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Aberdeen Proving Ground, Maryland 21010

ENVIRONMENTAL ASSESSMENT ARCSL-EA-83010

PROGRAMMATIC LIFE CYCLE ENVIRONMENTAL ASSESSMENT FOR SMOKE/OBSCURANTS

VOLUME 5 OF 5 VOLUMES

DYE COLORED SMOKES

PREPARED BY

JEROME J. CICHOWICZ
RANDALL S. WENTSEL, Ph.D.
ENVIRONMENTAL TECHNOLOGY DIVISION

FOR

PROJECT MANGER FOR SMOKE/OBSCURANTS

JULY 1983

Department of the Army
US Army Armament, Munitions and Chemical Command
Chemical Research and Development Center
Aberdeen Proving Ground, MD 21010

Programmatic Life Cycle Environmental Assessment for Smoke/Obscurants

Volume No. 5 of 5 Volumes

Dyes/Colored Smokes

July 1983

Prepared by:

Jerome J. Cichowicz

JEROME J. CICHOWICZ
General Engineer
Environmental Technology Division
Chemical Research and Development Center

Prepared by:

RANDALL S. WENTSEL Ph.D.
Environmental Scientist
Environmental Technology Division
Chemical Research and Development Center

Reviewed by:

C Reed Magness

C. REED MAGNESS
Supervisory Environmental Scientist
Environmental Technology Division
Chemical Research and Development Center

Reviewed by:

Janis D. Chase

JANIS D. CHASE
Environmental Coordinator
Chemical Research and Development Center

Reviewed for OPSEC:

Kenneth Kasai

KENNETH KASAI
Deputy Project Manager
Project Manager Smoke/Obscurants
AMCCOM

Approved by:

Morton S. Brisker

MORTON S. BRISKER
Colonel, CM
Project Manager Smoke/Obscurants
AMCCOM

3 Aug 83
DATE

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Colored smokes/dyes have been used extensively in the past to satisfy signaling and communication needs of the Armed Forces and will continue to be used as vital elements of the national defense posture. Associated with the need for colored smoke is the concern for noncarcinogenicity, nonmutagenicity, and minimal (reversible/nonincapacitating) toxicity to handling and user personnel and the environment. The environmental impacts and data relevant to the life cycle use of the standard dyes and the recommended replacement of safer dyes for future use are compiled in this report. With controled distribution and use of the (see reverse)

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SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered) colored smokes, that is adherence to safety aspects and regulations and the implementation of suggested mitigation, minimal adverse impacts to the quality of the human environment is predicted, and the conclusion is that proposed on-going smoke programs will not significantly affect the quality of the environment. Benzanthrone and Vat Yellow 4 have been discontinued for use and are only addressed in this report for the purpose of clarity.

PREFACE

This is Volume No. 5 of a five-volume document, which is to provide a general environmental assessment for the overall smoke/obscuration program. Volume No. 1 identifies oil smokes; Volume No. 2 provides pertinent information on red, white, and plasticized white phosphorus; Volume No. 3 identifies IR smokes; and Volume No. 4 covers HC smoke. The purpose of this volume is to provide a programmatic environmental assessment for signaling smokes (colored dyes). It includes the life cycle phases of research, development, testing, production, and deployment of colored smokes. Plans and schedules have been initiated to replace several of the standard dyes with nontoxic ones in the near future. Existing standard dyes and associated signaling smokes will continue to be used until approved replacement materials become available. This programmatic environmental assessment addresses both existing and proposed dyes as they are applicable to present usage.

This document is not site- or item-specific, however, it is intended to be used as a basic document in the preparation of related life cycle environmental documentation, as well as a major supportive reference for environmental documentation prepared for individual site-specific operations. Therefore, as new studies are completed and other items (smoke/dyes, munitions, etc.) are proposed, supplemental information will be developed and issued as appropriate.

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DYE COLORED SMOKES

I. PURPOSE AND NEED

As a result of the 1973 Yom Kippur War, the Army has reaffirmed the importance of both signaling and screening-smoke production as vital elements of its defense posture. The colored signaling dyes are an important means of communications. By prearrangement, colored smoke can be used to identify friendly units; to control the laying and lifting of artillery, mortar, and small arms fire; to identify targets, and to coordinate fire and maneuvering of combat arms engaged in local assault operations. Closely associated with the need for colored smoke is the requirement of noncarcinogenicity, nonmutagenicity, and minimal (reversible, nonincapacitating) toxicity to industrial personnel and the environment.

II. DESCRIPTION OF ACTION

A. Introduction.

Smoke signals were utilized in ancient times where hand and flag signals were not visible and when the sound of voice or horn was not audible. However, during the black gunpowder era, when battlefields were always enveloped in a thick haze, smoke could not be used for signaling. With the advent of smokeless powder, smoke signals again became feasible and are now an important means of identification and prearranged battlefield communications. Four characteristics of signaling smokes determine their value for use namely: color, visibility, duration, and volume.

1. Color.

A signaling smoke must be clearly distinguishable from the smoke incident to battle. The standard smokes are pyrotechnic mixes of fuel-oxidizer and a dye or dye combination, with a cooling agent sometimes added to prevent excessive decomposition of the dye which is evidenced by decolorization or flaming. When ignited, the mixtures burn and produce colored smoke clouds of red, violet green, and yellow, which afford good visibility and unmistakable identity.

2. Visibility.

At great distances all colors become gray and indistinguishable. A minimum visual range against a contrasting background is specified for each signaling munition. With the munitions now in use, the visual range varies from 3,000 feet (M22 rifle grenade) to 10,000 feet (M18 grenade).

3. Duration.

On the basis of duration, colored smoke munitions may be divided into two classes: fast-burning, which last about 1 minute, and slow-burning, which last about 2 minutes.

Signaling smokes are produced by volatilizing and condensing a mixture containing an organic dye. The heat produced by the fuel volatilizes the dye, which then condenses outside the munition to form colored smoke. The burning time can be regulate by adjusting the proportions of oxidant and combustible material, and by use of coolants. The fuel is either sulfur or sugar. The fuel-oxidizer mixture is sulfur/potassium chlorate ($KClO_3$) or sugar/$KCLO_3$. The fuel-oxidizer-coolant mixture is sugar/$KClO_3$/magnesium carbonate ($MgCO_3$).

B. Background.

Research studies indicate that some of the organic dyes presently used in colored smoke pyrotechnic formulations pose potential serious health hazards to occupationally exposed personnel. These component dyes include benzanthrone (7 H-benz (de) anthracene 7-one), C.I. Vat Yellow 4 (dibenzo (b, def) chrysene-7-14-dione) and Disperse Red 9 (1 - methylaminoanthraquinone). Benzanthrone causes dermatitis in man and affects the liver and autonomic nervous system. Both benzanthrone and Vat Yellow 4 are potential carcinogens. Disperse Red 9 is a skin irritant and sensitizer with possible carcinogenic activity. Research conducted in 1980 by the Oak Ridge National Laboratory revealed that all of the above dyes (yellow, green and red) and also 1, 4-diamino-2, 3-dihydro-anthraquinone violet dye, exhibited mutagenic activity. These health hazards are of concern as they give rise to a potential ban on production and use of colored-smoke munitions. The preferred solution is the substitution of dyes which are noncarcinogenic, nonmutagenic, and of minimal (reversible, nonincapacitating) toxicity to industrial personnel and the environment. Accordingly, two product improvement programs (PIP) have been conducted to provide safer dyes or dye mixes that can be substituted in the existing munitions without changing the item configuration or performance.[1,2]

C. Modes of Dissemination and Munition Types.

The pyrotechnic mixes of current colored smoke are put into cartridges (smoke markers) and hand grenades. Canisters for use with projectiles such as the 105-mm and 155-mm have been filled and stockpiled in the past, but no additional buys are anticipated; therefore, these canisters will not be addressed in this assessment. Colored smokes are used as point source devices for signaling and marking; therefore, payloads and area coverage are magnitudes less than for screening smokes. Payload estimates and dissemination characteristics are summarized in Table 1.

1. Smoke Markers.

Smoke cartridges (markers) are used to provide aerial indentification and location of troops on the ground and are designed to be fired from 40-mm grenade launchers. The cartridge consists of a cartridge case, projectile with pyrotechnic smoke payload, and a pyrotechnic impact fuze. The cartridge case is a dual-chamber aluminum container housing a brass propellant cup. The propellant cup is held in the case by a crimped base plug which provides a pressure type waterproof seal. The base plug houses a percussion primer. The projectiles utilize a one-piece, aluminum ogive and a steel base. The payload consists of a pyrotechnic smoke mixture pressed into the body ogive. The fuze is cemented to the base of the projectile and protudes into a cylindrical cavity of the smoke mixture.

Upon firing, the primer ignites the propellant charge. In turn, the projectile is accelerated down the launcher barrel where a spin of 3750 rpm is imparted by the barrel rifling. A muzzle velocity of 250 fps is attained. In addition to launching the projectile, the propellant gases ignite the first fire mixture of the fuze in the base of the projectile. The first fire mixture ignites a high-temperature transfer mixture contained in the steel cup. The transfer mixture burns during the first 15 meters of

Table 1. *Colored Smoke Munitions and Dissemination Characteristics*

Munition type(s)		Color	Military usage	Remarks	Status	Weight (lb)		Average burning time	Deployment mode
						Fill	Total		
Grenade M18		Red Yellow Green Violet	Signalling and marking	Considered in replacement program	PIP[a] action	0.73	1.10	50-90 seconds	Emplaced by hand (normally); ignited manually
Smoke Marker 40-mm	M713 M716 M715	Red Yellow Green	Aerial identification of ground objects	Considered in replacement program	PIP[b] action	0.16	0.40	-	40-mm grenade launcher
Grenade (train) M48		Red	Training	Currently no buys are set forth in the FYDP. PIP is applicable should there be future buys	-	-	-	5-25 seconds release to function time	Emplaced by hand; ignited manually

[a] Product Improvement Project (PIP) No: DA1-81-09-7320, Chemical Systems Laboratory project, Aberdeen, MD 21010

[b] PIP No: DA1-82-09-7324

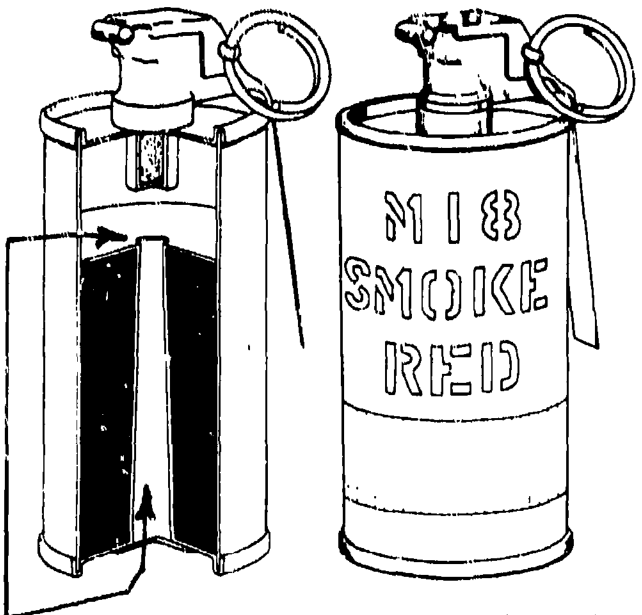
projectile flight. When the projectile is between 15 and 45 meters from the launcher muzzle, heat transferred through the steel cup ignites the delay mixture. Upon impact, the delay casing breaks, and the burning portion flies forward out of the fuze support, contacting and igniting the pyrotechnic smoke mixture. Ignition of the smoke mixture causes buildup of pressure, which dislodges the fuze support at the aft end of the projectile and the end seal at the forward end, thus allowing smoke to be emitted at either end of the projectile. Typical weight of the munition is 0.40 lb; length is 3.91 inches; smoke mixture payload typically is 75 grams.

2. Smoke Grenades.

Colored smoke grenades are used to mark or spot specific positions on the ground. They are normally emplaced by hand and ignited manually. The average soldier can throw a grenade 30 to 35 yards. Colored smoke is highly visible and would likely draw enemy fire when used in small quantities. So, it should never be used as a screening device.

The M18 smoke grenade is depicted in Figure 1 below. It is a self-contained unit filled (compacted) with a solid-fuel, smoke-producing agent by means of hydraulic rams. At the top of the grenade, a small chamber contains a starter system* filled with a specially developed chemical composition. Additional information on the M18 grenade can be found in the Operator's and Organization Maintenance Manual for Grenades.[3]

The grenades produce smoke by means of a reaction in which a carbohydrate-based fuel, such as sucrose, is oxidized by potassium chlorate. The heat liberated by this reaction serves to vaporize the dye, which is then ejected into the atmosphere along with other vaporized combustion products and, upon condensation, creates a cloud with the color of the vaporized dye.



ITEM:	M18 GRENADE
TYPE:	CORE BURNING
COLORS:	RED, VIOLET, GREEN, YELLOW
SIZE:	2.5-INCH DIAMETER, 4.5 INCHES LONG
WEIGHT : (TOTAL)	1.07 LB
(MIX)	.73 LB
FUZE:	M201A1 PYROTECHNIC FUZE
BURNING TIME:	50-90 SECONDS

Figure 1. M18 Colored Smoke Grenade

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*The starter mix is applied to the surface of the compacted smoke mix.

D. Signaling Smoke Formulations.

In the following paragraphs the various standard and substitute dye colors and associated compositions will each be identified separately. The dyes which may pose a health hazard and are scheduled for replacement are Disperse Red 9 (1-methylamino-anthraquinone), benzanthrone dye (7-H-benz (de) anthracene-7-one), Vat Yellow 4 (dibenzo (b, def) chrysene-7-14-dione) and Violet dye (1, 4-diamino-2, 3-dihydroanthraquinone). The proposed replacement dyes are depicted in Table 2 below.

Table 2. Standard versus Proposed Dye Replacements

Color smoke	Trade name (chemical nomenclature) Standard dye	Proposed replacement dye
Red	Disperse Red 9 (1-methylaminoanthraquinone)	Sudan R (0-methoxy-phenyl-azo-B-naphthol)
Green	Solvent Green 3 (1, 4-di-p-toluidinoanthraquinone)	Solvent Green 3
	Benzanthrone Dye (7 H-benz (de) anthracene-7-one)	Solvent Green 3 (increased percentage)
	Vat Yellow 4 (dibenzo (b, def) chrysene-7-14-dione)	Solvent Yellow 33 Dye (2-(2-quindolyl) - 1, 3-indandione)
Yellow	Vat Yellow 4 (same as above)	Solvent Yellow 33 Dye (same as above)
Violet	(1, 4-diamino -2, 3-dihydroanthraquinone)	Solvent Violet 36
	Disperse Red 9 (1-methylaminoanthraquinone)	Sudan R

Most of the Product Improvement Program (PIP) work accomplished so far has been for yellow and green smoke compositions. Not nearly as much information has been compiled for red and violet formulations. Preliminary testing for mutagenicity is being conducted to aid in determination of future red and violet dyes, while the yellow and green dyes have been tested and approved to start manufacturing yellow and green grenades. The green smoke will continue to use the standard Solvent Green 3 (at least for the present). A yellow dye, 2-(2-quinolyl)-1, 3-indandione, has been identified as having been successfully used as yellow smoke and, in combination with Solvent Green 3, as green smoke. It has been certified by the Food and Drug Administration (FDA) for use in externally applied drugs and cosmetics. The FDA designation for this dye is D&C Yellow No. 11. The synonym used by the Edgewood PIP program is Solvent Yellow 33. Ingestion and inhalation studies are underway by the US Army Medical Bioengineering Research and Development Laboratory (USAMBRDL), Fort Dietrick, Maryland.

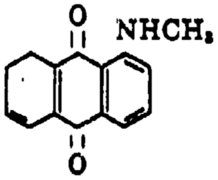
Where red and violet smokes are listed together and likewise yellow and green are grouped together in the following tables, it is because of their similarity in chemical ingredient formulations. Benzanthrone and Vat Yellow 4 are not addressed in the following sections because of their discontinued use.

1. Disperse Red 9 Dye.

1-Methylaminoanthraquinone is a disperse dye used by the Army to impart a red color to smokes. It is presently stockpiled for use but is scheduled for replacement. At current production rates, the Army uses 100,000 lb of this dye per year. This is approximately 12% of the civilian production capability.

(a) Alternate Names.

1-Methylaminoanthraquinone is a disperse dye with the chemical structure shown below:



The molecular formula of this dye is $C_{15}H_{11}NO_2$. Its molecular weight is 237.26 gm/mole. Pertinent alternate names for 1-methylaminoanthraquinone are:

CAS Registry No. 82-38-2

Replaces CAS Registry No.(s) 12226-87-8

CA Name (9CI) 9,10-anthracenedione, 1-(methylamino)

CA Name (8CI): anthraquinone, 1-(methylamino)

Wiswesser Line Notation L C666 BV IVJ DM1

Synonyms: Alpha-methyaminoanthraquinone; C.I. 60505; C.I. Disperse Red 9; C.I. Solvent Red 111; Calco Oil Red ZMQ; Celanthrene Red Y; Celliton Pink R; Diacelliton Fast Pink R; Duranol Red GN; Marcolex Red G; 1-methylamino-9-10-anthraquinone; 1-(methylamino) anthraquinone; N-methyl-1-anthraquinonylamine; 1-(N-methylamino) anthraquinone; Oil Red ZMQ; Serilene Fast Pink BT: Supracet Pink R; Waxoline Red MAA: Waxoline Red MP

(b) Physical Properties.

Physical form @ 20°C: solid

Color and crystalline form: yellow-red needles

MP: 170°C

Solubility: soluble in alcohol, benzene, chloroform, acetic acid, acetone, and linseed oil. Slightly soluble in carbon tetrachloride.

(c) Mix Formulations.

The colored smoke grenades produce smoke by volatilization of organic dyes. The dyes are intimately combined with a pyrotechnic mixture of a fuel, an oxidizer, and a coolant (burning rate modifier). The formulations of the standard smokes versus improved smokes are found in Tables 3 and 4.

Table 3. Standard Red and Violet Formulations

Chemical ingredient	Specification	Red smoke Parts by Weight	Violet smoke Parts by weight
Dye, Disperse Red 9,	MIL-D-3284C	40 % ±	
sodium bicarbonate,		25 % ±	24 % ±
potassium chlorate,		26 % ±	25 % ±
sulfur		9 % ±	9 % ±
Violet Smoke Mix*	MIL-D-3691B		42 %

*80± 2% 1, 4 diamino-2, 3-dihydroanthraquinone and 20± 2% of Disperse Red 9.

(d) Product Improvement Program Actions.

The purpose of the program (PIP DA1-81-09-7320) is to replace Disperse Red 9 (1-methyl-amino-anthraquinone) by developing substitute dyes. Specifically, areas targeted for investigation are:

1. Studies will continue to be conducted to derive red (and violet) smoke formulations. Grenades will be loaded and tested to optimize thermal efficiency, establish functional suitability, and verify the acceptability of colors.

2. Military specifications for substitute dyes will be prepared, including quality acceptance requirements.

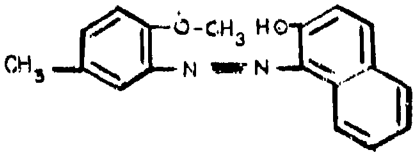
The primary replacement candidate to date is O-methoxy-phenyl-azo-B-napththol (Sudan R).

2. Sudan R Dye.

O-methoxy-phenyl-azo-B-naphthol is the proposed red dye to replace Disperse Red 9 in the M18 grenades and 40-mm smoke cartridges.

(a) Alternate Names

Pertinent alternate names for O-methoxyphenylazo-B-naphthol* are:



The molecular formula of this compound is

CAS Registry No. 6410-20-4

C.I. 12150

Synonyms: Oil Red G, Solvent Red 1

(b) Physical Properties.

Will be included as the data is obtained.

(c) Mix Formulations.

Table 4. Improved Red and Violet Formulations

Chemical ingredient	Specification	Red smoke Parts by weight	Violet smoke Parts by weight
Dye, Sudan R	MIL -	This table is to be completed as data becomes available.	
Violet Smoke Mix	MIL -		

(d) Product Improvement Program Actions.[2]

Included as part of the PIP will be the following actions:

The improved smoke formulations will be tested to assure they are safe and effective and meet the performance specifications. Hazards classifications will be assigned.

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*Other pertinent data will be included as it is developed.

A medical evaluation program (MEP) is being initiated which will completely assess the health effects of the substitute dye and the improved smoke formulations.

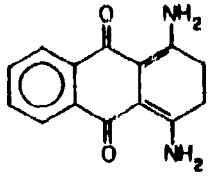
The technical data package for the M18 grenade will be amended to allow the production of red and violet smoke grenades with the substitute smoke formulations.

3. Violet Dye Mix.

A preblended mixture of 1, 4-diamino-2,3-dihydroanthraquinone (80% ± 2%) and Disperse Red 9 (20% ± 2%) constitute the violet dye mix that is used in smoke grenades to impart a violet color to the smoke. This dye is scheduled for replacement. The grenades are manufactured at Pine Bluff Arsenal. The use of the dye by the Army is sporadic. At current operating rates the Army uses only 0.7% of the civilian production of the dye; current Army production is 3,500 lb per year.

(a) Alternate Names.

1, 4-Diamino-2, 3-dihydroanthraquinone is a violet dye possessing the following chemical structure:



This compound has a molecular formula of $C_{14}H_{12}N_2O_2$ and a molecular weight of 240.26 gm/mole. Pertinent alternate names for 1, 4-diamino-2, 3-dihydroanthraquinone are:

CAS Registry No. 81-63-0

CA Names (9CI) 9, 10-anthracenedione.I.4-diamino-2, 3-dihydro-

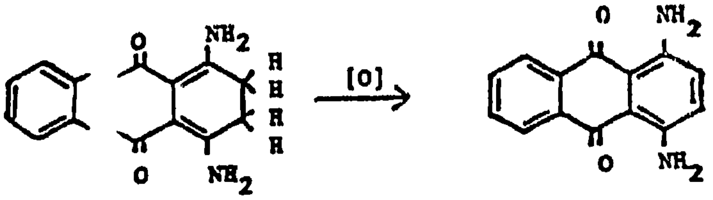
CA Names (8CI) anthraquinone, 1, 4-diamino-2, 3-dihydro-

(b) Physical Properties.

No physical properties of 1, 4-diamino-2,3-dihydroanthraquinone were found in this search.

(c) Chemical Properties

1, 4-diamino-2, 3-dihydroanthraquinone is easily oxidized to 1, 4-diaminoanthraquinone by either air or manganese dioxide.



In the environment this dye is expected to undergo photochemical decomposition. The rate of decomposition and the products formed will be dependent upon the surrounding conditions.

(d) Product Improvement Program Actions.

The purpose of the project (PIP DA1-81-09-7320) is to replace Violet Dye Mix and Disperse Red 9 (1-methyl-amino-anthraquinone) by developing substitute dyes. Specifically, areas targeted for investigation are:

1. Studies will continue to be conducted to derive violet smoke formulations. Grenades will be loaded and tested to optimize thermal efficiency, establish functional suitability, and verify the acceptability of colors.

2. Military specifications for substitute dyes will be prepared including quality acceptance requirements.

3. Candidate substitute dyes will be identified and developed.

4. A Medical Evaluation Plan (MEP) will be initiated.

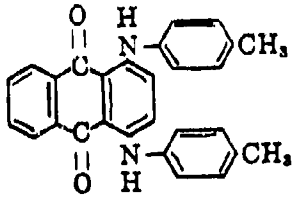
4. Solvent Green 3 Dye.

1, 4-di-p-toluidinoanthraquinone is a green dye used in smoke formulations to impart green color to the smoke. Current production is approximately 64,000 lb per year. Solvent Green dye has been used in conjunction with benzanthrone dye and Vat Yellow 4 Dye to create green smoke.

Benzanthrone and Vat Yellow 4, both yellow dyes, have been discontinued from use, and an engineering change proposal (ECP) to allow production of substitute dyes (Solvent Yellow 33 and increased percentages of Solvent Green 3) has been approved by the Configuration Control Boards (CCB) of CRDC and AMCCOM.

(a) Alternate Names.

1, 4-di-p-toluidinoanthraquinone is a green dye possessing the following chemical structure:



The molecular formula of this compound is $C_{28}H_{22}N_2O_2$ and its molecular weight is 418.50 gm/mole. Pertinent alternate names for 1, 4-di-p-toluidinoanthraquinone are:

CAS Registry No. 128-80-3

CA Name (9CI) 9, 10-anthracenedione; 1, 4-bis((4-methylphenyl) amino)

CA Name (8CI) anthraquinone, 1,4-bis(p-toluidino) anthraquinone

Wiswesser Line Notation: L C666 BV IVJ DMR D& GMR D

Synonyms: Ahcoquinoe Cyanine Green Base; Alizarine Cyanine Green Base; Alizarine Cyanine Green G Fat Soluble; Alizarine Green G Base; Amaplast Green OZ; Anthraquinone Green G Base; Arlosol Green B; Arlosol Green BS; Arlosol Green BSS; 1,4-bis(p-tolylamine) anthraquinone; C-green 10; C.I. 61565; C.I. Solvent Green 3; Cyanine Green G Base; D and C Green No. 6; 1, 4-bis(p-toluidino)anthraquinone; Fat Soluble Anthraquinon Green; 11091 Green; Green No. 202; Nitro Fast Green GB; Organol Fast Green J; Organol Green J; Quinazarin Green; Quinizarin Green SS; Quiniz-anine Green Base; Solvent Green 3; Sudan Green 4B; Toyo Oriental Oil Blue G; Waxoline Green; Waxoline Green G.

(b) Physical Properties.

Physical properties of 1, 4-di-p-toluidinoanthraquinone (Hawley, 1977, Colour Index, 1956):

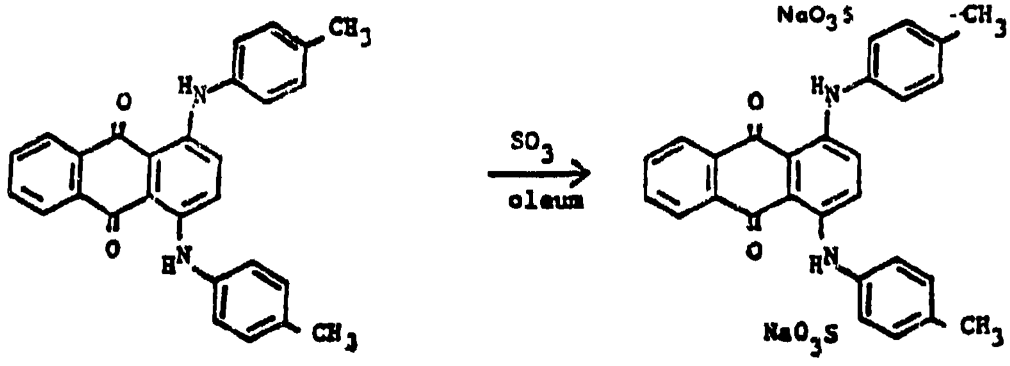
Physical Form @ 20°C: solid

MP: 213°C

Solubility. Slightly soluble in acetone, ethyl acetate, mineral oil, oleic acid, and stearic acid. Soluble in benzene and toluene

Chemical Properties.

1,4-di-p-toluidinoanthraquinone will undergo electrophilic substitution on the toluidine rings. This substitution occurs ortho to the amino function.



In the environment photodegradation of this dye can also occur. The rate and the products of the photodegradation will depend on surrounding conditions.

(c) Mix Formulations.

The standard smoke mixes are listed in Table 5, and Table 6 shows the improved replacement smoke mixes.

(d) Product Improvement Program Actions.

PIP action is not presently underway for Solvent Green 3 since all information to date indicate it is suitable for continued use. As already indicated, benzanthrone, a yellow dye, and Vat Yellow 4 have been replaced by increased percentages of Solvent 3 and Solvent Yellow 33. (An engineering effort is being performed under MMT project 5791403 for the dye replacement in the M18 grenade. A similar effort for the 40-min markers will be performed under PIP DA1-82-7324.)

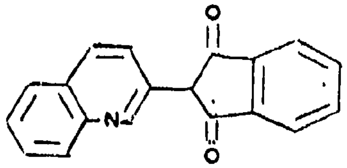
The medical evaluation program has been initiated which will completely assess the health effects of the substitute dye and the improved formulations.

5. Solvent Yellow 33 Dye.

2-(2-Quinolyl)-1, 3-indandione is a yellow dye which will impart yellow color to smoke. It is used in both yellow and green smoke munitions. The FDA designation for this dye is D&C yellow No. 11.

(a) Alternate Names.

2-(2-Quinolyl)-1,3-indandione has the following chemical structure:



CAS Registry No. 83-08-9

Color Index No. 47000

Synonyms: Chinoline yellow, quinoline yellow SS, C.I. Solvent Yellow 33, D&C Yellow 11

(b) Physical Properties.

These properties will be incorporated when data becomes available.

(c) Mix Formulations.

The following comments are pertinent to the new mixes in Table 6 and are derived from performance testing with smoke grenades.

1. Sulfur and sodium bicarbonate are unacceptable as fuel and coolant, respectively, in the new mixes. Yellow smoke grenades made with sulfur or sodium bicarbonate burn unevenly and the smoke color fades. Green smoke grenades made with sulfur burn unevenly and may explode.

Table 5. Standard Yellow and Green Smoke Mix Formulations

Chemical ingredient	Specification	Yellow Smoke VI		Green Smoke IV	
		Parts by weight	Tolerance	Parts by weight	Tolerance
Dye, Vat Yellow 4	MIL-D-0050029	14.0	±0.5	4.0	±0.5
Dye, benzanthrone	MIL-D-0050074	24.5	±1.0	8.0	±0.5
Dye, Solvent Green 3	MIL-D-003277	-	-	28.0	±1.0
Potassium chlorate	MIL-P-150, Grade B, Class 7	20.0	±2.0	27.0	±2.0
Sodium bicarbonate	O-S-576	33.0	±2.0	22.6	±2.0
Sulfur	MIL-S-487, Grade E	8.5	±1.0	10.4	±1.0

Table 6. Improved Yellow and Green Smoke Mix Formulations

Chemical ingredient	Specification	Yellow Smoke XII		Green Smoke VII	
		Parts by weight	Tolerance	Parts by weight	Tolerance
Dye, Solvent Yellow 33	DOD-D-51485	42.0	±1.0	12.5	±0.5
Dye, Solvent Green 3	MIL-D-003277	-	-	29.5	±1.0
Potassium chlorate	MIL-P-150, Grade B, Class 7	22.0	±1.5	24.5	±1.5
Magnesium carbonate	MIL-M-11361, Grade N	21.0	±2.0	17.0	±2.0
Powdered sugar	JJJ-S-791, Type I, Class (d)	15.0	±1.0	16.5	±1.0

NOTE: All proportions of potassium chlorate and sugar to other ingredients may be varied to yield the required burn time, but the ratio of potassium chlorate to sugar must be maintained in the proportions specificied in the table.

2. Powdered sugar (sucrose) and magnesium carbonate were the best fuel-coolant combination tested. Excellent smoke clouds of bright yellow and green were produced. The optimum formulations are shown in Table 6.

3. The oxidizer-fuel ratio (potassium chlorate-sugar) which gave the best grenade performance was determined to be 1.5:1.

4. Lactose was not acceptable as a fuel. Although lactose was preferred over sucrose, as the former is nonhygroscopic, yellow smoke grenades incorporating lactose burned unevenly and several green smoke grenades exploded.

5. Dextrin is not recommended as a Solvent Yellow 33 diluent, although its use is allowed in the other standard military smoke dyes. The presence of dextrin in the improved smoke mixes was found to have a significant effect on grenade burn time. Although smoke mixes which contained 2 or 4 percent dextrin were successfully formulated, the potential for producibility problems exists where the dextrin content varies from lot to lot.

6. Bright yellow smoke was produced using Solvent Yellow 33 alone. A bright green smoke, judged superior to the smoke of the standard green smoke grenade, was produced by a 70 to 30 (by weight) mixture of Solvent Green 3 and Solvent Yellow 33.

(d) Product Improvement Program Actions.

Solvent Yellow 33 was assessed under MMT Project No. 5791403 and the details are contained in a report by Smith.[4]

E. Impact Models (Environmental Fate).

The Environmental Technology Division of CRDC has access to an environmental fate model which uses the fugacity (defined as escaping tendency) of a chemical to predict the phases where a given chemical will concentrate. The phases are soil, water, air, sediment, and biota. The model assumes a steady state between phases. A more detailed explanation of the model is presented by Mackay and Paterson.[5]

The inputs for the model are:

molecular weight (mol wt)

temperature of environment (°C)

water solubility (mg/l)

vapor pressure (mm Hg at temperature of environment)

log octanol*/water partition coefficient (log kow)

amount released (moles)

As an example of this model, 1-methylaminoanthraquinone (MAA) was used. The molecular weight and temperature of MAA were known.

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*loc octanol = log koc which is calculated in the model

Estimates of water solubility and vapor pressure at 25°C was derived from data that was generated at higher temperatures. For the octanol/water partition coefficient (log kow),* two values were used to cover a range where the actual value would most likely fall. We assumed a water solubility value of 0.05 mg/gm at 25°C.

The results are presented in Table 7. The model indicates that MAA will primarily accumulate in the water. This model is a tool which can predict where a chemical will concentrate when released into the environment. The fugacity model requires a small amount of input and is good for initial environmental estimates. If necessary, more sophisticated models are available for environmental fate predictions.

Table 7. Environment Fate Model for 1-Methylaminoanthraquinone

		Percent of MAA in each phase				
Impact		Air	Water	Soil	Sediment	Biota
Molecule weight	237.1 gm/mol					
Temperature	25°C					
Water solubility	50 μg/l	32.6	59.6	1.4	6.4	< .1
Vapor pressure	.0002 PA					
log ow	3.00					
Molecule weight	237.1 gm/mol					
Temperature	25°C					
Water solubility	50 μg/l	0.0	99.6	.07	.34	< .1
Vapor pressure	.0002 PA					
log ow	1.5					

Anyone interested in using such models for their own predictions may contact the Environmental Technology Division, Chemical Research and Development Center at Aberdeen Proving Ground, MD 21010.

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*The log kow partition coefficient expresses the equilibrium concentration ratio of an organic chemical partitioned between n-octonal and water.

III. ENVIRONMENTAL LAWS AND REGULATIONS

Environmental laws and regulations are of two types: (1) those requiring assessment of environmental impacts of specific programs or actions, and (2) those requiring compliance with environmental pollution standards. The chemicals and facilities associated with smoke operations may be affected by one or more of the statutory requirements listed below. The primary purpose of this section is to identify general features and applications of those environmental regulations most likely to influence smoke operations during their life cycle. Specific applications will vary with individual items and should be addressed accordingly.

A. National Environmental Policy Act.

The National Environmental Policy Act (NEPA) of 1969 was created by congress to establish a national policy for protection of the environment and to provide the goals and means to avoid or minimize adverse environmental consequences by requiring that impacts of planned federal actions and alternatives be evaluated before being undertaken. As currently amended, this act is binding on the activities of all federal agencies, except where inconsistent with other statutory requirements. Certain provisions of NEPA are also incorporated into other federal legislation, including the National Historic Preservation Act of 1966 and the Endangered Species Act of 1973.

Army policy in NEPA matters is provided in AR 200-2, which establishes responsibilities and procedures for integration of environmental considerations into Army planning and decision making. Among these responsibilities are the identification and analysis of environmental risks for proposed actions and their most likely alternatives. The policy of the US Army Materiel Development and Readiness Command (DARCOM) requires environmental analysis and documentation for all items (including smokes) being developed under its program/project/production managers and research and development commands.

B. Resource Conservation and Recovery Act.

The Resource Conservation and Recovery Act (RCRA) of 1976 established a national program for management of waste, including hazardous waste (40 CFR parts 260-64; 266-267). Wastes are defined by RCRA as "hazardous:" (1) if specifically listed by regulations, or (2) if exhibiting any one of the characteristics of reactivity, corrosivity, ignitability, or EP toxicity (as defined in 40 CFR, 261.2). The present EPA list includes approximately 400 chemicals and 85 process wastes. State and local regulatory authorities may administer programs for hazardous waste management provided that the programs are at least as stringent as the federal program. Therefore, state and local programs should be evaluated for consistency with the federal regulations.

Under RCRA, the generator of waste has the responsibility for determining whether or not it is hazardous. If found to be hazardous, the waste is then subject to comprehensive "cradle to grave" record keeping requirements, including a manifest system to track and document the generation, transportation, and ultimate disposal of the material. It should be emphasized that substances are not classified by RCRA as wastes until they are ready to be discarded (i.e., regulations do not apply if substances - otherwise classifiable as wastes - are recycled for other industrial purposes).

The colored smokes/components are not listed by compound name as hazardous wastes under RCRA. However pyrotechnic smokes are classified as hazardous waste for disposal purposes, hence the colored dyes are pyrotechnic smokes. This classification for pyrotechnics is provided by Title 49 CFR 173.53 (r), which includes smoke generators and munitions filled with smoke and used in warfare as Class A explosive chemical ammunition. Title 40 CFR 261.23 (a) (8) states that Class A explosives as defined by 49 CFR 173.53 are hazardous wastes when disposed of.

C. Toxic Substance Control Act.

The Toxic Substance Control Act (TSCA) of 1976 addresses the manufacture, importation, distribution, and use of chemical substances. As amended (40 CFR, parts 704-710) this act authorizes the Environmental Protection Agency (EPA) to inventory commercial chemicals and, for chemicals listed after 31 December 1979, to require sufficient data to estimate health and environmental hazards of production use.

The standard colored smokes used by the Army for testing and training are listed on the initial TSCA inventory list (45 CFR 50544, 29 July 80). These standard dyes include Solvent Green 3, Disperse Red 9, Violet mix, benzanthrone, and Vat Yellow 4.

The new dyes, Sudan R and Solvent yellow 33, are also on the TSCA initial inventory list. Both have been used by industry for years in dye operations. Both Sudan R and Solvent yellow 33 were also developed before TSCA became effective and are on the initial inventory list.

D. Clean Air Act.

The Clean Air Act (CAA) of 1963 was created because of public concern over health problems associated with air pollution. As currently amended (40 CFR, parts 50-52), the CAA established National Ambient Air Quality Standards (NAAQS) for the control of criteria air pollutants to prevent adverse effects to air resources, human health, and the environment. NAAQS which may be affected by the smoke program are presented in Table 8. However, it is likely that an NAAQS would only be affected by smoke generation if it occurred frequently, on a large scale, and in the same general location. It is more feasible that smoke-generation exercises would exceed certain emission standards/nuisance laws established by state and local regulatory agencies. State and local municipalities may adopt standards that are more stringent than the NAAQS and local standards should be evaluated for consistency with national standards. Until recently, the emission of hydrocarbons was regulated by the NAAQS; however, on 30 December 1982, the hydrocarbon NAAQS was rescinded by the EPA. According to the EPA, because no consistent quantitative relationships between concentrations of ambient air ozone and hydrocarbon air quality levels exists, the original basis for the hydrocarbons standard could not be justified.

Under the CAA, the country is divided into 247 air quality control regions (AQCRs) to provide basic geographical units for air pollution control. States are required to prepare State Implementation Plans (SIPs) to implement and enforce criteria pollutant standards in those regions. AQCRs that have attained the NAAQS for a criteria pollutant are considered to be in "attainment" for that pollutant. AQCRs in violation of NAAQS for a criteria pollutant are considered "non-attainment" for that pollutant. Most standards specify two types of limitation - long term standards, which cannot be exceeded on an annual average, and short term-exposures, which cannot be exceeded for

Table 8. Federal Ambient Air Quality Standards for Certain Criteria Pollutants Relative to Colored Smokes

Chemical	National standards
Particulate matter	(A) 75 $\mu g/m^3$ annual geometric mean (B) 260 $\mu g/m^3$ - maximum 24-hour concentration not to be exceeded more than once per year.
Ozone	0.12 ppm (235 $\mu g/m^3$). The standard is attained when the expected number of days per calendar year with maximum hourly average concentrations above 0.12 parts per million (235 $\mu g/m^3$) is equal to or less than 1.0.
Hydrocarbons	EPA standard rescinded

brief periods (e.g., 3 hours and/or 24 hours). Because the deliberate generation of smokes during testing or training is directly counterproductive to air pollution abatement and the control efforts of the environmental regulatory agencies, the Army environmental coordinator at the individual test or training site should be consulted to determine whether a particular activity is regulated and to coordinate the smoke exercise with regulatory agencies for permits or variances, as required.

E. Federal Regulations Governing Hazardous Substance Release into the Environment.

Policy and procedures for control of discharges of hazardous substances into the environment are detailed in the Federal Water Pollution Control Act (FWPCA)* (PL95-576) and the Comprehensive Environmental Response Compensation and Liability Act of 1980 (CERCLA) (PL96-510). Section 311 of FWPCA describes requirements for handling discharges of hazardous substances into or upon navigable United States waters, adjoining shoreline, or the contiguous zone that may affect US natural resources.

EPA has promulgated regulations under the FWPCA which identify and establish reporting requirements for approximately 270 hazardous substances. Reporting requirements are bases on harmful quantities as defined by the regulation. Zinc chloride, the predominant aerosol product of HC smoke, is included on the FWPCA hazardous substance list.

An Installation Spill Prevention and Countermeasure Control (SPCC) Plan and an Installation Spill Contingency Plan (ISCP) establishes procedures to prevent spills and to ensure prompt reporting, containment, and cleanup of spills should they occur.

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*FWPCA is commonly known as the Clean Water Act.

Reporting procedures are outlined in Army Regulation 200-1, chapter 8, 15 June 1982. In that the smoke mixes are not liquid, the word(s) "leakage" or "accidental release" should be substituted for the word "spill."

CERCLA also establishes reporting requirements for the release of hazardous substances into the environment, including land, air, and water when release occurs in amounts equal to or greater than the reportable quantity. A hazardous substance as defined by CERCLA includes any substance designated or listed in: FWPCA, Section 307 and 311; RCRA, Section 3001; CAA, Section 12; and TSCA, Section 7. The "reportable quantity" for any hazardous substance is 1 pound, unless otherwise specified in Section 311 of the FWPCA. The reportable quantity under CERCLA for zinc chloride is therefore 5000 (2270 kg) lb or more per 24-hour period.

F. Regulations for the Transportation of Hazardous Materials.

1. Department of Transportation Regulations.

The Department of Transportation (DOT) is required by federal law to formulate regulations for safe transportation of hazardous material, poisonous substances, explosives, and other dangerous articles (Title CFR 49, parts 171-177). These regulations bind all carriers engaged in the transport of the above-mentioned hazardous material and are in accordance with the best known practices for assuring safety in transit. Of particular importance is part 172 of these regulations, which lists hundreds of materials by hazard class with guidelines for safe packaging and shipping.

Colored smoke munitions and bulk quantities are classified as a Class C explosives. Table 9 lists the hazard class and labels for these.

2. Military Regulations.

Explosives and other dangerous particles shipped or transported by the military services are subject to the applicable regulations of the military service involved. Modes of transportation covered by the regulations are:

(a) Surface Carriers.

AR 55-355 regulates the movement of military cargo within the United States by commerical vehicle.

(b) Air Shipments.

Air shipments are regulated by the TM 38-250 for safe transport of hazardous articles.

(c) Water Shipments.

AR 55-228 regulates shipment and transport of dangerous and hazardous articles by water in conjunction with US Coast Guard regulations.

Table 9. DOT Hazardous Materials (9 CFR 49, 172.101)
New "Product Improvement Program" Colored Smokes

Name	DOT Class	DoD Class	Ident No.	Labels required	Packing section of CFR 49	Maximum net quantity
Yellow, and green smoke mixes (bulk mixtures)[a]	C	1.3 G	None	Explosive C	173.108	50 lb passenger aircraft 200 lb cargo aircraft
Yellow, and green smoke munitions (grenades/cannisters)[a]	C	1.4 G	None	Explosive C	173.108	50 lb passenger aircraft 150 lb cargo aircraft
Red and violet smoke mixes (bulk mix)					These mixtures and end items need yet to be hazard tested and classifed.	
Red and violet smoke munitions (grenades/cannisters)						

[a] Classification of the bulk yellow and green pyrotechnic smoke mixtures and the end item improved grenades was accomplished by evaluation of test data obtained in accordance with chapter 5 of DOD Explosives Classification Procedures (draft) dated March 1979. Bulk mixtures were subjected to card gap, detonation, ignition and unconfined burning, impact, and thermal stability tests. Packaged end-item grenade tests included single package, stack, and external fire stack. This testing was performed at the National Aeronautics and Space Administration National Space Technology Laboratories, NSTL Station, Mississippi. The conclusions, which are published in a contractor report,[b] state that both bulk mixtures could be assigned a probable DOT Class C (DOD Class 1.3) and that both grenades could be assigned a probable DOT Class C (DOD Class 1.4). These classification assignments are the same as those for the standard yellow and green bulk mixes and end item munitions. The result of the tests were transmitted through the CRDC Safety Office to the Field Safety Activity, Charlestown, Indiana.

[b] McIntyre, F.L., Hazards Classification Testing for Bulk Pyrotechnic Mixtures and End Items. Unpublished. ARRADCOM Contractor Report (NASA). February 1981.

3. Other Regulations.

(a) In addition to the federal laws governing the transportation of flammables and hazardous materials, each state and nearly all municipalitites have laws or ordinances regulating the transportation of hazardous articles within their jurisdiction.

(b) Policies and procedures for environmental protection on military installations are provided in AR 200-1, "Environmental Protection and Enhancement" and respective supplements.

G. Regulations for the Storage of Hazardous Materials.

1. For ease of storing and handling, smokes are divided into chemical groups. Classification is based on the action of the item, and the degree and type of protection required. In accordance with DARCOM-R 385-100, munitions are assigned Chemical Group D and storage compatability Group G. Reference Table 10 for clarification and details.

H. Other Considerations.

1. Regulations on endangered species or historic preservation are primarily site specific. The environmental quality coordinators of the installation should be contacted to determine if these regulations are applicable.

2. The Department of the Army (DA), DARCOM, and Army Training Doctrine Command (TRADOC) prohibit open burning of colored smoke filled munitions. DARCOM policy as outlined in DARCOM Supplement 1 to AR 200-1, Chapter 4, para 4-4f states that the open burning of hexachloroethane (HC), white phosphorus (WP), and colored smokes is prohibited. Requests for exception to this policy should be forwarded to Commander, DARCOM, ATTN: DRCSG, with appropriate justification.

IV. TOXICITY AND HEALTH EFFECTS

A. Introduction.

In discussing the toxicity of colored smokes, each standard dye and all the proposed dyes will be addressed with the exception of benzathrone and Vat Yellow 4. These latter dyes are being phased out and their health effects have already been briefly addressed in Section I of this report. A review of the toxicology of colored smokes and colored dyes is contained in a report by Owens and Ward.[6] Data gaps exist on aquatic toxicity and the environmental impacts on flora and wildlife.

Toxicological testing. The candidate replacement, that was proven technically acceptable, Solvent Yellow 33 dye, must also be shown to be nononcogenic and of minimal toxicity. A medical evaluation program (MEP) has been planned to provide a toxicology data base to answer these questions. The MEP focuses on industrial site exposure of the worker and the environmental consequences of industrial waste and fallout during training.[7] The US Army Medical Research and Development Command (USAMRDC) through the USAMBRDL, Fort Detrick, Maryland, will provide the toxicological data base for the health hazard assessment required for the replacement smoke formulations. Some preliminary toxicological investigations have been completed or are in progress. A literature review[8] of the toxicity of D&C Yellow 11 (Solvent

Table 10. Storage Information and Shipping Classification[a]

Common name	Action of agent	Quantity distance	DOT chemical group agent[b]	Storage compatibility group[c]	Hazard class division	Color coding identification
Colored smoke dyes/ mixes and/or munitions (grenades or markers)	Signaling smoke	Table 17-13[a] Table 17-14[a]	Group D	Group G solid	1.3[d] mix/dye 1.4 munition	14

NOTE: The chemical and storage compatibility groups of the munition item shall be the same as that of the chemical material contained in the item.

[a] DARCOM-R 385-100 (17 August 1981)

[b] Group D = This group consists of signaling smokes and incendiary material for which conventional fire-fighting methods, except use of water, may be used. Protection from inhalation of smoke from burning incendiary mixtures is required.

[c] Group G = Fire works and illuminating, incendiary, smoke, or tear-producing ammunition other than ammunition that is activated by exposure to water or the atmosphere

[d] 1.3 = massive fire
1.4 = moderate fire, no blast

Yellow 33) was accomplished by Stanford Research Institute (SRI), International. Their report was primarily a review of data submitted to the Pharmaceutical Manufacturing Association by Hazelton Laboratories, Inc. The SRI report concluded that the available data indicated the D&C Yellow 11 is of very low toxicity. Research Division, Toxicology Branch, CSL, has tested both Solvent Yellow 33 and Solvent Green 3. Results to date indicate the dyes are of low toxicity. Studies of the combustion smoke aerosols have commenced also. Additionally, mutagenicity testing was recently begun by Oak Ridge Laboratory, Tennessee, under contract to USAMBRDL.

B. Disperse Red 9.

1. Mammalian Toxicity.[9,10,11,12]

Disperse Red 9 or 1-methylaminoanthraquinone (MAA) has been reported as a skin irritant and sensitizer when handled by loaders.

Female rats were dosed through a gastric tube with 500 mg/rat/dose every 3 days for 30 days.[6] The total dose was 5000 mg/rat. The rats were then observed for 9 months. The results are presented in Table 11. Cystic changes were noted in the kidneys of 14 rats. One rat developed tubular adenocarcinoma. However, carcinoma of the kidney was also observed in the controls. From this data, the authors concluded that the dye was noncarcinogenic to rats.[6]

The combustion products of MAA when it is combusted in a grenade and the by-products of MAA during manufacturing should be addressed. A draft report by Rubin <u>et al.</u>* characterized the combustion products of used smoke containing MAA. They found that the initial dye component was made up of 98% MAA, 0.6% 1-amino anthraquinone (AA), and 1.4% other fractions. When the used dye is combusted, the recovered material is 89% MAA, 6% AA, and 5% other fractions.

Further work at Oak Ridge National Laboratory (ORNL) on combustion products of Red Smoke Mix (RSM) indicates that 1-aminoanthraquinone makes up about 7 percent of the recovered particulate and 2-AA about 4 percent. The latter compound was not found in the uncombusted RSM. The 2-AA has been found to be a mammalian carcinogen in an NCI bioassay.[12]

2. Aquatic Toxicity.

No aquatic toxicity information was available on MAA. However, a similar compound, disperse blue 3, had a 96-hr LC50 in the fathead minnow of 1 mg/l at 15°C.[8]

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*Rubin, I. B., Buchanan, M. V., and Moneyhun, J. H. Chemical Characterization of Combusted Inventory Red and Violet Smoke Mixes. Oak Ridge National Laboratory, USAMBRDL. Unpublished data. October 1982.

Table 11. Evaluation of Carcinogenicity in Female Rat Mammary Glands After Doses of 1-Methylaminoanthraquinone and DMBA (Positive Control)[6]

Compound	Total dose	No. of rats remaining			No. autopsied	No. of rats with mammary lesions	Type and no. of mammary lesions	Other lesions
		0 days	45 days	9 mos				
	mg/rat							
1-Methylaminoanthraquinone	5000	19	18	14	18	1	Hyperplasia, 1	Tubular adenocarcinoma of kidney, 1
DMBA (positive control) 9,10-dimethyl-1, 2-benzanthracene	18	40	35	19	29	29	Carcinoma, 75; fibroadenoma, 10; hyperplasia, 47	Hyperplasia of lymph nodes, 2; carcinoma of pancreas, 1; lymphocytic infiltration of liver and lymph node, 2; abdominal reticulum cell granuloma, 1
Sesame oil		140	134	127	132	5	Carcinoma, 3; fibroadenoma, 1; hyperplasia, 5	

C. Sudan R.

1. Mammalian Toxicity.

A literature search was conducted under contract to CRDC on the mammalian toxicology of Sudan R. A report by Druckrey and Schmahl cited unpublished data on a carcinogenicity test of Sudan R in rats. The report stated that no tumors were found in 147 rats given 0.5-6.0 gm of Sudan R over a 60- to 300-day period.

This same literature search indicated more reliable toxicity data on two dyes which have a similar structure to Sudan R. Citrus Red No. 2 (2.5 - Dimethoxyphenylazo-B-naphthol) caused fatty degeneration of the liver in female mice which received 120 mg/kg/day in the diet for 80 weeks. A no effect levels was observed at 36 mg/kg/day.

Sudan I (phenylazo-B-naphthol) was found to reduce the life span of mice receiving 114-160 mg/kg/day in the diet for 12 months. From this data, it was estimated that Sudan R would have a low toxicity to mammals. However, information is required in the following areas:

a. more detailed toxicological studies;

b. identification of by-products in Sudan R;

c. identification of combustion products.

2. Aquatic Toxicology of Sudan R.

No information was found on the aquatic toxicity of Sudan R. This compound is reported as insoluble in water.

The following information is needed on:

a. chemical parameters, i.e., water solubility, vapor pressure, and chemical characterization of dye after use;

b. acute and chronic aquatic toxicity data for dyes and products after use;

c. bioaccumulation potential.

D. Violet Mix.

1. Mammalian Toxicity.[9,10,11]

Mammalian toxicity data could not be found on 1,4-diamino-2,3-dihydroanthraquinone (DDA). However, a mutagenicity study with five *Salmonella typhimurium* tester strains revealed that DDA was weakly mutagenic in strain TA 1537 and nonmutagenic in the other strains.

Unpublished ORNL data* stated that uncombusted violet smoke contained 80 percent DDA and 20 percent MAA. Upon combustion the DDA was quantitatively converted to 1,4 diaminoanthraquinone (DAA). The MAA was partially converted to AA.

In a Chemical Information System search in 1982, two toxicity studies on DAA were found. They reported the following toxic effects.

Animal	Administration	Dose (mg/kg)	Effect
rat	oral	4920	LDLO
rat	intraperitoneal	1300	LD50

In addition, DAA was lethal to earthworms in 20 hours at a concentration of 50 mg/l.

DAA was also estimated to be 10% degraded after 15 hours.

2. Aquatic Toxicity.

No information was found on the aquatic toxicity of this violet dye mix.

The following information is needed:

a. chemical parameters, i.e., water solubility, vapor pressure, and chemical characterization of dye after use;

b. acute and chronic aquatic toxicity data for dye and its reaction products after use;

c. bioaccumulation potential;

d. environmental fate (biodegradation, hydrolysis, vaporization, etc.).

E. Solvent Green 3.

1. Mammalian Toxicity.

Toxicity data for acute oral exposure to Solvent Green 3 (1,4-di-p-toluidinoanthraquinone) is presented in Table 12. The dye has a low acute oral toxicity in mammals.

The results from several toxicity tests conducted at Hazelton Laboratories in 1981 are summarized in Table 13. Two-year feeding studies were conducted with rats and dogs. No effects were observed with 3% of the dye in the diet.

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*Rubin, I. B., Buchanan, M. V., and Moneyhun, J. H. Chemical Characterization of Combusted Inventory Red and Violet Smoke Mixes. Oak Ridge National Laboratory, USAMBRDL. Unpublished data. October 1982.

Table 12. Acute Oral Toxicity of Solvent Green-3[8]

Animal	Dose gm/kg	Effect
rat	3.06	LD50
rat	10	LD50
rat	15	LD50
rabbit	10	LD50
rabbit	6	Minimum lethal dose

Table 13. Long-Term Studies of Green Dyes*
(Conducted at Hazelton Laboratories)

Dye	Species	Feeding - 2-year (Percent of dye in diet)	Repeated dermal (Percent of dye in solution)
Solvent Green DC Green 6	rats	0.25, 1.0, 3.0% - no microscopic alterations	rabbits - negative
CI61565 (Chemical Abstracts number)	dogs	same 3.0% - no effect level	mice - negative, 1%, 95 weeks
	rats	teratology - rats - negative 150, 450, 1500 mg/kg/day-gavage	
	rats	multigeneration - 10, 100, 300, 1000 mg/kg/day diet-negative	

*Weimer J. T. Status Report on CSL Toxicity Studies With Three Dyes. 16 July 1981. Unpublished data.

Teratogenicity tests with rats were negative at 1500 mg/kg/day. When dermal toxicity tests were conducted, Solvent Green 3 did not produce any toxicity. Tests of skin irritation in rabbits were also negative.

Mutagenicity tests (micronucleus tests) were conducted with Solvent Green 3. Mice were injected intraperitoneally with up to 100 mg/kg of the dye and micronuclei were examined for chromosome breakage. None was observed after Solvent Green 3. The available data indicate that this dye has a relatively low toxicity. Additional information is needed:

a. more detailed toxicological studies,

b. identification of by-products,

c. identification of combustion products.

2. Aquatic Toxicity.

No data are available; see C2 for a description of what data are needed.

F. Solvent Yellow 33/D&C Yellow 11.

1. Mammalian Toxicity.[13]

A literature review was conducted in 1980 on the mammalian toxicity of D&C Yellow 11 (2-(2-quinolyl)-1, 3-indandione).[13] The toxic oral dose of D&C Yellow 11 was reported to be greater than 10 gm/kg.

The results of chronic feeding studies and dermal application of D&C Yellow 11 are presented in Table 14. Morphologic changes in rats were noted at 1% levels of the dye in the diet.

Preliminary toxicity tests were conducted and no toxic effects were observed in rats receiving oral doses of 5 gm/kg of D&C yellow 11.*

D&C yellow 11 was also tested for dermal toxicity and skin irritation in rabbits.[15] In the dermal toxicity test, the rabbits were exposed to 2 gm/kg of dye paste. No toxic signs were observed. In the skin irritation test, the intact and abraded skin of rabbits was exposed to 500 mg of dye in 2.0 ml of H_2O for 24 hours. No effects were observed.

From the information available, D&C Yellow 11 (Solvent Yellow 33) has a low toxicity in mammals; however, further toxicity tests have been recommended. Also by-products and combustion products should be identified.

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*Weimer, J. T. Status Reports on CSL Toxicity Studies With Three Dyes. 16 July 1981. Unpublished data.

Table 14. Long-Term Studies of Yellow Dyes*
(Conducted at Hazelton Laboratories)

Dye	Species	Feeding (Percent of dye in diet)	Repeated dermal (Percent of dye in solution)
Solvent Yellow 33 Chinoline Yellow DC Yellow 11 CI 47000	rats	0.03, 0.1, 0.3, and 1.0% for 1 yr. Some pigment in kidney and liver of all animals. Morphologic alterations at 1% only.	<u>Rabbit</u> - 0.1 & 1.0% 15 of 64 applications. Negative. Microscopic indication of irritation but not carcinogenesis. <u>Mice</u> - 1%, 95 weeks. No effect on growth, survival less than controls. Enlargement in some organs.

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*Weimer J. T. Stauts Report on CSL Toxicity Studies With Three Dyes. 16 July 1981. Unpublished data.

2. Aquatic Toxicity.

No data are available; see C2 for description of what data are needed.

V. ENVIRONMENTAL IMPACTS - LIFE CYCLE

A. Research and Development.

1. Alternatives Considered.

Because of the health concerns already addressed, all standard dyes are being researched and tested for replacement except Solvent Green 3. This dye so far has proved to be satisfactory for use and is of low toxicity. Alternative action(s) which should be considered for implementation in addition to, or in lieu of, actions presently enforced include:

(a) No Action. Continue to use the standard dyes.

(b) Continue PIP efforts. To replace the standard dyes that are health hazards.

(c) Discontinue use of colored smoke. Delete all dyes from US inventories.

(d) Chamber Testing. Perform all R&D testing in an approved chamber.

2. Environmental Impacts.

(a) No Action.

Continue to use the standard dyes. The materials used in the standard munitions present toxic and carcinogenic hazards to R&D personnel exposed to the smoke. The standard yellow, green, and red dye mix formulations for the smoke cartridges are known health hazards. Elimination of these standard dyes further reduces hazardous waste water emissions and toxic gaseous waste streams resulting from manufacturing processes of the munition, consequently eliminating human health and environmental hazards from these sources. The identification and evaluation of combustion by-products from the standard colored smokes are data gaps. Some testing and evaluation of red and violet smokes have recently been conducted by the Oak Ridge National Laboratory in Tennessee, but nothing on the other colors. The results of red and violet tests are as follows:

The impact of the detonation on the red smoke mix was slight. The single dye component, 1-methylaminoanthraquinone, was reduced from 98 percent of the chloroform soluble portion of the original mix to 89 percent in the combusted mix, with apparent conversion to 1-aminoanthraquinone being the major factor in this change (6 percent, which is a tenfold increase from the original mix). The residue portion of the combusted red smoke mix contained sodium and potassium chlorides, elemental sulfur and undifferentiated carbonaceous matter in contrast to only the carbonaceous matter and some dye in the residue of the original mix.

The constituents of the vapor phase of the combusted red smoke mix included primarily toluene, styrene, and chloromethylbenzene and smaller amounts of aliphatic and aromatic hydrocarbons, substituted benzenes, and benzothiophene.

The violet smoke mix underwent a drastic change during combustion, with the 1,4-diamino-2,3-dihydroanthraquinone, which was the major constituent of the original smoke mix, being quantitatively converted to 1,4-diaminoanthraquinone. Highly volatile constituents trapped during the combustion of the violet smoke mix included carbon disulfide, alkyl benzenes, alkanes, thiophenes, acetophenone, and phenylacetaldehyde. Only a small proportion, about 4 percent, of the particulates of both mixes were water soluble. Data sheets on the residue and vapor products are contained in Appendix A.

(b) Continue Product Improvement Program Efforts to Replace the Standard Dyes.

This option is consistent with the directed actions of the Program Manager's Office for Smokes and Obscurants that attempt to circumvent the toxicological problems encountered with standard smokes. The Chemical Research and Development Center (CRDC) is conducting the PIP actions utilizing the latest technology in engineering and chemistry. Combustion studies and an assessment of toxicological risk should be performed to further justify their safe use.

(c) Discontinue Use of Colored Smoke.

This alternative would reduce the Army's communications capability on the battle field and jeopardize its defense posture. This option is not necessary since nontoxic, nonhazardous dyes can be substituted.

(d) Chamber Testing.

Perform all R&D testing in an approved chamber. Since signaling smoke testing requires only small amounts of (point source) smoke, this is a feasible alternative but maybe not the most desirable, completely viable alternative in this phase. Certainly there would be no adverse impacts, but meteorological effects would have to be considered.

3. Recommended Mitigation.

Mitigation is not required.

B. Manufacturing and Production.

1. Alternatives Considered.

Alternative action(s) which should be evaluated for implementation in addition to, or in lieu of, actions presently enforced include:

(a) No Action. Continue to manufacture and load standard smoke mixes.

(b) Continue PIP Action. To replace standard toxic smoke mixes.

(c) Discontinue colored smoke production. Delete all dyes from US inventories.

(d) Chamber Testing. Perform all training/testing in an approved chamber or controlled inclosure.

2. Environmental Impacts.

All colored smoke constituents are shipped from US locations to Pine Bluff Arsenal (PBA), Pine Bluff, Arkansas. The mission of PBA includes the formulation of mixes and the loading of all colored mixes in designed munitions. PBA has approved facilties for demilitarization and decontamination.

(a) No Action. Continue to manufacture and load standard smoke mixes. If this alternative is included, unneeded risks to manufacturing personnel will continue, although great strides have been made to vacuum clean the operations and contain manufacturing/formulation materials with closed system techniques.

(b) Continue Product Improvement Program Action to Replace Standard Toxic Smoke Mixes. This option is consistent with the directed actions from the Program Manager's Office for Smokes and Obscurants that attempt to circumvent the standard toxicological problems encountered with standard smokes.

(c) Discontinue Colored Smoke Production. Delete all dyes from US inventories. This option is inconsistent with the US defense efforts. This option is also not necessary since nontoxic, nonhazardous dyes can be substituted.

(d) Chamber Testing. Perform all testing in an approved chamber. This option is feasible and possibly desirable if testing during this life cycle phase is performed other then at PBA. PBA SOP's already require only chamber testing.

3. Recommend Mitigation.

For the recommended options mitigation is not applicable (options (b) and (d)).

C. Training and Testing Deployment.

1. Overview.

The Army has recently experienced a substantial revival of interest in using smoke for communications on the battlefield. The USA Chemical School located at Fort McClellan, Alabama, resumed training of personnel to support this program in 1980. This training provides experience in theory, generator operations, and practical application under field conditions.

Since training and testing occur in much the same type of environment and, in many cases, ranges serve both purposes, the impacts addressed below will be considered applicable to both situations, except as noted.

Training areas may be located adjacent to fishing ponds, hunting areas, areas leased for grazing beef and milk cattle, or off-post housing and cantonment areas. Although the toxicity of specific dyes is known or is being investigated, little is known about toxic substances which might be present in small but variable amounts in a chemical dye. Some studies to fill these data gaps are being conducted by USAMBRDL and will be addressed as results become known.

It is assumed that no future buys are scheduled or anticipated for the M48 colored-smoke training grenade. Therefore, the concern that this item could be a health threat, because it is intended as a riot control training round and not just a signaling point source smoke, is unwarranted at this time. Commanders in charge of training scenarios should be aware of this concern.

2. Alternatives Considered.

Alternative action(s) which should be evaluated for implementation in addition to, or in lieu of, actions presently enforced include:

(a) No Action. Continue to deploy standard, colored, signaling smoke.

(b) Cease Signaling Smoke Deployment. Either stop all signaling (communication) smoke, or use other means of communication.

(c) Chamber Testing. Conduct all training/testing in an approved chamber (or controlled area).

(d) Utilize PIP Actions. Use the improved dyes depending on resultant MED effect to deploy new dyes in open exercises or controlled chamber conditions.

3. Environmental Impacts.

(a) No Action. Continue to deploy standard colored, signaling smoke. This option would provide an unnecessary continuing health (carcinogenic) risk to test and training personnel. In addition, red dye smoke mix is known to be deleterious to health and has resulted in injuries such as dermatitis, temporary breathing impairment, and liver damage. There is no threat to troop personnel because it is not deployed over and near troop areas in large amounts as a screening smoke.

Tests are normally conducted in areas dedicated to testing military items to avert any public health hazard. As with any smoke munition, impact zones do not exceed 10 to 15 km downwind from the field test site, making the impacts local in nature.

(b) Cease Signaling Smoke Deployment. Either stop all signaling (communication) smoke, or use other means of communication. To discontinue the use of smoke on the battlefield would seriously reduce the US combat capability. Past deployment efforts have shown the value of smoke communications over more conventional types such as radio. There are times and occasions when the conventional method of communications have proven to be impossible, unavailable, and/or undesirable.

(c) Chamber Testing. Conduct all training/testing in an approved chamber (or controlled area). This is a feasible option if the expense of constructing and maintaining a chamber could be justified compared to the usage it would receive. Air to ground training/observations would not be feasible in a chamber.

(d) Utilize PIP Actions. Continue the product improvement studies and medical evaluation program to fully assess the substitution of safe dyes. This alternative is consistent with directives of the US Army and the Office of the Project Manager for Smoke and Obscurants to replace the problem dyes. Additional combustion studies will also have to be conducted to further justify their safe use.

Green and yellow smoke formulations have been tested in munitions and shown to be safe and effective and to meet performance specifications. The limited toxicity data collected to date shows all of the proposed dyes to be of low toxicity.

(e) Environmental Effects.

The following environmental impacts are general and applicable to all of the life cycle phases of R&D, manufacturing/production, and training.

(1) Effects on Plants.

Information could not be found in this area but is needed.

(2) Effects on Aquatic Organisms.

Combustion products (residue) can enter waters directly as fallout from colored smoke deployment, leaching from soils, or runoff. Additional aquatic data is not available for most of the dyes (see toxicity section), but is likewise needed.

(3) Effects on Domestic Animals and Wildlife.

Combustion products can become available to domestic animals and wildlife through fallout on water and grazing areas. More information is needed on these products and the amounts of fallout.

(4) Effects on Natural Populations.

Risks, while largely unavoidable for wildlife, may be mitigated by the observation that wildlife tend to leave during field testing. By timely posting and notification and area monitoring, persons and domestic animals can be cleared out of scheduled testing and training areas. In most cases testing and training ranges will not be populated and are off limits to unauthorized persons.

(5) Effects from Noise

Noise is not a problem with colored smoke munitions, i.e., point source grenades, cannisters, or grenade launchers.

(6) Effects from Wastes and/or Spills.

Wastes generated will consist mostly of test or training debris, i.e., expanded rounds and/or packaging materials or munition duds. SOP's and test plans which are required for each action shall ensure that all debris is collected and, in the case of duds, personnel of the Technical Escort Detachment shall direct the disposition. Installation Spill Contingency plans shall address the containment and cleanup of spills.

(7) Effects on Air Quality.

The generation of smokes/obscurants impacts directly on local air quality. The quality of this air is protected by federal, state, and local air pollution control regulations as discussed earlier. The primary pollutants discharged by the generation of these smokes are particulates and hydrocarbons. Because the deliberate generation of smokes/obscurants is directly counterproductive to the air pollution abatement and control efforts of the environmental regulatory agencies, operational scenarios should be coordinated with the appropriate agencies prior to smoke generation tests/training. In addition, sites for smoke-generation trials should be chosen so that they are far removed from populated and ecologically sensitive areas as well as installation boundaries.

Urban air may contain from 50-200 different hydrocarbons. Many hydrocarbons are harmful only in high concentration. Probably the most significant problem is the role of hydrocarbons in the formation of photochemical smog.

The effects of particulates are not as harmful as those from other pollutants, but particulate pollution is the one which most concerns the public because it is visible. People generally get concerned when they see giant clouds of black smoke billowing from a smokestack, but such emissions are generally not as harmful as invisible forms of pollution.

4. Recommended Mitigation.

(a) Appropriate weather conditions shall be selected which will assure that the smoke cloud will be confined to the military reservation/manuever area, while paying special attention to assure that it does not obscure vision on highly traveled roadways or cause damage to private property within the maneuver area. To avoid any undesirable downwind travel of colored smoke, weather conditions must be monitored before and during the exercise, and the exercise should be halted or not initiated should weather conditions dictate.

(b) The Post Chemical Officer, or a designated person in Range Control, should receive notification of smoke use in order to assure dispersion over time and space. When a pattern of excessive usage appears, coordination with the unit commander should be sufficient to resolve it. Areas and conditions for potential use should be precisely stated in range regulations, and the areas should be as large as possible to reduce concentrations. Areas of heavy use or repeated use should be monitored periodically for vegetation or other environmental change. This implies that there be some precise description of such areas before smoke use for a baseline comparison. Regulations and training scenarios should address proper maintenance of deployment equipment to prevent contamination from improper usage and fire damage from burning munitions.

(c) Before deployment of colored smokes, Range Control will coordinate with or notify the appropriate Air Pollution Control Authority, Post Fire Department, Post Forester airfield control tower, and other appropriate specified agencies. Road guards should be provided as necessary during unit training to provide warning of cloud limits along military-use roads. Some ground or air monitoring with positive communication between headquarters and the operators of the smoke equipment should be in effect to physically track the downwind edge of the cloud and to observe if it is drifting near the reservation boundary or a commercial highway.

(d) Individuals with respiratory conditions, including asthma, cardiac conditions, severe facial acne, or any active dermatitis should be evaluated by a medical officer before being allowed to participate in smoke field training. Commanders must ensure that in testing and training, exposures to smoke should be controlled in accordance with the occupational and environmental exposure guidance established by The Surgeon General as command policy.[*,**] "There are no specific known cases of physical impairment associated with smoke training. There is, however, similarity between the potential effects of current smoke agents and other known causes of physical disability associated with exposure aerosols. It is, therefore, prudent to take reasonable precautions in exposing personnel to field concentrations of smoke and to insure that respiratory protection (protective mask) is readily available." These guidelines as they may pertain to colored smokes are summarized as follows:

(1) Personnel will carry the protective mask when participating in exercises which include the use of smoke.[*,**]

(2) Personnel will mask when passing through or operating in dense smoke such as smoke blankets and smoke curtains, or when operating in or passing through a smoke haze in which the duration of exposure will exceed 5 minutes, or anytime exposure to smoke produces breathing difficulty or discomfort. Such effects in one individual will serve as a signal for all similarily exposed personnel to mask.[*,**]

(3) Bathing and laundering of clothing following exercises will eliminate the risk of skin irritations after exposure to smoke.

(4) Further buys and use of the M48 grenade for riot control training is not anticipated or recommended. However, should this decision be rescinded for any reason, then control over the distribution and use of the M48 grenade must be exercised by commanders to preclude undesired hazardous impacts to troops and others from training scenarios other than spotting or signaling.

(5) Special care must be taken when using smoke to ensure that appropriate protection is provided to all personnel who are likely to be exposed. When planning the use of smoke in training, specific consideration must be given to weather conditions and the potential downwind effects of the smoke. Positive controls (observation, control points, communications) must be established to prevent exposure of unprotected personnel.

(6) Publications should be reviewed to ensure that appropriate safety precautions for smoke are included in training and employment guidance.

(7) Females may particepate in training exercises involving colored smoke subject to all of the above guidelines and masking provisions.[*,**]

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[*] Letter, DRSTE-ST, TECOM, 25 March 1981, subject: "Health Hazards-Chemical Smoke Munitions Usage and Demilitarization."

[**] Messages, DAMO-SSC, subject: Smoke Safety, dated 281255Z Jul 78; DAMO-SCC, subject: Smoke Safety, dated 052005Z Sep 78, and DAMO-NNC, subject: Safety Considerations for Use of HC Smoke During Training, dated 211549Z Feb 80.

e. Smoke training/testing areas will be located so as to avoid the nesting areas of endangered wildlife.

f. Smoke and noise from these operations may disturb wildlife; however, no significant reduction in wildlife population would be likely.

g. When preparing deployment scenarios, test/training coordinators should evaluate the following measures as a checklist against downwind hazards.

(1) The proposed action should not extend beyond installation boundaries or exceed prescribed regulations.

(2) The substances necessary to produce the "no effects" concentrations and to predict associated downwind hazard distances should be calculated.

(3) The downwind hazard zone should not include any installation area containing personnel that are not test or training participants.

(4) Domestic animals should be absent from the downwind hazard zone.

D. Transportation and Storage.

Colored smoke dyes are shipped from various sections of the United States to PBA where the dyes are formulated into mixes and loaded into grenades and markers.

1. Transportation.

The tranportation and storage classifications and regulations are as indicated in Section III, paragraph F of this document.

a. Impacts of Activities.

The major impacts from transportation, whether it be the colored mix constituents or filled munitions, are leakage and fire, either of which could present a hazardous situation to workers and/or innocent bystanders. For either emergency, first aid procedures should be instituted and medical help sent for.

b. Recommended Mitigation.

(1) Signaling smokes are classified as Chemical Group D agents in accordance with DARCOM-R 385-100 paragraph 11-30. By definition these colored smoke mixtures contain a dye for the color of smoke desired and certain types of fuels.

(2) Persons not wearing suggested protective clothing and equipment should be restricted from areas of leakage. The area of leakage should be ventilated, especially in confined places. The installation leakage plan should be consulted for cleanup and disposal instructions.

(3) Special Protective Equipment for Chemical Group D Munitions.

Boxed and unboxed nonleaking munitions containing Chemical Group D agents may be handled without special protective equipment, but it is advisable to have respiratory protection available where incendiary materials or munitions items are involved. Protective masks will be worn when exposed to burning munitions or bulk chemicals.

(4) First Aid for Chemical Group D Munitions.

No unusual first aid treatment is required for personal injuries acquired in handling Chemical Group D munitions. Burns should be treated in the same manner as those caused by flame. Persons severely affected from high concentrations of smoke should be hospitalized.

(5) Leaking Chemical Group D Munitions.

Leaking Chemical Group D Munitions must be disposed of in accordance with approved procedures. These procedures may be obtained from Commander, ARRCOM, ATTN: DRSAR-DSM. Under emergency situations, such as a leaking smoke munition, general handling procedures should include wearing thick working gloves, safety goggles, and/or the universal gas mask. Appropriate clothing and equipment should be worn/used to prevent prolonged or repeated skin contact. The skin should be washed promptly with soap and water when it becomes contaminated.

(6) Fire in Magazines of Chemical Group D Munitions.

The primary efforts of fire fighters should be confined to preventing the spread of the fire in magazines containing Chemical Group D munitions (fire in igloo-type or Corbetta-type magazines will not be fought). Fires may be smothered by spraying with dry chemical from portable fire extinguishers or covering with sand. Fire in a magazine containing Chemical Group D munitions will not be fought with water except where large quantities of water are used in proportion to relatively small quantities of these type munitions.

2. Storage.

For the purpose of storing and handling bulk materials and chemical-filled munitions, they are divided into chemical groups. Classification is based on the action of the agent and the degree and the type of protection required. In accordance with DARCOM-R 385-100, colored signaling smoke mixes and associated munitions are assigned Chemical Group D and Storage Compatibility Group G. A more detailed breakdown of storage classification and requirements are included in Section III, paragraph G.

a. Impacts of Activities.

Hazards and/or area contamination from leakage or fire in storage will produce the same type of impacts indicated for transportation.

b. Recommended Mitigation.

Procedures in the "Spill (Leakage) Prevention Control and Countermeasure Plan" or guideline procedures noted under transportation in paragraph D.1.b. above should be followed.

E. Demilitarization/Disposal.

The technical manual[14] entitled, "General Instructions for Demilitarization/Disposal of Conventional Munitions" provides ready references to sources of information, regulations, and technical expertise for the purpose of insuring that demilitarization/disposal activities include the latest guidance and technical knowledge.

As a result of a serious incident whereby a cloud drifted off-post during demilitarization of smoke pots at Lexington-Blue Grass Depot, the following interim occupational and environmental exposure guidance was established and distributed from The Surgeon General for colored smoke. In disposal of colored smokes no open burning should be allowed. If other disposal options are undertaken, exposures of involved personnel to the dye components should be maintained below an 8-hour TWA of 0.2 mg/m^3. Exposures to by-products of the disposal process or the other components of these smokes should be maintained below permissible exposure limits established in 29 CFR 1910.1000.

Hazardous Waste Considerations.

The colored smokes, being pyrotechnics, upon disposal display the characteristic of reactivity (as defined by RCRA). This classification and guidance is contained in CFR 261.23 (a) (8) and 265.382. The Installation Environmental Quality Control Coordinator (IEQCC) should be consulted for proper disposal procedures.

1. Alternatives Considered.

Demilitarization/disposal procedures considered as approved alternatives for implementation during the various life cycle phases of smoke mix and/or munitions include (a) open burning, (b) Explosive Ordnance Demolitions (EOD) disposal, (c) incineration, and (d) Defense Property Disposal Office (DPDO) storage.

When demilitarization prior to disposal is a requirement for colored smoke munitions, it shall be conducted in accordance with the provisions of the Defense Demilitarization Manual, DOD 4160. 21-M-1, July 1979.

(a) Open Burning.

DARCOM Supplement 1 to AR 200-1, Chapter 4, para 4-4f, states that the open-burning demilitarization of hexachloroethane (HC), white phosphorus (WP), and colored smoke is prohibited. Requests for exception to this policy should be forwarded to Commander, DARCOM, ATTN: DRCSG, with appropriate justification. The moratorium on open burning was established by letter, DRSAR-MAD, 051400Z, subject Open Air Demilitarization of WP, HC, CS, and Colored Smoke-Filled Munitions.

(b) EOD Disposal.

Munitions containing colored smoke mixes that have malfunctioned/been damaged/declared excess and loose mix, which can be collected, will be demilitarized by EOD personnel for disposal. This procedure is especially applicable to test sites.

If a safety (handling) hazard exists with colored smoke munitions and for excess mix, the material may be demilitarized in place according to approved EOD procedures. Once demilitarized, disposal operations should be conducted only at permitted hazardous waste facilities unless the disposing activity qualifies as a small quantity generator under 40 CFR 261.5. In this case, the waste may be disposed of in the permitted sanitary landfill under the small generator exception. EOD will provide an after action report to the Environmental Quality Coordinator.

(c) Incineration.

Disposal by incineration is encouraged where approved incinerators exist and emission limits are monitored for compliance with state and federal requirements. Such incinerators exist where the smoke is collected and washed in scrubbing towers; the scrubbing water is then treated to conform to local requirements and NPDES permits. See TM 9-1300-277 which provides a listing of incineration facilities.

(d) DPDO Storage.

Storage of pyrotechnic/colored smoke waste at an installation must comply with DOD 4160.21-M-1 and AR 200-1 procedures while awaiting final demilitarization/disposition actions.

2. Environmental Impacts.

The impacts and risks associated with the alternatives depicted above should be nonexistent as their procedures and controls are well documented. These controls include the following, in addition to SOP's. Any emissions and effluents that may result from demilitarization/disposal, including incineration must be maintained within the limits set forth by EPA, local, and state air quality standards. Controls are enforced through Air Quality Standards, NPDES and RCRA requirements. All waste remaining after demilitarization must be disposed of at controlled facilities.

3. Recommended Mitigation of Activities.

Mitigation is contained in the above listed controls.

VI. AGENCIES AND PERSONS CONTACTED

1. Office of the Project Manager, Smoke/Obscurants, Aberdeen Proving Ground, MD 21005

Walter G. Klimek, DRCPM-SMK-T, Countermeasures and Test Division
Roger L. Schultz, DRCPM-SMK-M, Material Development and Technology Division

2. Chemical Research and Development Center, Aberdeen Proving Ground, MD 21010

Robert L. Dow, DRSMC-CLN-ST (A), Munitions Division
Charles S. Ferrett, DRSMC-CLN-SE (A), Munitions Division
Michael D. Smith, DRSMC-CLN-SE (A), Munitions Division
Ronald O. Pennsyle. DRSMC-CLY-A (A), Systems Development Division
John T. Weimer, DRSMC-CLB-TE (A), Research Division
Janis D. Chase, DRSMC-CLT-I (A), Environmental Technology Division
Steven R. Bennett, Ph.D., CPT, MSC, DRSMC-CLT-I (A), Environmental Technology Division

3. Traning and Doctrine Command Headquarters, Fort Monroe, VA 23651

Pennington, P.T., DAC	ATEN-S
Thomas E. Newkirk	HQ TRADOC, DCSENGR
William J. Weeks	HQ TRADOC, ATDO-C
Maj Lewis R. Williams, Jr	HQ TRADOC, STCD-MA
1LT Sharon Waligora	HQ TRADOC, STEN-FN
LTC Jimmy L. Young	HQ TRADOC, STEN-FN
Stanley Wolford	THREAT Dir., HQ TRADOC
Chris E. O'Connor, Jr.	HQ TRADOC, ATCD-FA
CPT James R. King	ODCST (ATTG-O) HQ TRADOC
Jan M. Gray	ATCD-MT
David J. Shaughnessy	THREAT DIR, HQ TRADOC

4. Training & Doctrine Command, Fort McClellan, NBC Defense School, AL

Ray Clark	USACMLS, DCD
E. Wayne Davis	USACMLS, DCD
CPT Michael Ward	USACMLS, DCD
CPT Harry E. Sutton	USACMLS, DOTD

5. Training & Doctrine Command, Fort Eustis

CPT Mckown	ATSC, ATIC-DST-DL Fort Eustis
Piers M. Wood	DAART, USATSC (ATIC-ART)

6. Smoke and Obscurant Test and Evaluation Center (TECOM), US Army, Dugway Proving Ground, Dugway, UT 84022

L. Dale King, STEDP-MT-L, Environmental & Life Sciences Division, Material Test Directorate
Edward Rengers, STEDP-MT-DA-M, Meteorological and Test Division

7. Headquarters, US Army Armament, Munitions and Chemical Command (AMCCOM), Rock Island, Illinois 61299

CPT Joseph A. Jakubowski, MSC, DRSAR-SG, Acting Staff Surgeon
Stan Lowe, DRSAR-ISE, Environmental Quality Division
Ronald T. Shinbori, DRSAR-ISE, Environmental Quality Division

8. US Army Medical Bioengineering Research and Development Laboratory, (USAMBRDL), Fort Dietrick, MD 21701

Dr. Mary C. Henry, Ph.D., Environmental Protection Research Division
CPT Gary Bratt, Environmental Protection Research Division

9. US Army Armament Research and Development Center (ARDC), Dover, New Jersey 07801

Frances J. Grego, DRSMC-PSE-EN (D), Environmental Division
Nicholas J. Mergel, DRSMC-PSE-EN (D), Environmental Coordinator

10. US Army Materiel Development and Readiness Command (USADARCOM), Alexandria, Virginia 22333

James E. Tragesser, DRCIS-A, Environmental Quality Division
Robert L. Lingo, DRCGC-S, Attorney Advisor

VII. CONCLUSIONS AND DATA GAP IDENTIFICATION

A. Conclusions.

1. It is a recognized fact that some of the colored smoke mixes and their combustion products may pose health hazards to manufacturing personnel and troops during training and testing exercises as detailed in the toxicological section of this report. Therefore, until the questionable colored smokes can be replaced by approved substitute mixes, control of their distribution and use should be conscientiously enforced. Controlled use means adherence to safety aspects and regulations and the use of suggested mitigation to minimize adverse impacts to the quality of the human environment. If operators of equipment take proper precautions to preclude inhalation and topical exposures and perform their duties adhering to industrial hygienic procedures, then health hazards for operators or test personnel can be eliminated. If tests are conducted in areas remote from civilian dwellings or communities, then public health hazards can be averted.

2. Testing and research should be initiated to provide data for identified gaps so that better guidelines may be established or corrective actions implemented to assure automatic, controlled use of colored smoke formulations.

3. Of the alternatives considered, the R&D Product Improvement Program and the possible use of chambers to support some testing and training exercises appear to be feasible courses of actions from the prospective of both health and cost, provided, of course, the meteorological differences do not alter the results too significantly.

4. The M48 colored training grenades presently stockpiled and the Disperse Red 9 dye should be disposed of or demilitarized, but under no circumstances should they be used under their present mission definition of riot control.

5. An Environmental Impact Statement is not recommended at this time and a Finding of No Significant Impact will be published.

B. Data Gap Identification.

The following information is needed to eliminate the data gaps which presently exist.

1. Dyes must be characterized to determine if toxicity is related to the dye component or to an impurity. If the toxicity is directly related to the non-dye fraction, a determination could be made as to whether the impurity could be removed; if removal is possible, a substantial amount of time/research dollars would be saved that are currently being expended to find substitute dyes. USAMBRDL has completed some toxicity studies on inventory red, violet, yellow, and green dyes, including work on mixtures, fractions, and pure components. A rough draft report is available. The same sequential testing is being done on candidate replacement dyes starting with yellow and green. The real concern is that toxic substances might be present in small but variable amounts in a chemical substance such as the dyes.

2. The combustion products of the colored smokes must be identified and quantified (percentages).

3. Toxicological and environmental fate information are much needed for all the colored dye mixes and constituents as well as for the by-products.

VIII. LITERATURE CITED

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9. Dacre, J. C. et al. USAMBRDL TR 7704. Physical, Chemical, Toxicological, and Biological Properties of Seven Chemicals Used in Pyrotechnic Compositions. Ft Detrick, MD. AD A090631. October 1979. UNCLASSIFIED Report.

10. Kitchens, J. F. et al. Preliminary Problem Definition Study of 43 Munitions - Vol III. Pyrotechnical Related Chemicals. USAMBRDL, Ft Detrick, MD. April 1978. A066309. UNCLASSIFIED Report.

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12. NCI Bioassay, National Cancer Institute Report. NCI-CG-TR-144. USDHEW-PHS, NHI. 1978.

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14. General Instructions for Demilitarization/Disposal of Conventional Munitions. TM 9-1300-277. March 1982.

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2. Vigus, E. S. and Deiner, A. ARCSL-TR-81054. Evaluation of Replacement Red Smoke Dyes for 1-N Methylaminoanthraquinone. October 1981.

3. King, D. L. Methology Investigation for Testing Effectiveness Smoke/Aerosol Munitions. Environmental Impact Assessment, US Army Dugway Proving Ground, Utah. October 1976.

4. Properties of Materials Used in Pyrotechnic Compositions. Engineering Design Handbook. Military Pyrotechnics Series. Part Three - AMCP 706-187. October 1963.

5. Smoke - An Obscuration Primer. Joint Technical Coordinating Group for Munitions Effectiveness No. 61 JTCG/ME-73-13. 13 March 1978.

6. Small Unit Smoke Operations. Training Circular No. 3-50-2. Headquarters, Department of the Army, Washington, DC. 29 December 1978.

7. Employment of Smoke. TRADOC Pamphlet, No. 525-3. 26 September 1980.

8. Chemical Reference Handbook FM 3-8. January 1967.

9. Military Chemistry and Chemical Compounds. FM 3-9/AFR 355-7. October 1975.

10. Safety Regulation, DARCOM 385-100, 17 August 1981.

11. Floating Smoke Grenade. Aircraft Armament Inc. DAAD05-69-C-0188.

12. Environmental Protection and Enhancement. Army Regulation 200-1. 15 July 1982.

13. DARCOM Supplement to AR 200-1. Environmental Protection and Enhancement. 29 June 1981.

14. Code of Federal Regulations, Volumes 40 and 49. Revised as of 1 October 81.

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16. Naval Sea Systems Command Report NWSC/CR/RDTR-36. Dinerman, C. E. and Gillian C. W. Ecological Disposal/Reclaim of Navy Colored Smoke Compositions. 1 June 1976.

17. Defense Disposal Manual. Department of Defense No. 4160.21-M-1. October 1981.

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APPENDIX A

CHEMICAL AND PHYSICAL PROPERTIES

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This appendix provides data sheets for the colored dyes, dye mix constituents and/or known combustion products. Data sheets were not found for all items but for those items that were found they are included within:

A. Dyes and constituents

Dextrin (diluent in mix)

1-4, diamino-2, 3-Dihydroanthraquinone (Violet)

1,4-di-p-Toluidinoanthraquinone (Solvent Green 3)

1-Methylaminoanthraquinone (Disperse Red 9)

B. Combustion Products

1-Aminoanthraquinone

Sulfur

Potassium Chlorate

Sodium Chlorate

Benzene

Carbon Disulfide

Styrene

Toluene

Chlorobenzene

Refs.

DEXTRIN

(Starch Gum, British Gum, Amylin, Gommelin, Vegetable Gum)

Dextrin or dextrines are obtained by treating starch in any one of a number of ways. These include controlled dilute acid hydrolysis of wet starch, the use of certain enzymes, and dry heat. The resultant products, whose properties vary with the source of the starch and the details of the treatment, are represented by the general chemical formula $(C_6H_{10}O_5)_n \cdot H_2O$. The n is, however, much smaller than in the original starch. The various dextrinization treatments of starch lead to complex mixtures resulting from three main types of reaction: 1, 16, 23, 24, 29, 70

1) Hydrolytic cleavage, which yields smaller and more water soluble compounds.
2) Transglucosidation, in which a 1-4 glucosidic bond between two $C_6H_{10}O_5$ units is broken and a 1-6 bond formed with a different $C_6H_{10}O_5$ unit, with the formation of a branch point. This reaction produces branched molecules and little change in molecular weight.
3) Some repolymerization and condensation of smaller molecules.

Because the polymolecularity of the original starches differ and various treatments result in a mixture of the three main reactions, the products differ in size, distribution of molecules, and in extent of branching, and thus have different properties.

Dextrins are distinguished from starch by the violet and red colors that dextrins give with iodine solution.

Dextrins are usually characterized by giving the source or kind of starch used, the color of the dry products, their solubility in water, and the viscosity of their water dispersions. The following table gives the more common treatments of starch to produce dextrins, together with some properties of the resulting starches.

CLASSIFICATION OF DEXTRINS 23

	White Dextrins	*Yellow or Canary Dextrins*	*British Gums*
Manuf. Conditions			
Usual catalyst	HCl	HCl	none or an alkali
Temperature, °C	79–121	149–218	135–218
Time, hrs.	3–8	6–18	10–20
Product Characteristics			
Color	white to light cream	buff to yellow or brown	buff to dark brown
Solubility (dispersibility), %	1–98	90–100	1–100
Useful diln., parts of water	2–5	1 or less	3–10

Source: Properties of Materials Used in Pyrotechnic Compositions, Engineering Design Handbook, AMCP 706-187.

Dextrin (page 2)

Specification:	JAN-D-232	

The specification covers two types of corn dextrin: Type I—white, and Type II—yellow. These vary in composition as indicated by a wide difference in water solubility.

Molecular Weight:	variable (appreciably less than starch)	
Color:	white to dark brown	
Density, g./ml.:	1.0384	1
Melting Point:	decomposes	
Specific Heat, cal./g./°C at 90°C:	0.292	1
Hygroscopicity:	very deliquescent	20V3
Health Hazard:	non toxic	93
Safety Classifications:		
OSM:	not listed	
ICC:	no shipping label required	
Use in Pyrotechnics:	fuel and binder	

Dextrins have strong adhesive properties and are used mainly as pastes.

Additional References:

1) B. Brimhall, Ind. Eng. Chem. *36*, 72 (1944)
2) J. Geerdes et al., J. Am. Chem. Soc. *79*, 4209 (1957)
3) "Chemistry and Industry of Starch," R. W. Kerr, Ed., Academic Press, Inc., New York (1950)
4) G. M. Christensen and F. Smith, J. Am. Chem. Soc. *79*, 4492 (1957)

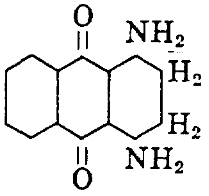
Source: AMCP 706-187

1.4-DIAMINO-2.3-DIHYDROANTHRAQUINONE

(1-4,diamino-2,3-dihydra-9,10-dihydro-9,10-diketoanthracene, Violet A 100)

		Refs.
Structural Formula:		82

$C_{14}H_{12}O_2N_2$



Specification No.:	MIL-D-3668	
Covers one grade with a minimum purity of 87%.		
Molecular Weight:	240.26	
Color:	violet	
Density, g./ml.:	(apparent) 0.35 ± 0.10	Spec.
Solubility:	soluble in 95% alcohol	Spec.

Health Hazard: Some toxicity as indicated by the specification requirement that each container be conspicuously labelled: "CAUTION—Avoid skin contact or breathing of dust fumes. Provide adequate ventilation in work areas."

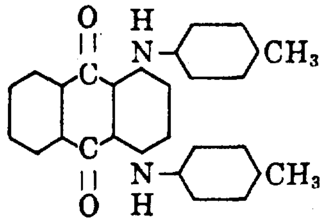
Safety Classifications:

OSM:	not listed
ICC:	not listed

Use in Pyrotechnics: To impart a violet color to burning smoke mixtures.

Source: AMCP 706-187

1,4-di-p-TOLUIDINOANTHRAQUINONE
(1,-4-di-p-tolyaminoanthraquinone, D & C Green No. 6, Quinizarine Green G Base, C.I. 61565, C.I. Solvent Green 3)



		Refs.
		92, 48A
Formula:	$C_{28}H_{22}N_2O_2$	
Specification No.:	MIL-D-3277	
Molecular Weight:	418.5	
Crystalline Form:	needles	88V14
Color: Green, from chlorobenzol—blue, from glacial acetic acid—dark violet		88V14 88V14
Density, g./ml.		
Apparent Density:	(Spec.) 0.45 ± 0.25	
Temperature Coefficient:	——	
Heat of Formation:	——	
Free Energy of Formation:	——	
Entropy:	——	
Melting Point:	491°K (218°C)	88V14
Heat of Fusion:	——	
Boiling Point:	——	
Transition Point:	——	
Heat of Sublimation:	——	
Heat Content or Enthalpy:	——	
Heat Capacity:	——	
Decomposition Temperature:	——	
Decomposition Products:	——	
Vapor Pressure:	——	
X-Ray Crystallographic Data:	——	
Hygroscopicity:	——	
Solubility Data: In alcohol (g./l.) at 60°C:	34	Addnl. Ref. 1
In aniline:	soluble with green color	88V14
In concentrated H_2SO_4:	soluble with violet-blue color or violet-red	
In chloroform and in benzene:	soluble	
Health Hazard:	unknown	92

Source: AMCP 706-187

1.4-Di-p-toluidinoanthraquinone (page 2)

Safety Classification:	
OSM:	not listed
ICC:	not listed
Fire and Explosion Hazard:	——
Electrostatic Sensitivity:	——
Use in Pyrotechnics:	to color smoke mixtures green

Additional References:

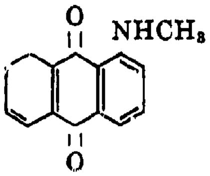
1) "The Dyeing Phenomena of Acetate Artificial Silk," V. Kartaschoff and G. Farine, Helv. Chim. Acta *2*, 822 (1928)

Source: AMCP 706-187

1-METHYLAMINOANTHRAQUINONE

		Refs.
(1-N-methylaminoanthraquinone, Celliton Pink R, Duranol Red GN, C.I. 60505, C.I. Disperse Red 9)		84, 48A

Formula: $C_{15}H_{11}NO_2$



Specification No.:	MIL-D-3824	
Spec. covers two grades differing in granulation.		
Molecular Weight:	237.11	
Crystalline Form:	needles	88V14
Color:	yellow-red	84
Density, g./ml.:		
Apparent Density:	(Spec) 0.35 ± .15	
Coefficient of Thermal Expansion:	——	
Heat of Formation:		
Free Energy of Formation:	——	
Entropy:	——	
Melting Point:	443°K (170°C)	84
Spec. grade II, min.:	442°K (169°C)	
Heat of Fusion:	——	
Boiling Point:	——	
Heat of Vaporization, Kcal./mole at 25°C and 1 atm.:	28.4 ± 0.7	Addnl. Ref. 3
Entropy of Vaporization, vapor at 1 atm., cal./mole/°C:	52.87 ± 0.30	Addnl. Ref. 1
Heat of Sublimation: Kcal./mole:	30.85	Addnl. Ref. 1
Heat Content or Enthalpy:	——	
Heat Capacity:	——	
Decomposition Temperature: For TGA see Ref. 80		
Decomposition Products:	——	
Vapor Pressure, $\log_{10}P$ (cm Hg) $= \frac{a}{T} + b$ $a = -6740$; $b = 13.435 \pm 0.036$; $T =$ abs. temp.		Addnl. Ref. 1
Energy of Activation for Volatilization (97% purity), Kcal./mole at 297–376°C:	19.6	80
X-Ray Crystallographic Data:	——	
Hygroscopicity:	——	

Source: AMCP 706-187

1-Methylaminoanthraquinone (page 2)

Solubility Data:		
In water, g./100 ml. at 25°C:	< .0002	Addnl. Ref. 5
at 80°C:	0.00055	
In alcohol (abs.) at 60°C:	14.96 g./l.	92, 88V14 I, 84
In $CHCl_3$, hot dil. HCl, glacial acetic acid:	soluble	
In benzene:	soluble, red	
In fuming H_2SO_4:	soluble, light yellow	
Health Hazard:	toxicity unknown	92, 93
Spec. requires each container be conspicuously labeled, "Caution—Avoid Skin Contact or Breathing of Dust or Fumes. Use with Adequate Ventilation."		
Safety Classifications:		
OSM:	not listed	
ICC:	not listed	
Fire and Explosion Hazard:	——	
Electrostatic Sensitivity:	——	
Use in Pyrotechnics:	to color smoke mixtures red	

Additional References:

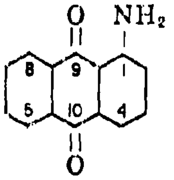
1) "Vapor Pressures of Some Dispersed Dyes," R. S. Bradley et al., Nature *178*, 998 (1956)
2) "The Dyeing Phenomena of Acetate Artificial Silk," V. Kartaschoff and G. Farine, Helv. Chim. Acta. *11*, 822 (1928)
3) "A Radioactive Ionization Gauge and Its Application to the Measurement of Latent Heat of Vaporization," J. H. Benyon and G. R. Nicholson, J. Sci. Instruments *33*, 376 (1956)
4) For Absorption Spectra see Ref. 66
5) J. Soc. Dyers Colourists *70*, 68-77 (1954)

Source: AMCP 706-187

1-AMINOANTHRAQUINONE. $C_{14}H_9NO_2$

(1-Amino-9,10-Dihydro-9,10-Dioxoanthracene; Fast Red Al; α-Anthraquinonylamine, C.I. 37275, Azoic Component 36)

Refs. 1, 84, 48A



		Refs.
Structural Formula:		
Specification No.:	MIL-D-3698	
Molecular Weight:	223.23	
Crystalline Form:	needles	
Color:	red	88V14
Density:	——	
Coefficient of Thermal Expansion:	——	
Heat of Formation:	——	
Free Energy of Formation:	——	
Entropy:	——	
Melting Point:	525°K (252°C) 526°K (253°C)	1 84
Heat of Fusion:	——	
Boiling Point:	sublimes	1, 88V14
Heat of Vaporization, Kcal./mole at 298°K and 1 atm.:	28.7 ± 0.1	Addnl. Ref. 1
Transition Point:	——	
Heat of Sublimation:	——	
Heat Content or Enthalpy:	——	
Heat Capacity:	——	
Decomposition Temperature:	——	
For DTA and TGA see Ref. 81	——	
Decomposition Products:	——	
Vapor Pressure:	——	
X-Ray Crystallographic Data:		
For absorption spectra see Ref. 66		
Hygroscopicity:	——	
Solubility Data:		Addnl. Ref. 2
In water, g./100 g. at 25°C:	0.00004	1, 28, 88V14
at 80°C:	0.0009	and V17
In ether, chloroform, benzene:	soluble	
In glacial acetic acid, 1 l. at 21.5°C:	dissolves 3.3 g.	

Source: AMCP 706-187

1-Aminoanthraquinone, $C_{14}H_9NO_2$ (page 2)

In 92-96% H_2SO_4:	dissolves with yellow color
In oleum, 20% SO_3:	dissolves with red color
In concentrated HCl:	dissolves
Health Hazard:	——
Safety Classifications:	
OSM:	not listed
ICC:	not listed
Fire and Explosion Hazard:	——
Electrostatic Sensitivity:	——

Use in Pyrotechnics: To color smoke mixtures red. Used in orange smoke mixtures.

Additional References:

1) "A Radioactive Ionization Gauge and its Application to the Measurement of Latent Heat of Vaporization," J. H. Beynon and G. R. Nicholson, J. Sci. Instr. *33*, 376 (1956)
2) J. Soc. Dyers Colourists *70*, 68-77 (1954)

Source: AMCP 706-187

BNZ

BENZENE

Common Synonyms
Benzol
Benzole

Watery liquid | Colorless | Gasoline-like odor

Floats on water. Flammable, irritating vapor is produced. Freezing point is 42° F.

Avoid contact with liquid and vapor. Keep people away.
Wear goggles and self-contained breathing apparatus.
Shut off ignition sources and call fire department.
Stop discharge if possible
Stay upwind and use water spray to "knock down" vapor.
Isolate and remove discharged material.
Notify local health and pollution control agencies.

Fire

FLAMMABLE.
Flashback along vapor trail may occur.
Vapor may explode if ignited in an enclosed area.
Wear goggles and self-contained breathing apparatus.
Extinguish with dry chemical, foam, or carbon dioxide.
Water may be ineffective on fire.
Cool exposed containers with water.

Exposure

CALL FOR MEDICAL AID.

VAPOR
Irritating to eyes, nose and throat.
If inhaled, will cause headache, difficult breathing, or loss of consciousness.
Move to fresh air.
If breathing has stopped, give artificial respiration.
If breathing is difficult, give oxygen.

LIQUID
Irritating to skin and eyes.
Harmful if swallowed.
Remove contaminated clothing and shoes.
Flush affected areas with plenty of water.
IF IN EYES, hold eyelids open and flush with plenty of water.
IF SWALLOWED and victim is CONSCIOUS, have victim drink water or milk.

Water Pollution

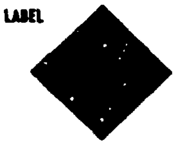
HARMFUL TO AQUATIC LIFE IN VERY LOW CONCENTRATIONS.
May be dangerous if it enters water intakes.
Notify local health and wildlife officials.
Notify operators of nearby water intakes.

1. RESPONSE TO DISCHARGE

(See Response Methods Handbook, CG 446-4)

Issue warning - high flammability
Restrict access

2. LABEL



3. CHEMICAL DESIGNATIONS

3.1 **Synonyms:** Benzol
Benzole
3.2 **Coast Guard Compatibility Classification:** Aromatic hydrocarbon
3.3 **Chemical Formula:** C_6H_6
3.4 **IMCO/United Nations Numerical Designation:** 3.2/1114

4. OBSERVABLE CHARACTERISTICS

4.1 **Physical State (as shipped):** Liquid
4.2 **Color:** Colorless
4.3 **Odor:** Aromatic, rather pleasant aromatic odor, characteristic odor

5. HEALTH HAZARDS

5.1 **Personal Protective Equipment:** Hydrocarbon vapor canister, supplied air or a hose mask; hydrocarbon-insoluble rubber or plastic gloves; chemical goggles or face splash shield; hydrocarbon-insoluble apron such as neoprene.
5.2 **Symptoms Following Exposure:** Dizziness, excitation, pallor, followed by flushing, weakness, headache, breathlessness, chest constriction. Coma and possible death.
5.3 **Treatment for Exposure:** SKIN: flush with water followed by soap and water; remove contaminated clothing and wash skin. EYES: flush with plenty of water until irritation subsides. INHALATION: remove from exposure immediately. Call a physician. If breathing is irregular or stopped, start resuscitation, administer oxygen.
5.4 **Toxicity by Inhalation (Threshold Limit Value):** 25 ppm
5.5 **Short-Term Inhalation Limits:** 75 ppm for 30 min
5.6 **Toxicity by Ingestion:** Grade 3; LD50 50 to 500 mg/kg
5.7 **Late Toxicity:** Leukemia
5.8 **Vapor (Gas) Irritant Characteristics:** If present in high concentrations, vapors may cause irritation of eyes or respiratory system. The effect is temporary.
5.9 **Liquid or Solid Irritant Characteristics:** Minimum hazard. If spilled on clothing and allowed to remain, may cause smarting and reddening of the skin.
5.10 **Odor Threshold:** 4.68 ppm

6. FIRE HAZARDS

6.1 **Flash Point:** 12°F C.C.
6.2 **Flammable Limits in Air:** 1.3% – 7.9%
6.3 **Fire Extinguishing Agents:** Dry chemical, foam, or carbon dioxide
6.4 **Fire Extinguishing Agents Not to be Used:** Water may be ineffective
6.5 **Special Hazards of Combustion Products:** Not pertinent
6.6 **Behavior in Fire:** Vapor is heavier than air and may travel considerable distance to a source of ignition and flash back
6.7 **Ignition Temperature:** 1097°F
6.8 **Electrical Hazard:** Class I, Group D
6.9 **Burning Rate:** 6.0 mm/min

7. CHEMICAL REACTIVITY

7.1 **Reactivity with Water:** No reaction
7.2 **Reactivity with Common Materials:** No reaction
7.3 **Stability During Transport:** Stable
7.4 **Neutralizing Agents for Acids and Caustics:** Not pertinent
7.5 **Polymerization:** Not pertinent
7.6 **Inhibitor of Polymerization:** Not pertinent

8. WATER POLLUTION

8.1 **Aquatic Toxicity:**
5 ppm/6 hr/minnow/lethal/distilled water
20 ppm/24 hr/sunfish/TLm/tap water
8.2 **Waterfowl Toxicity:** Data not available
8.3 **Biological Oxygen Demand (BOD):** 1.2 lb/lb, 10 days
8.4 **Food Chain Concentration Potential:** None

9. SELECTED MANUFACTURERS

1. Commonwealth Oil Refining Co., Inc.
   Commonwealth Petrochemicals Co.
   Penuelas, Puerto Rico 00724
2. Phillips Petroleum Co.
   Phillips Puerto Rico Core, Inc.
   Banco Popular Center
   Hato Rey, P. R. 00936
3. Shell Chemical Co.
   Petrochemicals Div.
   P. O. Box 2463
   Houston, Texas 77001

10. SHIPPING INFORMATION

10.1 **Grades or Purity:**

Industrial pure	99+%
Thiophene-free	99+%
Nitration	99+%
Industrial 90%	85+%
Reagent	99+%

10.2 **Storage Temperature:** Ambient
10.3 **Inert Atmosphere:** No requirement
10.4 **Venting:** Pressure-vacuum

11. HAZARD ASSESSMENT CODE

(See Hazard Assessment Handbook, CG 446-3)

A-T-U-V-W

12. HAZARD CLASSIFICATIONS

12.1 **Code of Federal Regulations:** Flammable liquid
12.2 **NAS Hazard Rating for Bulk Water Transportation:**

Category	Rating
Fire	3
Health	
Vapor Irritant	1
Liquid or Solid Irritant	1
Poisons	3
Water Pollution	
Human Toxicity	1
Aquatic Toxicity	3
Aesthetic Effect	2
Reactivity	
Other Chemicals	1
Water	0
Self-Reaction	0

12.3 **NFPA Hazard Classifications:**

Category	Classification
Health Hazard (Blue)	2
Flammability (Red)	3
Reactivity (Yellow)	0

13. PHYSICAL AND CHEMICAL PROPERTIES

13.1 **Physical State at 15°C and 1 atm:** Liquid
13.2 **Molecular Weight:** 78.11
13.3 **Boiling Point at 1 atm:** 176°F = 80.1°C = 353.3°K
13.4 **Freezing Point:** 42.0°F = 5.5°C = 278.7°K
13.5 **Critical Temperature:** 552.0°F = 288.9°C = 562.1°K
13.6 **Critical Pressure:** 710 psia = 48.3 atm = 4.89 MN/m²
13.7 **Specific Gravity:** 0.879 at 20°C (liquid)
13.8 **Liquid Surface Tension:** 28.9 dynes/cm = 0.0289 N/m at 20°C
13.9 **Liquid-Water Interfacial Tension:** 35.0 dynes/cm = 0.035 N/m at 20°C
13.10 **Vapor (Gas) Specific Gravity:** 2.7
13.11 **Ratio of Specific Heats of Vapor (Gas):** 1.061
13.12 **Latent Heat of Vaporization:** 169 Btu/lb = 94.1 cal/g = 3.94×10^5 J/kg
13.13 **Heat of Combustion:** −17,460 Btu/lb = −9698 cal/g = -406.0×10^5 J/kg
13.14 **Heat of Decomposition:** Not pertinent
13.15 **Heat of Solution:** Not pertinent
13.16 **Heat of Polymerization:** Not pertinent

(Continued on pages 5 and 6)

NOTES

CBB

CARBON BISULFIDE

Common Synonyms	
Carbon disulfide	Watery liquid Colorless to yellow Rotten egg to sweet odor Sinks in water. Flammable, irritating vapor is produced.

Avoid contact with liquid and vapor. Keep people away.
Wear goggles, self-contained breathing apparatus and rubber overclothing (including gloves).
Shut off ignition sources and call fire department.
Stop discharge if possible.
Stay upwind and use water spray to "knock down" vapor.
Isolate and remove discharged material.
Notify local health and pollution control agencies.

Fire

FLAMMABLE.
Flashback along vapor trail may occur.
Vapor may explode if ignited in an enclosed area.
Wear goggles, self-contained breathing apparatus, and rubber overclothing *(including gloves)*.
Extinguish with dry chemical or carbon dioxide.
Water and foam may be ineffective on fire.
Cool exposed containers with water.

Exposure

CALL FOR MEDICAL AID.

VAPOR
Irritating to eyes, nose and throat.
If inhaled, will cause nausea, vomiting, difficult breathing, or loss of consciousness.
Move to fresh air.
If breathing has stopped, give artificial respiration.
If breathing is difficult, give oxygen.

LIQUID
Will burn skin and eyes.
Harmful if swallowed.
Remove contaminated clothing and shoes.
Flush affected areas with plenty of water.
IF IN EYES, hold eyelids open and flush with *plenty of water*.
IF SWALLOWED and victim is CONSCIOUS, have victim drink water or milk and have victim induce vomiting.
IF SWALLOWED and victim is UNCONSCIOUS OR HAVING CONVULSIONS, do nothing except keep victim warm.

Water Pollution

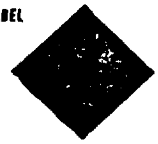
HARMFUL TO AQUATIC LIFE IN VERY LOW CONCENTRATIONS.
May be dangerous if it enters water intakes.
Notify local health and wildlife officials.
Notify operators of nearby water intakes.

1. RESPONSE TO DISCHARGE

(See Response Methods Handbook, CG 446-4)

Issue warning - high flammability
Restrict access
Evacuate area

2. LABEL



3. CHEMICAL DESIGNATIONS

3.1 **Synonyms:** Carbon disulfide
3.2 **Coast Guard Compatibility Classification:** Carbon disulfide
3.3 **Chemical Formula:** CS_2
3.4 **IMCO/United Nations Numerical Designation:** 3.1/1131

4. OBSERVABLE CHARACTERISTICS

4.1 **Physical State (as shipped):** Liquid
4.2 **Color:** Colorless
4.3 **Odor:** Faint sweetish; disagreeable, offensive, like that of decaying cabbage

5. HEALTH HAZARDS

5.1 **Personal Protective Equipment:** Only self-contained breathing mask with full face, approved by the United States Bureau of Mines, is recommended. If the vapor concentration exceeds 2% by volume or is unknown, supplied air respiratory equipment of appropriate design with full face masks should be used by all persons entering contaminated area. Masks should be used only for emergency situations and should be located accordingly. Almost any type of industrial clothing is satisfactory. Splashes of small quantity are not harmful to fabrics, and evaporation from clothing is quite rapid. Clothing should, however, be removed and the skin washed with water. Goggles should be used when there is any danger of CS_2 splashes or spray.

5.2 **Symptoms Following Exposure:** ACUTE EXPOSURE: mild to moderate irritation of skin, eyes, and mucous membranes from liquid or concentrated vapors; headache, garlicky breath, nausea, vomiting, diarrhea (even after vapor exposures), and occasionally abdominal pain, weak pulse, palpitations, fatigue, weakness in the legs, unsteady gait, vertigo, mania, hallucinations of sight, hearing, taste, and smell in acute massive vapor exposures; central nervous depression with respiratory paralysis; death may occur during coma or after a convulsion.

5.3 **Treatment for Exposure:** INHALATION: remove victim promptly from contaminated area. Administer oxygen and artificial respiration if needed. SKIN CONTACT: wash affected areas with copious quantities of water. INGESTION: induce vomiting and follow with gastric lavage and saline cathartics.

5.4 **Toxicity by Inhalation (Threshold Limit Value):** 20 ppm

5.5 **Short Term Inhalation Limits:** [illegible] ppm for [illegible] minutes; [illegible] ppm for [illegible] minutes; [illegible] ppm for [illegible] minutes; and [illegible] ppm for [illegible] minutes.

6. FIRE HAZARDS

6.1 **Flash Point:** −22°F C.C.
6.2 **Flammable Limits in Air:** 1.3% 50%
6.3 **Fire Extinguishing Agents:** Dry chemical, carbon dioxide
6.4 **Fire Extinguishing Agents Not to be Used:** Not pertinent
6.5 **Special Hazards of Combustion Products:** Toxic gases are generated, wear self-contained breathing apparatus
6.6 **Behavior in Fire:** Not pertinent
6.7 **Ignition Temperature:** 212°F
6.8 **Electrical Hazard:** Contact of the liquid or vapor with the surface of a lighted electric light bulb could result in ignition
6.9 **Burning Rate:** 2.7 mm/min

7. CHEMICAL REACTIVITY

7.1 **Reactivity with Water:** No reaction
7.2 **Reactivity with Common Materials:** No reaction
7.3 **Stability During Transport:** Stable
7.4 **Neutralizing Agents for Acids and Caustics:** Not pertinent
7.5 **Polymerization:** Not pertinent
7.6 **Inhibitor of Polymerization:** Not pertinent

8. WATER POLLUTION

8.1 **Aquatic Toxicity:** 35 ppm/48 hr/mosquito fish/TL_m/fresh water
8.2 **Waterfowl Toxicity:** Data not available
8.3 **Biological Oxygen Demand (BOD):** Data not available
8.4 **Food Chain Concentration Potential:** None

9. SELECTED MANUFACTURERS

1. FMC Corp.
   Inorganic Chemicals Div.
   633 Third Ave.
   New York, N. Y. 10017
2. PPG Industries Inc.
   Industrial Chemicals Div.
   Barberton, Ohio 44203
3. Stauffer Chemical Co.
   Industrial Chemicals Div.
   Delaware City, Delaware 19706

10. SHIPPING INFORMATION

10.1 **Grades or Purity:** Commercial; technical, USP
10.2 **Storage Temperature:** Ambient
10.3 **Inert Atmosphere:** Inerted
10.4 **Venting:** Pressure-vacuum

11. HAZARD ASSESSMENT CODE

(See Hazard Assessment Handbook, CG 446-3)

A-X-Y

12. HAZARD CLASSIFICATIONS

12.1 **Code of Federal Regulations:** Flammable liquid

12.2 **NAS Hazard Rating for Bulk Water Transportation:**

Category	Rating
Fire	4*
Health	
Vapor Irritant	2
Liquid or Solid Irritant	2
Poisons	3
Water Pollution	
Human Toxicity	1
Aquatic Toxicity	2
Aesthetic Effect	3
Reactivity	
Other Chemicals	2
Water	0
Self-Reaction	0

12.3 **NFPA Hazard Classifications:**

Category	Classification
Health Hazard (Blue)	2
Flammability (Red)	3
Reactivity (Yellow)	0

13. PHYSICAL AND CHEMICAL PROPERTIES

13.1 **Physical State at 15°C and 1 atm:** Liquid
13.2 **Molecular Weight:** 76.14
13.3 **Boiling Point at 1 atm:** 115°F = 46.3°C = 319.5°K
13.4 **Freezing Point:** −168.9°F = −111.6°C = 161.6°K
13.5 **Critical Temperature:** 523°F = 273°C = 546°K
13.6 **Critical Pressure:** 1100 psia = 76 atm = 7.7 MN/m²
13.7 **Specific Gravity:** 1.26 at 20°C (liquid)
13.8 **Liquid Surface Tension:** 32 dynes/cm = .032 N/m at 20°C
13.9 **Liquid-Water Interfacial Tension:** 48.4 dynes/cm = .0484 N/m at 20°C
13.10 **Vapor (Gas) Specific Gravity:** 2.6
13.11 **Ratio of Specific Heats of Vapor (Gas):** 1.292
13.12 **Latent Heat of Vaporization:** 153 Btu/lb = 85 cal/g = 3.559 × 10⁵ J/kg
13.13 **Heat of Combustion:** −5814 Btu/lb = −3230 cal/g = −135.2 × 10⁵ J/kg
13.14 **Heat of Decomposition:** Not pertinent
13.15 **Heat of Solution:** Not pertinent
13.16 **Heat of Polymerization:** Not pertinent

(Continued on pages 5 and 6)

5. HEALTH HAZARDS (Cont'd.)

5.6 **Toxicity by Ingestion:** Grade 2; rat LD_{50} = 0.1 - 0.99 g/kg
5.7 **Late Toxicity:** Non specific liver cell damage in rats; higher incidence of upper respiratory disease in humans.
5.8 **Vapor (Gas) Irritant Characteristics:** Vapors cause moderate irritation such that personnel will find high concentrations unpleasant. The effect is temporary.
5.9 **Liquid or Solid Irritant Characteristics:** Causes smarting of the skin and first-degree burns on short exposure, and may cause secondary burns on long exposure.
5.10 **Odor Threshold:** 0.21 ppm

Occupational Health Guideline for Carbon Disulfide

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: CS_2
- Synonyms: Carbon bisulfide
- Appearance and odor: Colorless to faintly yellow liquid with a strong, disagreeable or sweetish odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for carbon disulfide is 20 parts of carbon disulfide per million parts of air (ppm) averaged over an eight-hour work shift, with a ceiling level of 30 ppm, and an acceptable peak of 100 ppm for 30 minutes in an eight-hour work shift. NIOSH has recommended that the permissible exposure limit be reduced to 1 ppm averaged over a work shift of up to 10 hours per day, 40 hours per week, with a ceiling of 10 ppm averaged over a 15-minute period. The NIOSH Criteria Document for Carbon Disulfide should be consulted for more detailed information.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Carbon disulfide can affect the body if it is inhaled, if it comes in contact with the eyes or skin, or if it is swallowed. It may enter the body through the skin.

- **Effects of overexposure**

1. *Short-term Exposure:* Inhalation of carbon disulfide vapor may cause headache, nausea, drop in blood pressure, dizziness, unconsciousness, and death. Liquid carbon disulfide and high concentrations of the vapor may cause irritation of the skin, eyes, and nose. If the liquid is trapped under clothing, it may cause a burn. Swallowing carbon disulfide may cause loss of consciousness and convulsions. If small amounts are swallowed, vomiting, diarrhea, and headache may occur.

2. *Long-term Exposure:* Prolonged or repeated exposure to carbon disulfide may damage the nervous system and cause muscle weakness, numbness, feelings of pins and needles, unsteady walking, and difficulty in swallowing. Palsy, speech difficulty, and muscle spacticity may also occur. In addition, memory loss, headache, difficulty in sleeping, nervousness, fatigue, irritability, depression, suicidal tendencies, and psychosis may occur. Eye damage may occur with such symptoms as blind spots, narrowing of vision, and decreased ability to see in the dark. Increased arteriosclerosis may occur which may cause or increase damage to the heart and other organs. High blood pressure, kidney damage, liver damage, and stomach problems may occur. Repeated or prolonged exposure of the skin to carbon disulfide may cause a skin rash.

3. *Reporting Signs and Symptoms:* A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to carbon disulfide.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to carbon disulfide at potentially hazardous levels:

1. *Initial Medical Examination:*

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of the central and peripheral nervous systems, eyes, cardiovascular system, kidneys, and liver should be stressed. The skin should be examined for evidence of chronic disorders.

—Urinalysis: Since kidney damage has been observed in humans exposed to carbon disulfide, a urinalysis

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These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

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should be obtained to include, at a minimum, specific gravity, albumin, glucose, and a microscopic on centrifuged sediment.

—Liver function tests: Since liver damage has been observed in humans exposed to carbon disulfide, a profile of liver function should be obtained by using a medically acceptable array of biochemical tests.

—An electrocardiogram: Carbon disulfide has caused arrhythmias and electrocardiographic changes in humans. Periodic surveillance is indicated.

—Ophthalmic examination: Carbon disulfide has caused ocular changes in humans. An ophthalmic examination should be performed, including visual acuity.

—Medical warning: Workers should be informed of potential undesirable effects of exposure to carbon disulfide on reproduction (such as spermatic deficiences, menstrual disorders, and spontaneous abortions).

2. *Periodic Medical Examination:* The aforementioned medical examinations should be repeated on an annual basis.

- **Summary of toxicology**

Carbon disulfide vapor causes narcosis at high concentrations; repeated exposure to low concentrations causes damage to the central and peripheral nervous systems and may accelerate the development of or worsen coronary heart disease. Exposure of humans to 1150 ppm causes serious symptoms, and 4800 ppm for 30 minutes may be fatal. Carbon disulfide intoxication can involve all parts of the central and peripheral nervous systems, including damage to the cranial nerves and development of polyneuritis with paresthesias and muscle weakness in the extremities, unsteady gait, and dysphagia. In extreme cases of intoxication, a Parkinson-like syndrome may result, characterized by speech disturbances, muscle spasticity, tremor, memory loss, mental depression, and marked psychic symptoms; permanent disability is likely. Reproductive disorders occur, such as aspermia, menstrual irregularities, and spontaneous abortion. Psychosis and suicide are established risks of overexposure to carbon disulfide. Other reported effects of exposure to carbon disulfide are ocular changes (retinal degeneration, corneal opacities, disturbances of color vision, corneal anesthesia, diminished pupillary reflexes, microscopic aneurysms in the retina), gastrointestinal disturbances (chronic gastritis and achlorhydria), renal impairment (albuminuria, microhematuria, elevated blood urea nitrogen, diastolic hypertension), and liver damage. Effects commonly caused by repeated exposure to carbon disulfide vapor are exemplified by a group of workers with a time-weighted average (TWA) exposure of 11.2 ppm (range 0.9 to 127 ppm) who complained of headaches and dizziness; in other workers with a TWA of 186 ppm (range 23 to 378 ppm) complaints also included sleep disturbances, fatigue, nervousness, anorexia, and weight loss; the end-of-day exposure coefficient of the iodine azide test on urine was a good indicator of workers who were or had been symptomatic. Overexposure to carbon disulfide has long been regarded as potentially atherogenic for cerebral, renal, and coronary arteries; recent epidemiologic studies of viscose rayon workers have confirmed a 2.5- to 5-fold increase in risk of death from coronary heart disease as compared with the experience of unexposed workers. Other cardiovascular effects observed in workers repeatedly exposed to carbon disulfide are bradycardia, tachycardia, arrhythmias, and electrocardiographic changes consistent with both nonspecific and ischemic wave changes. Splashes of the liquid in the eyes cause immediate and severe irritation; dermatitis and vesiculation may result from skin contact with the vapor or the liquid. Although ingestion is unlikely to occur, it may cause coma and convulsions.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 76.1
2. Boiling point (760 mm Hg): 46.3 C (115 F)
3. Specific gravity (water = 1): 1.27
4. Vapor density (air = 1 at boiling point of carbon disulfide): 2.6
5. Melting point: −111.5 C (-169 F)
6. Vapor pressure at 20 C (68 F): 300 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 0.2
8. Evaporation rate (butyl acetate = 1): 22.6

- **Reactivity**

1. Conditions contributing to instability: Containers may burst when heated.
2. Incompatibilities: Contact with strong oxidizers, and chemically active metals (such as sodium, potassium, and zinc), azides, and organic amines may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as sulfur dioxide and carbon monoxide) may be released in a fire involving carbon disulfide.
4. Special precautions: Liquid carbon disulfide will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: −30 C (-22 F) (closed cup)
2. Autoignition temperature: 90 C (194 F)
3. Flammable limits in air, % by volume: Lower: 1.3; Upper: 50
4. Extinguishant: Dry chemical, carbon dioxide for small fires

- **Warning properties**

1. Odor Threshold: The *Handbook of Organic Industrial Solvents* states that at less than 1 ppm, carbon disulfide has a disagreeable odor. Summer gives an odor threshold of 7.7 ppm , and May gives 0.0011 ppm and 0.0081 ppm. The AIHA *Hygienic Guide* gives an odor threshold of 1.2 ppm.
2. Eye Irritation Level: Carbon disulfide is not known to be an eye irritant.
3. Evaluation of Warning Properties: Since the odor threshold of carbon disulfide is below the permissible

exposure limit, it is treated as a material with good warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **Eight-Hour Exposure Evaluation**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Ceiling Evaluation**

Measurements to determine employee ceiling exposure are best taken during periods of maximum expected airborne concentrations of carbon disulfide. Each measurement should consist of a fifteen (15) minute sample or series of consecutive samples totalling fifteen (15) minutes in the employee's breathing zone (air that would most nearly represent that inhaled by the employee). A minimum of three (3) measurements should be taken on one work shift and the highest of all measurements taken is an estimate of the employee's exposure.

- **Peak Above Ceiling Evaluation**

Measurements to determine employee peak exposure should be taken during periods of maximum expected airborne concentration of carbon disulfide. Each measurement should consist of a 30-minute sample or a series of consecutive samples totalling 30 minutes in the employee's breathing zone (air that would most nearly represent that inhaled by the employee). A minimum of three measurements should be taken on one work shift and the highest of all measurements taken is an estimate of the employee's exposure.

- **Method**

Sampling and analyses may be performed by collection of carbon disulfide vapors using an adsorption tube with subsequent desorption with benzene and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure carbon disulfide may be used. An analytical method for carbon disulfide is in the *NIOSH Manual of Analytical Methods,* 2nd Ed., Vol. 3, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00261-4).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent skin contact with liquid carbon disulfide, where skin contact may occur.
- Non-impervious clothing which becomes contaminated with carbon disulfide should be removed promptly and not reworn until the carbon disulfide is removed from the clothing.
- Any clothing which becomes wet with liquid carbon disulfide should be removed immediately and not reworn until the carbon disulfide is removed from the clothing.
- Clothing wet with liquid carbon disulfide should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of carbon disulfide from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the carbon disulfide, the person performing the operation should be informed of carbon disulfide's hazardous properties.
- Employees should be provided with and required to use splash-proof safety goggles where liquid carbon disulfide may contact the eyes.

SANITATION

- Skin that becomes contaminated with carbon disulfide should be promptly washed or showered with soap or mild detergent and water to remove any carbon disulfide.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to carbon disulfide may occur and control methods which may be effective in each case:

Operation	Controls
Use in manufacture of viscose rayon during xanthation of cellulose and spinning and cutting operations; use as a xanthating agent in manufacture of cellophane; use during manufacture of pesticides	Process enclosure; local exhaust ventilation; general dilution ventilation; temperature control; personal protective equipment
Use as a fumigant and spray application on grains, and space fumigation of agricultural premises	General dilution ventilation; temperature control; personal protective equipment
Use in synthesis of carbon tetrachloride	Process enclosure; local exhaust ventilation; general dilution ventilation; temperature control; personal protective equipment
Use in synthesis of intermediates and manufacture of dyes, pharmaceuticals, rubber chemicals, pesticides, and flotation agents	Process enclosure; local exhaust ventilation; general dilution ventilation; temperature control; personal protective equipment
Liberation during destructive distillation of coal in manufacture of coal gas and coal tar	Process enclosure; local exhaust ventilation; general dilution ventilation; temperature control; personal protective equipment
Use as a solvent in dry spinning of polyvinyl chloride; as a solvent in oil wells; use in manufacture of optical glass	Process enclosure; local exhaust ventilation; general dilution ventilation; temperature control; personal protective equipment
Use during rubber manufacture in cold curing operations; during extraction processing of oils, fats, resins, and waxes; use in manufacture of matches	Process enclosure; local exhaust ventilation; general dilution ventilation; temperature control; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If liquid carbon disulfide gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation is present after washing, get medical attention. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If liquid carbon disulfide gets on the skin, immediately wash the contaminated skin using soap or mild detergent and water. If liquid carbon disulfide soaks through the clothing, remove the clothing immediately and wash the skin using soap or mild detergent and water. Get medical attention promptly.

- **Breathing**

If a person breathes in large amounts of carbon disulfide, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When liquid carbon disulfide has been swallowed and the person is conscious, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If carbon disulfide is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities, absorb on paper towels. Evaporate in a safe place (such as a fume hood). Allow sufficient time for evaporating vapors to completely clear the hood ductwork. Burn the paper in a suitable location away from combustible materials. Large quantities can be reclaimed or collected and atomized in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device. Carbon disulfide should not be allowed to enter a confined space, such as

a sewer, because of the possibility of an explosion. Sewers designed to preclude the formation of explosive concentrations of carbon disulfide vapors are permitted.

- Waste disposal method:

Carbon disulfide may be disposed of by atomizing in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

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RESPIRATORY PROTECTION FOR CARBON DISULFIDE

Condition	Minimum Respiratory Protection* Required Above 20 ppm
Vapor Concentration	
200 ppm or less	Any chemical cartridge respirator with an organic vapor cartridge(s). Any supplied-air respirator. Any self-contained breathing apparatus.
500 ppm or less	Any chemical cartridge respirator with a full facepiece and an organic vapor cartridge(s). A gas mask with a chin-style or a front- or back-mounted organic vapor canister. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece. A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.
Greater than 500 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Chlorobenzene

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: C_6H_5Cl
- Synonyms: Monochlorobenzene; chlorobenzol; phenyl chloride; MCB
- Appearance and odor: Colorless liquid with a mild aromatic odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for chlorobenzene is 75 parts of chlorobenzene per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 350 milligrams of chlorobenzene per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Chlorobenzene can affect the body if it is inhaled or if it comes in contact with the eyes or skin. It can also affect the body if it is swallowed.

- **Effects of overexposure**

1. Short-term Exposure: Chlorobenzene may cause drowsiness, incoordination, and unconsciousness. It may also cause irritation of the eyes, nose, and skin. Exposure to high levels might also cause liver damage.

2. Long-term Exposure: Prolonged or repeated skin contact with chlorobenzene liquid may cause skin burns. Prolonged or repeated exposure to this chemical might also result in liver, kidney, or lung damage.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to chlorobenzene.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to chlorobenzene at potentially hazardous levels:

1. Initial Medical Screening: Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from chlorobenzene exposure.

—Skin disease: Chlorobenzene can cause dermatitis on exposure. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.

—Liver disease: Chlorobenzene is known as a liver toxin in animals. The importance of this organ in the biotransformation and detoxification of foreign substances should be considered before exposing persons with impaired liver function.

—Kidney disease: Although chlorobenzene is not known as a kidney toxin in humans, the importance of this organ in the elimination of toxic substances justifies special consideration in those with impaired renal function.

—Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of chlorobenzene might cause exacerbation of symptoms due to its irritant properties.

2. Periodic Medical Examination: Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

Chlorobenzene vapor is a narcotic. Cats exposed to 8,000 ppm showed severe narcosis after ½ hour and died 2 hours after removal from exposure, but 660 ppm for 1 hour was tolerated. Exposed animals showed eye and nose irritation, drowsiness, incoordination, and coma followed by death from the most severe exposures. Several species of animals exposed to 1,000 ppm for 7 hours/day, 5 days/week over a period of 44 days showed histopathologic changes in the lungs, liver, and

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U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

September 1978

kidneys, but at 475 ppm there was only slight liver histopathology in guinea pigs. Toxicologic studies and experience indicate that chlorobenzene does not cause the type of blood changes seen with benzene exposure. In man, eye and nasal irritation begin to occur at 200 ppm, and at that level the odor is pronounced and unpleasant; industrial experience indicates that occasional short exposures are not likely to result in more than minor skin irritation, but prolonged or frequently repeated contact may result in skin burns. In one case of accidental poisoning from ingestion of the liquid by a child there was pallor, cyanosis, and coma, followed by complete recovery. Occupational intoxication has not been reported.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 112.5
2. Boiling point (760 mm Hg): 132 C (270 F)
3. Specific gravity (water = 1): 1.1
4. Vapor density (air = 1 at boiling point of chlorobenzene): 3.9
5. Melting point: −44 C (-47 F)
6. Vapor pressure at 20 C (68 F): 8.8 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 0.05
8. Evaporation rate (butyl acetate = 1): 1

- **Reactivity**

1. Conditions contributing to instability: Heat
2. Incompatibilities: Contact with strong oxidizers may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as hydrogen chloride, phosgene, and carbon monoxide) may be released in a fire involving chlorobenzene.
4. Special precautions: Liquid chlorobenzene will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: 28.9 C (84 F) (closed cup)
2. Autoignition temperature: 638 C (1180 F)
3. Flammable limits in air, % by volume: Lower: 1.3; Upper: 7.1
4. Extinguishant: Carbon dioxide; dry chemical, foam

- **Warning properties**

According to both Deichmann and Gerarde and the AIHA *Hygienic Guide*, the odor of chlorobenzene is "barely perceptible" at 60 ppm, a concentration below that of the permissible exposure. Chlorobenzene is considered to have good warning properties. It is an eye irritant, as stated by Patty, but the exact concentrations at which this irritation occurs are not mentioned.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by collection of vapors using an adsorption tube with subsequent desorption with carbon disulfide and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure chlorobenzene may be used. An analytical method for chlorobenzene is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 2, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00260-6).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with liquid chlorobenzene.
- Clothing wet with liquid chlorobenzene should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of chlorobenzene from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the chlorobenzene, the person performing the operation should be informed of chlorobenzene's hazardous properties.
- Any clothing which becomes wet with liquid chlorobenzene should be removed immediately and not

reworn until the chlorobenzene is removed from the clothing.

- Employees should be provided with and required to use splash-proof safety goggles where liquid chlorobenzene may contact the eyes.

SANITATION

- Skin that becomes wet with liquid chlorobenzene should be promptly washed or showered with soap or mild detergent and water to remove any chlorobenzene.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to chlorobenzene may occur and control methods which may be effective in each case:

Operation	Controls
Use in manufacture of phenol in synthesis of polymeric materials	Local exhaust ventilation
Use as an intermediate in manufacture of ortho- and para-nitrobenzenes for use in dye manufacture; manufacture of DDT, aniline, picric acid, beta-chloroanthraquinone, and other chemicals; manufacture of rubber adhesives and adhesives	Process enclosure
Use as fiber swelling agent and dye carrier in textile processing	Local exhaust ventilation
Use as tar and grease remover in cleaning and degreasing operations	Local exhaust ventilation
Use as solvent in surface coatings and surface coating removers	Process enclosure; local exhaust ventilation; personal protective equipment
Use as extractant in manufacture of diisocyanates, rubber, perfumes, and pharmaceuticals	Local exhaust ventilation

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If chlorobenzene gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention immediately. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If chlorobenzene gets on the skin, promptly wash the contaminated skin using soap or mild detergent and water. If chlorobenzene soaks through the clothing, remove the clothing immediately and wash the skin using soap or mild detergent and water. If irritation persists after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of chlorobenzene, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

If chlorobenzene has been swallowed, do not induce vomiting. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If chlorobenzene is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities, absorb on paper towels. Evaporate in a safe place (such as a fume hood). Allow sufficient time for evaporating vapors to completely clear the hood ductwork. Burn the paper in a suitable location away from combustible materials. Large quantities can be reclaimed or collected and atomized in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device. Chlorobenzene should not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion. Sewers designed to preclude the formation of explosive concentrations of chlorobenzene vapors are permitted.

- Waste disposal method:

Chlorobenzene may be disposed of by atomizing in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

reworn until the chlorobenzene is removed from the clothing.

- Employees should be provided with and required to use splash-proof safety goggles where liquid chlorobenzene may contact the eyes.

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- Skin that becomes wet with liquid chlorobenzene should be promptly washed or showered with soap or mild detergent and water to remove any chlorobenzene.

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The following list includes some common operations in which exposure to chlorobenzene may occur and control methods which may be effective in each case:

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Use as fiber swelling agent and dye carrier in textile processing	Local exhaust ventilation
Use as tar and grease remover in cleaning and degreasing operations	Local exhaust ventilation
Use as solvent in surface coatings and surface coating removers	Process enclosure; local exhaust ventilation; personal protective equipment
Use as extractant in manufacture of diisocyanates, rubber, perfumes, and pharmaceuticals	Local exhaust ventilation

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In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If chlorobenzene gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention immediately. Contact lenses should not be worn when working with this chemical.

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If chlorobenzene gets on the skin, promptly wash the contaminated skin using soap or mild detergent and water. If chlorobenzene soaks through the clothing, remove the clothing immediately and wash the skin using soap or mild detergent and water. If irritation persists after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of chlorobenzene, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

If chlorobenzene has been swallowed, do not induce vomiting. Get medical attention immediately.

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Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

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- Waste disposal method:

Chlorobenzene may be disposed of by atomizing in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

REFERENCES

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- International Labour Office: *Encyclopedia of Occupational Health and Safety*, McGraw-Hill, New York, 1971.
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- Sax, N. I.: *Dangerous Properties of Industrial Materials* (3rd ed.), Van Nostrand Reinhold, New York, 1968.
- von Oettingen, W. F.: *The Halogenated Aliphatic, Olefinic, Cyclic, Aromatic, and Aliphatic-Aromatic Hydrocarbons Including the Halogenated Insecticides, Their Toxicity and Potential Dangers*, U.S. Public Health Service Publication No. 414, U.S. Government Printing Office, Washington, D.C., 1955.

RESPIRATORY PROTECTION FOR CHLOROBENZENE

Condition	Minimum Respiratory Protection* Required Above 75 ppm
Vapor Concentration	
1000 ppm or less	A chemical cartridge respirator with a full facepiece and an organic vapor cartridge(s).
2400 ppm or less	A gas mask with a chin-style or a front- or back-mounted organic vapor canister. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
Greater than 2400 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

PCR	POTASSIUM CHLORATE

Common Synonyms	Solid	White	Odorless
Potcrate Chlorate of potassium Chlorate of potash	Mixes with water.		

Call fire department.
Keep people away.
Isolate and remove discharged material.
Notify local health and pollution control agencies.

Fire	Not flammable. May cause fire on contact with combustibles. POISONOUS GASES ARE PRODUCED IN FIRE. Flood discharge area with water
Exposure	Call for medical aid. DUST Irritating to eyes, nose and throat. Move victim to fresh air. If in eyes, hold eyelids open and flush with plenty of water. SOLID Irritating to skin and eyes. If swallowed will cause nausea, vomiting or loss of consciousness. Remove contaminated clothing and shoes. Flush affected areas with plenty of water. IF IN EYES, hold eyelids open and flush with plenty of water. IF SWALLOWED and victim is CONSCIOUS, have victim drink water or milk and have victim induce vomiting. IF SWALLOWED and victim is UNCONSCIOUS OR HAVING CONVULSIONS, do nothing except keep victim warm.
Water Pollution	Effect of low concentrations on aquatic life is unknown. May be dangerous if it enters water intakes. Notify local health and wildlife officials. Notify operators of nearby water intakes.

1. RESPONSE TO DISCHARGE

(See Response Methods Handbook CG 446-4)

Issue warning—oxidizing material, water contaminant
Restrict access
Disperse and flush

2. LABEL

3. CHEMICAL DESIGNATIONS

3.1 **Synonyms:** Chlorate of potash, Chlorate of potassium; potcrate
3.2 **Coast Guard Compatibility Classification:** Not applicable
3.3 **Chemical Formula:** $KClO_3$
3.4 **IMCO/United Nations Numerical Designation:** 5.1/1485

4. OBSERVABLE CHARACTERISTICS

4.1 **Physical State (as shipped):** Solid
4.2 **Color:** White
4.3 **Odor:** None

5. HEALTH HAZARDS

5.1 **Personal Protective Equipment:** Dust mask; rubber gloves, goggles; protective clothing to prevent contact with skin
5.2 **Symptoms Following Exposure:** Inhalation of dust can irritate nose and throat. Contact with eyes or skin causes irritation. Ingestion causes abdominal pain, nausea, vomiting, cyanosis, collapse.
5.3 **Treatment for Exposure:** EYES: flush with water for at least 15 min. SKIN: wash with soap and water. INGESTION: dilute by drinking soapy or salty water to induce vomiting; call physician.
5.4 **Toxicity by Inhalation (Threshold Limit Value):** Data not available
5.5 **Short-Term Inhalation Limits:** Data not available
5.6 **Toxicity by Ingestion:** Grade 2, LD$_{50}$ 0.5 to 5 g/kg
5.7 **Late Toxicity:** Data not available
5.8 **Vapor (Gas) Irritant Characteristics:** Data not available
5.9 **Liquid or Solid Irritant Characteristics:** Data not available
5.10 **Odor Threshold:** Not pertinent

6. FIRE HAZARDS

6.1 **Flash Point:** Not flammable, but may cause fire upon contact with ordinary combustibles
6.2 **Flammable Limits in Air:** Not pertinent
6.3 **Fire Extinguishing Agents:** Water on adjacent fires
6.4 **Fire Extinguishing Agents Not to be Used:** Not pertinent
6.5 **Special Hazards of Combustion Products:** Toxic fumes are formed in fires
6.6 **Behavior in Fire:** Decomposes when hot to form oxygen, which increases severity of fire
6.7 **Ignition Temperature:** Not pertinent
6.8 **Electrical Hazard:** Not pertinent
6.9 **Burning Rate:** Not pertinent

7. CHEMICAL REACTIVITY

7.1 **Reactivity with Water:** No reaction
7.2 **Reactivity with Common Materials:** Contact with combustible material may cause fire.
7.3 **Stability During Transport:** Stable
7.4 **Neutralizing Agents for Acids and Caustics:** Not pertinent
7.5 **Polymerization:** Not pertinent
7.6 **Inhibitor of Polymerization:** Not pertinent

8. WATER POLLUTION

8.1 **Aquatic Toxicity:** Data not available
8.2 **Waterfowl Toxicity:** Data not available
8.3 **Biological Oxygen Demand (BOD):** None
8.4 **Food Chain Concentration Potential:** None

9. SELECTED MANUFACTURERS

1. Pennwalt Corporation
Chemicals Division
Three Parkway
Philadelphia, Pa. 19102

2. Hooker Chemical Corporation
Specialty Chemicals Division
P. O. Box 344
Niagara Falls, N. Y. 14302

3. Mallinckrodt Chemical Works
Industrial Chemicals Division
Second and Mallinckrodt Streets
P. O. Box 5439
St. Louis, Mo. 63160

10. SHIPPING INFORMATION

10.1 **Grades or Purity:** Commercial: 99.7+%, Reagent: Purified
10.2 **Storage Temperature:** Ambient
10.3 **Inert Atmosphere:** No requirement
10.4 **Venting:** Open

11. HAZARD ASSESSMENT CODE

(See Hazard Assessment Handbook CG 446-3)

SS

12. HAZARD CLASSIFICATIONS

12.1 **Code of Federal Regulations:** Oxidizing material
12.2 **NAS Hazard Rating for Bulk Water Transportation:** Not listed
12.3 **NFPA Hazard Classifications:**

Category	Classification
Health Hazard (Blue)	1
Flammability (Red)	0
Reactivity (Yellow)	2 OXY

13. PHYSICAL AND CHEMICAL PROPERTIES

13.1 **Physical State at 15°C and 1 atm:** Solid
13.2 **Molecular Weight:** 122.6
13.3 **Boiling Point at 1 atm:** Not pertinent (decomposes)
13.4 **Freezing Point:** 680°F = 360°C = 633°K
13.5 **Critical Temperature:** Not pertinent
13.6 **Critical Pressure:** Not pertinent
13.7 **Specific Gravity:** 2.34 at 20°C (solid)
13.8 **Liquid Surface Tension:** Not pertinent
13.9 **Liquid-Water Interfacial Tension:** Not pertinent
13.10 **Vapor (Gas) Specific Gravity:** Not pertinent
13.11 **Ratio of Specific Heats of Vapor (Gas):** Not pertinent
13.12 **Latent Heat of Vaporization:** Not pertinent
13.13 **Heat of Combustion:** Not pertinent
13.14 **Heat of Decomposition:** −176 Btu/lb = −98 cal/g = -4.1×10^5 J/kg
13.15 **Heat of Solution:** 147 Btu/lb = 81.9 cal/g = 3.43×10^5 J/kg
13.16 **Heat of Polymerization:** Not pertinent

(Continued on pages 5 and 6)

NOTES

SDC

SODIUM CHLORATE

Common Synonyms
Chlorate of soda

Solid crystals or powder — Colorless to pale yellow — Odorless

Sinks and mixes with water.

Stop discharge if possible.
Avoid contact with solid
Isolate and remove discharged material
Notify local health and pollution control agencies.

Fire

Not flammable.
CONTAINERS MAY EXPLODE IN FIRE.
May cause fire on contact with combustibles

Combat adjacent fires from a safe distance or protected location
Flood discharge area with water
Cool exposed containers with water
Continue cooling after fire has been extinguished

Exposure

CALL FOR MEDICAL AID.

SOLID
Irritating to skin and eyes.
Harmful if swallowed.

Flush affected areas with plenty of water.
IF IN EYES, hold eyelids open and flush with plenty of water.
IF SWALLOWED and victim is CONSCIOUS, have victim drink water or milk and have victim induce vomiting
IF SWALLOWED and victim is UNCONSCIOUS OR HAVING CONVULSIONS, do nothing except keep victim warm.

Water Pollution

Dangerous to aquatic life in high concentrations.
May be dangerous if it enters water intakes.

Notify local health and wildlife officials.
Notify operators of nearby water intakes.

1. RESPONSE TO DISCHARGE

(See Response Methods Handbook, CG 446-4)

Issue warning—high flammability
Should be removed
Disperse and flush

2. LABEL

3. CHEMICAL DESIGNATIONS

3.1 **Synonyms:** Chlorate of soda
3.2 **Coast Guard Compatibility Classification:** Not applicable
3.3 **Chemical Formula:** $NaClO_3$
3.4 **IMCO/United Nations Numerical Designation:** 5.1/1495

4. OBSERVABLE CHARACTERISTICS

4.1 **Physical State (as shipped):** Solid
4.2 **Color:** Pale yellow to white
4.3 **Odor:** Odorless

5. HEALTH HAZARDS

5.1 **Personal Protective Equipment:** Clean work clothing (must be washed well with water after each exposure), rubber gloves and shoes; where dusty, goggles and an approved dust respirator. Do NOT use oils, greases, or protective creams on skin.
5.2 **Symptoms Following Exposure:** Ingestion of a toxic dose (at least 1/2 oz.) leads to severe gastroenteric pain, vomiting, and diarrhea. Possible respiratory difficulties, including failure of respiration. Kidney and liver injury may also be produced. The lethal oral dose for an adult is approximately 15 gm. Contact with eyes causes irritation.
5.3 **Treatment for Exposure:** INGESTION: induce vomiting and follow with gastric lavage, saline cathartics, fluid therapy, and oxygen. EYES: wash thoroughly with water.
5.4 **Toxicity by Inhalation (Threshold Limit Value):** Not pertinent
5.5 **Short-Term Inhalation Limits:** Not pertinent
5.6 **Toxicity by Ingestion:** Grade 3, LD_{50} 50 to 500 mg/kg
5.7 **Late Toxicity:** Data not available
5.8 **Vapor (Gas) Irritant Characteristics:** Non volatile
5.9 **Liquid or Solid Irritant Characteristics:** Prolonged exposure to solid or dust may irritate skin
5.10 **Odor Threshold:** Not pertinent

6. FIRE HAZARDS

6.1 **Flash Point:** Not flammable but supports combustion
6.2 **Flammable Limits in Air:** Not pertinent
6.3 **Fire Extinguishing Agents:** Water
6.4 **Fire Extinguishing Agents Not to be Used:** Fire blankets
6.5 **Special Hazards of Combustion Products:** In fire situations oxygen may be liberated and increase the intensity of the fire
6.6 **Behavior in Fire:** Melts, then decomposes to give oxygen gas that increases the intensity of fire. Reacts explosively, either as a solid or a liquid, with all organic matter and some metals
6.7 **Ignition Temperature:** Not pertinent
6.8 **Electrical Hazard:** Not pertinent
6.9 **Burning Rate:** Not pertinent

7. CHEMICAL REACTIVITY

7.1 **Reactivity with Water:** No reaction
7.2 **Reactivity with Common Materials:** Chlorates are powerful oxidizing agents and can cause explosions when heated or rubbed with wood, organic matter, sulfur, and many metals. Even water solutions react in this way if stronger than 30%, especially when warm
7.3 **Stability During Transport:** Starts at 572°F with evolution of oxygen gas. Decomposition may be self-sustaining. Oxygen increases intensity of fires
7.4 **Neutralizing Agents for Acids and Caustics:** Not pertinent
7.5 **Polymerization:** Not pertinent
7.6 **Inhibitor of Polymerization:** Not pertinent

8. WATER POLLUTION

8.1 **Aquatic Toxicity:**
11,000 ppm/perch/threshold toxicity/fresh water
3.8 ppm/scenedesmus/threshold toxicity/fresh water
8.2 **Waterfowl Toxicity:** Data not available
8.3 **Biological Oxygen Demand (BOD):** None
8.4 **Food Chain Concentration Potential:** None

9. SELECTED MANUFACTURERS

1. Kerr-McGee Chemical Corp.
Kerr-McGee Bldg.
Oklahoma City, Okla. 73102

2. Occidental Petroleum Corp.
Hooker Chemical Co.
Industrial Chemicals Division
Niagara Falls, N. Y. 14302

3. Penn-Olin Chemical Co.
Calvert City, Ky. 42029

10. SHIPPING INFORMATION

10.1 **Grades or Purity:** Technical (99.5% minimum), treated (99.0% minimum)
10.2 **Storage Temperature:** Ambient
10.3 **Inert Atmosphere:** No requirement
10.4 **Venting:** Open

11. HAZARD ASSESSMENT CODE

(See Hazard Assessment Handbook, CG 446-3)

SS

12. HAZARD CLASSIFICATIONS

12.1 **Code of Federal Regulations:** Oxidizing material
12.2 **NAS Hazard Rating for Bulk Water Transportation:** Not listed
12.3 **NFPA Hazard Classifications:**

Category	Classification*	
Health Hazard (Blue)	0	1
Flammability (Red)	0	0
Reactivity (Yellow)	2 oxy	2 oxy

*First column refers to non-fire situation

13. PHYSICAL AND CHEMICAL PROPERTIES

13.1 **Physical State at 15°C and 1 atm:** Solid
13.2 **Molecular Weight:** 106.45
13.3 **Boiling Point at 1 atm:** Decomposes
13.4 **Freezing Point:** 478°F = 248°C = 521°K
13.5 **Critical Temperature:** Not pertinent
13.6 **Critical Pressure:** Not pertinent
13.7 **Specific Gravity:** 2.49 at 15°C (solid)
13.8 **Liquid Surface Tension:** Not pertinent
13.9 **Liquid-Water Interfacial Tension:** Not pertinent
13.10 **Vapor (Gas) Specific Gravity:** Not pertinent
13.11 **Ratio of Specific Heats of Vapor (Gas):** Not pertinent
13.12 **Latent Heat of Vaporization:** Not pertinent
13.13 **Heat of Combustion:** Not pertinent
13.14 **Heat of Decomposition:** Not pertinent
13.15 **Heat of Solution:** Not pertinent
13.16 **Heat of Polymerization:** Not pertinent

(Continued on pages 5 and 6)

NOTES

STY

STYRENE

Common Synonyms
Styrol
Vinylbenzene
Phenylethylene

Watery liquid Colorless to light yellow Sweet pleasant odor

Floats on water. Flammable, irritating vapor is produced.

Avoid contact with liquid and vapor. Keep people away
Wear chemical protective suit with self-contained breathing apparatus
Stop discharge if possible
Call fire department
Isolate and remove discharged material
Notify local health and pollution control agencies

Fire

FLAMMABLE
CONTAINERS MAY EXPLODE IN FIRE
Flashback along vapor trail may occur.
Vapor may explode if ignited in an enclosed area
Wear chemical protective suit with self-contained breathing apparatus
Combat fires from safe distance or protected location.
Extinguish with dry chemical, foam, or carbon dioxide
Water may be ineffective on fire
Cool exposed containers with water.

Exposure

CALL FOR MEDICAL AID.

VAPOR
Irritating to eyes, nose and throat.
If inhaled, will cause dizziness or loss of consciousness.
Move to fresh air
If breathing has stopped, give artificial respiration.
If breathing is difficult, give oxygen.

LIQUID
Will burn skin and eyes
Harmful if swallowed
Remove contaminated clothing and shoes.
Flush affected areas with plenty of water.
IF IN EYES, hold eyelids open and flush with plenty of water
IF SWALLOWED and victim is CONSCIOUS, have victim drink water or milk
DO NOT INDUCE VOMITING

Water Pollution

HARMFUL TO AQUATIC LIFE IN VERY LOW CONCENTRATIONS.
Fouling to shoreline.
May be dangerous if it enters water intakes.
Notify local health and wildlife officials.
Notify operators of nearby water intakes.

1. RESPONSE TO DISCHARGE

(See Response Methods Handbook, CG 446-4)

Issue warning — air contaminant
Mechanical containment
Should be removed
Chemical and physical treatment

2. LABEL

3. CHEMICAL DESIGNATIONS

3.1 **Synonyms:** Phenethylene, Phenylethylene Styrol, Styrolene, Vinylbenzene

3.2 **Coast Guard Compatibility Classification:** Olefin

3.3 **Chemical Formula:** $C_6H_5CH{=}CH_2$

3.4 **IMCO/United Nations Numerical Designation:** 3.3/2055

4. OBSERVABLE CHARACTERISTICS

4.1 **Physical State (as shipped):** Liquid

4.2 **Color:** Colorless

4.3 **Odor:** Sweet at low concentrations, characteristic pungent, sharp, disagreeable

5. HEALTH HAZARDS

5.1 **Personal Protective Equipment:** Air supplied mask or approved canister, rubber or plastic gloves, boots, goggles or face shield

5.2 **Symptoms Following Exposure:** Moderate irritation of eyes and skin. High vapor concentrations cause dizziness, drunkenness, and anesthesia

5.3 **Treatment for Exposure:** INHALATION: remove to fresh air, keep warm and quiet, use artificial respiration if needed. INGESTION: do NOT induce vomiting, call physician, no known antidote. SKIN OR EYE CONTACT: flush with plenty of water, for eyes get medical attention

5.4 **Toxicity by Inhalation (Threshold Limit Value):** 100 ppm

5.5 **Short-Term Inhalation Limits:** 100 ppm for 30 min

5.6 **Toxicity by Ingestion:** Grade 2; LD_{50} 0.5 to 5 g/kg

5.7 **Late Toxicity:** Data not available

5.8 **Vapor (Gas) Irritant Characteristics:** Vapors cause moderate irritation such that personnel will find high concentrations unpleasant. The effect is temporary

5.9 **Liquid or Solid Irritant Characteristics:** Causes smarting of the skin and first-degree burns on short exposure, may cause secondary burns on long exposure

5.10 **Odor Threshold:** 0.148 ppm

6. FIRE HAZARDS

6.1 **Flash Point:** 93°F O.C.; 88°F C.C.

6.2 **Flammable Limits in Air:** 1.1%–6.1%

6.3 **Fire Extinguishing Agents:** Water fog, foam, carbon dioxide, or dry chemical

6.4 **Fire Extinguishing Agents Not to be Used:** Water may be ineffective

6.5 **Special Hazards of Combustion Products:** Not pertinent

6.6 **Behavior in Fire:** Vapor is heavier than air and may travel considerable distance to a source of ignition and flash back. At elevated temperatures such as in fire conditions, polymerization may take place which may lead to container explosion

6.7 **Ignition Temperature:** 914°F

6.8 **Electrical Hazard:** Class I, Group D

6.9 **Burning Rate:** 5.2 mm/min

7. CHEMICAL REACTIVITY

7.1 **Reactivity with Water:** No reaction

7.2 **Reactivity with Common Materials:** No reaction

7.3 **Stability During Transport:** Stable

7.4 **Neutralizing Agents for Acids and Caustics:** Not pertinent

7.5 **Polymerization:** May occur if heated above 150°F. Can cause rupture of container. Metal salts, peroxides, and strong acids may also cause polymerization

7.6 **Inhibitor of Polymerization:** Tertiary-butylcatechol, 10-15 ppm

8. WATER POLLUTION

8.1 **Aquatic Toxicity:** 22 ppm/96 hr/bluegill/TL_m/fresh water

8.2 **Waterfowl Toxicity:** Data not available

8.3 **Biological Oxygen Demand (BOD):** 18% (theor.), 412 days

8.4 **Food Chain Concentration Potential:** None

9. SELECTED MANUFACTURERS

1. Amoco Chemicals Corp.
   910 South Michigan Ave.
   Chicago, Ill. 60605
2. Dow Chemical Co.
   Midland, Mich. 48640
3. Monsanto Co.
   Monsanto Polymers & Petrochemicals Co.
   800 North Lindbergh Blvd.
   St. Louis, Mo. 63166

10. SHIPPING INFORMATION

10.1 **Grades or Purity:** 99.5+%

10.2 **Storage Temperature:** Ambient

10.3 **Inert Atmosphere:** No requirement

10.4 **Venting:** Open (flame arrester)

11. HAZARD ASSESSMENT CODE

(See Hazard Assessment Handbook, CG 446-3)

A-T-U-Z

12. HAZARD CLASSIFICATIONS

12.1 **Code of Federal Regulations:** Flammable Liquid

12.2 **NAS Hazard Rating for Bulk Water Transportation:**

Category	Rating
Fire	3
Health	
Vapor Irritant	2
Liquid or Solid Irritant	2
Poisons	2
Water Pollution	
Human Toxicity	1
Aquatic Toxicity	3
Aesthetic Effect	2
Reactivity	
Other Chemicals	2
Water	0
Self Reaction	3

12.3 **NFPA Hazard Classifications:**

Category	Classification
Health Hazard (Blue)	2
Flammability (Red)	3
Reactivity (Yellow)	2

13. PHYSICAL AND CHEMICAL PROPERTIES

13.1 **Physical State at 15°C and 1 atm:** Liquid

13.2 **Molecular Weight:** 104.15

13.3 **Boiling Point at 1 atm:** 293.4°F = 145.2°C = 418.4°K

13.4 **Freezing Point:** −23.1°F = −30.6°C = 242.6°K

13.5 **Critical Temperature:** 703°F = 373°C = 646°K

13.6 **Critical Pressure:** 580 psia = 39.46 atm = 4.00 MN/m^2

13.7 **Specific Gravity:** 0.906 at 20°C (liquid)

13.8 **Liquid Surface Tension:** 32.14 dynes/cm = 0.03214 N/m at 19°C

13.9 **Liquid-Water Interfacial Tension:** 35.48 dynes/cm = 0.03548 N/m at 19°C

13.10 **Vapor (Gas) Specific Gravity:** Not pertinent

13.11 **Ratio of Specific Heats of Vapor (Gas):** 1.074

13.12 **Latent Heat of Vaporization:** 156 Btu/lb = 86.8 cal/g = 3.63×10^5 J/kg

13.13 **Heat of Combustion:** Not pertinent

13.14 **Heat of Decomposition:** Not pertinent

13.15 **Heat of Solution:** Not pertinent

13.16 **Heat of Polymerization:** −277 Btu/lb = −154 cal/g = -6.45×10^5 J/kg

(Continued on pages 5 and 6)

NOTES

Occupational Health Guideline for Styrene

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $C_6H_5CH=CH_2$
- Synonyms: Phenylethylene; vinylbenzene; cinnamene; styrene monomer
- Appearance and odor: Colorless liquid with a sweet aromatic odor at low concentrations. Sharp, penetrating, and disagreeable odor at higher concentrations.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for styrene is 100 parts of styrene per million parts of air (ppm) averaged over an eight-hour work shift, with a ceiling level of 200 ppm and an acceptable peak of 600 ppm for 5 minutes in any three-hour period. The American Conference of Governmental Industrial Hygienists has issued a Notice of Intended Changes of its recommended Threshold Limit Value for styrene from 100 ppm to 50 ppm.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Styrene can affect the body if it is inhaled, is swallowed, or comes in contact with the eyes or skin.

- **Effects of overexposure**

1. Short-term Exposure: Styrene may irritate the eyes, nose, throat, and skin. High concentrations may cause a person to become sleepy or to become unconscious.

2. Long-term Exposure: Repeated skin contact with styrene may produce a skin rash.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to styrene.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to styrene at potentially hazardous levels:

1. Initial Medical Screening: Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from styrene exposure.

—Central nervous system disorders: Since exposure to styrene vapor or liquid on the skin has been observed to result in central nervous system depression and occasional abnormalities in the electroencephalogram, persons with pre-existing disorders may be unusually susceptible to these effects.

—Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of styrene might cause exacerbation of symptoms due to its irritant properties or psychic reflex bronchospasm.

—Skin disease: Styrene is a defatting agent and can cause dermatitis on prolonged exposure. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.

—Kidney disease: Although styrene is not known as a kidney toxin in humans, the importance of this organ in the elimination of toxic substances justifies special consideration in those with possible impairment of renal function.

—Liver disease: Although styrene is not known as a liver toxin in humans, the importance of this organ in the biotransformation and detoxification of foreign substances should be considered before exposing persons with impaired liver function.

2. Periodic Medical Examination: Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

Exposure to concentrations of styrene above 200 ppm

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service   Centers for Disease Control
National Institute for Occupational Safety and Health

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

September 1978

causes irritation of the eyes and upper respiratory tract. There is cracking and inflammation of the skin due to defatting. Higher exposures depress the central nervous system. Electroencephalographic changes have been reported. Styrene is excreted fairly rapidly in the urine, largely as hippuric acid.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 104
2. Boiling point (760 mm Hg): 145 C (293 F)
3. Specific gravity (water = 1): 0.90
4. Vapor density (air = 1 at boiling point of styrene): 3.6
5. Melting point: −30.6 C (−23 F)
6. Vapor pressure at 20 C (68 F): 4.5 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 0.03
8. Evaporation rate (butyl acetate = 1): 0.49

- **Reactivity**

1. Conditions contributing to instability: Styrene is stabilized by a polymerization inhibitor (often tert-butylcatechol). If this is not present in adequate concentrations, styrene can polymerize and explode its container. The polymerization is also speeded up by temperatures above 66 C (150 F).
2. Incompatibilities: Avoid contact with oxidizing agents and catalysts for vinyl polymerization, such as peroxides, strong acids, and aluminum chloride.
3. Hazardous decomposition products: Toxic gases and vapors (such as carbon monoxide) may be released in a fire involving styrene. Styrene fumes are very acrid.
4. Special precautions: Styrene will corrode copper and copper alloys and dissolve rubber.

- **Flammability**

1. Flash point: 32 C (90 F) (closed cup)
2. Autoignition temperature: 490 C (914 F)
3. Flammable limits in air, % by volume: Lower: 1.1; Upper: 6.1
4. Extinguishant: Dry cemical, foam, or carbon dioxide

- **Warning properties**

1. Odor Threshold: May reports that the odor threshold of styrene is 0.08 ppm.
2. Eye Irritation Level: The AIHA *Hygienic Guide* reports that "styrene vapor at concentrations of 200 to 400 ppm was found to have transient irritant effects on the eyes."
4. Evaluation of Warning Properties: Since the odor threshold of styrene is below the permissible exposure limit, it is treated as a material with adequate warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **Eight-Hour Exposure Evaluation**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Ceiling Evaluation**

Measurements to determine employee ceiling exposure are best taken during periods of maximum expected airborne concentrations of styrene. Each measurement should consist of a fifteen (15) minute sample or series of consecutive samples totalling fifteen (15) minutes in the employee's breathing zone (air that would most nearly represent that inhaled by the employee). A minimum of three (3) measurements should be taken on one work shift and the highest of all measurements taken is an estimate of the employee's exposure.

- **Peak Above Ceiling Evaluation**

Measurements to determine employee peak exposure should be taken during periods of maximum expected airborne concentration of styrene. Each measurement should consist of a 30-minute sample or a series of consecutive samples totalling 30 minutes in the employee's breathing zone (air that would most nearly represent that inhaled by the employee). A minimum of three measurements should be taken on one work shift and the highest of all measurements taken is an estimate of the employee's exposure.

- **Method**

Sampling and analyses may be performed by collection of styrene vapors using an adsorption tube with subsequent desorption with carbon disulfide and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure styrene may be used. An analytical method for styrene is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 2, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00260-6).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National

Institute for Occupational Safety and Health.

- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with liquid styrene.
- Clothing wet with liquid styrene should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of styrene from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the styrene, the person performing the operation should be informed of styrene's hazardous properties.
- Non-impervious clothing which becomes contaminated with liquid styrene should be removed promptly and not reworn until the styrene is removed from the clothing.
- Any clothing which becomes wet with liquid styrene should be removed immediately and not reworn until the styrene is removed from the clothing.
- Employees should be provided with and required to use splash-proof safety goggles where liquid styrene may contact the eyes.

SANITATION

- Skin that becomes contaminated with liquid styrene should be promptly washed or showered with soap or mild detergent and water to remove any styrene.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to styrene may occur and control methods which may be effective in each case:

Operation	Controls
Liberation during spray-up manufacture of glass fiber, reinforced styrene-polyester articles	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use during spray application of styrene polyester surface coatings	Process enclosure; local exhaust ventilation; personal protective equipment
Use during hand lay-up of glass fibers, reinforced styrene-polyester articles	Local exhaust ventilation; general dilution ventilation, personal protective equipment
Use during molding of articles or potting electrical components with polystyrene	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use during manufacture of tires and other rubber goods using styrene-butadiene elastomers (SBR)	General dilution ventilation
Use in manufacture of concretes	General dilution ventilation; personal protective equipment
Use during bag lay-up manufacture of glass fiber, reinforced styrene-polyester articles; during use of surface coatings containing styrene-butadiene copolymer resins	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Liberation during die molding of articles made from styrene-polyester resins; during brush application of surface coatings	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in process operations for production of polystyrene, acrylonitrile-butadiene styrene (ABS), styrene-acrylonitrile (SAN), and styrene-butadiene copolymers	Local exhaust ventilation; personal protective equipment
Use in manufacture of surface coatings; use in miscellaneous processes as an elastomer, intermediate, or starting material; use during manufacture of ion-exchange resins (styrene-divinylbenzene copolymer)	Local exhaust ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If styrene gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If styrene gets on the skin, promptly flush the contaminated skin with water. If styrene soaks through the clothing, remove the clothing immediately and flush the skin with water When there is skin irritation, get medical attention.

- **Breathing**

If a person breathes in large amounts of styrene, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

If styrene has been swallowed, do not induce vomiting. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If styrene is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities, absorb on paper towels. Evaporate in a safe place (such as a fume hood). Allow sufficient time for evaporating vapors to completely clear the hood ductwork. Burn the paper in a suitable location away from combustible materials. Large quantities can be collected and atomized in a suitable combustion chamber. Combustion may be improved by mixing with a more flammable liquid.

- Waste disposal methods:

Styrene may be disposed of:

1. By absorbing it in vermiculite, dry sand, earth or a similar material and disposing in a secured sanitary landfill.
2. By atomizing in a suitable combustion chamber. Combustion may be improved by mixing with a more flammable liquid.

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RESPIRATORY PROTECTION FOR STYRENE

Condition	Minimum Respiratory Protection* Required Above 100 ppm
Vapor Concentration	
400 ppm or less	Any chemical cartridge respirator with an organic vapor cartridge(s).** Any supplied-air respirator.** Any self-contained breathing apparatus.**
1000 ppm or less	A chemical cartridge respirator with a full facepiece and an organic vapor cartridge(s).
5000 ppm or less	A gas mask with a chin-style or a front- or back-mounted organic vapor canister. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
Greater than 5000 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

**If eye irritation occurs, full-facepiece respiratory protective equipment should be used.

SULFUR (SULPHUR). S. *Refs.*

(Flowers of Sulfur, Milk of Sulfur, Brimstone)

Specification No.: JAN-S-487

The specification covers five grades of ground S:

A, ground crude S used for black powder.

B, ground crude S used for pyrotechnics compositions.

C, ground crude S used for pyrotechnics compositions.

D, ground refined S used for nongaseous powders and primer compositions.

E, ground crude S used for pyrotechnic compositions. The grades differ slightly in purity and in granulation.

Molecular Weight: 256.53

Crystalline Form: (α) rhombic, (β) monoclinic, (γ) amorphous 1, 46

Color: yellow

Forms of Sulfur: Solid sulfur (S) exists in two crystalline forms, rhombic and monoclinic, and also as an elastomer. The rhombic form is stable at ordinary temperatures. Above the transition temperature of 95.4°C and up to the boiling point monoclinic S is the stable variety. Elastic S is prepared by rapidly chilling liquid S which has been heated to elevated temperatures. The infrared spectrum is identical with that of liquid S. On melting, S becomes a straw-yellow transparent liquid, designated as λ S. The liquid may be supercooled in bulk far below its freezing point to room temperature in the form of droplets which in time may solidify to a clear yellow glass. At about 160°C, the liquid is dark brown. Its color deepens as the temperature is raised, and above 250°C, it turns brownish-black. Apparently the structure of the liquid undergoes an abrupt change at about 160°, and this transformation is accompanied by the absorption of 2.751 cal./g. The sudden and enormous increase in viscosity which occurs at this temperature is one indication of a structural alteration. Other properties show a marked discontinuity. Long chain polymers referred to as μ S, in equilibrium with rings of octatomic molecules, apparently exist in the liquid above 160°. Beyond 230° the viscosity decreases but the color remains dark up to the boiling point, 444.6°C. If S at the boiling point is cooled slowly, it passes through the changes described above in the reverse order. 46 20V3

"Flowers" of sulfur is a term applied to the mined molten S which is finely ground. It is the type used for pyrotechnic purposes.

Density, g./ml.: 1, 46

(solid)	rhombic	2.07
	monoclinic	1.96
	amorphous	1.92

Coefficient of Thermal Expansion: 46

Temp. °C	*Linear (rhombic)*	*Cubic (rhombic)*
0–13	4.567×10^{-5}	13.70×10^{-5}
13–50	7.433×10^{-5}	22.30×10^{-5}
50–78	8.633×10^{-5}	25.90×10^{-5}
78–97	20.67×10^{-5}	62.01×10^{-5}
97–110	103.2×10^{-5}	309.6×10^{-5}

Source: AMCP 706-187

Sulfur (Sulphur) S_8 (page 2)

Heat of Formation, Kcal./mole at 298°K:	(gas) 53.25	1, 9
Free Energy of Formation, Kcal./mole at 298°K:	(gas) 43.57	9
Entropy, cal./deg./mole at 298°K:	(rhombic) 7.62 (monoclinic) 7.78	5, 9 5, 9
See Tables a, b, c, d		
Melting Point, °C: (α) 112.8 (β) 119.25 (γ) about 120		1
Heat of Fusion, cal./g.:	(rhombic) 11.9 (monoclinic) 9.2	9
Boiling Point, °C:	444.6	1, 46
Heat of Vaporization, cal./mole at 717.75°K:	2300	5
Transition Point, °C:		
(rhombic → monoclinic)	95.4	46
(liquid → viscous)	159.9	46
Heat of Transition, cal./g.:		
(rhombic to monoclinic)	2.992	46
(liquid to viscous)	2.751	
Heat of Sublimation, cal./mole at 298°K:	S_8 24,350 S_2 330,840	5
Heat Content or Enthalpy, cal./mole at 298°K:	(solid) 1053	5
See Tables a, b, c, and d		

a. HEAT CONTENT AND ENTROPY OF S (c, l)

(Base, rh–crystals at 298.15°K) 4

T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole
350	290	0.90
368.6 (rh). . . .	400	1.20
368.6 (mon) . . .	485	1.43
392 (mon)	630	1.82
392 (l)	965	2.67
400	1030	2.83
500	1940	4.85
600	2780	6.38
700	3650	7.72
717.8	3810	7.95

S (rh):

Enthalpy: $H_T - H_{298.15} = 3.58T + 3.12 \times 10^{-3}T^2 - 1345$ (0.2 percent; 298–368.6°K)

Heat Capacity: $C_p = 3.58 + 6.24 \times 10^{-3}T$; $\Delta H_{368.6} = 85$

S (mon):

Enthalpy: $H_T - H_{298.15} = 6.20T - 1800$ (0.1 percent; 368.6–392°K)

Heat Capacity: $C_p = 6.20$; ΔH_{392} (fusion) $= 335$

S (l):

Enthalpy: $H_T - H_{298.15} = 8.73T - 2457$ (0.6 percent; 392–717.8°K)

Heat Capacity: $C_p = 8.73$

Source: AMCP 706-187

b. HEAT CONTENT AND ENTROPY OF S (g)

(Base, ideal gas at 298.15°K)

4

T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole	T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole
400	570	1.65	1900	8320	9.79
500	1120	2.88	2000	8830	10.06
600	1660	3.86	2200	9850	10.54
700	2190	4.68	2400	10,875	10.99
800	2715	5.38	2600	11,910	11.40
900	3235	5.99	2800	12,950	11.79
1000	3750	6.53	3000	13,995	12.15
1100	4260	7.02	3500	16,650	12.96
1200	4770	7.46	4000	19,340	13.68
1300	5280	7.87	4500	22,065	14.32
1400	5790	8.25	5000	24,810	14.90
1500	6295	8.60	6000	30,330	15.91
1600	6800	8.92	7000	35,860	16.76
1700	7305	9.23	8000	41,390	17.50
1800	7815	9.52			

S (g):

Enthalpy: $H_T - H_{298.15} = 5.26T - 0.05 \times 10^{-3}T^2 - 0.36 \times 10^5T^{-1} - 1443$
(0.6 percent; 298-2400°K)

Heat Capacity: $C_p = 5.26 - 0.10 \times 10^{-3}T + 0.36 \times 10^5T^{-2}$

Enthalpy: $H_T - H_{298.15} = 4.96T + 0.05 \times 10^{-3}T^2 - 0.60 \times 10^5T^{-1} - 1282$
(0.2 percent; 2400-8000°K)

Heat Capacity: $C_p = 4.96 + 0.10 \times 10^{-3}T + 0.60 \times 10^5T^{-2}$

c. HEAT CONTENT AND ENTROPY OF S_2(g)

(Base, ideal gas at 298.15°K)

4

T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole	T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole
400	810	2.34	1500	10,430	13.79
500	1640	4.18	1600	11,325	14.37
600	2485	5.72	1700	12,225	14.91
700	3345	7.05	1800	13,125	15.43
800	4220	8.22	1900	14,025	15.92
900	5095	9.25	2000	14,925	16.38
1000	5975	10.17	2200	16,730	17.24
1100	6855	11.01	2400	18,545	18.03
1200	7745	11.79	2600	20,360	18.76
1300	8635	12.50	2800	22,175	19.43
1400	9535	13.17	3000	23,995	20.06

Source: AMCP 706-187

$S_2(g)$:

Enthalpy: $H_T - H_{298.15} = 8.72T + 0.08 \times 10^{-3}T^2 + 0.90 \times 10^5T^{-1} - 2909$
(0.3 percent; 298–3000°K)

Heat Capacity: $C_p = 8.72 + 0.16 \times 10^{-3}T - 0.90 \times 10^5T^{-2}$

d. HEAT CONTENT AND ENTROPY OF $S_8(g)$ 4
(Base, ideal gas at 298.15°K)

T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole	T, °K	$H_T - H_{298.15}$ cal./mole	$S_T - S_{298.15}$ cal./deg. mole
400	3935	11.32	800	20,580	40.06
500	7985	20.37	900	24,850	45.09
600	12,125	27.90	1000	29,140	49.62
700	16,330	34.39			

$S_8(g)$:

Enthalpy: $H_T - H_{298.15} = 42.54T + 0.52 \times 10^{-3}T^2 + 5.04 \times 10^5T^{-1} - 14{,}420$
(0.1 percent; 298–1000°K)

Heat Capacity: $C_p = 42.54 + 1.04 \times 10^{-3}T - 5.04 \times 10^5T^{-2}$

Decomposition Temperature: For DTA see Addnl. Ref. 5

Decomposition Products: ——

Vapor Pressure:

Press. mm.	1	10	40	100	400	760	M.P.
Temp. °C	183.8	243.8	288.3	327.2	399.6	444.6	112.8

Form	*Range*	*Equation (P in mm., T in °K)*
rhombic	20–80	$\log P = 11.664 - \frac{5166}{T}$
monoclinic	96–116	$\log P = 11.364 - \frac{5082}{T}$
liquid	25–74	$\log P = 8.70 - \frac{4055}{T}$
	120–325	$\log P = 14.7000 - .0062238T - \frac{5405.1}{T}$
	325–550	$\log P = 7.43287 - \frac{3268.2}{T}$

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X-Ray Crystallographic Data:

System	*Space Group*	*a*	*b*	*c*	*Atoms/ Unit Cell*
rhombic	V_h^{24}	10.37	12.845	24.369	128 (16 eight-membered rings)
monoclinic	C_{2h}^{1}	10.90	10.96	11.02	48 (6 eight-membered rings)

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Hygroscopicity:

Spec. grade, % gain at 70°F in 168 hr.:	none at 40, 50, and 70% R.H. 0.01 at 90% R.H.

33

Source: AMCP 706-187

Sulfur (Sulphur) S. (page 5)

Solubility Data:		
In water:	insoluble	20
In alcohol and ether:	slightly soluble	
In carbon disulphide, 70 g./100 g.:	soluble	
In light petroleum, hot benzene, toluene and benzyl chloride:	soluble	46
Health Hazard: Believed to be nontoxic. Tank car shipments of molten sulfur may accumulate poisonous H_2S gas, which is also flammable and explosive. In unloading operations suitable precautions should be taken.		93, 46
Safety Classifications:		
OSM:	not specified	
Probably class 2 as a pyrotechnic material.		
ICC:	not mentioned	
U.N.	an inflammable solid	
Coast Guard:	hazardous	
Fire and Explosion Hazard: When ignited, molten S will burn in air producing acrid fumes of SO_2, which are irritating, suffocating and lachrymatory, and inhalation should be avoided. Burning S can react vigorously with oxidizing materials. Sulfur when compounded with chlorates and some other oxidizing agents, forms sensitive explosive mixtures. When mixed with carbon, lampblack, fats and oils, S forms mixtures which can ignite spontaneously. It should be stored away from oxidizing agents. To fight fire use water.		12, 14, 46, 75
Electrostatic Sensitivity: When rubbed with most substances it becomes negatively charged.		
Minimum energy required for ignition by an electric spark, millijoules:	15	26
Ignition Temperature, in air at atmospheric pressure, °C:	248-261	46
closed cup:	405°F	75
open cup:	440°F	
Minimum Explosive Concentration of dust, mg./l.:	35	26
	30	22
Heat of Combustion, Kcal./g.:	(monoclinic) 2.240	1
	(rhombic) 2.200	

Additional References:

1) "The Sulphur Data Book," W. N. Tuller, Ed., McGraw-Hill Book Co., New York (1954)
2) "The National Fire Codes, Vol. II, Combustible Solids, Dusts, Chemicals and Explosives," National Fire Protection Association, Inc., Boston, Mass. (1958)
3) "The National Fire Codes, Vol. II, The Prevention of Dust Explosions." National Fire Protection Association, Inc., Boston, Mass. (1952)
4) "Sulfur May Have Helical Structure," C & EN, p. 44 (Sept. 5, 1960)
5) Trans. Faraday Soc. 55, No. 444, 2221 (1959)

Source: AMCP 706-187

TOL | TOLUENE

Common Synonyms
Toluol
Methylbenzene
Methylbenzol

Watery liquid | **Colorless** | **Pleasant odor**

Floats on water. Flammable, irritating vapor is produced

Stop discharge if possible. Keep people away.
Shut off ignition sources and call fire department
Stay upwind and use water spray to "knock down" vapor
Avoid contact with liquid and vapor.
Isolate and remove discharged material
Notify local health and pollution control agencies

Fire

FLAMMABLE
Flashback along vapor trail may occur
Vapor may explode if ignited in an enclosed area

Wear goggles and self-contained breathing apparatus
Extinguish with dry chemical, foam, or carbon dioxide
Water may be ineffective on fire
Cool exposed containers with water

Exposure

CALL FOR MEDICAL AID

VAPOR
Irritating to eyes, nose and throat.
If inhaled, will cause nausea, vomiting, headache, dizziness, difficult breathing, or loss of consciousness.

Move to fresh air.
If breathing has stopped, give artificial respiration.
If breathing difficult, give oxygen.

LIQUID
Irritating to skin and eyes.
If swallowed, will cause nausea, vomiting or loss of consciousness.

Remove contaminated clothing and shoes.
Flush affected areas with plenty of water.
IF IN EYES, hold eyelids open and flush with plenty of water
IF SWALLOWED and victim is CONSCIOUS, have victim drink water or milk
DO NOT INDUCE VOMITING

Water Pollution

Dangerous to aquatic life in high concentrations.
Fouling to shoreline.
May be dangerous if it enters water intakes.

Notify local health and wildlife officials.
Notify operators of nearby water intakes

1. RESPONSE TO DISCHARGE

(See Response Methods Handbook, CG 446-4)

Issue warning: high flammability
Evacuate area

2. LABEL

3. CHEMICAL DESIGNATIONS

3.1 **Synonyms:** Methylbenzene
Methylbenzol
Toluol

3.2 **Coast Guard Compatibility Classification:** Aromatic hydrocarbon

3.3 **Chemical Formula:** $C_6H_5CH_3$

3.4 **IMCO/United Nations Numerical Designation:** 3.2/1294

4. OBSERVABLE CHARACTERISTICS

4.1 **Physical State (as shipped):** Liquid

4.2 **Color:** Colorless

4.3 **Odor:** Pungent, aromatic, benzene-like; distinct, pleasant

5. HEALTH HAZARDS

5.1 **Personal Protective Equipment:** Air-supplied mask; goggles or face shield; plastic gloves

5.2 **Symptoms Following Exposure:** Vapors irritate eyes and upper respiratory tract; cause dizziness, headache, anesthesia, respiratory arrest. Liquid irritates eyes and causes drying of skin. If aspirated, causes coughing, gagging, distress, and rapidly developing pulmonary edema. If ingested causes vomiting, griping, diarrhea, depressed respiration.

5.3 **Treatment for Exposure:** INHALATION: remove to fresh air; give artificial respiration and oxygen if needed; call a doctor. INGESTION: do NOT induce vomiting; call a doctor. EYES: flush with water for at least 15 min. SKIN: wipe off, wash with soap and water.

5.4 **Toxicity by Inhalation (Threshold Limit Value):** 100 ppm

5.5 **Short-Term Inhalation Limits:** 600 ppm for 30 min

5.6 **Toxicity by Ingestion:** Grade 2; LD_{50} 0.5 to 5 g/kg

5.7 **Late Toxicity:** Kidney and liver damage may follow ingestion

5.8 **Vapor (Gas) Irritant Characteristics:** Vapors cause a slight smarting of the eyes or respiratory system if present in high concentrations. The effect is temporary.

5.9 **Liquid or Solid Irritant Characteristics:** Minimum hazard. If spilled on clothing and allowed to remain, may cause smarting and reddening of the skin.

5.10 **Odor Threshold:** 0.17 ppm

6. FIRE HAZARDS

6.1 **Flash Point:** 40°F C.C.; 55°F O.C.

6.2 **Flammable Limits in Air:** 1.27%-7%

6.3 **Fire Extinguishing Agents:** Carbon dioxide or dry chemical for small fires, ordinary foam for large fires

6.4 **Fire Extinguishing Agents Not to be Used:** Water may be ineffective

6.5 **Special Hazards of Combustion Products:** Not pertinent

6.6 **Behavior in Fire:** Vapor is heavier than air and may travel a considerable distance to a source of ignition and flash back

6.7 **Ignition Temperature:** 997°F

6.8 **Electrical Hazard:** Class I, Group D

6.9 **Burning Rate:** 5.7 mm/min

7. CHEMICAL REACTIVITY

7.1 **Reactivity with Water:** No reaction

7.2 **Reactivity with Common Materials:** No reaction

7.3 **Stability During Transport:** Stable

7.4 **Neutralizing Agents for Acids and Caustics:** Not pertinent

7.5 **Polymerization:** Not pertinent

7.6 **Inhibitor of Polymerization:** Not pertinent

11. HAZARD ASSESSMENT CODE

(See Hazard Assessment Handbook, CG 446-3)

A-T-U

12. HAZARD CLASSIFICATIONS

12.1 **Code of Federal Regulations:** Flammable liquid

12.2 **NAS Hazard Rating for Bulk Water Transportation:**

Category	Rating
Fire	3
Health	
Vapor Irritant	1
Liquid or Solid Irritant	1
Poisons	2
Water Pollution	
Human Toxicity	1
Aquatic Toxicity	3
Aesthetic Effect	2
Reactivity	
Other Chemicals	1
Water	0
Self-Reaction	0

12.3 **NFPA Hazard Classifications:**

Category	Classification
Health Hazard (Blue)	2
Flammability (Red)	3
Reactivity (Yellow)	0

8. WATER POLLUTION

8.1 **Aquatic Toxicity:** 1180 mg/l/96 hr/sunfish/TLm/fresh water

8.2 **Waterfowl Toxicity:** Data not available

8.3 **Biological Oxygen Demand (BOD):** 0%, 5 days; 38% (theor.), 8 days

8.4 **Food Chain Concentration Potential:** None

9. SELECTED MANUFACTURERS

1 Exxon Chemical Co.
Houston, Tex. 77001

2 Shell Chemical Co.
Petrochemicals Division
Houston, Tex. 77001

3 Sun Oil Co.
St. Davids, Pa. 19087

10. SHIPPING INFORMATION

10.1 **Grades or Purity:** Research, reagent, nitration: all 99.8+%; industrial contains 94+%, with 5% xylene and small amounts of benzene and nonaromatic hydrocarbons; 90/120: less pure than industrial

10.2 **Storage Temperature:** Ambient

10.3 **Inert Atmosphere:** No requirement

10.4 **Venting:** Open (flame arrester) or pressure-vacuum

13. PHYSICAL AND CHEMICAL PROPERTIES

13.1 **Physical State at 15°C and 1 atm:** Liquid

13.2 **Molecular Weight:** 92.14

13.3 **Boiling Point at 1 atm:** 231.1°F = 110.6°C = 383.8°K

13.4 **Freezing Point:** −139°F = −95.0°C = 178.2°K

13.5 **Critical Temperature:** 605.4°F = 318.6°C = 591.8°K

13.6 **Critical Pressure:** 596.1 psia = 40.55 atm = 4.108 MN/m^2

13.7 **Specific Gravity:** 0.867 at 20°C (liquid)

13.8 **Liquid Surface Tension:** 29.0 dynes/cm = 0.0290 N/m at 20°C

13.9 **Liquid-Water Interfacial Tension:** 36.1 dynes/cm = 0.0361 N/m at 25°C

13.10 **Vapor (Gas) Specific Gravity:** Not pertinent

13.11 **Ratio of Specific Heats of Vapor (Gas):** 1.089

13.12 **Latent Heat of Vaporization:** 155 Btu/lb = 86.1 cal/g = 3.61×10^5 J/kg

13.13 **Heat of Combustion:** −17,430 Btu/lb = −9686 cal/g = -405.5×10^5 J/kg

13.14 **Heat of Decomposition:** Not pertinent

13.15 **Heat of Solution:** Not pertinent

13.16 **Heat of Polymerization:** Not pertinent

(Continued on pages 5 and 6)

NOTES

REVISED 1978

Occupational Health Guideline for Toluene

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $C_6H_5CH_3$
- Synonyms: Toluol; phenylmethane; methylbenzene
- Appearance and odor: Colorless liquid with an aromatic odor, like benzene.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for toluene is 200 parts of toluene per million parts of air (ppm) averaged over an eight-hour work shift, and during any such work shift, 300 ppm toluene may not be exceeded except that a peak of 500 ppm toluene is permitted for 10 minutes during the eight-hour work shift. NIOSH has recommended that the permissible exposure limit be reduced to 100 ppm toluene averaged over an eight-hour work shift with a ceiling level of 200 ppm averaged over a ten-minute period. The NIOSH Criteria Document for Toluene should be consulted for more detailed information.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Toluene can affect the body if it is inhaled, if it comes in contact with the eyes or skin, or if it is swallowed. It may enter the body through the skin.

- **Effects of overexposure**

1. Short-term Exposure: Toluene may cause irritation of the eyes, respiratory tract, and skin. It may also cause fatigue, weakness, confusion, headache, dizziness, and drowsiness. Peculiar skin sensation may be produced such as a "pins and needles feeling" or numbness. Very high concentrations may cause unconsciousness and death. The liquid splashed in the eye may cause irritation and temporary damage. Inhalation may also cause difficulty in seeing in bright light. If liquid toluene is splashed in the eyes, it will cause temporary irritation.

2. Long-term Exposure: Repeated or prolonged exposure to liquid toluene may cause drying and cracking of the skin.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to toluene.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to toluene at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of the central nervous system, liver and kidneys should be stressed. The skin should be examined for evidence of chronic disorders.

—Urinalysis: Since proper kidney function is necessary for biologic monitoring, a urinalysis should be obtained to include at a minimum specific gravity, albumin, glucose, and a microscopic on centrifuged sediment. The urine should be analyzed for hippuric acid to obtain a background level.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis. Hippuric acid level in urine may be an indicator of the level of toluene exposure.

- **Summary of toxicology**

Toluene vapor causes narcosis. Controlled exposure of human subjects to 200 ppm for 8 hours produced mild fatigue, weakness confusion, lacrimation, and paresthesia; at 600 ppm for 8 hours there were also euphoria, headache, dizziness, dilated pupils and nausea; at 800

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

ppm for 8 hours, symptoms were more pronounced, and after-effects included nervousness, muscular fatigue, and insomnia persisting for several days. Severe but reversible liver and kidney injury occurred in a person who was a glue-sniffer for 3 years; the chief component of the inhaled solvent was toluene (80% V/V); other ingredients were not listed. In workers exposed for many years to concentrations in the range of 80 to 300 ppm, there was no clinical or laboratory evidence of altered liver function. Toluene exposure does not result in the hematopoietic effects caused by benzene; the myelotoxic effects previously attributed to toluene are judged by more recent investigations to be the result of concurrent exposure to benzene present as a contaminant in the commercial toluene used. Most of the toluene absorbed from inhalation is metabolized to benzoic acid, conjugated with glycine in the liver to form hippuric acid, and excreted in the urine; the average amount of hippuric acid excreted in the urine by individuals not exposed to toluene is approximately 0.7 to 1.0 g/l of urine. The liquid splashed in the eyes of two workers caused transient corneal damage and conjunctival irritation; complete recovery occurred within 48 hours. Repeated or prolonged skin contact with liquid toluene has a defatting action, causing drying, fissuring, and dermatitis.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 92.1
2. Boiling point (760 mm Hg): 111 C (231 F)
3. Specific gravity (water = 1): 0.86
4. Vapor density (air = 1 at boiling point of toluene): 3.14
5. Melting point: −95 C (−139 F)
6. Vapor pressure at 20 C (68 F): 22 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 0.05
8. Evaporation rate (butyl acetate = 1): 2.24

- **Reactivity**

1. Conditions contributing to instability: Containers may burst at elevated temperatures.
2. Incompatibilities: Contact with strong oxidizers may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as carbon dioxide and carbon monoxide) may be released in a fire involving toluene.
4. Special precautions: Toluene will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: 4 C (40 F) (closed cup)
2. Autoignition temperature: 480 C (896 F)
3. Flammable limits in air, % by volume: Lower: 1.27; Upper: 7.1
4. Extinguishant: Carbon dioxide, dry chemical, foam

- **Warning properties**

1. Odor Threshold: The American National Standards Institute (ANSI) states that "the odor of toluene is detectable by most people at concentrations in the range of 10 to 15 ppm. The odor has little value as a warning property."

Patty points out that olfactory fatigue occurs rapidly upon exposure to toluene.

2. Eye Irritation Level: Grant states that "the vapors of toluene cause noticeable sensation of irritation to human eyes at 300 to 400 ppm in air, but even at 800 ppm irritation is slight."

ANSI reports that "irritation of eyes, mucous membranes, and upper respiratory tract may occur while workers are exposed to low concentrations of toluene. There is a considerable range of variation (100 to 500 ppm) between individuals, some finding any concentration of toluene objectionable. Commercial grades of toluene vary in irritant properties."

3. Evaluation of Warning Properties: Because of its irritant effects, toluene is judged to have good warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **Eight-Hour Exposure Evaluation**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Ceiling Evaluation**

Measurements to determine employee ceiling exposure are best taken during periods of maximum expected airborne concentrations of toluene. Each measurement should consist of a ten (10) minute sample or series of consecutive samples totalling ten (10) minutes in the employee's breathing zone (air that would most nearly represent that inhaled by the employee). A minimum of three (3) measurements should be taken on one work shift and the highest of all measurements taken is an estimate of the employee's exposure.

- **Peak Above Ceiling Evaluation**

Measurements to determine employee peak exposure should be taken during periods of maximum expected airborne concentration of toluene. Each measurement should consist of a 10-minute sample or a series of consecutive samples totalling 10 minutes in the employee's breathing zone (air that would most nearly represent that inhaled by the employee). A minimum of three measurements should be taken on one work shift and the highest of all measurements taken is an estimate of the employee's exposure.

- **Method**

Sampling and analyses may be performed by collection of vapors using an adsorption tube with a subsequent desorption of toluene with carbon disulfide and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure toluene may be used. An analytical method for toluene is in the *NIOSH Manual of Analytical Methods,* 2nd Ed., Vol. 3, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00261-4).

Methods for Set V" (order number PB 262 524).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with liquid toluene.
- Any clothing which becomes wet with liquid toluene should be removed immediately and not reworn until the toluene is removed from the clothing.
- Clothing wet with toluene should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of toluene from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the toluene, the person performing the operation should be informed of toluene's hazardous properties.
- Employees should be provided with and required to use splash-proof safety goggles where liquid toluene may contact the eyes.
- Where there is any possibility that employees' eyes may be exposed to toluene, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

- Skin that becomes wet with liquid toluene should be promptly washed or showered with soap or mild detergent and water to remove any toluene.
- Employees who handle liquid toluene should wash their hands thoroughly with soap or mild detergent and water before eating or smoking.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to toluene may occur and control methods which may be effective in each case:

Operation	Controls
Use as a solvent in pharmaceutical, chemical, rubber, and plastics industries; as a thinner for paints, lacquer, coatings, and dyes; as a paint remover; insecticides	Process enclosure; general dilution ventilation; local exhaust ventilation; personal protective equipment
Use as starting material and intermediate in organic chemical and chemical synthesis industries	Process enclosure; general dilution ventilation; local exhaust ventilation; personal protective equipment
Use in manufacture of artificial leather; fabric and paper coatings; photogravure ink production; spray surface coating; as a diluent (cellulose ester lacquers)	Process enclosure; general dilution ventilation; local exhaust ventilation; personal protective equipment
Use as constituent in formulation of automotive and aviation fuels	Process enclosure; general dilution ventilation; local exhaust ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If liquid toluene gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation is present after washing, get medical attention. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If liquid toluene gets on the skin, promptly wash the contaminated skin using soap or mild detergent and water. If liquid toluene soaks through the clothing, remove the clothing immediately and wash the skin using soap or mild detergent and water. If irritation persists after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of toluene, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When toluene has been swallowed, get medical attention immediately. Do not attempt to make the exposed person vomit.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If toluene is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities, absorb on paper towels. Evaporate in a safe place (such as a fume hood). Allow sufficient time for evaporating vapors to completely clear the hood ductwork. Burn the paper in a suitable location away from combustible materials. Large quantities can be reclaimed or collected and atomized in a suitable combustion chamber. Toluene should not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion. Sewers designed to preclude the formation of explosive concentrations of toluene vapors are permitted.

- Waste disposal method:

Toluene may be disposed of by atomizing in a suitable combustion chamber.

ADDITIONAL INFORMATION

To find additional information on toluene, look up toluene in the following documents:

- Medical Surveillance for Chemical Hazards
- Respiratory Protection for Chemical Hazards
- Personal Protection and Sanitation for Chemical Hazards
- NIOSH Criteria Document for Toluene (July 1973)

These documents are available through the NIOSH Division of Technical Services, 4676 Columbia Parkway, Cincinnati, Ohio 45226.

REFERENCES

- American Conference of Governmental Industrial Hygienists: "Toluene," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.
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- "Occupational Exposure to Toluene," *Federal Register*, 40:46206-46219, October 6, 1975.
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- Union Carbide Corporation, Industrial Medicine and Toxicology Department: *Toxicology Studies - Toluene*, New York, 1970.

RESPIRATORY PROTECTION FOR TOLUENE

Condition	Minimum Respiratory Protection* Required Above 200 ppm
Vapor Concentration	
500 ppm or less	Any chemical cartridge respirator with an organic vapor cartridge(s). Any supplied-air respirator. Any self-contained breathing apparatus.
1000 ppm or less	A chemical cartridge respirator with a full facepiece and an organic vapor cartridge(s).
2000 ppm or less	A gas mask with a chin-style or a front- or back-mounted organic vapor canister. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
Greater than 2000 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

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APPENDIX B

HAZARD FAULT TREE ANALYSIS

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The attached hazard assessment tree in Figure 2 depicts undesired events and the effects which could result from accidental releases of hazardous chemicals. These events can be applied to statistical probabilities and indicate the singular or combination occurrences required to produce undesired effects. It can be used to assess modes of transportation and handling procedures and to evaluate accidental releases of colored smoke mixes or their smoke by-products.

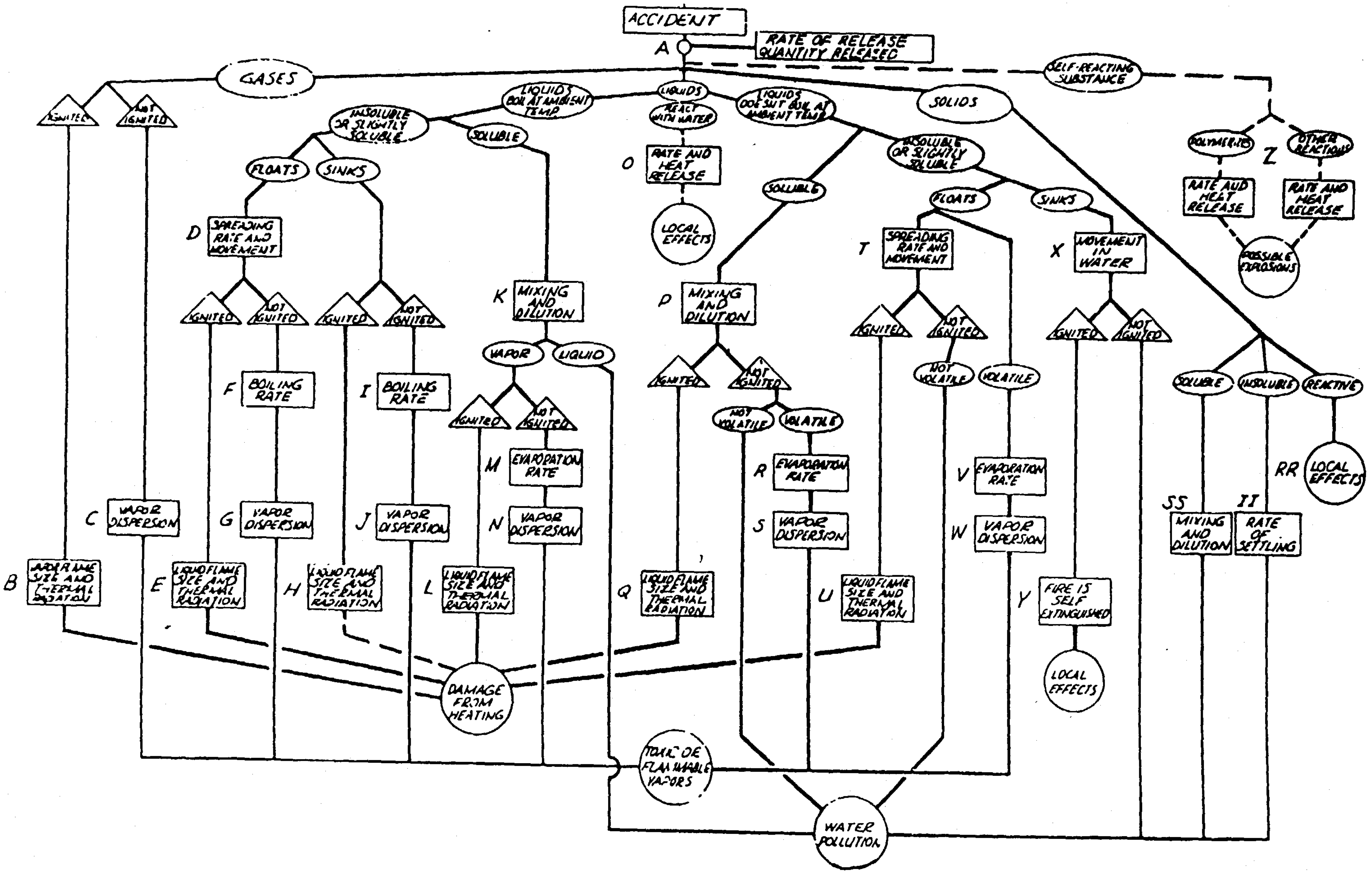

Figure 2. Hazard Assessment Tree

APPENDIX C

THE EFFECTS OF CLIMATIC AND GEOLOGICAL CONDITIONS ON DISPERSION CLOUDS

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The effects of weather, particularly wind speed and direction, and terrain conditions are important factors to be considered in smoke operations. The movement of smoke depends upon the speed and direction of the wind. Wind direction and velocity are important in estimating the amount of smoke required and the effects produced. Another factor is atmospheric stability - temperature, humidity, precipitation, and cloud cover.

1. Winds*

Transport (steering) winds have the greatest influence on smoke operations. Transport of the smoke plume from a surface source may occur in one or more layers extending several hundred meters above the surface. Heat is released when smoke is produced and the heat may cause some of the smoke plume to rise to high levels. Accurate estimates of transport wind require measurements in these layers.

The movement of smoke depends on the speed and direction of the wind. These factors are important in determining the number of smoke-producing sources needed and the requirements for munitions for a given smoke operation. Placement of smoke varies with windspeed. Difficulties are encountered with smoke generators if windspeed is outside the desired range (4-10 knots). Some smokes tend to rise when the wind is less than 4 knots and are torn apart by winds greater then 13 knots. Additional generators may be required to establish and maintain a colored smoke signal at high windspeeds. Windspeed also has a major influence on persistence and duration of a screen, as well as on the distance of travel. The effects of wind direction on smoke clouds are depicted in Figure 3.

Appropriate placement of smoke sources varies, depending on the wind direction encountered in the target area (Figure 3).

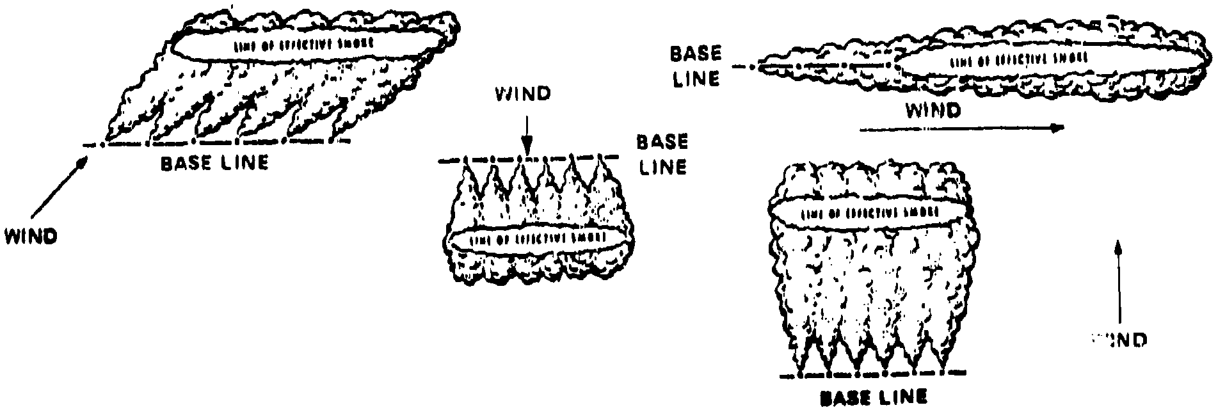

Figure 3. Effect of Prevailing Wind Direction

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*Data included in this Climatic and Geological Conditions section was gathered from the following sources.

1. Smoke, an Obscuration Primer, Joint Technical Coordinating Group for Munitions Effectiveness, 61 JTCG/ME-77-13, 13 March 1978 (UNCLASSIFIED).

2. Rengers, E., Dugway Proving Ground, Utah, Personal Communications, May 1983.

2. Atmospheric Stability - Temperature.

The rate of vertical spread from a source on a stationary surface depends on air stability. In unstable air, smoke will rise more quickly than in stable air. Conditions of atmospheric stability that are of interest are inversion, neutral, and lapse; these result from temperature differences of the air from the surface upward. From these gradients, it can be predicted whether a smoke cloud will remain at a constant altitude (inversion), rise at a moderate rate (neutral), or rise rapidly (lapse). The effect of temperature on smoke is slight. The only effect is the relationship of temperature to relative humidity and a warning of the smoke cloud due to solar radiation.

(a) Land Inversion.

An inversion exists when there is an increase in air temperature with an increase in height above the ground. During an inversion, smoke spreads and diffuses slowly. These conditions are favorable for production of a smoke haze or area screen (Figure 4) and occur on clear calm nights.

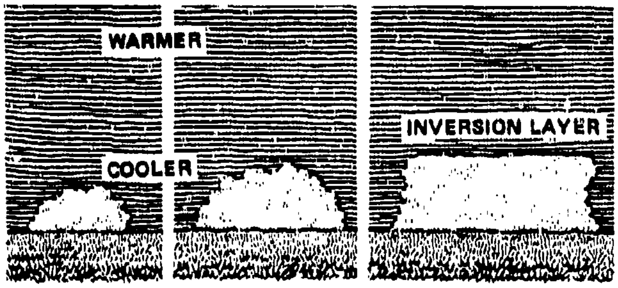

Figure 4. Development of Smoke Cloud - Inversion

(b) Land Neutral.

Neutral conditions have characteristics between lapse and inversion, since no temperature gradient exists. Neutral tending toward lapse is favorable for smoke curtains; neutral tending toward inversion is favorable for area screens (Figure 5). These conditions occur an hour or so before and after sunrise or sunset.

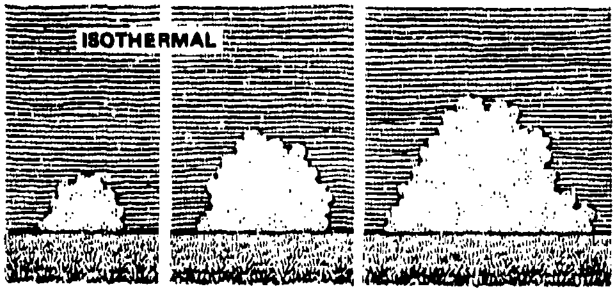

Figure 5. Development of Smoke Cloud - Neutral

(c) Land Lapse.

A lapse condition exists when there is a decrease in air temperature with an increase in height above the ground. The air is unstable, with much air turbulence; smoke tends to rise and diffuse rapidly (Figure 6). The lapse condition is favorable for production of smoke curtains and is least favorable for smoke screens. It occurs on clear days when winds are light.

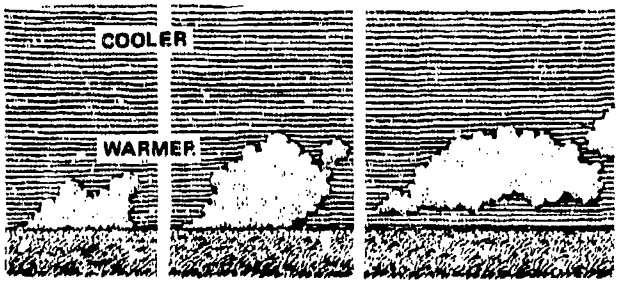

Figure 6. Development of Smoke Cloud - Lapse

(d) The Land-Air Interface.

In the evening and at night following cooling of the earth, there is a rapid cooling of air close to the surface; therefore, the heavier, cooler air is beneath a warmer layer. This is the most stable condition. Over land, the lapse condition is most probable on clear summer days from about 2 hours after sunrise to about 2 hours before sunset; this results in an onshore breeze during the day. At night, warm air rising from the water results in offshore breezes.

3. Humidity.

Colored smoke particles absorb moisture and increase in size, thereby increasing their density and making the smoke more effective. Therefore, high humidity is a favorable employment condition.

4. Precipitation.

Rain and snow reduce visibility but will not adversely affect colored smoke too much. Against a snowy background, the colors will be more visible.

5. Cloud Cover.

When the sky is more than 70 percent covered with clouds, a neutral temperature gradient prevails. The atmosphere is moderately stable, and conditions are generally favorable for smoke.

6. Terrain.

Since smoke is carried by the wind, it normally follows the earth's contours. On flat or unbroken terrain and over water, smoke streamers take longer to spread out and mix. On the other hand, trees and buildings tend to mix smoke streamers and increase smoke coverage. Large hill masses and rugged terrain cause strong crosscurrents which disperse smoke, causing holes and unevenness.

(a) Arctic.

Smoke operations in arctic regions or other cold weather areas present special problems common to all types of units. Preventive maintenance for individual equipment in cold climates is given in appropriate technical manuals. On clear days, stable conditions exist over snowy surfaces and are strongest about sunrise. Smoke tends to remain near the surface and may travel for long distances before dissipating. In extremely cold, smoke clouds last longer than under more temperate conditions.

(b) Desert.

All deserts have certain characteristics in common -- lack of water, absence of vegetation, large areas of sand, extreme temperature ranges, and brilliant sunlight. Desert sands absorb heat from the sun and cause appreciable differences in horizontal temperature, which in turn may cause whirlwinds. The soil is heated during the day to such an extent that smoke operations become extremely difficult because of strong unstable conditions. Smoke tends to pillar because of rising air currents. High winds and dust storms occur throughout the year. Smoke is more effective in early morning and late evening, or on an overcast day when neutral atmospheric conditions exist.

(c) Mountain.

Mountain operations are characterized by the difficulties encountered due to terrain. Because of transportation difficulties and probable limited resupply quantities, screening smokes are a problem. This is not true with the smaller quantities required for signaling and deployment using grenade launchers. Steep hills split winds so they eddy around and over the hill. Thermally induced slope winds occur throughout the day and night. These conditions make it extremely difficult to utilize smoke signals. Wind currents, eddies, and turbulence must be continuously studied and observed.

(d) Jungle.

Smoke used in dense vegetation tends to spread slowly downwind and downslope and to follow creek beds and gullies. Jungle weather is usually hot, humid, and characterized by sudden changes. Windspeed in jungle areas normally does not exceed 3 kilometers per hour.

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Science Applications Inc.
ATTN: Mr. Robert E. Turner 1
1010 Woodman Drive, Suite 200
Dayton, OH 45432

Creative Optics 1
25 Washington St
Bedford, MA 01730

McDonnell Douglas Astro Co
ATTN: John Adams (A-3-210,11-1) 1
5301 Bolsa Ave
Huntington Beach, CA 92647

BMD Program Office
ATTN: Dick McAtee, Rm. 7S14 1
5001 Eisenhower Ave
Alexandria, VA 22333

Dr. W. Michael Farmer, Assoc Prof, Physics
University of Tennessee Space Institute 1
Tullahoma, TN 37388

Commander
Tooelle AD
ATTN: SDSTE-AE (Dr. J.L. Bishop) 1
Tooele, UT 84074

ARNG
Operating Activity Center
ATTN: NGB-ARI-E/Bldg E6810 1
Aberdeen Proving Ground, MD 21010

Commander
USA Environmental Hygiene Agency
ATTN: HSHB-O (B. Donovan) 2
ATTN: Librarian, Bldg 2100 1
Aberdeen Proving Ground, MD 21010