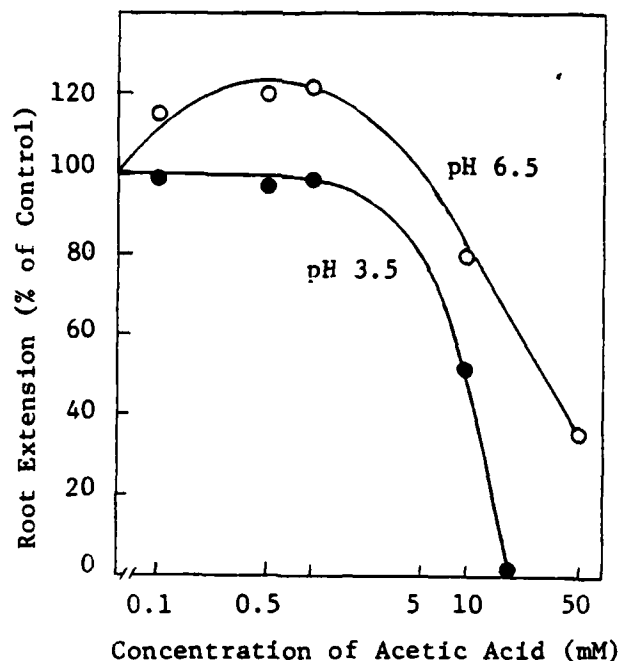


Figure VII-4. Effect of Acetic Acid on Root Extension of Barley Seedlings (Lynch, 1977)

Low concentrations (<5mM) of acetic acid stimulated root growth at pH 6.5 while higher concentrations inhibited the extension of roots. The phytotoxic effect of acetic acid appears pH-dependent. At pH 3.5, the inhibitory effect was increased and at a concentration of 15mM, all seeds were completely inhibited from germinating.

6. Environmental Fate

n-Butyl acetate is readily degraded in the environment by a variety of mechanisms including hydrolysis, microbial degradation and photochemical degradation. Degradation products in aqueous solution should be readily metabolized and incorporated into microbial cell mass.

7. Availability of Literature for Phase II

n-Butyl acetate is a widely used solvent. Several studies have been conducted to evaluate the toxicological and environmental hazards of this compound. Thus, there is sufficient literature available for a Phase II study.

H. Regulations and Standards

The U.S. OSHA standard for n-butyl acetate in air is 150 ppm (TWA) (Federal Register, 1974). The Soviet and Czechoslovakian limits are 45 ppm and 85 ppm, respectively (American Conference of Governmental Industrial Hygienists, 1977).

n-Butyl acetate is a flammable solvent. DOT requires the shipping label to read: flammable liquid (Federal Register, 1976a).

No EPA effluent guidelines for n-butyl acetate were found in the literature (Federal Register, 1976b.) However, this compound is listed in EPA Hazardous Substances List. n-Butyl acetate is a class D compound (toxicity range 100 µg/l LC50 <500 µg/l) (Federal Register, 1978).

I. Conclusions and Recommendations

n-Butyl acetate has been used in Army munitions production in the past. However, at the present time only very small quantities of n-butyl acetate are being used by the Army.

n-Butyl acetate presents a low hazard to mammals. It is degraded in the environment and thus does not present a long term environmental hazard.

In view of the limited use of n-butyl acetate by the Army, it is recommended that any future Army sponsored toxicological or environmental studies on this compound should be a low priority.

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PRELIMINARY PROBLEM DEFINITION STUDY ON MUNITIONS-RELATED CHEMI--ETC(U)

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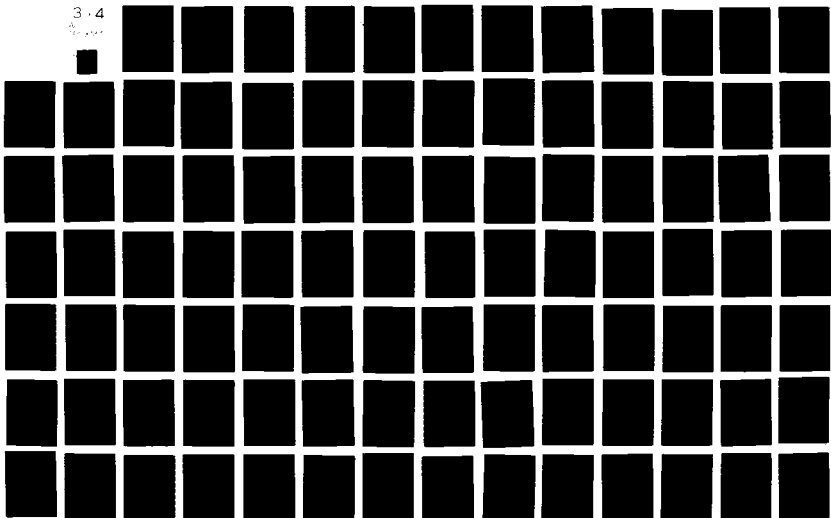
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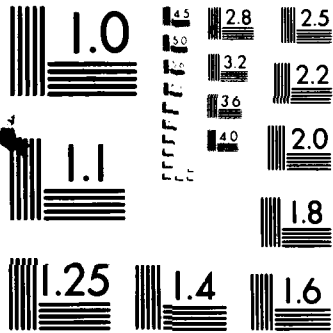
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PRELIMINARY PROBLEM DEFINITION STUDY ON
MUNITIONS-RELATED CHEMICALS
TETRANITROCARBAZOLE

SUMMARY

Tetranitrocarbazole is a component of the yellow first-fire mixture formulated at Longhorn AAP. This mixture is used in almost every round produced at Longhorn AAP. Current usage of tetranitrocarbazole is 4,375 lb/year. This usage will increase to ~10,000 lb/year at full mobilization. The tetranitrocarbazole is produced by Sodyeco for military use. Less than 25 lb of this chemical per year are used by the civilian community. Thus, tetranitrocarbazole is a military unique compound.

Only limited toxicological information on tetranitrocarbazole was found in the literature. The information suggests that tetranitrocarbazole is moderately toxic to mammals.

The available literature on tetranitrocarbazole is very limited. Further information on the toxicological and environmental fate of this compound will have to come from laboratory studies. These studies should include:

- verification of the LD50 to rats
- Ames mutagenicity tests
- 96 hour static aquatic toxicity tests to fish and *Daphnia magna*
- bioaccumulation and biodegradation studies
- chemistry and photochemistry studies

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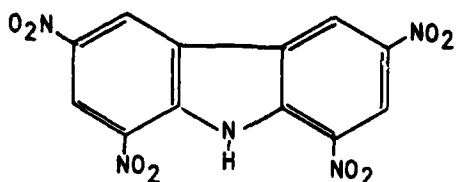
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VIII. TETRANITROCARBAZOLE

A. Alternate Names

Tetranitrocarbazole has a molecular formula of $C_{12}H_5N_5O_8$ corresponding to a molecular weight of 347.20. It has the following molecular structure:



Other pertinent alternate names for tetranitrocarbazole are listed below:

CAS Registry No.:	4543-33-3
CA Name (8CI):	Carbazole, 1,3,6,8-tetranitro
CA Name (9CI):	9H Carbazole, 1,3,6,8-tetranitro
Wiswesser Line Notation:	T B656 HN BHJ CNW ENW JNW LNW
Synonyms:	Nirosan; TNC; 1,3,6,8-tetranitrocarbazole

B. Physical Properties

The physical properties of tetranitrocarbazole are listed in Table VIII-1. The infrared spectrum of tetranitrocarbazole is shown in Figure VIII-1.

Table VIII-1. Physical Properties of Tetranitrocarbazole*

Physical Form at 20°C:	Powder
Color:	Yellow
M.P.:	285°C - 300°C
Flash Point:	470°C
Heat of Combustion:	3773 cal/g
Solubility:	Soluble in hot acetone Slightly soluble in nitrobenzene Insoluble in water

* Kirk and Othmer, 1965; Sodyeco, 1965.

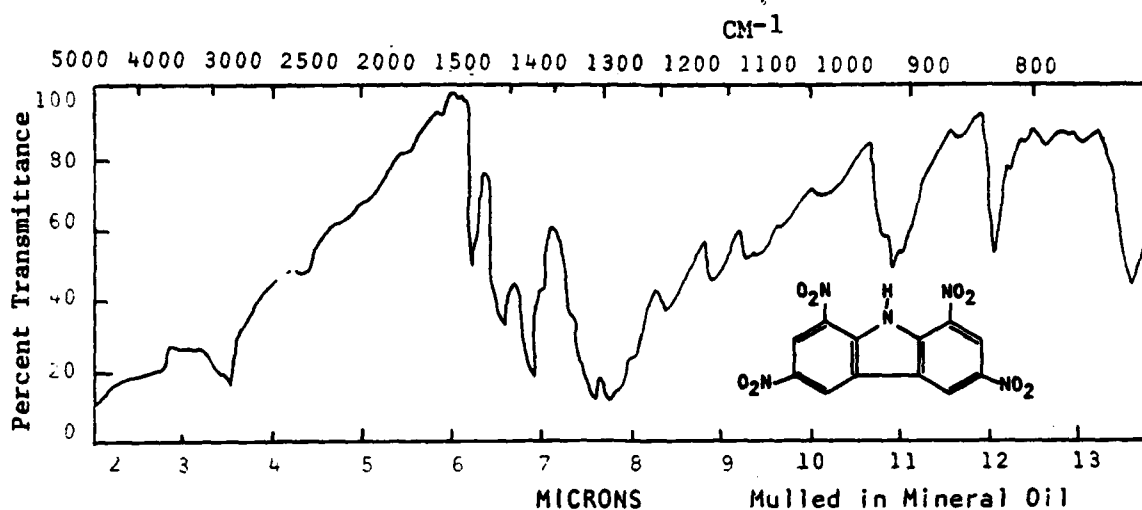
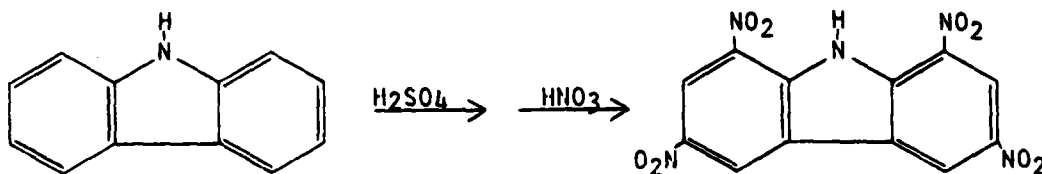


Figure VIII-1. Infrared Spectrum of 1,3,6,8-Tetranitrocarbazole
 © Sadtler Research Laboratories, Inc. (1962)

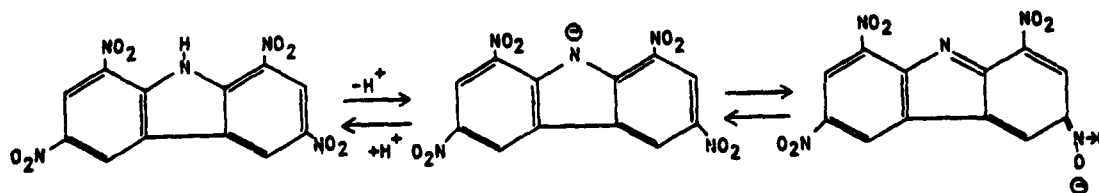
C. Chemical Properties

1. General Reactions

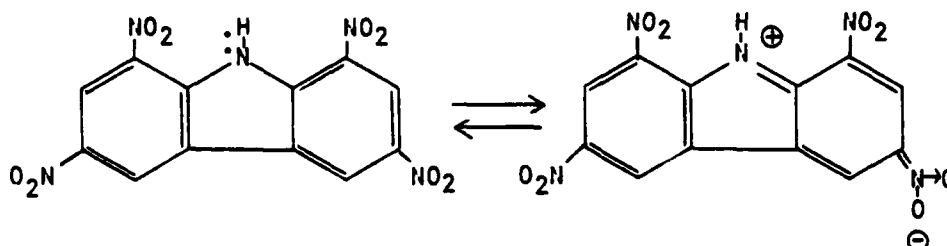
Tetranitrocarbazole is produced by the mixed acid nitration of carbazole (Sodyeco, 1979; Kirk and Othmer, 1965).



The presence of the four nitro groups conjugated to the amine function lends an acidic character to the molecule (Raileanu *et al.*, 1973).



Tetranitrocarbazole could also function as a base. However, due to the delocalization of the nitrogen lone pair, the basicity of tetranitrocarbazole is slight under ordinary conditions.

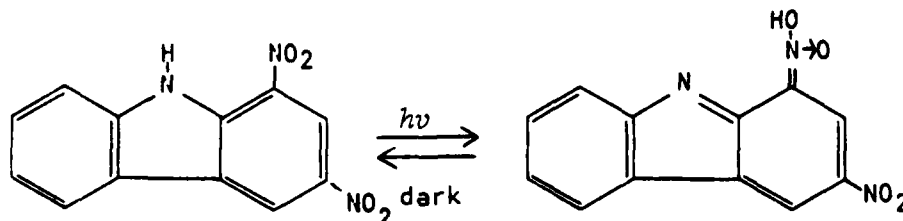


In strong acid media, however, the nitrogen should be protonated to some extent.

As an aromatic compound, tetranitrocarbazole might be expected to undergo electrophilic substitution, however, due to the deactivation of the nitro substituents no further substitution is possible. The nitro substituents do give the molecule the property of functioning as an electron acceptor in charge transfer complexes. Several complexes of this type have been reported including adducts with carbazole, anthracene, phenanthrene, benzidine, diphenylamine, phenothiazine, α and β -naphthol and piperazine (Raileanu *et al.*, 1973). The complexes containing oxygen and nitrogen donors were assumed to be localized σ complexes. The complexes with carbazole, anthracene and phenanthrene were said to be delocalized.

2. Environmental Reactions

The environmental chemistry of tetranitrocarbazole has not been reported. The photochemistry will probably be dominated by photochromism analogous to that reported for 2,4-dinitrodiphenylmethane (Dessauer and Paris, 1963).



Photochemical reduction of the nitro groups is also a possibility.

3. Sampling and Analysis

The analysis of tetranitrocarbazole was not reported in the literature searched. High pressure liquid chromatography appears to be the most promising technique for analysis of this compound.

D. Uses in Army Munitions

1. Purpose

Tetranitrocarbazole is used by Longhorn AAP as a minor constituent a yellow first-fire mixture. This mixture is used in almost every round produced by Longhorn AAP. The first-fire mixture is used to ignite the primary explosive charge. Yellow first-fire mix has the following composition:

Barium nitrate	50%
Tetranitrocarbazole	10%
Silicon	20%
Zirconium hydride	15%
Laminac 4116 polyester	5%

The mixture is produced by Longhorn AAP in 25-50 lb batches. In addition to the above constituents, 6.2 ml of Lupersol DDM is used in each 25 lb batch as a curing agent for the Laminac 4116 polyester resin.

First-fire mixtures are prepared by weighing and blending the dry ingredients. The binder is added and blended into the mixture. The particles formed are sieved and dried, then loaded into the rounds.

2. Quantities Used

During 1976 and 1977, about 3500-4000 lb/year of tetranitrocarbazole was used at Longhorn AAP. During 1978, 4,375 lb were used. The estimated requirement of tetranitrocarbazole at full mobilization is 10,000 lb/year or 833 lb/month.

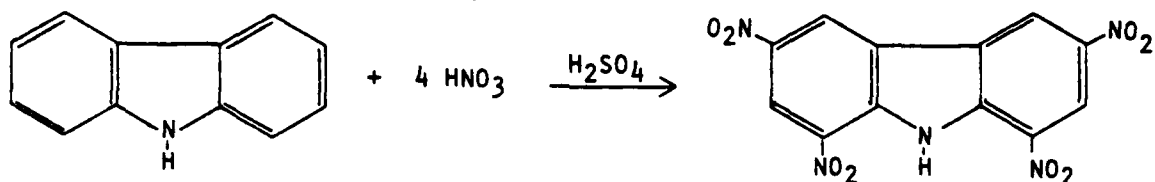
3. Documented or Speculated Occurrences in Air or Water

Tetranitrocarbazole use at Longhorn AAP results in an estimated current loss of 2-4 lb/month. At full mobilization, losses of 4-8 lb/month would be expected. These figures are based upon an estimate by Maley (1978). It is estimated that 0.5 to 1.0% of the amount of primer and tracer materials handled is lost to waste streams. Wastes generated at Longhorn AAP are washed into sumps and transported by truck to an evaporation pond. This pond has accumulated solid residues from munitions wastes for many years. A second pond is being considered, as the ability of the existing pond to handle future wastes is uncertain.

E. Uses in the Civilian Community

1. Production Methodology

1,3,6,8-Tetranitrocarbazole is produced by mixed acid nitration of carbazole (Sodyeco, 1979; Kirk and Othmer, 1965):



Typically a sulfuric acid solution of carbazole is added to nitric acid at 50-60°C. The reaction is then quenched with water, filtered and washed with water, ammonia and water before drying. The tetranitrocarbazole thus formed contains from 5-10% of 1,2,6,8-tetranitrocarbazole and/or trinitrocarbazole.

2. Manufacturers, Production and Capacities

Tetranitrocarbazole is presently manufactured by Sodyeco Division of Martin Marieta Chemicals. Yearly production is typically 5000-6000 pounds. Up to 40,000 pounds per year were produced during the Vietnam conflict. Production capacity is approximately 100,000 pounds per year.

3. Usages

Essentially 100% of the tetranitrocarbazole produced is for military purposes. Less than 25 pounds per year are consumed for civilian purposes. In the past, tetranitrocarbazole has been employed in the manufacture of fireworks.

4. Future Trends

There are no projected civilian demands for tetranitrocarbazole, although there has been speculation as to its application as an insecticide.

5. Speculated or Documented Occurrences in the Environment

Occurrences of tetranitrocarbazole in the environment from civilian manufacture have not been reported. Amounts of tetranitrocarbazole entering the environment from production are expected to be less than 1% of the amount produced, or 60 lb/year under current production conditions.

F. Comparison of Military and Civilian Uses and Pollution

The military uses essentially all the 1,3,6,8-tetranitrocarbazole manufactured in the United States. This compound is manufactured to military specifications by Sodyeco. Thus, tetranitrocarbazole is a military unique compound. The major source of entry into the environment of this compound is the lagoon at Longhorn AAP.

G. Toxicological and Environmental Hazards

1. Mammalian Toxicity

Very little information is available on the toxicity of tetranitrocarbazole. An LD50 for rats of 250 mg/kg was reported by Sodyeco (1979). This information would indicate that tetranitrocarbazole is moderately toxic to mammals.

2. Environmental Hazards

No information was found on the toxicity of tetranitrocarbazole to aquatic organisms, microorganisms or plants.

3. Availability of Literature for Phase II

Only limited information is available on tetranitrocarbazole in the general literature. Toxicological and environmental hazards information for Phase II will have to come from the manufacturers files, foreign manufacturers and researchers.

H. Regulations and Standards

There are no U.S. effluent guidelines on industrial hygiene standards for tetranitrocarbazole. Tetranitrocarbazole is listed in EPA "*Toxic Substances Candidate List of Chemical Substances* (1977)."

I. Conclusions and Recommendations

Tetranitrocarbazole is manufactured by one U.S. civilian company exclusively for use by the Army in yellow first-fire mixture. Thus, tetranitrocarbazole is a military unique compound.

Limited toxicological information on tetranitrocarbazole indicates that it is moderately toxic to mammals.

In view of the military uniqueness of tetranitrocarbazole and the limited toxicological information found in this study, a further Army sponsored studies this compound are recommended. These studies should be aimed at definition of the environmental fate of this compound including its chemistry, photochemistry, biodegradability and bioaccumulation. Additional toxicology studies should include verification of the LD50 to rats, Ames test and 96-hour static aquatic toxicity to fish and *Daphnia magna*.

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PRELIMINARY PROBLEM DEFINITION STUDY ON
MUNITIONS-RELATED CHEMICALS
LEAD 2-ETHYLHEXANOATE (H101)

SUMMARY

Lead 2-ethylhexanoate (H101) is widely used in the civilian community as a drier in paints and inks. Civilian production of this compound is ~2 million lb/year. Pollution of lead 2-ethylhexanoate from civilian production and formulation, use and disposal of paints and inks is expected to be high and widespread.

In contrast, Army use of lead 2-ethylhexanoate is ~22,000 lb/year under current operating conditions. This figure would increase to only 30,000 lb at full mobilization. This chemical is used in the N-5 propellant and AAH casting powder produced at Radford AAP. Pollution resulting from the use of lead 2-ethylhexanoate at Radford AAP is estimated at less than 1000 lb/year under full mobilization operating schedules.

Lead 2-ethylhexanoate is a chronic toxicity hazard to mammals. Long term exposure of this chemical leads to the symptoms of chronic lead poisoning.

In view of the limited Army use and pollution of lead 2-ethylhexanoate in munitions production. It is recommended that further Army sponsored toxicological or environmental studies on this compound should be a low priority.

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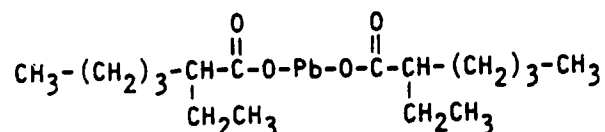
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IX. LEAD 2-ETHYLHEXANOATE (H101)

A. Alternate Names

Lead 2-ethylhexanoate is a salt of 2-ethylhexanoic acid with a molecular formula of $C_{16}H_{30}O_4Pb$ and corresponding molecular weight of 493. Lead 2-ethylhexanoate has the following molecular structure



Other pertinent alternate names for lead 2-ethylhexanoate are listed below. When used in propellant formulations, lead 2-ethylhexanoate is designated H101.

CAS Registry No.:	16996-40-0
CA Name (9CI):	Hexanoic acid, 2-ethyl-, lead salt
Synonyms:	Lead 2-ethylhexoate; Lead Octoate; Nuxtra Lead 24%; Nuxtra Lead 36%; Lead Catalox 24%; 24% Hex Cem Liquid; Lead 2-ethylhexoate; H101.

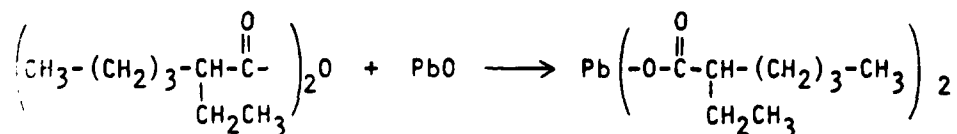
B. Physical Properties

Lead 2-ethylhexanoate is usually supplied in a hydrocarbon solvent containing specific amounts of lead. The physical properties of these solutions are presented in Table IX-1.

C. Chemical Properties

1. General Reactions

Lead 2-ethylhexanoate can be prepared by the action of 2-ethylhexanoic anhydride on lead oxide (Goldschmidt, 1970).



It can also be prepared by heating lead powder with 2-ethylhexanoic acid in the presence of oxygen (Hahl, 1962).

Table IX-1. Physical Properties of Lead 2-ethylhexanoate*

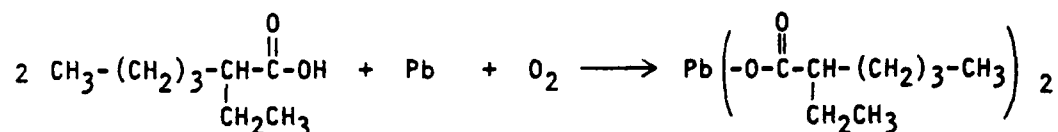
24% Lead Formula

Physical Form @ 20° C:	liquid
Specific Gravity:	1.08 @ 77°F
Flash Point:	104° F
Boiling Range:	305° - 380° F
Vapor Pressure:	6 mm @ 77° F Hg
Vapor Density (air = 1):	3.9
Flammable Limits (% Vol):	1.1% lower limit 6.0% upper limit
Solubility:	soluble in most organic solvents insoluble in water
Gardner Color:	2

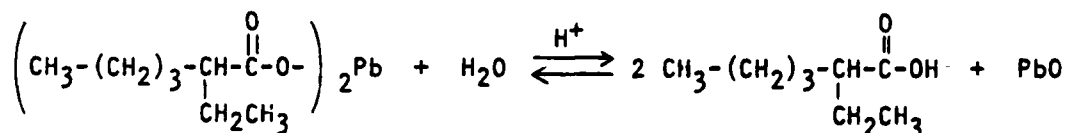
36% Formula

Specific Gravity:	1.34 @ 77°F

* Witco Chemical, 1976; Tenneco Chemicals, Inc., 1972; Kirk and Othmer, 1965.



The chemistry of lead 2-ethylhexanoate has not been reported. Hydrolysis should take place at low pH.



2. Environmental Reactions

The environmental chemistry of lead 2-ethylhexanoate has not been reported. Hydrolysis should be the major reaction.

3. Sampling and Analysis

The analytical procedures for lead 2-ethylhexanoate involve separate analysis of the hydrolysis products, i.e., lead and 2-ethylhexanoic acid. Thin layer chromatography of lead 2-ethylhexanoate in the presence of other lead and copper carboxylates has been reported by Habermann (1971).

Quantitative determination of organolead compounds may be accomplished by removing the organic moiety by oxidation and analysis of the remaining lead oxide by atomic absorption. Alternatively lead may be determined colorimetrically with dithizone by absorption at 520 nm (Franson, 1975).

D. Uses in Army Munitions

1. Purposes

Lead 2-ethylhexanoate is used in the production of both solvent and solventless double base propellants at Radford AAP. The primary uses of lead 2-ethylhexanoate are in AHH casting powder which is made by the solvent process and N-5 propellant produced by the solventless process. Lead 2-ethylhexanoate is also used in the RAP F/155 mm and RAP F/8 inch solventless formulations, although these items are not currently being manufactured.

In the solvent process, nitrocellulose and nitroglycerine mixtures are dehydrated by addition of ethanol, then pressed to form a block containing about 25% ethanol. The wet block is broken up and ether is added to the extent of about 50% of the wet weight. Any desired propellant additives are premixed with the ether. The propellant is then pressed at 3000 psi and extruded into cords of the desired diameter. The propellant particles are

placed in warm water to reduce solvent content to 1 to 5%, then air dried.

In the solventless process, a premix is made of nitrocellulose, nitroglycerine and the desired additives dispersed in water. The water is then removed by centrifuging. The paste is air dried then passed through roll calenders to form sheets of the desired thickness. The sheets are cut into strands. These strands do not contain any volatile materials and are dimensionally stable.

The amount of lead 2-ethylhexanoate used in the various formulations is shown below:

<u>Formulation</u>	<u>% Lead 2-Ethylhexanoate in Formulation</u>
AHH Casting Powder	2.3
N-5 Propellant	1.2
RAP F/155, F/8	2.0

2. Quantities Used

a. Historical Use

The quantities of AHH Casting Powder and N-5 propellant produced at Radford AAP in recent years are shown in Table IX-2.

Table IX-2. Production History at Radford AAP, lb
(Watts, 1978)

	<u>1972</u>	<u>1973</u>	<u>1974</u>	<u>1975</u>	<u>1976</u>	<u>1977</u>
AHH	118,500	193,900	291,900	-	-	337,800
N-5	-	-	59,000	382,300	1,044,400	2,281,600

These production rates account for an average use rate of lead 2-ethylhexanoate of 11,150 lb/year. The low use rate was 2,725 lb in 1972. The high use rate for this period was 35,150 lb in 1977. The total amount of lead 2-ethylhexanoate purchased by Radford AAP since 1972 was 121,000 lb (Dickenson, 1979). Over 90% of the material was used for AHH and N-5. The remainder was used for the RAP propellants.

b. Current Use

The current use rate of lead 2-ethylhexanoate at Radford AAP is 21,600 lb/year (Dickenson, 1979). All of this amount is used for production

of AHH casting powder and N-5 propellant.

c. Use at Full Mobilization

The full mobilization use rate of lead 2-ethylhexanoate would be 30,200 lb/year or 2517 lb/month.

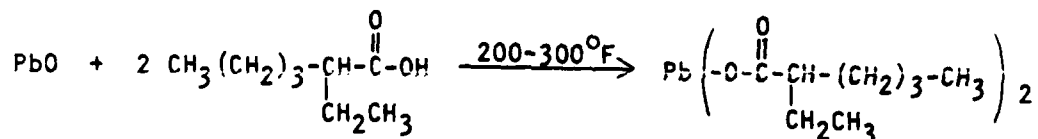
3. Documented or Speculated Occurrences in Air or Water

Losses from propellant processing operations average 5.3% for the solventless process and 6.6% for the solvent process (Smith and Dickenson, 1974; Glennon, 1977). Based upon these figures, current losses of lead 2-ethylhexanoate to the environment are on the order of 100-200 lb/month. At full mobilization, the loss rates would be 130-160 lb/month. Based on the limited solubility of tetranitrocarbazole in water, it is estimated that approximately one-third of these amounts would eventually enter the New River.

E. Uses in the Civilian Community

1. Production Methodology

Lead 2-ethylhexanoate is produced by the reaction of lead oxide with 2-ethylhexanoic acid or anhydride according to the following equation



2. Manufacturers, Production and Capacity

The U.S. manufacturers of lead 2-ethylhexanoate are listed in Table IX-3.

Table IX-3. Manufacturers of Lead 2-ethylhexanoate
(SRI International, 1978)

Ferro Corp. Chem. Div.	Bedford, Ohio
Interstab Chems. Inc	New Brunswick, N.J.
Mooney Chems., Inc.	Franklin, Pa.
The Shepherd Chem. Co.	Cincinnati, Ohio
Tenneco Inc., Tenneco Chems., Inc.	Elizabeth, N.J. Long Beach, Calif.
Troy Chem. Corp.	Newark, N.J.
Witco Chem. Corp., Organics Div.	Clearing, Ill. Lynwood, Calif.

Historical U.S. production and sales of lead 2-ethylhexanoate are presented in Table IX-4.

Table IX-4. U.S Production and Sales of Lead 2-ethylhexanoate
(U.S. Tarriff Commission, 1973-1977)

	<u>1973</u>	<u>1974</u>	<u>1975</u>	<u>1976</u>	<u>1977</u>
Production (1000 lb)	891	2442	1769	2595	1896
Sales (1000 lb)	615	2473	1743	2499	1899

3. Usages

Lead 2-ethylhexanoate is used primarily as a drier and in industrial product finishing (Tenneco, 1979). Driers are used in paint, varnish, printing ink and linoleum industries.

4. Future Trends

No major changes in the lead 2-ethylhexanoate market are anticipated. Production and sales should remain around the 2 million lb/year level.

5. Documented or Speculated Occurrences in the Environment

Large amounts of lead 2-ethylhexanoate will enter the environment from disposal of waste paints and inks, and from the formulation and use of these products. The exact amount of lead 2-ethylhexanoate entering the environment from these sources is not known.

F. Comparison of Civilian and Military Uses and Pollution

Under current production schedules, lead 2-ethylhexanoate is used only at Radford AAP. This installation uses about 21,600 lb/year. At full mobilization the amount of lead 2-ethylhexanoate needed by Radford AAP would be ~30,000 lb/year. Thus current military use rate of this chemical is only ~1% of the civilian production of 2 million lb/year. Pollution resulting from lead 2-ethylhexanoate use in munitions production is <1000 lb/year at full mobilization. This quantity is negligible in comparison to losses from civilian production, formulation, uses and disposal of paints and inks containing lead 2-ethylhexanoate.

G. Toxicological and Environmental Hazards

1. Mammalian Toxicity

Cohen *et al.* (1974) fed lead 2-ethylhexanoate to infant baboons. As shown in Table IX-5, they observed an increase in blood lead levels and a decrease in δ -aminolevulinic acid dehydratase (ALA-D) activity. Blood lead levels increased linearly over the 2-5 months of daily ingestion of 100-500 ug/kg of lead 2-ethylhexanoate. They also observed that lead 2-ethylhexanoate was not absorbed into the blood as fast as lead acetate.

2. Aquatic Toxicity

There is no information available on the aquatic toxicity of lead 2-ethylhexanoate.

3. Toxicity to Microorganisms

No specific data on the toxicity of lead 2-ethylhexanoate 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 unstable 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.

The microbial degradation of hexanoic acid has been investigated by several researchers. McKenna and Coon (1970) reported that an inducible hydroxylase which catalyses the conversion of fatty acids from C₆ to C₁₂ to their ω -hydroxylase derivatives has been isolated from *Pseudomonas oleovorans*. Oxidation of hexanoic acid by fungi of the genus *Fusarium* has been documented (Varbanets *et al.*, 1969). Activated sludges from municipal waste treatment

Table IX-5. Response of Baboons to Ingestion of Lead
2-ethylhexanoate Drier in Olive Oil (Cohen
et al., 1974)

Baboon number	Dose rate, $\mu\text{g/kg-day}$	Blood, lead, $\mu\text{g}\%$	ALA-D $\frac{\text{nmole PBG}}{\text{ml RBC/hr}}$
B-656	Pre-exposure ¹	8.0	386
B-656	100 ²	21.0	163
B-191	Pre-exposure	8.0	612
B-191	500	24.0	175
B-654	Pre-exposure	11.0	419
B-654	500	28.0	146

¹ All pre-exposure values are the means of six determinations made during the 2-week period immediately preceding the start of lead ingestion.

² Values represent the means of data accumulated during the 9-day period following the start of ingestion.

plants in Columbus, Ohio immediately oxidized saturated fatty acids up to undecane acid (Malaney and Gerhold, 1969). However, the activated sludges did not acclimate to rapid oxidation of the dicarboxylic acids after 24 hours exposure. Toxicity appeared with several of the acids of intermediate chain length in two of the sludges. Hexanoic acid inhibited cultures of *Streptococcus cremoris*, *S. lactis*, *S. diacetilactis*, *Leuconostoc citrovorum*, *Escherichia coli*, *Salmonella typhimurium*, and *Staphylococcus aureus* at a concentration of 10,000 to 100,000 ppm (Kulshrestha and Marth, 1970).

4. Phytotoxicity

No phytotoxicity information on lead 2-ethylhexanoate was encountered. However, phytotoxic data on lead 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).

D'Souza and Mistry (1970) studied the uptake of ^{210}Pb in red kidney bean plants (*Phaseolus vulgaris*). After 15 days in the test solution, accumulation of ^{210}Pb occurred predominantly in roots and only very small amounts were translocated to the shoots. Lagerwerff (1971) observed that increasing the soil pH from 5.9 to 7.2 resulted in decreases in yield and Pb content in radishes.

When *Minuartia verma* and *Thlaspi alpestre* plants were grown in soils containing 82-900 ppm lead, the expressed juice of *T. alpestre* contained 0.01 - 0.04 mg/ml lead while that of *M. verma* contained 0.01 - 0.02 mg/ml lead (Ernst, 1968). Abnormally large amounts of lead were absorbed by carrot plants growing in plots treated with sludge containing significant concentrations of Pb while globe beet and potato plants did not accumulate significant amounts (LeRiche, 1968).

Garber (1970) studied the content of lead, zinc, and copper in plants in the vicinity of metallurgical factories. He observed that plant growth was inhibited in soils enriched by high concentrations of lead. Beans (Kentucky Wonder) grown in lead-treated soil (200 ml/kg dry soil of 1% lead acetate solution) exhibited a mildly toxic reaction in the form of spotty chlorotic discolorations of the foliage (Berg, 1969). Peanuts reportedly were not inhibited by the lead treatment.

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-6 (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,

Table IX-6. 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 to Solution			
		Roots		Shoots	
(ppm)	(μ g)	(ppm)	(μ g)	(ppm)	(μ g)
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

the roots act as a barrier which restricts the movement of lead salt through the plant to growing animals. During winter months when plant growth is low, a considerable increase in the lead contents of the ryegrass shoots was observed. An 8-fold increase in total lead content of a soil did not cause any significant increase in the lead content of bromegrass grown on the soil in a greenhouse (Motto *et al.*, 1970).

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 change 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).

5. Availability of Literature for Phase II

Only limited information on the toxicological and environmental hazards of lead 2-ethylhexanoate is available in the general literature. Phase II information would have to come from U.S. and foreign manufacturers files or be inferred from literature on lead and 2-ethylhexanoic acid.

H. Regulations and Standards

1. Air and Water Standards

There are no air or water standards specific for lead salicylate or lead β -resorcyate. However, criteria have been set for lead in potable water (Federal Register, 1979). For protection of human health, the lead content of potable waters can be no greater than 50 g/l. Proposed fresh water criteria for protection of aquatic life have been revised for lead taking into account water hardness (Federal Register, 1979). The equation for the 24-hour average concentration is $1.51 \ln(\text{hardness}) - 3.37$. The maximum allowable concentration is $1.51 \ln(\text{hardness}) - 1.39$.

2. Human Exposure Standards

No specific standards for lead 2-ethylhexanoate have been set for occupational exposure to this chemical. However, a criteria document has recommended an air standard of $150 \mu\text{g}(\text{Pb})/\text{m}^3$ for lead stearate (NIOSH, 1977). A similar TLV for lead 2-ethylhexanoate should afford workers adequate protection. As formulated in oil, lead 2-ethylhexanoate is classified as a Class 2 flammable liquid by OSHA (Tenneco, 1972).

3. Department of Transportation

DOT classifies lead-2-ethylhexanoate in oil as a "Combustible Liquid."

1. Conclusions and Recommendations

H101 or lead 2-ethylhexanoate is used by the Army in the formulation of N-5 propellant and AHH casting powders at Radford AAP. Only about 1% of the civilian production of lead 2-ethylhexanoate is used by the Army in the munitions production. Pollution of lead 2-ethylhexanoate at Radford AAP is estimated at less than 1000 lb/year at full mobilization usage of this chemical. In contrast, widespread pollution from the civilian production, formulation into paints and inks and uses and disposal of these paints and inks is expected to occur.

Chronic exposure to lead 2-ethylhexanoate leads to increased blood lead levels. Thus long-term exposure through inhalation, ingestion and possibly skin contact can lead to chronic lead poisoning.

It is recommended that any further toxicological and environmental studies on lead 2-ethylhexanoate by the Army should be low priority. This recommendation is based on the low use and pollution of lead 2-ethylhexanoate by Army munitions production in comparison to civilian production, uses and disposal.

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PRELIMINARY PROBLEM DEFINITION STUDY ON
MUNITIONS-RELATED CHEMICALS
DI-N-BUTYL SEBACATE

SUMMARY

Di-n-butyl sebacate is a plasticizer for PVC used when low temperature flexibility of the plastic is necessary. Only one civilian manufacturer, Union Camp Corporation, currently produces di-n-butyl sebacate. However, other manufacturers have facilities which could be used to produce di-n-butyl sebacate if the demand for this plasticizer increases. Currently civilian production of di-n-butyl sebacate is in a decline because of high prices of starting materials.

The Army utilizes di-n-butyl sebacate in Otto II torpedo fuel produced at Radford AAP. Significant quantities of Otto II fuel have been produced at Radford in the years 1972-1977. However, no current production is scheduled nor is any production of this fuel anticipated in the near future.

Di-n-butyl sebacate is an ester of low toxicity. The LD50's for this compound are ~18 g/kg. In the environment, di-n-butyl sebacate is readily degraded by microorganisms. Thus it does not pose a long term threat to the environment.

Due to the curtailed use of di-n-butyl sebacate by Radford AAP, no immediate Army sponsored studies on this compound are recommended.

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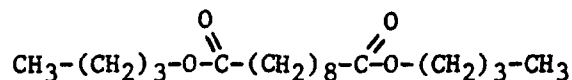
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X. DI-n-BUTYL SEBACATE

A. Alternate Names

Di-n-butyl sebacate is an aliphatic di-ester with a molecular formula of $C_{18}H_{34}O_4$ and corresponding molecular weight of 314.47. It has the structural formula:



Pertinent alternate names for di-n-butyl sebacate are listed below:

CAS Registry No.:	109-43-3
Replaces CAS Registry No.:	39393-66-3
CA Name (8CI):	Sebacic acid, dibutyl ester
CA Name (9CI):	Decanedioic acid, dibutyl ester
Wiswesser Line Notation:	40V8V04
Synonyms:	Bis(n-butyl) sebacate; Dibutyl sebacate; Di-n-butyl sebacate; Polycizer DBS; Stayflex DBS; Kodaflex DBS; PX 404.

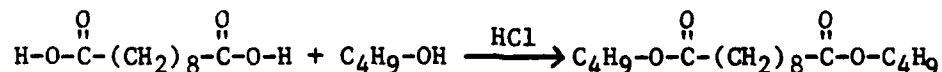
B. Physical Properties

The physical properties of di-n-butyl sebacate are listed in Table X-1. The infrared and NMR spectra of di-n-butyl sebacate are shown in Figures X-1 and X-2.

C. Chemical Properties

1. General Chemistry

Di-n-butyl sebacate is conveniently obtained by esterification of sebacic acid with n-butanol in the presence of hydrogen chloride (Prager and Jacobson, 1920).



The sebacic acid is in turn obtained by heating of castor oil or ricinoleic acid with sodium hydroxide. An alternate synthesis for di-n-butyl sebacate involves the electrolytic oxidation of potassium butyl adipate which results in decarboxylation and dimerization.

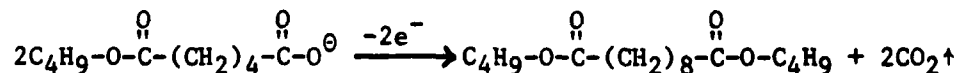


Table X-1. Physical Properties of Di-n-butyl Sebacate*

Physical Form at 20°C:.	liquid
Color:	clear
Odor:	none
Melting Point:	-11°C
Boiling Point:	349°C @ 760 mm Hg 180°C @ 3 mm Hg
Flash Point (COC):	350°F
Autoignition Point (COC):	412°F
Refractive Index:	1.4395 @ 25°C
Specific Gravity:	0.936 (20/20°C)
Weight/Gallon:	7.81 lb
Saponification No.:	355
Solubility:	soluble in ether insoluble in water
Viscosity:	8.6 cps.

*Union Camp Corp., 1972

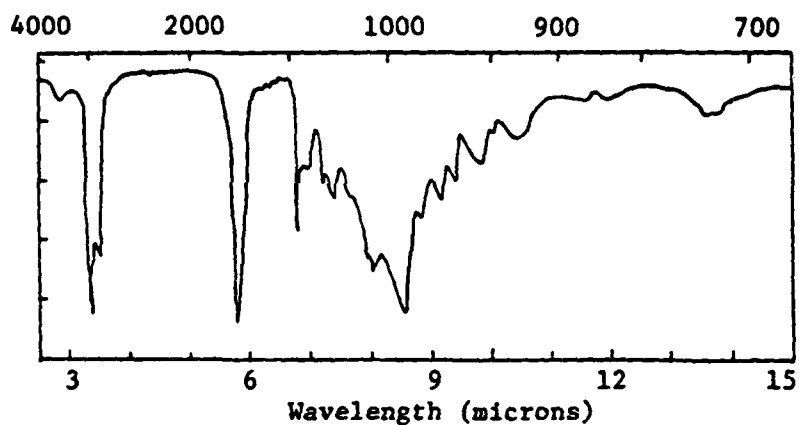


Figure X-1. Infrared Spectrum of Di-n-butyl Sebacate
(Haslam and Willis, 1965)

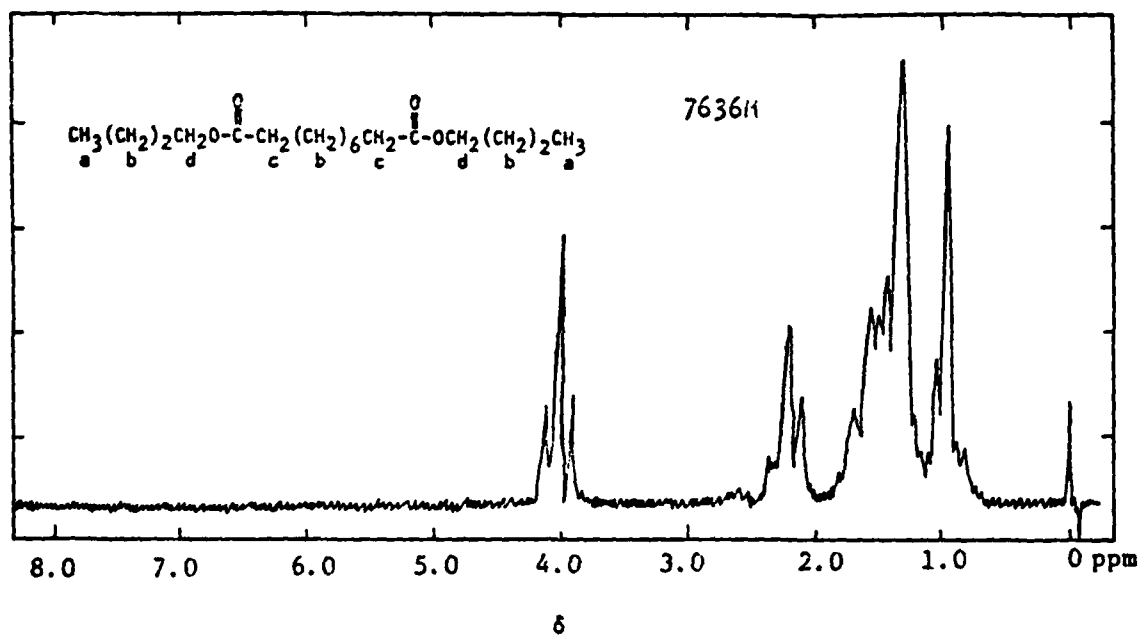
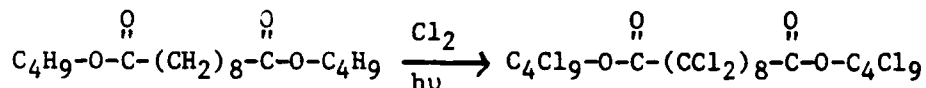
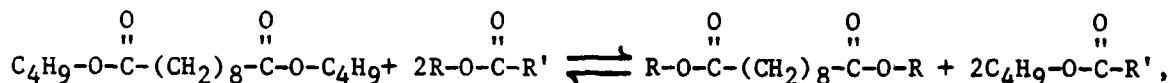


Figure X-2. NMR Spectrum of Di-n-butyl Sebacate
© Sadtler Research Laboratories, Inc. (1967)

Despite an abundance of literature regarding the applications for di-n-butyl sebacate very little has been published regarding its chemistry. Di-n-butyl sebacate reacts with chlorine in sunlight to produce a perchlorinated analog (Prager and Jacobsen, 1920).



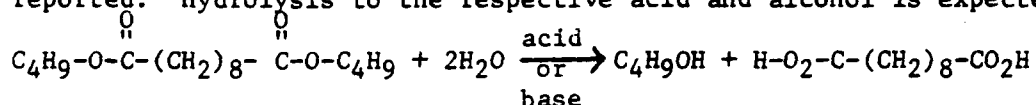
Transesterification reactions are also likely,



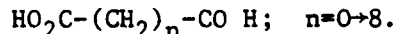
and have been used to advantage in the analysis of di-n-butyl sebacate (Wandel and Tengler, 1965; Craig *et al.*, 1963).

2. Environmental Reactions

The environmental chemistry of di-n-butyl sebacate has not been reported. Hydrolysis to the respective acid and alcohol is expected:



Oxidation of either di-n-butyl sebacate or sebacic acid is likely to yield a series of homologous dicarboxylic acids:



3. Sampling and Analysis

Qualitative analysis for di-n-butyl sebacate has been accomplished by employing a color test involving treatment with resorcinol in sulfuric acid. Following neutralization and dilution, a yellow color is indicative of sebacates (Wandel and Tengler, 1965). Whitnack (1975) has used a single sweep polarographic technique for analysis of di-n-butyl sebacate.

The most widely used quantitative analysis method for di-n-butyl sebacate is gas chromatography. Analysis has been accomplished using a 0.4% Apiezon M on quartz column at 220°C (Saltanova *et al.*, 1971), a 10% Apiezon L on S-22 Celite column at 230°C (Feofanov *et al.*, 1968), a 5% SE-30 column (Wandel and Tengler, 1965), and a 3% SE-30 on Chromsorb W column (Kessick *et al.*, 1978). Sampling of aqueous solutions can be accomplished by extraction with benzene (Kessick *et al.*, 1978).

D. Uses in Army Munitions

1. Purpose

Di-n-butyl sebacate is used by Radford AAP in the production of

Otto Fuel II. Di-n-butyl sebacate represents 22.5% of the Otto Fuel formula, the remainder being as shown below:

<u>Constituent of Otto Fuel II</u>	<u>Quantity</u>
Propyleneglycoldinitrate (PGDN)	75.8-76.2%
2-nitrodiphenylamine	1.4-1.6%
Sodium	0-0.8 ppm

Otto Fuel II is used as a torpedo propellant. It is produced at Radford AAP in the Nitroglycerine #1 Area. The principal processing step is nitration of propylene glycol to form PGDN. The stabilizers (di-n-butyl sebacate and 2-nitrodiphenylamine) are then added to form the finished propellant (Dickenson, 1979).

2. Quantities Used

Since 1972, Radford AAP has used 166,000 lb of di-n-butyl sebacate in the production of Otto Fuel II. This represents an average use rate of 27,700 lb/year during the years of production, 1972 to 1977. There is no current use of di-n-butyl sebacate at Radford AAP, nor is any use anticipated in the foreseeable future. The mobilization schedule does not call for any production of Otto Fuel II, so the full mobilization use rate is also zero.

3. Documented or Speculated Occurrences in Air or Water

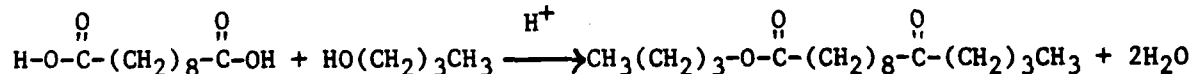
There is no current loss of di-n-butyl sebacate to the environment at Radford AAP, as none is in use. The full mobilization losses would also be zero, since Otto Fuel II is not required by the mobilization schedule.

During the 1972-1977 period, the losses of di-n-butyl sebacate are estimated at 70-115 lb/month. This quantity represents 3-5% of the amount used which is considered to be a typical loss level (Dickenson, 1979). Since di-n-butyl sebacate is insoluble in water, only 1/3 of the amount lost in the production, 23-38 lb/month, probably found its way into the effluent streams and the New River.

E. Uses in the Civilian Community

1. Production Methodology

Di-n-butyl sebacate is produced by esterification of sebacic acid with n-butanol (Union Camp Corp., 1979).



Details of the production technology were considered proprietary and were not released. Esterifications generally involve an equilibrium situation which requires either the use of a large excess of alcohol, removal of the water of reaction or both (Kirk and Othmer, 1965). Purification in all likelihood would involve reduced pressure distillation.

2. Manufacturers, Production and Capacity

Union Camp Corporation, Chemical Products Division, in Dover, Ohio, is the only active United States manufacturer of di-n-butyl sebacate. Past production levels are presented in Table X-2. Di-n-butyl sebacate accounts for $\sim 1/2$ the sebacate esters produced each year by Union Camp Corp.

Table X-2. Historical Production of Di-n-butyl Sebacate

	<u>1973</u>	<u>1974</u>	<u>1975</u>	<u>1976</u>	<u>1977</u>
Sebacic Acid esters (1000 lb)	6882	7665	5614	1705	4482
Di-n-butyl sebacate (1000 lb)	3696 (actual)	4062 (est.)	2976 (est.)	904 (est.)	2420 (est.)

3. Usages

Di-n-butyl sebacate is primarily used in cellulose, PVC type food wraps and as a low temperature plasticizer for nitrile rubbers. It is also used as a lubricant in electric pre-shave lotions, dielectric liquid and flavoring (Union Camp, 1972).

4. Future Trends

Future trends in di-n-butyl sebacate use are expected to decrease if the price of sebacic acid continues to rise. No major changes in the di-n-butyl sebacate industry are anticipated.

5. Documented or Speculated Occurrences in the Environment

Large amounts of di-n-butyl sebacate would be lost to the environment as a solid waste from food wraps. It is estimated that $\sim 1\%$ of the di-n-butyl sebacate produced is lost to the environment from either the production process or through its uses. Thus, $\sim 24,200$ lb of this compound are released into the environment each year.

F. Comparison of Civilian and Military Uses and Pollution of Di-n-butyl Sebacate

The only military use of di-n-butyl sebacate is in Otto Fuel II. This fuel was produced at Radford AAP, however, there is no current or anticipated future production. Only one U.S. company currently produces di-n-butyl sebacate. Production over the years from 1973 to 1977 averaged an estimated 2,811,000 lb/year. The military use of this chemical was only 1% of the U.S. production. Military pollution, when di-n-butyl sebacate is in use, is estimated at $\sim 1.5\%$ of the civilian losses.

G. Environmental and Toxicological Hazards of Di-n-butyl Sebacate

1. Mammalian Toxicity

The results of acute toxicity tests with di-n-butyl sebacate are presented in Table X-3. In a program to evaluate the toxicity of dental materials, Lawrence *et al.* (1974) determined the acute toxicity of di-n-butyl sebacate to mice. They found di-n-butyl sebacate to have a low acute toxicity. The LD50 for oral gavage was >32.0 ml/kg. By intraperitoneal injection, the LD50 was determined to be 14.70 ml/kg.

Table X-3. Acute Mammalian Toxicity of Di-n-butyl Sebacate

<u>Animal</u>	<u>Administration</u>	<u>Dose in g/kg</u>	<u>Effect</u>	<u>Reference</u>
Mice	oral	>32.0	LD50	Lawrence <i>et al.</i> , 1974
Mice	intraperitoneal	14.7	LD50	"
Rats	oral	5.0	no effect	Wallace, 1976
Rats	oral	17-32	tolerated	Smith, 1953

Komarova (1976) investigated the toxic properties of certain plasticizers including di-n-butyl sebacate. Acute studies indicated that a no effect dose of di-n-butyl sebacate for white mice was 10 g/kg and 5 g/kg for white rats. The LD50 for white mice was 18.1 g/kg and 17.2 g/kg for white rats. Pathological examination of deceased mice and rats revealed hemorrhages and pulmonary edema, plethora of the heart muscles, kidneys, brain matter and intestinal walls, and panesis of the stomach. No changes were reported in the condition of surviving mice and rats which had been given di-n-butyl sebacate in dosages of 5, 10, 15 and 20 g/kg.

In a chronic feeding study, di-n-butyl sebacate (1/50 LD50) in sunflower oil was fed to white mice over a period of 9 months. No changes occurred in the dosed mice when compared to the controls. Analysis of long term and chronic poisoning showed that di-n-butyl sebacate appeared to be practically non-toxic and lacked cumulative effects (Komarova, 1976).

Mild irritation was observed when di-n-butyl sebacate was applied to the skin of rabbits (Wallace, 1976) and guinea pigs (Komarova, 1976). Some conjunctive redness was also found in rabbit eye irritation studies with di-n-butyl sebacate (Wallace, 1976).

In conclusion, the toxicity of di-n-butyl sebacate to mammals by the oral route is very low. Smith (1953) reported di-n-butyl sebacate to be safe for use in food wrappers.

2. Aquatic Toxicity

No information was recovered on the aquatic toxicity of di-n-butyl sebacate.

3. Microorganism Toxicity

No information indicating that di-n-butyl sebacate is toxic to microorganisms was encountered. The literature reviewed indicates that di-n-butyl sebacate is readily degraded by fungi. Klausmeier *et al.* (1970) reported that added nutrients stimulated *Asperigillus terreus* growth and degradation of di-n-butyl sebacate. *Asperigillus terreus* was able to metabolize di-n-butyl sebacate as a source of energy and carbon. It was observed that metabolites that accumulated during early growth were further metabolized in later growth stages.

4. Phytotoxicity

No information was found on the effects of di-n-butyl sebacate on plants.

5. Environmental Fate

The literature indicates that di-n-butyl sebacate is readily degraded in the environment. Microorganisms are capable of using this compound as a carbon source. Chemical hydrolysis in the environment is also expected to occur.

6. Literature Availability for Phase II

Di-n-butyl sebacate is used as a plasticizer in food wrappers. Toxicological and environmental data are available from a wide variety of sources in sufficient quantities for a Phase II study.

H. Regulations and Standards

There are no OSHA or EPA standards or regulations specific for di-n-butyl sebacate. It is approved for use as a plasticizer on food wrappers under Food Additive Regulations, Par. 121, Title 21 of the Federal Register (Union Camp Corp., 1972).

I. Conclusions and Recommendations

Di-n-butyl sebacate is used as a plasticizer in Otto II torpedo fuel. Otto II torpedo fuel has been produced in large quantities at Radford AAP in past years, however, there are no current or future plans for production of this fuel. Thus, the Army's use of this compound has essentially dropped to zero.

Civilian use of di-n-butyl sebacate has also declined in recent years. Only one manufacturer is currently producing this plasticizer. Increase in civilian use of di-n-butyl sebacate will depend on prices of sebacic acid and the availability and prices of comparable plasticizers.

The mammalian toxicity of di-n-butyl sebacate is low with LD50's >10 g/kg. In the environment, di-n-butyl sebacate is readily degraded to non-toxic products by microorganisms. Thus, this compound does not pose any long term environmental hazard.

In view of the current limited use of di-n-butyl sebacate in Army munitions and the low environmental and toxicological hazards from this compound, further Army sponsored studies on di-n-butyl sebacate should be a low priority item.

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PRELIMINARY PROBLEM DEFINITION STUDY ON
MUNITIONS-RELATED CHEMICALS
DI-N-PROPYL ADIPATE

SUMMARY

Di-n-propyl adipate is a plasticizer that is used almost exclusively in solid propellant formulations produced at Radford AAP. There are no civilian uses of this compound. Radford AAP buys di-n-propyl adipate from Hatco Chemical. This company produces the compound on special order. Thus Radford AAP is the main source of environmental pollution by di-n-propyl adipate.

Di-n-propyl adipate has a low acute toxicity to mammals (g/kg). However, it has been shown to be teratogenic in rats receiving an acute dose. No aquatic toxicity information on di-n-propyl adipate was found in this literature search.

In view of the military uniqueness of this compound and its potential teratogenicity, a Phase II study of the environmental and toxicological hazards of di-n-propyl adipate is recommended.

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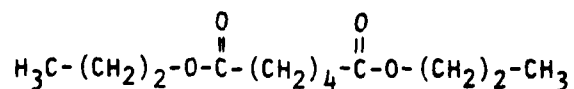
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XI. Di-n-Propyl Adipate

A. Alternate Names

Di-n-propyl adipate is an ester of adipic acid, an aliphatic dicarboxylic acid. It has a molecular formula of $C_{12}H_{22}O_4$ and has the molecular weight of 230.31 g/mole. The structural formula for di-n-propyl adipate is:



Other pertinent alternate names for di-n-propyl adipate are listed below:

CAS Registry No.: 106-19-4
Synonyms: Hexanedioic acid, dipropyl ester
Wiswesser Line Notation: 30V4V03

B. Physical Properties

The physical properties of di-n-propyl adipate are listed in Table XI-1.

Table XI-1. Physical Properties of Di-n-Propyl Adipate*

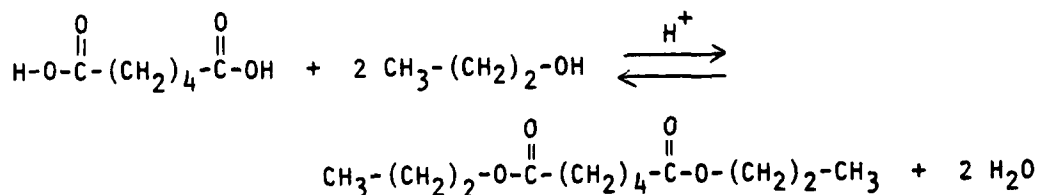
Physical Form at 20°C:	clear liquid
Color:	straw
Odor:	mild
MP:	-20.3°C to -15.7°C
BP:	155°C/10 mm Hg
Density:	0.979 ₄ ²⁰
Refractive Index n_D^{20} :	1.4314
Viscosity:	(high)
Solubility:	insoluble in water soluble in ethanol, ether, chloroform

*Windholz, 1976; Hawley, 1977

C. Chemical Properties

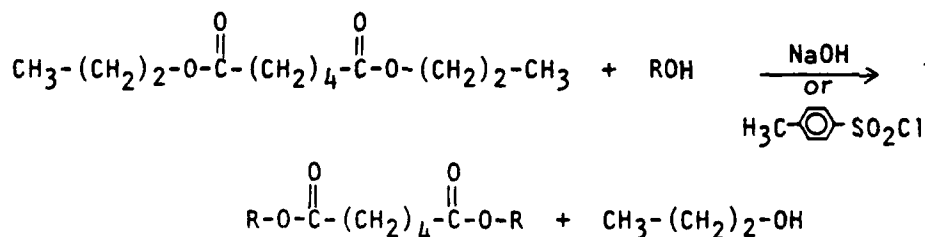
1. General Chemistry

Di-n-propyl adipate is a typical dialkylester of adipic acid. Adipic acid is easily esterified by the reaction of adipic acid and n-propanol (Kirk and Othmer, 1978).

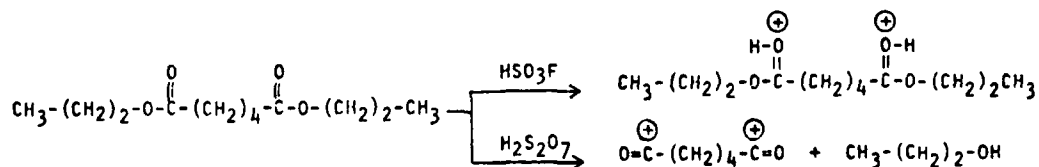


This reaction proceeds well with or without the acid catalyst. Without acid, either a large excess of alcohol is required or water must be removed by distillation. Hydrolysis, the reverse reaction, is therefore favored in excess water. Adipic acid is generally formed by the oxidation of either cyclohexanol or cyclohexanone.

Transesterification reactions have been reported (Bondar *et al.*, 1971). Propanol was removed by distillation to increase the yield.



The behavior of di-n-propyl adipate in flourosulphuric and disulphuric acids has also been reported (Malhotra and Sehgal, 1974). Deprotonation occurs in HSO_3F while in $\text{H}_2\text{S}_2\text{O}_7$ an oxycarbonum ion forms:



Oxidation of di-n-propyl adipate has been shown to give CO₂ and CO and CH₃(CH₂)₂-O₂C(CH₂)_n-CO₂H n=1,4 (Fedorishcheva *et al.*, 1972). No oxidation takes place on the propyl groups.

2. Environmental Reactions

The environmental chemistry of di-n-propyl adipate has not been investigated. Almost certainly, however, the predominant reaction is hydrolysis to adipic acid and propanol. Oxidative decarboxylation of the resultant monopropylester or adipic acid itself is also expected to occur yielding glutamic, succinic, malonic and/or oxalic acids.

3. Sampling and Analysis

Analysis for di-n-propyl adipate has been accomplished by gas chromatography. Non polar (0.5% SE-30) and polar (0.5% neopentylglycolpolysebacate) stationary phases have been employed at 200°C (Zulaica and Guiochon, 1962; Zulaica and Guiochon, 1963). Similar results were obtained with Apiezon M at 130°C and Ucon oil at 100 and 120°C on stainless-steel capillary columns (Strauss, 1973). A flame ionization detector was employed. Di-n-propyl adipate has also been determined in propellant compositions (Alley and Dykes, 1972). Three columns (3.8% OV-101, 2.5% OV-210 and 1.1% OV-225) were employed. Oven temperatures were programmed between 70 and 220°C at 6°C/min and a flame ionization detector was used.

D. Uses in Army Munitions

1. Purpose

Di-n-propyl adipate is used at Radford AAP in the production of double base propellants by the solventless process. The formulations which require di-n-propyl adipate are listed below:

<u>Formulation</u>	<u>% di-n-propyl Adipate in Formulation</u>
M-36	2.0
N-12	5.85
N-14	0.4
NOSIH-AA-2	1.6
NOSIH-AM-2	1.2
NOSIH-AA-6	2.0

In the solventless process, a premix is made of nitrocellulose, nitroglycerine and the desired additives. These materials are dispersed in water. The water is then removed by centrifuging. The paste is air dried and passed through roll calendars to form sheets of the desired thickness. The sheets are cut into strands. The strands do not shrink, as they do not contain any volatile materials.

2. Quantities Used

a. Historical Use

Historical production rates of propellants containing di-n-propyl adipate are presented in Table XI-2.

Table XI-2. Production History at Radford AAP, lb
(Watts, 1978)

	<u>1972</u>	<u>1973</u>	<u>1974</u>	<u>1975</u>	<u>1976</u>	<u>1977</u>
M-36					125,900	504,900
N-12	33,600	57,900	98,900	80,100	25,900	37,800
N-14	1,600	1,700	9,600	-	-	11,400
NOSIH-AA-2	25,600	-	-	-	-	4,700
NOSIH-AA-6	1,192,700	2,011,900	2,011,900	1,228,900	50,600	-
NOSIH-AM-2	-	-	4,300	16,400	91,900	71,200

The average use rate of di-n-propyl adipate over this period was 26,000 lb/year. The low use rate was 4,300 lb in 1977. The high rate for this period was 46,000 lb in 1974.

b. Current Use

The current use rate of di-n-propyl adipate at Radford AAP is 4,800 lb/year or 400 lb/month.

c. Use at Full Mobilization

The mobilization schedule calls for use of di-n-propyl adipate at the rate of 312 lb/month. The propellants which use di-n-propyl adipate are not called for in large quantities in the mobilization schedule.

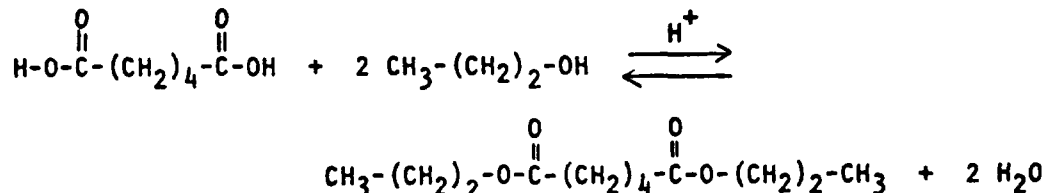
3. Documented or Speculated Occurrences in Air and Water

Losses from propellant processing operations average 5.3% for the solventless process (Smith and Dickenson, 1974; Glennon, 1977). Based upon this figure, current losses of di-n-propyl adipate to the environment would be 20-25 lb/month. At full mobilization, the loss rate would be 15-20 lb/month. It is estimated that about one-half of these amounts would eventually enter the New River.

E. Uses in the Civilian Community

1. Production Methodology

Di-n-propyl adipate is produced by esterification of adipic acid with n-propanol.



The reaction proceeds with or without the acid catalyst. However, without the acid a large excess of n-propanol must be used and the water removed by distillation.

2. Manufacturers, Production and Capacity

Hatco Chemical in Fords, N.J. is the sole source manufacturer of di-n-propyl adipate for Radford AAP. (Dennis, 1979). They manufacture di-n-propyl adipate to military specifications (Hatco Chemical, 1979). Di-n-propyl adipate is not manufactured for use by the civilian community. Several manufacturers could make this ester if a large need arises. However, they have not and do not expect to produce this compound on a regular basis.

3. Usages

There are no civilian uses for di-n-propyl adipate.

4. Future Trends

No civilian uses of di-n-propyl adipate are anticipated in the future.

5. Documented or Speculated Occurrences in the Environment.

The only potential civilian source of entry of di-n-propyl adipate into the environment is from the custom manufacture of this chemical by Hatco Chemical. It is estimated that no more than 1% of the amount produced is lost in the processing. These losses would be sporadic.

F. Comparison of Military and Civilian Uses and Pollution of Di-n-Propyl Adipate

The only current use of di-n-propyl adipate is as a plasticizer in solid propellant formulations. These propellants are currently produced only

at Radford AAP. Di-n-propyl adipate is produced to military specifications on order by one manufacturer. Civilian pollution of di-n-propyl adipate is sporadic and minimal. Losses of this compound to the New River from propellant manufacture at Radford AAP are estimated at 8-13 lb/month depending on the use rates.

G. Toxicological and Environmental Hazards

1. Toxicity to Mammals

The acute toxicity of di-n-propyl adipate to Sprague-Dawley rats is 3.7858 ml/kg by intraperitoneal administration. In spite of the low acute toxicity of this compound, some teratogenic effects have been observed (Singh *et al.*, 1973). In this study, pregnant Sprague-Dawley rats were injected with di-n-propyl adipate by the intraperitoneal route on the fifth, tenth and fifteenth day of pregnancy. Five rats were utilized at each of four dosage levels. On the 20th day of gestation, the rats were sacrificed by ether inhalation. The numbers of corpus lutea, resorption sites, viable and dead fetuses, and fetal weights were recorded. The fetuses were examined for gross, skeletal and visceral abnormalities. The results of this study are compared in Table XI-3 to those obtained from controls receiving blunt needle injections, distilled water, normal saline or cottonseed oil injections. An increase in the number of resorptions and the number of abnormalities and a decrease in fetal weight were observed with increasing dosage of di-n-propyl adipate. From the results of this study, a safe level for no teratogenic effects for di-n-propyl adipate appears to be 0.1262 ml/kg or 1/30 the LD50.

2. Aquatic Toxicity

No information was found on the toxicity of di-n-propyl adipate to aquatic organisms.

3. Toxicity to Microorganisms

No information was found on the toxicity of di-n-propyl adipate to microorganisms. However, adipic acid at concentrations of 100 mg/l had no affect on bacteria or protozoa (Meinck *et al.*, 1970).

4. Phytotoxicity

No specific information on the physiological effects of di-n-propyl adipate to vegetation was encountered in the literature search. Several

Table XI-3. Teratogenic Effects of Di-n-Propyl Adipate in the Rat
(Singh *et al.*, 1973)

Treatment Group	Volume Injected, ml/kg	No. of Corpus Lutea	Number of Resorptions (Z)	Number of Dead Fetuses (Z)	Number of Live Fetuses (Z)	Mean Weight of Fetuses, g	Abnormalities		
							Gross (Z)	Skeletal (X)	Visceral (Y)
Controls									
Blunt Needle	-	69	4(6.0)	0	63(94.0)	3.91±0.02	0	1(3.0)	0
Distilled Water	10.00	59	4(6.8)	0	55(93.2)	4.40±0.33	0	0	-
Normal Saline	10.00	62	7(11.5)	0	54(88.5)	4.10±0.13	1(1.9)	4(14.3)	-
Cottonseed Oil	10.00	71	5(7.5)	0	62(92.5)	3.89±0.09	1(1.6)	2(6.3)	0
Di-n-propyl adipate	0.1262	66	2(3.2)	0	61(96.8)	3.90±0.09	0	0	0
Di-n-propyl adipate	0.3786	61	6(10.9)	0	49(89.1)	3.77±0.17	1(2.0)	0	0
Di-n-propyl adipate	0.7572	64	6(9.8)	0	55(90.2)	3.63±0.11	2(3.6)	0	0
Di-n-propyl adipate	1.2619	56	9(20.0)	0	36(80.0)	3.61±0.22	2(5.6)	1(5.3)	0

references concerning the phototoxicity of adipic acid indicate that it is relatively non-toxic to plants in moderate concentrations. Meinck *et al.* (1970) reported that no adverse effects were observed in algae at a concentration of 100 mg/l. Prill *et al.* (1949) observed that a 1.25 M concentration of adipic acid resulted in 50% inhibition in the growth of wheat seedling roots.

5. Environmental Fate

Di-n-propyl adipate is expected to be readily degradable in the environment. Hydrolysis or microbial degradation will lead initially to n-propanol, monopropyl adipate and adipic acid. Further microbial degradation of these initial products will lead to incorporation of the carbons into the cell mass.

6. Literature Availability for Phase II

Due to the low use of di-n-propyl adipate, only a limited amount of toxicological and environmental data are available on this chemical. Thus, toxicological and environmental hazards of this compound will have to be inferred from similar esters.

H. Regulations and Standards

There are no U.S. regulations or standards specific for di-n-propyl adipate. This compound has a low toxicity. However, some teratogenic effects have been observed. Therefore, it is recommended that exposure of pregnant women to di-n-propyl adipate should be avoided.

I. Conclusions and Recommendations

Di-n-propyl adipate is a plasticizer used in a variety of propellants manufactured at Radford AAP. Radford AAP uses ~26,000 lb of this compound per year. Radford AAP purchases its di-n-propyl adipate from Hatco Chemical. Hatco Chemical produces di-n-propyl adipate in accordance to military specifications on special order. There are no civilian uses of this chemical.

Although the acute mammalian toxicity of di-n-propyl adipate is low (g/kg), teratogenic effects in rats have been observed. No aquatic toxicity information on di-n-propyl adipate was found in the literature. In the environment, di-n-propyl adipate should be chemically and/or microbially degraded.

Di-n-propyl adipate is a military unique compound. Radford AAP effluents are the major source of environmental pollution by this compound. Therefore, it is recommended that further environmental and toxicological studies on di-n-propyl adipate be undertaken. These studies should include a detailed toxicological and environmental evaluation of di-n-propyl adipate in Phase II. Aquatic toxicity and fish egg survival tests are warranted if the Phase II study does not uncover information in these areas.

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PRELIMINARY PROBLEM DEFINITION STUDY ON
MUNITIONS-RELATED CHEMICALS
METHYL CENTRALITE

SUMMARY

Methyl centralite is an N,N' disubstituted urea used as a coating for IMR propellants. These propellants are currently manufactured only at Radford AAP. The use of methyl centralite by the Army for this purpose is less than 400 lb per year. Pollution resulting from this use is negligible.

There are no civilian manufacturers or users of methyl centralite in the United States. All methyl centralite purchased by the Army is obtained from foreign manufacturers.

Based on the limited information available, the toxicological and environmental hazards of methyl centralite appear to be similar to the more widely used ethyl centralite.

Even though methyl centralite is a military unique chemical, it is used in small quantities and is thus not a military problem chemical. Any further Army sponsored studies on this compound should be a low priority.

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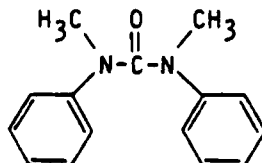
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XII. METHYL CENTRALITE

A. Alternate Names

Methyl centralite is an N,N' disubstituted urea with a molecular formula of $C_{15}H_{16}N_2O$ and corresponding molecular weight of 240.31. It has the following structural formula:



Other alternate names are listed below:

CAS Registry No.:	611-92-7
CA Name (8CI):	Carbonilide, N,N'-Dimethyl diphenyl
CA Name (9CI):	Urea, -N,N'-Dimethyl-N,N'diphenyl
Synonyms:	Centralite-2; Centralite II; N,N'-Dimethylcarbonilide; N,N'-Dimethyl-N,N'-Diphenylurea; 1,3-Dimethyl-1,3-Diphenylurea α,β -Dimethylcarbanilide
Wisweisser Line Notation:	1NR & VN18R

B. Physical Properties

The physical properties of methyl centralite are listed in Table XII-1.

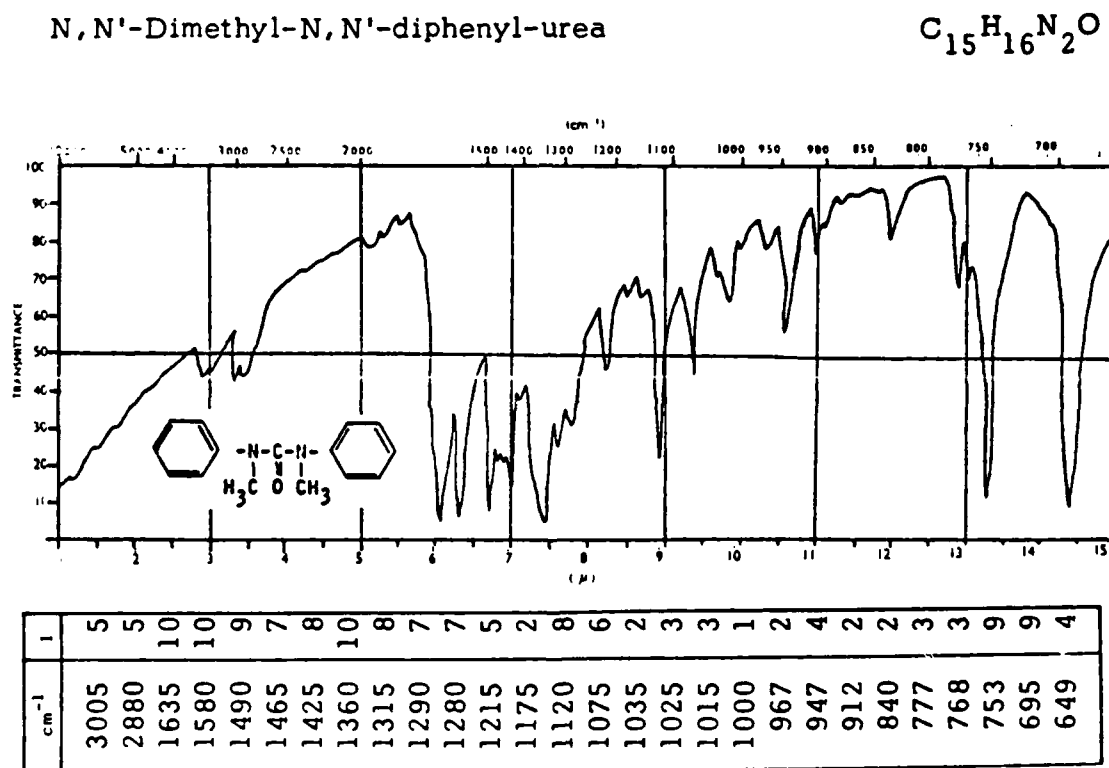
Table XII-1. Physical Properties of Methyl Centralite *

Physical Form @ 20°C :	crystalline
Color:	white
M.P.:	120.5 - 122°C
B.P.:	295°C
Density:	1.180 g/cm ³
Solubility:	soluble in petroleum ether, isopropyl ether, methanol, ethanol, carbon disulfide, ethyl acetate, acetone

* Military Specification (1960), Brodman *et al.*, 1974

The UV absorbance maximum for methyl centralite is reported as 244 nm (Maurer, 1970). The infrared spectrum of methyl centralite is shown in Figure XII-1.

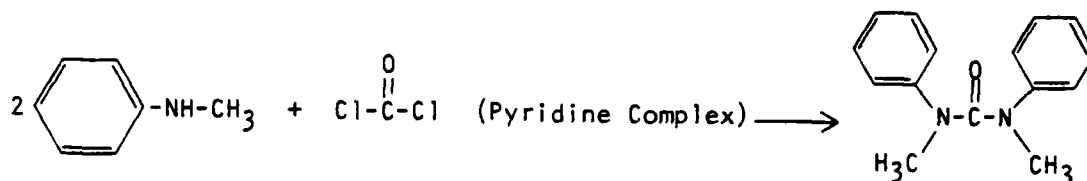
Figure XII-1. Infrared Spectrum of Methyl Centralite
(Mecke and Langenbucher, 1965)



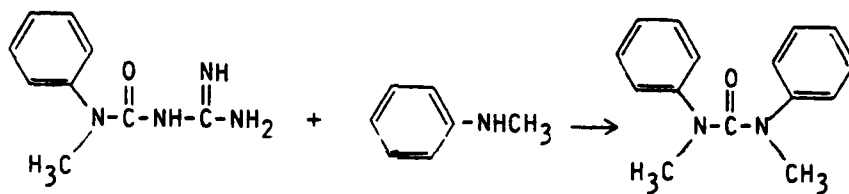
C. Chemical Properties

1. General Reactions

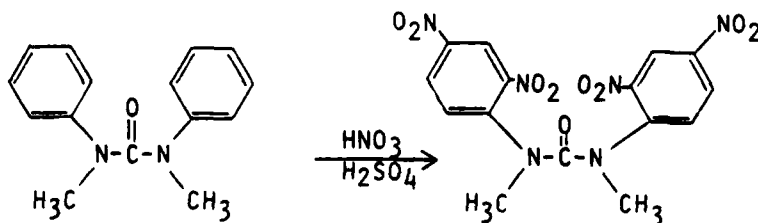
Methyl centralite is synthesized by treating N-methylaniline with phosgene (Scholtissek, 1956):



It has also been synthesized by treating 1-methyl-1-phenyl-3-amidinourea with N-methylaniline (Urbanski *et al.*, 1959):



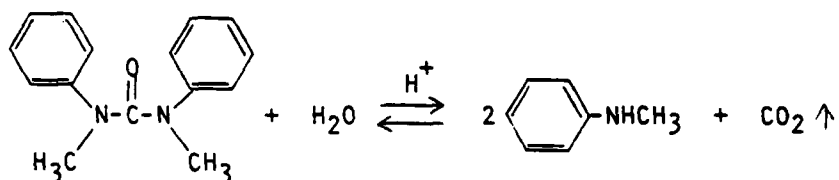
Methyl centralite forms a 2:1 complex with uranium tetrachloride and bromide and a 3:1 complex with thorium tetrachloride (Bagnall *et al.*, 1971). Methyl centralite is very susceptible to electrophilic substitution and has been nitrated in mixed acid (Lepore *et al.*, 1976).



2. Environmental Reactions

The environmental chemistry of methyl centralite has not been reported. The hydrolysis of ethyl centralite is slow (Roy, 1968) and the analogous reaction for methyl centralite should also be slow. However,

hydrolysis is expected to be the primary environmental reaction.



Photolysis of methyl centralite should lead to similar products as the irradiation of amides generally leads to cleavage of the carbon-nitrogen bonds (Calvert and Pitts, 1966).

3. Sampling and Analysis

Methyl centralite has been determined by its ultraviolet absorption at 244 nm (Maurer *et al.*, 1970). Thin layer chromatography has also been employed to advantage. Ripper (1967) used silica gel plates with a mobile phase of 30% isopropylether/petroleum ether. Sinha (1964) employed 1:1 benzene/petroleum ether mobile phase on silica gel plates. Methyl centralite has also been analyzed by gas chromatography with flame ionization detection. Stationary phases which have been used include 15% Apiezon L on Chromosorb W at 250°C (Alston *et al.*, 1966) and silicone oil SE-30 on Chromosorb G at 160°C (Sommer, 1976). No detection limits were given.

D. Uses in Army Munitions

1. Purpose

Methyl centralite is used by Radford AAP as a coating for small arms propellants. Specifically, methyl centralite is used with IMR single base propellants. These propellants are used in the 5.56 mm and 25 mm rounds.

Single base propellants are produced in the "C" propellant line at Radford AAP using the solvent process. In this process, nitrocellulose, containing 28% moisture, is dehydrated by addition of ethanol. The material is then pressed into a block containing about 75% nitrocellulose and 25% of ethanol.

The wet block is then broken up and transferred to a mixer. Ether, containing any desired additives, is added and the ingredients mixed for one hour. The mixture is pressed and extruded into cords. The cords are cut to the desired length. The remaining solvents are removed by immersion in warm water followed by air drying. The propellant is sometimes glazed with a coating of graphite, or in the case of IMR propellant, methyl centralite.

2. Quantities Used

During the 1972-1977 period, Radford AAP used a total of 872 lb of methyl centralite. This quantity represents an average annual use rate of 145 lb/year. The current use rate is 352 lb/year or 29.3 lb/month. At full mobilization, no methyl centralite would be used, as IMR propellants are not called for on the mobilization schedule.

3. Documented or Speculated Occurrences in Air or Water

Losses of methyl centralite to the environment occur during preparation operations such as weighing, grinding or classification. Additional losses occur during the propellant coating step. It is estimated that 2-3% of the materials used are lost during preparation and 1-2% during coating operations (Dickenson, 1978). At current production rates, a total of 1 to 1.5 lb/month of methyl centralite is lost to the environment. At full mobilization, methyl centralite losses would drop to zero, as IMR propellants are not on the mobilization schedule.

E. Civilian Uses

Radford AAP receives methyl centralite solely from the Naval Ordnance Station, Indian Head, Md. (Dennis, 1979). The Naval Ordnance Station imports methyl centralite from Canada (Eldridge, 1979). Methyl centralite is not produced in the United States (SRI International, 1978), nor are there any plans for future civilian production of this chemical.

F. Comparison of Military and Civilian Uses and Pollution of Methyl Centralite

There are no U.S. civilian producers of methyl centralite. All the methyl centralite used by Radford AAP is purchased from foreign manufacturers. Thus, in the United States, methyl centralite is a military unique chemical. However, the use of methyl centralite in munitions production is minor, less than 400 lb/year. The pollution resulting from this use is also negligible.

G. Toxicological and Environmental Hazards

1. Mammalian Toxicity

The lowest effective dose of methyl centralite to rats is 500 mg/kg (Dieke *et al.*, 1947). From this data, it appears that methyl centralite is similar in toxicity to ethyl centralite.

2. Aquatic Toxicity

There is no information on the aquatic toxicity of methyl centralite. A similar compound, ethyl centralite, is toxic in the low ppm range. Methyl centralite is used in very small amounts at Radford AAP and should present no hazard to the aquatic community in the New River.

3. Toxicity to Microorganisms

No specific references concerning the toxicity of methyl centralite to microorganisms were located while reviewing the literature. Information on the effects of ethyl centralite and a degradation product, 4-nitroaniline, on microorganisms are documented. Ethyl centralite levels greater than 10 ppm inhibited the growth of saprophytic microflora and retarded the degradation of organic pollutants (Korolev *et al.*, 1976). The toxicity threshold of 4-nitroaniline to *Pseudomonas putida* was reported by Bringman and Kuhn (1977) to be 3.8 ppm.

4. Phytotoxicity

No information was found on the phytotoxic activity of methyl centralite. Limited information was located on the effects of N-ethyl-aniline, a potential degradation product of the closely related structure ethyl centralite. The effects of N-ethylaniline and related compounds to algae are presented in Table XII-2.

Batterton *et al.* (1978) reported that N-ethylaniline had a low toxicity to a blue-green algae (*Agmenellum quadruplicatum*), when compared to other substituted anilines.

5. Environmental Fate

Once released into the environment from Radford AAP effluents, methyl centralite will accumulate in the sediment. Chemical and microbial degradation is expected to occur only slowly. Some bioaccumulation is also expected, but the extent of accumulation is not known.

6. Availability of Literature for Phase II

Only a few references to methyl centralite appear in the literature. Thus, any information on the toxicological or environmental hazards of this compound would have to come from foreign manufacturers, Army and Navy researchers, or by analogy to related compounds such as ethyl centralite.

H. Regulations and Standards

No U.S. effluent or industrial hygiene standards exist for methyl centralite. This compound is not listed in the EPA "Toxic Substances Control Act Candidate List of Chemical Substances" (1977). For a related compound, ethyl centralite, Korolev *et al.* (1976) suggested a Russian maximum permissible level of 0.5 ppm in water.

Table XII-2. Toxicity of Potential Ethyl Centralite Degradation Products and Related Compounds to Algae

Algae	Compound	Hardness (ppm as CaCO ₃)	Temperature °C	Dose	Effect	Reference
Blue Green (<i>Agmenellum quadricaudatum</i>)	n-ethylaniline	-	-	500 µg/plate	5% inhibition of growth	Batterton <i>et al.</i> (1978)
"	aniline	-	-	10 µg/plate	100% inhibition of growth	"
Green (<i>Scenedesmus quadricauda</i>)	4-nitroaniline	16	25	11.0 ppm	toxicity threshold	Bringmann and Kuhn (1977)
"	aniline	16	25	8.3 ppm	toxicity threshold	"

I. Conclusions and Recommendations

Methyl centralite is a compound which is used by the Army in very small quantities and on a sporadic basis. Since no civilian companies make or use methyl centralite, it is a military unique compound.

Only limited information is available on the toxicological and environmental hazards of methyl centralite. From the little information available, it appears that methyl centralite behaves in a manner similar to the more widely used ethyl centralite.

Even though methyl centralite is a military unique chemical, the use rate of this chemical by the Army is negligible. Therefore, any future Army sponsored studies on this compound should be a low priority.

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PRELIMINARY PROBLEM DEFINITION STUDY ON
MUNITIONS-RELATED CHEMICALS
GLYCOL DINITRATES

SUMMARY

The glycol dinitrates are manufactured for their explosive and plasticizer properties. The most commonly used of these compounds include:

- ethylene glycol dinitrate
- diethylene glycol dinitrate
- triethylene glycol dinitrate
- 1,2-propylene glycol dinitrate
- 1,3-propylene glycol dinitrate

Diethylene glycol dinitrate was evaluated in a previous problem definition study. This study completes the evaluation of the Army use of the remaining glycol dinitrates.

Of the four remaining glycol dinitrates, only 1,2-propylene glycol dinitrate is used to any extent in Army munitions production. This compound is used as a component of Otto II torpedo fuel produced at Radford AAP. Historical use of 1,2-propylene glycol dinitrate is ~137,000 lb/year. However there is no current or anticipated near future production of Otto II fuel.

In contrast, the civilian community produces glycol dinitrate for use in dynamite as a freezing point depressant. The quantity of ethylene glycol dinitrate produced in the U.S. each year is estimated at ~10 million lb.

The glycol dinitrates are moderately toxic by all routes of administration. Humans exhibit adverse responses such as headache, visual and balance impairment at concentrations as low as 0.1 - 0.2 ppm in air. The environmental fate of these compounds has not been studied. However, hydrolysis and photochemical decomposition are expected to be the major environmental reactions.

In spite of the effects of the glycol dinitrates on humans, a Phase II study of these compounds by the Army should be a low priority unless Otto II fuel production is resumed in high volume.

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XIII. GLYCOL DINITRATES

A. Introduction

The glycol nitrates are a class of compounds manufactured mainly for their plasticizer and explosive properties. The most common of the glycol nitrates include:

- ethylene glycol dinitrate
- diethylene glycol dinitrate
- triethylene glycol dinitrate
- 1,2-propylene glycol dinitrate
- 1,3-propylene glycol dinitrate
- propylenetriol trinitrate

Propylenetriol trinitrate (nitroglycerin) has been the subject of many previous studies and thus was not included in this preliminary problem definition study. Diethylene glycol dinitrate was included in an earlier problem definition study (Kitchens *et al.*, 1978). Therefore, to complete the study of the glycol dinitrates, the Army usages of ethylene glycol dinitrate, triethylene glycol dinitrate, 1,2-propylene glycol dinitrate and 1,3-propylene glycol dinitrate are evaluated in this report.

B. Alternate Names

The glycol dinitrates are aliphatic nitrate esters. The alternate names, molecular and structure formula and molecular weights of these esters are presented below:

Ethylene glycol dinitrate

Empirical Formula:	$C_2H_4N_2O_6$
Structural Formula:	$O_2N-O-(CH_2)_2-O-NO_2$
Molecular Weight:	152
CAS Registry No.:	628-96-6
CA Name (9CI):	1,2-ethanediol, dinitrate
CA Name (8CI):	Ethylene glycol, dinitrate
Wiswesser Line Notation:	WNO2ONW
Synonyms:	Ethylene dinitrate; Ethylene nitrate; Glycol dinitrate; Nitroglycol; EGDN

Triethylene glycol dinitrate

Empirical Formula: $C_6H_{12}N_2O_8$
Structural Formula: $O_2N-O-(CH_2)_2-O-(CH_2)_2-O-(CH_2)_2-O-NO_2$
Molecular Weight: 240
CAS Registry No.: 111-22-8
CA Name (9CI): Ethanol, 2,2'-(1,2-ethanediylbis(oxy))
bis-,dinitrate
CA Name (8CI): Triethyleneglycol dinitrate;
Synonyms: TEGDN; TEGN
Wiswesser Line Notation: WNO20202ONW

1,2-Propylene glycol dinitrate

Empirical Formula: $C_3H_6N_2O_6$
Structural Formula: $O_2N-O-CH_2-\overset{\text{O}-NO_2}{\underset{|}{CH}}-CH_3$
Molecular Weight: 166
CAS Registry No.: 6423-43-4
CA Name (9CI): 1,2-propanediol, dinitrate
Synonyms: Propylene dinitrate; Propylene glycol
dinitrate; Propylene nitrate; Iso-
propylene nitrate; PGDN
Wiswesser Line Notation: WNO1Y1 and ONW

1,3-Propylene glycol dinitrate

Empirical Formula: $C_2H_6N_2O_6$
Structural Formula: $O_2N-O-(CH_2)_3-O-NO_2$
Molecular Weight: 166
CAS Registry No.: 3457-90-7
CA Name (9CI): 1,3-Propanediol, dinitrate
Synonyms: 1,3-Propylene glycol dinitrate;
Trimethylene nitrate; Trimethylene
dinitrate
Wiswesser Line Notation: WNO3ONW

C. Physical Properties

The physical properties of ethylene glycol dinitrate, triethylene glycol dinitrate, 1,2-propylene glycol dinitrate and 1,3-propylene glycol dinitrate are listed in Table XIII-1.

D. Chemical Properties

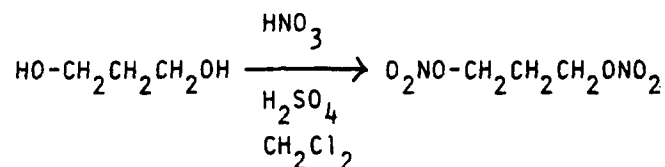
1. General Reactions

The glycol dinitrates have a very similar chemistry and will be considered as a group. The preparation of alkyl nitrates can be accomplished in a variety of ways. The most general method is the mixed acid nitration of alcohols (Boschan *et al.*, 1955). For example, 1,3-propylene glycol dinitrate can be prepared by the action of nitric and sulfuric acids on 1,3-propanediol in methylene chloride (Marken *et al.*, 1977):

Table XIII-1. Physical Properties of the Glycol Dinitrates*

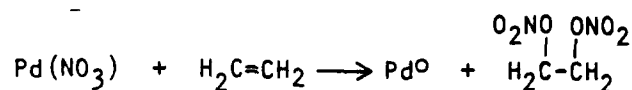
Property	Ethylene glycol dinitrate	Triethylene glycol dinitrate	1,2-Propylene glycol dinitrate	1,3-Propylene glycol dinitrate
Physical Form at 20°C	Oily liquid	Liquid	Liquid	Liquid
Color	Yellow	Colorless	Colorless	Colorless
Odor	-	-	Disagreeable	-
Melting Point	-20°C	-19°C	-	-
Boiling Point	-	-	92°C @ 10 mm Hg	180°C @ 10 mm Hg
Vapor Pressure	0.0044 mm Hg @ 0°C 0.038 mm Hg @ 20°C 0.26 mm Hg @ 40°C 1.3 mm Hg @ 60°C 5.9 mm Hg @ 80°C 22.0 mm Hg @ 100°C	<0.001 mm Hg @ 25°C		
Volatility @ 60°C		0.04 mg/hr cm ²	-	-
Density, d_{4}^{20}	1.4918	1.3291 (d_{16}^{16})	1.3774	1.3952
Refractive Index	1.4452 (n_D^{20})	1.454 (n_{∞}^{20})	1.4270 (n_{∞}^{20})	1.43476 (n_{∞}^{20})
Viscosity @ 20°C	4.2 cP	13.2 cP	4.65 cP	5.8 cP
Dielectric Constant	28.26	-	26.80	18.97
Heat of Combustion	1764 cal/g	3428 cal/g	-	-
Heat of Explosion	-	357 cal/g	-	-
Heat of Formation	366 cal/g	-	-	-
Solubility	Soluble in water	Soluble in water; alcohol; 2:1 ether; alcohol; acetone	soluble in water	

*Urbanski, 1965

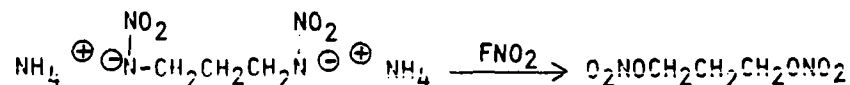


Other techniques which have been employed include:

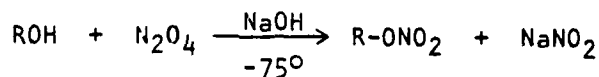
- the treatment of alkenes with palladium nitrate for the preparation of ethylene glycol dinitrate and 1,2-propylene glycol dinitrate (Likholobov *et al.*, 1974):



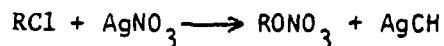
- the reaction of the ammonium salts of primary nitramines with nitryl fluoride for the preparation of ethylene glycol dinitrate and 1,3-propylene glycol dinitrate (Gafurov *et al.*, 1971):



- the reaction of alcohols with N_2O_4 at -75°C (Bachman and Cannon, 1967):

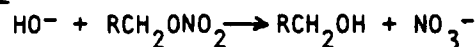


- the reaction of alkylhalides with silver nitrate (Boschan *et al.*, 1955):

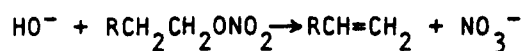


The glycol dinitrates hydrolyze rapidly in base, somewhat more slowly in acid and only at elevated temperatures in water alone (Johnson, 1975). The hydrolysis of alkyl nitrates can lead to a variety of products including the parent alcohol, alkenes, aldehydes and carboxylic acids as shown in Figure XIII-1 (Johnson, 1975; Boschan *et al.*, 1955).

a) SN_1 or SN_2



b) E_2



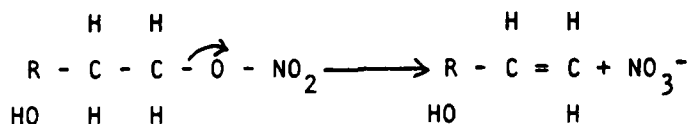
c) Elimination of an α proton



Figure XIII-1. Nitrate Ester Hydrolysis.

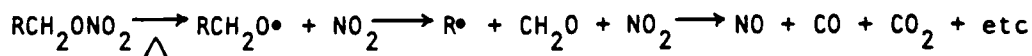
Reaction A) involves displacement of the nitrate group by nucleophilic hydroxide anion. In near neutral solutions water molecules may act as nucleophiles. Most esters undergo bimolecular substitution (SN_2) with nucleophilic addition and elimination of nitrate occurring simultaneously. Sterically hindered nitrate esters generally are hydrolyzed via SN_1 processes involving initial loss of nitrate to form a carbonium ion followed by rapid addition of a water molecule.

Reaction B) involves simultaneous elimination of a β proton and the NO_3^- moiety.



Reaction C) proceeds with abstraction of an α proton with simultaneous cleavage of the O-N bond rather than the C-O bond (Boschan *et al.*, 1955).

Thermal decomposition of alkyl nitrates initially yields alkoxy radicals which react further to give complex mixtures (Boschan *et al.*, 1955).



Photolysis also gives complex mixtures including NO_2 , NO , N_2O , N_2 , H_2 , CO , CO_2 , CH_2O , etc. (Boschan *et al.*, 1955).

2. Environmental Reactions

The environmental fate of glycol dinitrates has not been reported; however, the likely reactions are hydrolysis and photolysis. These reactions will yield complex mixtures of nitrogen oxides and short chain alcohols, alkenes and carbonyls.

3. Sampling and Analysis

Several methods have been developed to determine the alkylpoly-nitrates in air and water samples. Quantitative separation and analysis of alkylpolynitrates by gas chromatography with a hot wire detector was reported by Camera and Pravisanì (1964). They used short columns and low temperatures to prevent decomposition reactions. The method gave good separations and high precision. However, no lower detection was given.

Detection of nitrate esters in water to the 20 ppb level is possible using a single-sweep polarographic method (Whitnack and Becktel, 1976). This system was developed for the Navy to monitor 1,2-propylene glycol dinitrate in their effluent. The method can be used as a continuous monitor in a range of 0.10 to 1000 ppm 1,2-propylene glycol dinitrate in water.

Two methods of analysis of low concentrations of nitrate esters in air are reported in the literature. One method is based upon nitration of m-xylene in a sulfuric acid collection solution. The nitroxylene is determined colorimetrically after isolation by steam distillation (Yagoda and Goldman, 1943). In a gas chromatographic method, Camera and Pravisanì (1967) collected air samples by bubbling through ethanol. The ethanol solutions were injected directly into a gas chromatograph equipped with an electron capture detector. With a 10 liter air sample volume, the sensitivities for various nitrate esters were

- ethyleneglycol dinitrate 0.08 mg/m³
- 1,2-propyleneglycol dinitrate 0.02 mg/m³

E. Uses in Army Munitions

Of the four glycol dinitrates included in this study, only one compound, 1,2-propylene glycol dinitrate has been recently used in Army munitions production. The Army use of 1,2-propylene glycol dinitrate is discussed in this section.

1. Purpose

1,2-Propylene glycol dinitrate is used by Radford AAP in the production of Otto Fuel II. 1,2-Propylene glycol dinitrate is the principal constituent of Otto Fuel II, comprising 75.8 to 76.2% of the formulation. Radford AAP manufactures 1,2-propylene glycol dinitrate from 1,2-propylene glycol which is purchased from commercial sources.

Otto Fuel II is a mixture of 1,2-propylene glycol dinitrate, di-n-butyl sebacate (22.5%), 2-nitro diphenylamine (1.4-1.6%) and up to 0.8 ppm sodium. Otto Fuel II is used as a torpedo propellant. It is produced at Radford AAP in the Nitroglycerine #1 Area. The principal processing step is nitration of propylene glycol to form 1,2-propylene glycol dinitrate. The stabilizers (di-n-butyl sebacate and 2-nitrodiphenylamine) are then added to form the finished propellant (Dickenson, 1979).

2. Quantities Used

Since 1972, Radford AAP has used 820,000 lb of 1,2-propylene glycol dinitrate in the production of Otto Fuel II. This represents an average annual use rate of 136,700 lb/year from 1972 to 1977. There is no current use of 1,2-propylene glycol dinitrate. The full mobilization use rate is zero, as the mobilization schedule does not call for the production of Otto Fuel II.

3. Documented or Speculated Occurrences in Air or Water

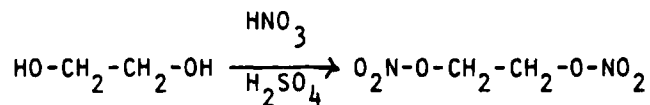
As there is no current use of 1,2-propylene glycol dinitrate at Radford AAP, no losses to the environment occur. Since there is no mobilization requirement for Otto Fuel II, no future production is foreseen. No near future losses of 1,2-propylene glycol dinitrate are expected.

During the 1972-1977 period, the losses of 1,2-propylene glycol dinitrate were 340 to 570 lb/month. This represents 3-5% of the amount used, which is considered to be a typical loss level (Dickenson, 1978).

F. Uses in the Civilian Community

1. Production Methodology

The only one of the glycol dinitrates that has a civilian use is ethylene glycol dinitrate. This chemical is used as freezing point depressant for low freezing dynamites. Ethylene glycol dinitrate is produced by mixed acid nitration of ethylene glycol. The reaction temperature must be kept low (10-15°C) to prevent hydrolysis and oxidation.



The water content of the acid is usually less than 15%. Yields are ~90.5% of the theoretical values (Urbanski, 1965). In practice, glycerine and glycol in a 50:50 mixture are usually nitrated simultaneously to make dynamite in one operation.

2. Manufacturer, Production and Capacity

Ethylene glycol dinitrate is manufactured by International Minerals and Chemical Corporation, IMC Chemical Group, Inc. Subsidiary in Seiple, Pennsylvania. Approximately 250 million lb of dynamite were produced in the U.S. in 1976 (NIOSH, 1978a). These dynamites contained 5-50% nitroglycerine: ethylene glycol dinitrate.

3. Usage

The only civilian usage of ethylene glycol dinitrate is in the production of dynamite.

4. Future Trends

The dynamite industry is in competition with new types of explosives that have better low and high temperature properties. Dynamite production is expected to slowly decline. Only 10% of the blasting agents used in the U.S. are dynamites containing ethylene glycol dinitrate (NIOSH, 1978a).

5. Documented or Speculated Occurrences in the Environment

There is no information available on losses of the glycol dinitrates to the environment from civilian manufacture or uses.

G. Comparison of Military and Civilian Usages and Pollution

Both civilian and military use of the glycol dinitrates is low. Of the four chemicals in this study, 1,2-propylene glycol dinitrate has the highest Army use in the production of Otto II torpedo fuel. However, this fuel is not in current production and no near future production is planned. The civilian manufacture of ethylene glycol dinitrate for use in dynamite is low. There are no other civilian uses of this chemical. Pollution of the glycol dinitrates from both civilian and military uses is also low.

H. Toxicological and Environmental Hazards

1. Toxicity to Mammals

The data on the toxicity of the glycol dinitrates to mammals indicate that these compounds are moderately toxic by all routes of administration. The acute toxicity response of these compounds to various mammals are presented in Table XIII-2. The main cause of death is anoxia due to the conversion of hemoglobin to methemoglobin.

Acute studies with ethylene glycol dinitrate (93% in a gel) were conducted to determine the rate of absorption of this compound through the skin. The initial absorption rate of ethylene glycol dinitrate was

Table XIII-2. Acute Toxicity of the Glycol Dinitrate to Mammals

Compound	Species	Route of Administration	Dose mg/kg	Effect	Reference
Ethylene glycol dinitrate	Rat	oral	616	LD50	NIOSH, 1977
"	Cat	s.c.	50	LDLo	NIOSH, 1977
"	Rabbit	s.c.	300	LDLo	NIOSH, 1977
"	Human	oral	5	LDLo	NIOSH, 1977
Triethylene glycol dinitrate	Rat	oral	1000	LD50	NIOSH, 1977
"	Rat	i.p.	995	LD50	Anderson <i>et al.</i> , 1976
"	Rat	s.c.	2520	LD50	NIOSH, 1977
"	Mouse	i.p.	945	LD50	NIOSH, 1977
"	Guinea Pig	i.p.	700	LD50	NIOSH, 1977
Propylene glycol dinitrate	Rat	oral	250	LD50	NIOSH, 1977
"	Rat	oral	1190	LD50	Clark and Litchfield, 1967
"	Rat	s.c.	463	LD50	NIOSH, 1977
"	Rat	i.p.	479	LD50	NIOSH, 1977
"	Mouse	s.c.	1208	LD50	NIOSH, 1977
"	Mouse	i.p.	1047	LD50	NIOSH, 1977
"	Monkey	i.v.	410	LDLo	NIOSH, 1977

~10 mg/cm²/hr. As shown in Table XIII-3, significant deaths were observed with doses of 300 mg/kg and greater.

Table XIII-3. Effects of Acute Percutaneous Exposure of Rats to Ethylene Glycol Dinitrate (NIOSH, 1978a).

Exposure mg/kg	Percentage of Deaths in 12 Hours
100	2
200	0
300	18
400	22
500	19
600	30

Chronic inhalation studies with ethylene glycol dinitrate on cats were conducted by Gross *et al.*, 1942. The experimental conditions and results are summarized in Table XIII-4.

Table XIII-4. Inhalation Toxicity of Ethylene Glycol Dinitrate (Gross *et al.*, 1942)

No. of Animals	Dose	Duration	Effects
1	13 mg/m ³	8 hr/day 5 days/week for 1000 days	Few effects - decreased erythrocytes during days 30-120, then return to normal; no methemoglobin.
1	134 mg/m ³	8 hr/day 5 days/week for 1000 days	anemia; increased leukocyte count, Heinz bodies; up 29% methemoglobin
1	140 mg/m ³	8 hr/day 5 days/week for 273 days	death at 273 days; normoblastic anemia
1	170 mg/m ³	8 hr/day 5 days/week for 102 days	death at 102 days; normoblastic anemia
1	170 mg/m ³	8 hr/day 5 days/week for 97 days	death at 97 days; normoblastic anemia

The results of this study indicate severe toxicological responses at concentrations greater than 134 mg/m³.

Several epidemiological and occupational exposure studies have been conducted to determine the effects of glycol dinitrate and 1,2-propylene glycol dinitrate on humans. The initial symptoms of intoxication by these compounds are headache, fall in blood pressure due to vasodilation, visual and balance impairment and irritability. These symptoms have been reported to occur in volunteers exposed to concentrations of greater than 0.1 ppm ethylene glycol dinitrate and 0.2 ppm 1,2-propylene glycol dinitrate (American Conference of Governmental Industrial Hygienists, 1977). Methemoglobin formation occurs at higher doses. Death can result from anoxia in high doses or from withdrawal symptoms due to intermittent low doses.

2. Environmental Hazards

No information was found on the environmental hazards of the glycol dinitrates. Hydrolysis is expected to be the major environmental reaction of these compounds. Photochemical decomposition could also occur.

3. Availability of Literature for Phase II

A large number of toxicological studies have been conducted with the glycol dinitrates. Thus there is sufficient toxicological information for a Phase II study. However, the environmental literature on these compounds is practically non-existent.

I. Regulations and Standards

The current OSHA standard for ethylene glycol dinitrate is 1 mg/m³ (ceiling concentration) in air (NIOSH, 1978b). The recommended exposure limit is a ceiling concentration of 0.1 mg/m for 20 minutes (NIOSH, 1978b). The TLV for 1,2-propylene glycol dinitrate is 0.2 ppm. A ceiling TLV of 0.05 ppm is recommended (American Conference of Governmental Industrial Hygienists, 1977).

The manufacture of the glycol dinitrates would be classified under explosive manufacturing subcategory A (Manufacture of Explosives) (EPA, 1976). The effluent limit recommendations based on Best Practicable Control Technology Currently Available (BPCTCA); Best Available Demonstrated Control Technology (BADCT) and the Best Available Technology Economically Achievable (BATEA) are listed in Table XIII-5.

J. Conclusions and Recommendations

The purpose of this preliminary problem definition study was to assess the Army's responsibility for conducting further studies on the glycol dinitrates - ethylene glycol dinitrate, triethylene glycol dinitrate, 1,2-propylene glycol dinitrate and 1,3-propylene glycol dinitrate. Of these compounds, only

Table XIII-5. Recommended Effluent Limitations for Explosives
Point Source Subcategory A (EPA, 1976)

Effluent Characteristic	Type of Limitation	Effluent Limitations		
		Average of Daily Values for 30 Consecutive Days		Maximum for any One Day
		Shall not Exceed	kg/kg production	
		mg/l	mg/l	mg/l
BOD ₅	BPCTCA	0.24		0.72
COD	BPCTCA	2.59		7.77
TSS	BPCTCA	0.084	50	0.25
				150
BOD ₅	BADCT	0.22		0.35
COD	BADCT	2.3		3.6
TSS	BADCT	0.034	20	0.067
				40
BOD ₅	BATEA	0.067		0.11
COD	BATEA	0.55		0.85
TSS	BATEA	0.017	10	0.034
				20

1,2-propylene glycol dinitrate is used to any extent by the military. This compound is manufactured at Radford AAP by the mixed acid nitration of 1,2-propylene glycol for use in Otto II torpedo fuel. Past use of 1,2-propylene glycol dinitrate has been ~137,000 lb/year. No current or near future use of this chemical by the Army is anticipated.

In contrast ethylene glycol dinitrate is used in the civilian community for the production of low freezing dynamite. Although the exact production figures are not available, civilian production of ethylene glycol dinitrate is probably around 10 million lb/year. Thus the military production and use of the glycol dinitrates is minor compared to the civilian production of dynamites.

The glycol dinitrates are toxic through all routes of administration. The acute toxicity of these compounds to most mammals is moderate. However effects on humans such as headache, fall in blood pressure and balance and visual impairment are observed at low doses (>0.1 ppm).

Since there are no current Army uses of the glycol dinitrates, a Phase II detailed toxicological and environmental study of these compounds should be a low priority.

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PRELIMINARY PROBLEM DEFINITION STUDY ON
MUNITIONS-RELATED CHEMICALS
TOLUIDINE RED TONER

SUMMARY

Toluidine red toner is an azonaphthol derivative used as a red colorant. In the civilian community, the main use of this pigment is in paints for industrial and agricultural equipment. The Army uses toluidine red toner in igniter mixes formulated at Lake City AAP. Toluidine red toner is a minor constituent of these mixes and is used as a colorant. Only 75 lb/year of toluidine red toner are currently used by the Army at Lake City AAP. Under full mobilization schedules this usage would increase to 400 lb/year.

Only one study was found on the toxicological hazards of toluidine red toner. In this subacute study, no effects were observed with rats fed doses up to 2% of their diet. However, other closely related compounds are proven carcinogens in animals.

Based on the limited use of toluidine red toner, it is recommended that any further Army sponsored studies on this compound should be a low priority.

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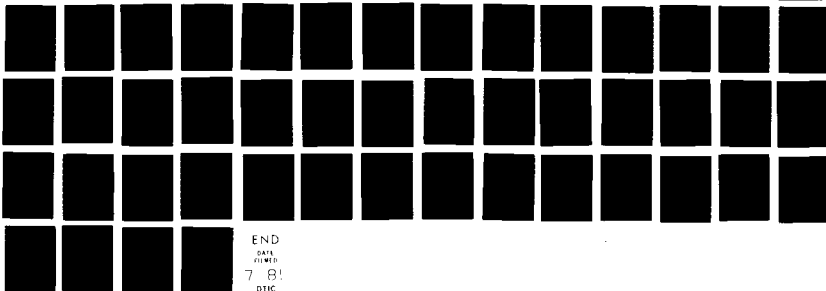
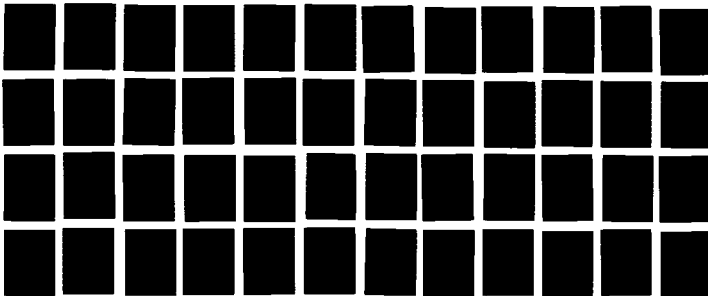
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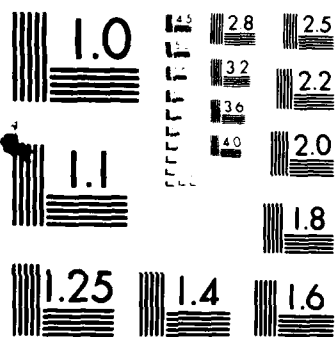
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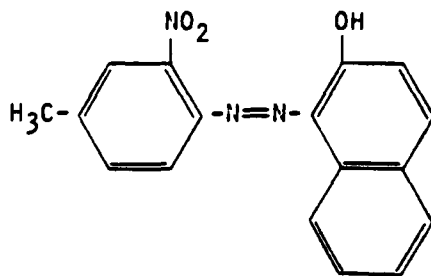
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XIV. TOLUIDINE RED

A. Alternate Names

Toluidine red is an azo dye with a molecular formula of $C_{17}H_{13}N_3O_3$ and corresponding molecular weight of 311. It has the following molecular structure:



Other pertinent alternate names for toluidine red are listed below:

CAS Registry No.:	2425-85-6
CA Name (8CI):	2-Naphthalenol, 1-(4-methyl-2-nitrophenyl)azo-
Synonyms:	C.I. Pigment red 3; D&C Red No. 35 Permanent Red 4R; Pigment scarlet R; Pigment Scarlet (Russian); Pigment Ruby; Hansa Red B; Toluidine Red
Color Index No.:	12120

B. Physical Properties

The physical properties of toluidine red are listed in Table XIV-1. The visible reflective spectra of toluidine red tint at ratios of 1:1, 1:10 and 1:99 to white are shown in Figure XIV-1.

C. Chemical Properties

1. General Reactions

Toluidine red is produced by the coupling reaction of β -naphthol and 2-nitrotoluidine (Hawley, 1977). Azo coupling reactions of this sort generally involve the formation of the diazonium salt of a primary aromatic amine (2-nitrotoluidine in this case) and the subsequent coupling with a phenolic compound in basic solution (Streitwieser and Heathcock, 1976).

Table XIV-1. Physical Properties of Toluidine Red*

Physical Form @ 20°C:	solid
Melting Point:	258°C
Surface Free Energy:	39.7 dynes/cm
Crystal Structure Data:	monoclinic
	$a = 16.300 \pm 0.010 \text{Å}$
	$b = 12.901 \pm 0.008 \text{Å}$
	$c = 6.982 \pm 0.004 \text{Å}$
	$\beta = 102.33 \pm 0.08^\circ$
Space Group:	$P2_1$ or $P2_1/m$

* Colour Index, 1956; Wu and Brzozowski, 1971; Chung, 1971.

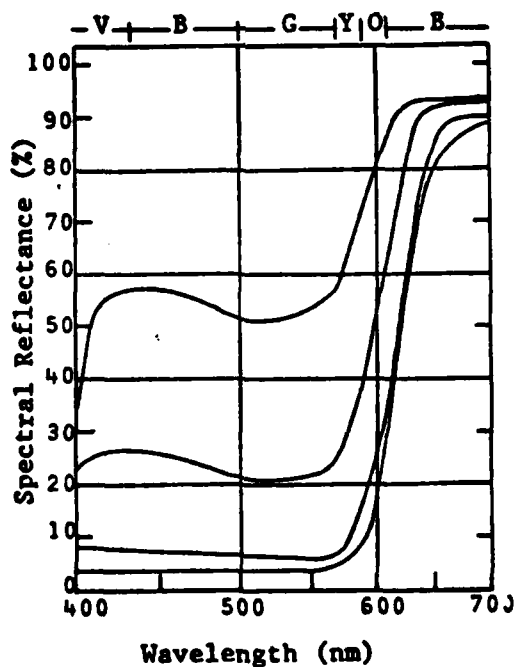
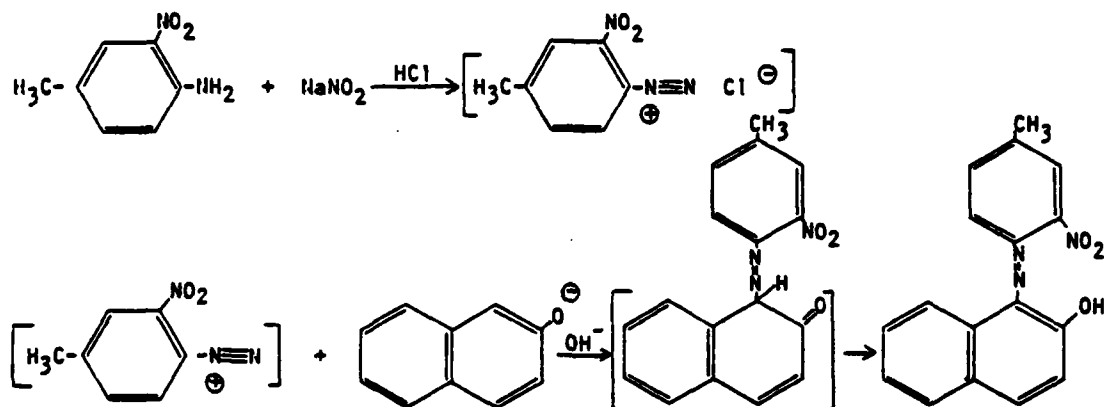
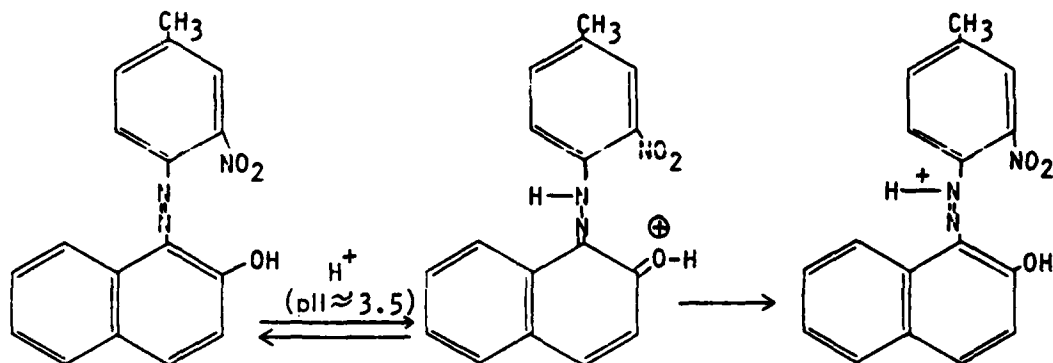


Figure XIV-1. Spectral Reflectance Curves for Toluidine Red (PR-3)/Ti₂ (Stubbs, 1973)

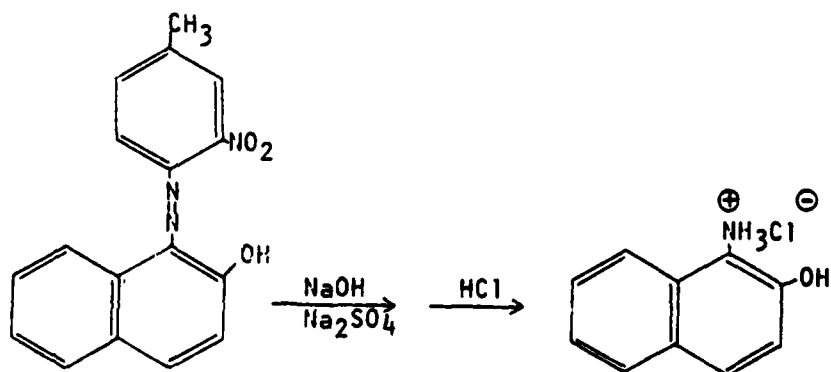
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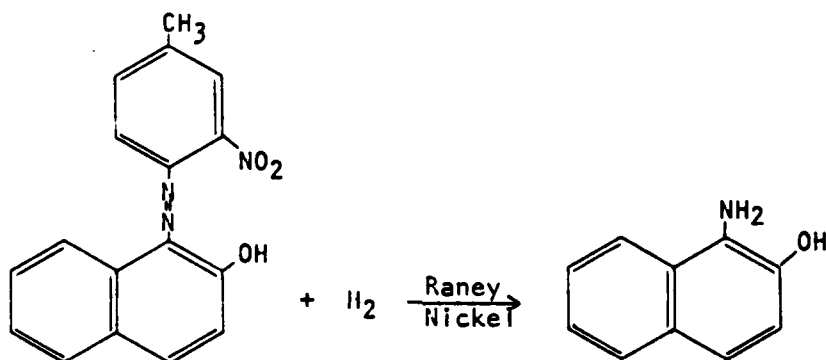
Azo dyes are generally quite stable to mild acid or base. Although the nitrogens have lone pairs of electrons capable of exhibiting basic properties, generally a fairly strong acid solution is required to yield significant protonation (Streitwieser and Heathcock, 1976).



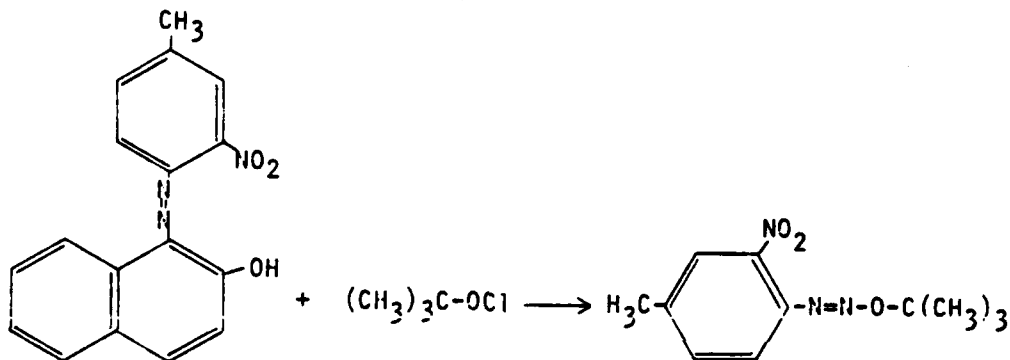
Azo dyes can be reduced to amino phenols by sodium hydrosulfite (Streitwieser and Heathcock, 1976)



or by hydrogenation with Raney nickel (Whitmore and Revukas, 1940).



Toluidine red reacts with t-butyl hypochlorite resulting in an electrophilic displacement of the diazonium moiety.



2. Environmental Reactions

The environmental fate of toluidine red has not been reported. Likely reactions are reduction to 1-amino- β -naphthol and 2-nitro-toluidine or a photochemical decomposition. Photochemical decomposition of azo compounds generally results in fragmentation yielding nitrogen gas (Calvert and Pitts, 1966). Radicals generated by this fragmentation can either recombine or react with other compounds present in the environment.

3. Sampling and Analysis

Toluidine red has been analyzed by high performance liquid chromatography (Ohnishi *et al.*, 1977). A Li Chrosorb SI 100 column using a concave gradient technique with 5% chloroform/hexane and 50% chloroform/hexane. A visible photometer detector was employed at 420 nm.

D. Uses in Army Munitions

1. Purpose

Toluidine Red Toner is used by Lake City AAP in the production of the following formulations:

<u>Formulation</u>	<u>%Toluidine Red Toner in Formulation</u>
Igniter Mix I-508	0.5 ± 0.1
Igniter Mix I-136	<0.1
Igniter Mix I-276A	0.48
LCA #3 Inert Mix	0.02

In these formulations, toluidine red toner serves as a colorant only. It is inert with respect to the combustion properties of the igniter mixes.

This chemical is also a constituent of paints used by Longhorn AAP. No toluidine red toner is purchased by Longhorn AAP as the pure substance, however.

2. Quantities Used

During 1978, Lake City AAP used a total of 75 lb of toluidine red toner. Similar amounts were used during the 1975-1977 period. At full mobilization, the annual use rate of this compound would increase to about 400 lb/year.

3. Documented or Speculated Occurrences in Air or Water

Typical losses from manufacture of primers and tracers average 1-2% of the amount handled (Melton, 1978). Based upon the current use rate of toluidine red toner at Lake City AAP, the estimated losses are 0.06 to 0.12 lb/month. At full mobilization, the loss rate would increase to 0.3 to 0.7 lb/month. This material is discharged into the Lake City AAP industrial waste treatment facility.

E. Uses in the Civilian Community

1. Production Methodology

Toluidine red toner is manufactured by a coupling reaction between 2-nitrotoluidine and β -naphthol (Hercules, Inc., 1979) (See Section C. 1.).

2. Manufacturers, Production and Capacity

The U.S. manufacturers of toluidine and toner are listed in Table XIV-2. Historical production and sales of toluidine red toner are listed in Table XIV-3.

3. Usages

Toluidine red toner has varied civilian uses. The main use of the toner is in paints for industrial and farm equipment (Hercules Inc., 1979; Harshaw Chemical Co., 1979). It also is soluble in plasticizers and can be used in art

Table XIV-2. U.S. Manufacturers of Toluidine Red Toner
(SRI International, 1978; Hercules Inc., 1979)

<u>Manufacturer</u>	<u>Location</u>
Hercules Inc.	Glens Falls, N.Y.
Harshaw Chem. Co.	Cleveland, Ohio
Chemetron Corp. Chem. Group, Pigment Div.	Holland, Mich. Huntington, W. Va.
American Cyanamid Org. Chem. Div.	Willow Is., W. Va.

According to the U.S. Tarriff Commission (1977) the following companies also make toluidine red toner:

Flint Ink Corp.
Coal/Ink Div.

E.I. duPont de Nemours & Co., Inc.

Keystone Color Works, Inc.

H. Kohnstamm & Co., Inc.

Sterling Drug, Inc.
Hilton-Davis Chemical Co. Div.

Sun Chemical Corp.
Pigments Div.

Paul Uhlich & Co., Inc.

Table XIV-3. Historical Production and Sales of Toluidine
Red Toner (U.S. Tarriff Commission, 1973-1977)

	<u>1973</u>	<u>1974</u>	<u>1975</u>	<u>1976</u>	<u>1977</u>
Production, 1000 lb	1790	2240	1660	2168	1583
Sales, 1000 lb	1771	1807	1287	1635	1313

finishes. Because toluidine red toner bleeds it cannot be used in automotive equipment (Harshaw Chemical Co., 1979).

4. Future Trends

The U.S. annual production of toluidine red has declined from 3.15 million lb in 1950 to a level between 1.5 and 2.0 million lb/year. It is expected to remain at this level.

5. Documented or Speculated Occurrences in the Environment

Toluidine red toner will enter the environment from its production and formulation into paints and plasticizers. Waste paint products are also expected to be a source of environmental contamination by this toner. The amount of toluidine red toner entering the environment from these sources has not been documented.

F. Comparison of Civilian and Military Uses and Pollution

Toluidine red toner is used in small quantities (75-400 lb/year) in four mixes formulated at Lake City AAP. Pollution from the formulation and use of these mixes is estimated at 0.3 to 0.7 lb/month at full mobilization use rates. In contrast, there are several U.S. civilian manufacturers of toluidine red toner. This toner is used as a colorant in red paints formulated for use on agricultural and industrial equipment. The pollution resulting from civilian manufacture and use of this toner is expected to be widespread. In comparison, the pollution from munitions production at Lake City AAP is insignificant.

G. Toxicological and Environmental Hazards

1. Mammalian Toxicity

Graham and Davis (1968) conducted a study to evaluate the effects of toluidine red on rats. Toluidine red was fed to the rats in levels of up to 2% for 90 days. No effects were found in hematology, growth or mortality. No pathological changes were found in this study. No carcinogenic effects were noted in this short-term study. However, three related compounds have been shown to be carcinogenic in animals. The structures of these chemicals and their effects are presented in Table XIV- 4.

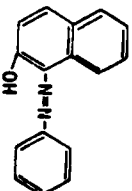
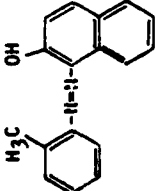
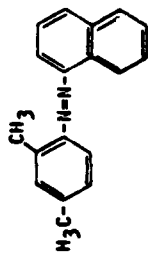
2. Environmental Hazards

A review of available literature failed to yield any references concerning the effects of toluidine red toner to aquatic life, plants or microorganisms.

3. Availability of Literature for Phase II

The literature on the environmental and toxicological hazards is very limited. Information for a Phase II study would have to come from U.S. and foreign manufacturers files and current research.

Table XIV-4. Toxicity of Compounds Similar in Structures
Toluidine Red

Compound	Structure	Animal	Route of Administration	Dose mg/kg	Effect	Reference
1-(phenylazo)- 2-naphthol		mouse	implant	80	LDLo neoplasms	NIOSH, 1977
"	"	mouse	subcutaneous	6000	LDLo neoplasms	NIOSH, 1977
1-(o-totylazo)- 2-naphthol		mouse	subcutaneous	6000	LDLo carcinogenic	NIOSH, 1977
"	"	rat	oral	5000	LDLo	NIOSH, 1977
1-(2,4-xylylazo)- 2-naphthol		mouse	implant	80	LDLo	NIOSH, 1977

H. Regulations and Standards

There are no U.S. effluent or industrial hygiene regulations or standards specific for toluidine red toner. Toluidine red toner is not listed in EPA's "*Toxic Substances Control Act Candidate List of Chemical Substances*" (1977) or *Suspected Carcinogens* (Christensen et al., 1975).

I. Conclusions and Recommendations

The goal of this problem definition study was to determine the Army's responsibility for conducting further studies on toluidine red toner. This toner is used as a colorant in mixes made at Lake City AAP. Only small amounts (75-400 lb/year) of toluidine red are used by the Army for this purpose. There are several civilian manufacturers of this toner. It finds widespread use as a red pigment in paints for agricultural and industrial equipment. Army use of toluidine red toner in munitions production is minor by comparison to civilian production paint formulation and use. Therefore, any further toxicological or environmental studies on this compound by the Army should be a low priority. However, adequate precautions should be taken to protect workers from any potential carcinogenic effects of this compound.

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PRELIMINARY PROBLEM DEFINITION STUDY ON
MUNITIONS-RELATED CHEMICALS
STRONTIUM OXALATE

SUMMARY

Strontium oxalate is used as a constituent of R-256 tracer mix formulated at Lake City AAP. At current production levels, Lake City AAP uses ~700 lb of strontium oxalate per year. This quantity represents ~10% of the current civilian production which is ~7000 lb/year. However, under full mobilization conditions, Lake City AAP would require 30,000 lb of strontium oxalate per year in order to meet production schedules. Thus under full mobilization schedules, all the strontium oxalate manufactured in the U.S. would be used in Army munitions production. The only civilian use of strontium oxalate is in radiator cleaners.

No toxicological or environmental hazards data specifically for strontium oxalate were found in the literature search. Information on other strontium salts indicates that they generally have a low toxicity to mammals and aquatic organisms.

In view of the high Army use of strontium oxalate and other strontium compounds at full mobilization and the limited information found on the toxicological and environmental hazards of strontium oxalate, a Phase II study is recommended. This study should include all strontium salts used in Army munitions production and the interaction of these salts with other metals in the environment.

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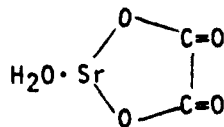
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XV. STRONTIUM OXALATE

A. Alternate Names

Strontium oxalate monohydrate, a salt of oxalic acid, has the empirical formula of $\text{SrC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ and the molecular weight of 193.64 g/mole. It has the structural formula:



Other names for strontium oxalate are:

CAS Registry No.:	814-95-9
Replaces CAS Registry No.:	14529-93-2
CA Name (8CI):	Oxalic acid, strontium salt
CA Name (9CI):	Ethanedioic acid, strontium salt
Synonyms:	Oxalic acid, monostrontium salt; Ethanedioic acid, strontium salt

B. Physical Properties

The physical properties of strontium oxalate are listed in Table XV-1.

Table XV-1. Physical Properties of Strontium Oxalate*

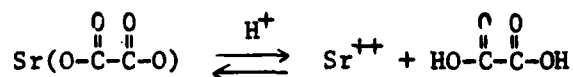
Physical form at 20°C:	crystalline powder
Color:	colorless
Odor:	odorless
Melting Point:	150°C (loses H_2O)
K_{sp} at 25°C	$7.8 \times 10^{-8} \text{ mole}^2/\text{l}^2$
Heat of dissociation:	38.40 Kcal/mole
Solubility:	slightly soluble in water; soluble in acetic acid; readily soluble in HCl , HNO_3

*Weast, 1970; Hawley, 1977; Windholz, 1976, Gardner and Nancollas, 1976

C. Chemical Properties

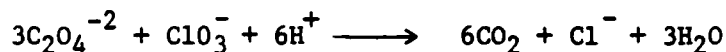
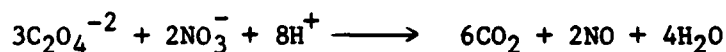
1. General and Environmental Reaction

The main reaction of strontium oxalate is hydrolysis to form strontium and oxalic acid.

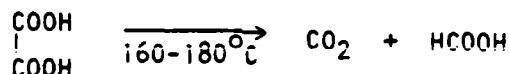


Strontium forms insoluble salts with carbonate ($K_{sp} = 7 \times 10^{-10}$) and sulfate ($K_{sp} = 7.6 \times 10^{-7}$) (Hogness and Johnson, 1957). Hydrolysis followed by precipitation of the strontium as the carbonate will be the main environmental reaction of strontium oxalate.

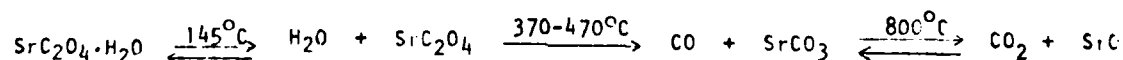
The oxalic acid formed in the hydrolysis is easily oxidized with nitric acid or hypochlorite (Ayres, 1958).



Oxalic acid can also be decomposed by heating (Roberts and Caserio, 1964).



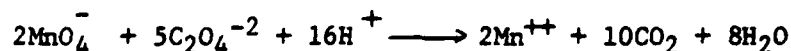
Strontium oxalate can also be thermally decomposed. The initial step in the decomposition is the loss of a water molecule followed by formation of strontium carbonate and finally strontium oxide (Derouane *et al.*, 1975).



2. Sampling and Analysis

Strontium oxalate may be determined either as strontium or as oxalic acid. 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 $\mu\text{g/l}$ (Franson, 1975).

Oxalic acid can be determined by titration with potassium permanganate. In the reaction, the oxalate is oxidized to CO_2 (Ayres, 1958).



D. Uses in Army Munitions

1. Purpose

Strontium oxalate is used at Lake City AAP as a constituent of R-256 tracer mix. This formulation is used in the M-17 50 caliber tracer rounds. The composition of the R-256 mix is shown below:

<u>Constituent</u>	<u>% in R-256 Tracer Mix</u>
Strontium nitrate	33.3 ± 1
Magnesium	26.7 ± 1
Strontium peroxide	26.7 ± 1
Calcium resinate	8.3 ± 1
Strontium oxalate	5 ± 1

The production of primer and tracer mixes is generally a dry process. The process for making the R-256 mix is shown in Figure XV-1.

2. Quantities Used

Lake City AAP used 700 lb of strontium oxalate during 1978. The use rate during the 1975-1977 period is shown below:

<u>Year</u>	<u>Lb Strontium Oxalate Used to Produce R-256 Tracer Mix</u>
1975	300
1976	1,500
1977	670

At full mobilization, the use rate for this chemical would increase to about 30,000 lb/year.

3. Documented or Speculated Occurrences in Air or Water

Typical losses from manufacture of primer and tracer mixes average 1-2% of the amount handled (Melton, 1978). Based upon the current use rate of Lake City AAP, the estimated losses of strontium oxalate are 0.6 to 1.2 lb/month. At full mobilization, the losses would increase to 25 to 50 lb/month. This material is discharged into a conventional industrial waste treatment facility. The treatment plant consists of a mixing well, a Parshall flume and two parallel series of three partitioned treatment basins (USAEHA-ES, 1971). In the first two treatment basins, oil and grease are skimmed off. 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 supernatant liquid is discharged into the West Fire Prairie Creek which ultimately drains into the Little Blue River. Based on

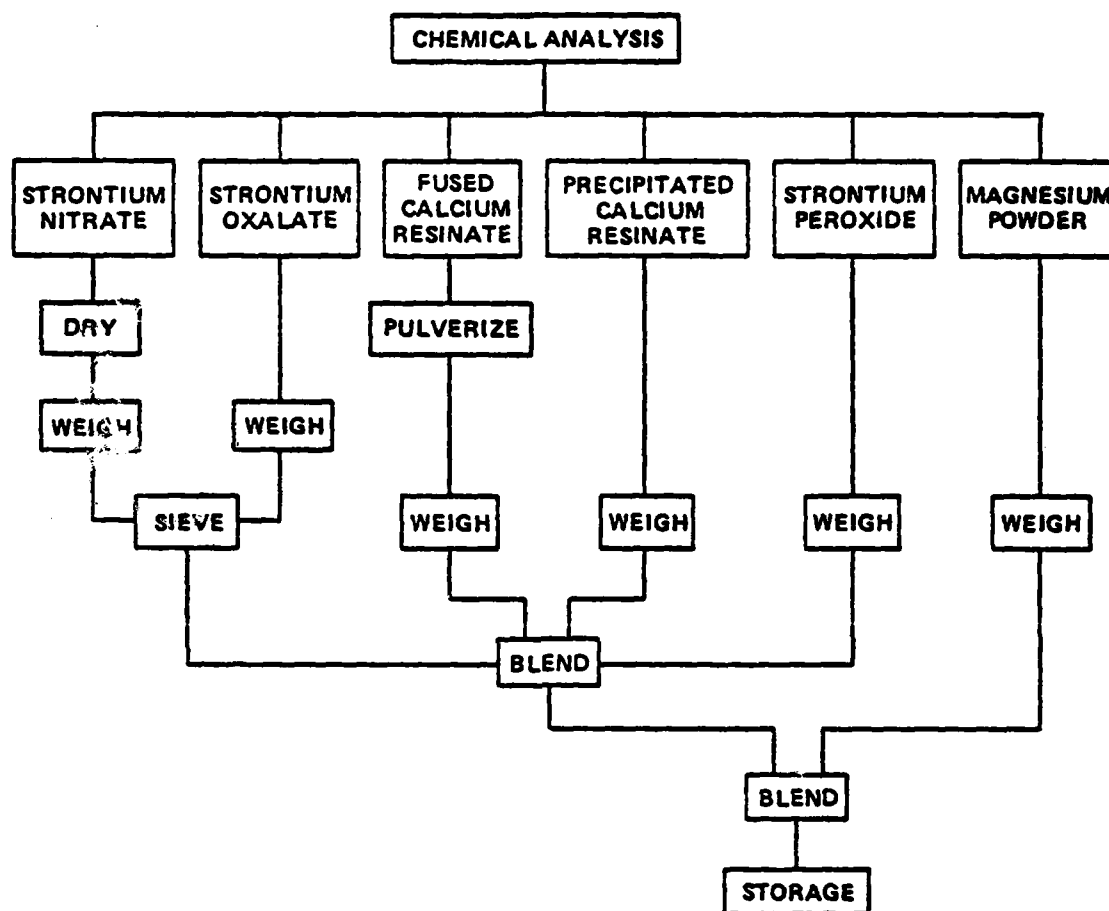


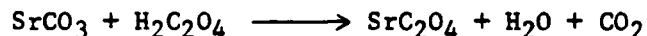
Figure XV-1. Process Flow Sheet - Tracer Composition R-256

solubilities, the maximum strontium concentration which could be discharged from the Industrial Waste Plant is 3.53 ppm.

E. Uses in the Civilian Community

1. Production Methodology

Strontium oxalate is manufactured by reacting oxalic acid with strontium carbonate (Hummel Chem., 1979).



2. Manufacturers, Production and Capacity

The U.S. manufacturers and production of strontium oxalate are listed in Table XV-2.

Table XV-2. U.S. Manufacturers of Strontium Oxalate (SRI International, 1978)

<u>Manufacturer</u>	<u>Location</u>	<u>1978 Production (lb/yr)</u>
Barium and Chemicals Inc.	Steubenville, Ohio	~2000*
Hummel Chem. Co. Inc.	South Plainfield, N.J.	~5000**

*(Barium and Chemicals, 1979)

** (Hummel Chem., 1979)

3. Usages

Strontium oxalate is used to some extent as a radiator cleaner (Barium and Chemicals, 1979).

4. Future Trends

No major changes in the strontium oxalate industry are anticipated.

5. Documented or Speculated Occurrences in the Environment

The use of strontium oxalate as a radiator cleaner will discharge all the chemical employed for this purpose into the environment.

F. Comparison of Civilian and Military Uses and Pollution

Current combined civilian and military uses of strontium oxalate are

less than 7000 lb/year. Lake City AAP is only using 700 lb of this chemical per year or about 10% of the civilian production. However, at full mobilization, Lake City AAP would require 30,000 lb/year of strontium oxalate for munitions production. Thus, under full mobilization schedules, the Army would use essentially 100% of the strontium oxalate produced.

At the present time, the civilian use of strontium oxalate as a radiator cleaner accounts for the major source of environmental contamination by this compound. However, under full mobilization operations, the Army munitions production would become the major source of environmental contamination of strontium oxalate and other strontium compounds.

G. Toxicological and Environmental Hazards

1. Toxicity to Mammals

No information was found on the toxic effects of strontium oxalate to mammals. Generally the toxicity of strontium is relatively low. The oral LD50 of strontium chloride is 2250 mg/kg to rats; for mice the oral LD50 is 3100 mg/kg (NIOSH, 1977).

2. Aquatic Toxicity

No information is available on the aquatic toxicity of strontium oxalate. However, strontium compounds generally have a low toxicity to aquatic organisms. The data in Table XV-3 verifies this observation.

Table XV-3. Aquatic Toxicity of Strontium Compounds

<u>Compound</u>	<u>Organism</u>	<u>Level (in ppm)</u>	<u>Effect</u>	<u>Reference</u>
Sr(NO ₃) ₂	Stickleback (<i>Gasterosteus acuteatus</i>)	3000	average survival at 96 hr	Jones (1939)
SrCl ₂	Water flea (<i>Daphnia magna</i>)	125	LC50 48 hr	Biesinger and Christensen (1972)
"	" "	42	16% repro- ductive impairment	"

3. Toxicity to Microorganisms

No specific information was retrieved on the toxicity of strontium oxalate to microorganisms.

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 (1965) demonstrated that the complete substitution of strontium for calcium at levels of 18 mg Sr/l in the nutrient medium of 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 the bacteria.

Bringmann and Kuehn (1976) reported that inhibition of cell multiplication in *Pseudomonas putida* by oxalic acid started at 41 mg/l. Cell inhibition in *Piputida* for a neutralized solution started at 1550 mg/l. The perturbation level of oxalic acid for *Vorticella campanula* and *Paramecium caudatum* was 50 mg/l (Bringmann and Kuehn 1976).

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 did not 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.

Table XV-4. Effects of Strontium Salts on Microorganisms.

Microorganism	Salt	Sr Concn. mg/l	Reported Effect	Reference
Protozoa				
<i>Microregna heterostoma</i>	SrCl ₂	329	28 hr toxic threshold for feeding	Bringmann and Kuehn, 1959
<i>Paramecium</i>	SrCl ₂	8000	All dead in 4.5 hr	Dale, 1913
Bacteria				
<i>Bacillus anthracis</i>	SrCl ₂	23 X 10 ³	Growth inhibition threshold	Eisenberg, 1919
<i>Bacillus anthracis</i>	SrCl ₂	26 X 10 ³	Growth inhibition	Eisenberg, 1919
<i>Sarcina tetragena</i>	SrCl ₂	17 X 10 ³	Growth inhibition threshold	Koulumies, 1946
<i>Micrococcus phogenes</i>	SrCl ₂	17 X 10 ³	Growth inhibition threshold	Eisenberg, 1919
<i>Micrococcus canadensis</i>	SrCl ₂	13 X 10 ³	Growth inhibition threshold	Eisenberg, 1919
<i>Corynebacterium diphtheriae</i>	SrCl ₂	6700	Growth inhibition threshold	Eisenberg, 1919
<i>Corynebacterium diphtheriae</i>	SrCl ₂	10 X 10 ³	Growth inhibition	Koulumies, 1946
<i>Corynebacterium pseudodiphtheriae</i>	SrCl ₂	10 X 10 ³	Growth inhibition threshold	Eisenberg, 1919
<i>Corynebacterium pseudodiphtheriae</i>	SrCl ₂	4 X 10 ³	Growth inhibition	Koulumies, 1946
<i>Bacillus typhi</i>	SrCl ₂	30 X 10 ³	Growth inhibition threshold	Eisenberg, 1919
<i>Bacillus pneumoniae</i>	SrCl ₂	13 X 10 ³	Growth inhibition threshold	Eisenberg, 1919
<i>Bacillus pyrocyanus</i>	SrCl ₂	10 X 10 ³	Growth inhibition threshold	Eisenberg, 1919
<i>Bacillus vulgare</i>	SrCl ₂	27 X 10 ³	Growth inhibition threshold	Eisenberg, 1919
<i>Vibrio cholerae</i>	SrCl ₂	1700	Growth inhibition threshold	Eisenberg, 1919
<i>Escherichia coli</i>	SrCl ₂	27 X 10 ³	Growth inhibition threshold	Eisenberg, 1919

Table XV-4 (continued)

<i>Escherichia coli</i>	SrCl ₂	22 X 10 ³	Growth inhibition threshold	Hotchkiss, 1923
<i>Escherichia coli</i>	SrCl ₂	18 X 10 ³	Growth inhibition	Koulumies, 1946
<i>Salmonella paratyphi B</i>	SrCl ₂	10 X 10 ³	Growth inhibition	Koulumies, 1946
<i>Salmonella paratyphi A</i>	SrCl ₂	10 X 10 ³	Growth inhibition	Koulumies, 1946
<i>Eberthella typhosa</i>	SrCl ₂	18 X 10 ³	Growth inhibition	Koulumies, 1946
<i>Proteus vulgaris</i>	SrCl ₂	18 X 10 ³	Growth inhibition	Koulumies, 1946
<i>Shigella paradyseriae</i>	SrCl ₂	7 X 10 ³	Growth inhibition	Koulumies, 1946
<i>Brucella abortus</i>	SrCl ₂	7 X 10 ³	Growth inhibition	Koulumies, 1946
<i>Pasteurella peustis</i> (Tjevidei)	SrCl ₂	7 X 10 ³	Growth inhibition	Koulumies, 1946
<i>Pasteurella pestis</i> (Soensdang)	SrCl ₂	22 X 10 ³	Growth inhibition	Koulumies, 1946
<i>Hemophilus pertussis</i>	SrCl ₂	10 X 10 ³	Growth inhibition	Koulumies, 1946
<i>Hemophilus influenza</i>	SrCl ₂	10 X 10 ³	Growth inhibition	Koulumies, 1946
<i>Neisseria catarrhalis</i>	SrCl ₂	18 X 10 ³	Growth inhibition	Koulumies, 1946
<i>Neisseria gonorrhoeae</i>	SrCl ₂	10 X 10 ³	Growth inhibition	Koulumies, 1946
<i>Staphylococcus aureus</i>	SrCl ₂	10 X 10 ³	Growth inhibition	Koulumies, 1946
<i>Staphylococcus albus</i>	SrCl ₂	10 X 10 ³	Growth inhibition	Koulumies, 1946
<i>Streptococcus pyrogenes</i>	SrCl ₂	10 X 10 ³	Growth inhibition	Koulumies, 1946
<i>Streptococcus viridans</i>	SrCl ₂	10 X 10 ³	Growth inhibition	Koulumies, 1946
<i>Diplococcus pneumoniae</i>	SrCl ₂	10 X 10 ³	Growth inhibition	Koulumies, 1946
<i>Actinomyces graminis</i>	SrCl ₂	44 X 10 ³	Growth inhibition	Koulumies, 1946
<i>Mycobacterium tuberculosis</i>	SrCl ₂	7 X 10 ³	Growth inhibition	Koulumies, 1946

Table XV-4 (continued)

<i>Mycobacterium tuberculosis</i>	SrCl ₂	7 X 10 ³	Growth inhibition	Koulumies, 1946
<i>Clostridium</i> (7 species)	SrCl ₂	7 to 10 X 10 ³	Growth inhibition	Koulumies, 1946
<i>Leptospira icterohaemorrhagiae</i> (3 strains)	SrCl ₂	7 to 10 X 10 ³	Growth inhibition	Koulumies, 1946
Fungi				
<i>Epidermophyton Kaufmann-Wolff</i>	SrCl ₂	26 X 10 ³	Growth inhibition	Koulumies, 1946
<i>Trichophyton</i> (3 species)	SrCl ₂	26 to 52 X 10 ³	Growth inhibition	Koulumies, 1946
<i>Penicillium</i> (Orion)	SrCl ₂	70 X 10 ³	Growth inhibition	Koulumies, 1946
<i>Mucor corymbifer</i>	SrCl ₂	26 X 10 ³	Growth inhibition	Koulumies, 1946
<i>Cladissporium mansonii</i>	SrCl ₂	44 X 10 ³	Growth inhibition	Koulumies, 1946
<i>Scopularia brevicaulis</i>	SrCl ₂	66 X 10 ³	Growth inhibition	Koulumies, 1946
<i>Aspergillus fumigatus</i>	SrCl ₂	70 X 10 ³	Growth inhibition	Koulumies, 1946
<i>Altenaria</i>	SrCl ₂	66 X 10 ³	Growth inhibition	Koulumies, 1946
<i>Altenaria tenuis</i>	Sr(NO ₃) ₂	30 X 10 ³	ED50, germination inhibition	Somers, 1959; 1961
<i>Botrytis fabae</i>	Sr(NO ₃) ₂	13 X 10 ³	ED50, germination inhibition	Somers, 1961
Algae				
<i>Coccomyxa pring-shetmi</i>	----	5 - 10	Inhibition of growth and calcium utilization	Walker, 1953
<i>Chlorella vulgaris</i>	SrCl ₂ -6H ₂ O	>13 X 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. (g)	Average weight per grain.(g)	Weight of straw.(g)
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 g of strontium nitrate	369	11.9065	.0323	44.50
Pot 4+5 g of strontium nitrate	555	19.6108	.0353	52.00
Average	462	15.7586	.0338	48.25
Pot 5+10 g of strontium nitrate	561	17.6505	.03146	62.00

Bringman and Kuehn (1976) studied the effects of oxalic acid on algae. They reported that 42 mg/l inhibited cell multiplication in *Microcystis aeruginosa* while a neutralized solution started inhibiting *M. aeruginosa* at 80 mg/l.

5. Availability of Literature for Phase II

Very little information on the toxicological and environmental properties of strontium oxalate is available in the general literature. Information for Phase II will have to come from manufacturers files or inferred from data on strontium and oxalic acid.

H. Regulations and Standards

There are no U.S. effluent or industrial hygiene standards specific for strontium oxalate.

I. Conclusions and Recommendations

Approximately 10% of the strontium oxalate produced in the United States is currently used in Army munitions production. However, under full mobilization schedules, the Army's need for strontium oxalate would be ~4 times the current civilian production. Thus, under these conditions, strontium oxalate would be a military unique chemical.

Based on the potential high use rate of strontium oxalate in Army munitions and the relatively small amount of information available on this compound, it is recommended that strontium oxalate be included in a Phase II study. This Phase II study also should include the interaction of strontium with other metals in the aquatic environment and their effects on aquatic organisms and plants.

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PRELIMINARY PROBLEM DEFINITION STUDY ON
MUNITIONS-RELATED CHEMICALS
DECHLORANE (MIREX)

SUMMARY

Dechlorane is an organochlorine compound which has been used as a pesticide and a flame retardant for plastics. The use of dechlorane (or mirex as it is called when formulated into pesticides) as a pesticide has received widespread attention. This attention is due to the persistence and mobility of dechlorane in the environment and its bioconcentration and biomagnification through the food chain. In mammals, dechlorane has been shown to be a teratogenic and there is appreciable evidence that it is also carcinogenic. Based on the toxicological and environmental hazards associated with dechlorane, EPA has restricted the use of this chemical in pesticide formulations. As a result of the litigations, Allied Chemical ceased manufacture of dechlorane and sold the patent rights to the Mississippi Authority. Thus, this chemical is no longer manufactured in the U.S.

The Army's main use of dechlorane is in tracer mixes manufactured at Lone Star AAP. Approximately 1500 lb/year are currently procured by Lone Star AAP from importers. At full mobilization, ~5000 lb of dechlorane per year would be required in munitions production. The dechlorane wastes from tracer mixes are currently ~4 lb/month. These wastes are placed in holding ponds. However, due to the mobility of dechlorane in the environment, these ponds could be a significant source of contamination by dechlorane.

Sufficient literature summaries on the toxicological and environmental properties of dechlorane already exist. The Army could reference these summaries in their evaluations. Therefore, a Phase II study is not recommended at this time.

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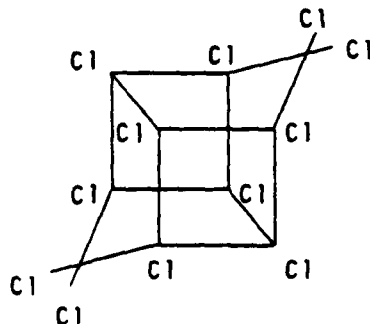
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XVI. DECHLORANE

A. Alternate Names

Dechlorane is an organochlorine pesticide with the empirical formula $C_{10}Cl_{12}$ and a molecular weight of 545.59 g/mole. It has the following structural formula:



Other names for dechlorane include:

CAS Registry No.:

2385-85-5

CA Name (9CI):

1,1a,2,2,3,3a,4,5,5,5a,5b,6-Dodecachlorooctahydro-1,3,5-metheno-1H-cyclobuta (cd) pentalene

Wiswesser Line Notation:

L545 B4 C5 D 4ABCE JTJ-/G 1 2

Synonyms:

Bichlorendo; Cyclopentadiene, hexachloro-, dimer; Dodecachlorooctahydro-1,3,5-metheno-2H-cyclobuta (c,d)pentalene; Dodecachloropentacyclodecane; Dodecachloropentacyclo (3,3,2,0^{2,6},0^{3,9},0^{7,10})decane; ENT 25,719; GC 1283; Hexachlorocyclopentadiene dimer; HRS 1276; Mirex; Perchloropentacyclo (5.2.1.0^{2,6}.0^{3,9}.0^{5,8})decane; 1,3-Cyclopentadiene,1,2,3,4,5,5-hexachloro-, dimer; Dechloroane; Perchloropentacyclodecane; Dechlorane Plus 515; Perchlorodihomocubane; Dechlorane 515; Dechlorane Plus; Dechlorane 4070; CG-1283

B. Physical Properties

The physical properties of dechlorane are listed in Table XVI-1.

Table XVI-1. Physical Properties of Dechlorane *

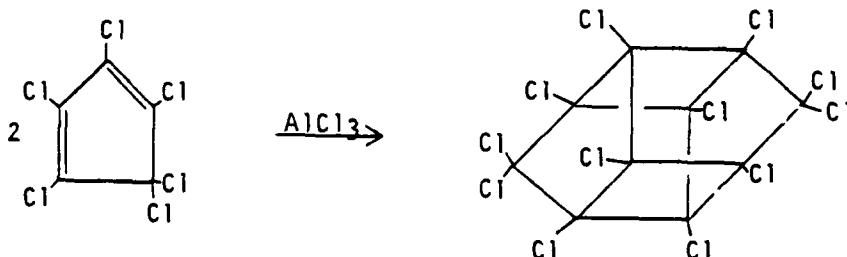
Physical form at 20°C:.	crystalline solid
Color:	white
Odor:	odorless
Melting Point:	485°C
Solubility:	practically insoluble in water; soluble in dioxane, xylene, benzene, carbon tetrachloride, methyl ethyl ketone

* Hawley, 1977; Windholz, 1976

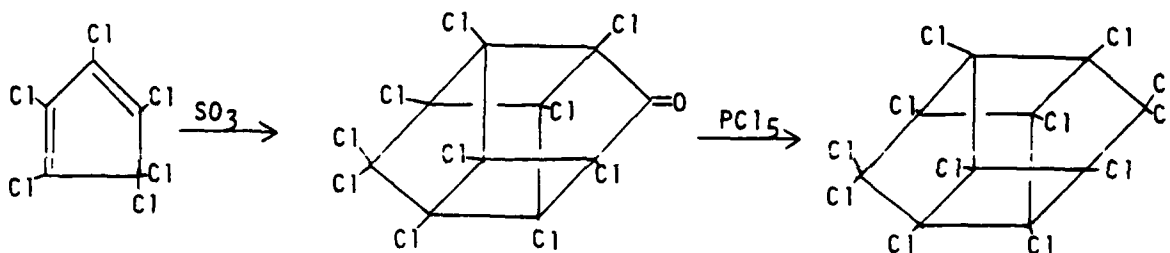
C. Chemical Properties

1. General Reactions

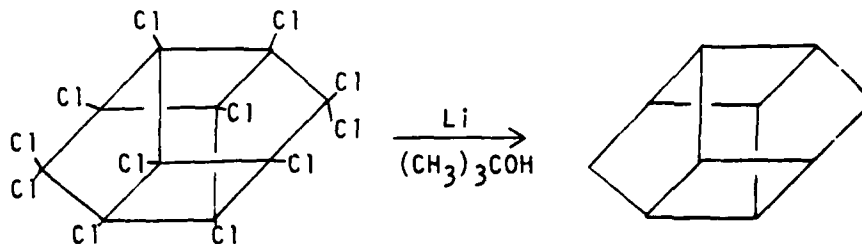
Dechlorane 510, or Mirex is produced in high yield by the solventless reaction of hexachlorocyclopentadiene with aluminum chloride (Tracey, 1964) or a similar reaction in hexachlorobutadiene solvent (Johnson, 1961):



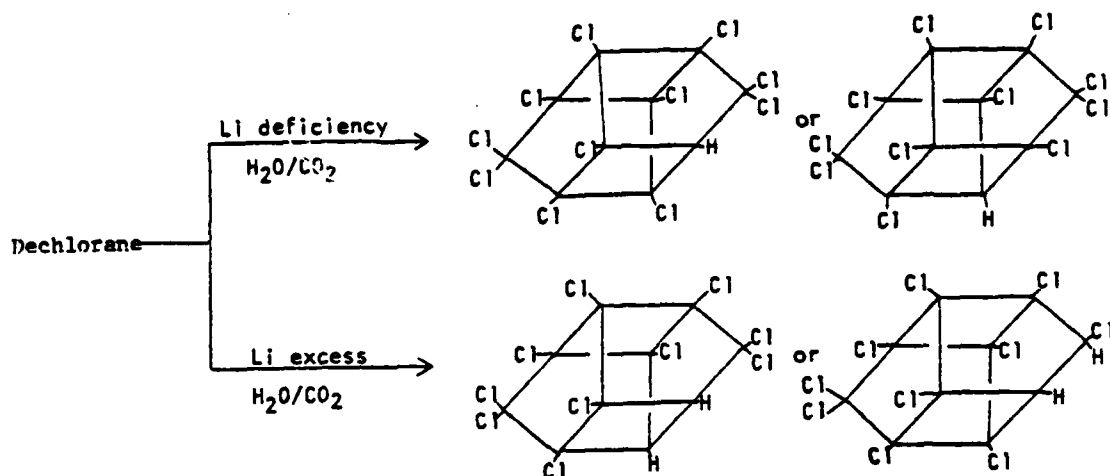
An alternative preparation involves an initial reaction with sulfur trioxide yielding kepone followed by conversion to mirex by phosphorous pentachloride (Johnson, 1961):



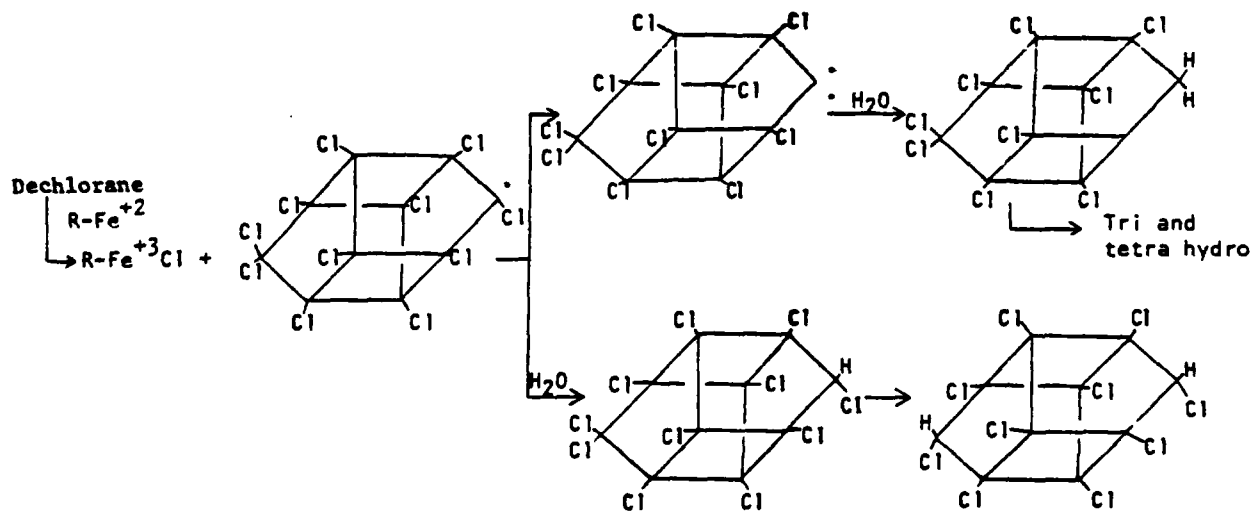
Dechlorane can be reduced to its parent hydrocarbon compound by reaction with lithium and t-butanol (Dilling *et al.*, 1967):



Partial reduction can be afforded with either excess or deficiency of lithium in water and dry ice yielding mono and dihydro compounds.

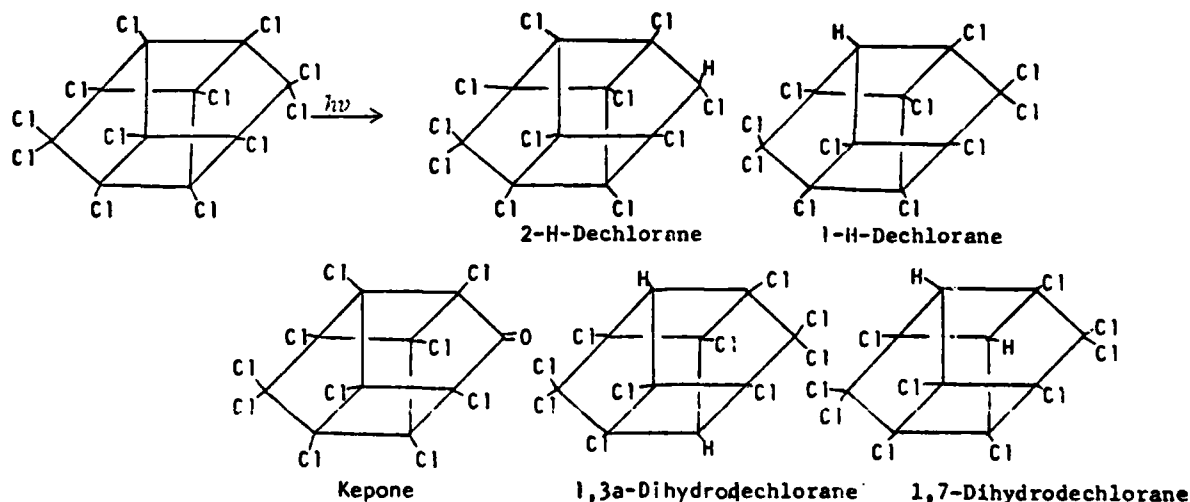


Dechlorane is also reduced by reaction with reduced hematin yielding mono, di, tri and tetra hydro derivatives (Holmstead, 1976).



2. Environmental Reactions

The main environmental reaction of dechlorane is the photochemical dechlorination. Several reports (Alley *et al.*, 1974; Alley *et al.*, 1973; Carlson *et al.*, 1976; Lewis *et al.*, 1976) have appeared in the literature pertaining to the photolysis of dechlorane. Two monohydro derivatives (1-H and 2-H) and kepone have been shown to be photoproducts of dechlorane (Carlson *et al.*, 1976). Alley *et al.* (1974) identified the 1-H monohydro derivative and a dihydro derivative as photoproducts of dechlorane. The dihydro derivative is either the 1,7 or 1,3a-dihydro dechlorane. The structures of the dechlorane byproducts are shown below:



3. Sampling and Analysis

Dechlorane has been analyzed by thin layer chromatography using silica gel 60F-254 with a heptane mobile phase (Holmstead, 1976), silica gel G and alumina ALOX N with several mobile phases (Antoine *et al.*, 1977) and silica gel G with heptane (Carlson *et al.*, 1976). Gas chromatography has also been employed. Gas chromatography has been performed on 0.35% SE-30 on glass beads at 220°C along with three other columns (Alley *et al.*, 1973; Alley *et al.*, 1974) using a flame ionization detector. Antoine *et al.* (1977) used an electron capture detector and three columns, DC-11, QF1 and OV17 on Chromosorb W at 170°, 180° and 180°C respectively for the analysis of dechlorane. Lewis *et al.* (1976) used 15% OV-17/1.95% OV-210 and .4% SE-30/6% OV210 on Gas Chrom Q both at 200°C with an electron capture detector. The lower detection limit is 10-12 g with the electron capture detector.

Gas chromatography - chemical ionization mass spectroscopy has also been used effectively. Holmstead (1976) employed a 3% DEX11-300 on Varoport-30 column at 200°C while Carlson *et al.* (1976) employed 3% SE-30, 3% DC-200, and 1.5% OV 17/1.95% QF1 columns as inlets to chemical ionization mass spectrometers.

D. Uses in Army Munitions

1. Purpose

Dechlorane is used at Lake City AAP in the production of formulations R-512 and R-516. The amount of dechlorane in each mix is shown below:

<u>Formulation</u>	<u>% Dechlorane in Formulation</u>
R-512	3.1
R-516	1.5

In these mixes, dechlorane serves only as a color intensifier. It has no effect on the performance of the formulations, which can be produced without dechlorane if desired.

The Army Chemical Systems Laboratory has used dechlorane to produce experimental white smoke mixture E158/E159. The constituents of this formulation are:

Dechlorane	41.5 $\pm$ 1%
Zinc oxide	43.0 $\pm$ 1%
Potassium chlorate	8.0 $\pm$ 1%
Sugar	5.0 $\pm$ 1%
Nitrocellulose	2.5 $\pm$ 0.5%

The dechlorane serves as a chlorine carrier in this mixture.

Lone Star AAP uses dechlorane to produce M-12, M-13 tracer mix. The formulation is shown below:

Dechlorane	6-7%
Mg powder, Type I	21 $\pm$ 2%
Mg powder, Type II	21 $\pm$ 2%
Strontium nitrate	44 $\pm$ 2%
Vinyl alcohol nitrate resin	7-8%

2. Quantities Used

Lake City AAP used 10 lb of dechlorane in 1978 for production of experimental tracer mixes. The full mobilization use rate of dechlorane at this facility would be about 200 lb/year or 16.7 lb/month.

Smoke mixtures using dechlorane are not currently produced, nor is any future production planned. The experimental mixtures using dechlorane made by the Chemical Systems Laboratory are no longer being considered. The quantities used for the experimental formulations involved only a few pounds of dechlorane (Fortner, 1979).

The major Army use of dechlorane is at Lone Star AAP. This facility used about 1500 lb/year of dechlorane over the 1975-1978 period. The full mobilization use rate would be 416 lb/month.

3. Documented or Speculated Occurrences in Air or Water

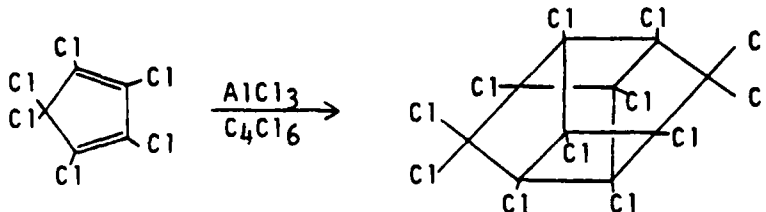
Actual losses of dechlorane at Lone Star AAP have not been measured. Typically, 1-2% of the tracer materials handled are lost to waste streams (Alexander, 1978). Current losses of dechlorane are estimated to be 1-3 lb/month. At full mobilization, the loss would be in the range of 4-9 lb/month.

At Lone Star AAP, wastes generated from production operations are collected in stainless steel vats. They are then treated with sodium nitrite and acetic acid to destroy explosive components. The effluent is disposed of in gravel bottom leaching pits. There is a potential for ground water contamination by percolation from the leaching pits. The extent of such contamination has not been determined.

E. Uses in the Civilian Community

1. Production Methodology

Dechlorane 510/4070 or Mirex is not presently being produced in the civilian economy. The production methodology was originally patented by Hooker Chemical Corp. and involved the Friedel-Crafts condensation of hexachlorocyclopentadiene (Johnson, 1961)



in hexachlorobutadiene solvent and later a similar solventless technique (Tracey, 1964). The crude product is vacuum distilled to remove solvent and unreacted starting material and recrystallized from benzene.

2. Manufacturers, Production and Capacities

Dechlorane is not presently being produced. The production patents have been purchased by the state of Mississippi (Boundy, 1979). Lone Star AAP purchases their dechlorane from Phillips Bros. Div. of Englehard Industries of California. This company imports dechlorane.

3. Usages

Civilian applications for dechlorane include its application as a fire retardant in a variety of polymers and its use as an insecticide especially for the control of fire ants (Holmstead, 1976).

4. Future Trends

Future applications of dechlorane are doubtful due to EPA restrictions, however, the state of Mississippi apparently has some plans for its use in the control of their fire ant problem (Boundy, 1979).

5. Speculated and Documented Occurrences in the Environment

There have been several reports related to documentation of dechlorane in the environment. It was first discovered in substantial amounts in Lake Ontario fish near the Hooker Chemical Corporation plant in Niagara Falls, N.Y. (Brauer, 1977). It has been identified in soil 12 years after an area was treated for fire ant control, and up to 10% of the residue had been converted to kepone (Brauer, 1977; Carlson *et al.*, 1976). Although much of the controversy regarding dechlorane involves its use as a pesticide, the problem seems quite a bit more widespread. Nearly 75% of the dechlorane distributed by Hooker from 1957 to 1975 went for non-pesticide use, mainly as a flame retardant and plasticizer in synthetic fibers and other plastics products (Brauer, 1977). Part of the problem seems to center around the ambiguity in the nomenclature, *i.e.* Mirex, the pesticide, versus dechlorane the fire retardant. The former has attracted much attention while the latter has not, despite its greater usage.

F. Comparison of Military and Civilian Uses of Dechlorane

Civilian use of dechlorane as a fire retardant in plastics and as a pesticide declined to near zero in 1972 when civilian production of this chemical ceased. Dechlorane is now used only in experimental quantities as a pesticide for controlling fire ants in Mississippi.

The military use of dechlorane in tracer mixes is only ~1500 lb/year although the Army's need for this chemical would increase to ~5000 lb/year. Thus, under these production schedules the Army would be a major user of dechlorane.

G. Toxicological and Environmental Hazards

1. Toxicity to Mammals

Dechlorane is moderately toxic to mammals when administered in an acute dose. Deaths occurred in rats fed 306 mg/kg (NIOSH, 1977). Absorption through the skin also occurs. The LD50 for acute skin exposure to rabbits is 800 mg/kg (NIOSH, 1977). When Sprague-Dawley rats were fed a single dose of (0.2 mg/kg) radiolabeled dechlorane, only 18% of the radiolabeled carbon was eliminated during the first 7 days after administration (Gibson *et al.*, 1972). Approximately 85% of this amount was eliminated as unmetabolized dechlorane in the feces within 48 hr. Dechlorane showed strong lipophilic tendencies. Concentrations of dechlorane equivalents in the fat were 0.9 seven days after dosing. The fat levels did not decrease during the 28 days of the experiment. The monohydroprotoproduct of dechlorane behaved similarly. However, there was some evidence that this compound was metabolized to a greater extent

than dechlorane.

Dechlorane has been shown to have teratogenic properties when administered to rats and mice. Rats fed .25 ppm dechlorane in their food for as little as 45 days had fewer pups born alive than did controls. Also, fewer of these pups survived to weaning and many of them developed cataracts (Gaines and Kimbrough, 1970). Passage of dechlorane through the placental barrier and excretion into the milk were confirmed by analyses of the milk and fetuses.

In addition to being a teratogen in mammals, there is also evidence that dechlorane is a carcinogen. Several studies have been conducted in order to evaluate the carcinogenic potential of this chemical. In the initial study conducted by Litton Bionetics in 1969, male and female mice were fed 26 ppm dechlorane daily from age 7 days till death. This report stated that there was a significant increase in liver hepatomas. However, different pathologists disagreed on the interpretation of the slides. This disagreement centered on whether hepatocellular carcinoma were actually present or if the observed changes were hyperplastic nodules (Federal Register, 1976).

In a second study conducted by Litton Bionetics, Inc., Charles River caesarian derived rats were fed daily doses of 100 ppm or 50 ppm of dechlorane for 18 months. Again pathologists disagreed on whether hepatocellular carcinomas or hyperplastic modules were present (Federal Register, 1976).

2. Toxicity to Birds

Dechlorane at levels of 600 ppm in the diets of laying hens did not alter egg production. However, the hatchability and survival rate of the chicks was significantly lower than that of the controls (Naber and Ware, 1965).

3. Aquatic Toxicity

The toxicity of dechlorane to aquatic invertebrates is presented in Tables XVI-2 and XVI-3. Dechlorane is highly toxic to these organisms. Ludke *et al.* (1971) found that 65% of the crayfish, *Procambarus hayi*, died when exposed to 0.1 ppb of dechlorane for 48 hours. They also observed that dechlorane was accumulated in crayfish tissues 940 - 27,210 times over water concentration.

Dechlorane is relatively non-toxic to fish. At high concentration gill and kidney lesions are observed (Van Valin *et al.*, 1968). However, fish tend to bioaccumulate dechlorane from their food (Lowe *et al.*, 1971). As shown in Table XVI-4, dechlorane levels in fish populations never exposed to this compound are high. These data suggest a high mobility of dechlorane in the environment.

Table XVI-2. Toxicity of Dechlorane to Aquatic Invertebrates
(Naqvi and De la Cruz, 1973)

<u>Organism</u>	<u>Level (ppm)</u>	<u>Effect</u>
Water Strider (<i>Gerris remigis</i>)	.13	72 hr. LC50
Gyrinus Beetle (<i>Dineutes americanus</i>)	2.06	"
Shrimp (<i>Palaemonetes kadiakensis</i>)	1.01	
Dragonfly nymph (<i>Macronia sp</i>)	1.0	96% death at 144 hr.
Amphiod (<i>Hyallela azteca</i>)	.001	54% death at 600 hr.

Table XVI-3. Dechlorane Toxicity to Crayfish
(Ludke *et al.*, 1971)

<u>Crayfish</u>	<u>Level (ppb)</u>	<u>Length of Exposure (hours)</u>	<u>Lethal Response</u>
<i>Procambarus blandius</i>	1.0	144	95% dead; 5 days after transfer to clean water
"	5.0	6	76% dead; 10 days after transfer to clean water
"	5.0	24	50% dead; 10 days after transfer to clean water
"	5.0	58	98% dead; 10 days after transfer to clean water
<i>P. hayi</i>	0.1	48	65% dead; 4 days after transfer to clean water
"	0.5	48	71% dead; 4 days after transfer to clean water

Table XVI-4. Background Levels of Dechlorane in Fish

Fish	Part	Dechlorane (ppm)	Reference
Northern Longnose gar (<i>Lepistosteus osseus</i>)	gonads	.020	Kaiser (1974)
	viscera, fat	.041	"
	liver	.047	"
Northern pike (<i>Esox lucius</i>)	pectoral to		
	pelvic fin	.025	"
	post-anal fin	.050	"
Catfish	whole body	.008-2.59	Collins <i>et al.</i> (1973)

4. Toxicity to Microorganisms

The metabolism of dechlorane in the estuarine environment and its effects on estuarine microorganisms has been studied. Brown *et al.* (1975) reported that 10 ppm dechlorane did not inhibit the metabolic activity of estuarine pond water, but did inhibit primary productivity. A concentration of 1000 ppm dechlorane did not effect the growth curves of bacterial cultures or significantly alter the mixed microbial populations and activities of estuarine sediments. Degradation products of dechlorane such as kepone and reduced kepone exhibited far more toxicity to microorganisms.

Andrade *et al.* (1975) studied the metabolism of dechlorane by anaerobic digester sludge organisms. It was found that 10-monohydrodechlorane was formed after 2 months incubation of 50 mg dechlorane at 30°C, with 250 ml anaerobic sludge.

5. Phytotoxicity

De la Cruz and Naqvi (1973) observed progressive photosynthetic inhibition in naturally occurring plankton populations exposed to 1 ppb dechlorane. Sixteen percent inhibition occurred after 6 days and 33% at 18 days exposure. A pure culture of *Chlamydomonas* showed a 55% photosynthetic reduction after exposure to 1 ppm dechlorane for 168 hours. The respiration rates of plankton and higher organisms initially increased to a maximum of 62% at low dechlorane concentrations or during the early incubation period, but decreased to <50% at elevated concentrations or after extended exposure at low concentrations.

6. Environmental Fate of Dechlorane

Dechlorane is an environmentally persistent compound. The major environmental reactions of this compound are the formation of monohydrodechlorane and kepone by photodehalogenation or by the action of microorganisms. Bioconcentration of dechlorane by many lower forms of life and biomagnification through the food chain are the major environmental pathways of dechlorane.

7. Availability of Literature for Phase II

The use of dechlorane as a pesticide and the recognition of its persistence in the environment have prompted several studies on the effects of dechlorane on non-target species. Therefore, there is sufficient literature available for a detailed Phase II toxicological and environmental study.

H. Regulations and Standards

Dechlorane has been the subject of deliberations since March 18, 1971. On this date, EPA issued a notice of intent to cancel registrations of pesticide products containing dechlorane. These hearings proceeded intermittently until 1976 when Allied ceased formulation of dechlorane into pesticide baits

and transferred its registration to the Mississippi Authority (Federal Register, 1976).

EPA cancelled all the registrations for dechlorane held by Mississippi Authority effective December 31, 1977. However, some experimental use permits have been issued to the Mississippi Authority for fire ant control.

Water quality criteria of 0.001 ppb of dechlorane for protection of fresh water aquatic organisms has been suggested by EPA (1976).

I. Conclusions and Recommendations

Dechlorane was widely used in the civilian community as a flame retardant for plastics and fibers and as a pesticide for controlling fire ants. There is no current civilian production of this compound although the State of Mississippi may initiate production of this compound for control of fire ants.

The Army uses dechlorane in tracer mixes produced at Lone Star AAP. Other AAPs have used this chemical in the past. However, they are not using dechlorane presently nor do they have any future plans for use of this chemical. Lone Star AAP currently uses dechlorane at a rate of 1500 lb/year. At full mobilization, the Army's need for this compound would be 5000 lb/year. In the future, dechlorane may be difficult to obtain if imports are not allowed and manufacture of dechlorane is not reinitiated. Thus, the Army may need to find a substitute for dechlorane in tracer mixes. Currently, the Army is one of the major users of dechlorane. Formulation of tracer mixes currently results in an estimated 1-3 lb of dechlorane entering the environment each month. This amount would increase to 4-9 lb/month at full mobilization. Although this effluent is placed in holding ponds, dechlorane has been shown to be highly mobile in the environment.

Dechlorane is extremely toxic to aquatic invertebrates. It is bioconcentrated by many organisms and bioaccumulated through the food chain. Dechlorane has also been shown to be teratogenic and carcinogenic to mammals.

Sufficient literature summaries on the toxicological and environmental properties of dechlorane already exist. The Army could reference these summaries in their evaluations. Therefore, a Phase II study is not recommended at this time.

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ABBREVIATIONS AND SYMBOLS

°	
Å	- Angstrom
@	- at
AAP	- Army Ammunition Plant
ANOVA	- Analysis of Variance
~	- Approximately
BADCT	- Best Available Demonstrated Control Technology
BATEA	- Best Available Technology Economically Achievable
BDNPA	- Bis(2,2-dinitropropyl)acetal
BDNPF	- Bis(2,2-dinitropropyl)formal
BOD ₅	- Biochemical Oxygen Demand
B.P.	- Boiling Point
BPCTCA	- Best Praticable Control Technology Currently Available
BTU	- British Thermal Unit
°C	- Degrees Centigrade
Cal	- Calorie
CEF	- Tris(chloroethyl)phosphate
cm	- Centimeter
cm ⁻¹	- Wavenumber
cm ³	- Cubic Centimeter
COC	- Cleveland Open Cup
COD	- Chemical Oxygen Demand
C _p	- Heat Capacity at Constant Pressure
cP	- Centipoise
d	- Density
D	- Detonation Speed
δ	- Chemical Shift
DOT	- Department of Transportation
ΔH _c	- Heat of Combustion
ΔH _f	- Heat of Fusion
DMSO	- Dimethylsulfoxide

ABBREVIATIONS AND SYMBOLS (continued)

DNTCB	- 2,4-dinitro-1,3,5-trichlorobenzene
ϵ	- Molar Absorptivity Coefficient
EGDN	- Ethylene Glycol Dinitrate
E_m	- Molar Absorptivity Coefficient
EPA	- Environmental Protection Agency
est	- Estimated
$^{\circ}\text{F}$	- Degree Fahrenheit
f	- Faint
FIR	- Far Infrared Red
g	- Gram
gal	- Gallon
H^+	- Hydrogen Ion
HMX	- Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine
HPLC	- High Performance Liquid Chromatography
h ν	- Light Energy
in	- Inch
i.p.	- Intraperitoneal
i.v.	- Intravenous
J	- Joule
$^{\circ}\text{K}$	- Degree Kelvin
kbar	- Kilobar (unit of pressure)
kcal	- Kilocalorie
kg	- Kilogram
kgg	- Thousand Kilograms
kp	- Partition Coefficient
Ksp	- Solubility Product Constant
l	- Liter
λ	- Wavelength
lb	- Pound
LC20	- Concentration Required to Kill 20% of the Exposed Population

ABBREVIATIONS AND SYMBOLS (continued)

LC50	- Concentration Required to Kill 50% of the Exposed Population
LC100	- Concentration Required to Kill 100% of the Exposed Population
LD50	- Dosage Required to Kill 50% of the Exposed Population
LDLO	- Lowest Dosage for Which an Effect is Observed
$\lambda_{\max}$	- Wavelength of Absorption Maxima
m	- Meter
m^3	- Cubic meter
μ	- Micron
m/e	- Mass to Charge Ratio
μg	- Microgram
mg	- Milligram
MGD	- Million Gallons per Day
MIR	- Mid Infrared
ml	- milliliter
mm	- Millimeter
μm	- Micrometer
mM	- Millimoles
mm Hg	- Measure of Vapor Pressure
mol	- Moles
M.P.	- Melting Point
N	- Newton
n_D	- Refractive Index
NIOSH	- National Institute of Occupational Safety and Health
nm	- Nanometer
NMR	- Nuclear Magnetic Resonance
NNM	- N-Nitrosomorpholine
OSHA	- Occupational Safety and Health Administration
π	- Pi (a constant ≈ 3.1416)
Pa	- Pressure in Newtons per Square Meter
Pcv	- Detonation Pressure at Constant Volume

ABBREVIATIONS AND SYMBOLS (continued)

PGDN	- Propylene Glycol Dinitrate
pH	- Negative Log of Hydrogen Ion Concentrations
ppb	- Parts Per Billion
ppm	- Parts Per Million
R	- Refractive Index
RDX	- Hexahydro-1,3,5-trinitro-1,3,5-triazine
s	- Strong
sc	- Subcutaneous
sec	- Second
SEX	- 1-acetyloctahydro-3,5,7-trinitro-1,3,5,7-tetrazocine
T	- Temperature, °Kelvin
TATB	- Triaminotrinitrobenzene
TAX	- 1-acetylhexahydro-3,5-dinitro-1,3,5-triazine
TBA	- Tumor Bearing Animals
ICLO	- Lowest Effective Toxic Concentration
TCTNB	- Trichlorotrinitrobenzene
TEGDN	- Triethylene Glycol Dinitrate
TEGN	- Triethylene Glycol Dinitrite
TF	- Tumor Free
TLC	- Thin Layer Chromatography
TLV	- Threshold Limit Value
TNT	- Trinitrotoluene
Torr	- Unit of Pressure
TSS	- Total Suspended Solids
TWA	- Time Weighed Average
UV	- Ultraviolet
V	- Very
vol	- Volume
V.P.	- Vapor Pressure
wk.	- Week
wt	- Weight
yr	- Year

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