POLLUTION PREVENTION SCOPING

FOR

CHLOROETHANE

APRIL 3, 1991

CMA 052320

LIFECYCLE ANALYSIS AND POLLUTION PREVENTION SCOPING FOR CHLOROETHANE
APRIL 3, 1991

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CMA 052321

TABLE OF CONTENTS

SUMMARY AND DISPOSITION ALTERNATIVES: CHLOROETHANE APRIL 3, 1991

INTRODUCTION

Chloroethane was identified during preliminary screening (pre-RM1) as a high volume chemical with substantial air and water releases reported in TRI. A recent NTP bioassay shows chloroethane to be a potent multi-site mouse carcinogen.

RM1 screening determined chloroethane to be a good candidate for the Risk Reduction List due to high air releases. The RM1 decision meeting recommended that health effects information gathered on chloroethane be referred to OSHA for consideration and that an informal exchange of health effects information with the FDA would be beneficial. In addition, some follow up work regarding chloroethane's use in topical anesthetics was suggested, and a confirmation of the slope factor used in the RM1 risk characterization was requested.

A preliminary RM2 meeting set a date for scoping potential pollution prevention oriented approaches to mitigating potential environmental problems associated with chloroethane. In addition, informati n was requested concerning the use of chloroethane in foamed plastics. ETD was assigned the lead to develop the framework of a pollution prevention scoping exercise using chloroethane as an example.

A workgroup was convened, made up of the staff and Section Chief participants in the RM1 sc-eening exercise. A lifecycle analysis and pollution prevention opportunities scoping methodology was designed which would utilize data developed during the RM1 screening activities to develop appropriate risk reduction alternatives. The methodology arranges the RM1 data to correspond with use categories. This arrangement allows for quick identification of missing data and its importance to developing technical alternatives. The standardization provided by the methodology facilitates quick review by staff and management. Information within each use is arranged in a logical order flowing from identification of uses, description of use processes, identification of releases, estimates of exposures, characterization of risks, and evaluation of how the risk reduction hierarchy of source reduction, recycling/reuse and control technologies could be used to achieve a goal of pollution prevention in the target uses. The additional work required to effect scoping for chloroethane included primarily:

- o the rearrangement of information into the new pattern,
- o RM1 screening level information gathered by RIB, CEB and ICB for each of the use areas,
- o a screening level effort by CEB to evaluate the hierarchy of controls for each of the uses.

(A "screening level" of effort is defined as 10 hours or less per item, in this case per use for each topic. Thus, market information for each use was between 30-40 hours of additional effort over the information collected for RM1.)

The results obtained from this exercise confirmed the recommendations obtained during RM1 and provided greater certainty for those recommendations (referral to OSHA and FDA). This exercise has identified a new area of possible concern, namely consumer exposure to foamed plastic used in construction, and identified a role for OTS in coordinating pollution prevention and cross-media issues in OAR rulemaking. In addition, this methodology has allowed for specific identification of areas where future work may be necessary pending results of the proposed ODW test rule. Finally, this document provides the basis for developing future investigatory work, by clarifying the relationship between the various parts of the analysis which are necessary to characterize risk and evaluate risk reduction opportunities in each use.

INDUSTRY PROFILE

Manufacturers

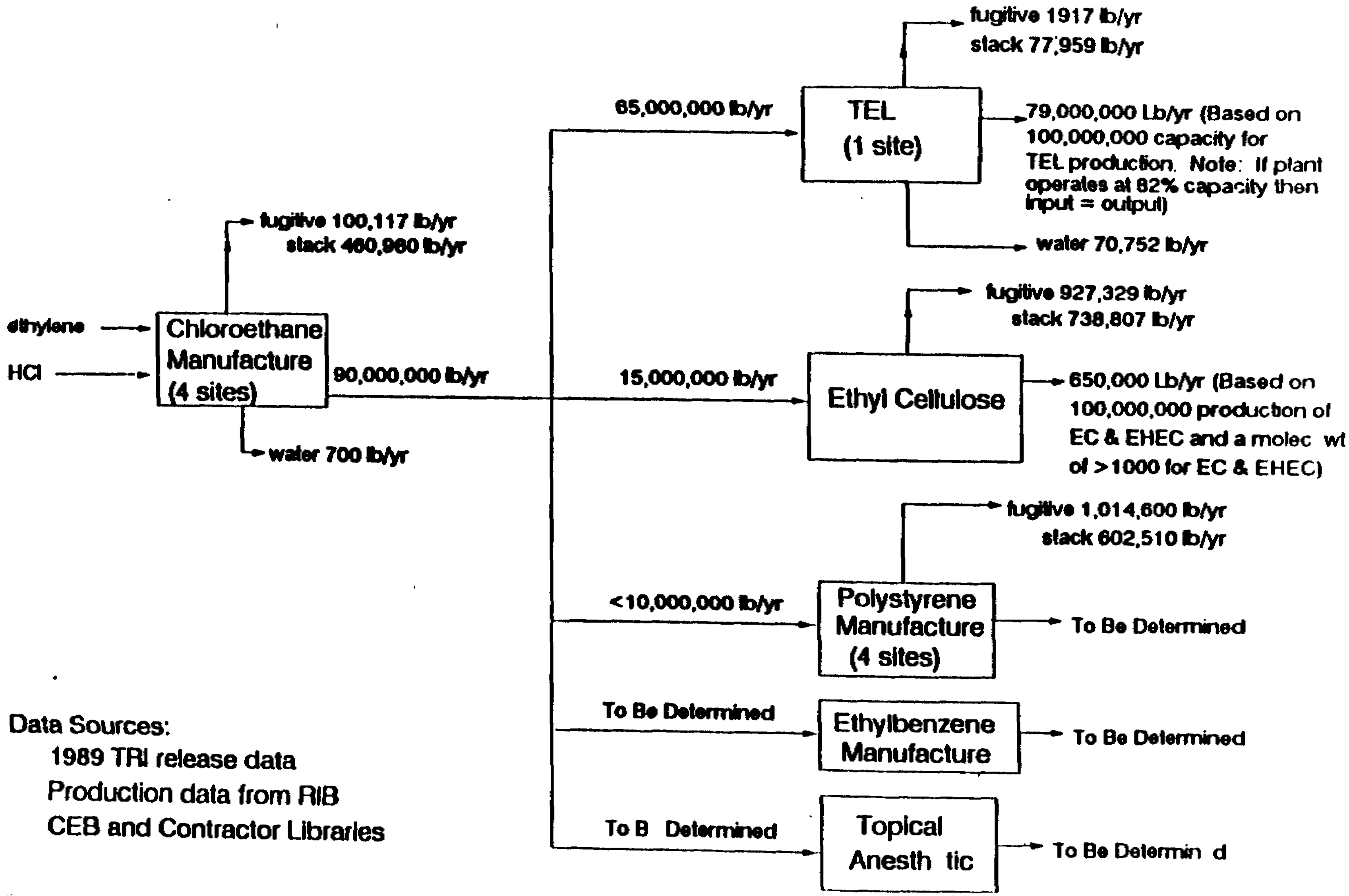
Dow Chemical
DuPont
Ethyl Corp.
PPG Industries Inc.

Total Production Volume: 1989 - 120 million lbs.
U.S. consumption: 90 million lbs.
Export: 30 million lbs.

Market Trends: U. S. consumption of chloroethane has decreased steadily since 1970 because of phaseout of lead in gasoline. U. S. production of chloroethane in the last four years, however, has been stable because of strong export demand, eg., the Far East, Middle East, Africa and Latin America. Western Europe still uses lead alkyl antiknock mixes as its most important octane enhancer. PPG and DuPont report that they will stop producing lead based antiknock mixtures by the end of the year.

Uses	% of choloroethane used
1. Tetraethyllead (TEL)	75%
Used as gasoline additive for purposes of octane boosting and valve lubrication	
2. Ethyl cellulose (EC) and Ethyl Hydroxyethyl cellulose (EHEC)	10-20 %
Used as a film forming resin in lacquer, adhesives, varnishes, paints plastic products, laundry detergents	
3. Ethyl benzene manufacturing	<10%
4. Polystyrene manufacturing	<10%
4. Topical anesthetic	minimal

Chloroethane Lifecycle Diagram



Data Sources:
1989 TRI release data
Production data from RIB
CEB and Contractor Libraries

Figure 1

3

CMA 052325

AREAS OF POTENTIAL CONCERN:

Manufacturing:

Air: Significant releases both fugitive and stack. The risk appears to be low from these releases, however, considerable uncertainty exists in the risk modeling. Analysis of total waste generation using TRI treatment codes to quantify pollution prevention possibilities could be undertaken.

Water: Minimal TRI reported releases to water. May be deposition of air releases in water. May want to evaluate risks from low level contaminants in drinking water.

Occupational: See TEL

TEL

Air: Significant releases both fugitive and stack. The risk appears to be low from these releases, however, considerable uncertainty exists in the risk modeling. Analysis of total waste generation using TRI treatment codes to quantify pollution prevention possibilities could be undertaken.

Water: TRI reported water releases. Economic data shows that U. S. TEL production is being phased out as leaded gasoline is phased out, in the near term.

Occupational: Monitoring data from OSHA and NIOSH show worker exposures well below the PEL. PEL = 1000 ppm = 2600 mg/m^3. OSHA generally does not establish PELs above 1000ppm. PEL was developed prior to information received regarding carcinogenic and developmental toxicity endpoints. The level of concern for these endpoints is several orders of magnitude below the PEL. (EED received new information from IRIS, RfC Online 4/2.)

Ethyl Cellulose and Ethyl 2-Hydroxyethyl Cellulose

Air: Significant releases both fugitive and stack. The risk appears to be low from these releases, however, considerable uncertainty exists in the risk modeling. Analysis of total waste generation using TRI treatment codes to quantify pollution prevention possibilities could be undertaken.

Water: Minimal TRI reported releases to water. May be deposition of air releases in water. May want to evaluate risks from low level contaminants in drinking water.

Occupational: See TEL

Consumer: Potential exposure from use in consumer products.

Ethylbenzene

Air: No reported TRI releases, therefore, unknown.

Water: Unknown

Occupational: See TEL

Areas of Potential Concern, cont'd

Polystyrene

Air: Significant releases both fugitive and stack are reported in TRI only for polystyrene producers. The risk appears to be low from these releases, however, considerable uncertainty exists in the risk modeling.

Water: Minimal TRI reported releases to water. May be deposition of air releases in water. May want to evaluate risks from low level contaminants in drinking water.

Occupational: See TEL

Consumer: Possible consumer exposure exists due to use of polystyrene in construction.

Topical Anesthetic:

No TRI reports were available. Air release during use as a spray anesthetic and consequent exposure to health related occupations and consumers is possible.

REGULATORY STATUS

CAAA Hazardous Organic National Emission Standard for Hazardous Air Pollutant (NESHAP)
[CAA = Clean Air Act Amendments; Hazardous Organic NESHAP = HON]

Defines Maximum Achievable Control Technology (MACT) to be in-place by 1995. Note MACTs are not risk based. Multimedia impacts may be considered by HON Workgroup.

Chloroethane is on Hazardous Air Pollutant List (HAP). It and most of its derivatives will be targeted for air release reductions of 90% in a November, 1991 Proposed Rule.

Fugitive Release NESHAP

NESHAP for emission sources such as equipment leaks emanating from flanges and pumps was developed through a negotiated rulemaking. Will be included in the HON Proposed rule. Fugitive emissions will be reduced by leak detection and repair programs (LDAR).

Office of Drinking Water (ODW) Proposed Test Rule

- Oral 14-day repeated dose and oral 90-day subchronic toxicity studies would be performed for chloroethane and four other chlorinated compounds. Data will be used to develop Health Advisories for unregulated drinking water contaminants.

RISK REDUCTION ALTERNATIVES OR MISSING PIECES

Air: Because this is a volatile chemical, most opportunities may be in better containment. Most releases are reported to air and most sources of releases identified in the pollution prevention screening support this conclusion. At the current time regulations under development in the Office of Air and Radiation (OAR) may address these concerns.

Water: Most reported water releases are from TEL production. TEL production is being phased out so no risk reduction action appears necessary in this area. Other water concerns would involve very low levels of releases (too low to be reported in TRI) or deposition from air releases. The OAR regulatory effort may address the air release problem as it may reduce water deposition. There may be other sources of chloroethane in water. The ODW Test Rule will provide results on the level of concern in drinking water. OTS may wish to revisit this area of concern after the results of the test rule have been received.

Occupational: Develop information for OSHA, FDA

Consumer: Investigate possible exposure from variety of uses of ethyl cellulose in consumer products. Investigate possible exposure from foamed plastics used in construction.

Waste: Investigate TRI release codes to determine waste generation in releases (i.e. whether releases are pre-treatment or post-treatment.)

POTENTIAL PROGRAM ACTIVITIES

- **Further Investigatory Work:** Investigate possible exposure from variety of uses of ethyl cellulose in consumer products.
  Investigate possible exposure from foamed plastics used in construction.
  Investigate TRI release codes to determine waste generation in releases (i.e. whether releases are pre-treatment or post-treatment.)

Voluntary Action: None identified at this time

Information Dissemination: None identified at this time

Information Rules: None identified at this time

Test Rules: Rule has been proposed, awaiting "B" decision.

Referral: Refer new endpoint hazard information to OSHA
Refer new endpoint hazard information to FDA
Refer to OAR for CFC Substitutes study

Section 6 Rules: No action identified at this time

CMA 052328

FURTHER WORK

TASK	DIVISION	RESOURCES	TIME
1) Refer health data to ACGIH, OSHA; Refer concerns on topical anesthetic use to FDA	HERD & ECAD	minimal	---
2) Follow up on exposure from rigid foam. (Clarify use of chloroethane in ethyl benzene and polystyrene manufacture and potential for consumer exposure.) Investigate appropriateness of referral to OAR/OTS CFC Substitutes project (may not be considered a CFC substitute).	EED & ETD	<.1FTE, $10k	2 months
3. Analyze TRI Release and Treatment data to Quantify Waste Generation (Return to RM2 to report and consider further activity. Possible candidate for information dissemination.)	ETD	<$10k	2 months
4. Follow up on exposure from use of chloroethane in ethyl cellulose. (Identify uses and potential for exposure.)	ETD EED	.1 FTE, $20k .1 FTE. $10l Total	4 months 2 months 4 - 6 months

CHLOROETHANE

BASIC CHEMICAL PROPERTIES

Chloroethane (ethyl chloride) CAS # 75-00-3; C_2H_5Cl, mw 64.52, mp -139 °C, bp 12.3 °C, density 0.891, log K_{ow} 1.47 (estimate), water solubility 5.7 g/liter (20 °C), vapor pressure 1199 mm Hg (25 °C). All data except log K_{ow} are measured values.

Environmental Fate Summary:

Most of the compound would go to air, even if the major releases were not to air, because of relatively rapid volatilization from water, and low adsorption. There is little potential for bioaccumulation. The half-life in air is expected to exceed a week under most conditions (USEPA, 1989 reported a range of roughly one week to two months). Leifer estimated 27 days for the troposphere (personal communication).

HEALTH HAZARD

Summary of Health Hazard Concern for Chloroethane .

The primary health hazard concern for chloroethane is cancer. When chloroethane was tested at a single dose level (15,000 ppm) for carcinogenicity by the inhalation route in rats and mice, there was clear evidence of carcinogenic activity for female mice, as indicated by carcinomas of the uterus. There was high to moderate concern for neurotox at RM-1.

Chloroethane has not been reviewed/verified by CRAVE, i.e., there is no carcinogen classification for chloroethane. There is, however, an April 1, 1991 inhalation RfC of 10 mg/m^3 based on developmental toxicity (delayed fetal ossification in mice). This is a recent data development.

Quantitative Dose-Response Assessment for Chloroethane

In September 1990, EED carried out a preliminary quantitative dose-response assessment for chloroethane and estimated a slope factor of 2.9×10^{-3} per (mg/kg)/day [inhalation unit risk: 8.3×10^{-4} per mg/m^3] based on an 86% incidence of uterine carcinomas of endometrial origin in female mice exposed to 15,000 ppm in air for 6 hours/day, 5 days/week for 100 weeks in an NTP study. The linearized multistage procedure was employed, but EED expressed reservations about using this slope factor because the study employed only the one positive dose plus control. Preliminary experiments indicated that a higher dose than 15,000 ppm could have been tolerated; the maximum-tolerated dose (MTD) was not reached.

Two more reactive analogues selected by the Oncology Branch of HERD, bromoethane and 1,2-dichloroethane, have estimated slope factors of 8.3×10^{-3} and 9.1×10^{-2} per (mg/kg)/day, respectively. The first slope factor was derived by EED; the second obtained from the IRIS database. These slope factors are, as expected, higher but still consistent with the estimated value for chloroethane.

USES/VOLUMES

Manufacturers: Dow Chemical
DuPont
Ethyl Corp.
PPG Industries Inc.

Total Production Volume: 1989 - 120 million lbs.
U.S. consumption: 90 million lbs. Export: 30 million lbs.

Market Trends: U. S. consumption of chloroethane has decreased steadily since 1970 because of phaseout of lead in gasoline. U. S. production of chloroethane in the last four years, however, has been stable because of strong export demand, eg., the Far East, Middle East, Africa and Latin America. Western Europe still uses lead alkyl antiknock mixes as its most important octane enhancer. PPG and DuPont report that they will stop producing lead based antiknock mixtures by the end of the year. Once this production shuts down, domestic production of chloroethane should decrease drastically.

Uses	% of choloroethane used
1. Tetraethyllead (TEL)	75%
2. Ethyl cellulose (EC) and Ethyl Hydroxyethyl cellulose (EHEC)	10-20 %
3. Foamed plastics: initiator for ethyl benzene for styrene, polystyrene and alkyl catalyst	<10%
4. Topical anesthetic	minimal

Source: Telephone conversations with Julie Sheehy, CEH, 3/26-4/3, 1991.

REGULATORY STATUS

CAAA Hazardous Organic NESHAP (HON)

Defines Maximum Achievable Control Technology (MACT) to be in-place by 1995. Note MACTs are not risk based. Multimedia impacts may be considered by HON Workgroup.

Chloroethane is on Hazardous Air Pollutant List (HAP). It and most of its derivatives will be targeted for air release reductions of 90% in a November, 1991 Proposed Rule.

Fugitive Release NESHAP

NESHAP for emission sources such as equipment leaks from flanges and pumps was developed through a negotiated rulemaking. This will be included in the HON Proposed rule. Fugitive emissions will be reduced by leak detection and repair programs (LDAR).

ODW Proposed Test Rule

Oral 14-day repeated dose and oral 90-day subchronic toxicity studies would be performed for chloroethane four other chlorinated compounds. Data will be used to develop Health Advisories for unregulated drinking water contaminants.

MANUFACTURING

INDUSTRIAL CHEMISTRY AND PROCESSES DESCRIPTION

Chloroethane is manufactured at 4 sites:

Dow Chemical, TX
DuPont, NJ
Ethyl Corp, TX
PPG, LA

The majority of chloroethane is produced by the hydrochlorination of ethylene. This reaction is carried out in the presence of a catalyst such as aluminum chloride. The reaction product is sent to a separator where the lower boiling ethyl chloride is removed and further refined by fractionation. See Figure 2 for a typical chloroethane manufacturing block diagram.

Chloroethane is most commonly produced by hydrochlorination of ethylene in the presence of aluminum chloride ($AlCl_3$):

$$CH_2{=}CH_2 + HCL \xrightarrow{AlCl_3} CH_3\text{-}CH_2\text{-}Cl$$

RELEASE ANALYSIS

TRI Data 1989

Facility	Environmental Releases (lb/yr) Air		Water	Other
	Fugitive	Stack		
Dow Chemical, TX	20,000	2,000	300	0
DuPont, NJ[1]	1,917	38,980	0	0
Ethyl, TX	4,200	0	0	0
PPG, LA	74,000	420,000	400	0
TOTAL	100,117	460,980	700	0

(1) DuPont, NJ is both a manufacturer and user (in tetraethyl lead) of chloroethane. For this analysis, it was assumed that 50% of the air releases were attributable to manufacture.

EXPOSURE ANALYSIS

General Population

Atmospheric exposure (inhalation) was evaluated. Ambient levels and populations potentially exposed from both manufacturing and user sites were previously estimated by EED from pre-1989 TRI data. See Table displayed below, following Figure 2.

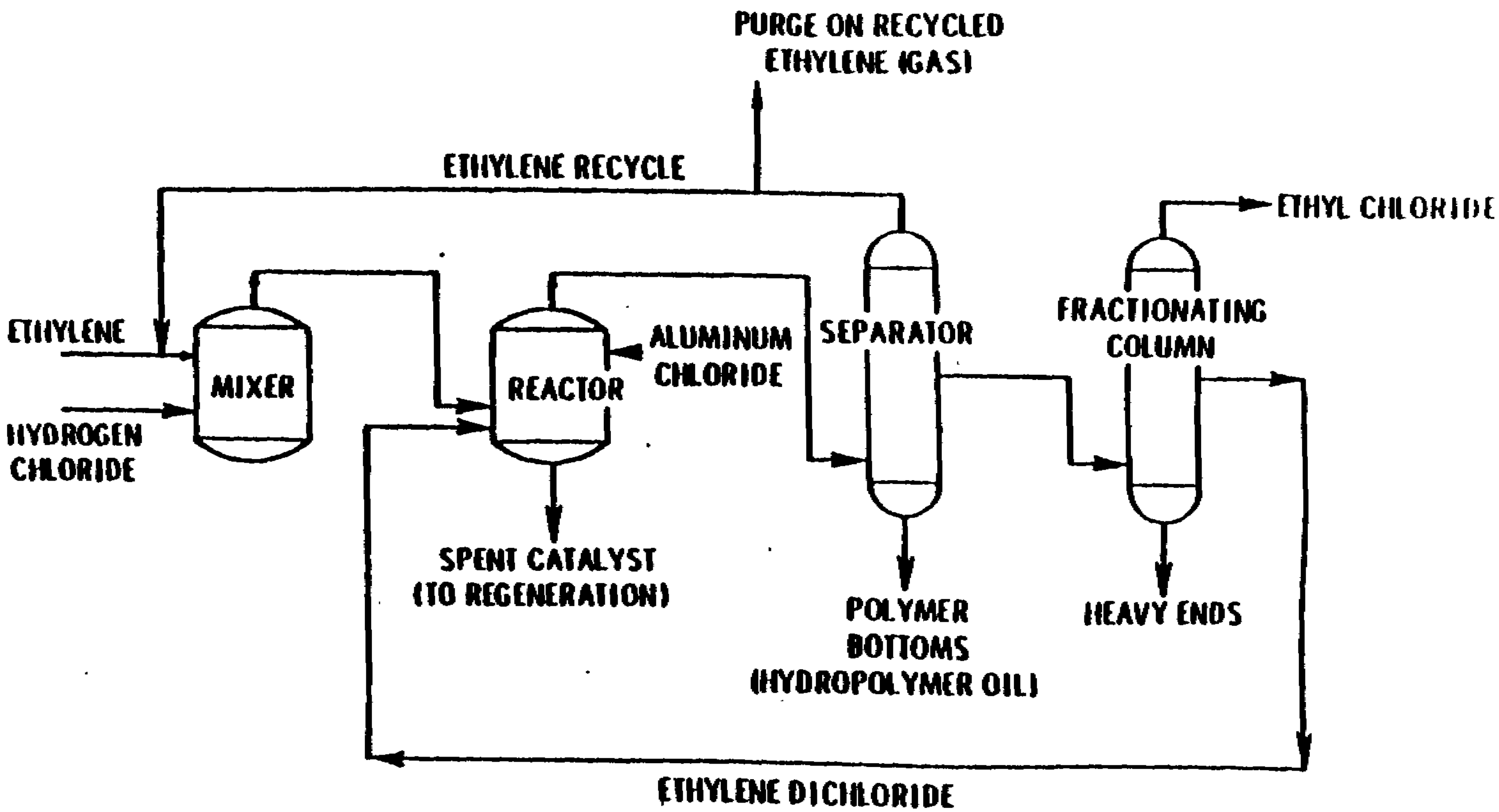


Figure 2 Process Schematic: Hydrochlorination of Ethylene

Exposure, cont'd

Occupational

PEL = 1000 ppm = 2600 mg/m^3
OSHA generally does not establish PELs above 1000ppm.
Monitoring data refers only to TEL production. See Use 1.

Environment

Data collected only for TEL manufacturing. See Use 1.

RISK CHARACTERIZATION

General Population

From Manufacturing and User Sites

EED calculated a cancer slope factor for chloroethane based on an incidence of uterine carcinomas of endometrial origin ($2.9x10^{-3}$ per (mg/kg)/day). Since only one nonzero dose was tested, the uncertainty of this slope factor is more than normally accepted. Because of this uncertainty, risks for chloroethane using analogues (bromoethane and 1,2-dichloroethane) were also calculated. However, because the two analogues used are both more reactive than chloroethane, derived risk estimates probably overestimate the risk. The risk numbers presented in the following sections are intended as a means of gaining some perspective on the significance of the estimated exposure levels. These risk numbers should not be viewed as rigorous estimates of actual cancer risk. The overall number of predicted cancer cases based on these risk numbers is relatively small.

AMBIENT AIR EXPOSURES PROJECTED FROM 1987 TRI RELEASES
From Manufacturing and User Sites

EXPOSURE LEVEL ($\mu g/m^3$)	LIFETIME AVERAGE DAILY DOSE (mg/kg)/day	UPPER BOUND INDIVIDUAL RISK LEVEL	EXPOSED POPULATION	UPPER BOUND EXCESS LIFETIME CANCER CASES
3.8E+01	1.1E-02	3E-05	2,222	7E-02
2.5E+01	7.1E-03	2E-05	10,777	22E-02
1.0E+01	2.8E-03	8E-06	5,649	5E-02
7.5E+00	2.1E-03	6E-06	1,898	1E-02
5.0E+00	1.4E-03	4E-06	21,859	9E-02
2.5E+00	7.1E-04	2E-06	58,984	12E-02
1.0E+00	2.8E-04	8E-07	12,233	1E-02
......	......	......	......	......
1.0E-07	2.8E-11	8E-14	95,505	8E-09
TOTALS:			41,406,867	6E-01

(Maximum Calculated Concentration: 6.1 mg/m^3)

Risk Characterization, cont'd.

By this estimate there could be an upper bound of less than 1 (0.6) excess life-time cancer cases among a total exposed population of 41,406,867. If the slope factors of the two analogues, bromoethane or 1,2-dichloroethane, are used in the calculation, the upper bound on excess life-time cancer cases is estimated at 2 or 18, respectively. There are uncertainties associated with this evaluation.

Occupational Exposures

Exposure at the OSHA PEL of 2600 mg/m^3 for a working lifetime corresponds to an individual upper bound lifetime cancer risk of greater than 10^{-1}. New data on developmental toxicity also indicates that the PEL may not be sufficiently protective for this endpoint. Monitoring data refers only to TEL production.

Drinking Water Exposures

No separate assessment for manufacturing sector. See Use 1.

SOURCE ASSESSMENT

Identification of releases/wastes of concern

- o Nearly all chloroethane emissions are to air .
- o Examples of major stack release sources are storage tanks and process vents
- o Examples of fugitive air emissions sources are valve leaks and other equipment leaks
- o Analyses of data have focussed on end of pipe TRI releases. Analyses of waste generation could be undertaken using TRI treatment codes.

SOURCE REDUCTION OPPORTUNITIES

PROCESS CHANGE ASSESSMENT

- o Develop understanding on the size of purge stream on ethylene recycle line and its contribution to total air emissions

- o Research whether there are catalysts which would reduce amount of ethylene throughput, spent catalyst regeneration, polymer bottoms production, heavy end production in fractionating column

MANAGEMENT PRACTICES ASSESSMENT

- o LDAR (leak detection and repair) programs within facility to limit fugitive emissions will be promulgated in HON.

RECYCLE OPPORTUNITIES

Potential opportunities that could be investigated are:

- o Condensers or carbon adsorbers in stack vents and storage tanks to recover VOC's followed by separation (if necessary) and recycling
- o Separation/recycling unit for cooling water streams contaminated with chloroethane
- o Recovery chloroethane from polymer bottoms, heavy ends and spent catalyst regeneration

CONTROL TECHNOLOGIES

Improved treatment technologies that may be worthy of further investigation:

- o Vent VOC's to existing boiler or process heater for energy recovery
- o Incinerate gas from process vents, storage tanks and transfer operations
- o Condensers in stack vents to recover VOC's and VOC's sent to flare

Improved disposal technologies:

USE 1: TETRAETHYLLEAD (TEL)

INDUSTRY/USE PROFILE

Manufacturers: Ethyl Corp (U.S. plant on stand-by); PPG (reportedly will cease production of TEL by end of 1991), and DuPont.

Function: TEL is an antiknock or octane booster additive for gasoline mixes. TEL also provides valve lubrication.

Processors: A DuPont site located in Deepwater,NJ makes TEL. A strong export market exists, although as other countries develop regulations for leaded gasoline, the export market may decline. Also some lead is still used which accounts for the stable production over the last three years. About 60% of the antiknock mix is a lead alkyl, either TEL or TML (tetramethyl ethyl lead). TEL is cheaper than TML and is often used with TML for motor gasoline. For aviation additives, only TML is used. As of 1990, E.I. duPont with an estimated 100 million lbs./year TEL capacity at Deepwater, N.J. probably provides most TEL to the market. A majority, 50% - 80% of the TEL produced was exported. On 3/18/91, duPont announced it will stop making TEL by mid-1991. (CMR) The only North American supplier after that will be an Ethyl Corp. plant in Canada. Amounts needed to meet North American demand in next year is about 40 million lbs. (Source: CMR & Jamil Wakim, CEH, telephone conversation, 4/3/91.) Lead may still be allowed in gasoline for farm and military uses.

INDUSTRIAL CHEMISTRY AND PROCESS DESCRIPTION

The first process used for the manufacture of tetraethyllead involved a batch reaction between sodium-lead alloy and chloroethane. This basic approach, with improvements and variations, was the predominant commercial route to tetraethyllead from the early 1920s to the early 1960s.

DuPont's facility in Deepwater, NJ uses chloroethane to manufacture tetraethyl lead. See figure 3 for a typical tetraethyl lead manufacturing block diagram.

Sodium-lead alloy is reacted with chloroethane in the presence of a catalyst (usually acetone) to form tetraethyl lead (TEL). After reaction is complete, unreacted chloroethane is vented and the reactor contents are moved to a stripper for separation of the TEL from the reaction slurry. The reaction bottoms are washed to remove sodium chloride and to recover the lead. The TEL is sent to a blending unit for the antiknock mixture. The use of TEL in gasoline is illegal for most uses in the U.S. and is gradually being phased out in other areas of the world, such as western Europe.

RELEASE ANALYSIS

1989 TRI data:

Facility: DuPont, NJ

Air	Fugitive:	1,917 lb/yr
	Stack:	77,959 lb/yr
Water		70,752 lb/yr

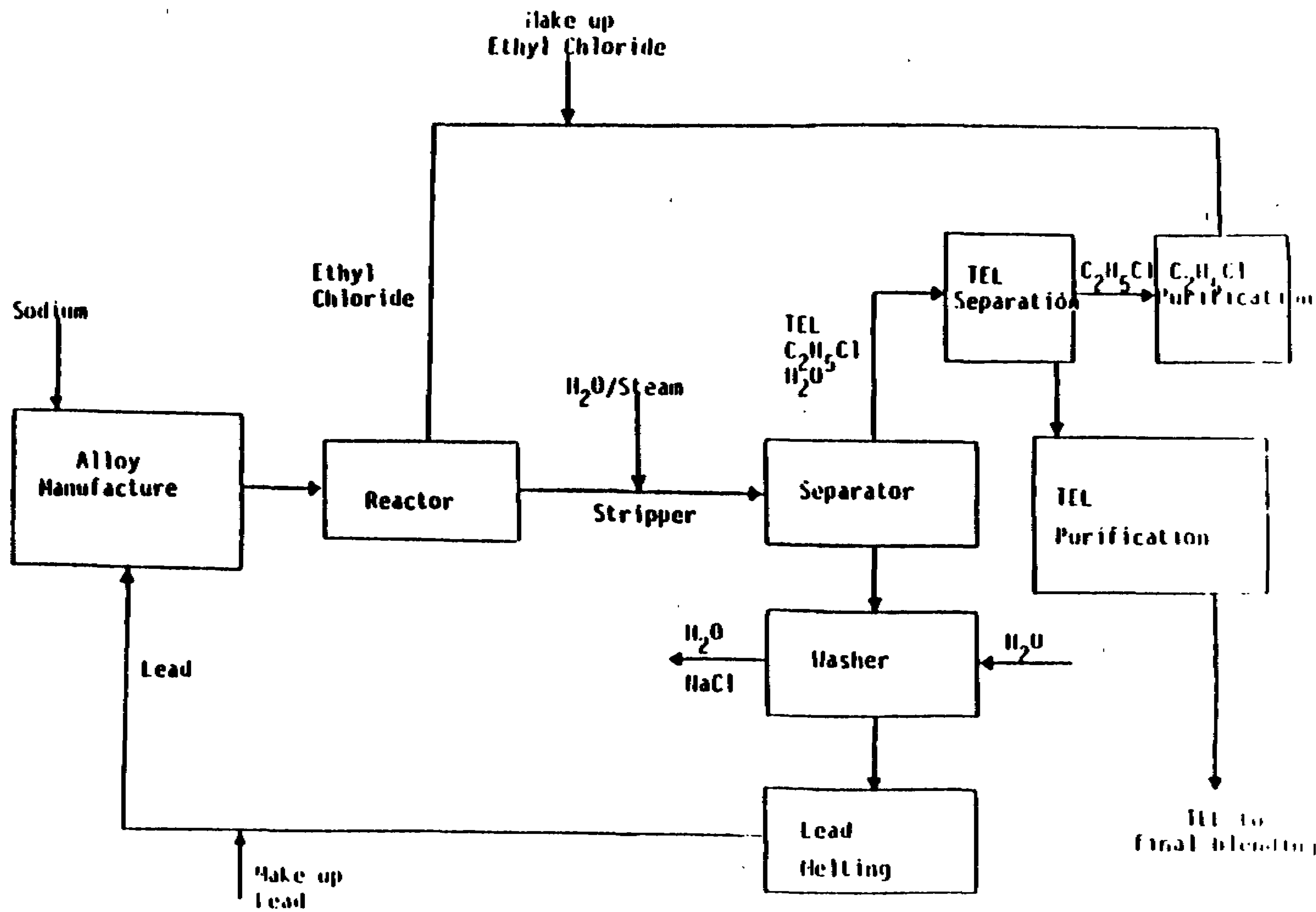


Figure 3 Simplified Block Diagram: Tetraethyl Lead from Sodium-Lead Alloy

Figure 3

EXPOSURE ANALYSIS

General Population

Occupational

PEL = 1000 ppm = 2600 mg/m^3
OSHA generally does not establish PELs above 1000ppm.
Available OSHA and NIOSH monitoring data was substantially below PEL.

Environment

The levels in water resulting from pre-1989 TRI reported releases were all estimated to be below 1 ppb. They ranged from 0.005 mg/L to 0.54 mg/l (ppb). No nearby drinking water utilities were found.

RISK CHARACTERIZATION

General Population

Separate analysis not performed for scoping. See analysis prepared in Manufacturing Section

Occupational

Exposure at the OSHA PEL of 2600 mg/m^3 for a working lifetime corresponds to an individual upper bound lifetime cancer risk of greater than 10^{-1}. A NIOSH survey at a tetraethyl lead plant showed average exposures to chloroethane of 0.4 mg/m^3. Exposure at this level for a working lifetime corresponds to a lifetime upper bound individual cancer risk of about $4E10^{-5}$.

Drinking Water

No reported TRI releases are located upstream of drinking water intakes. Furthermore, releases to water appear to be low and modeled ambient water concentrations are very low, resulting in an overall low level of concern for water exposures.

SOURCE ASSESSMENT

Identification of releases/wastes of concern

- o Approximately half of the chloroethane emissions are to air and the other half to water.
- o Examples of major stack release sources are storage tanks and process vents.
- o Examples of fugitive air emission sources are valve leaks and other equipment leaks.
- o The major water source is from washing of reactor bottoms.
- o Analyses of data have focussed on end of pipe TRI releases. Analyses of waste generation could be undertaken using TRI treatment codes.

SOURCE REDUCTION OPPORTUNITIES

SUBSTITUTE ASSESSMENT

Market Information

Tetramethyl ethyl lead (TML) is better quality; more expensive than TEL. When leaded gasoline is phased out completely, there will no longer be a need for lead alkyl antiknock mixes. Other substances will be used. DuPont cited declining domestic demand and tightening environmental controls as reason for closing U. S. plant, despite strong export demand.

Chemical Criteria for Substitute Performance

Since TEL may not be produced domestically in the future, there may be no need to substitute for chloroethane in TEL production. If substitutes were of interest, the following would apply:

The most fundamental criteria for an alternative to using chloroethane in the preparation of tetraethyllead is for the alternative substance to provide an ethyl ($-C_2H_5$) moiety. An electrochemical process for tetraethyllead which does not utilize chloroethane was developed by K. Ziegler in the early 1960s (U.S. Patent 3,372,097 March 5, 1968; K. Ziegler and H. Lehmkuhl). It is not clear to what extent the Ziegler process is used commercially, but essentially molten potassium-aluminum-complex ($KAl(C_2H_5)_4$) is electrolyzed to yield tetraethyllead by the following equation;

$$4\ KAl(C_2H_5)_4 + Pb \longrightarrow Pb(C_2H_5)_4 + 4\ K + 4\ Al(C_2H_5)_3$$

The preparation of the potassium-aluminum-ethyl complex is accomplished by combining ethylene and hydrogen with potassium and aluminum. Yield of tetraethyllead is virtually quantitative.

Systems Analysis of Use Function:

Not necessary for this scoping.

Hazard Review of Substitutes:

Not necessary for this scoping.

PROCESS CHANGE ASSESSMENT

Technological opportunities may include:

- Research other routes to TEL synthesis other than Sodium-Lead Alkylation
- Research other methods for removing sodium chloride other than water washing which may be a large source of chloroethane release.

MANAGEMENT PRACTICES ASSESSMENT

- LDAR (leak detection and repair) programs within facility to limit fugitive emissions will be promulgated in HON.

RECYCLE/REUSE OPPORTUNITIES

Potential opportunities that could be investigated are:

- Condensers or carbon adsorbers in stack vents and storage tanks to recover VOC's followed by separation (if necessary) and recycling
- Improved separation/recycling unit for wash water/stripping streams contaminated with chloroethane may be worthy of investigation

CONTROL TECHNOLOGY

IMPROVED TREATMENT TECHNOLOGY OPPORTUNITIES MAY INCLUDE:

- Vent VOC's to existing boiler or process heater for energy recovery
- Incinerate gas from process vents, storage tanks and transfer operations

IMPROVED DISPOSAL TECHNOLOGIES

Not applicable.

USE 2: ETHYL CELLULOSE (EC) AND ETHYL 2-HYDROXYETHYL CELLULOSE (EHEC)

INDUSTRY/USE PROFILE

Dow vacated business in 1989. The only U. S. site currently producing EC & EHEC is in Parlin, N.J. (periodic production as demanded) and is owned by Aqualon Co. This is a company formed by a merger with Hercules & Henkel's water-soluble polymers businesses. The EC & EHEC equipment was transferred from a site in Kennedy, Texas. About 10 million lbs. of EC & EHEC is produced in the U. S. The functional use for EC & EHEC is as a film forming resin, whether used as an ink or a surface coating. Can be formulated into lacquer, adhesives, varnishes, and plastic products. It produces a candy-apple effect such as coating for bowling balls. The way it is manufactured in the U.S., it is a non-water-soluble material.

Processors could include industrial coating companies, manufacturers of bowling balls, etc.

Importer: Berol, importing water soluble EC & EHEC, but under 100,000 lbs.

Source: telephone conversation with Mr. John Goin, Business Manager for Water Soluble Ethers and Markets, Chemical Economics Research, SRI, 4/3/91.

INDUSTRIAL CHEMISTRY AND PROCESS DESCRIPTION

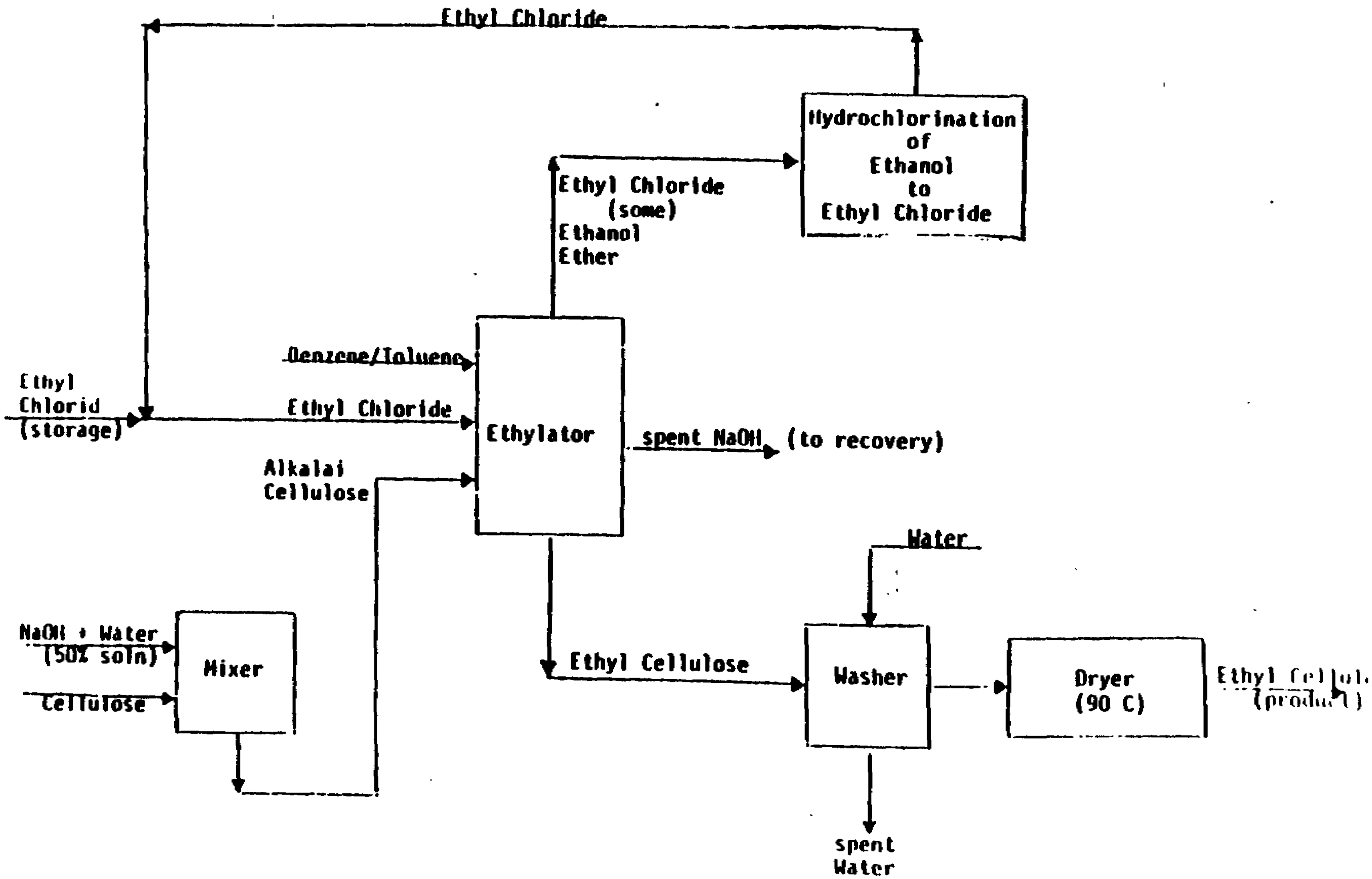
Their syntheses involve the reaction of alkali cellulose with chloroethane (ethyl cellulose) or chloroethane and ethylene oxide (ethyl 2-hydroxyethyl cellulose).

Chloroethane is used as an intermediate to make ethyl cellulose. This occurs at five Dow Chemical sites.

Alkali cellulose solution is added along with chloroethane, to an agitated, nickel-lined, pressurized vessel where it is ethylated between 90 and 150 deg. C for 6-12 hours. The ethyl cellulose product is purified by washing with water in a stainless steel vessel then dried and packaged. See Figure 4 for a typical ethylcellulose manufacturing block diagram.

CMA 052342

Figure 4



Block Diagram: Ethyl Cellulose

RELEASE ANALYSIS

1989 TRI Data:

Facility	Environmental Releases (lb/yr) Air Fugitive	Air Stack	Water
Dow Chemical, Il	240,000	130,000	0
Dow Chemical, CT	208,000	164,000	0
Dow Chemical, GA	336,200	139,000	0
Dow Chemical, CA	140,000	150,000	0
Dow Chemical, MI	3,129	148,987	8
TOTAL	927,329	738,807	8

EXPOSURE ANALYSIS

Occupational

PEL = 1000 ppm = 2600 mg/m^3
OSHA generally does not establish PELs above 1000ppm.

General Population

Environment

Separate analysis not performed for Scoping. See analyses performed in Manufacturing Section for both General Population and Environment.

Consumer

Possible exposure in consumer products.

RISK CHARACTERIZATION

Occupational

Exposure at the OSHA PEL of 2600 mg/m^3 for a working lifetime corresponds to an individual upper bound lifetime cancer risk of greater than 10^{-1}. New data on developmental toxicity also indicates that the PEL may not be sufficiently protective for this endpoint. Monitoring data refers only to TEL production.

General Population, Environment, Drinking Water

Separate analysis not performed for Scoping. See Manufacturing Section.

SOURCE ASSESSMENT

Identification of releases/wastes of concern

- Nearly all chloroethane emissions are to air
- Examples of stack release sources are storage tanks and process vents
- Examples of fugitive air emission sources are valve leaks and other equipment leaks
- Analyses of data have focussed on end of pipe TRI releases. Analyses of waste generation could be undertaken using TRI treatment codes.

SOURCE REDUCTION OPPORTUNITIES

SUBSTITUTE ASSESSMENT

Market Information

Other cellulose ethers are likely substitutes for EHEC such as hydroxylethyl cellulose, hydroxypropyl cellulose and methyl cellulose; water soluble solvents. The market is declining--expect to continue to decrease because there are no new applications and competition from water-soluble solvents. EC and EHEC is described by CEH as a fine functional chemical that is intrinsically a solvent.

Chemical Criteria for Substitute Performance

The most fundamental criteria for an alternative to using chloroethane in the preparation of ethyl cellulose or ethyl 2-hydroxyethyl cellulose from cellulose is for the alternative substance to provide an ethyl ($-C_2H_5$) moiety. Examples of such substances having similar alkylating ability to that of chloroethane are bromoethane and iodoethane. It does not appear, however, that bromoethane or iodoethane are used during the commercial synthesis of ethyl cellulose or ethyl 2-hydroxyethyl cellulose.

Systems Analysis of Use Function

Not necessary for this scoping.

Hazard Review of Substitutes

Bromoethane and iodoethane are more toxic than chloroethane.

PROCESS CHANGE ASSESSMENT

Technological opportunities may include:

- Examine extent to which wash water in ethyl cellulose manufacture is contaminated with chloroethane.
  Research other methods of washing ethyl cellulose product or reduce the amount of wash water used.
- Research ethylator operating conditions so as to minimize chloroethane losses
- Research use of filtration step to remove excess NaOH from alkali cellulose production before ethylator step

MANAGEMENT PRACTICES ASSESSMENT

- LDAR (leak detection and repair) programs within facility to limit fugitive emissions will be promulgated in HON

RECYCLE/REUSE OPPORTUNITIES

Potential opportunities that could be investigated are:

- Condensers or carbon adsorbers in stack vents, storage tanks and ethyl cellulose dryer to recover VOC's followed by separation (if necessary) and recycling
- Improved separation/recycling unit for cooling water, ethyl cellulose wash water and possibly spent NaOH streams contaminated with chloroethane may be worthy of investigation

CONTROL TECHNOLOGY

IMPROVED TREATMENT TECHNOLOGIES MAY INCLUDE:

- Vent VOC's to existing boiler or process heater for energy recovery
- Incinerate the gas from process vents, storage tanks and transfer operations

IMPROVED DISPOSAL TECHNOLOGIES

Not necessary for this scoping.

USE 3: ETHYL BENZENE

INDUSTRY/USE PROFILE

Chloroethane is used as an initiator for the production of ethylbenzene.

U. S. Producers of ethylbenzene:

Amoco, Atlantic Richfield, Chevron

The quantity of ethylbenzene produced in 1988 in the U. S. was about 10 billion lbs. Almost all ethylbenzene produced is used for styrene. U. S. production of styrene in 1990 was approximately 8.5 billion lbs.

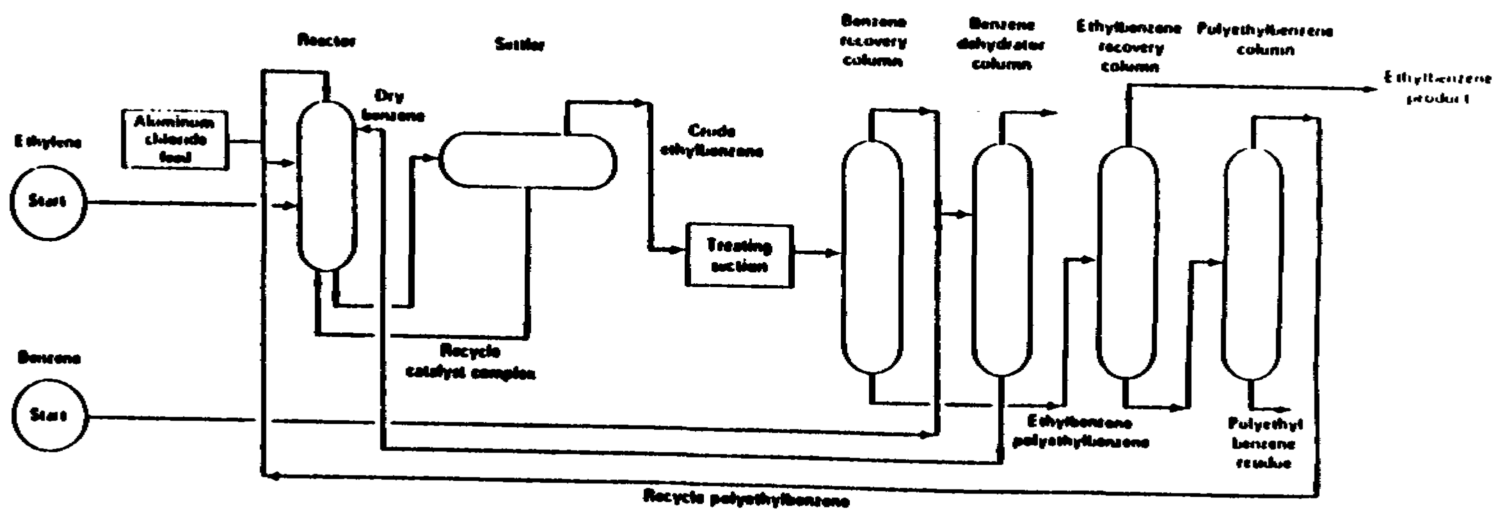
INDUSTRIAL CHEMISTRY AND PROCESSES DESCRIPTION

Chloroethane is used as an initiator in the production of ethylbenzene. The number of sites and their locations are unknown at this time (and no manufacturers of ethylbenzene reported for chloroethane in TRI).

Chloroethane is combined with aluminum chloride and recycled alkylated benzenes to form a catalyst-complex phase. This complex is mixed with benzene in a reactor to disperse the catalyst-complex phase. Ethylene is sparged into the reaction mixture and essentially complete conversion of ethylene is obtained.

The organic phase is washed with caustic and water to remove traces of catalyst. The crude ethylbenzene is sent to a series of three distillation columns for recovery of crude ethylbenzene. See Figure 5 for a typical process flow diagram.

Figure 5



Union Carbide/Badger ethylbenzene process. Courtesy of *Hydrocarbon Processing*.

RELEASE ANALYSIS

1989 TRI Data: No reports

EXPOSURE ANALYSIS

Occupational

PEL = 1000 ppm = 2600 mg/m^3
OSHA generally does not establish PELs above 1000ppm.

General Population

Environment

No separate analysis done for Scoping. See analysis under Manufacturing.

RISK CHARACTERIZATION

Occupational

Exposure at the OSHA PEL of 2600 mg/m^3 for a working lifetime corresponds to an individual upper bound lifetime cancer risk of greater than 10^{-1}. New data on developmental toxicity also indicates that the PEL may not be sufficiently protective for this endpoint. Monitoring data refers only to TEL production.

General Population, Environment, Drinking Water

Separate analysis not performed for Scoping. See analyses performed in Manufacturing Section.

SOURCE ASSESSMENT

Identification of releases/wastes of concern

- Nearly all chloroethane emissions are to air
- Examples of stack release sources are storage tanks and process vents
- Examples of fugitive air emission sources are valve leaks and other equipment leaks
- Analyses of data have focussed on end of pipe TRI releases. Analyses of waste generation could be undertaken using TRI treatment codes.

SOURCE REDUCTION OPPORTUNITIES

SUBSTITUTE ASSESSMENT

Market Information

Not readily available

Chemical Criteria for Substitute Performance

The most fundamental criteria for the synthesis of ethylbenzene from benzene is the addition of an ethyl ($-C_2H_5$) moiety onto the benzene ring. Most commercial syntheses of ethylbenzene involve reacting benzene with ethylene in the presence of a catalyst complex which usually consists of aluminum chloride and chloroethane. In such syntheses ethylene provides the requisite ethyl moiety; chloroethane serves as a constituent of the catalyst complex. A synthetic procedure that does not utilize chloroethane is the Mobil/Badger ethylbenzene process. This process was developed during the 1970s and was based on a synthetic zeolite catalyst, ZSM-5, developed by the Mobil Oil Corporation. The catalyst is basically silica-alumina and the reaction, which utilizes benzene and ethylene, provides ethylbenzene in nearly quantitative yield. Many companies have adopted this synthetic approach.

Systems Analysis of Use Function

Not necessary for this scoping.

Hazard Review of Substitutes

Not necessary for this scoping.

PROCESS CHANGE ASSESSMENT

Technological opportunities may include:

- Optimize use of chloroethane as catalyst-promoter
- Use hydrogen chloride (HC1) as catalyst in place of chloroethane
- Investigate the use of other catalyst-promoters other than HC1 or chloroethane

MANAGEMENT PRACTICES ASSESSMENT

- LDAR (leak detection and repair) program within facility to limit fugitive emissions will be promulgated in HON.

RECYCLE/REUSE OPPORTUNITIES

Potential opportunities that could be investigate are:

- Recover chloroethane from wash water in treating section.
- Condenser in Benzene dehydrator stack section to recover chloroethane followed by recycling into reactor

CONTROL TECHNOLOGY

IMPROVED TREATMENT TECHNOLOGIES MAY INCLUDE

None

IMPROVED DISPOSAL TECHNOLOGIES

None

USE 4: POLYSTYRENE

INDUSTRY/USE PROFILE

Chloroethane is used as in polystyrene production. No references have been found for the use of chloroethane as a blowing agent in the market literature.

U. S. Producers of polystyrene:

Dow, El Paso Products, Huntsman Chemical Corp., Koch Industries, Sterling Chemicals, Inc.

Styrene is used to produce polystyrene. Approximately 65% of styrene is used for polystyrene production. Total polystyrene production was 4.8 billion lbs. in 1987.

The use of ethylbenzene in producing polystyrene is in the polymerization process. The ethylbenzene diluent is mixed with the styrene monomer; if only a relatively small amount of diluent (e.g. 5-15%) is used, process is generally considered a modified mass polymerization process. If greater amounts of diluent are employed, the process is considered a solution process. Pentane, not chloroethane, is used as a blowing agent. (Telephone conversation with Eleanor Conolly, CEH, 4/4/91.)

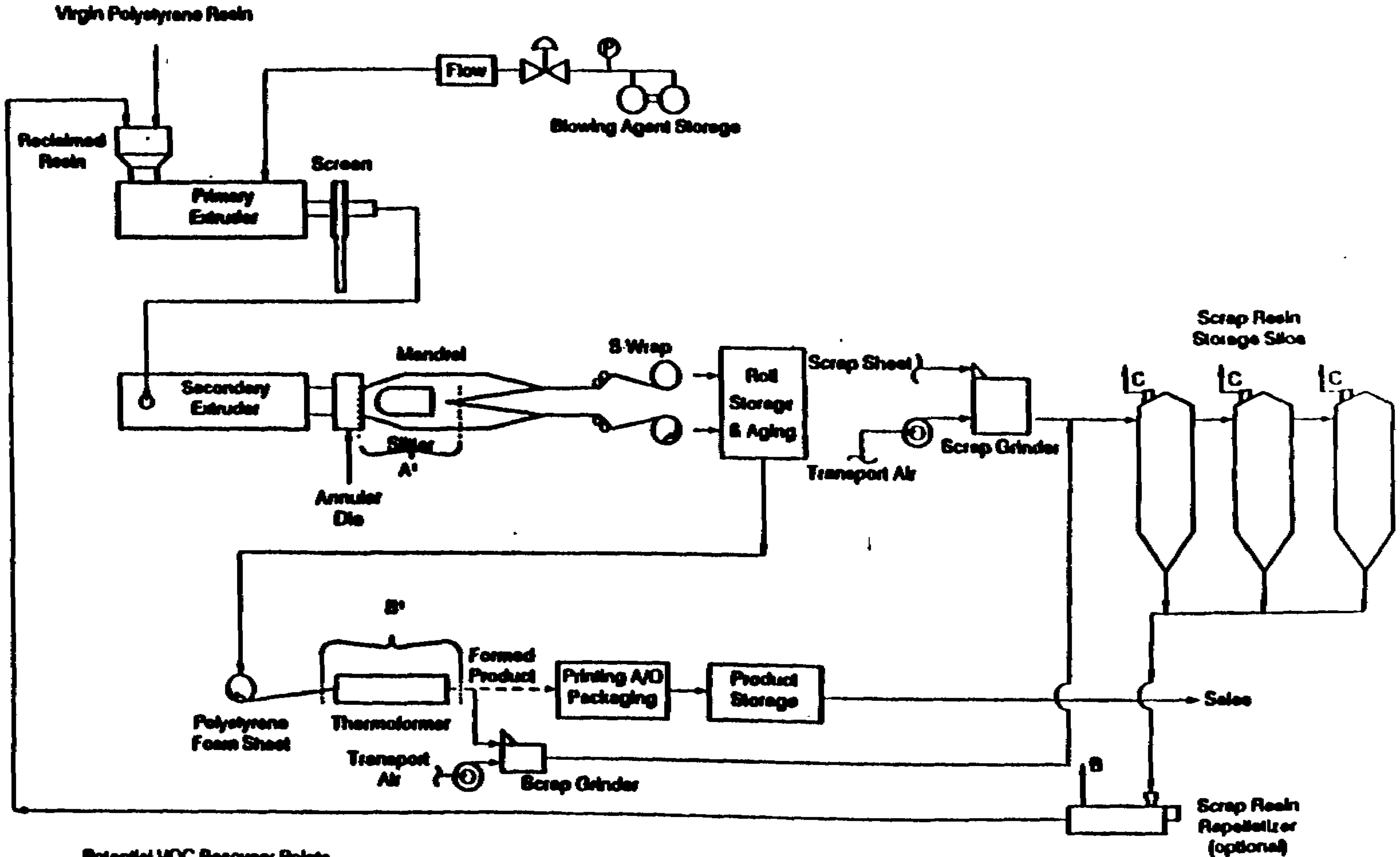
The bulk of extruded (as opposed to bead-molded) polystyrene foam board, used as an insulation board in construction, is produced by Dow, V.C. Industries, and Amoco. U. S. Consumption of polystyrene in construction was about 540 mil. lbs. in 1987. Approximately half of that is extruded foam board which used mostly for roofing.

INDUSTRIAL CHEMISTRY AND PROCESSES DESCRIPTION

Chloroethane is used as a blowing agent in the production of polystyrene foam. This operation occurs at the following sites:

Dow Chemical at MO, and 2 Ohio sites
AMOCO Foam Products, VA

Resin and nucleating agent are fed into the first stage of the primary extruder and melted. Liquefied blowing agent is metered through the barrel into the second stage of the primary extruder, where it is thoroughly mixed with resin and nucleating agent. This mixture is pumped into the secondary extruder where it is stirred, cooled and advanced to the die. As the gaseous polymer melt exits the dye, the pressure is released causing the blowing agent to vaporize and form the foam cells. See figure 6 for a typical polystyrene foam manufacturing block diagram.



Potential VOC Recovery Points

- A Outside and Inside Extruded Bubble
- B Repelletizer Extruder Vent
- C Exhaust from Pneumatic Transfer of Reground Scrap Foam to Silos

Note:

[1] Capture system is not existing. Need to be developed.

Figure 6

Flow Diagram of a Typical Polystyrene Foam Sheet Manufacturing Process

RELEASE ANALYSIS

1989 TRI Data:

Facility	Environmental Releases (lb/yr) Fugitive	Stack
Dow, MO	330,000	390,000
Dow, OH	282,000	212,000
Dow, OH	12,600	510
AMOCO, VA	390,000	0
TOTAL	1,014,600	602,510

EXPOSURE ANALYSIS

Occupational

PEL = 1000 ppm = 2600 mg/m^3
OSHA generally does not establish PELs above 1000ppm.

General Population

Environment

No separate analysis done for General Population or for Environment for Scoping. See analysis under Manufacturing.

RISK CHARACTERIZATION

Occupational

Exposure at the OSHA PEL of 2600 mg/m^3 for a working lifetime corresponds to an individual upper bound lifetime cancer risk of greater than 10^{-1}. New data on developmental toxicity also indicates that the PEL may not be sufficiently protective for this endpoint. Monitoring data refers only to TEL production.

General Population, Environment, Drinking Water

Separate analysis not performed for Scoping. See analyses performed in Manufacturing Section.

SOURCE ASSESSMENT

Identification of releases/wastes of concern

- Nearly all chloroethane emissions are to air
- Examples of stack release sources are storage tanks and process vents
- Examples of fugitive air emission sources are valve leaks and other equipment leaks
- Analyses of data have focussed on end of pipe TRI releases. Analyses of waste generation could be undertaken using TRI treatment codes.

SOURCE REDUCTION OPPORTUNITIES

SUBSTITUTE ASSESSMENT

Market Information

Not readily available

Chemical Criteria for Substitute Performance

Not necessary for Scoping.

Systems Analysis of Use Function

Hazard Review of Substitutes

PROCESS CHANGE ASSESSMENT

Technological opportunities may include:

- Optimize amounts of blowing agents used in the process
- Investigate the use of chloroethane with other materials such as water to reduce the amount of chloroethane used
- Substitute another blowing agent

MANAGEMENT PRACTICES ASSESSMENT

- LDAR (leak detection and repair) program within facility to limit fugitive emissions will be promulgated in HON.

RECYCLE/REUSE OPPORTUNITIES

Potential opportunities that could be investigate are:

- Capture vented blowing agent from secondary extruder
- Condensers in stack vents and on storage tanks to recover VOC's followed by separation (if necessary) and recycling
- Improved separation/recycling unit for cooling water streams contaminated with chloroethane may be worthy of investigation
- Recovery of blowing agent emitted from degassing from stored foam

CONTROL TECHNOLOGY

IMPROVED TREATMENT TECHNOLOGIES MAY INCLUDE

- Vent VOC's to existing boiler or process heater for energy recovery
- Incinerate the gas from process vents, storage tanks and transfer operations

IMPROVED DISPOSAL TECHNOLOGIES

Not necessary for scoping.

USE 5: TOPICAL ANESTHETIC

INDUSTRY/USE PROFILE

The use of chloroethane as a topical anesthetic can be traced back as early as 1848. Although its use as a topical anesthetic has declined over the past decade, many medical institutions still use chloroethane for this purpose. In fact, some sources have claimed that the use of chloroethane as a topical anesthetic will *increase* as a result of the sudden increase in outpatient plastic surgery. Extensive literature now exists on theories and mechanisms of anesthesia, and it is believed that the local anesthetic properties of chloroethane are attributable to nonspecific interference with nerve conduction.

A possible use exists as a recreational drug sold through specialty stores. The product is labeled "Ethyl-Gaz" and the contents include chloroethane.

INDUSTRIAL CHEMISTRY AND PROCESSES DESCRIPTION

Not performed for Scoping.

RELEASE ANALYSIS

All chloroethane used as a topical anesthetic will be released to air, since it is used as a spray.

EXPOSURE ANALYSIS

Occupational

PEL = 1000 ppm = 2600 mg/m^3
OSHA generally does not establish PELs above 1000ppm.

Possible exposure to health care personnel.

General Population

Not necessary for this scoping.

Consumer

Possible consumer exposure as it is used.

Environment

Not necessary for this scoping.

RISK CHARACTERIZATION

Occupational

Possible risk through inhalation during spray use.

General Population, Environment, Drinking Water

Separate analysis not performed for Scoping. See analyses performed in Manufacturing Section.

Consumer

Possible Consumer risk through inhalation and/or dermal absorption. In addition, potential abuse through home use. (Reported five cardiovascular related deaths in 1990 through use as inhalant/stimulant.) Not developed for Scoping.

SOURCE ASSESSMENT

Not necessary for this scoping.

SOURCE REDUCTION OPPORTUNITIES

SUBSTITUTE ASSESSMENT

Market Information

Not readily available.

Chemical Criteria for Substitute Performance

In general, an ideal substitute for chloroethane as a topical anesthetic should have the following characteristics: (1) be nonflammable; (2) be inexpensive; (3) require uncomplicated equipment for administration; (4) provide adequate anesthesia; (5) produce rapid and uncomplicated induction and emergence; (6) have no effect on myocardium or respiration at anesthetic doses; (7) be chemically and metabolically stable; (8) have a reasonable margin of safety.

An alternative product that is equally as efficacious as ethyl chloride as a topical anesthetic is methyl fluoride (Fluori-Methane®). The advantages of methyl fluoride over ethyl chloride are 1. nonflammable; 2. little or no cancer concerns; 3. not as chilling (will not promote frostbite); and 4. provides the same degree of anesthesia.

Systems Analysis of Use Function

Not necessary for this scoping.

Hazard Review of Substitutes

Not necessary for this scoping.

The following analyses were not necessary for this scoping:

TECHNOLOGY/PROCESS CHANGE ASSESSMENT

MANAGEMENT PRACTICES ASSESSMENT

RECYCLE/REUSE OPPORTUNITIES

CONTROL TECHNOLOGY

IMPROVED TREATMENT TECHNOLOGIES
IMPROVED DISPOSAL TECHNOLOGIES