

**Design for the Environment
Cleaner Technology Substitutes Assessment
Outline with Examples**

Created for a DfE Printing Project Meeting
March 10, 1993

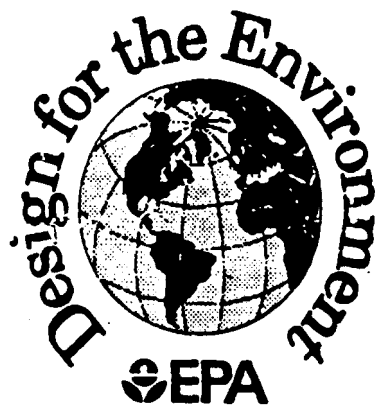


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- 1. Lifecycle Risk Analysis**
- 2. Pollution Prevention Opportunities**
- 3. Comparative Performance & Cost**

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- 1. Lifecycle Risk Analysis**
- 2. Pollution Prevention Opportunities**
- 3. Comparative Performance & Cost**

C. ETC.

You will find the Profile of Use Cluster Application, Functional Subgroup Identification and Definitions, and Substitute Identification pieces for Lithographic Blanket Washes and Screen Reclamation/Stencil Removal in separate documents called Introductory Outline of Cleaner Technology Substitutes Assessments (CTSAs). Below is an outline of the types of information found in those sections of the CTSA documents.

PROFILE OF USE CLUSTER APPLICATION

- A. Definition of application
 - chemistry of use (e.g., inks used in lithography)
 - desired performance characteristics
- B. Market Information (profile of use, e.g. inks) [Baseline]
 - volume, annual amount used
 - manufacturers of chemical
 - users of chemical
 - # of companies producing chemical
 - trends
- C. Identification of Substitute Chemicals, Technologies, Processes [products]

Description

- list of potential substitutes
- for chemical products:
 - chemistry of use
 - performance characteristics
 - percentage used in clustered products
- for alternative technologies: (e.g. possibly heat sensitive paper which avoids ink)
 - description of technology
 - performance characteristics
 - chemical use implications of alternative

The Use Cluster Analysis of the Printing Industry, a background document which includes a market profile and defines the processes, chemicals and technologies used by the industry, provides the information for this part of the CTSAs. An EPA economist researched the draft document and industry representatives are working with the DfE Printing Project to revise the analysis for publication.

FUNCTIONAL SUBGROUP IDENTIFICATION

[This may be omitted if it is not needed. Where substitutes consist of a product, this section may be used to identify the function of the component chemicals in the mixture.]

List functions performed by chemicals within the products

e.g. for inks: solvents, dispersants, pigments, etc.

Industry workgroup members identified the functional subgroups for the selected use clusters. This information will be reviewed for accuracy by an **EPA chemist** and/or **chemists from the industry**.

FUNCTIONAL SUBGROUP 1 (e.g. solvents)

(Note: There may be several functional subgroups within a product.)

Definition of function

- chemistry of use (e.g., solvent used as ink pigment dispersant)
- desired performance characteristics

Market Information

- volume, annual amount used
- manufacturers of chemical
- users of chemical
- # of companies producing chemical
- trends

Definition of function is submitted by industry workgroup members and reviewed by an **EPA chemist**.

Market information is submitted by **industry** or researched by an **EPA economist**.

SUBSTITUTES IDENTIFICATION

Description

- list of potential substitutes

for chemical substitutes:

- chemistry of use
- performance characteristics
- percentage used in clustered products

for alternative technologies:

- description of technology
- performance characteristics
- chemical use implications of alternative

Substitutes are defined, for purposes of the analysis, in the broadest sense of the term, including alternative chemicals, technologies and processes. In order to have complete information on current trends in the industry, we need industry to identify alternatives and submit information for to assist in the assessment of risk, performance and costs of substitutes.

Please see the attached letter (Exhibit 1 a/b) sent out to **suppliers** describing the type of information on alternatives we are seeking. To address company concerns about confidentiality, third parties are collecting the data for the project, thus maintaining anonymity for those submitting information. **Printers** are asked to submit information on alternative work practices as well.

EPA staff have formed a workgroup responsible for analyzing the alternatives.



**Environmental Conservation Board
of the Graphic Communications Industries**

A Cooperative Voice for Environmental Action

1899 Preston White Drive
Reston, VA 22091-4367
703/648-3218 • FAX 703/648-3219

February 18, 1993

Dear Printing Industry Supplier:

We are contacting you regarding a project known as the Design for the Environment (DfE) Printing Project. Specifically, the DfE Printing Project, a cooperative initiative between the graphic communications industry and the United States Environmental Protection Agency (EPA), requests that you consider providing information on alternatives to currently used chemicals or technologies in the area of blanket washes for offset lithography. The goal of the DfE program is to assist the industry in making informed, environmentally responsible design choices by providing standardized analytical tools for industry application and providing information on the comparative characteristics of alternative chemicals and technologies.

We have enclosed additional information on the DfE Printing Project in order to give you further background on the project, and to bring you up to date on its current status. To summarize the work to date, after several meetings in 1992, the group working on offset lithography has focused its efforts on the issue of blanket washes. To date, the committees working on those assessments have collected chemical and volume information for "traditional" blanket washes.

The next step in the assessment process is collection of data on various alternatives. Alternatives are those products or technologies which are defined by industry as alternatives to traditional methods. For example, products that have lower VOCs, or eliminate regulated chemicals such as CFCs. A technology that eliminated or required less of a chemical product would also qualify as an alternative process or technology.

In the case of chemical product alternatives, we are looking for chemicals, and volume in the alternatives. For technology alternatives, we would like a description of the technology, and performance, cost and use information associated with the new technology.

After information on alternatives has been collected it is the project's goal to provide accurate information to printers so that they are able to make informed judgements on the products and technologies they choose to use in their facilities. The DfE project will work with manufacturers and printers to develop case studies outlining the use of alternative products and technologies. The case studies will be available to the offset lithographic community.

EXHIBIT 1a



Printing Industry Supplier
February 18, 1993
Page 2

In order to alleviate concerns about proprietary information, we have been requested to act as intermediaries in the submission of product and technology information to EPA, keeping the supplier's company confidential. We encourage you to use this mechanism for supplying information to the project. Please send information to either:

Mark J. Nuzzaco
Executive Director
ECB
1899 Preston White Drive
Reston, VA 22091
Tel: 703/648-3218
Fax: 703/648-3219

Thomas Purcell
Core Group Industry Co-Chair
Printing Industries of America
100 Daingerfield Road
Alexandria, VA 22314
Tel: 703/519-8114
Fax: 703/548-3227

We hope that you will agree that a proactive approach to this EPA initiative is in the best interest of suppliers and their customers. We thank you in advance for your participation in the project. Additionally, we hope to see you at the upcoming DfE Printing Project's Industry Workgroup meeting on March 10-11 at the Washington D.C. Marriott. Please contact us if you have any questions.

Sincerely,



Mark J. Nuzzaco
Executive Director

Enclosure

MJN/sm

cc: ECB Board of Directors
ECB Member CEOs
ECB Technical Committee
John M. Nannes
Kathy Ramus
Ken Schnettler

SUBSTITUTE 1

(Note: This analysis is completed for each substitute.)

BASIC CHEMICAL PROPERTIES

The physical and chemical characteristics of the chemical will be detailed. This includes such information as chemical name and any synonyms; CAS number; structure; molecular formula; molecular weight; physical state, melting point; boiling point; vapor pressure; water solubility; other solubilities; density; flash point.

The following is an example (Exhibit 2) of the information the **EPA chemist** is providing for the chemicals in the clusters. **Industry** is encouraged to provide this information on alternative chemicals when they are submitted for the assessment.

RM1 ICB FORM
(Readily Available Information)

Chemical Name: 2-Methoxyethanol acetate (ester)

Molecular Formula: C₅H₁₀O₃

CAS Number: 110-49-6

Molecular Weight: 118

Chemist: Fred L. Metz

Physical State: Colorless, flammable liquid with mild ethereal odor

Structure: CH₃OCH₂CH₂OOCCH₃

Synonyms: 2-MEA; Ethylene glycol monomethyl ether acetate

Trade Name: Methyl Cellosolve acetate

Melting Point: -65°C (M)

Water Solubility: Miscible (M)

Boiling Point: 145°C (M)

Density: 1.005 (M)

Vapor Pressure: 5.3 mm Hg (M) at 25°C

Flash Point: 55.6°C (open cup)
55.6°C (closed cup)

Other Solubilities:

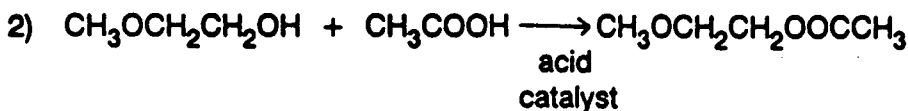
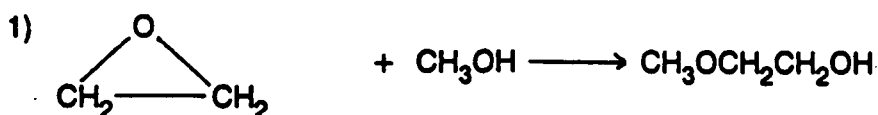
Above data is either measured (M) or estimated (E).

Additional Pertinent Chemical Information:

One major function of 2-methoxyethanol acetate is to dissolve various components of mixtures, in both aqueous and nonaqueous systems, for the uses described below, and to keep them in solution until the last stages of evaporation. It is these dispersive applications that cause the greatest concern for widespread human and environmental exposure.

Common Industrial Synthesis:

2-Methoxyethanol acetate is produced by the reaction of ethylene oxide with methanol, followed by esterification with acetic acid, acetic acid anhydride, or acetic acid chloride together with an acid catalyst.



Chemistry of Use:

2-Methoxyethanol acetate and the other ethylene glycol ethers have a wide range of uses as solvents, with particular applications in paints, stains, inks, lacquers, and the production of food-contact plastics. In addition, they are used as resin solvents in surface coatings and inks for silkscreen printing and in photographic and photolithographic processes, as solvents for dyes in textile and leather finishing, and as general solvents in a wide variety of home and industrial cleaners.

HAZARD SUMMARY

- Summary of Health Hazard Concern
- Quantitative Dose Response Assessment
- Summary of Safety Hazard Concerns
- Summary of Ecological Concern
- Quantitative Level of Concern

Health and ecological hazard information is an important component of the exposure assessment from which risk of chemicals is derived. Hazard information is available in EPA data bases and will be compiled from the **DfE Scoring System** and by **Health and Environmental Review Division (HERD)** on the use cluster chemicals. See the attached Exhibits 3 a/b/c for examples of text and tables provided in EPA documents evaluating human and environmental health hazards of chemicals.

In some cases readily available information may not be sufficient to establish comparative risks for chemicals in the cluster. In these cases **HERD** will look for structural analogs from which they can derive the necessary information.

Industry associations with additional hazard information may submit relevant test results to the **HERD** for inclusion in the hazard review.

HEALTH AND ENVIRONMENTAL HAZARD

Summary of Health Hazard Concerns and Quantitative Dose-Response Assessment

Although AN is a very acutely toxic chemical and there is also evidence for reproductive and developmental toxicity concerns, the driving health hazard concern is for carcinogenicity. It has an EPA carcinogen classification of B1, "probable human carcinogen", based on the observations of (1) a statistically significant increase in incidence of lung cancer in exposed workers and (2) tumors, generally brain astrocytomas, in studies in two rat strains exposed by various routes (drinking water, gavage, and inhalation).

O'Berg (1980) conducted an occupational epidemiology study on 1345 male workers exposed to AN at a DuPont textile fiber plant in Camden, SC at some time between 1950 and 1966. A trend of increased cancer incidence was seen with increased duration of exposure and increased length of follow-up time.

Quast (1980) administered AN in drinking water to rats of both sexes for 2 years. Statistically significant increases were observed in tumors of the CNS (astrocytomas), Zymbal gland, stomach, tongue, small intestine, and mammary gland. In general, the increases were dose-related. Similar results were seen in the Quast (1980) inhalation study. The IRIS oral slope factor is $5.4E-1$ per mkd; it should be used only for dietary intake. This value is a geometric mean derived from individual slope factors calculated for three different rat drinking water bioassays. The overall risk of tumors was determined from the number of animals having tumors that were statistically significant at any site.

The drinking water unit risk is $1.5E-5$ per $\mu\text{g/L}$, but should not be used if the water concentration exceeds $600 \mu\text{g/L}$.

The IRIS inhalation unit risk is $6.8E-5$ per $\mu\text{g/m}^3$, but should not be used if the air concentration exceeds $1E+2 \mu\text{g/m}^3$. The unit risk was derived from a relative risk using the epidemiological data of O'Berg. The cohort was sufficiently large and followed for an adequate time period. An increased risk of respiratory cancer remained after adjustment for smoking.

Summary of Environmental Hazard and Quantitative Level of Concern

Acute toxicity values for AN as listed in the Aquire data base range from $<1-100 \text{ mg/L}$ for invertebrates and fish. Crustaceans are especially sensitive to AN, with acute values from $1-11 \text{ mg/L}$. The value commonly cited as a chronic toxicity value (2.6 mg/L) is drawn from Henderson *et al.*, (1961); however this is not correct because this value is not a true chronic test endpoint. The endpoints of survival, growth, development, and reproduction that are commonly measured in current chronic tests were not determined by Henderson *et al.*

In 1990, Analytical Biochemistry Laboratories, Inc. conducted a chronic fish early life stage test. Statistically significant decreases in growth were obtained at the lowest tested concentration, 0.34 mg/L . The no-observed-effect concentration (NOEC) is probably near or lower than this concentration. A level of concern was calculated using this lowest test value (0.34 mg/L). An uncertainty factor of 10 was then applied to this value to account for the variations and error due to the differing sensitivities of the tested species, the type of organism tested, and extrapolations from the laboratory to the natural environment.

For AN, this results in a concern level of $34 \mu\text{g/L}$ (34 ppb). This value is considerably lower than modeled stream concentrations during low (7Q10) flow conditions. (The modeled maximum low flow concentration is $1493 \mu\text{g/L}$ or 1500 ppb .) Under these conditions toxicity to aquatic populations is a substantial concern.

Health Hazard Table

Table 3. Summary of Toxicity Data on Aerosol Spray Paint Components Ranked from High to Moderate Concern by SAT

Chemical	CAS No.	Component Type	SAT Hazard Rank	Weight-of-Evidence Classification ¹	Oral Slope Factor (mg/kg-day) ⁻¹	Oral RfD (mg/kg-day)	Inhal. RfC (mg/m ³)	Inhal. Unit Risk (μg/m ³) ⁻¹	Drinking Water Unit Risk (μg/L) ⁻¹
Methylene chloride	75-09-2	Solvent	H	B2	7.5E-3	6E-2	Under review	4.7E-7	2.1E-7
Cadmium orange/red lithopone	12656-57-4	Pigment	H	B1 ²	-	5E-4 ²	Under review ²	1.8E-3 ²	-
Lead molybdate	10190-55-3	Pigment	H	None	-	-	-	-	-
Lead sulfate	7446-14-2	Pigment	H	None	-	-	-	-	-
Lead chromate	7758-97-6	Pigment	H	None	-	-	-	-	-
Molybdate orange	12656-85-8	Pigment	H	Under review ⁴	-	Under review	-	-	-
Chromium lead molybdenum oxide	12709-98-7	Pigment	H	A ³	-	-	-	1.2E-2 ³	-
Toluene	108-88-3	Solvent	MH	D	-	2E-1	4E-1	-	-
Diethylene glycol dimethyl ether	111-96-6	Solvent	MH	None	-	-	-	-	-
Aluminum	7429-90-5	Pigment	MH	None	-	-	-	-	-
1,1,1-Trichloroethane	71-55-6	Solvent	M						
Hexane	110-54-3	Solvent	M	Under review	-	Under review	2E-1	-	-
Tetrachloroethylene	127-18-4	Solvent	M	Under review	-	1E-2	-	-	-
1,1,2-Trichloroethane	79-00-5	Solvent	M	C	5.7E-2	4E-2	Under review	1.6E-5	1.6E-6
Trichloroethylene	79-01-6	Solvent	M	Under review	-	Under review	Under review	-	-
Ammonia	7664-41-7	pH stabilizer	M ⁶						

Ecological Hazard Table

RELATIONSHIP OF 1988 TRI RELEASES REPORTED BY SPECIFIC SEGMENTS OF THE AN INDUSTRY TO ESTIMATES OF EXCESS LIFETIME CANCER CASES AND MAXIMUM AQUATIC CONCENTRATIONS					
REPORTING TRI FACILITIES AND PROCESSING ACTIVITIES	RELEASES (lb)		EXCESS LIFETIME CANCER CASES		MAXIMUM AQUATIC CONCENTRATION (ppb) <small>(CHRONIC CONCERN LEVEL IS 34 PPB)</small>
	STACK/FUGITIVE AIR	SURFACE WATER	FROM AIR	FROM DRINKING WATER	
AN MANUFACTURE American Cyanamid BP International Sterling Chemicals DuPont Monsanto	637,000	5,380	6	7	1493
ADIPONITRILE MANUFACTURE Monsanto	90,000	1,800			
ACRYLAMIDE MANUFACTURE American Cyanamid Dow Chemicals Nalco	24,000	2,882			
ACRYLIC FIBERS MANUFACTURE American Cyanamid DuPont Monsanto TMG Group	802,000	7,348	13	<1	<1
ABS/SANS RESINS MANUFACTURE Dow Chemical GE Plastics Monsanto	2,235,000	108,000	40	<1	507
NITRILE ELASTOMER MANUFACTURE BF Goodrich Armtek Goodyear Uniroyal	149,000	430,000	6	<1	<1

SUMMARY AND
DISPOSITION OPTIONS

ACRYLONITRILE
NOVEMBER 20, 1991

EXHIBIT 3c

VOLUME INFORMATION

Market Information

[general information regarding manufacture of the chemical and its use in manufacturing the product in question]

- volume, annual amount used, % used in product
- manufacturers of substitute 1
- users of substitute 1
- trends

Volume and formulation information are also important components of the exposure model which defines the comparative risk of selected chemicals. Industry workgroup members are the major source of this information. Necessary data includes: volume of chemicals in products in the use cluster; percentage (ranges and averages) of chemicals in products; and, total volume manufactured per year of chemicals in use cluster. The EPA chemist and economist will oversee the collection of this information.

Attached is an example (Exhibit 4 a/b) of the type of formulation information needed for the analysis and a form for submitting this information to the project.

Design for the Environment Printing Project

FORMULATION DATA FOR BLANKET WASHES & STENCIL REMOVAL

Quantitative evaluation of the exposures and risks associated with a product requires data on the product formulation. The most useful information is a complete list of all chemicals in a product and the concentration (range and average) of each chemical in the product. A brief description of each chemical's function, e.g. solvent, surfactant, can also be useful for assessment and communication purposes. Specific product names are *not* necessary. (see Example 1 below)

A less desirable but still useful alternative to reporting specific chemical concentrations is to list the chemicals associated with each functional component and provide the concentration of that entire component. For example, someone might report that ethyl acetate and isopropanol make up the solvent component of their product and that the solvent component comprises 25% by weight of the product. (see Example 2 below)

EXHIBIT 4a

Product category	Chemical name	CAS #	Weight % of chemical in product as used		Function	Weight % of functional component as used		Product name (optional)
			range	avg		range	avg	
blanket wash	2-propanol	67-63-0	10-20%	15%	solvent			Example 1
	2-butanone	78-93-3	9-25%	15%	solvent			
	acetone	67-64-1	25-40%	30%	solvent			
stencil removal	ethyl acetate	141-78-6			solvent	20-35%	25%	Example 2
	2-propanol	67-63-0						
	sodium hypochlorite	7681-52-9		5%	oxidizer			

Tom Purcell
Printing Industries of America, Inc.
100 Daingerfield Road
Alexandria, VA 22314
tel. 703-519-8114 fax 703-548-3227

Mark Nuzzaco
Environmental Conservation Board of the
Graphic Communications Industry
1899 Preston White Dr.
Reston, VA 22091-4367
tel. 703-648-3218 fax 703-648-3219

Marcie Kinter
Screen Printing Association International
10015 Main St.
Fairfax, VA 22031-3489
tel. 703-385-1335 fax 703-273-0456

[illegible]

REGULATORY STATUS

This section of the analysis contains a description of existing regulations, i.e., OSHA Pels, and on going regulatory actions by government agencies for the chemicals in the cluster. This information is collected from the scoring system data base by an EPA chemical engineer. Two examples (Exhibits 5 a/b) of regulatory status information follow.

Lists which contain the Chemical:
108-88-3 BENZENE, METHYL-

COUNT OF RECORDS = 14

Code	List
> CAA 111	STANDARDS OF PERFORMANCE FOR NEW STATIONARY SOURCES OF
> CAA 112	NATIONAL EMISSION STANDARDS FOR HAZARDOUS AIR POLLUTANTS
> CERCLA	COMPREHENSIVE ENVIRONMENTAL RESPONSE, COMPENSATION AND
> CWA 304	INFORMATION AND GUIDELINES
> CWA 307(A)	TOXIC POLLUTANTS
> CWA 311	CLEAN WATER ACT SECTION 311 HAZARDOUS SUBSTANCES
> NPDWR	NATIONAL PRIMARY DRINKING WATER REGULATIONS
> PARA-4C	PRE-TREATMENT POLLUTANTS
> PRIO POLL	PRIORITY POLLUTANTS
> RCRA U LIST	OTHER DISCARDED COMMERCIAL CHEMICAL PRODUCTS
> SARA 110	SUPERFUND SITE PRIORITY CONTAMINANT LIST
> SARA 313	EPCRA SECTION 313 LIST OF TOXIC SUBSTANCES
> TSCA 8A PAIR	TOXIC SUBSTANCES CONTROL ACT (PRELIMINARY ASSESSMENT
> TSCA 8D	HEALTH AND SAFETY DATA REPORTING RULES

- - - END OF REPORT - - -

Table A-2. Existing Aerosol Spray Paint Chemical Regulations

Component/Chemical	CAS No.	Volatility	SAT Hazard Ranking	Existing Chemical Regulations						
				SDWA MCL ^a (µg/L)	SDWA MCLG ^a (µg/L)	CERCLA RQ ^b (lb)	RCRA TC ^c (µg/L)	OSHA PEL ^d (ppm) ^e / (mg/m ³) ^f	ACGIH TLV ^g (ppm) ^h / (mg/m ³) ⁱ	Other
Solvents										Calif.
Aliphatic Hydrocarbons										
Hexane	110-54-3	Volatile	M					50 ^j		
Naphthas										
Petroleum naphtha	8030-30-6	Volatile	LM					100 ^j		
VM&P naphtha	8032-32-4	Volatile	LM					400 ^j		
Octane	111-65-9	Volatile	LM					500 ^j		
Alcyclic Hydrocarbons										
Cyclohexane	110-82-7	Volatile	LM					300 ^j		
Methylcyclohexane	108-87-2	Volatile						400 ^j		
Methylcyclopentane	96-37-2	Volatile								
Aromatic Hydrocarbons										
Toluene	108-88-3	Volatile	MH	1,000	1,000	1,000		200 ^j	100	
m-Xylene	108-38-3	Volatile	LM	10,000	10,000			100 ^j		
o-Xylene	95-47-6	Volatile	LM	10,000	10,000	1,000		100 ^j		
p-Xylene	106-42-3	Volatile	LM	10,000	10,000	1,000		100 ^j		
Ethylbenzene	100-41-2	Volatile		700	1,000	1,000		100 ^j	100	
Chlorinated Solvents										
Methylene chloride	75-09-2	Volatile	H					100 ^j		CAA ^k
Perchloroethylene (Tetra-)	127-18-4	Volatile	M	5.0	0	100	0.7	100 ^j	50	CAA ^k
1,1,1-Trichloroethane	71-55-6	Volatile		200	200	1,000		350 ^j	350	CAA ^k
1,1,2-Trichloroethane	79-00-5	Volatile	M	5.0	3.0	100		10 ^j	10	
1,1,2-Trichlorotrifluoroethane	76-13-1	Volatile	LM					1,000 ^j		
Trichloroethylene	79-01-6	Volatile	M	5.0	0	100	0.5	100 ^j	50	CAA ^k
Ketones & Esters										
Acetone	67-64-1	Volatile	L					750 ^j		
Methyl ethyl ketone	78-93-3	Volatile	LM			5,000	200	200 ^j	200	
Methyl isobutyl ketone	108-10-1	Volatile	LM			5,000		100 ^j	50	
Alcohols										
Butyl alcohol	71-36-3	Volatile	LM					100 ^j		
Isopropyl alcohol	67-63-0	Volatile	LM					400 ^j		

INDUSTRIAL CHEMISTRY AND PROCESSES DESCRIPTION

- I. The chemistry and process of manufacturing the chemical will be discussed.

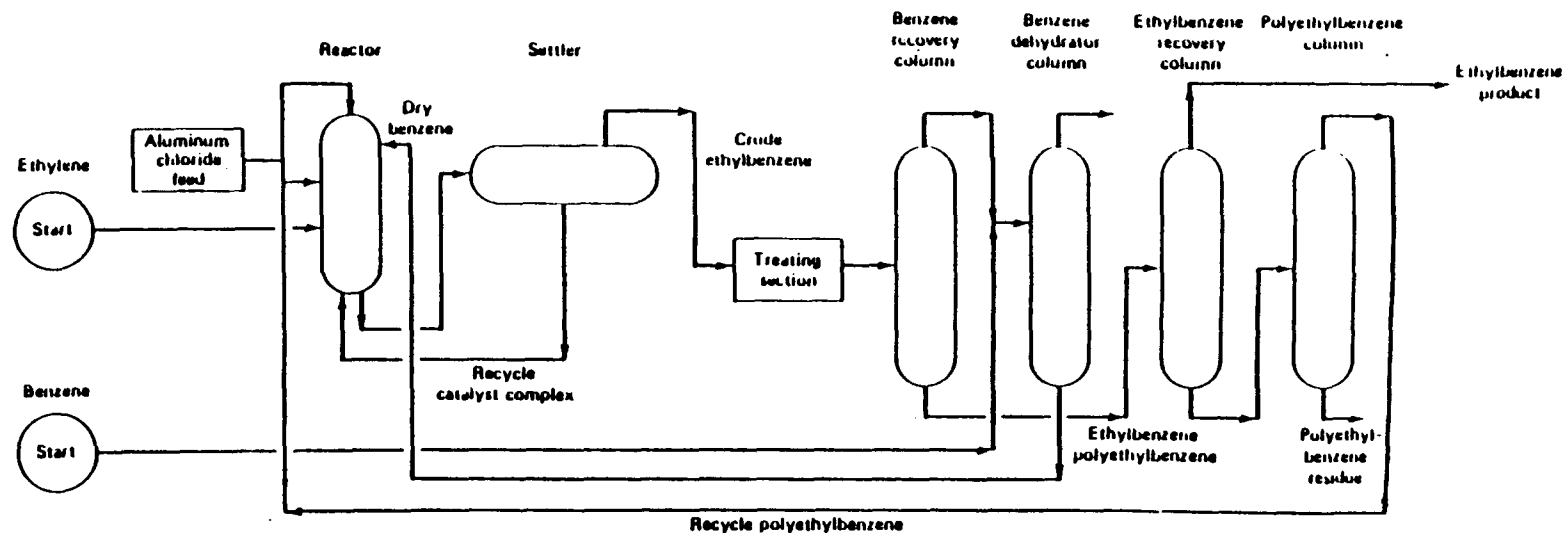
[Include process diagram]

- II. The chemistry and process of manufacturing the products which are the subject of this use cluster will be discussed.

[Include process diagram]

Chemistry and process flow diagrams provide the basis for determining possible sources of releases within the manufacture of a chemical or production of a product in a use cluster. In cases where the volume of a chemical used in the use cluster product is negligible when compared to the total volume manufactured of that chemical, one can elect not to perform analysis for I. above.

It may be sufficient to create one process flow diagram for the manufacture of the use cluster product if there is one primary process used by the industry. **Industry representatives** can work with **EPA** to develop the process flow diagram(s). See Exhibit 6 for an example of a process flow diagram.



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

SOURCE RELEASE ASSESSMENT

This assessment identifies potentially harmful releases and waste from chemicals in the identified use cluster. This release information informs the exposure model which estimates possible risks to humans or the environment. In addition, release reduction/mitigation strategies will be identified in the pollution prevention and control technology opportunity assessment sections described below using this release information. Uncertainties will be characterized.

Industry will work with **EPA** to identify releases/wastes of concern from chemicals in the use cluster in each of these areas:

- I. Manufacture of chemical/ Disposal
- II. Manufacture of products/ Disposal
- III. Use of products/ Disposal

In cases where the chemical volume used in the use cluster product is negligible compared to the total volume manufactured, then I. can be skipped. See Exhibit 7 for an example of information provided in the source assessment.

SOURCE ASSESSMENT: IDENTIFICATION OF RELEASES/WASTES OF CONCERN

- The largest waste stream in AN production consists of still bottoms from the wastewater stripper, the final purification of AN, the distillation of acetonitrile, and the purification of acetonitrile. These four waste streams are RCRA listed hazardous wastes (K011, K013, and K014) and are generally managed by storage in a deep well pond with subsequent deep well injection. Air releases from the holding pond may be significant. Phone calls to the facilities may be required to verify that holding ponds are still in use in light of the RCRA Land Disposal Restrictions. TRI releases via deep well injection total 4,333,900 pounds for 1988.
- The second largest release source is stack emissions, with fugitive emissions also close to this amount. Examples of major stack release sources are the absorber vent and distillation column purge vents.
- Examples of fugitive air emissions sources are valve leaks, pump and compressor seals, product storage tanks, transfer operations and emissions from the deep well ponds.
- HCN is a major by-product which may be either recycled or disposed of. Efforts to increase the reutilization of HCN should be encouraged.

EXPOSURE ANALYSIS AND RISK CHARACTERIZATION

I. Manufacture of chemical

Occupational

Environment

Human Health Endpoint

Air

Water

Land

Non-human Endpoint

Air

Water

Land

Safety Concerns

Disposal

II. Manufacture of product/ Disposal

same as above

III. Use of products/ Disposal

same as above

EPA staff will estimate exposure in the above areas in order to provide information for the risk characterization of the selected cluster. Exposure scenarios will be developed for each area above with the help of **industry**. **EPA** will create the risk characterization section of the CTSA. See Exhibits 8 a/b/c/d/e/f for examples of an exposure assessment and risk characterization write-up. (Note that the attached examples focus on product use, not manufacture and do not include analyses on water or land releases.)

4.0 EXPOSURE ASSESSMENT

Indoor Air exposure to aerosol paint can occur through the following routes:

- Inhalation of gas and vapor components (e.g., solvent or propellant) of spray paint;
- Inhalation of paint solids and resins (e.g., colorant and binders) from overspray; and
- Dermal exposure to paint solids and non-volatile components through incidental contact of exposed skin with paint mist in air and incidental or accidental spraying of hands and fingers.

4.1 Occupational Exposure Assessment

4.1.1 Worker Population

The total estimated worker population in the United States who use or are exposed to aerosol spray paint in an indoor environment is approximately 970,000. Aerosol spray paints are predominantly utilized in the following occupational settings:

Construction Industry - lay out of building grids;

Building Maintenance - heat resistant products on furnaces, boilers, grills, stoves, etc; paints are also used for applying safety markings;

Vehicle Maintenance and Repair - touch-up/finish of auto bodies; painting of other vehicle parts;

Floral Industry - preparation of floral arrangements;

Carpentry - finishing;

Household furniture - finishing;

Aircraft and Parts - touch-ups and repairs; and

Advertising - making signs, etc.

For the purposes of this assessment, the number of workers potentially exposed to aerosol spray paints by spray usage and industry type was estimated (SAIC 1992) using the assumption that only 25% of the workforce in the selected industries actually use or are exposed to spray paint, and of those, approximately 40% use or are exposed to spray paint indoors. Therefore, approximately 10% of the estimated worker population in each industry is assumed to be exposed to spray paint indoors.

Estimates of the number of employees exposed to aerosol spray paint according to usage and industry type are presented in Table A-1 of Appendix A. The industry codes have been categorized into five groups of estimated usage (volume and frequency). The groups are categorized as follows:

Group 1: 2 cans per day (highest);

Group 2: 1 can per day;

Group 3: 1 can per week;

Group 4: 1 can per month; and

Group 5: 1 can per four months (lowest).

4.1.2 Worker Exposure Analysis

Appendix B presents the detailed exposure assessment methodology and major assumptions used by SAIC (1992) to estimate worker exposures. Tables 5 and 6 present the results of the occupational exposure assessment for volatile and non-volatile components, respectively. Estimated daily doses based on one can of spray paint used per 8-hour workday are presented in column 5 of Table 5 and 6. Potential dose rate estimates for dermal contact, based on use of one can of spray paint per 8-hour workday, are presented in column 12 of Table 6. Lifetime Average Daily Dose ($LADD_{pot}$) and Average Daily Dose (ADD) estimates for workers are presented in columns 8 and 11 of Table 5 and 6, respectively. The averaging time for the $LADD_{pot}$ was 70 years (i.e., a person's) and for ADD was 40 years (i.e., a person's working life).

4.2 Consumer Exposure Assessment

4.2.1 Consumer Population

Based on information from a 1987 national usage survey of household solvent products (Westat 1987) and 1988 U.S. Bureau of Census data, approximately 68.2 million people in the United States are potentially exposed to components of aerosol spray paints. Of these, approximately 51% (33.2 million) are male and 49% (35.0 million) are female. Typical consumer applications of aerosol spray paints include painting or refinishing furniture, trim and shutters, and appliances and other household items; hobbies; and automobile touch-up and refinishing. Approximately 18 percent of aerosol spray paint activities take place entirely indoors (excluding the garage), and another 16 percent take place in a garage. Consequently, it was assumed that indoor use of aerosol spray paints by consumers ranges from approximately 18 to 34 percent. Activities occurring in the garage were assumed to occur while the door was closed thereby mimicking an indoor air exposure. Automotive aerosol spray paint products are typically used outdoors.

4.2.2 Consumer Exposure Analysis

Appendix B presents the exposure assessment methodology and major assumptions used by Versar (1992a) to estimate consumer potential dose rates. Central tendency and high-end potential dose rate estimates for short-term (24-hour) consumer exposure to volatile and non-volatile components of aerosol spray paints are presented in column 6 and 7 of Tables 5 and 6, respectively. Estimates of the central tendency and high-end potential Lifetime Average Daily Dose ($LADD_{pot}$) for volatile and non-volatile components are presented in columns 9 and 10 of Tables 5 and 6, respectively.

Exposure estimates were obtained using the Multi-Chamber Concentration and Exposure Model (MCCEM), which offers both short-term and long-term exposure calculations (GEOMET 1991). A generic house was used which assumed that the aerosol spray paint was used in the kitchen. The short-term exposures and $LADD_{pot}$ s of the individual volatile and non-volatile components were extrapolated, based on weight-%, from those calculated for total volatiles and total non-volatiles.

The consumer exposure assessment estimated individual exposures for twelve scenarios based on the varying the following parameters: inhalation rate, exposure frequency, exposure duration, amount of product used per event, percent of time event takes place indoors, and time spent in room after event. By selecting median and/or mean values for all parameters and choosing high values for certain minor parameters, four scenarios were developed in an attempt to estimate the central tendency value. The central tendency is either the mean or median exposure value. Eight scenarios were developed to estimate high end exposures to result in values which are estimated to fall above the 90th percentile of the potential dose rate distribution. Although 8 high end scenarios were developed, 4 scenarios were not used due to concerns that the combination of high values for each

parameter may have pushed these scenarios off the curve to a bounding estimate. A bounding estimate is an estimate to which no real person is exposed.

4.3 Major Data Gaps and Uncertainties

For any exposure scenario there are uncertainties inherent in the assumptions and methods used to calculate the corresponding exposure levels. Additionally, the parameters that comprise the exposure models exhibit some degree of variability. Identification of uncertainties, therefore, are required to provide decision-makers with the complete spectrum of information regarding the quality of an assessment, including the major data gaps and the effect the data gaps have on the accuracy or reasonableness of the exposure estimates developed. This section discusses the sources of error, areas of uncertainty, and data gaps which, conceivably, may weaken any conclusions that may be drawn from this assessment.

4.3.1 Occupational Exposure Assessment

The scarcity of published aerosol spray paint studies and exposure models requires that exposure estimates be made by adapting other models. Quantification of exposure is best accomplished with measurements made during spray paint can use, but little data was available for this specific work task. The major areas of uncertainty in the exposure estimates presented in this report include the following:

Exposed population - Information was not available regarding the specific occupations or SIC codes that use aerosol spray paints. Professional judgment was used to select the SIC codes of the exposed population and in the estimation of the number of workers exposed within each code.

Occupational use estimate - While a significant amount of the spray paint used occupationally is purchased in retail stores, no information was available regarding the actual end use (i.e., household vs. workplace). The estimate that approximately 50% of the units produced have an occupational end use is based on input from an industry source and professional judgment.

Use of the CEB Dermal Exposure Model - The CEB dermal exposure model requires an estimate of the amount of material remaining on the skin (Q). The CEB assessment manual provides a table of estimated Q values, which are based on the immersion of hands into liquids of varying viscosity. Aerosol spray paint use would likely result in far less material on the skin than liquid immersion. Therefore, the dermal exposure estimates from this model are likely to be conservatively high.

Constituents in the spray paint - The formulations of spray paint products are highly variable. The estimates of constituent percentages presented in this report are derived from actual product data and reference data bases. The variability between spray paint products translates into uncertainty in the estimated exposures.

4.3.2 Consumer Exposure Assessment

Although there are indications that the majority of aerosol spray paint consumed in the United States is used by consumers, the end-use markets are characterized poorly with no accurate breakdown of consumption by user groups. Consequently, it is possible to enumerate the consumer population expected to be exposed to components of aerosol spray paint only by comparison of national population statistics with the results of the Westat survey. Attempts at enumerating the population by questioning trade associations and other professional organizations were unsuccessful.

The accuracy of the MRI database used to obtain information on the concentration of volatile components was low for some of the results. Specifically, the true values for the first study were $\pm 30\%$ of the reported concentrations with recoveries of 96-115%. For the second study, the true values were ± 0.2 -5.0 times the reported concentrations with recoveries of 70-135%. Additionally, concentration data for non-volatile components of aerosol paints were limited to dated information from Clinical Toxicology of Commercial Products (Gosselin and Hodge, 1984). Use of these data add a degree of uncertainty to the exposure assessment.

MCCEM, the model used in this assessment to estimate the potential short-term and lifetime exposures to total volatiles and total non-volatiles in aerosol spray paint used average assumptions with regard to room volume, and infiltration and exfiltration rates. In addition, assumptions regarding such input parameters such as the overspray fraction of the paint, aerosol settling velocity, the fraction of overspray available for inhalation, and the activity pattern of the individual all add uncertainty to the exposure estimates. Perhaps the most important contributor to uncertainty is the assumption regarding the number of times paint is used per lifetime. The exposure frequency was based on the Westat survey response regarding the time since last painting. This is not the same as the time between painting events. This discrepancy tends to inflate the frequency of use. Therefore, the time since last painting was divided by 2 in order to decrease the frequency of use. A factor of 2 was used based on the fact that, on average, the survey question would have been asked of people half way between events. Since this was found to be the most sensitive parameter in the exposure calculation, more data are needed in order to estimate a more reliable exposure frequency.

Tables 5 and 6 present a summary of the occupation and consumer exposure to volatile and non-volatile chemicals, respectively, and are sorted by chemical and component class. It also provides a summary of the SAT hazard ratings for specific chemical components not previously identified in the moderate to high concern table (i.e., Table 3).

Aerosol Spray Paints

Table 5. Summary of Volatile Component Occupational and Consumer Inhalation Potential Dose Rate Findings by Chemical and Component Type

CAS #	Chemical	Chemical Component Type	SAT Hazard Rank	Short-Term			Long-Term		
				Occupational Daily Dose (mg/kg-day)	Consumer Daily Dose Range (mg/kg-day)		Occupational ADD ¹ (mg/kg-day) (range)	Consumer LADD _{pot} Range (mg/kg-day)	
					Central Tendency	High-End		Central Tendency	High-end
67-64-1	Acetone	Solvent	L	2.366	9.82E+00 - 1.64E+01	5.45E+01 - 7.86E+01	0.0203 - 3.2400	3.33E-03 - 1.05E-02	1.84E-02 - 5.03E-02
110-82-7	Cyclohexane	Solvent	LM	0.037	1.42E-01 - 2.37E-01	7.88E-01 - 1.14E+00	0.0003 - 0.0500	4.81E-05 - 1.52E-04	2.67E-04 - 7.28E-04
100-41-4	Ethylbenzene	Solvent	LM	0.18	6.15E-01 - 1.03E+00	3.41E+00 - 4.93E+00	0.0015 - 0.2400	2.08E-04 - 6.58E-04	1.16E-03 - 3.15E-03
110-54-3	Hexane	Solvent	M	0.473	1.75E+00 - 2.92E+00	9.72E+00 - 1.40E+01	0.0040 - 0.6400	5.93E-04 - 1.87E-03	3.29E-03 - 8.97E-03
108-87-2	Methyl Cyclohexane	Solvent		0.12	3.55E-01 - 5.92E-01	1.97E+00 - 2.84E+00	0.0010 - 0.1640	1.20E-04 - 3.80E-04	6.66E-04 - 1.82E-03
96-37-7	Methyl Cyclopentane	Solvent	LM	0.041	1.66E-01 - 2.76E-01	9.19E-01 - 1.33E+00	0.0004 - 0.0560	5.61E-05 - 1.77E-04	3.11E-04 - 8.49E-04
75-09-2	Methylene Chloride	Solvent	H	1.779	6.55E+00 - 1.09E+01	3.64E+01 - 5.25E+01	0.0150 - 2.4000	2.22E-03 - 7.01E-03	1.23E-02 - 3.36E-02
78-93-3	Methyl Ethyl Ketone	Solvent	LM	0.651	2.55E+00 - 4.27E+00	1.42E+01 - 2.05E+01	0.0056 - 0.9000	8.65E-04 - 2.73E-03	4.80E-03 - 1.31E-02
108-10-1	Methyl Isobutyl Ketone	Solvent	LM	0.531	1.96E+00 - 3.28E+00	1.09E+01 - 1.57E+01	0.0045 - 0.7200	6.65E-04 - 2.10E-03	3.69E-03 - 1.01E-02
111-65-9	Octane	Solvent	LM	0.053	2.13E-01 - 3.55E-01	1.18E+00 - 1.71E+00	0.0005 - 0.0720	7.21E-05 - 2.28E-04	4.00E-04 - 1.09E-03
80-56-8	α -Pinene	Solvent		0.0186	4.73E-02 - 7.90E-02	2.63E-01 - 3.79E-01	0.00010 - 0.0162	1.60E-05 - 5.06E-05	8.89E-05 - 2.43E-04

RISK CHARACTERIZATION

Risks were estimated for both occupational and consumer settings. The following exposure routes were evaluated: 1) inhalation of vapor components such as solvents and propellants, 2) inhalation of aerosols of paint solids and resins such as colorants and binders, 3) dermal exposure to paint solids and other non-volatile components through incidental contact.

Both short-term and long-term exposures were estimated: 24-hour dose, average daily dose (ADD) during a 40-yr working lifetime, and total lifetime (70-yr) average daily dose (LADD). Central tendency (mean or median) and high end (>90th percentile) estimates were developed by constructing scenarios in which major input parameters vary. The variables included: inhalation rate, exposure frequency, exposure duration, quantity of product used per event, concentration of chemical in product, percent of time event takes place indoors, and time spent in room after event.

Carcinogenic risks were evaluated by estimating upper-bound individual lifetime risks. Carcinogenic risk for a chemical is calculated by multiplying the estimated exposure level and the chemical's carcinogenic potency estimate. For example a lifetime average exposure level of 3 $\mu\text{g}/\text{m}^3$ to a chemical with a carcinogenic potency (unit risk) of $5 \times 10^{-7}/\mu\text{g}/\text{m}^3$ would result in a lifetime risk of 1.5×10^{-6} . Other toxicologic endpoints were evaluated by calculating a "hazard index," which is the ratio of the exposure level to a Reference Dose (RfD) or Reference Concentration (RfC). EPA defines a Reference Dose or Reference Concentration (for inhalation exposures) as a daily lifetime exposure level that is unlikely to present an appreciable risk of deleterious effects. A Reference Dose is expressed as a mg/kg/day dose and a Reference Concentration as a mg/m³ air concentration. A hazard index value greater than one (i.e. the exposure level is above the RfD or RfC level) is assumed to present a potential concern. Hazard index values below one are assumed to represent minimal concern. Sample risk estimates for some of the aerosol spray paint chemicals are shown in the table below.

Preliminary Risk Estimates

Chemical	Hazard quotient		Upper bound cancer risk	
	Occ. range	Consumer high end	Occ. range	Consumer high end
methylene chloride	0.25 - 40	0.21 - 0.56	1E-05 - 2E-03	2E-05 - 6E-05
Cd orange/red lithopone	0.28 - 44	0.46 - 1.3	6E-04 - 8E-02	1E-03 - 4E-03
CrPbMo oxide			4E-03 - 5E-01	1E-02 - 3E-02
Toluene	84 - 13500	70 - 191		
Hexane	70 - 11000	58 - 160		

The risk estimates shown above should be regarded as only rough, screening level estimates because of many uncertainties and limitations in both the underlying data and the mathematical models employed. The exposure modeling relied heavily on extrapolations from generic data and assumptions based on professional judgment.

INTRODUCTION TO POLLUTION PREVENTION AND CONTROL TECHNOLOGY OPPORTUNITY ASSESSMENT

This assessment will provide a summary of available information regarding pollution prevention and control technology opportunities which may reduce/mitigate industrial releases of a chemical or chemicals under review. Specific individual processes for chemical manufacturing and use for which possible human and/or environmental risks will be identified in each of the components of the risk reduction hierarchy. The hierarchy essentially consists of:

- 1) source reduction (including technology changes and improved management practices)
- 2) responsible recycling/reuse
- 3) improved treatment technologies
- 4) improved disposal technologies

Information collected will address worker exposure issues, so as to identify all cost and performance issues associated with the use of a particular chemical or technology.

If relevant information does not exist to compile portions of this assessment, then the resulting information needs will be clearly identified as areas for potential future investigation.

An EPA chemical engineer will work with industry to identify opportunities for pollution prevention and will then assess these alternatives.

Source reduction and pollution prevention opportunities will be identified by industry and the EPA chemical engineer in the following areas:

An example of the information included in this analysis follows as Exhibit 9.

SOURCE REDUCTION OPPORTUNITIES

Process Change Assessment

Information gathering and engineering assessments will be performed on process changes and conditions that reduce releases. Such information includes equipment modifications and altered process conditions.

Management Practices Assessment

The impact of altered management practices to reduce releases will be examined. Examples of such management practices include the incorporation of periodic monitoring and maintenance of areas where fugitive air releases may occur.

RECYCLE OPPORTUNITIES

Areas where improved recycling would reduce releases will be examined. Examples include the use of condensers in stacks to recover volatile organics followed by separation and recycle.

CONTROL TECHNOLOGIES

Treatment technologies that result in mitigated releases will be examined. Examples include the use of incinerators to burn organic waste for energy.

Disposal technologies that result in mitigated releases will be examined. Examples include the use of vitrification for highly toxic metals.

SOURCE REDUCTION OPPORTUNITIES

Process Change Assessment

- Continue to conduct research into process changes that will eliminate the need to water strip the AN product.
- Improvements could be investigated in the separation of AN product and water generated from the reaction such as improved distillation or extraction following distillation.

Management Practices Assessment

- LDAR (leak detection and repair) programs within the facility to limit fugitive emissions.
- Investigate improving the efficiency of the incinerator/flare.

RECYCLE OPPORTUNITIES

Potential opportunities that could be investigated are:

- Water scrubbers or carbon absorbers on AN holding and storage tanks to recover AN in emissions and recycle to the process.
- Use of nitrogen blanket or purge to address explosive potential by reducing oxygen content in product stream and allow start-up emissions to be sent to absorber.
- Routing of startup emissions to a combined water scrubber/carbon adsorption or other technology that may overcome explosive potential and allow for recycling of the AN.

CONTROL TECHNOLOGIES

Improved control technologies that have been employed or may be worthy of further investigation:

- Thermal incineration of absorber off-gas.
- Process flare to receive emissions from column vents.
- Floating roof tanks in place of fixed roof tanks to reduce AN emissions from storage tanks.
- Double mechanical seals.
- Rubber seals on process sewers and sumps with drainage to central sump and dedicated process sewer to eliminate emissions from open sewers.
- Insulated storage tanks to reduce thermal breathing.
- Enclosed sampling system for product/process sampling.
- Conversion of holding pond to tanks or into covered units.

Improved treatment technologies that may be worthy of investigation include:

- Incinerate hazardous wastewaters and bottoms streams in a hazardous waste incinerator; eliminate holding ponds.
- Extraction of hydrocarbons from the wastewater prior to being sent to the holding pond or for reuse (e.g., carbon adsorption, solvent extraction).

PERFORMANCE

Information relating to the comparative performance of the substitute will be presented. These issues will include the affect on performance of any necessary risk reduction equipment or procedures.

Include information on multiple functions of specific chemicals, i.e. may act as pigment and solvent. Also, certain chemicals may only work with specific other chemicals in other functional subgroups, e.g. solvent x may only work with a specific rosin.

COST

Information relating to the comparative cost of the substitute will be presented. This will include the cost of any necessary risk reduction equipment or procedures.

Include information on chemicals, processes or technologies that do not perform as well therefore requiring greater quantities of materials and incurring a greater cost.

Information on performance and cost of alternatives will be collected through industry performance testing of substitutes using industry approved parameters. EPA will assist in developing parameters and testing methodologies. Testing will seek to document, in case study form, quality trade offs, work practice changes and cost considerations involved in using process, chemical and technology alternatives. See Exhibit 10 a for an outline of what performance testing goals and schedule.

**PERFORMANCE TESTING
DESIGN FOR THE ENVIRONMENT PRINTING PROJECT**

There are two purposes for performance testing in the DfE Printing Project. First, printer performance testing will be used to create a baseline for the performance and cost analyses in the substitute assessments. This means that traditional as well as new alternatives need to be identified and tested by printers to form a basis for comparison between products.

Second, performance testing will document any quality trade offs and work practice changes so printers will have the information necessary to try alternative products in their plants. Thus, information from the performance tests will be included in the substitute assessment analysis and will be written as case studies for printers. It is important that the performance information be based on documented standardized tests, as much as possible, so that quality trade offs and cost considerations can be considered along with risk trade-offs.

Proposed Outline

I. Study Design and Printer Identification

GATF/SPTF with the help of the EPA's Office of Research and Development/Office of Pollution Prevention and Toxics and industry printers and suppliers (Performance Committee) will develop a study design. The committee will identify parameters/variables as well as agree upon an acceptable level of uncertainty for the test.

Baseline testing will be performed in controlled conditions at selected test sites, like GATF and SPAI. In addition, printers will be identified through the committee or technical assistance organizations in the states and asked to provide case studies on performance.

II. Product Identification

Products with representative formulas will be chosen using Material Safety Data Sheets to provide a sampling of approximate chemical data for traditional products and new alternatives. Traditional products need to be tested simultaneously with new alternatives in order to create baseline information (i.e. comparing products on an equal basis). The committee will select the representative products which will be masked for the test. Masked MSDS forms will also be created to provide proper documentation when the chemicals come into the print shops.

III. Product Testing

Two steps in performance testing have been identified. First, a controlled test at one site will be performed for a number of traditional and alternative products to test the study design. While the parameters will all be tested for in a scientific manner, documentation will be by case study method, explaining that absolute certainty can not be attached to the results of the tests.

Second, identified, masked products will be tested by printer who have volunteered the use of their shops. An organization, like GATF or SPAI, or an other contractor, will provide technical assistance to printers and will help the printers document the test results using the Study Design. Again, the goal of the tests is not to provide absolute certainty as to the substitutability of the product. Rather the goal is to document, in a structured manner, how the product worked, any work practice or other modifications it required, any quality trade offs identified by the pressman, as well as issues which may affect cost. This information will inform the substitute assessment and printers who are interested in knowing about alternative products.

IV. Documentation of Results

The contractor, with the assistance of EPA's Office of Research and Development, will provide test results to the substitute assessments and will write case studies for printers which document the impressions and judgements of the pressmen as well as providing factual information.

Proposed Timeline

I and II.

Study Design, Printer and Product Identification - 2 months

III..

Initial Controlled Test and Printer Testing - 3 months

IV.

Documentation of Results - 2 months

Revised: 3/7/93

ENERGY IMPACTS

Discuss the energy requirements for manufacture of the chemical and for manufacture of the product, using this chemical. Discuss sources of energy.

Industry will provide information for this analysis from the performance testing results.

RESOURCE CONSERVATION

Discuss natural resource issues; what impacts on non renewable resources the manufacture of this chemical or product have.

EPA staff and industry will work together to define the data needs for this piece.

INTERNATIONAL TRADE ISSUES

Discuss the international trade in this chemical and any issues surrounding this trade. Also include discussion of any international agreements which may affect the use of this chemical or product.

The above sections will be integrated into a social cost/benefits issues piece written by the EPA economist on the project.