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Environmental Profile for N-Methylpyrrolidone

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ENVIRONMENTAL PROFILE FOR N-METHYLPYRROLIDONE

By

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Foreword

The U. S. Environmental Protection Agency is charged by Congress with protecting the Nation's land, air, and water resources. Under a mandate of national environmental laws, the Agency strives to formulate and implement actions leading to a compatible balance between human activities and the ability of natural systems to support and nurture life. To meet this mandate, EPA's research program is providing data and technical support for solving environmental problems today and building a science knowledge base necessary to manage our ecological resources wisely, understand how pollutants affect our health, and prevent or reduce environmental risks in the future.

The National Risk Management Research Laboratory is the Agency's center for investigation of technological and management approaches for reducing risks from threats to human health and the environment. The focus of the Laboratory's research program is on methods for the prevention and control of pollution to the air, land, water and subsurface resources; protection of water quality in public water systems; remediation of contaminated sites and groundwater; and prevention and control of indoor air pollution. The goal of this research effort is to catalyze development and implementation of innovative, cost-effective environmental technologies; develop scientific and engineering information needed by EPA to support regulatory and policy decisions; and provide technical support and information transfer to ensure effective implementation of environmental regulations and strategies.

This publication is a product of the Laboratory's Life Cycle Engineering and Design research program, an effort to develop life cycle assessment and evaluation tools that can be applied for improved decision-making by individuals in both the public and private sectors. Life Cycle Assessment is a part of the Laboratory's strategic long-term research plan. This document is published and made available by EPA's Office of Research and Development to assist the user community and to link researchers with their clients.

E. Timothy Oppelt, Director
National Risk Management Research Laboratory

Abstract

This project is sponsored by the U.S. Department of Defense's (DoD's) Strategic Environmental Research and Development Program (SERDP) and led by the U.S. Environmental Protection Agency's (EPA's) Life Cycle Assessment (LCA) Research Team at the National Risk Management Research Laboratory (NRMRL). The research effort described in this report was conducted to support the Life Cycle Engineering and Design (LCED) Program, a cooperative program of both DoD and EPA. Among the objectives of the LCED is demonstrating the effectiveness of analytical tools and environmental techniques to reduce impacts to the environment and costs of operation while maintaining performance standards. The lessons learned from LCED projects will be incorporated into a design guide for DoD process engineers and designers. Environmental information on N-methylpyrrolidone (NMP) is required for the development of the design guide. This report presents information related to the potential environmental implications of NMP.

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Acronyms

BCF	Bioconcentration factor
BOD	Biological oxygen demand
CAA	Clean Air Act
CARC	Chemical agent-resistant coating
CAS	Chemical Abstract Service
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
COD	Chemical oxygen demand
cP	Centipoise
DoD	U.S. Department of Defense
EC	Effective concentration
EPA	U.S. Environmental Protection Agency
EPCRA	Emergency Planning and Community Right-to-Know Act
HAP	Hazardous air pollutant
LCA	Life cycle assessment
LCED	Life Cycle Engineering and Design Program
LD_{50}	Lethal dose to 50 percent of test animals
MEK	Methyl ethyl ketone
MSDS	Material safety data sheet
NFPA	National Fire Protection Association
NMP	N-methylpyrrolidone
Pa	Pascals
PC	Propylene carbonate
ppm	Parts per million
POTW	Publicly owned treatment works
PVA	Polyvinyl acetate
PVC	Polyvinyl chloride
RCRA	Resource Conservation and Recovery Act
SARA	Superfund Amendments and Reauthorization Act
SERDP	Strategic Environmental Research and Development Program
TLV	Threshold limit value
TOC	Total organic carbon
TSCA	Toxic Substances Control Act
VOC	Volatile organic compound
°C	Degrees Celsius
°F	Degrees Fahrenheit

1.0 Introduction

The research effort described in this report was conducted under cooperating programs of both the Department of Defense (DoD) and the Environmental Protection Agency (EPA). Among the shared objectives of the cooperators is demonstrating the effectiveness of analytical tools and environmental techniques to reduce environmental impacts and costs of operation while maintaining performance standards. This project was sponsored by DoD's Strategic Environmental Research and Development Program (SERDP) and conducted by EPA's Life Cycle Assessment Research Team at the National Risk Management Research Laboratory (NRMRL).

STRATEGIC ENVIRONMENTAL RESEARCH AND DEVELOPMENT PROGRAM

SERDP was established 2 years ago in order to sponsor cooperative research, development, and demonstration activities for environmental risk reduction. Funded with DoD resources, SERDP is an interagency initiative between DoD, the Department of Energy (DOE), and EPA. SERDP seeks to develop environmental solutions that improve mission readiness for federal activities. In addition, it is expected that many techniques that are developed will have applications across the public and private sectors.

LIFE CYCLE ASSESSMENT RESEARCH PROGRAM

Since 1990, the NRMRL has been at the forefront in the development of life cycle assessment (LCA) as a methodology for environmental assessment. In 1994, NRMRL established an LCA Team to organize individual efforts into a comprehensive research program. The LCA Team coordinates work in both the public and private sectors with cooperators ranging from members of industry and academia to federal facility operators and commands. The team has published project reports and guidance manuals, including *Life Cycle Assessment: Inventory Guidelines and Principles* and *Life Cycle Design Guidance Manual.* The work described in this report is a part of an expanding program of research in LCA taking place under the direction of NRMRL in Cincinnati, OH.

The research effort described in this report was conducted under the Life Cycle Engineering and Design (LCED) program, a cooperative program of both the DoD and EPA. Among the objectives of the LCED program is demonstrating the effectiveness of analytical tools and environmental techniques to reduce impacts to the environment and costs of operation while maintaining performance standards. To do this, LCED has sponsored three LCA and life cycle-based projects at DoD installations:

- Propylene Carbonate (PC) Blend 2, a depainting alternative to methyl ethyl ketone (MEK)
- Chemical agent-resistant coating (CARC)
- GBU-24 energetics model.

The lessons learned from these three projects will be incorporated into a design guide for DoD process engineers and designers. Environmental information on N-methylpyrrolidone (NMP) is required for the development of the design guide. This report presents information related to the potential environmental implications of NMP.

1.1 Goals and Scope of this Research

The overall goal of this research is to document the environmental impacts of NMP to assist DoD in assessing the life cycle environmental implications of NMP and NMP-based formulations as viable alternative materials, products, and techniques to paint, depaint, and corrosion control DoD aircraft, vehicles, and equipment in common applications at federal facilities.

A life cycle study encompasses the cradle-to-grave stages of a product, process, or activity, from the acquisition of raw materials to the final disposition. Consistent with life cycle concepts, the study boundaries for the use of NMP in painting and depainting operations include the following elements:

- Raw materials acquisition
- Production of intermediate chemicals and materials
- Production of NMP
- Use of NMP
- Storage and disposal of residual NMP.

Although all stages of the NMP life cycle were considered, greater emphasis was placed on the use, storage, and disposal stages because these are the stages over which DoD facilities can exert the most control.

1.2 Research Approach

Identifying the life cycle environmental implications of NMP in DoD painting and depainting operations requires not only a comprehensive search for the use of NMP in those

operations but also a search for information related to the production, use (in other applications), and disposal of NMP.

To develop an environmental profile for NMP, the following tasks were conducted and documented:

- Conducted a literature search of NMP for all environmental impact information and data that can be reasonably acquired
- Collected analyses of the environmental impacts of NMP as used in painting and depainting operations
- Contacted responsible individuals in the aerospace industry who have evaluated NMP and NMP substitutes, as well as those currently using NMP
- Provided detailed information on the known ecological and human health impacts of NMP, including occupational health and safety implications of the use of NMP in aerospace cleaning and depainting operations
- Collected relevant case histories on the use of NMP for cleaning and depainting operations.

1.3 Report Organization

This report is organized according to the following sections:

2.0 Production and Use of NMP
3.0 Impact Categories
4.0 Data Review
5.0 Impact Assessment
6.0 Environmental Regulations
7.0 Summary
8.0 References.

Section 2.0 provides background information on NMP and presents several case studies focusing on its use in depainting operations. Key human health and environmental impact categories are identified in Section 3.0. Section 4.0 discusses sources of information, physical and chemical properties, environmental fate and transport, and the toxicology of NMP. Section 5.0 identifies the populations at risk of exposure and summarizes the available data on potential impacts to natural resources and ecosystems. Current environmental regulations are reviewed in Section 6.0, and a summary is provided in Section 7.0.

2.0 Production and Use of NMP

The process used to manufacture NMP is summarized below. The relatively low vapor pressure and high flash point of NMP, as compared to other solvents, make it suitable for use in painting and depainting operations. However, there has been some concern about the potential environmental and human health impacts associated with the use of NMP. In particular, focus has been placed on the human reproductive impacts of NMP.

A life cycle evaluation of NMP requires an assessment of all potential impacts associated with its production and use. Section 2.1 summarizes the steps involved in the manufacture of NMP, starting with the extraction and processing of natural gas to the manufacture of the final NMP product. Section 2.2 contains summaries of case histories regarding the use of NMP in paint and depainting operations, as well as other applications that provide similar exposure scenarios.

2.1 Production

A flow diagram and description of the process required to manufacture NMP are presented in *Life Cycle Assessment for the PC Blend 2 Aircraft Radome Depainter* (U.S. EPA, 1996a). N-methylpyrrolidone is manufactured by combining γ-butyrolactone with methylamine. Production of methylamine begins with the production and processing of natural gas. Natural gas and steam are fed into a reformer over a nickel catalyst, where 70 percent of the feed is converted into hydrogen and carbon dioxide. The remaining hydrocarbons are fed into a second reformer, where air is introduced to supply nitrogen. The nitrogen and hydrogen react to form ammonia. Methanol, which is manufactured from methane-rich natural gas, is used to alkalize the ammonia in the presence of a dehydrating catalyst to produce methylamine.

The γ-butyrolactone used in NMP production is produced from the combination of acetylene and formaldehyde. First, acetylene and formaldehyde are reacted at 90 to 100 °C and an acetylene partial pressure of 500 to 600 kPa. 1,4-Butynediol, which is produced from the reaction, is then hydrogenated to 1,4-butanediol through the Reppe process. The γ-butyrolactone is then manufactured by dehydrogenation of 1,4-butanediol.

NMP production is accomplished by condensing γ-butyrolactone with methylamine at 200 to 350 °C and 10 MPa. The total energy required to produce 1,000 pounds of NMP from raw material acquisition through NMP production equal 28,526,000 Btu for material resources,

16,934,000 Btu for process energy, and 918,000 Btu for transportation. A flow diagram of this process is shown on page A-4 of *Life Cycle Assessment for the PC Blend 2 Aircraft Radome Depainter* (U.S. EPA, 1996a).

N-methylpyrrolidone is primarily manufactured in the United States by three chemical companies:

- BASF, Inc.
- ARCO Chemical Company
- International Specialty Products (ISP) Technologies Inc.

U.S. Patent Nos. 5,049,300, 5,049,314, 5,478,491, and 5,575,859 contain information about various paint strippers that use NMP in their composition.

2.2 Use

The low volatility and high flash point of NMP make it suitable for use in painting and depainting and other industrial stripping and cleaning operations. This sections contains summaries of case studies conducted using NMP in painting and depainting operations, as well as in other applications that entailed similar exposure scenarios to the painting and depainting operations. The case studies are summarized here to highlight applications and situations where the performance of NMP has been evaluated and documented.

More extensive case study summaries are provided in Appendix A.

Pollution Prevention Demonstration and Evaluation of Paint Application Equipment and Alternatives to Methylene Chloride and Methyl Ethyl Ketone (J.M. Elion et al., EPA/600/SR-96/117, October 1996).

This research provides results of a demonstration of NMP as a possible alternative to methylene chloride and MEK. The demonstration was conducted at the Marine Corps Logistics Base in Albany, GA. N-methylpyrrolidone was chosen because it effectively removed CARCs in laboratory tests, is nonflammable, and is not classified as a hazardous air pollutant (HAP) by EPA. However, NMP had to be heated to be effective in the demonstration. If employed, this substitution would potentially reduce HAPs at the base by 11 percent from 1992 levels.

Surface Tension Modification of NMP-based Paint Strippers (W.C. Walsh, BASF Corporation, Chemicals Division, Mount Olive, NJ).

Five NMP-based formulas, ranging in weight percent content from 12 to 80 percent, were reviewed in this study to determine their effectiveness as paint strippers. All of these formulations demonstrated good paint-stripping ability in the removal of commonly used paints and coatings. During testing, performance data were developed on the ability of these products

to strip acrylic latex, alkyd, polyurethane, and epoxy coatings from wood substrates. Characteristics evaluated in this study included work area solvent concentrations, material recyclability, waste generation, waste disposal, and stripping cost. In addition, by lowering the surface tension of these NMP formulas, the time required for their use may be decreased by as much as 40 percent. Even after reducing the time required to strip urethane enamel and household epoxy, the NMP formulas were slower than the methylene chloride product. N-methylpyrrolidone works slower but provides the user a working environment containing less solvent vapor.

Initial Screening of Chemical Ingredients and Substitutes in Consumer and Small Shop Paint Stripper Formulations (Sherry Wise, Regulatory Impacts Branch, Economics, Exposure and Technology Division, Office of Pollution Prevention and Toxics, U.S. Environmental Protection Agency, Washington, D.C., June, 1994).

This report contains information on chemical ingredients of commercially available paint stripper products used to remove paint and other finishes by consumer do-it-yourselfers or small shop operators (e.g., furniture restorers and refinishers). Coatings in the evaluations included alkyd enamels, latex semigloss enamels, flat acrylic latexes, spar varnishes, urethane varnishes, latex exterior enamels, interior vinyl acrylics, epoxies, marine paint, and marine varnish. Eight NMP-based strippers were rated below methylene chloride-based products on all coatings but above ATM strippers (mixtures of acetone and/or toluene and/or methanol), with the exception of enamel, where both NMP and ATM were rated equally. N-methylpyrrolidone was the fastest of the "safe" products (15 minutes to more than 1 hour, depending on the concentration of NMP). Each NMP-based product also had a slight odor and was nonflammable. However, they cost nearly twice as much as methylene chloride removers. They can also cause dizziness and nausea after prolonged exposure.

Replacement of MEK with N-Methylpyrrolidone (NMP) in Coatings Plant Resin Clean Up Operations (W.C. Walsh, BASF Corporation, Chemicals Division, Mount Olive, NJ).

This research discusses work conducted by a manufacturer of high-solids, oven-cured, clear-coat, and base-coat coatings for Original Equipment Manufacturer (OEM) automotive and heavy equipment, as well as for some industrial applications, to evaluate replacing its MEK cleaning solvent with NMP systemwide. Results from the study showed that over a 10-month test period there was a 5-fold decrease in MEK emissions from the facility and that cleaning costs rose by 40 percent over total MEK costs. But, this result was due to the inexperience of the facility in initially using NMP. The total volume of cleaning solvent passing through the plant decreased by 39 percent, 69 percent of which could be accounted for by decreases in virgin MEK purchases. Also, the total volume of MEK passing through the plant decreased by almost 72 percent.

Met-Ed/Penelec Business and Industry, Technology Excellence Center (BITEC), BITEC Assistance Report for James River Corporation, Lehigh Valley, PA (Concurrent Technologies Corporation, 1450 Scalp Avenue, Johnstown, PA, May 1996).

James River Corporation manufactures both wax-coated paper and plastic (high-impact polystyrene polymer) drinking cups at its Lehigh Valley, PA, facility. The plastic cups are manufactured using aluminum thermoforming tools, with up to 100 vent holes in each tool. These tools were removed and placed in an immersion tank filled with Tower 19 paint thinner, a mixture of 80 percent toluene and 20 percent acetone, for 15 to 30 minutes and then allowed to air-dry. Once dry, the vent holes were manually probed to remove the accumulated polystyrene using a drill bit.

Based on a visual examination, NMP was the most effective of the three cleaners tested, removing residues from recessed areas and small holes. N-methylpyrrolidone also did not emit obvious odors during testing. Drying times were relatively high -- some parts were still wet after drying for 20 to 25 minutes at ambient temperature. At the time, NMP was available for approximately $2.35/lb or approximately $1,000 to $1,150/55-gal drum.

3.0 Impact Categories

A life cycle evaluation of the potential impacts of NMP requires consideration of impacts both to the environment and to human health. To assist in guiding the search for information related to NMP, impact categories and subcategories were established. Numerous impact categories have been proposed for life cycle impact assessment, and most LCAs to date have selected from these previous efforts in lieu of defining their own impact categories. However, impact categories are typically selected so that the goals of the study may be satisfied.

This section lists the categories and subcategories of impacts to the environment and to human health that were selected as starting points for the evaluation of NMP. For each category and subcategory, quantitative and qualitative impact information was searched for and compiled, as appropriate. Any additional impacts found that were not part of the original listing were subsequently added.

3.1 Ecological Impacts

Potential ecological impacts of NMP as used in painting and depainting operations result primarily from the production, use, and disposal stages of its life cycle, where emissions are released directly into the environment. Examples of activities that might result in environmental impacts could include the extraction and processing of natural gas, the volatilization of NMP during use, or the leaching of residual NMP into the soil or ground water. To establish a baseline set of ecological impact categories for this research, LCA guidance documents and case studies were consulted. The resulting list of ecological impact categories is shown in Table 3-1. The impacts have been categorized by their mechanism of action, mainly whether they result from chemical or nonchemical pollutants or from resource depletion.

3.2 Human Health Impacts

Potential human health impacts of NMP as used in painting and depainting operations result primarily from the use stage of its life cycle, where workers may be directly exposed to NMP emissions. Additional human health impacts may result from emissions released during the production and disposal stages of the life cycle. To establish a baseline set of human health impact categories for this research, LCA guidance documents and case studies were consulted. The resulting list of human health impact categories is shown in Table 3-2. Again, the impacts have been categorized by their mechanism of action, mainly whether they result from chemical or nonchemical pollutants.

Table 3-1. Ecological Impact Categories Related to Chemical and Nonchemical Stressors and Resource Depletion

Chemical	Nonchemical	Resource Depletion
• Global warming • Ozone depletion • Acid deposition • Photochemical oxidant formation • Tropospheric ozone • Aquatic toxicity • Eutrophication • Visibility alterations • pH alterations • Chemical/biological content alteration • Oxygen depletion • Aquifer contamination • Land use	• Ionizing radiation • Heat • Noise • Environmental disturbance -habitat alteration -physical change to water -physical change to soil • Regional climate change • Species change -composition -total diversity	*Nonrenewable* • Fossil fuels • Minerals *Renewable* • Water • Renewable energy • Agricultural resources • Wilderness resources

Table 3-2. Human Health Impact Categories Related to Chemical and Nonchemical Stressors

Chemical	Nonchemical
• Human carcinogen • Inhalation toxicity • Irritant (eye, lung, skin, gastrointestinal) • Respiratory system effects • Central nervous system effects • Mutagenicity • Developmental toxicity • Allergenicity • Blood dyscrasias • Odors • Cardiovascular system effects • Reproductive effects • Behavioral effects • Bone effects • Renal effects	• Heat • Noise • Light • Nuisance

4.0 Data Review

A joint literature search was conducted for NMP and PC. Both of these chemicals are components of PC2, which is used in depainting. This section discusses the literature search and summarizes the available information on NMP's physical and chemical properties, environmental fate and transport, and toxicity. However, Tables 4-1 and 4-2 are inclusive of both NMP and PC.

4.1 Sources

Research Triangle Institute (RTI) conducted an extensive literature search for NMP and PC. In addition to searching online databases, manufacturers were contacted, government reports were located, and an Internet search was conducted. Results of the literature and Internet searches are summarized in the following sections.

4.1.1 *Literature Search*

A literature search was performed using the databases listed in Table 4-1. The databases were searched from 1990 to the present using N-methyl-pyrrolidone and propylene carbonate as key words. The number of relevant articles found in each database is listed in Table 4-1.

Table 4-1. Literature Search for NMP and PC

Name of Database	Database Topic	Number of Articles Found
MEDLINE	Health and medicine	6
Enviroline	Environmental subjects	1
Wilson Applied Science and Technology Abstracts	Science and technology	54
Pollution Abstracts	Pollution topics	1
Environmental Bibliography	Environmental subjects	6
NTIS: National Technical Information Services	Government technical reports	2
Ei Compendex	Engineering	86
World Surface Coatings Abstracts	Coating, paints, inks	14

A second search was performed using the following key words related to NMP and PC: greenhouse, global warming, acid rain, smog, photochemical, ozone, air dispersion, air aging, air transport, aquatic, plant life, eutrophication, visibility, weather, thermal, alterations, oxygen depletion, aquifer, thermal change, and oxygen depletion. Table 4-2 lists the databases searched, the dates searched, and the number of articles found in each database.

Table 4-2. Specific Topic Literature Search for NMP and PC

Name of Database	Database Topic	Number of Articles Found	Dates Searched
Meteorological and Geoastrophysical Abstracts	Meteorological and environmental	0	June 1970-1997
Enviroline	Environmental subjects	2	August 1975-1997
GeoArchive	Geosciences	0	August 1974-1997
WATERNET	Water topics	0	1971-1997
Water Resources Abstracts	Water resource topics	8	August 1967-1997
GEOBASE	Ecology	0	August 1980-1997
BIOSIS	Biological abstracts	22	September 1969-1997
Aquatic Sciences and Fisheries Abstracts	Marine and freshwater environments	0	September 1979-1997
Environmental Bibliography	Environmental subjects	6	October 1974-1997
MEDLINE	Health and medicine	14	November 1966-1997
CANCERLIT	Cancer	3	September 1975-1997
PsycINFO	Pyschology, health	0	October 1967-1997
TOXLINE	Toxicological literature	34	August 1965-1997
EMBASE	Biomedical literature	49	August 1974-1997
IAC Health and Wellness Database	Health	1	1976-1997

Government sources and manufacturers contacted included the EPA Office of Pollution Prevention and Toxics (OPPT), the Toxic Substances Control Act (TSCA) Administrative Record, the U.S. Coast Guard, BASF Corporation, Huntsman Specialty Chemical, ISP, and ARCO Chemical Company.

OPPT provided the following reports:

- *Lifecycle Analysis and Pollution Prevention Assessment for N-Methylpyrrolidone (NMP) in Paint Stripping* (U.S. EPA, 1993)

- *Initial Screening of Chemical Ingredients and Substitutes in Consumer and Small Shop Paint Stripper Formulations* (U.S. EPA, n.d.)

- *Consumer/Small Shop Paint Stripping Use Cluster AR-161 Risk Management Report Public Comment Draft* (U.S. EPA, 1996b).

A report entitled *Consumer Paint Stripping Products Containing N-Methylpyrrolidone - Draft Final Report* (Eastern Research Group Inc., n.d) was obtained from the Administrative Record, File AR-075, in the TSCA Non-Confidential Information Center.

Although the U.S. Coast Guard is currently evaluating alternatives to using methylene chloride for small aircraft paint stripping, no information on NMP is now available.

BASF Corporation in Wyandotte, MI, could not provide a list of companies using its NMP-based products; however, it did provide the following reports:

- *1,4-Butanediol Derivatives Flow Chart* (BASF, n.d. a)

- *Acetylenic Chemicals Reaction Flow Chart* (BASF, n.d. b)

- *Formulating Paint Strippers with N-Methylpyrrolidone* (BASF, 1990)

- *N-Methylpyrrolidone Application Profile - Immersion Paint Stripping* (BASF, n.d. c)

- *N-Methylpyrrolidone Biodegradability* (BASF, n.d. d)

- *N-Methyl Pyrrolidone (NMP Technical Tips): Chemical Warfare Resistant Coatings (CARC) Removal from Metal Surfaces* (BASF, n.d. e)

- *N-Methyl Pyrrolidone (NMP Technical Tips): Reclaiming or Recycling of NMP* (BASF, n.d. f)

- 1-*Methyl-2-Pyrrolidone, Material Safety Data Sheet* (BASF, 1997)

- *Replacement of MEK with N-Methylpyrrolidone in Coatings Plant Resin Clean Up Operations* (BASF, n.d. g)

- *Surface Tension Modification of NMP-Based Paint Strippers* (BASF, n.d. h)

- *N-Methylpyrrolidone (NMP): Formula for Success* (BASF, n.d. i).

In addition, BASF's New Jersey branch supplied the following data sheet:

- *Data Sheet for NMP* (IUCID, n.d).

The data sheet summarizes all toxicity testing of NMP performed by U.S. and international companies. The report lists the type of test (i.e., LD_{50}), animal species, value, method, year, test substance, result, and source. The two (primary) sources for test data were BASF AG Ludwigshafen and ISP Europe GUILDFORD. Most of the comments in the results were in German, and most of the data have not been published.

Huntsman Specialty Chemical in Houston, TX, provided the following information:

- *Test Procedures for the Degradability and Bacterial Toxicity of Chlorinated Hydrocarbon Replacements* (Kayser et al., n.d.)

- *Permeability of Commercial Solvents Through Living Human Skin* (Ursin et al., 1995).

ISP supplied a toxicity overview for NMP (ISP, n.d.), and ARCO Chemical Company, Newtown Square, PA, provided data sheets covering environmental fate and ecological toxicity of NMP (ARCO, n.d.).

4.1.2 *Internet Search*

Several Internet searches were conducted to gather environmental profile data for NMP. The following keywords were used for the searches: n-methylpyrrolidone, n-methyl-2-pyrrolidone, NMP, methylene chloride substitution, methyl ethyl ketone substitution, solvent replacement, solvent substitution, depainting solvents, painting solvents, aircraft depainting, paint removal, health effects (n-methylpyrrolidone), environmental effects (n-methylpyrrolidone), ecological effects (n-methylpyrrolidone), radome depainting, paint stripping, toxicity (n-methylpyrrolidone), aerospace painting, and aerospace depainting. Table 4-3 provides a list of Internet sites that were found for NMP.

Table 4-3. Internet Searches for NMP Environmental Profile Data

Title	Address	Type of Information
N-Methylpyrrolidone (NMP) -- General Information	http://sage.rti.org/nmp_gen.htm	Background
List of 286 Chemicals Added to the Toxics Release Inventory (TRI)	http://rtk.net/E8209T660	Background
Hazardous Substances Data Bank (HSDB)		Background, populations at risk (workers), toxicity (lab animal data), use, and environmental fate and transport
Worksafe Australia	http://www.allette.com.au/worksafe/haz/AZ/NMethyl2pyrrolidone.htm	Populations at risk (workers)
Health and Safety Page	http://ntp-db.niehs.nih.gov/NTP_Reports/NTP_Chem_H&S/NTP_Chem8/Radian872-50-4.txt	Populations at risk (workers)
National Fire Protection Association (NFPA) Chemical Hazard Labels	http://www.orcbs.msu.edu/chemical/nfpa/hazardinformation(m).html	Populations at risk (workers)
Site Specific Procedures for Carcinogens	http://www.cc.rochester.edu/Admin/EHAS/sitespec/sts_carc.htm	Populations at risk (workers)
Chemfinder	http://chemfinder.camsoft.com/	Physical and chemical properties
Chemical Sampling Information	http://www.osha-slc.gov/ChemSamp_data/CH_254480.html	Physical and chemical properties
DuPont NonWovens Chemical Abstract Number Search Page	http://www.dupont.com/Tyvek/protective-apparel/Chemical-Data/cas.htm	Physical and chemical properties
The Environmental Chemicals Data Information Network (ECDIN) Data Bank	http://ulisse.etoit.eudra.org/cgibin_ecd/inter_query	Identification, physical and chemical properties, production and use, legislation and rules, occupational health and safety, toxicity, concentrations and fate in the environment, detection methods, hazards and emergency response

(continued)

Table 4-3. (Continued)

Title	Address	Type of Information
Welcome to Fisher Scientific	http://www.fisher1.com/fb/itv?16..f97.4.msf0007.69.1...	Physical and chemical properties, hazards identification, toxicological information, regulatory information
National Center for Manufacturing Sciences	http://solvdb.ncms.org	Physical and chemical properties, health and safety data, regulatory information, environmental fate data
N-methylpyrrolidone (NMP) - Representative Material Safety Data Sheet (MSDS) Summaries	http://clean.rti.org/nmp_msds.htm	Physical and chemical properties, toxicity data, reactivity data
Guide to National Institute for Occupational Safety and Health/Occupational Safety and Health Administration (NIOSH/OSHA) Air Sampling Methods	http://www.skcinc.com/NIOSH1/FILE1120.HTM	Physical and chemical properties
The Carcinogenic Potency Project	http://potency.berkeley.edu/pub/tables/hybrid.rodents.text	Toxicity (lab animal data)
8(e) Triage Chemical Studies Database	http://www.epa.gov/docs/8e_triag	Toxicity (lab animal data)
Envirosense Solvent Substitution Data Systems	http://es.inel.gov/ssds/ssds.html	Use
Fiberglass Mold Cleaning -- General Information	http://clean.rti.org/fibr_gen.htm	Use
P2 in Plastics Manufacturing	http://nben.org.p2tech/plastics.html	Use
P2 Tech Archive	http://gopher.great-lakes.net:2200/R4935...80-1m/mailarc/p2tech	Use
Air Force Link -- Official web site of the U.S. Air Force	http://www.af.mil/index.html	Use
Chem Systems Inc. -- Special Reports	http://www.chemsystems.com/special.htm#butanediol	Background
National Library of Medicine -- PubMed	http://ncbi.nlm.nih.gov/PubMed	Toxicity (human data)

(continued)

Table 4-3. (Continued)

Title	Address	Type of Information
National Library of Medicine -- Internet Grateful Med	http://igm.nim.nih.gov	Toxicity (human data)
SERDP Keyword Search	http://www.hgl.com/SERDP/keyword/default.htm	Use
DoD Defense Environmental Network and Information eXchange	http://es.inel.gov/program/p2dept/defense/denix.html	N/A
Agency for Toxic Substances and Disease Registry (ATSDR) World Wide Web (WWW) Document Text Search	http://atsdr1.atsdr.cdc.gov:8080/atsdrhome.html	N/A
Environmental Health Perspectives Search Form	http://ehpnet1.niehs.nih.gov/docs/ehp_search.html	Toxicity
National Institute of Standards and Technology (NIST) Chemistry WebBook	http://webbook.nist.gov/chemistry	Thermochemical and thermophysical properties
University of Utah MSDS Archive	http://www.chem.utah.edu/MSDS/M/1-METHYL-2-PYRROLIDONE	Physical and chemical properties, toxicity data, reactivity data
Solvent Handbook Database System -- M-PYROL	http://wastenot.inel.gov/shds	Air efficiency data, paint stripping data, paint corrosion data, recycling data, cleaning efficiency data, corrosion data, compatibility data
Environmental Science Center Experimental Log P (octanol/water partition coefficient) Database	http://esc.syrres.com/~ESC/database.htm	Experimental log p (octanol/water partition coefficient)
Physical Properties Database (PHYSPROP)	Commercially available database	Chemical structures, names, and physical properties

(continued)

Table 4-3. (Continued)

Title	Address	Type of Information
Environmental Fate Database (EFDB)	Commercially available database	Environmental fate and exposure data including adsorption, bioconcentration, biodegradation, dissociation constant, effluent concentrations, monitoring, occupational concentrations, and photo-oxidation
Toxic Substances Control Act Test Submission (TSCATS) Database	Commercially available database	Unpublished technical reports submitted by industry concerning health effects, environmental effects, and environmental fate
Chemical Pointer File	Commercially available database	Regulatory information, toxicity, environmental fate and transport
Compilation of Ozone Depletion Potentials (ODP) and Global Warming Potentials (GWP)	http://esc.syrres.com/~ESC/ODPGWP.htm	N/A
Atmospheric Oxidation Database	http://esc.syrres.com/~ESC/aopexp.htm	N/A
DefenseLINK (Links to Army, Air Force, Navy, and Marine Corps homepages)	http://www.defenselink.mil	N/A

N/A = no information on NMP was available at this site.

4.2 Physical and Chemical Properties

N-methylpyrrolidone is a slow-evaporating, highly polar, aprotic, organic solvent. Its molecular formula is C_5H_9NO. It is a colorless, low-viscosity liquid with a faint amine odor and is fully miscible with water. N-methylpyrrolidone is the lactam of 4-methylaminobutyric acid and a very weak base. Commercial NMP has a typical pH of 8.0 to 9.5 (BASF, 1997). NMP exhibits high solvent activity over a variety of resins commonly used in paint and coating formulations including acrylic and polyurethane systems as well as lacquer-type systems. The rate of solvent activity can be increased by increasing the temperature of the formulation containing NMP or the substrate to be stripped (BASF, 1990). Table 4-4 presents the physical and chemical properties of NMP.

Table 4-4. NMP Physical and Chemical Properties

Physical State[1]	**Liquid**
Appearance[1]	Clear colorless liquid
Odor[1]	Mild, amine-like
Vapor density[1]	3.4 (air = 1)
Boiling point (Fahrenheit)[2]	395.6
Freezing point (Fahrenheit)[2]	-11.92
Specific gravity[2]	1.033
Viscosity (cP)[2]	1.666
Vapor pressure (mmHg)[2]	0.341
Surface tension (dynes-cm^2)[2]	40.7
Flash point (Fahrenheit)[2]	197.6
Explosion limit % (upper)[2]	9.5
Explosion limit % (lower)[2]	1.3
Evaporation rate[1]	0.03 (butyl acetate = 1)
Molecular weight[3]	99.13
Solubility (water)[3]	>=100 mg/mL @ 20 °C (rad)
Solubility (95% ethanol)[3]	>=100 mg/mL @ 20 °C (rad)
Solubility (acetone)[3]	>=100 mg/mL @ 20 °C (rad)
Solubility (dimethyl sulfoxide [DMSO])[3]	>=100 mg/mL @ 20 °C (rad)
Typical pH[4]	8.0 to 9.5
Autoignition temperature (Fahrenheit)[5]	518
Reactivity[5]	Stable. Avoid heat, fire, and ignition sources. Incompatible with strong oxidizing or reducing agents.
Percent volatiles by volume[6]	100

(continued)

Table 4-4. (Continued)

Physical State[1]	Liquid
Bulk density[7]	1.028
Critical temperature (K)[8]	7.218 E+02
Critical pressure (Pa)[8]	4.780 E+06
Experimental log p (octanol/water partition coefficient)[9]	-0.38

References

[1] Fisher Scientific, 1996. http://www.fisher1.com/fb/itv?16..f97.4.msf0007.69.1... *1-Methyl-2-pyrrolidinone Material Safety Data Sheet.*

[2] National Center for Manufacturing Sciences. http://solvdb.ncms.org/*SOLV-DB: – Methylpyrrolidone.*

[3] Health and Safety Page. 1991. http://ntp-db.niehs.nih.gov/NTP_Reports/ NTP_Chem_ H&S/NTP_Chem8/Radian872-50-4.txt. *NTP Chemical Repository (Radian Corporation, August 29, 1991): N-Methyl-2-pyrrolidone.*

[4] N-Methylpyrrolidone (NMP) -- General Information. 1997. http://sage.rti.org/nmp_gen.htm. *N-Methylpyrrolidone.*

[5] N-methylpyrrolidone (NMP) -- Representative MSDS Summaries. 1997. http://clean.rti.org/nmp_msds.htm. *N-Methylpyrrolidone.*

[6] J.T. Baker Chemical, n.d.

[7] BASF Corporation, 1997.

[8] Zhao, Renhong. U.S. EPA Systems Analysis Branch.

[9] Environmental Science Center Experimental Log P (octanol/water partition coefficient) Database. http://esc.syrres.com/~ESC/database.htm.

4.3 Environmental Fate and Transport

N-methylpyrrolidone is highly mobile in soil (soil adsorption coefficient estimate of 9.6) but unlikely to absorb to sediment or suspended organic matter to any significant degree. It may slowly volatilize from dry soil but not from moist soil. N-methylpyrrolidone also has a low volatility from water because of its high solubility and low Henry's law constant. Its estimated half-life for volatilization from a model river (1 m deep, 1 m per flow, 3 m per s wind speed) is 2,335 days. N-methylpyrrolidone has a calculated bioaccumulation factor (BCF) of 0.16 and is unlikely to bioconcentrate significantly in aquatic organisms or the food chain (ARCO, n.d.).

Biodegradation occurs under aerobic conditions in aquatic or terrestrial environments; however, a short log phase may occur. The half-life of NMP was determined to be 4.0, 8.7, and 11.5 days in clay, loam, and sandy soils, respectively. Rapid gas-phase reactions with hydroxyl radicals would be expected in the atmosphere (estimated $t^{1/2} = 5.2$ hours). Significant removal by

reaction with ozone is not likely. Reactions in the atmosphere can also be described as slow oxidation to hyperoxides, accelerated by light (ARCO, 1997).

An aerobic degradation measurement of 73 percent biological oxygen demand (BOD) in 28 days was determined for NMP. This test consisted of incubation of 100 mg/L with 30 mg activated sludge for 4 weeks. Other biodegradability findings reported by ARCO (1997) include the following:

- 95 percent removal in 2 weeks (static die-away system, sewage sludge inoculum)
- 95 percent removal in 7 days (average) (semicontinuous, activated sludge)
- > 98 percent removal in 24 hours (210-mg/L initial concentration, sewage sludge inoculum)
- 94 percent removal chemical oxygen demand (COD) screening study, 1-day lag (150-mg/L initial concentration, activated sludge inoculum)
- >98 percent removal 18-hour retention (model flow-through treatment, 300 mg/L activated sludge)
- >90 percent removal screening study, lag of 3-5 days (static, sewage sludge).

The biodegradability of NMP was tested using a variety of test methods. All test results indicated that NMP is practically fully biodegradable. Table 4-5 summarizes these test results (BASF, n.d. d).

Table 4-5. NMP Biodegradability Test Results

Test	Dissolved Organic Carbon--Degradation (%)
Coupled-Units	99
Zahn-Wellens	98
MITI	95
Sturm	97
OECD-Screening	99

An NMP biodegradability test conducted by the University of Stuggart designed to simulate as closely as possible conditions in a publicly owned treatment works (POTW) produced the following results (BASF, n.d. d):

a) A municipal sewage treatment plant (POTW) has a base capacity to eliminate spontaneously up to 10 mg/L without adaptation.

b) The adaptation to higher NMP concentrations is very fast.

c) No deadaptation occurs if the supply of NMP is interrupted for 1 week.

d) If a POTW is not overloaded, virtually complete elimination of NMP in domestic sewage can be expected.

NMP was found to be nontoxic to most aquatic life and readily degraded by typical wastewater treatment plant organisms.

Another biodegradability test, conducted by the Singapore Department of Scientific Services, examined the biodegradability of NMP using a static die-away system and a semicontinuous activated sludge system. The NMP concentrations of the influent for the activated sludge process were around 100 ppm. Results of the die-away test showed that 95 percent biodegradability of NMP was obtained after a 2-week period of incubation and, therefore, was readily degradable in a static system. Ninety-five percent biodegradability was accomplished after 5 days of incremental acclimation in the semicontinuous activated sludge test. It was also found, however, that the metabolite of the degradation was a carbonyl compound having a significant COD that could not be broken down completely under these conditions (Chow and Ng, 1983).

A study was conducted to examine the possibility of biochemical oxidation of NMP at high starting concentrations (up to 1,200 mg/L) and to determine the aeration time necessary to attain a required degree of cleanup. Testing was performed in an aeration tank with a capacity of 20 to 50 L per tank. Sludge containing NMP at concentrations of 200 to 400 mg/L was adapted in the tanks for 2 weeks. Later, the NMP concentration was increased to 600 to 800 mg/L and then to 1,200 mg/L. The results of this study indicate that in concentrations up to 1,200 mg/L NMP does not adversely affect active sludge and can be subjected to biochemical destruction in aeration tanks. In addition, sorption dominates over bio-oxidation in the initial NMP removal period (Ivanov et al., 1989).

4.4 Toxicity

NMP has undergone fairly extensive toxicity testing under TSCA; however, much of the data is unpublished. Several summaries were obtained from the manufacturers that provide a brief overview of the toxicology data. In general, NMP has a low order of acute, subchronic, and chronic toxicity. It is mildly irritating to skin but is moderately to severely irritating to the eyes. The available data indicate that NMP is not likely to be mutagenic or carcinogenic, but there is some evidence of reproductive and developmental effects in laboratory animals at high doses. The following sections present an overview of the available information.

4.4.1 *Human Data*

Very few reports on human exposure and toxicity were located for NMP. The available studies examined skin irritation in workers, acute effects in volunteers, pharmacokinetics, and skin permeability.

Leira et al., 1992. Irritant Cutaneous Reactions to N-Methyl-2-Pyrrolidone (NMP).

After 2 days of work with NMP, 10 of the 12 workers in an Safety electrotechnical company in Norway experienced acute irritant contact dermatitis of the hands. The material safety data sheet (MSDS) of a Norwegian sales firm contained no information on cutaneous hazards, but the MSDS of an American producer of NMP stated the risk of severe dermatitis (blister, edema, cracking, redness) upon prolonged or repeated contact. This information was based on unpublished case reports where undiluted NMP had been used for cleaning purposes over prolonged periods without cutaneous protection. Butyl rubber was identified as the best glove material to prevent NMP penetration. Polyvinyl acetate (PVA) was listed as a suitable material as well, but latex, neoprene, nitrile, and polyvinyl chloride (PVC) were not recommended. In this case, latex glove use was continued, with cotton gloves worn underneath to prevent moisture buildup, and the gloves were changed hourly. With this precaution, skin problems ceased. This study indicates that NMP is a stronger skin irritant than previously reported.

Akesson and Paulsson, 1997. Experimental Exposure of Male Volunteers to N-Methyl-2-Pyrrolidone (NMP): Acute Effects and Pharmacokinetics of NMP in Plasma and Urine.

Six male volunteers were exposed for 8 hours on 4 different days to 0, 10, 25, and 50 mg/m^3 NMP. The subjects were exposed two at a time in an exposure chamber with an air turnover rate of 20 per hour. There was an exposure free period of about 5 minutes after 2, 4, and 6 hours of exposure for examination and biological sample collection. NMP exposure was assessed by four consecutive 2-hour sampling periods in the personal breathing zone of each subject. Blood samples were taken before the start of the exposure, immediately after the exposure, and 16 hours after the exposure. Changes in nasal volume and airway resistance were measured. The geometry of the nasal cavity was assessed by continuous acoustic rhinometry before exposure and 2, 4, 6, and 8 hours after the start of exposure. In the 10 to 50 mg/m^3 exposure range, no subjective self-reported sensations of eye, nasal, or respiratory irritation occurred. Pulmonary functions and nasal cavities were not affected by NMP exposure. N-methylpyrrolidone was readily eliminated in the urine. The mean half-lives were 4 hours and 4.5 hours for plasma and urine, respectively. Only 2 percent was excreted in urine as unmetabolized NMP. At the end of the exposure, there was a close correlation between exposures and the plasma concentration and urinary excretion of NMP, which indicated that biological monitoring of exposure to NMP or risk from NMP is possible. Results indicate that NMP is a mild irritant.

Ursin et al., 1995. Permeability of Commercial Solvents through Living Human Skin.

The steady-state rate of permeation of commercial solvents through living human skin was measured. Skin was removed from healthy females during plastic surgery of the breast. The samples were thinned by removing the dermal tissue from the epidermis and then stretched to a thickness of 300 to 600 μm. Each piece of surgically removed skin usually provided sufficient material to run nine permeation experiments. The permeability rate of NMP was determined to be 171 g/m^{2}h, which was about three times faster than MEK and seven times faster than methylene chloride. This study indicates that NMP is readily absorbed through human skin.

4.4.2 *Laboratory Animal Data*

Acute toxicity of NMP has been studied in rats, mice, guinea pigs, rabbits, and quail. The reported oral lethal dose to 50 percent of test animals (LD_{50}) ranged from about 3.5 to 7.5 g/kg, indicating a very low order of acute toxicity (ISP, n.d.). Subchronic (ingestion and inhalation) studies and reproductive and developmental studies have been conducted in a number of laboratory animals. These studies are briefly reviewed below.

Bartsch et al., 1976. Acute Toxicity of Various Solvents in the Mouse and Rat.

Various solvents are frequently used to improve the solubility of poorly soluble compounds in pharmacological and toxicological experiments. This study was conducted to assess the toxicity of each solvent to avoid a false assessment of the compound being tested. Nine different solvents, including NMP, were examined to find lethal dose levels in the mouse and the rat. The solvents were administered into the tail vein and orally through a stomach tube to a group of 10 animals (5 males and 5 females) of both mice and rats. The solvents were administered in quantities such that at least 3 mortality values between 16 and 84 percent were obtained. The three LD_{50} values for NMP in mice were 3.5 IV, 4.3 IP, and 7.5 PO. NMP's LD_{50} values for rats were 2.2 IV, 2.4 IP, and 3.8 PO. From these data, it was concluded that no more than a quarter of the LD_{50} of the solvent should be used in pharmacological and toxicological experiments to avoid interference between the substance under investigation and the solvent.

Becci et al., 1983. Subchronic Feeding Study in Beagle Dogs of N-Methylpyrrolidone.

This study was conducted to evaluate the toxicological effects of NMP following dietary administration for 13 weeks to male and female dogs. Dose levels were 0, 25, 79, and 250 mg/kg body weight per day. Dosage groups consisted of 6 male and 6 female dogs. Examinations conducted to study possible toxicological and pathological effects included body weight gain and food consumption; hematological and clinical chemical data; and ophthalmic, gross, and histopathological examinations. A dose-dependent decrease in body weight and an increase in platelet count correlating with increased megakaryocytes were noted. Serum cholesterol in males

decreased with the increasing doses of NMP. Feeding NMP to dogs at levels of up to 250 mg/kg body weight per day resulted in no statistically significant toxicological or pathological effects.

Malek et al., 1997. Repeated Dose Toxicity Study (28 Days) in Rats and Mice with N-methylpyrrolidone (NMP).

The repeated dose toxicity of NMP was evaluated in a 28-day feeding study in rats and mice. Groups of 5 male and 5 female rats each were fed either 0, 2,000, 6,000, 18,000, or 30,000 ppm NMP and groups of 5 male and 5 female mice each were fed either 0, 500, 2,500, 7,500, or 10,000 ppm. Compound-related mortality did not occur during the study in either sex of the rats. Lower mean body weight values and body weight gain values (reflecting decreased food consumption) were seen in male rats fed diets containing 18,000 ppm or greater NMP and female rats fed diets containing 30,000 ppm NMP. Clinical chemical changes were also observed in the rats at 18,000 ppm in males and at 30,000 ppm in both sexes, indicating possible compound-related alterations in lipid, protein, and carbohydrate metabolism. No histopathological changes in rats were judged to be directly related to NMP exposure. In the mice, cloudy swelling of the epithelia of the distal parts of the renal tubuli was observed in 4 males and 3 females at 10,000 ppm and in 2 males at 7,500 ppm. Abnormal urine coloration was observed in mice at 2,500 ppm and above and in rats at 18,000 ppm and above. Although the urine discoloration was compound-related, no adverse effects were noted in either species.

Engelhardt and Fleig, 1993. 1-Methyl-2-Pyrrolidinone (NMP) Does Not Induce Structural and Numerical Chromosomal Aberrations in Vivo.

N-methylpyrrolidone, a widely used industrial and commercial solvent, has been shown through several studies to be neither a point mutagenic nor a clastogenic agent. However, it has been found to induce aneuploidy in vitro using *Saccharomyces cerevisiae*. Aneuploidy is associated with spontaneous abortions, congenital malformations, birth abnormalities, and carcinogenesis; therefore, it poses a serious hazard to humans. Micronucleus tests and chromosome analysis test were performed using male and female mice and Chinese hamsters, respectively. In the micronucleus tests, doses of 3,800, 1,900, and 950 mg/kg NMP were given to test groups. Animals in the highest dose group were observed 16, 24, and 48 hours after treatment, while lower dosage groups were observed 24 hours after treatment. For the chromosome analysis, 3,800 or 1,900 mg/kg NMP was given. Bone marrow was sampled after 24 hours in the lower dosage group and after 24 hours and 48 hours in the higher dosage group. In the micronucleus tests, NMP did not increase the frequency of polychromatic erythrocytes containing either small or large micronuclei, indicating that NMP has neither a clastogenic effect nor a spindle poison effect in vivo. In the chromosome analysis tests, the administration of NMP did not result in an increase in the number of mitoses containing structural chromosomal alterations, numerical chromosomal alterations, or numerical chromosomal aberrations. NMP did not reveal any clastogenic or aneugenic activity. Both NMP tests failed to show a mutagenic

effect, the number of polychromatic etrythrocytes containing either small or large micronuclei and the frequency of aberrant mitoses always falling in the range of the negative controls.

Hass et al., 1995. Developmental Toxicity of Inhaled N-Methylpyrrolidone in the Rat.

Fifty-five rats were mated and split into a control group (27 rats) and an experimental group (28 rats). On days 4 through 20 of pregnancy, the rats were exposed for 6 hours per day to clean air and to air containing the highest technically possible concentrations of NMP (about 165 ppm). The animals were observed daily after exposure for signs of toxicity. Body weight and food consumption were recorded on days 4, 7, 14, and 21 of pregnancy. On day 21 of pregnancy, rats were decapitated. The following data were recorded: weight of intact uterus; number of corpora lutea; and number of implantations and fetuses alive, dead, or resorbed. The live fetuses were weighed, their sex determined, and then examined for external malformations. No clinical signs of maternal toxicity were seen during the exposure period. There were no statistically significant differences between the two groups on the number of corpora lutea, implantations, and resorptions or live fetuses per dam. A higher incidence of preimplantation loss and significantly more dams with preimplantation loss were observed in the exposed group. The mean fetal body weight in the litters was slightly lower in the exposed group but was not statistically significant. There was an increase in delayed ossification observed among litters of rats exposed to NMP. The number was statistically significant for cervical vertebrae and for digital bones. Further studies are needed to assess the dose-response relationship as the implications of the results of this study are that NMP may not be a harmless replacement for other organic solvents.

Hass, 1990. Prenatal Toxicity of N-methylpyrrolidone in Rats: Postnatal Study.

Groups of pregnant rats were exposed to either 150 ppm NMP or to clean air 6 hours per day on days 7 through 20 of gestation. After delivery, the development of the pups was observed. Milestones such as pinnae development, incisor eruption, and eye opening were recorded along with development of reflexes (surface righting, auditory startle, air righting) and homing response. After weaning, 2 males and 2 females were selected for further testing. Onset of puberty (vagina opening, complete separation of frenulum) and growth until day 100 were recorded. The males were further investigated for motor ability, activity, learning, and memory. The pups born to the exposed mothers had a lower mean body weight than the control group. This difference in mean body weight persisted into adulthood. The exposed group also exhibited delays in several developmental milestones and reflexes.

Becci et al., 1982. Teratogenicity Study of N-Methylpyrrolidone after Dermal Application to Sprague-Dawley Rats.

In this dose range finding study, the dose levels of NMP used were 500, 1,100, and 2,500 mg/kg body weight per day. Rats were mated, 1 male to 1 female. After mating, 5 pregnant females were assigned to each treatment group. On day 5 of gestation, an application site was

prepared by carefully clipping the fur on the back of each animal. From days 6 to 15 of gestation, material was spread over the skin and rubbed in. The test materials remained on the animals for 8 hours per day, at which time any residual material was removed. Body weights of the dams were taken on days 0, 6, 9, 12, 15, and 20. The females were euthanized with chloroform on day 20 of gestation. In the teratogenicity study, the dose levels for NMP were 75, 237, and 750 mg/kg body weight per day. All procedures for this study were the same as for the dose range finding study, except that each treatment group consisted of 25 females and each fetus was examined for teratologic effects. Results of the dose range finding study showed that at all dosage levels, treatment with NMP was associated with patches of dry skin at the application area and a bright yellow color of the urine. At the high dosage level (2,500 mg/kg), all dams died or spontaneously aborted prior to day 20 of gestation. At 1,100 mg/kg of NMP, all but 1 of the 66 fetuses were resorbed. At the low dosage level (500 mg/kg), NMP had no adverse effect on pregnancy, dam body weights, implantations, or gestation when compared to negative controls. Results of the teratology study showed that dams treated with NMP showed patches of dry skin, the severity of which increased with the dose. Treatment with NMP at the highest dosage level resulted in a decrease in the number of viable offspring, an increase in the mean number of resorption sites per dam, and a decrease in the mean fetal weight. No effect on pregnancy, implantation, or gestation was noted in the middle or low dosage levels of NMP. Fetuses in the high dosage group exhibited an increased incidence of several skeletal abnormalities. Soft tissue examinations revealed no dose-related differences in the type or frequency of anomalies observed in fetuses from dams treated with NMP when compared to control groups.

Hass et al., 1994. Effects of Prenatal Exposure to N-methylpyrrolidone on Postnatal Development and Behavior in Rats.

This study was conducted to assess the effects that prenatal exposure to NMP has on the development of rats. Two groups of pregnant rats were exposed to either 150 ppm NMP or to clean air for 6 hours a day on gestation days 7 through 20. There was no evidence of maternal toxicity resulting from exposure to NMP. The only change attributable to NMP was a bright yellow coloring of the urine from the rats in the exposed group. Litters from the exposed mothers had a lower mean body weight, from birth throughout the preweaning period, than pups in the control group. The exposed pups' physical development was delayed, and they were significantly delayed in some recorded developmental milestones and in the ontogeny of the surface righting reflex. There were no differences between the exposed and control groups for the age of sexual maturation, motor function, activity level, and performance in learning tasks with a low grade of complexity. However, performance was impaired in the exposed offspring in more difficult tasks.

Solomon et al., 1995. 1-Methyl-2-Pyrrolidone (NMP): Reproductive and Developmental Toxicity Study by Inhalation in the Rat.

This study was conducted to assess the effect of prolonged exposure to NMP before and during the reproductive period on reproductive and developmental processes. Rats used in the

experiment were split into two groups. The first group of male and female rats served as the P_0 generation. The second group of rats served as unexposed mates for the F1 generation. Rats within the P_0 group were distributed randomly into seven groups (10 males and 20 females per group). At 34 days old, the rats were exposed to 10, 51, or 116 ppm NMP for 6 hours a day, 7 days a week. Males were exposed for a minimum of 100 days, while females were exposed for a minimum of 106 days. At 119 days of age, each male was placed with 2 females from the same treatment group. Pregnant females were not exposed to NMP from day 20 of gestation to day 4 postpartum. The produced offspring were designated as the F1 generation. On day 70 postpartum, 1 male and 1 female were selected from each litter to mate with the unexposed rats from the previous group to produce an F2 generation. For the developmental phase, both male and female rats inhaled 0 or 116 ppm NMP. Results of the study indicate that reproductive performances did not differ between the exposure groups. Rats exposed to 116 ppm NMP did have a detectable decrease in response to sound; however, they showed no other signs of NMP-related toxicity. A slight decrease in fetal weight was recorded among the F1 offspring whose parents both inhaled NMP at 116 ppm. No detectable or developmental effects appeared in the 10- or 51-ppm groups.

Lee et al., 1987. Toxicity of N-Methyl-2-Pyrrolidone (NMP): Teratogenic, Subchronic, and Two-Year Inhalation Studies.

The toxicity of NMP was tested on rats in a teratogenic study, a 4-week inhalation study and a 2-year inhalation study. In the teratogenic study, groups of 25 pregnant rats were exposed to 0.1 and 0.36 mg/L of NMP in air for 6 hours a day on days 6 through 15 of gestation. A control group was exposed to air in a similar chamber. During the first 3 days of exposure, several of the rats experienced sporadic lethargy and irregular respiration. However, these signs were not seen after that period or during the 10-day recovery period. NMP exposure did not affect the pregnancy or embryonal growth rate. A 4-week inhalation study was conducted using a total of 60 male and 60 female rats divided into four groups of 15 rats of each sex. These rats were exposed to 0.1, 0.5, and 1.0 mg/L NMP for 6 hours a day, 5 days a week, for 4 weeks. A control group was treated under similar conditions using only air. Exposure was discontinued after 10 days in the 1.0 mg/L group due to an excessive mortality rate. These rats had focal pneumonia, bone marrow hypoplasia, and atrophy of lymphoid tissue in the spleen and thymus. No clinical signs or pathological lesions were found in rats at the lower exposure levels. A third group of rats was exposed to 0, 0.04, or 0.4 mg/L NMP for 6 hours a day, 5 days a week, for 2 years. There were no evident life-shortening toxic or carcinogenic effects observed in this group.

4.4.3 *Toxicokinetics*

N-methylpyrrolidone is well-absorbed from all three primary routes of exposure (ingestion, inhalation, and skin). Following absorption, NMP is rapidly metabolized and excreted in the urine. Studies in rats indicate that about 90 percent of the dose is eliminated within 24 hours and studies in human volunteers indicate a plasma half-life of about 4 hours. N-methylpyrrolidone is rapidly distributed to all major organs, but uptake is low. The highest

tissue concentrations occur in the liver and intestines (about 2 and 3 percent of the total dose, respectively). The major metabolic pathway is ring hydroxylation, and 5-hydroxy-N-methylpyrrolidone is the primary metabolite (ISP, n.d.; Wells and Digenis, 1988). Several toxicokinetic studies are reviewed below.

Akesson and Jönsson, 1997. Major Metabolic Pathway for N-Methyl-2-Pyrrolidone in Humans.

The metabolic pathway for NMP was studied in humans. Three male volunteers were administered 100 mg NMP orally. All urine was collected during nine consecutive 24-hour sampling periods. Gas chromatography/mass spectrometry (GC/MS) was used to identify and quantify metabolites in the urine. The metabolites included NMP, 5-hydroxy-N-methyl-2-pyrrolidone (5-HNMP), N-methylsuccinimide (MSI), and 2-hydroxy-N-methylsuccinimide (2-HMSI) and were measured at levels of 0.8 percent, 44 percent, 0.4 percent, and 20 percent, respectively. The increasing half-lives of NMP, 5-HNMP, MSI, and 2-HMSI suggest the existence of a metabolic pathway where NMP is first hydroxylated to 5-HNMP, then further oxidized to MSI, and then hydroxylated to 2-HMSI. The half-lives for 5-HNMP, MSI, and 2-HMSI in urine were approximately 4, 8, and 17 hours, respectively. One-third of the oral dose of NMP was not found as any of the above compounds, which may reflect incomplete absorption from the gastrointestinal tract or the presence of metabolites undetected by the assay.

RTI, 1991. Absorption, Distribution, Metabolism and Elimination of N-Methyl-2-Pyrrolidone (NMP) in Rats after Oral and Dermal Administration.

The disposition of oral and dermal doses of ^{14}C-labeled NMP was studied in 28 male Fischer rats. Rats were given oral doses of NMP of 5 and 500 mg/kg by gavage. Oral doses of NMP were mainly excreted in the urine, with 75 percent (plus or minus 3 percent) of the 500 mg/kg dose and 84 percent (plus or minus 3 percent) of the 5 mg/kg dose excreted in the first 24 hours post-dosing. Elimination of radioactivity in feces or as volatile components in breath was low, and only 1.7 percent of the doses were converted into CO_2. Dermally administered NMP was absorbed very well and excreted primarily through the urine. About 50 percent of the 0.2 and 2.0 mg/cm^2 doses and 75 percent of the 20 mg/cm^2 dose were absorbed, suggesting that NMP enhances its own absorption. Blood level equivalents of NMP in animals given a dermal application of 240 mg NMP in a dose site of 12 cm^2 rose to a maximum of 640 μg-equivalents/g blood at about 8 hours. At least four metabolites were present in the urine; little or no NMP was excreted unchanged. The profile of urinary metabolites present after dermal exposures was similar to those after oral administration. Up to 60 percent of the administered doses were excreted as a single metabolite, 5-HNMP.

Akhter and Barry, 1985. Absorption through Human Skin of Ibuprofen and Flurbiprofen; Effect of Dose Variation, Deposited Drug Films, Occlusion and the Penetration Enhancer N-Methyl-2-Pyrrolidone.

The penetration of ibuprofen and flurbiprofen, nonsteroidal inflammatory agents, was tested on cadaver skin using NMP as a penetration enhancer for the carboxylic acids. Strips of Caucasian abdominal skin were mounted in glass diffusion cells. Ibuprofen and flurbiprofen at three dose levels each were applied in 50 uL acetone. The penetration profile was monitored for 180 hours. During the first 60 hours, penetration was from acetone and from a deposited drug film. One-hundred microliters of NMP was added toward the end of the experiment to cover the skin. The addition of the NMP produced a sudden increase in the penetration rate of the ibuprofen and flurbiprofen by changing the diffusional resistance of the membrane. The quantity of drug permeating across the skin was increased due to the decreased loss of the drug to evaporation.

Wells and Digenis, 1988. Disposition and Metabolism of Double-Labeled N-Methyl-2-Pyrrolidinone in the Rat.

N-methylpyrrolidone is frequently used as a solvent in the formulation of pesticides and as a solubilizing agent in parenteral and topical veterinary pharmaceutical products. Despite this, the in vivo disposition of NMP in man or animals is largely unknown. This study was developed to evaluate the disposition and metabolism of NMP in the rat. Specifically, the work was designed to study the pharmacokinetics and tissue distribution of single- and double-labeled NMP after a single intravenous dose in the rat and to identify the major metabolic pathways. Male rats were anesthetized and their jugular veins were cannulated with tubing. Each rat was injected with a 5.0-μCi dose of either [methyl-^{14}C]-, [ring-^{14}C]-, or [4-^{3}H]NMP in isotonic saline (0.2 to 0.35 mL). For double-labeled radioisotopic studies, animals were coadministered 5.0 μCi of [4-^{3}H]NMP and 2.5 μCi of either [methyl-^{14}C]- or [ring-^{14}C]NMP. Urine and feces were collected every 6 hours for the duration of the study. Expired air was collected for 24 hours following dosing. A second group of rats was treated with single isotope doses of 8.0 μCi and double-labeled isotope doses of 8.0 μCi of [4-^{3}H]NMP and 4.0 μCi of either [methyl-^{14}C]- or [ring-^{14}C]NMP. Serial blood samples were withdrawn at the following times after dosing: 5, 10, 15, 20, 30, 45, 60, 90, 120, 240, and 360 minutes. In a third group, rats were anesthetized and remained anesthetized throughout the study. Double-labeled isotope doses of 5.0 μCi of [4-^{3}H]NMP and 2.5 μCi of [ring-^{14}C]NMP were administered through the jugular vein and the bile duct. Bile was collected at the following times after dosing: 15, 30, 45, 60, 75, 90, 105, 120, 150, 180, 210, and 240 minutes. After a single IV injection, NMP was rapidly distributed to tissues and then showed a slow elimination profile from plasma, suggesting that NMP may be slowly released from a storage deport such as fat. N-methylpyrrolidone was extensively distributed to all the major organs, with appreciable amounts found in the liver and the kidneys at 6 hours. The major route of excretion of radioactivity was through the urine and accounted for about 70 percent of the dose within 12 hours. After 24 hours, the cumulative excretion in urine represented about 80 percent of the dose.

Midgley et al., 1992. Percutaneous Absorption of Co-Administered N-Methyl-2-[^{14}C]Pyrrolidinone and 2-[^{14}C]Pyrrolidinone in the Rat.

This study was designed to assess the oral route as a valid alternative to dermal application for systemic toxicity studies of NMP and 2-pyrrolidinone (2-P). Oral doses of the mixture in solution were given to 66 rats (33 of each sex) by gastric intubation. The doses were equal to 112 mg NMP and 75 mg 2-P/kg body weight. Topical doses of the same mixture were applied to 66 other rats on a shaven area of the animal's back. The treated area was covered with aluminum foil to avoid oral ingestion of the topical dose. Blood was withdrawn from each animal by cardiac puncture under halothane anesthesia followed by cervical dislocation to kill them. Plasma, urine, cage washings, contents of expired air traps, occlusive dressing digests and extracts, application-site washings, skin digests, and carcass digests were separately mixed with a special scintillator for measurement of radioactivity. Concentrations of unchanged NMP and 2-P were determined in the plasma of orally and topically dosed rats by high-performance liquid chromatography (HPLC) with an online radioactivity detector. Radioactivity was excreted predominately in the urine following either dermal or oral administration routes. At 2 hours after oral dosing, plasma concentrations reached peak values and remained relatively uniform during 1 to 6 hours after application to the skin. This rate suggests constant percutaneous absorption during this period. N-methylpyrrolidone was absorbed through the skin at a faster rate than 2-P, and total percutaneous absorption was faster in females than in males. The oral route was considered to be a valid alternative to the dermal route due to the extensive percutaneous absorption and little first-pass metabolism of the two pyrrolidinones.

Wells et al., 1992. Isolation and Identification of the Major Urinary Metabolite of N-Methylpyrrolidone in the Rat.

Male rats were injected with either unlabeled NMP or a 5-μCi dose of [methyl-^{14}C]NMP in isotonic saline. Unlabeled NMP in saline was coadministered with [methyl-^{14}C]NMP to achieve a dose of 45 mg/g. Urine was collected from 0 to 12, 12 to 24, and 24 to 48 hours after dosing. Using GC/MS, 5-HNMP was identified as the major urinary NMP metabolite.

5.0 Impact Assessment

This section reviews the available data on environmental fate and transport and toxicity to determine potential impacts to human populations and the environment from exposure to NMP.

5.1 Human Populations at Risk

U.S. EPA (1993) has prepared an LCA for NMP in paint-stripping. Because of limited data on NMP, much of the LCA was based on data for methylene chloride and extrapolated to NMP based on known or expected differences in physicochemical characteristics, production volume, method of use, and so on. No case reports for NMP releases were identified. According to U.S. EPA (1993), NMP releases were not reported and recorded in the TRI database and no TRI reports since 1993 were found for NMP.

Human populations at risk include workers who use NMP and residents who may be exposed through contamination of water supplies, soil, air, or food or who may use NMP products at home. Because of NMP's low volatility, inhalation exposures are expected to be low. However, inhalation exposures can occur when used in a poorly ventilated area, when sprayed on, and/or when NMP solutions are heated during use. Because NMP is readily absorbed through the skin, dermal contact can be a significant exposure pathway. The U.S. EPA (1993) LCA report indicated that workers involved in the manufacture of NMP or the use of NMP in depainting operations and workers in consumer/small shop paint-stripping were at risk of reproductive and developmental effects if personal protective equipment, particularly proper gloves, was not worn. This report also concluded that risk from exposure to the general population and to the environment under normal circumstances of manufacture and use is minimal. Exposure from food is not likely to be significant because NMP does not bioaccumulate and is biodegradable. However, NMP spills could pose a threat to ground water and water supplies because of low soil adsorption and high solubility. Available case studies are summarized below.

Beaulieu and Schmerber, 1991. M-Pyrol (NMP) Use in the Microelectronics Industry.

This study was conducted to establish a threshold limit value (TLV) for NMP. Previously, no TLV had been set; however, the GAF Corporation had recommended a time-weighted average (TWA) exposure of 100 ppm.

N-methylpyrrolidone is used in the microelectronics industry to strip phenolic residue from packages and photoresist resins on wafer surfaces and as a vehicle for "die-coat"

application. Occupational exposure and stack emission sampling for NMP vapor was performed at two microelectronic fabrication facilities. Site A, constructed in 1979, was a class 100 (100 particles per cubic foot of air) wafer fabrication facility with better particle control achieved through process microenvironments. Site B, built in 1985, was a class 10 control of particulate matter in air in the wafer fabrication areas. Twenty-five air samples were collected from each facility. Industrial hygiene evaluations were performed in the die-coat application areas, in the NMP cleaning rooms, and in rooftop stack exhausts. Several conclusions were drawn from this study. The manufacturer's recommended TLV of 100 ppm for NMP vapor is unacceptable. Many of the employees developed headaches and chronic eye irritation at exposure levels of 0.7 ppm. This study indicates that semiconductor industry employees have typical exposures ranging from 0.02 to 1.5 ppm NMP. The results of this study also indicate that employee exposure should be controlled to less than 0.1 ppm through local exhaust ventilation, good work practices, and the use of personal protective equipment.

Solomon et al., 1996. Stillbirth after Occupational Exposure to N-Methyl-2-Pyrrolidone.

A laboratory technician worked at a chemical manufacturing company in a multiroom quality control (QC) laboratory, analyzing samples for production runs. The woman's responsibilities included operating two atomic absorption spectrophotometers where she dissolved each solid sample in NMP. During her pregnancy, the woman was given a half-face air-purifying respirator in addition to her other protective equipment, which included a laboratory coat, safety goggles, and latex gloves. At the 16th week of gestation, there was a spill of NMP at work, which the woman cleaned up. The NMP dissolved the latex gloves, causing extensive direct skin contact to her hands, including a break in the skin. Over the next 4 days, the woman felt ill with malaise, headache, nausea, and vomiting. She was removed from work on sick leave about 4 weeks after the incident and later returned to office duties with no further exposures to NMP. By the 20th week of gestation, she had been exposed to NMP an average of 42 hours a week. At 25 weeks' gestation, an ultrasound showed early intrauterine growth retardation, at which the growth of the fetus corresponded with a 21-week gestational age. Five weeks later, no fetal activity or fetal heart sounds were detected from the ultrasound. The patient was induced and delivered a stillborn fetus. At 31 weeks of gestation, the fetus appeared to be at 29 weeks' gestation. After leaving the exposed environment, the woman had a successful full-term pregnancy without complication. A review of available literature found that NMP has consistently been demonstrated to have fetotoxic effects on animals. N-methylpyrrolidone adversely affects the fetus in all tested animal species at or slightly below levels that cause mild signs of toxicity in adult animals. The effect is shown through fetal loss or delayed fetal development. From this case and animal literature, NMP should be considered fetotoxic in humans. Companies, and laboratories in particular, should have reproductive health policies in effect that allow for nondiscriminatory voluntary removal of prospective parents in situations of possible exposure.

Anundi et al., 1993. High Exposures to Organic Solvents among Graffiti Removers.

This study was designed to measure the exposures to solvents and possible related health effects among graffiti removers and to eventually promote the use of personal protection. Twelve men participated in the study. The men ranged in age from 18 to 36 years and had worked as graffiti removers between 3 months and 4.5 years. Their job involved removing graffiti from underground stations by spraying solvent on the contaminated surfaces and swabbing with a tissue or applying thickened solvent with a brush and washing with heated high-pressure water spray. Organic solvents used to remove graffiti include dichloromethane (DCM), NMP, trimethylbenzenes, and the glycol ethers dipropylenglycolmonomethylether (DPGME) and propylenglycolmono-n-butylether (PGBE). The workers did not use respirator masks, and gloves, when used, were made of leather and were frequently soaked with solvent. Four workers were studied per day using a battery-operated personal air sampler. Air was aspirated at a flow rate of 15 mL per minute through a charcoal tube and an XAD-2 tube. Fifteen-minute samples were also collected during different work procedures with a pump flow rate of 150 mL per minute. A questionnaire was filled out by each worker to assess previous occupations and nonoccupational exposure to organic solvents, estimated use of the different cleaning products in their present work, and use of protective equipment. High exposures of DCM were found among the workers, with 50 percent of the workers exceeding the permissible exposure limit (PEL) for this solvent. The highest short-term levels were up to 17 times the occupational limit value. N-methylpyrrolidone is easily absorbed through intact skin and, therefore, should be seen as a potential risk. Health effects most readily observed among graffiti removers consisted primarily of irritative effects in the upper respiratory tract and the eyes. Workers were advised to use half-mask respirators and also to protect their skin against spillage.

Zellers and Sulewski, 1993. Modeling the Temperature Dependence of N-Methylpyrrolidone Permeation through Butyl- and Natural-Rubber Gloves.

Gloves selected for testing included one butyl-rubber glove and three other gloves composed of either natural rubber or a blend of natural rubber with small percentages of nitrile and neoprene rubbers. Permeation tests were conducted at four temperatures from 25 to 50 °C using the ASTM F739-85 permeation test method. After 4 hours of exposure to NMP, the butyl-rubber gloves showed no breakthrough at any temperature. For the remaining gloves, permeation resistence decreased significantly as the temperature increased. Breakthrough values in the gloves decreased by factors of 7 to 10 when temperatures were increased from 25 to 50 °C. Temperatures were then extrapolated to 70 and 93 °C, the temperatures at which degreasing is often performed. In all types of gloves, these temperatures yielded breakthrough values of less than 2 minutes and less than 30 seconds, respectively. Gloves were also exposed to NMP at 25 °C and dried overnight. With the exception of the butyl-rubber gloves, low levels of NMP vapor were detected off-gassing from the inner surfaces of the gloves. The results of this study suggest that butyl-rubber gloves should be used for protection from NMP in cases where particulate contamination (resulting from talc treatment of the gloves for adhesion inhibition) can be tolerated.

5.2 Natural Resources/Ecosystems

No specific reports of ecological damage following a spill of NMP were found. As mentioned in the previous section, NMP was not included in TRI reporting. N-methylpyrrolidone has been found to have a low to intermediate reactivity toward ozone (ARCO, n.d.). It is biodegradable, does not bioaccumulate, and has a low acute toxicity to aquatic life. The biological oxygen demand (BOD_5), chemical oxygen demand (COD), and total organic content (TOC) have been reported as 1,100 mg/mL, 1,600 mg/mL, and 600 mg/mL, respectively (BASF, n.d d). Aquatic toxicity data are summarized below.

5.2.1 *Aquatic Toxicity*

Tests to determine the acute toxicity of NMP at concentrations of 100 mg/L for a period of 4 days on guppies (*Lebistes reticulatus*) showed no toxic symptoms or effects (BASF, n.d. i). The effective concentration (EC_{50}) (48 hours) for the Golden orf (*Leuciscus idus*) was found to be between 4,600 and 10,000 mg/L. The EC_{50} (96 hours) for the Rainbow trout (*Oncorhynchus mykiss*) was found to be >500 mg/L. The EC_{50} (24 hours) for the water flea (*Daphnia magna Straus*) was found to be >1,000 mg/L (BASF, n.d. d). Table 5-1 presents the findings of other NMP aquatic toxicity tests (ISP, n.d.). N-methylpyrrolidone demonstrated low toxicity in all of these tests.

Table 5-1. Results of NMP Aquatic Toxicity Testing

Species	LC_{50} (mg/L)
Sunfish	0.8[1]
Fathead minnow	1.1[1]
Trout	3.0[1]
Water flea	4.9[1]
Scud	4.7[1]
Mud crab	1.6[1]
Grass shrimp	1.1[1]
Guppy	1.3[2]

[1] GAF, 1979.

[2] Weisbrod and Seyring, 1980.

The EC_{50} (72 hours) for algae (*Scenedesmus subspicatus*) was found to be >500 mg/L. For bacteria (*Pseudomonas putida*), the EC_{50} (48 hours) was determined to be >9,000 mg/L (BASF, n.d. d). The no-observed-effect concentration (NOEC) for NMP for algae and bacteria is 5,000 mg/L (ARCO, 1996).

5.2.2 *Data Needs*

Of the list of ecological impact categories presented in Section 3.1, data were available for aquatic toxicity and oxygen depletion. Although NMP has shown reproductive and developmental effects in mammals, reproductive studies in aquatic organisms were not available. Other data needs include information concerning global warming potential, photochemical oxidant (smog) formation, visibility alterations, weather alterations, pH alterations, chemical/biological content alterations, aquifer contamination, land use, and natural resource depletion.

6.0 Environmental Regulations

The Chemical Abstracts Service (CAS) Number for NMP is 872-50-4. N-methylpyrrolidone is currently listed in the Toxic Substances Control Act (TSCA) Inventory. N-methylpyrrolidone is listed under the Superfund Amendments and Reauthorization Act (SARA) 313 Title III Emergency Planning and Community Right-to-Know Act (EPCRA), Section 313(d)(2)(B), serious or irreversible chronic health effects. The effective date was January 1, 1995, and the first reports were due July 1, 1996. A full discussion can be found in the *Federal Register* dated November 30, 1994, Vol. 59, No. 229, pp. 61,432-61,485. N-methylpyrrolidone is not listed under the Clean Air Act (CAA), the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA), or the Resource Conservation and Recovery Act (RCRA).

Table 6-1 provides a summary of the regulatory information related to NMP.

Table 6-1. Regulatory Information for NMP

Regulation	Applicability to NMP
CAA	Not listed
CERCLA	Not listed
RCRA	Not listed
SARA	Yes
CWA[1]	Not listed
OSHA[2]	Not listed
ACGIH[3]	Not listed
IARC[4]	Not listed
NIOSH[5]	Not listed
NTP[6]	Not listed

[1] Clean Water Act
[2] Occupational Safety and Health Administration
[3] American Conference of Governmental and Industrial Hygienists
[4] International Agency for Research on Cancer
[5] National Institute for Occupational Safety and Health
[6] National Toxicology Program

In addition to the regulations listed in Table 7, NMP has a National Fire Protection Association (NFPA) health hazard rating of 2 (BASF, 1997). This rating includes materials that may cause temporary incapacitation or residual injury upon intense or continued exposure without the provision of prompt medical treatment. Such treatment includes requiring the use of respiratory protective equipment with an independent air supply. N-methylpyrrolidone has an NFPA flammability rating of 2. This rating includes materials that must be exposed to relatively high ambient temperatures before ignition occurs. Materials with this rating could produce hazardous atmospheres with air under moderate heating or high ambient temperatures. N-methylpyrrolidone has an NFPA reactivity rating of 0, meaning that the solvent is normally stable, even under fire exposure conditions, and does not react with water.

7.0 Summary

N-methylpyrrolidone is a general-purpose organic solvent with a wide variety of industrial applications, including as an ingredient in process chemicals, engineering plastics, coatings, and agricultural chemicals, and in paint stripping and cleaning operations (BASF, n.d. i). This environmental profile was prepared to compile and review the available data regarding potential impacts to human health and the environment from the use of NMP and NMP-based formulations in painting and depainting DoD aircraft, vehicles, and other equipment. This research included identifying case studies of NMP formulations in painting and depainting operations or other applications with similar exposure scenarios, compiling toxicology and environmental fate and transport data, and collecting analyses of environmental impacts.

Several case studies were identified and reviewed (see Section 2.2 and Appendix A). These studies indicate that NMP formulations work slower and may be more expensive than MEK or methylene chloride formulations, but they are generally effective, reduce emissions, and reduce worker exposure.

Very little environmental impact data were available for NMP because TRI reporting has not been required. N-methylpyrrolidone is highly mobile in soil and would be expected to leach into ground water if spilled onto soil. It readily biodegrades in soil under aerobic conditions, with estimated half-lives of 4 to 11.5 days, and in wastewater. Volatilization from soil and water is slow; however, once released into the air, it reacts with hydroxyl radicals and degrades (estimated t½ of about 5 hours). N-methylpyrrolidone does not bioaccumulate in aquatic organisms or in the food chain. The available aquatic data indicate a low order of toxicity.

Much of the toxicity information apparently has not been published; however, data are available on acute toxicity, subchronic toxicity, chronic toxicity, mutagenicity, carcinogenicity, and reproductive and developmental toxicity. N-methylpyrrolidone is readily absorbed through all routes of exposure and is rapidly distributed, metabolized, and excreted in the urine. It is a skin and eye irritant, and dermal contact should be avoided through use of proper gloves and other personal protective equipment. Case reports of workers using NMP have shown acute contact dermatitis after 2 days' exposure. Overall, the acute, subchronic, and chronic toxicity of NMP is low. The LD_{50} in laboratory animals ranges from about 3.5 to 7.5 g/kg, and subchronic studies in rodents have shown no adverse effects at concentrations as high as 6,000 mg/kg. The available data suggest that NMP is not mutagenic or carcinogenic; however, it has produced reproductive and developmental effects in several laboratory animal tests following high-dose oral or inhalation exposures. In addition, at least one case report indicates that occupational exposure to NMP may have resulted in a stillbirth.

Populations at greatest risk from exposure include workers and individuals using NMP-based products at home. Exposure to the general population should be minimal under most circumstances unless a water supply has been impacted from a spill. At least one study has indicated that the manufacturer's recommended threshold limit value (TLV) of 100 ppm is too high and that NMP airborne concentrations should not exceed 0.1 ppm to protect against headaches and chronic eye irritation. Although NMP is not readily volatilized, it can pose inhalation hazards if adequate ventilation is not provided, if it is heated, or if it is sprayed. Therefore, both respiratory and skin protection should be used to reduce exposure.

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Appendix A
N-METHYLPYRROLIDONE CASE STUDIES

Depainting Case Studies

Pollution Prevention Demonstration and Evaluation of Paint Application Equipment and Alternatives to Methylene Chloride and Methyl Ethyl Ketone (J. M. Elion et. al., EPA/600/SR-96/117, October 1996).

Introduction

This research provides results of a demonstration of NMP as a possible alternative to methylene chloride and MEK. The demonstration was conducted at the Marine Corps Logistics Base in Albany, GA. This demonstration took place where base vehicles were depainted by methylene chloride through immersion. For this demonstration, NMP was chosen to replace methylene chloride because it effectively removed CARCs in laboratory tests, is nonflammable, and is not classified as an HAP by the EPA. If employed, this substitution would potentially reduce HAPs at the base by 11 percent from 1992 levels.

Results and Discussion

To accommodate the NMP, an existing immersion tank was retrofitted by adding plumbing to heat the tank with steam and a recirculating pump to provide enough agitation to ensure a uniform temperature throughout the bath. An adjacent rinse tank required a pump to draw recycled NMP for rinsing stripped parts. Finally, a vacuum distillation unit was installed to reclaim used solvent from the stripping bath and to provide recycled NMP for rinsing. After initial water testing, the tank was emptied and filled with an initial charge of 38, of the 208-L barrels of technical-grade NMP. An additional 10 barrels were added later in the test.

The NMP, when heated to 66±6 °C, was able to remove multiple layers of CARC and strip parts to the bare metal within 3 to 4 h. The heated NMP was able to successfully remove Plastisol®, a plastic coating, from battery tie-down brackets. These parts were previously stripped in a hot alkaline bath, followed by scraping and blasting to remove the coating. Also, NMP was able to soften epoxy-based topcoats, but removal usually required overnight soaking.

From this study, NMP substitution for methylene chloride would potentially reduce HAPs at the Marine base by 11 percent from 1992 levels.

Disadvantages of using NMP include the following: (1) NMP must be heated to be effective, and (2) NMP is subject to reporting under SARA.

The annualized costs for NMP stripping are lower than for methylene chloride stripping, but implementation requires high capital investment.

Surface Tension Modification of NMP-based Paint Strippers (W.C. Walsh, BASF Corporation, Chemicals Division, Mount Olive, NJ).

Introduction

Solvents traditionally used in paint strippers include methylene chloride, methanol, acetone, and MEK. In comparing these products with NMP-based paint removers, the primary tradeoffs are stripping speed versus solvent inhalation and product cost versus usage cost. NMP-based paint removers work at a slower rate but have dramatically lower vapor pressures, thus reducing the chances of solvent inhalation. In addition, by lowering the surface tension of these NMP formulas, the time required for their use may be decreased by as much as 40 percent.

Results and Discussion

Five NMP-based formulas, ranging in weight percent content from 12 to 80 percent, were reviewed in this study to determine their effectiveness as paint strippers. All of these formulations demonstrated good paint-stripping ability in the removal of commonly used paints and coatings. During testing, performance data were developed on the ability of these products to strip acrylic latex, alkyd, polyurethane, and epoxy coatings from wood substrates. They were applied to test substrates by both brush and roller and given sufficient time to penetrate the coating. Characteristics evaluated in this study included work area solvent concentrations, material recyclability, waste generation, waste disposal, and stripping cost.

One method of judging the relative risk of inhalation is by comparing the ratios of equilibrium vapor concentrations (EVCs) to PELs (8-h average) for each solvent. Ratios for the NMP formulations ranged from 3 to 26 compared to the ratios for the conventional solvents, which ranged from 320 to 900.

The modified NMP blends were tested against the original formulas, as well as against Zip-Strip, a common methylene chloride-based product, to observe the time required to lift various coatings from wood substrates at room temperature. The resultant stripping times, ranging in minutes, are shown in Table A-1.

Even after reducing the time required to strip urethane enamel and household epoxy, the NMP formulas were slower than the methylene chloride product. N-methylpyrrolidone works slower, but it provides the user a working environment containing less solvent vapor.

Table A-1. Comparative Stripping Times (minutes)

Paint type	NMP-based[a] stripping times, min.	Zip-Strip stripping times, min.
Alkyd (3 layers)	5-8	2.0
Urethane enamel (2 layers)	19-110	2.0
Household epoxy (2 layers)	9-24	1.5
Acrylic latex (2 layers)	7-8	2.0
Urethane finish (1 layer)	4-100	1.5

[a] Results for modified and unmodified formulations.

A significant amount of the spent stripper is potentially a reusable solvent. If a sufficient volume of thickened residue were isolated, a filter press could be used to separate the spent solvent. This solvent could then be recycled through distillation and reused.

Results from this research show that a relatively minor amount of the stripper will evaporate from the substrate, even after 25 h. After 3 h, 98 percent of the stripper formulation remained on the surface. Waste disposal of the stripped paint/solvent residue, as well as any paper cloth debris, was packaged in a thick-walled polyethylene or polyvinylidene chloride bag.

Appendices attached to the report describe sample preparation and surface coverage comparison calculations.

In the study, the volume of the NMP blend required for a single application was approximately 38 percent less than that required for Zip-Strip. This amount represents a substantial savings in the actual material required to strip any given surface area.

Initial Screening of Chemical Ingredients and Substitutes in Consumer and Small Shop Paint Stripper Formulations (Sherry Wise, Regulatory Impacts Branch, Economics, Exposure and Technology Division, Office of Pollution Prevention and Toxics, U.S. Environmental Protection Agency, Washington, D.C., June, 1994).

Introduction

This report contains information on chemical ingredients of commercially available paint stripper products used to remove paint and other finishes by consumer do-it-yourselfers or small shop operators (e.g., furniture restorers and refinishers). Coatings in the evaluations included alkyd enamels, latex semigloss enamels, flat acrylic latexes, spar varnishes, urethane varnishes, latex exterior enamels, interior vinyl acrylics, epoxies, marine paint, and marine varnish.

Results and Discussion

NMP-based strippers accounted for 12 percent of the products reviewed, or a total of 9 products. Three of the 9 products reported NMP concentrations of 20 to 80 percent, 21 to 30 percent, and greater than 67 percent, by weight.

The evaluation results showed that NMP was satisfactory in possibly stripping most paints. However, the NMP products required slightly longer times to achieve effective stripping compared with methylene chloride. In *Wood Magazines* (1992), NMP-based products performed less than satisfactorily compared with products containing methylene chloride but better than products based on dibasic ester (5 of 7 finishes) and caustics (also 5 of 7 finishes).

Appendix B used a range of methodologies to evaluate the paint strippers. Some consumer-oriented evaluations select a single representative stripping application and test the performance of several retail formulations. Others simulate a variety of coating removal situations (by using different types of coatings and substrates) and test both commercial products and laboratory formulations. Some tests vary the cure time and exposure of the coating and try to correlate stripping effectiveness with these variables.

Eight NMP-based strippers were rated below methylene chloride-based products on all coatings but above ATM strippers (mixtures of acetone and/or toluene and/or methanol), with the exception of enamel, where both NMP and ATM received an average score of 2.4. Average ratings were between 2.4 and 2.9 on the 1- to-4 scale.

N-methylpyrrolidone was the fastest of the "safe" products (15 minutes to more than 1 hour, depending on the concentration of NMP). Each NMP-based product also had a slight odor and was nonflammable. However, they were expensive, costing nearly twice as much as methylene chloride removers. They can also cause dizziness and nausea after prolonged exposure.

Other Studies - Cleaning

Replacement of MEK with N-Methyl Pyrrolidone (NMP) in Coatings Plant Resin Clean Up Operations (W.C. Walsh, BASF Corporation, Chemicals Division, Mount Olive, NJ).

Introduction

This research discusses work conducted by a manufacturer of high-solids, oven-cured, clear-coat, and base-coat coatings for Original Equipment Manufactures (OEM) automotive and heavy equipment, as well as for some industrial applications, to evaluate replacing its MEK cleaning solvent with NMP systemwide. It was anticipated that the cleaning system at the plant would maintain the same standard of cleanliness throughout all stages of the coating production, while using a chemical that created a lower amount of organic emissions. In addition to this,

NMP was selected because of its heat-stable molecular structure, making it an ideal candidate for recycling through distillation processes.

Results and Discussion

MEK was used at this facility to clean up small reactors and to process holding tanks, transfer lines, large blending tanks, transfer pumps, production floors, spray guns, and returnable tote tanks. However, as MEK was continually used to solvate the more complex resin systems, the amounts of MEK evaporating also increased. But, NMP's volatility is not as great as MEK and, therefore, NMP does not evaporate as quickly as MEK.

Testing was conducted over a 10-month period to evaluate the capability of NMP to replace MEK as a cleaning solvent in the manufacturing facility. Results from the study showed that over a 10-month period there was a 5-fold decrease in MEK emissions from the facility and that cleaning costs rose by 40 percent over total MEK costs. But, this increase was due to the inexperience of the facility in initially using NMP. The total volume of cleaning solvent passing through the plant decreased by 39 percent, 69 percent of which could be accounted for by the decreases in virgin MEK purchases. Also, the total volume of MEK passing through the plant decreased by almost 72 percent.

Met-Ed/Penelec Business and Industry, Technology Excellence Center (BITEC), BITEC Assistance Report for James River Corporation, Lehigh Valley, PA (Concurrent Technologies Corporation, 1450 Scalp Avenue, Johnstown, PA, May 1996).

Introduction

James River Corporation manufactures both wax-coated paper and plastic (high-impact polystyrene polymer) drinking cups at its Lehigh Valley, PA, facility. The plastic cups are manufactured using aluminum thermoforming tools, with up to 100 vent holes in each tool. These tools were removed and placed in an immersion tank filled with Tower 19 paint thinner, a mixture of 80 percent toluene and 20 percent acetone, for 15 to 30 minutes and then allowed to air-dry. Once dry, the vent holes were manually probed to remove the accumulated polystyrene using a drill bit.

James River originally used solvent-based chemicals to clean the aluminum thermoforming tools. Due to health and safety concerns, these chemicals were replaced by an ultrasonic cleaning system using aqueous chemicals. The aqueous chemicals proved to be unsatisfactory for the tool-cleaning application.

James River's goal was to replace the Tower 19 paint thinner with a safer, low volatile organic compound (VOC) cleaning chemical, preferably by using the ultrasonic cleaning system. Thus, the objective of this study was to conduct a bench-scale test of three alternative solvents to

evaluate their overall performance in the ultrasonic cleaning system. Factors such as cleaning quality and drying time were evaluated and recommendations were made based on these results.

Results and Discussion

Several soiled aluminum thermoforming tools were submitted for testing. Each contained a buildup of styrene residue in the vent holes. A test plan was developed to evaluate the following alternative paint-stripping solvents:

- NMP
- Ethyl lactate
- Oxysol.

The bench-scale ultrasonic cleaning unit was too small to accommodate the size of some of the parts from James River, so 4-oz. souffle cups were used to hold the parts. The cups had to be rotated during the cleaning test. The parts were immersed at ambient temperature for approximately 15 to 20 minutes and subjected to ultrasonic energy. The unit provides 110 W of sonic power at 85 kHz and holds approximately half a gallon. After cleaning, the parts were visually inspected and the drying time noted. James River's goal was to achieve a 15-minute drying time.

Based on the visual examination, NMP was the most effective of the three cleaners tested, removing residues from recessed areas and small holes. N-methylpyrrolidone also did not emit obvious odors during testing; however, drying times were relatively high. Some parts were still wet after drying for 20 to 25 minutes at ambient temperature.

At the time, NMP was available for approximately $2.35/lb or approximately $1,000 to $1,150/55-gal drum.

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