# Environmental, Safety, and Health Considerations— Composite Materials in the Aerospace Industry

*Compiled by*
Huai-Pu Chu
*NASA Goddard Space Flight Center*
*Greenbelt, Maryland*

National Aeronautics
and Space Administration

**Goddard Space Flight Center**
Greenbelt, Maryland 20771

**1994**

# PREFACE

The Aerospace Industries Association, Suppliers of Advanced Composite Materials Association, and the National Aeronautics and Space Administration co-sponsored a conference on "Environmental, Safety, and Health Considerations—Composite Materials in the Aerospace Industry." The conference was held in Mesa, Arizona, on October 20-21, 1994. Seventeen papers were presented in four sessions including general information, safety, waste, and emissions from composites. Topics range from product stewardship, best work practice, biotransformation of uncured composite materials, to hazardous waste determination and offgassing of composite materials.

The general conclusion of the conference was that more research needed to be conducted on the effects of composites on environment, safety, and health throughout the product lifecycle. It was recommended that task groups such as the composite dust task group and best working practices group should forge ahead in their research efforts. Moreover, it was felt that the conference should be held bi-annually to allow for new research to be completed and for timely dissemination of research results so as to further promote safe and efficient use of composites in the aerospace industry.

Huai-Pu Chu

# CONTENTS

## SESSION I: GENERAL INFORMATION
### Chairman: Huai-Pu Chu, NASA

## SESSION II: SAFETY
### Chairman: Shana Goldberg, AIA

## SESSION III: ENVIRONMENTAL—WASTE
### Chairman: Denis Bourcier, The Boeing Company

PRECEDING PAGE BLANK NOT FILMED

# CONTENTS

## SESSION IV: ENVIRONMENTAL—EMISSIONS
### Chairman: Jennifer Heth, ICI Fiberite

# A ROADMAP FOR REGULATORY SURVIVAL IN THE 1990s

Authors
**R. S. Sayad**
**S. B. McCollister**
**R. D. Olson**
**The Dow Chemical Company**
**Midland, Michigan**

*1995116609*

There have been many changes over the last several years in the ways that we're required to label, handle, and dispose of the products of our manufacturing processes...and we all know there will be _more_, not fewer, environmental regulations to deal with in the years to come.

Many of the easily solved environmental problems are gone. Those that remain are complex and sometimes global in nature: acid rain, the "greenhouse effect," stratospheric ozone depletion, atmospheric ozone increases, hazardous wastes, and abandoned waste sites.

These problems are manifestations of what some of us may call "environmental gridlock" -- when industry, government and the public feel overwhelmed by the tough decisions and actions that must still be taken -- and misunderstanding may get in the way of cooperative productive action to preserve the environment.

There is a way to break out of this gridlock, and to lay the groundwork for a future where both our businesses and our environment can survive and thrive. It demands that we not only comply with the regulations of today, but that we take the initiative in continuously improving our environmental performance.

Industry must keep abreast of and in compliance with the regulatory requirements that already exist and respond proactively with responsible manufacturing and disposal practices that will keep our business running profitably tomorrow.

This sounds like a tall order -- but it's based on the belief that no matter what kind of hazard a chemical presents, we in industry can help find ways to work with it safely from manufacturing through disposal. We must challenge ourselves to take the lead role in addressing safe handling and environmental issues, before we are forced to do so by law.

And there are plenty of people standing by to see how well we respond to that challenge. Our industry, for example, is watched over by the EPA and OSHA, among other governmental agencies. We follow TSCA, CERCLA, CAA, SARA, RCRA, and MSDS requirements. In addition, there are requirements for premanufacturing notices, consent orders, hazard communications, and labeling. In addition, as our industry has become global, we must also be aware of regulations in other countries.

To better understand how all these requirements fit together, let's take a look at what we call a "Regulatory Road Map" -- a schematic view of some of the federal regulations and state initiatives that impact our MSDS, labels, and overall compliance requirements. (See Table 1)

It's important to be aware of how a chemical is listed by federal or state regulations or recommending bodies. For example, if a chemical has been listed by OSHA, IARC (International Agency for Research on Cancer), or NTP (the National Toxicology Program) as a carcinogen, this listing will trigger hazard communication requirements. It may also cause restrictions on the levels of a chemical that you may release into the air or water, as well as how you manage your plant wastes.

Understanding how a chemical is listed is the first critical step in overall compliance. Once a chemical makes one of these lists as a hazardous material or a carcinogen, your emissions, labeling, or MSD sheets may need to be changed in order to comply with federal or state regulations. Being fully aware of how the chemicals you use are listed by all pertinent bodies is the essential compass that you must have to follow the regulatory road map. As an example of how the regulatory road map works, let's look at a chemical which is listed by either IARC, NTP or OSHA and follow its compliance requirements for MSDS, labels, and other state and federal regulations.

## Regulatory Road Map -- Federal Hazard Communication Requirements

The OSHA Hazard Communication Standard, 29 CFR 1910.1200, was promulgated in 1983 and went into effect on November 25, 1985. It initially required that chemical manufacturers and importers label shipping containers and provide Material Safety Data Sheets for all hazardous chemicals they manufacture.

In addition, if chemicals considered hazardous under OSHA are present at 1.0% or greater in a mixture, all of the hazardous effects reported for the component must be addressed on the MSDS unless the mixture as a whole has been tested. Carcinogens, as determined by OSHA, IARC or NTP, must be addressed on the MSDS if they are present at 0.1% or higher, again, unless the mixture containing the carcinogen has been tested and found not to be a carcinogenic. For example Methylene Dianiline (MDA) has recently been listed as a carcinogen by OSHA and therefore must be shown on MSD sheets to levels of 1,000 ppm or 0.1%.

The procedures and criteria used by OSHA, NTP, and IARC to classify carcinogens, vary somewhat. OSHA classifications result from the standard-setting process that the agency uses to regulate chemicals and presently includes Methylene Di Aniline, the others are listed on Table 2.

NTP has a two-pronged approach:
    1) - "Substances or groups of substances, occupational exposures associated with a technological process, and medical treatments that are known to be carcinogenic," and
    2) - those which may "reasonably be anticipated to be carcinogens," which are defined as "those for which there is a limited evidence of carcinogenicity in humans or sufficient evidence or carcinogenicity in experimental animals."

IARC has its own evaluation scheme.
    Group I - Carcinogenic to humans, based on sufficient evidence of carcinogenicity in humans;
    Group 2A - Probably carcinogenic to humans, based on limited evidence in humans and sufficient evidence in experimental animals;
    Group 2B - Possibly carcinogenic to humans, based on limited human evidence in the absence of sufficient evidence in humans.
    Group 3 - Materials are not classifiable as to carcinogenicity to humans.
    Group 4 - Chemicals are considered probably not carcinogenic.

The carcinogen classifications determine whether or not a statement for carcinogenicity should appear on the label. OSHA has issued guidance for such determinations, as shown in Table 3.

As the Table shows, for chemicals regulated by OSHA, on the NTP list or categorized by IARC in Group 1 or 2A, a notation of carcinogenicity is expected to be on the label.

The OSHA Hazard Communication Standard also requires that other "chronic effects" be noted on the label, although the agency's guidance is not as clear as it is for carcinogenicity. Chronic hazards to be included on a label can be selected by a weight-of-evidence assessment. If the effect is "well-substantiated", then it should be noted on the label.

Of course, OSHA isn't the only agency on the regulatory road map. The Superfund Amendments and Reauthorization Act of 1986 ("SARA") was enacted into law in October 1986. Title III of SARA significantly impacts a manufacturing facility's legal requirement for hazard communication in the community in which it operates.

Sections 303 and 304 require that facilities cooperate in emergency planning and report releases of certain extremely hazardous substances to the community.

Section 311 of SARA Title III requires that the MSDSs for chemicals considered hazardous under OSHA Haz Com (or a listing of those chemicals) be provided to state and local emergency response organizations and to local fire departments.

Section 312 requires that for those chemicals, the facility submit an inventory form to the above agencies on an annual basis.

Section 313 covers a list of toxic chemicals initially derived from several state right-to-know lists. The law requires annual reporting of releases of these chemicals to EPA for the Toxic Release Inventory (TRI). A list of the Section 313 chemicals can be obtained from a EPA office.

In addition, a manufacturing or supplier must notify a customer of the fact that a chemical component in a mixture is on the 313 list. Such notification must be included with the MSDS, if an MSDS is required for a product.

As these regulations have evolved over the last eight years, the road map has become increasingly complex.

## State Initiatives and
## Right-To-Know Laws

Some states have also taken a role in regulation. Right-to-know laws are now on the books in New Jersey and Pennsylvania, among others - and more states are likely to follow with various other requirements.

And although state laws are effective only for operations within that state, the logistics of assuring compliance can be complicated.

For example, the New Jersey statute covers workers and communities. It applies to any hazardous substances used, studied, produced, or handled at a facility in the state.

The law includes requirements for labeling and training. It also mandates environmental and workplace surveys by employers. Any person may request copies of the surveys, and employers must send copies to local police and fire departments.

The Pennsylvania state law requires labeling and MSD sheets for substances which the state has listed.

Manufacturers must prepare MSD sheets for each hazardous substance they produce or import, and must provide all purchasers with copies of the sheets for the hazardous substances purchased. MSD sheets are also made available to the public upon request.

New Jersey and Pennsylvania have Right-to-Know laws requiring that labels include statements of the presence of chemicals at various concentrations. Pennsylvania requires this type of information on the MSDS as well. Some products containing specific state listed chemicals may need to list these chemicals on labels/MSD Sheets at levels as low as 100 ppm. Of course, the state lists can be obtained by asking the state for this information.

### Proposition 65

California's Proposition 65, the Safe Drinking Water and Toxic Enforcement Act of 1986, is a citizen initiative approved by 65 percent of state voters.

The law requires the governor to publish a list of chemicals "known to the state to cause cancer or reproductive toxicity." It establishes two prohibitions regarding use of the listed chemicals.

First, no person may knowingly discharge or release a listed chemical into drinking water or into or onto land where it will pass into a source of drinking water.

Second, no person may knowingly expose any individual to a listed chemicals without first providing a "clear and reasonable warning" of significant risk to the individual if an assessment indicates a certain risk level. For carcinogens, the trigger is a risk of $10^4$ i.e., in 1 in 10,000, as determined by the linearized multistage model for risk assessment.

For reproductive toxins, the trigger is the no-observed-effect-level divided by 1,000.

Warnings must then be provided for environmental, workplace, and, most significantly, consumer-product exposure of an individual to the state listed chemicals. If warnings are necessary they may be included on labels, MSD sheets or fax sheets. In addition, they may also be placed in the workplace or other areas to indicate to the public that there may be a warning necessary for that particular product which contains a state listed chemical.

### The impact of other Initiatives

In addition to being aware of and in compliance with the federal and state regulations we've already discussed, industry also needs to be aware of how a chemical can be affected by the many branches within the EPA, particularly the offices of Air and Radiation and Solid Waste.

A primary focus in the Office of Air and Radiation is Clean Air Act implementation and ambient air quality. Also important is the Emissions Standards and Engineering Division, which develops standards to regulate air pollutants.

In addition to knowing how a chemical is regulated or listed by various EPA offices, we must also be aware of how a listed carcinogenic or hazardous chemical is regulated by the EPA.

If a particular chemical is listed by EPA as a hazardous waste, one must be aware of how it is to be disposed of properly. The identification of a chemical as a hazardous waste may also include process chemicals, by-products, or still bottoms that are listed under the Resource Conservation and Recovery Act or RCRA. The Waste Management Division in the office of Solid Waste, is seeking further ways for industry to reduce pollution through waste treatment, minimization or elimination, and recycling.

## How to Survive

There is no question that concern for the environment has place a significant responsibility on all of us. And while the costs of compliance are often high, the costs of non-compliance can be many times higher.

In order to survive, we must see ourselves and be seen by others as part of the solution, not part of the problem. That means we must voluntarily reduce emissions and waste further. This voluntary action will build our credibility and show lawmakers and the public that regulation isn't the only way to make progress in protecting our environment.

At Dow, we've been trying to do our part. In the last several years, we've significantly reduced both air and water emissions. For example, we've reduced our emissions to the air by 85 percent since the early 80's. Also, for many years, we've been committed to handling our non-water waste internally in state-of-the-art incineration facilities.

And in the last six years, we've invested over a billion dollars in capital alone to make environmental, health, and safety improvements in our plants around the world.

In addition to making real, measurable improvements, we must also all work harder to acknowledge the legitimacy of the public's concerns and to encourage greater public involvement in environmental policy making.

We should open our facilities for tours and invite visits from neighbors, elected officials, and special interest groups. By working together, we will lessen the misunderstandings, increase the level of communication, and demonstrate our willingness to cooperate and negotiate.

The third thing we can do is strengthen our participation in various trade and industry organizations, like SACMA and AIA, etc. This can help us achieve consistency in environmental and health and safety policy by promoting reasonable, scientifically based federal regulations and a more influential EPA and OSHA. Trade associations provide an opportunity for industry and government to work together on common issues. They can also help you better understand the regulations being addressed and how your company can achieve compliance at an early stage.

A good example of this kind of effort is Responsible Care®, a voluntary program being adopted by chemical companies in the U.S., Canada, Australia, New Zealand, the United Kingdom, and France. All participants agree to adhere to specific principles and management practices which require them to continuously improve their environmental, health, and safety performance in the areas of community awareness and emergency response, distribution and transportation safety, waste and release reduction, safe plant operations, worker safety, waster management, product stewardship, and more. By participating in Responsible®, the chemical industry is making a public commitment that their environmental performance will improve -- in ways that government and the public can measure. (See Table 4 for the guiding principle of Responsible Care®.

Ultimately, the answer to survival in the 1990s is awareness. Make use of the many resources available to keep abreast of how the chemicals you use are listed and what regulations you must comply with.

Make sure you know how the chemicals you use are listed by NTP, OSHA and IARC, as well as staying up to date on the requirements of the EPA and individual states.

A healthy environment and a healthy economy are both achievable goals. By responding proactively, working together, and communicating openly, we can help ensure that the 1990s are remembered as the decade of environmental progress throughout industry.

**Please note: This paper is being presented in good faith, but is not intended as a substitute for legal advice. If you require legal advice, consult a legal professional who is well-informed as to the latest regulatory developments for the specific chemicals you use in your operations. Reference should also be made to primary legal sources to verify that the most recent developments are considered. The authors are not attorneys.**

1/94

# Regulatory Road Map



TABLE 1

9
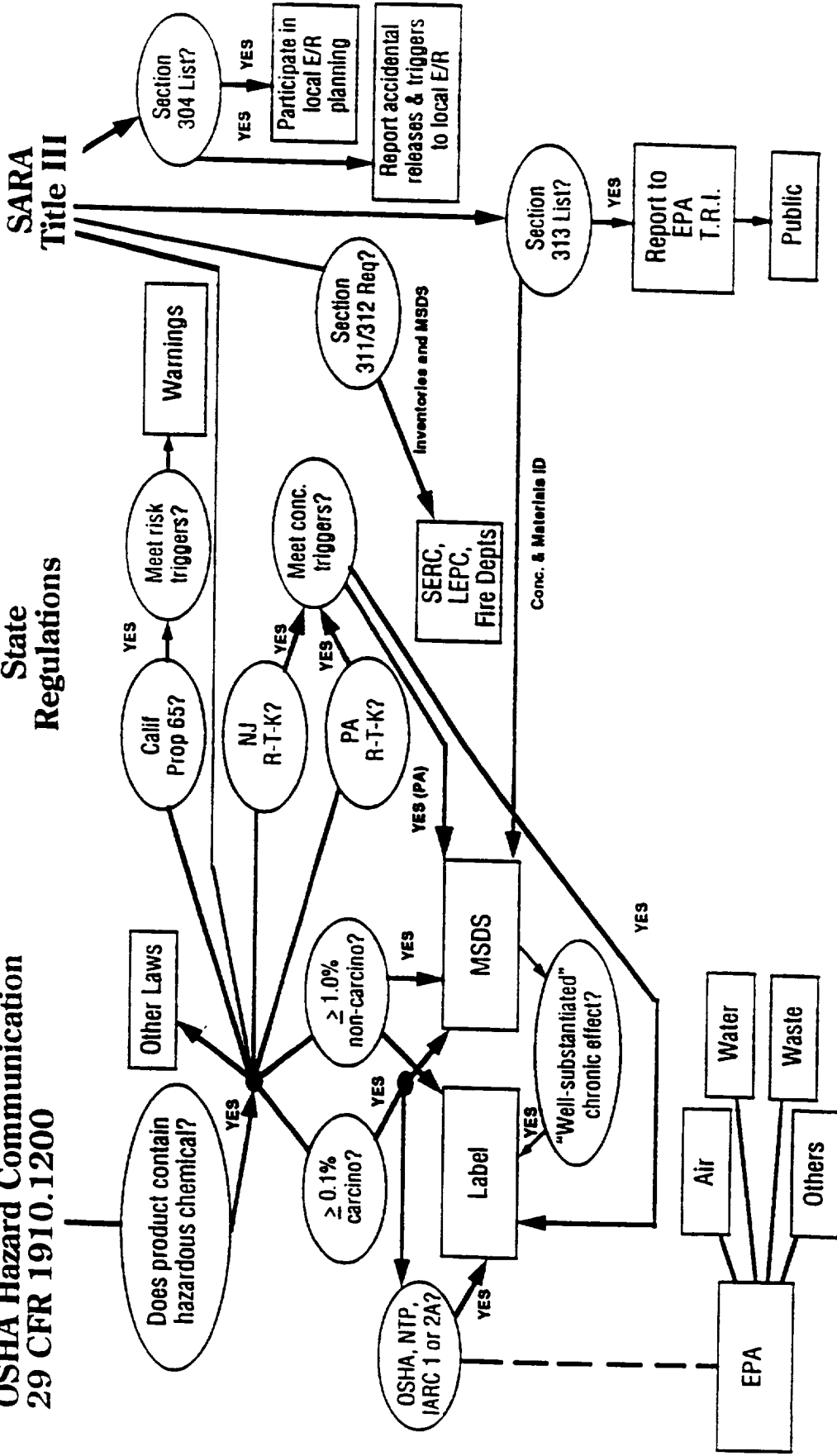
# Occupational Safety And Health Standards

## Subpart Z - Toxic and Hazardous Substances

Sec.

Sec.

1910.1001  Asbestos, tremolite, anthophylite, and actinolite. (eff. 7-21-86)

1910.1002  Coal tar pitch volatiles; interpretation of term.

1910.1003  4-Nitrobiphenyl.

1910.1004  alpha-Naphthylamine.

1910.1006  Methyl chloromethyl ether.

1910.1007  3,3-Dichlorobenzidine (and its salts).

1910.1008  bis-Chloromethyl ether.

1910.1009  beta-Naphthylamine.

1910.1010  Benzidine

1910.1011  4-Aminodiphenyl.

1910.1012  Ethyleneimine.

1910.1013  beta-Propiolactone.

1910.1014  2-Acetylaminofluorene.

1910.1015  4-Dimethylaminoazobenzene.

1910.1016  N-Nitrosodimethylamine.

1910.1017  Vinyl chloride.

1910.1018  Inorganic arsenic.

1910.1025  Lead.

1910.1028  Benzene.

1910.1029  Coke oven emissions.

1910.1043  Cotton dust.

1910.1044  1,2-dibromo-3-chloropropane

1910.1045  Acrylonitrile.

1910.1047  Ethylene oxide.

1910.1048  Formaldehyde,

TABLE 2

# Guidance For MSDS And Label Notations For Carcinogens

| Source | MSDS | Label |
|---|---|---|
| Regulated by OSHA as a carcinogen | X | X |
| Listed on NTP Carcinogen Report | X | X |
| IARC--Group 1 | X | X |
| IARC--Group 2A | X | X |
| IARC--Group 2B | X | Not Required |
| IARC--Group 3 | Not Required | Not Required |
| IARC--Group 4 | Not Required | Not Required |
| One Positive Study - Animal Only | X | Not Required |
| Multiple Animal Studies | X | Depends on weight of evidence; N.O. review needed. |
| One Positive Study - Some Human Evidence | X | X |

TABLE 3.

11

# Responsible Care® Guiding Principles

1. To recognize and respond to community concerns about chemicals and our operations.

2. To develop and produce chemicals that can be manufactured, transported, used and disposed of safely.

3. To make health, safety and environmental considerations a priority in our planning for all existing and new products and processes.

4. To report promptly to officials, employees, customers and the public, information on chemical-related health or environmental hazards and to recommend protective measures.

5. To counsel customers on the safe use, transportation and disposal of chemical products.

TABLE 4

12

# Responsible Care® Guiding Principles

6. To operate our plants and facilities in a manner that protects the environment and the health and safety of our employees and the public.

7. To extend knowledge by conducting or supporting research on the health, safety and environmental effects of our products, processes and waste materials.

8. To work with others to resolve problems created by past handling and disposal of hazardous substances.

9. To participate with government and others in creating responsible laws, regulations and standards to safeguard the community, workplace and environment.

10. To promote the principles and practices of Responsible Care® by sharing experiences and offering assistance to others who produce, handle, use, transport or dispose of chemicals.

TABLE 4

13

# PRODUCT STEWARDSHIP
# IN
# THE COMPOSITES INDUSTRY

Dr. Donald C. Aldrich
Dr. Edmund A. Merriman

DUPONT ADVANCED MATERIALS SYSTEMS

# OVERVIEW

- What is Product Stewardship and what does it mean to your business

- How can **you** make Product Stewardship work for you

- How does the Product Stewardship Code of Management Practice apply to the Advanced Composites and Aerospace Industries

- How does Product Stewardship fit into your business organization

- What is life cycle thinking and how does it impact your business decisions

# WHAT IS PRODUCT STEWARDSHIP?

Product Stewardship is a system for identifying and managing safety, health and environmental risks throughout all stages of a product's life cycle and continuously seeking ways to reduce the adverse impact upon human health and the environment

Product Stewardship means providing information and support, as an integral part of our business offering, so that our contractors and customers can use our products safely and without environmental harm.

# WHAT IS THE PURPOSE OF PRODUCT STEWARDSHIP?

The Purpose of Product Stewardship is to make **health, safety and environmental protection an integral part** of designing, manufacturing, using, recycling and disposing of your products.

Janos Schulze
Director of Regulatory Affairs
Ciba-Geigy Corporation

SACMA Presentation
October 1993

# WHY DO PRODUCT STEWARDSHIP?

**GOOD BUSINESS.** You can improve your offering by responding to the needs, concerns, and outrage of customers and society

It helps you be responsive to society's expectations

Some is required by regulatory and liability considerations

Required of members of the Chemical Manufacturer's Association (CMA)

Corporate Policy

**<u>GOOD BUSINESS</u>**

# A DOZEN WAYS TO MAKE PRODUCT STEWARDSHIP WORK FOR YOU

1. Review the safety, health, and environmental information you provide your customers for one product. Is it the <u>best</u> information you can provide? Can your customers use this product safely? Are they likely to?

2. Summarize the principle safety, health and environmental hazards of one of your products. Do competitive products have less serious hazard? How might this impact your business?

3. Examine the risk associated with one of your products

$$Risk = Hazard \ (fact) + Outrage \ (perception)$$

Do competitive products have less serious risk? How might this impact your business?

# A DOZEN WAYS TO MAKE PRODUCT STEWARDSHIP WORK FOR YOU
## (cont.)

4. Determine how your customers use one of your products. Do employees of your customers have sufficient information to work with your product safely? Are the customers' employees using correct personal protective equipment? What happens to residual product? How can you help reduce hazards and minimize emissions?


5. Review how you and a customer dispose of a material. Does your business have some continuing "liability" for this material?


6. Does the management of your company have a policy of supporting Product Stewardship? Do you have goals and responsibilities for implementing Product Stewardship? If not, would this improve your company's offering or reduce your liabilities?

# A DOZEN WAYS TO MAKE PRODUCT STEWARDSHIP WORK FOR YOU
## (cont.)

7. Examine your employees' perception of your company's SH&E performance. Can you improve by involving them more?

8. Review your systems to design, develop or improve products and processes. Do your systems make health, safety and environmental impact key considerations?

9. Consider what your site looks like to the public. Do they know how well you manage environmental risks? Have you established a relationship of trust with community opinion leaders?

# A DOZEN WAYS TO MAKE PRODUCT STEWARDSHIP WORK FOR YOU
## (cont.)

10. Determine how a contractor is using your products. Are all appropriate safeguards in place to manage hazards and minimize emissions? Is potential liability to your business being properly managed?

11. Review transportation incidents with one of your products. How can these be minimized?

12. Consider one of your key suppliers. Do they provide you appropriate health, safety and environmental information and guidance on their products? Is their operations such that you can be assured of continuing supply of critical raw materials?

# THE RESPONSIBLE CARE® CODE OF MANAGEMENT PRACTICE

Responsible Care® is a Chemical Manufacturers Association-led initiative to improve the industry's responsible management of chemicals

## Code of Management Practice

Community Awareness and Emergency Response

Pollution Prevention

Process Safety

Distribution

Employee Health and Safety

Product Stewardship

Adoption of these codes and an annual self-evaluation is required for CMA members.

If you are not a CMA member, why should you be interested in Responsible Care®?

# WHY DO IT?

- Responsible Care® developed in response to society's concern about the chemical industry

- Composites are part of the chemical industry

- Society's concerns regarding chemicals impact composite manufacturers and users

- SH&E "risk" is not limited to hazardous or toxic chemicals. It is defined by the public's perceptions

- Growing regulatory requirements

- Following the principles of Responsible Care® is good business

# RESPONSIBLE CARE®
## PRODUCT STEWARDSHIP MANAGEMENT PRACTICES


Management Leadership and Commitment


Information and Characterization


Risk Management

# PRODUCT RISK CHARACTERIZATION

1.  Make Hazard Assessment

    Prepare summary of physical, human and ecological hazards and understanding of data gaps

2.  Identify potential for human and environmental exposures

    Describe product trail: where, how much, to whom, how used and disposed by customer and distributor

3.  Combine Hazard information and potential exposures

    Are appropriate systems and procedures in place to protect users of your products and the environment from the identified hazards?

4.  Identify potential outrage issues.

# PRODUCT STEWARDSHIP PLUS
# LIFE CYCLE ASSESSMENT
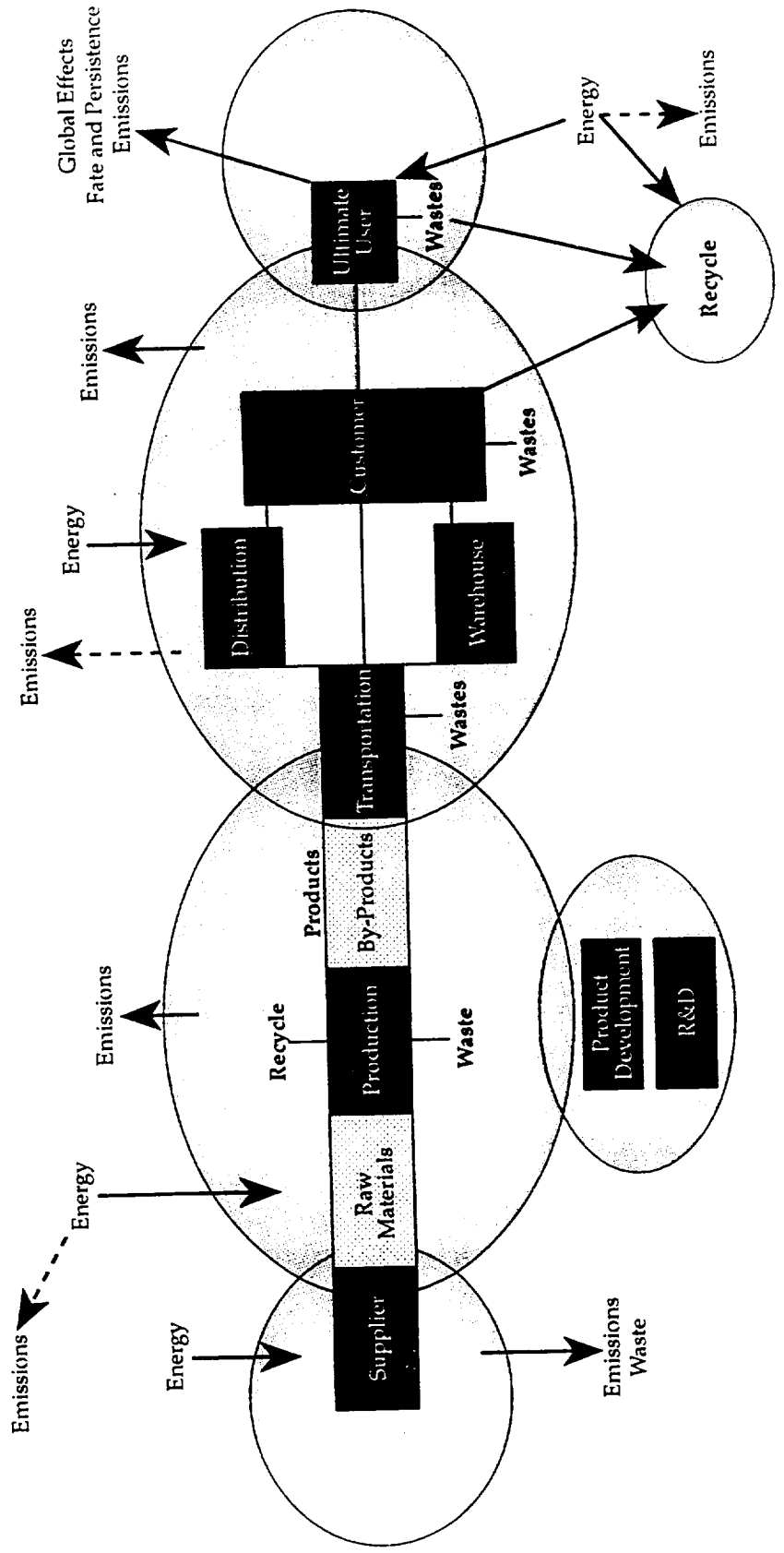
# SUMMARY

Product Stewardship is good business

Product Stewardship is a frame of mind

Product Stewardship is proactive action

Good Product Stewardship is important for growth of composites

Product Stewardship is good business

# Health, Safety and Environmental Requirements for Composite Materials

## Kathleen A. Hazer
### representing
## Aerospace Industries Association

## Conference on Environmental, Safety and Health Considerations - Composite Materials in the Aerospace Industry

## October 20, 1994

o **Data required by chemical users to evaluate new materials**

o **Many data elements are regulatory requirements**

o **Data elements are grouped by the stage of product development**

- **emphasis on practical aspects of use**

- **tied to SACMA/AIA working groups**

# PHASE I (PRE-ENGINEERING) EVALUATION

## I. General Data: for the product

- o Chemical identification for each chemical

- o % (wt.) of each chemical present in product, including impurities

- o CAS number for all chemicals

- o Physical properties of the material

  - - vapor pressure at 25°C

  - - VOC content (mass percent which is volatile per 40 CFR 51.165)

# PHASE I (PRE-ENGINEERING) EVALUATION

## II. Toxicology: for resins, fibers, adhesives and their constituents

- o Primary skin and eye irritation

- o Oral LD-50 or inhalation LD-50; dermal LD-50

- o Guinea pig sensitization

- o Genotoxicity-Ames test

# PHASE I (PRE-ENGINEERING) EVALUATION

**III.**     **Industrial Hygiene: for the product**

- o **Manufacturer's handling procedures**

- o **Initial glove material and protective clothing material recommendation**

# PHASE I (PRE-ENGINEERING) EVALUATION

## IV.  Medical Concerns

- o  **Existing medical condition(s) potentially aggravated by exposure**

- o  **First-aid treatment**

# PHASE I (PRE-ENGINEERING) EVALUATION

## V. Fire/Safety: for the product

- o **Storage requirements**

- o **Incompatibilities**

- o **Flash point**

- o **NFPA rating**

- o **Exotherms**

    - Conditions for occurrence

    - How to handle exotherm

    - Chemical identity of chemicals/classes that are released

# PHASE I (PRE-ENGINEERING) EVALUATION

**VI.  Environmental:  for  the product**

    o  **Toxic Substances Control Act Status**

    o  **SARA 313 listing**

    o  **SARA 311/312 hazard classifications**

    o  **Shipping codes (DOT, IATA, UN/NA)**

    o  **RCRA waste codes**

# PHASE II (ENGINEERING) EVALUATION

I. **Toxicology: for resins, fibers, adhesives and their constituents**

   o **One to four week subchronic toxicity**

      - **inhalation or dermal**

      - **tied to effects shown in acute tox tests**

   o **Genotoxicity**

      - **Mouse Lymphoma**

      - **In Vivo Rat Bone Marrow Cytogenetics**

# PHASE II (ENGINEERING) EVALUATION

II. Industrial Hygiene: for the product

o Identification of chemicals that off-gas

- when taken from cold storage to room temperature

- during hot-iron operations in lay-up

- when a heat gun is used during cure

- during normal cure cycle

# PHASE II (ENGINEERING) EVALUATION

## II. Industrial Hygiene: for the product (continued)

- o Physical characterization of dust from machining operations on cured materials

  - % fibers/ % particulates

  - % respirable

- o Chemical characterization of dust from machining operations on cured materials

  (eg., are original sensitizing constituents being released)

# PHASE III  (PRE-PRODUCTION) FEASIBILITY

## I.  Toxicology

o  **Need for specific studies to be based on an evaluation by manufacturer's and user's toxicologists**

o  **Specific studies should be tied to health effects revealed in completed tox tests or effects observed in the workforce**

# PHASE III (PRE-PRODUCTION) FEASIBILITY

## II. Industrial Hygiene

- o **Monitoring methods for air and surfaces**

  - - collection medium

  - - analytical method

- o **Recommended TWA/STEL**

- o **Is a "SKIN" notation needed for TWA?**

- o **Specific glove material and protective clothing material recommendation**

# PHASE III (PRE-PRODUCTION) FEASIBILITY

**III.     Medical Concerns**

    **o   Bio-monitoring methods for early exposure monitoring**

    **o   Special clinical exams**

        **-   part of routine, annual physical**

        **-   additional exams indicating exposure**

# PHASE III (PRE-PRODUCTION) FEASIBILITY

## IV. ENVIRONMENTAL: for the product and constituents

- o **TSCA PAIR/CAIR Status**

- o **TSCA Inventory status Section 8(b) and Section 5**

- o **Section 8(d) list status**

- o **Section 4 test rule status**

- o **Section 8(e) submissions**

- o **Aquatic toxicology**

    - **Acute LC-50 daphnia**

    - **Acute LC-50 minnows**

# Advanced Composite Material Manufacturing Operations

# Safety and Health

# Work Practice Observations and Recommendations

JACKIE LUCA
NORTHROP GRUMANN CORPORATION

**A**erospace
**I**ndustries
**A**ssociation

**Environmental, Safety & Health Committee**

**Composites Task Group**

**July 1994**

# AIA COMPOSITES SURVEY

## Aerospace Industries Association (AIA)

o    Newspaper articles on adverse health effects of
        composites in 1988

o    Aerospace Industries Association wanted more
        information

o    HR Council tasked Safety & Health Committee to study

o    Task Group formed in 1988

# AIA COMPOSITES SURVEY

## AIA Composites Task Group Actions

o   Sent letters to all AIA member companies requesting
    basic information  (28 responses)


o   Requested MSDSs from all companies for each composite
    material used (15 responses)


o   MSDSs categorized by composite type
    (1000 usable MSDSs)


o   Distributed "User Experience Survey Forms" to collect
    specific data on each composite material
    (12 responses)

# AIA COMPOSITES SURVEY

## AIA Task Group Actions (continued)

o    Collected data on ventilation controls, PPE used, medical
     and exposure monitoring, employee symptoms

o    Collected 677 User forms covering 258 different
     materials

o    Grouped into 8 categories:
     Aliphatic amine curing agents
     Aromatic amine curing agents
     Epoxy resin systems
     Phenolic resin systems
     Polyester resin systems
     Polyimide resin systems
     Silicon resin systems
     Thermoplastics

o    Gathered toxicity and exposure route information from
     published sources and on-line data bases

# AIA COMPOSITES SURVEY

<u>Results/Findings</u>

BARRIER CREAMS--Used in conjunction with gloves
>    70% of companies responding used with aliphatic and
>    aromatic compounds
>    Between 20-40% of companies used with the other
>    materials

SMOCKS
>    57% used with phenolics
>    48% used with polyimides
>    26% or fewer used with other materials

GLOVES--Most prevalent PPE requirement
>    ~100% used with aliphatics
>    57% used with phenolics
>    All others fell in between

RESPIRATORS
>    >70% used with aliphatics and aromatics
>    27% used with polyimides
>    22% used with phenolics

# AIA COMPOSITES SURVEY

## Results/Findings--Composite-Specific Observations

ODOR COMPLAINTS
> 56% reported complaints from phenolics
> 52% reported complaints from polyimides
> 12% or less reported complaints from others

SENSITIZATION
> 35% complained of polyimides
> 19% complained of phenolics
> 16% complained of aliphatics
> 15% complained of epoxies

DERMATITIS
> 42% complained of phenolics and polyimides
> 20% complained of epoxies
> 12% complained of aliphatics

# AIA COMPOSITES SURVEY

## Summary Recommendations

1. Wear gloves and coveralls/smocks when handling uncured composite materials and when handling cured or uncured dusts.

2. Wear cut-resistant gloves when cutting composite materials.

3. Use high velocity, low volume local exhaust when drilling, sanding, grinding, etc.

4. Use spray booths when handling large volumes of hazardous or irritating materials or when conducting spray applications of composite materials.

5. Have good general ventilation for other operations.

# AIA COMPOSITES SURVEY

## More information needed:

On certain raw materials to understand how they react under various conditions

## More attention needed:

On communicating potential hazards to users

On exposure monitoring and medical surveillance

## CONCLUSION:

Composite materials can be handled safety if proper work practice procedures are followed.  Some operations will require additional, more stringent controls than others due to the nature of the particular chemicals present.

Companies should respond promptly to employee concerns.

Communication to employees on new composite technologies is essential to provide employees with the information and tools to minimize health risks.

# ADVANCED COMPOSITE MATERIAL MANUFACTURING OPERATIONS

# SAFETY AND HEALTH

# WORK PRACTICE OBSERVATIONS AND RECOMMENDATIONS

**Aerospace Industries Association**

**Environmental, Safety, and Health Committee**

**Composites Task Group**

**November 1994**

# Acknowledgments

---

This report does not purport to identify all potential health and safety risks stemming from the use of advanced composite materials in the aerospace industry, nor can it guarantee that the work practice procedures described herein will prevent any potential adverse health and safety effects related to use of advanced composite materials. The report's recommendations are provided only as guidelines and should be treated accordingly. As control technologies continue to improve and additional toxicological data becomes available, "best practice" work recommendations will continue to evolve.

# Executive Summary

In 1988, the Aerospace Industries Association (AIA) anticipated that its member companies would significantly increase their use of advanced composite materials in the future as a means of improving product performance, because use of composites as a substitute for conventional materials would reduce product weight, improve product strength, and increase payload capacity of aircraft, missiles, and space vehicles. These changes would require modifications to be made to the work environment to accommodate new materials and processes. Additionally, the product improvements would require safety and health professionals to evaluate new occupational exposure risks and to address the concerns of employees at AIA member companies about safety and health issues related to handling these new materials.

These challenges encouraged the Human Resources Council of AIA to direct its Occupational Safety and Health Committee to establish a Composites Task Group. The task group included safety and health professionals from several AIA member companies. The group's charter was to gain a better understanding of effective work practice controls for use in composite manufacturing operations. This was accomplished by reviewing toxicological data, surveying industry's experiences and control methods for various composites and processes, and interacting with other professional organizations as the basis for establishing safe work practice recommendations and identifying information needs. This strategy was considered a cost-effective approach to gathering information for the benefit of the group and minimizing duplication of effort.

Effective controls that were identified were compiled by composite type and by manufacturing operation and are presented in the following report. In summary:

1. Gloves and coveralls/smocks are recommended when handling uncured composite materials and when handling cured or uncured composite dusts, to prevent potential dermatitis from resins and fibers, to prevent exposure to chemicals that can be absorbed through intact skin, and to minimize transfer of resins and dusts from the immediate work environment.

2. Cut-resistant gloves are recommended when cutting composite materials.

3. High-velocity, low-volume local exhaust ventilation is recommended when performing dust-generating tasks (e.g., drilling, sanding, and grinding) to minimize skin, eye, nose, and throat irritation from chemical and mechanical properties of fibrous resin dusts.

4. Use of booths is recommended for spray applications of composite materials and when large volumes of hazardous and/or irritating materials are handled, to minimize health risks and to improve employee comfort and productivity.

5. Good general ventilation (3-5 air changes per hour) is recommended for most other composite manufacturing operations.

As engineering controls continue to evolve with changing technology, occupational safety and health recommendations will change accordingly.

Results of the AIA Composites Task Group survey indicate that some employees experience adverse reactions to composite materials when performing various tasks. The frequency of complaints associated with certain composite material components suggests an association between the specific chemical/process and the degree of protection. The data indicated that use of controls presently available can have a significant impact on minimizing these adverse effects.

The result of the toxicological review indicated that employees can be protected from exposure to composite materials using conventional engineering and personal protective equipment controls. Additional information is needed for certain raw materials to better understand how they react under various conditions. Communicating potential hazards to users is an area that needs additional attention to ensure that employee concerns are addressed. Also, occupational exposure monitoring and medical surveillance procedures need to be refined and standardized so that monitoring and surveillance results can be compared and decisions made using the greatest amount of information possible.

Based on the data presently available, composite materials can be handled safely if proper work practice procedures are followed. Some composite operations will require additional, more stringent controls than others because of certain chemicals present; however, current technology is available to satisfy these special requirements. Companies should respond to employee concerns about new materials and processes. Communication to the work force on new composite technologies is essential to provide employees with the information and tools to minimize health risks. ■

# CONTENTS

# I    Introduction

In an effort to gain a better understanding of effective safety and health work practice controls for composite manufacturing operations, the Aerospace Industries Association (AIA) Occupational Safety and Health Committee* established a Composites Task Group. Initially, the group included safety and health professionals from eight AIA member companies:

The Boeing Company
General Dynamics Corporation
General Electric Corporation
IBM Corporation
Kaman Aerospace Corporation
Lockheed Corporation
McDonnell Douglas Corporation
Northrop Corporation

The group's task was to provide AIA members with recommendations for minimizing occupational exposure risk and to determine research needs and information gaps. The strategy included a review of toxicological information on composites, a review of member company experience and control methods, and interaction with other professional organizations who share an interest in composite work practices. ■

---

* The AIA Occupational Safety & Health Committee was combined with the Environmental Affairs Committee in January 1994, to form the AIA Environmental, Safety & Health Committee. This committee functions as AIA's only free-standing committee and reports directly to the AIA president.

# II   Information Resources

## A. Toxicological Review

Toxicity and exposure route information was needed to determine which controls were most effective, from a theoretical perspective, to minimize exposures while performing various manufacturing tasks. On-line databases, including MED-LINE and TOX-LINE, were utilized in addition to current toxicology sources[1].

## B. Member Company Experience Survey

The member company experience survey was the primary source of practical information used to evaluate the effectiveness of various controls. The survey was conducted to collect information from composite users on controls being used and was compiled by composite type and by manufacturing task. This plan enabled the group to identify trends and to outline control recommendations for "like" materials and processes.

## C. Task Group Interaction With Other Organizations

The AIA Composites Task Group established formal dialog with other organizations that have an interest in improving composites technology and enhancing manufacturing process performance.

The AIA Composites Task Group and the Suppliers of Advanced Composite Materials Association (SACMA) formed a joint composites working group. This group has since formed several ad hoc committees to review common topics of interest, such as information on Material Safety Data Sheets (MSDS), composite dusts, combustion products, neurotoxicity/synergistic effects, and test/development protocol.

The National Center for Advanced Technologies (NCAT) is a professional organization that provides information about advanced technologies, including composites. The AIA Composites Task Group presented an overview of AIA task group activities at the NCAT-sponsored Advanced Composite Materials Conference in December 1990, to encourage organization members to consider health effects of composite materials when implementing new materials and processes[2].

The Department of Defense (DoD), in cooperation with AIA and SACMA, sponsored a symposium on health effects of composite materials held in Dayton, Ohio, in February 1989. Many of the AIA Occupational Safety and Health Committee members contributed to the symposium. The conference proceedings were later published by DoD[3] and later in a technical journal[4].

The American Conference of Governmental Industrial Hygienists (ACGIH) is a professional organization that establishes guidelines for occupational exposures to chemical and physical hazards. The AIA Composites Task Group presented a paper at the ACGIH-sponsored Conference on Advanced Composites in February 1991, to reinforce the need to develop standards using input from the user community. The conference papers were later published by ACGIH[5].

The American Industrial Hygiene Association (AIHA) is a worldwide organization dedicated to facilitating communications among industrial hygienists. The AIA Composites Task Group presented information at the AIHA annual conference in May 1991, to demonstrate how data can be collected industry-wide, to establish work practice guidelines[6]. ■

61

# III    Scope of Survey

## A. Composite Materials Reviewed

Composite materials included in the survey were those that the group defined as "Advanced Composite Materials":

> *Advanced composite materials refer to a group of high performance resin/fiber systems that are being developed as replacements for conventional materials, such as metals, to improve product performance. Advanced composites typically contain high strength fibers that are embedded in an organic polymeric matrix. The resin-impregnated fibers are blended or oriented and cured (hardened) to give the end product superior strength, toughness, and/or temperature resistance properties.*

To better focus the scope of the survey to composites used by AIA-member companies, company contacts were requested to submit one MSDS for each composite material used at their company. MSDSs were reviewed and categorized by composite type based on the chemical composition of the material. Categories included aliphatic amine curing agents, aromatic amine curing agents, epoxy, phenolic, polyester, polyimide and silicone resin systems and thermoplastics. Even though aliphatic and aromatic amine curing agents are not "stand alone" composite systems, these resin components are subject to unique handling and use requirements. Therefore, aliphatic and aromatic amine curing agents are treated separately in this report. Section IV (B)(2) includes a summary of industry experience with these materials, a description of each composite category, toxicological properties and safe work practice recommendations.

## B. Manufacturing Operations Reviewed

The industry survey focused on composite manufacturing operations most frequently performed by AIA member companies such as assembly, bagging, curing, wet and dry lay-up, rework, trimming, sanding, machining, research and development and tooling. Engineering controls, administrative actions, and personal protective equipment requirements or provisions were reviewed to determine those that are most effective in minimizing exposures to various materials.

Section IV (B)(3) describes each operation reviewed, presents the results of the industry survey and toxicological findings, and provides safe work practice recommendations.

## C. Toxicological Review

A toxicological review was conducted to determine potential health effects, routes of entry, and information gaps for various components of composite materials using on-line databases and other toxicological references. This information was used to determine the types of controls that would be most effective from a theoretical perspective.

Exposure routes are discussed in Section IV.A. A toxicological summary for each composite type is included in Section IV.B.2. Control recommendations based on toxicological findings are integrated into recommendations contained in Sections IV.B.2 and IV.B.3. Information needs are discussed in Section IV.C.

## D. Industry Experience Survey

An industry experience survey was conducted concurrently with the toxicological review. AIA member companies were surveyed to identify composite users and their experience with composites during various manufacturing tasks. Data was used to identify controls that are most effective from a practical perspective. The following is a more detailed description of the survey:

**(1)   Phase I:** AIA member companies were surveyed to identify composite users and a contact person at each company and/ or facility to establish a correspondence database. Companies were also requested to report on the number of years experience that they had with composites, floor space dedicated to composites work, and the number of employees who work in these areas.

Of the 70 companies surveyed, 28 used composites. On the average, member companies had 19 years experience with composites, dedicated 4,750 square feet of floor space to composite operations, and employed about 343 people in composite work areas. Ninety-one percent of respondents did not manufacture raw composite-related

materials, 88 percent cured vendor-supplied composites, and 94 percent machined cured composites.

**(2) Phase II:** MSDSs were requested from each company for each composite material used. Each MSDS was reviewed and categorized by composite type, based on chemical composition. Information on each material and user was entered into a "demographics" database.

Fifteen companies submitted over 1,700 MSDSs to be reviewed for applicability to this survey, of which approximately 1,000 were accepted. The 700 unused MSDSs all concerned solvents, paints, adhesives, and/ or other materials not meeting the definition of "advanced composites."

**(3) Phase III:** Information collected during Phase II was used to generate a "User Experience Survey Form" for each composite material used at each company. Forms were sent to each company contact, who was instructed to complete a separate form for each manufacturing operation where the material was used and where data was available. The form included questions on ventilation controls, personal protective equipment requirements or provisions, medical monitoring, and employee complaints regarding odor, sensitivity, and dermatitis. Results from this survey were used to generate a "User Experience" database, which is a relational database capable of reorganizing data by data field.

A total of 12 companies, with one or more subsidiary location reporting from each company, participated in Phase III of this project :

**Member Companies Contributing to DataBase**
The Boeing Company
General Dynamics Corporation
Grumman Corporation
Hexcel Corporation
Kaman Aerospace Corporation
Lockheed Corporation
Martin Marietta Corporation
McDonnell Douglas Corporation
Northrop Grumman Corporation
Rohr, Inc.
United Technologies Corporation
Westinghouse Electric Corporation

A total of 677 survey forms were collected, representing 258 different materials and 10 primary manufacturing operations. Sixty-five percent of responses were related to use of epoxy resins, 9 percent for polyimide resins, 8 percent for aliphatic amine curing agents, 7 percent for aromatic amine curing agents, 6 percent for phenolic resins, 2 percent for silicone resins, 3 percent for polyester resins and less than 1 percent for thermoplastics. Results from this phase were entered into a relational database.

## E. Work Practice Recommendations

The final step involved integrating information that was compiled during the toxicological review with information compiled during the user experience survey. Reports were generated by composite type and by manufacturing operation to evaluate the effectiveness of various controls. This report represents the end product of the composites task group study. ■

# IV   Results/Recommendations

## A. Exposure Routes

Reacted composite resins are polymeric and not highly volatile or readily absorbed through the skin. However, the unreacted resin base materials, including hardening agents, may be volatile and released from a pre-preg or resin material. Resins are somewhat reactive in the uncured state, but hazards are generally limited to skin irritation and sensitization. The potential for a resin to produce these effects can vary significantly, even within a single resin type.

The route of exposure pertains to the manner in which a toxicant enters the body. Major differences are noted between routes of exposure for uncured resins, partially cured prepregs, and fully cured composites.

### 1) Ingestion

Potential for exposure via the oral route is considered low for most composite operations. However, certain conditions may increase the potential by this route. For example, chemicals can be ingested through foods or food service utensils contaminated when in contact with working surfaces, or if hands and face are not washed prior to eating, drinking, or smoking. Also, oral intake of a dust may occur when materials are removed from the respiratory tract via ciliary transport and then swallowed.

Those materials which are irritants and systemic toxicants are of special concern. Irritants can produce significant gastrointestinal disturbance when swallowed. Systemic toxicants may be dissolved in the stomach or intestine, absorbed, and distributed to target tissues. The contribution of oral dose is difficult to assess. Biological monitoring combined with air monitoring, in some cases, might be used to estimate the relative significance of the oral route.

### 2) Inhalation

Inhalation is a major potential route of exposure when dealing with composite materials, especially when uncured materials are heated, or cured materials are sanded, drilled, cut, or ground. The types of materials encountered may range from particles to vapors and the toxicity may be exhibited by local lung tissue effects or by systemic toxicity. The contribution of inhalation dose can be estimated via personal air monitoring or, in some cases, by biological monitoring if all other sources of exposure are controlled.

### 3) Dermal

The dermal route of exposure is also a major potential route for uncured and partially cured composite chemicals, because a large proportion of work tasks involve significant handling of these materials. An example of extensive dermal contact occurs during the hand lay-up process, where large surface areas of pre-preg are rubbed with the fingers and palms. Protection for skin surfaces is of utmost importance in preventing direct dermal contact. Secondary dermal contact can also occur when contaminated clothing or gloves come in contact with the skin.

Dermal dose can be estimated by biological monitoring, controlling for inhalation exposure. The ability of a material to be available for absorption through the skin can be estimated by wipe samples taken from the surface of skin and gloves, or from workplace surfaces where skin contact is likely. The potential for a material to be absorbed through the skin can be calculated or measured experimentally by in-vivo and in-vitro absorption studies using a laboratory animal model.

## B. Work Practice Recommendations

This section discusses work practice recommendations that were compiled with input from the toxicological review and the industry-wide user experience survey. These recommendations are provided only as guidelines and should be treated accordingly. As control technologies continue to improve and additional toxicological data becomes available, "best practice" work recommendations will continue to evolve. The following are current observations and recommendations:

### 1) Engineering/Personal Protective Equipment Controls

The user experience survey form requested information on the types of engineering and personal protective equipment controls that are being utilized for various materials and manufacturing operations. The toxicology

## Use of Barrier Creams for Selected Composites
*(Figure 1)*



Figure 1: Use of Barrier Creams for Selected Composites. Chart showing % Yes Responses (0–100) versus Composite Types: Aliphatic, Aromatic, Epoxy, Phenolic, Polyester, Polyimide.

## Use of Coveralls/Smocks for Selected Composites
*(Figure 2)*



Figure 2: Use of Coveralls/Smocks for Selected Composites. Chart showing % Yes Responses (0–100) versus Composite Types: Aliphatic, Aromatic, Epoxy, Phenolic, Polyester, Polyimide.

review evaluated routes of entry for various composites and manufacturing operations. The following discusses various engineering and personal protective equipment options and provides an overall summary of recommended use:

### (a) Barrier Creams

Barrier creams are often provided as a non-mandatory protective measure to reduce skin contact with composite materials. Many employees choose to use barrier creams in conjunction with gloves to help retain skin moisture and help resist solvent penetration. Use of barrier creams in lieu of gloves for protection from chemicals is not recommended for three reasons: (a) barrier creams may be removed either mechanically or chemically while working and gives employees a false sense of security, (b)

barrier creams may contaminate surfaces of composites and adversely affect the bonding strength of these materials, and (c) there is limited experimental evidence that barrier creams can effectively prevent skin contact/permeation of composite resins or their components. Use of barrier creams are recommended as an enhancement to an effective glove program. Figure 1 illustrates responses from the industry-wide survey regarding use of barrier creams by composite type.

### (b) Coveralls/Smocks

Use of coveralls, sleeves, and smocks are recommended in areas where bodily contact with uncured resins or cured or uncured composite dusts is likely. Use of coveralls and sleeves minimizes the risk of having contaminated clothing leave the work area and allows employees to move from regulated areas to unregulated areas with little effort. The degree of protection required is dependent on the physical contact that an employee has with the composite materials and the degree of hazard associated with the material. Figure 2 includes responses from the industry-wide survey regarding use of coveralls and smocks by composite type.

### (c) Gloves

Use of gloves was found to be the most prevalent personal protective equipment requirement in the composites work environment. Gloves are recommended for manufacturing operations that involve skin contact with uncured resins, cured or uncured composite dusts, and where there is potential for hand lacerations. Most companies try to use gloves that are impervious to the resins, fibers, and solvents being used, but are thin enough to provide the employee with enough dexterity to perform the task. When cutting is involved, cut-resistant gloves are recommended, and, if this task also involves a chemical exposure hazard, the cut-resistant glove is recommended to be worn over an impervious glove to prevent hand lacerations and to prevent puncturing the impervious glove.

The type of glove or combination of gloves are specific to the materials being handled and the operation being performed. Use of gloves is not recommended when working near revolving equipment, as this may result in serious hand injuries.

## Use of Gloves for Selected Composites (Figure 3)

**Use of Gloves for Selected Composites** *(Figure 3)*

[Bar chart: % Yes Responses vs Composite Types. Y-axis 0–100. Composite Types: Aliphatic, Aromatic, Epoxy, Phenolic, Polyester, Polyimide]

**Use of Respirators for Selected Composites** *(Figure 4)*

[Bar chart: % Yes Responses vs Composite Types. Y-axis 0–100. Composite Types: Aliphatic, Aromatic, Epoxy, Phenolic, Polyester, Polyimide]

Each job needs to be evaluated on a case-by-case basis. Use of glove charts can help identify the appropriate glove material. Glove try-out is recommended to enable employees to evaluate the comfort factor of similar glove materials and sizes. Figure 3 displays industry use of gloves by composite type.

### (d) Respirators

Use of particulate air-purifying respirators is recommended if high-velocity, low-volume local exhaust ventilation is not available when performing dust-generating operations, but only if the protection factor of the respirator is determined to adequately minimize dust exposure. Otherwise, higher levels of respiratory protection is recom-

mended, such as powered air-purifying or air-supplied respiratory protection. If local exhaust ventilation is provided, it is recommended that respirators be made available as an optional use item.

Use of organic vapor air-purifying respirators are recommended to be made available as an optional use item to minimize nuisance odors when performing tasks such as mixing materials or applying wet resins in absence of good general ventilation. Respirators should be required when exposures approach recommended limits, but only if industrial hygiene evaluations indicate that airborne levels are within the assigned protection factors for the respirator and when warning properties of the materials provide the user with sufficient notice of breakthrough. Otherwise, higher levels of respiratory protection are recommended, such as powered air-purifying or air-supplied respiratory protection.

Air-supplied respirators are recommended when spraying composite materials in areas where there is direct exposure to sprayed material or when good booth ventilation is not available. Figure 4 illustrates responses from the industry-wide survey regarding use of respirators by composite type.

### (e) Ventilation

The four primary ventilation controls used in composite manufacturing operations include good general ventilation, local exhaust, downdraft tables, and booth ventilation:

- **Good General Ventilation:** Good general ventilation (typically 3-5 air changes per hour) is adequate for most composite work areas, such as where pre-preg lay-up operations are being performed or in general areas where parts are being prepped for processing. If dust is being generated (i.e., drilling, grinding, sanding, etc.) or when the composite resin has a very strong odor that may adversely affect employee comfort and productivity, then high-velocity, low-volume local exhaust, downdraft tables, or booth ventilation should be considered.

- **Local Exhaust:** High-velocity, low-volume local exhaust ventilation at the point-of-operation is recommended for controlling dusts generated during cutting, drilling, and sanding operations. These dusts cause mechanical and chemical irritation of

## Incidence of Odor Complaints for Selected Composites

*(Figure 5)*

**% Yes Responses** (y-axis: 0, 20, 40, 60, 80, 100)

**Composite Types** (x-axis: Aliphatic, Aromatic, Epoxy, Phenolic, Polyester, Polyimide)

## Incidence of Sensitization for Selected Composites

*(Figure 6)*

**% Yes Responses** (y-axis: 0, 20, 40, 60, 80, 100)

**Composite Types** (x-axis: Aliphatic, Aromatic, Epoxy, Phenolic, Polyester, Polyimide)

## Incidence of Dermatitis for Selected Composites

*(Figure 7)*

**% Yes Responses** (y-axis: 0, 20, 40, 60, 80, 100)

**Composite Types** (x-axis: Aliphatic, Aromatic, Epoxy, Phenolic, Polyester, Polyimide)

the skin, eyes, nose, and throats of some employees. There is also the possibility that incompletely cured composite dusts containing small amounts of unreacted monomers could be absorbed through the skin or respiratory system. Use of local exhaust ventilation minimizes the need to provide employees with respiratory protection and minimizes contamination of adjacent work areas. Exhaust ventilation is also recommended to evacuate gases from autoclaves that are used to cure composites.

• **Downdraft Tables:** Downdraft tables are recommended in areas where composites that have a strong odor are being handled or where significant dusts are being generated. The size and orientation of the part relative to the table will determine the effectiveness of this control (i.e., there must be enough downward air velocity around the part to capture contaminants at the source). The system filtration method of choice will depend on the hazard being controlled and on whether the filtered air is recirculated back into the work area or exhausted directly outside.
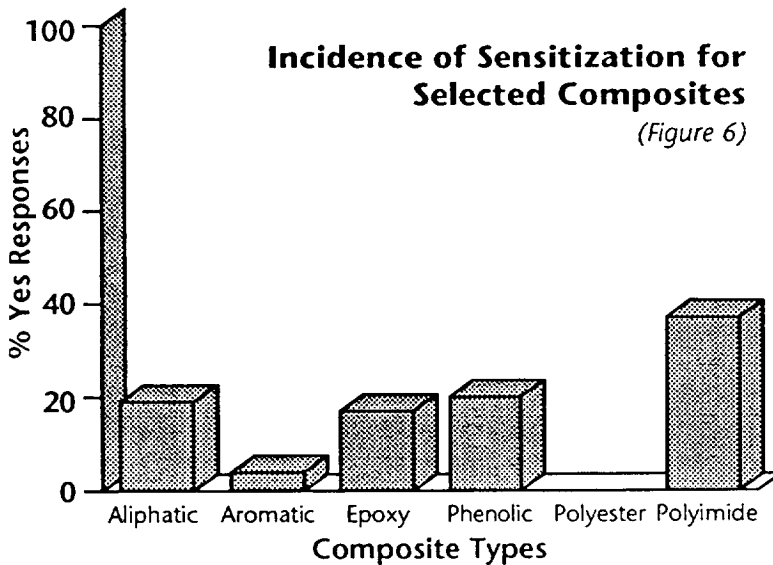
• **Booth Ventilation:** Booth ventilation is recommended when composite materials are being sprayed or when large volumes of volatile materials are being handled. If areas can be isolated where hazardous operations are being performed, it is often more cost-effective to perform the task within the confines of a booth to minimize air handling costs and prevent odors from adversely affecting personnel in adjacent work areas.

### 2) Composite-Specific Observations/ Recommendations

The following is a summary of observations from the user experience survey, including data on odor complaints, incidence of sensitization and dermatitis, and information pertaining to medical surveillance.

The user experience survey indicated significant differences in how employees perceive odors from various composites. Figure 5 illustrates a comparison of odor complaints by composite type. Responses indicate that one or more employees reported a given effect for a given material.

The occurrence of sensitization (Figure 6) and dermatitis (Figure 7) from survey responses may provide additional justification for preventing exposures when handling

## Incidence of Preplacement Medical for Selected Composites

*(Figure 8)*



Incidence of Preplacement Medical for Selected Composites (Figure 8) — bar chart of % Yes Responses by Composite Types: Aliphatic, Aromatic, Epoxy, Phenolic, Polyester, Polyimide.

## Incidence of Periodic Medical for Selected Composites

*(Figure 9)*



Incidence of Periodic Medical for Selected Composites (Figure 9) — bar chart of % Yes Responses by Composite Types: Aliphatic, Aromatic, Epoxy, Phenolic, Polyester, Polyimide.

specific materials. Responses indicate that one or more employees reported a given effect for a given material.

Most companies provide medical evaluations to monitor the health status of personnel assigned to composite work areas. Figure 8 illustrates the percentage of respondents who provide pre-placement medical evaluations and Figure 9 illustrates the percentage of respondents who provide periodic evaluations.

The following observations and control recommendations are based on user experiences and toxicological considerations and are reported by composite type. Percentages are based on the total number of responses for each question and indicate that one or

more individuals reported a given affect for a given material:

## (a) Epoxy Resin Systems

### Description:

Epoxy resin systems are the most common composite materials used in the aerospace industry. This group represents about 65 percent of the total number of materials reviewed. They are typically used on exterior surfaces of aircraft as a general building material or as structural components on doors and sidewalls. They are generally used in areas where temperatures will not exceed 300 degrees F.

The epoxy resin (part A) typically consists of the reaction product between epichloro-hydrin and bisphenol A. A curing agent (part B) is required to cross-link polymers to create the end product.

### Toxicology:

As is the case with all resin systems, the degree of hazard presented is dependent on the manner in which it is handled and processed as well as its physical state. Even though much confusion is created when attempting to describe the specific physical state of resin (e.g., reactive components, pre-cured mixtures, B-staged resins, pre-preg at room temperature, pre- and post-cured resin dust, etc.), each of these physical states and associated work processes present different hazard exposure conditions.

A significant amount of work has been done in characterizing the toxicity of epoxy resins and epoxy components, diluents, and hardeners. Much of the work reported was performed on the neat chemicals. Borgstedt and Hine[7] in a detailed review of the literature on the subject, developed the following categories of epoxy materials: Epoxy compounds, amine curing agents, related materials (other hardeners, diluents non-reactive solvents, etc.) the curing mixture, and the fully cured resin. Specific chemical resin components and applicable work processes have been described in a white paper prepared by the Suppliers of Advanced Materials Association (SACMA), a trade association representing suppliers of advanced composites[8].

The pre-cured individual resin components are considered the most reactive and are sufficiently volatile to give rise to sys-

temic effects, the components of notable toxicity being epichlorohydrin and ethylene oxide. Although epichlorohydrin is usually fully reacted in a cured epoxy resin system, the unreacted epichlorohydrin is a suspect carcinogen. Also, a variety of aromatic amine curing agents are used in the resin systems, including methylene dianiline (MDA), m-phenylene diamine (M-PDA), and diamino diphenyl sulfone (DDS). MDA is a suspect bladder carcinogen. However, these materials are present in very small quantities (usually less than 1 percent for epichlorohydrin) in the reacted epoxy system. The irritant properties of the unreacted resin are important factors in large single doses or repeated exposure to individual epoxy resin components. These have been reported to produce damage to the liver, the blood, and blood-forming organs, as well as causing oncogenic effects in animals.

Probably the most significant occupational health concern with epoxy resins is the potential for skin sensitization. Sensitization has been produced in animals and monitored in humans in contact with certain resin components as well as some formulated and partially cured resin materials[7,9,10,11].

Inhalation exposure to dusts released from uncured resin prepreg as well as cured composites is also of concern when composites are processed.

The research completed thus far indicates that for non-aramid-based cured materials, the fibrogenic potential of these dusts was much less than crystalline silica dusts, but greater than control "nuisance" dusts[12,13]. It has been shown that aramid based composites, upon machining, may produce fibrils characterized morphologically as fibers and which have been shown to produce fibrogenic and tumorogenic responses in animals[8]. Additionally, machining and processing of cured composites may generate enough heat to evolve combustion byproducts of the resin. For example, laser cutting of cured epoxy composite has resulted in formation of chemically diverse gaseous byproducts of varying toxicities and concentrations, polycyclic aromatic hydrocarbons being the predominant species[14].

The majority of toxicology data on cured composites has been generated with epoxy resin systems and therefore, extrapolation of this data to other resin systems often occurs. This may become less practical as the diversity of new resin components expands.

**Observations:**

(1) **General Comments:** A total of 417 responses were received from 16 companies/subsidiaries. In summary, comments included concern for skin and nose irritation (both chemical and mechanical in nature). Most companies did not report odor complaints unless the material was heated, such as with heat guns or during exotherms. Irritation from the dust generated during cutting operations was also reported. One company reported swelling around eyes. There were two reports of yellow discoloration of skin (hands and fingers). Some of these effects may be related to the curing agent used concurrently in these processes.

(2) **Odors:** Eleven percent of responses reported that some employees complain of odors.

(3) **Sensitization:** Fifteen percent of responses reported that some employees experience sensitization to epoxy resin composites.

(4) **Dermatitis:** Twenty percent of responses indicated that some employees experience dermatitis when working with epoxy resins.

(5) **Personal Protective Equipment:** Seventy-two percent of the responses indicated that gloves are required, 30 percent provide barrier creams (optional use), and 15 percent require use of coveralls/smocks over street clothes. Forty-one percent require use of respirators for certain manufacturing tasks. Most respirators are used for protection from dusts.

(6) **Ventilation:** Forty-four percent of responses reported use of good general ventilation when using epoxy resin composites, 12 percent local exhaust, 10 percent downdraft tables, 2 percent hood and 1 percent booth ventilation. Cutting and dust-generating operations typically used local or downdraft ventilation.

(7) **Medical Monitoring:** Sixty-seven percent of responses reported that pre-placement medical evaluations are performed on employees and 65 percent indicated that periodic follow-up exams are provided.

## Recommendations:

It is recommended that work surfaces be kept clean from accumulation of dust and uncured resin to prevent possible dermatitis and skin sensitization. Incidence of dermatitis was moderate in the industry survey, some of which is attributed to mechanical irritation from fibers. Reporting of sensitization among the worker population is consistent with literature data confirming that epoxy resins and some components are skin sensitizers[10]. Odor complaints about resins at room temperatures were relatively low unless materials were heated or the work area lacked good general ventilation. Therefore, use of good general ventilation (3-5 air changes per hour) is recommended during lay-up operations. If materials are heated, exhaust gases should be ventilated away from the work area. Although cured composite dusts are not believed to pose a significant health risk, high-velocity, low-volume local exhaust ventilation at the point of operation is recommended to minimize exposure to dusts that may result in respiratory and skin irritation (chemical and mechanical) and adversely affect production efficiencies. If there is a possibility of skin exposure to dusts or resins, skin protection, including gloves and coveralls, should be utilized to minimize dermatitis and sensitization potential. Pre-placement medical evaluations and periodic medical evaluations are recommended. Employees should be trained on the potential health effects of epoxies and on how to minimize risk. Training should be reinforced periodically, such as annually.

### (b) Polyimide Resin Systems

### Description:

Polyimide resins are typically used where high-temperature resistance is required (over 500 degrees F). They provide superior impact resistance, toughness, and delamination strength. However, they are more difficult to process.

"Polyimide resins" refer to a group of structurally similar polymers, including bismaleimides (BMI). The "imide" unit of the polymer is usually a cyclic, five-member ring and can be fused to one or more cyclic or aromatic rings to maximize thermal resistance.

## Toxicology:

The toxicity and sensitization potential of the molding powder ranges from low to high depending upon ingredients and the completeness of reactions. The effect would appear to be dependent on the aromatic diamine used. Certain curing agents, such as MDA, are suspect carcinogens. In addition, other curing agents may pose serious potential health effects and should be evaluated very carefully before use (see Section IV.B.2.g., "Aromatic Amine Curing Agents").

The health effects of polyimide resins as a group have not been studied extensively. The data gathered thus far indicates that the resin systems may produce skin irritation and sensitization reactions, however, significant variability in claimed health effects exists among different products based on MSDS data. These differences may be due to the residual level of reaction products present in the resin formulation and the actual extent of cure in the product. The relative concentrations of unreacted 4,4, - methylene dianiline or 4,4 - diaminodiphenyl-ether, two possible components of polyimide systems, may be responsible for differences in the above-mentioned effects. These amine reactants have been reviewed and determined to exhibit carcinogenic/mutagenic effects in test animals (16) (see Section IV.B.2.g, "Aromatic Amine Curing Agents").

## Observations:

(1) General Comments: A total of 60 responses were received from 11 companies/ subsidiaries. In summary, comments included concern for odors that cause headaches and dizziness; one company was concerned about sensitization from exotherms; and one company reported employee concern for dusts generated from some materials.

(2) Odors: Fifty-two percent of responses reported that some employees complain of odors, compared to 11 percent for epoxies.

(3) Sensitization: Thirty-five percent of responses reported that some employees experience sensitization to polyimide resin composites, compared to 15 percent for epoxy resins.

**(4) Dermatitis:** Forty-two percent of responses indicated that some employees experience dermatitis when working with polyimide resins, compared to 20 percent for epoxy resins.

**(5) Personal Protective Equipment:** Seventy-three percent of the companies surveyed require use of gloves, 22 percent provide barrier creams (optional use) and 48 percent require use of coveralls/smocks over street clothes. Twenty-seven percent require use of respirators when performing certain manufacturing tasks. Required use of gloves and clothing cover is slightly higher for polyimide resins than for epoxy resins.

**(6) Ventilation:** Thirty-four percent of responses reported that they utilize good general ventilation when using polyimide resin composites, 12 percent local exhaust and 2 percent downdraft tables.

**(7) Medical Monitoring:** Forty-four percent of responses reported that pre-placement medical evaluations are performed on employees and 31 percent indicated that periodic follow-up exams are provided. Required medical exams are lower for this group as compared to the epoxy resin composite users.

**Recommendations:**

The industry experience survey indicated that use of polyimide resins resulted in the highest overall adverse reaction experience rate, especially during pre-preg lay-up operations. Odor, dermatitis, and sensitivity experience was high relative to other composites. According to the toxicological review, odor, dermatitis, and sensitization potential for the polyimide resin itself is low. Therefore, reported adverse experiences may be due to the curing agents being used concurrently with the polyimide resin. Special precautions should be observed. Toxicological data on the curing agents should be carefully evaluated and adequate exposure controls should be placed on the operations before the material is approved for use (see Section IV.B.2.g, "Aromatic Amine Curing Agents").

It is recommended that work surfaces be kept clean from accumulation of dust and uncured resin to prevent possible dermatitis and skin sensitization. Good general ventilation should be used as a minimum and, if possible, local exhaust or downdraft systems should be used to control odors. If there is a possibility of exposure to dusts or resin, skin protection, including gloves and coveralls, should be utilized. Use of barrier creams will enhance the effectiveness of a good glove program. If materials are heated, exhaust gases should be vented away from the work area. Although cured composite dusts do not pose a significant health risk, high-velocity, low-volume local exhaust ventilation at the point of operation is recommended for dust generating operations to minimize exposure to dusts that may result in respiratory and skin irritation (chemical and mechanical). Furthermore, the slight (or theoretical) potential exists for small amounts of some unreacted monomers to remain on dust particles and be absorbed into the body. Pre-placement medical evaluations and periodic medical evaluations are recommended. Employees should be trained on the potential health effects of polyimides and on how to minimize risks. Training should be reinforced periodically, such as annually.

### (c) Phenolic Resin Systems

**Description:**

Phenolic resins are more temperature resistant than conventional epoxy resins, but are not as temperature-resistant as polyimides. The service temperature of phenolic resins is typically 350-370 degrees F; these resins are used as materials for fire barriers and hot air ducts. They are also used as materials for interior aircraft parts.

Polymerization of phenolic resins includes a reaction between the phenol monomer and an aldehyde (typically formaldehyde). Reactions are retarded with inhibitors and accelerated using catalysts and/or heat.

**Toxicology:**

Phenolic resin composites are reported to produce dermatitis, most likely resulting from exposure to the phenolic monomer component in the resin[10]. Phenol is a potent primary irritant, and resorcinol, furfural, and formaldehyde are irritants and sensitizers[11]. Formaldehyde is a suspect carcinogen.

Contact dermatitis is probably the best characterized health effect resulting from worker contact with the phenolic resins[17]. Additionally, skin sensitization reactions to

71

specific phenol-formaldehyde reaction products have been described[18].

Although the amount of free phenol and formaldehyde present in the reacted resin is usually regarded as trace, both phenol and formaldehyde are skin, eye, and respiratory tract irritants. All contact with the uncured resin during curing/heating should be avoided as well as direct skin contact with prepregs containing resin.

Formaldehyde is a potential skin sensitizer and animal carcinogen[19]. Phenol is systemically toxic and is well absorbed through the skin in its vapor, liquid or solid form[20].

## Observations:

**(1) General Comments:** A total of 36 responses were received from 10 companies/subsidiaries. In summary, comments included concern for dermatitis, both mechanical and chemical in nature. Dermatitis was reported to appear "occasionally" or "in clumps" then disappear. Throat irritation was reported by one company.

**(2) Odors:** Fifty-six percent of responses reported that some employees complain of odors, compared to 11 percent for epoxies.

**(3) Sensitization:** Nineteen percent of responses reported that some employees experience sensitization to phenolic resin composites, compared to 15 percent for epoxies.

**(4) Dermatitis:** Forty-two percent of responses indicated that some employees experience dermatitis when working with phenolics, compared to 20 percent for epoxy resins.

**(5) Personal Protective Equipment:** Fifty-seven percent of the companies surveyed require use of gloves, 24 percent provide barrier creams (optional use) and 57 percent require use of coveralls/smocks over street clothes. Twenty-two percent require use of respirators for certain manufacturing tasks.

**(6) Ventilation:** Thirty-two percent of responses reported that they utilize good general ventilation when using phenolic resin composites, 40 percent use local exhaust ventilation. Use of local exhaust ventilation is over twice as high for phenolic composites compared to epoxies.

**(7) Medical Monitoring:** Fifty percent of responses reported that pre-placement medical evaluations are performed on employees and 33 percent of responses indicated that periodic follow-up exams are provided. Required medical exams are slightly lower for this group as compared to epoxy users.

## Recommendations:

The industry experience survey indicated that adverse experience with phenolics use was primarily due to odors and dermatitis resulting from the chemical and mechanical properties of the resins and fibers. There may be an association between the reports of limited glove usage and increased dermatitis/sensitization in operations utilizing phenolics. Odor complaints were noted for most operations, especially in absence of good general ventilation.

It is recommended that work surfaces be kept clean from accumulation of dust and uncured resin to prevent possible dermatitis. Good general ventilation is recommended as a minimum during lay-up operations. If materials are heated, exhaust gases should be vented away from the work area. Although cured composite dusts do not pose a significant health risk, high-velocity, low-volume local exhaust ventilation at the point of operation is recommended for dust generating operations to minimize exposure to dusts that may result in respiratory and skin irritation (chemical and mechanical). If there is a possibility of exposure to dusts or resin, skin protection, including gloves and coveralls, should be utilized to minimize dermatitis. Pre-placement medical evaluations and periodic medical evaluations are recommended. Employees should be trained on the potential health effects of phenolics and on how to minimize risk. Training should be reinforced periodically, such as annually.

## (d) Polyester Resin Systems

### Description:

Polyester resins are typically used for high-temperature applications and where low dielectric strength properties are desirable (low absorbency). "Polyester resins" are made by polymerizing a polyester pre-polymer, usually a condensed alcohol, with a vinyl monomer, usually styrene. Additional modifiers or ingredients can be

added, such as phenolic resins, epoxy resins, and fire retardants, and cross-linked by air oxidation of the unsaturated groups to obtain the desired end product[23].

## Toxicology:

The unsaturated polyester thermoset resins are prepared with styrene as the cross-linking group between polymer units. Additives such as methylmethacrylate (increases resistance to weathering) and dimethylaniline (accelerator) may be used in the formulation and may be important in the characterization of the potential health significance of exposure to the wet resin.

Narcosis and mucosal irritation due to styrene monomer exposure is reported as the most frequently experienced health effect due to the use of polyester resins, the latter being so severe upon exposure that contact with the material is generally avoided[12, 22]. Dimethylaniline is a CNS depressant and can produce methemoglobinemia resulting in cyanosis. Both styrene and dimethylaniline can enter the bloodstream by either inhalation or absorption through the skin[23].

Exposure to dusts containing cured polyester resins has produced respiratory irritation and potential changes in lung functionality in workers[24]. Also, similar to other resin dusts, mechanical irritation of the skin can occur.

## Observations:

(1) General Comments: A total of 16 responses were received from three companies/subsidiaries. There were no specific concerns reported on polyester composites. This may be due to the high level of control when using these materials and the relatively low usage within the aerospace industry.

(2) Odors: There were no reports of employee complaints concerning odors, compared to 11 percent for epoxies.

(3) Sensitization: There were no reports of employee sensitization to polyester resin composites, compared to 15 percent for epoxies.

(4) Dermatitis: There were no reports of employee dermatitis as a result of working with polyester resin composites, compared to 20 percent for epoxies.

(5) Personal Protective Equipment: Seventy-five percent of responses indicated that gloves are required, compared to 72 percent with epoxies, and 44 percent provide barrier creams (optional use). None of the companies reported that they require use of coveralls/smocks over street clothes when working with polyester resin composites, compared to 15 percent for epoxy resins.

(6) Ventilation: Fifty percent of responses reported that they utilize good general ventilation when using polyester resin composites, 17 percent use local exhaust ventilation and 17 percent use downdraft tables. Use of ventilation is about the same for polyester resins as it is for epoxies.

(7) Medical Monitoring: Sixty-four percent of responses reported that pre-placement medical evaluations are performed on employees and 64 percent indicated that periodic follow-up exams are provided. Required medical exams are similar for this group as compared to epoxy users.

## Recommendations:

The industry experience survey indicated that most companies had very little adverse information on use of polyester resin composites. Odor complaints and incidence of dermatitis and sensitization were extremely low or non-existent. It appeared that use of neoprene and natural latex gloves were effective in preventing dermatitis and that use of local exhaust and downdraft ventilation was effective in minimizing airborne dusts and odors. Additional recommendations are the same for polyester resin systems as were noted in the second paragraph of recommendations for phenolic resin systems.

### (e) Silicone Resin Systems

## Description:

Silicone resins can resist high temperatures, but have a relatively low-strength capacity. They are typically used as insulation in high-temperature areas (above 350 degrees F) and where flexible bonding is desirable.

"Silicon resins" are any of a large group of organic siloxane polymers that are highly cross-linked. The basic building blocks include a silicate where various organic

groups are attached as replacements for oxygen atoms on the side chains[1].

## Toxicology:

The order of toxicity is low for all routes of entry except the eyes, in some cases. The inhalation hazard is also low because the vapor pressure of the liquid component is low[13].

The order of toxicity of this class of resins is considered low, the primary health hazard being skin, eye and respiratory irritation upon contact with the resin reactants, dialkylsilicon dihalides and organo peroxy curing compounds[21,25]. The cured material is considered biologically inert[21] and therefore is not expected to be a hazard from an inhalation standpoint. Mechanical irritation of the skin may occur, as will occur with sufficient contact to any cured resin dust.

## Observations:

(1) **General Comments:** A total of 11 responses were received from two companies/subsidiaries. One company reported employee concern for skin irritation.

(2) **Odors:** Eight percent of responses reported that some employees complain of odors, compared to 11 percent for epoxies.

(3) **Sensitization:** Eight percent of responses reported that some employees experienced sensitization to silicone resin composites, compared to 15 percent for epoxies.

(4) **Dermatitis:** Eight percent of responses reported that some employees experience dermatitis as a result of working with silicone resin composites, compared to 20 percent for epoxies.

(5) **Personal Protective Equipment:** Twenty-seven percent of the responses indicated that gloves are required, compared to 72 percent for epoxies. None provide barrier creams (optional use) or require use of coveralls/smocks over street clothes when working with silicone resin composites, compared to 15 percent for epoxies.

(6) **Ventilation:** Sixty-four percent of responses reported that they utilize good general ventilation when using silicone resin composites, compared to 44 percent for epoxies. Seven percent use local exhaust ventilation and 7 percent use hood ventila-

tion. Good general ventilation is used more frequently than specialized ventilation, such as local exhaust and downdraft systems as compared to epoxies.

(7) **Medical Monitoring:** Thirty-six percent of responses reported that pre-placement medical evaluations are performed on employees and 73 percent indicated that periodic follow-up exams are provided.

## Recommendations:

The industry experience survey indicated that there is very little adverse information on odors, dermatitis, or sensitivity as a result of working with silicone resin composites. Additional recommendations are the same for silicone resin systems as were noted in the second paragraph of recommendations for phenolic resin systems.

## (f) Aliphatic Amine Curing Agents

### Description:

Aliphatic amine curing agents are typically used to cure epoxy resin systems. They have a short pot life (30 minutes or less) and are used where relatively low service temperatures (150-200 degrees F) are expected. They are often used in small quantities for repair applications.

Aliphatic amines are derivatives of ammonia where one or more hydrogens are replaced by an alkyl or alkanol group. Aliphatic amine curing agents (part B) are mixed with a resin (part A) to create a reactive mixture that results in cross-linking of polymer groups.

### Toxicology:

Aliphatic amine curing agents are considered highly irritating and corrosive and may cause damage on contact with eyes, skin, and the respiratory tract. Skin absorption is a problem; many are capable of cutaneous hypersensitization[5]. Systemic symptoms from inhalation are headache, nausea, faintness, and anxiety. These systemic symptoms are usually transient[6]. These amines are strongly basic (pH 13-14) and can produce chemical burns of the skin. Some contain dye bases that may yellow the skin upon oxidation. Cutaneous amine reactions cause erythema, intolerable itching, and severe facial swelling. Blistering with weeping of serous fluid, crusting, and scaling may occur[6].

74

Aliphatic and cycloaliphatic amine hardeners are basic compounds characterized by their corrosive properties. These materials are components of epoxy resins and are severe skin, eye, and respiratory tract irritants as well as sytemically toxic. Some of the amines are implicated in skin and respiratory tract sensitization responses. The skin reaction symptoms are similar enough to those from epoxy resin that they cannot specifically be attributed to either constituent[7].

## Observations:

(1) **General Comments:** A total of 51 responses were received from 7 companies/subsidiaries. In summary, some companies reported complaints of odor and headache when the product was heated or sanded. One company reported swelling around eyes and another reported yellowing of hands. When comparing these observations with those from epoxy resin systems, it should be noted that many epoxy resin systems contain aliphatic amine curing agents.

(2) **Odors:** Twelve percent of responses reported that some employees complain of odors, compared to 11 percent for epoxies.

(3) **Sensitization:** Sixteen percent of responses indicated that some employees experienced sensitization to aliphatic amine curing agents, compared to 15 percent for epoxies.

(4) **Dermatitis:** Twelve percent of responses reported that some employees experience dermatitis as a result of working with aliphatic amine curing agents, compared to 20 percent for epoxies.

(5) **Personal Protective Equipment:** Ninety-six percent of the responses indicated that gloves are required, compared to 72 percent with epoxy resins, 73 percent provide barrier creams (optional use) and 9 percent require use of coveralls/smocks over street clothes when working with these materials, compared to 25 percent for epoxy resins.

(6) **Ventilation:** Fifty-nine percent of responses reported that they utilize good general ventilation when using aliphatic amine curing agents, compared to 44 percent for epoxies, 23 percent use downdraft ventilation and five percent use slot hood ventilation. Use of ventilation

systems is more common when handling aliphatic amine curing agents than when handling epoxies.

(7) **Medical Monitoring:** Eighty-four percent of responses reported that pre-placement medical evaluations are performed on employees, compared to 67 percent for epoxies, and 84 percent indicated that periodic follow-up exams are provided, compared to 65 percent for epoxies.

## Recommendations:

Toxicological information indicates that aliphatic amine curing agents are corrosive and are considered primary irritants. Exposure to these resins may result in dermatitis and sensitization. The industry experience survey indicates that employees complain of odors, dermatitis, and sensitivity when working with these materials. Additional recommendations are the same for aliphatic amine curing agents as were noted in the second paragraph of recommendations for phenolic resin systems.

### (g) Aromatic Amine Curing Agents

## Description:

Aromatic amine curing agents are typically used to cure epoxy resin systems. They provide the product with superior temperature-resistance properties where service temperatures may reach 300-350 degrees F.

Aromatic amines include aromatic hydrocarbons where at least one of the hydrogens has been replaced with an amino group. Aromatic amine curing agents (part B) are mixed with a resin (part A) to create a reactive mixture that results in cross-linking of polymer groups.

## Toxicology:

Aromatic amine curing agents are generally considered systemic toxics because some are readily absorbed through the skin and react with internal systems, such as the liver and bladder. "The most dominant toxic effects are methemoglobin formation and cancer of the urinary tract. Other toxic effects include hematuria, cystitis, anemia, and skin sensitization."[7]

Aromatic amines are used in epoxy resins as curing agents and as reactants in some polyimide resins. The amines may be mono or diphenyl compounds, with the latter

being separated by either an aliphatic chain or a sulfone (S=O).

The potential health effects presented by this class of chemicals is somewhat dependent on the chemical structure of the members. Certain characteristics are exhibited. Most are mild irritants and may produce liver damage. Some aromatic amines may produce irreversible retinal degeneration upon overexposure. All members are absorbed well through the skin and are not appreciably volatile except when subjected to elevated temperatures, and therefore skin exposure is critical.

Some of the members of the class, most notably 4,4 - methylene dianiline (MDA), are similar to their structural analog benzidine in being classified as a potential bladder carcinogen.

The primary concern with this group of chemicals is their potential to be absorbed through the skin. It is not surprising that airborne monitoring of worker exposure has not been considered an accurate estimate of worker uptake of the chemical. Instead, biological monitoring is prescribed[26].

### Observations:

**(1) General Comments:** A total of 45 responses were received from six companies/subsidiaries. In summary, one company reported complaints of odor during exotherm, one reported nausea and vomiting and one reported that medical monitoring includes biomonitoring. As is the case with aliphatic amines, aromatic amines are used in many epoxy resin systems.

**(2) Odors:** Nine percent of responses reported that some employees complain of odors, compared to 11 percent for epoxies.

**(3) Sensitization:** Five percent of responses indicated that some employees experienced sensitization to aromatic amine curing agents, compared to 15 percent for epoxies.

**(4) Dermatitis:** Five percent of responses reported that some employees experience dermatitis as a result of working with aromatic amine curing agents, compared to 20 percent for epoxies.

**(5) Personal Protective Equipment:** Eighty-nine percent of the responses indicated that gloves are required, compared to

72 percent with epoxies, 70 percent provide barrier creams (optional use), and 26 percent require use of coveralls/smocks over street clothes when working with aromatic amine curing agents, compared to 25 percent for epoxies.

**(6) Ventilation:** Fifty-three percent of responses reported that they utilize good general ventilation when using aromatic amine curing agents, compared to 44 perecnt for epoxies, 21 percent use downdraft ventilation and 11 percent use local exhaust ventilation.

**(7) Medical Monitoring:** Eighty-two percent of responses reported that pre-placement medical evaluations are performed on employees, compared to 67 percent for epoxies, and 84 percent indicated that periodic follow-up exams are provided, compared to 65 percent for epoxies.

### Recommendations:

The industry experience survey indicates that companies receive moderate amounts of feedback from employees concerning odor, dermatitis, and sensitivity as a result of working with aromatic amine curing agents. Toxicological data indicates that the primary effect of many aromatic amine curing agents is that they are readily absorbed through the skin and have an adverse effect on internal organs. Additional recommendations are the same for aromatic amine curing agents as were noted in the second paragraph of recommendations for phenolic resin systems.

### (h) Thermoplastics

### Description:

Thermoplastics are used where weight savings is desirable, and they provide the product with superior toughness and impact resistance. Materials are more expensive than conventional composites but processing time is significantly less.

"Thermoplastics" refer to a group of plastics that can be softened with heat and hardened on cooling, such as vinyls, acrylics, and polyethylene[14].

### Toxicology:

Thermoplastics typically do not cause skin irritation or toxic effects. Some are so inert, such as fluoroplastics, that they are used for

human organ prostheses. Other thermoplastics, such as acrylics, can cause respiratory and cutaneous irritation but do not cause cumulative or chronic toxic health affects. Fumes from molding operations have been reported to cause eye irritation.

Since thermoplastic resins are generally processed from fully polymerized materials, the hazards to workers manufacturing parts from these precursors is limited to exposure to polystyrene during heating and to polyphenylenesulphide (PPS) breakdown products during molding operations[8]. Health effects of styrene monomer have been discussed in the treatment of polyester resins (Section IV.B.2.d). PPS can thermally degrade to produce a wide range of possible gaseous breakdown products, including hydrogen cyanide, sulfur oxides, and carbon monoxide, which are all acutely toxic upon inhalation exposure. Control of released decomposition byproduct vapors during heat/pressure forming of thermoplastics is important.

**Observations:**

Thermoplastic materials are sometimes treated separately since the material form and work process (i.e., thermoform operations) are somewhat different than that of

mechanical or hand lay-up. The potential for dermal and inhalation exposure may be greatly reduced since the operation is conducted with a minimum number of employees in the immediate area around the thermoform unit. Additionally, the fact that the material is present as a pre-formed sheet results in minimal dermal contact and limited inhalation exposure in terms of the number of individuals as well as the relative level of airborne contaminants, assuming that appropriate ventilation controls are in place.

There were not enough responses on thermoplastics to develop a profile of user experiences. However, based on the toxicological review, the following recommendations are provided:

**Recommendations:**

General recommendations are the same for thermoplastics as were noted in the second paragraph of recommendations for phenolic resin systems.

### 3) Operation-Specific Observations/ Recommendations

The following is a summary of observations and recommendations based on the toxicology review and the industry experience survey on health effects of composite materials reported by manufacturing operation. Percentages are based on the total number of responses for each question and indicate that one or more individuals reported a given effect when performing a given task. Table 1 illustrates potential hazards and target effects by operation.

**(a) Assembly**

**Description:**

Includes joining pieces together to form sub-assemblies, or joining sub-assemblies together to form a finished product.

**Observations (42 responses):**

Twenty-nine percent of all responses indicated that some employees experienced dermatitis, 23 percent complained of odors and 12 percent reported sensitization when performing assembly work. Most other complaints noted concern for dust inhalation.

**Recommendations:**

It is recommended that gloves be worn when manually handling uncured compos-

| Hazards by Manufacturing Operation | | | | | | |
|---|---|---|---|---|---|---|
| | Potential Hazards | | | Target Effects | | |
| Operation | Dust | Fiber | Volatiles | Skin | Inhal. | Eyes |
| Assembly | X | X | | X | X | |
| Bagging | | X | X | X | X | X |
| Curing | X | | X | X | X | X |
| Kitting | | X | X | X | X | X |
| Lay-up (wet) | | X | X | X | X | X |
| Lay-up (pre-peg) | X | X | X | X | X | X |
| Rework | X | X | X | X | X | X |
| Trim/Sand Machine | X | X | | X | X | X |
| Research & Development | X | X | X | X | X | X |
| Tooling | X | X | X | X | X | X |

(Adapted from Reference (12))    *(Table 1)*

ite materials, and to prevent skin contact with composite dusts. Good general ventilation (3-5 air changes per hour) is adequate for most assembly operations but if dusts are generated, use of high-velocity, low-volume local exhaust ventilation is recommended.

### (b) Bagging

**Description:**

Uncured parts are covered with absorbent matting to absorb excess resin bleeding from the part during cure, and is sealed with a vacuum bag to evacuate gases and help retain product shape during the curing process.

**Observations (57 responses):**

Nineteen percent of all responses indicated that some employees experience dermatitis, 7 percent complain of odors and 5 percent reported sensitization when performing bagging work.

**Recommendations:**

It is recommended that gloves be worn when manually handling uncured composite materials and bagging materials containing uncured resins to prevent skin contact that may result in dermatitis and/or sensitization. Good general ventilation is recommended for bagging operations.

### (c) Curing

**Description:**

The bagged part is placed in an oven, autoclave, or press and is processed over a period of time to expedite the chemical reaction between components of the composite mixture.

**Observations (85 responses):**

Fourteen percent of all responses indicated that some employees experience dermatitis, 18 percent complain of odors and 17 percent reported sensitization when performing curing work.

**Recommendations:**

It is recommended that gloves be used when handling uncured composites, that ventilation systems be used to exhaust gases from autoclaves, and that good general ventilation be provided in all other areas where curing operations are performed. Ventilation systems should be designed to effectively remove decomposition products of exotherms from the work area.

### (d) Kitting

**Description:**

Frozen pre-peg is removed from a freezer and cut to the desired size and shape required prior to pre-peg lay-up. For wet lay-up applications, the cloth or fabric part of the two-part system is cut and sized. Dusts and fibers may be produced from both wet lay-up and pre-peg operations, volatiles, and possibly aerosols from the resin system may be produced from pre-peg systems during cutting as well as during removal of pre-peg backing prior to lay-up.

**Observation:**

Information from this process is included in the observations sections below for wet and pre-peg lay-up.

**Recommendations:**

See sections (e) and (f).

### (e) Wet Lay-Up

**Description:**

Uncured resins are applied to dry fibrous materials in alternating layers in the desired orientation on lay-up tools to obtain the desired shape.

**Observations (56 responses):**

Fifteen percent of all responses indicated that some employees experience dermatitis, 26 percent complain of odors and 18 percent reported sensitization when performing wet lay-up work.

**Recommendations:**

Odor was the most prevalent complaint observed during wet lay-up operations and the majority of those were reported in areas where only limited ventilation was provided. It is recommended that good general ventilation be used as a minimum and that hood ventilation or downdraft tables be used as needed to control odors. Use of impervious gloves and coveralls/smocks are also recommended to minimize skin contact with uncured resins.

### (f) Pre-Preg Lay-Up

**Description:**

Pieces of pre-preg cloth or tape (fibrous materials impregnated with resin and partially cured) are cut and placed in the desired orientation on lay-up tools in multiple plies to obtain the desired shape.

78

**Observations (131 responses):**

Forty-four percent of all responses indicated that some employees experience dermatitis, 25 percent complain of odors and 34 percent reported sensitization when performing pre-preg lay-up work.

**Recommendations:**

Dermatitis, odors, and sensitization were all significant adverse reactions reported by companies that perform pre-preg lay-up operations. The fact that pre-preg operations require intimate contact with uncured composites and that the task requires employees to perform this task for many hours per day justifies the need for special precautions.

It is recommended that employees use impervious gloves when performing pre-preg lay-up operations. Depending on the scope of work performed, gloves should be impervious to the resin and solvents used in the process. Most lay-up operations also involve cutting composite materials so the cut-resistance of the glove should be considered when selecting an impervious glove, or a cut-resistant glove should be worn over the impervious glove. Use of good general ventilation is recommended as a minimum and use of downdraft tables should be considered for composites that emit strong odors or generate dust when cut.

**(g) Rework**

**Description:**

Repair of damaged or defective parts to restore them to original specification.

**Observations (62 responses):**

Eleven percent of all responses indicated that some employees experience dermatitis, none complained of odors and 4 percent reported sensitization when performing rework operations. Most companies that responded to this section utilized downdraft tables to control airborne dusts and fumes.

**Recommendations:**

Rework operations are typically small-scale, short-duration projects that, according to responses, are well controlled with local exhaust ventilation, downdraft tables, and use of gloves. It is recommended that high-velocity, low-volume local exhaust ventilation be used to control dust-generating operations at the point of operation and

that coveralls and gloves be used to prevent skin contact that may result in dermatitis from chemical and mechanical properties of the materials.

**(h) Sand/Machine/Trim**

**Description:**

Cured parts are rough trimmed, net trimmed, deburred, sanded, drilled or processed via machining.

**Observations (79 responses):**

Six percent of all responses indicated that some employees experience dermatitis, 6 percent complained of odors and 5 percent reported sensitization when performing trimming, sanding or machining operations. Most companies that responded to this section utilized local exhaust ventilation, downdraft tables and gloves to control personnel exposures.

**Recommendations:**

It is recommended that high-velocity, low-volume local exhaust ventilation be used to control dusts and that employees use personal protective equipment, including coveralls and gloves to prevent skin contact that may result in dermatitis from the chemical and mechanical properties of the materials. Use of gloves and loose clothing is not recommended near revolving equipment.

**(i) Research & Development**

**Description:**

Research and development includes laboratory testing of new materials and processes to determine optimum manufacturing conditions.

**Observations (85 responses):**

Four percent of all responses indicated that some employees experience dermatitis, 10 percent complained of odors and 6 percent reported sensitization when performing trimming, sanding, or machining operations. Most companies that responded to this section utilized good general ventilation, local exhaust, downdraft tables, and gloves to control personal exposures. Most complaints originated in areas where there was less than good general ventilation provided.

**Recommendations:**

It is recommended that good general ventilation be used as a minimum for small scale, low hazard tasks and that high velocity, low volume local exhaust be used to control dust generating operations. Downdraft ventilation or booth/hood ventilation should be considered to control odors. Use of personal protective equipment including coveralls and gloves are also recommended to prevent skin contact that may result in dermatitis from the chemical and mechanical properties of the materials.

## (J) Tooling

**Description:**

Tooling includes preparation of the tool, which is made of composite materials and serves as a working surface and a master model for the finished part.

**Observations (36 responses):**

Four percent of all responses indicated that some employees experience dermatitis, 10 percent complained of odors and 6 percent reported sensitization when performing trimming, sanding, or machining operations. Most companies that responded to this section utilized good general ventilation, local exhaust, downdraft tables, and gloves to control personnel exposures. Most complaints originated in areas where there was less than good general ventilation provided.

**Recommendations:**

It is recommended that good general ventilation be used as a minimum for small-scale, low-hazard tasks and that high-velocity, low-volume local exhaust be used to control dust generating operations. Downdraft ventilation or booth/hood ventilation should be considered to control odors. Use of personal protective equipment, including coveralls and gloves, are also recommended to prevent skin contact that may result in dermatitis from the chemical and mechanical properties of the materials.

## C. Information Needs

While gathering data on current knowledge and industry experiences with composite materials, information needs were also identified. This section outlines the most significant of these information needs and provides recommendations on how to fill these knowledge gaps to improve evaluation and communication processes:

## 1) Toxicology of Raw Materials

A review of toxicological data pertaining to composite raw materials indicates that additional information is needed to provide safety and health professionals with information to better assess risk potential of these products, particularly the new resin systems, pre-pregs, and fibrous dusts. Probably the largest information gap is a lack of data on the ability of resin components to permeate the skin. This makes control of exposure difficult, since it is not always clear what control levels of airborne contamination are necessary or what level of dermal protection to use. Secondly, there is a need to facilitate communications between manufacturers and users about known hazards, such as those that are reportable to the Environmental Protection Agency (EPA) under the Toxic Substance Control Act (TSCA), Section 8(e), because of the chemicals' potential to cause significant adverse effect on health or the environment.

**Recommendation:**

Major toxicology data gaps relative to raw materials should be identified by manufacturers and users, and a plan should be established to provide funding for industry and/or government to conduct additional research, including epidemiological studies. Additional emphasis should be placed on the elimination of the sources of obnoxious resin odors, if possible, to improve employee comfort and increase productivity. Hazard information pertaining to these materials should be transferred to users via Material Safety Data Sheets.

## 2) Occupational Exposure Monitoring

New materials have been introduced into the work environment and many of these materials have not had sampling and analytical methods or recommended exposure limits established. As a result, several different procedures may be used to collect and measure the same analyte. This practice makes it difficult to evaluate data industry-wide and to determine if exposures are within safe limits.

**Recommendation:**

Sampling and analytical methods and guidelines for occupational exposure should

be established for air, surface, and biological samples. Specific areas which could be addressed are sampling of pre-pregs for dust and fibers since some of these products are being found to generate dust during process-ing even in the uncured state. Other areas include sampling and analysis of pre-preg solvents, resin raw materials, diluents, etc. Air sampling procedures should include measurement of volatile components of resins, formulation byproducts, and com-posite dusts.

For many pre-preg and resin products, the amount of volatile materials present in the products may not cause significant exposure by the inhalation route. Skin contact is often the major route of potential exposure, and, as a consequence, surface sampling and biological monitoring could be used to better assess risk. Surface sampling proce-dures include wipe tests of pre-preg to identify the relative availability of a resin component and wipe tests of work surfaces are used to identify the extent of contamina-tion. Biological sampling could serve a useful purpose to measure relative exposures via skin absorption or ingestion and he used to prioritize corrective actions. Biological monitoring techniques should be estab-lished for composite components which are of sufficient toxicity and are readily ab-sorbed dermally.

### 3) Medical Surveillance

Medical monitoring protocols should be established through review of the product hazards combined with information regard-ing relative exposure levels to which workers are exposed. In many cases, neither of these parameters are known and therefore, the fundamental information needed to estab-lish a medical monitoring program cannot be readily determined.

### Recommendation:

Definition is needed of medical monitoring programs already in existence and those which are planned in the composites indus-try. Additionally, the manufacturers should be encouraged to share toxicology informa-tion about chemicals with occupational medicine personnel representing the user industry. Lastly, accurate exposure measure-ments should be made.

### 4) Hazard Communication

Often, components are listed by generic name or by general class of chemicals to which they belong. The terms "epoxy resin" or "amine curing agent" are not acceptable to the product users. Users of composites are unable to evaluate the potential health effects of materials for which only general chemical information is supplied. They are also unable to provide employees with effective guidance on appropriate personal protective equipment without specific information provided by the manufacturer. Also, the formulated resin or partly cured product may present a hazard much differ-ent than the reactant material.

At times, composite raw material labels do not contain accurate information on the manufacturer, the product identification, health hazard warnings or the repackaging company name. This creates difficulties identifying materials and making a link between the label and the MSDS.

### Recommendation:

Appropriate health hazard information should be notated on the MSDS. The MSDS serves as an educational tool and should be used to communicate specific and accurate information to employees. There are only two acceptable options for listing of materi-als which are hazardous. The first is listing the specific chemical identity, including the Chemical Abstracts Service (CAS) number, and the second is a statement that the identity of the chemical is proprietary.

The potential health effects of the mate-rial should be clearly stated on the MSDS, including appropriate methods to control exposures. General statements such as "may cause skin irritation" and "impermeable gloves should be worn" should be avoided. In terms of protective gloves, a specific type of glove shown to be effective against permeation should be designated. Details about break-through times should also be included. ■

# V    Conclusion

Results of the AIA Composites Task Group study indicate that some persons who work with composite materials do experience adverse reactions to these materials when performing various manufacturing tasks. The frequency of the complaints associated with certain composite materials suggests that there is an association between the chemical/process and the source of employee concern. However, the data also indicates that there are effective controls presently available that can significantly minimize the risk of experiencing these adverse effects. Based on the data presently available, composite materials can be handled safely if safe work practices are observed.

Some composite operations will require additional, more stringent controls than others, depending upon the chemicals involved, but technology is presently available to address these special requirements. Companies should respond to employee concerns about new materials and processes. Communication to the workforce on new composite technologies should be restructured when needed to provide employees with the information and tools to minimize health risk. Furthermore, internal company enforcement policies should be strengthened regarding the wearing of gloves and other personal protective equipment. Proper ventilation systems should be designed, installed, and maintained where appropriate.

As composite technology continues to advance and mature, safety and health professionals and manufacturing engineers need to work together to provide employees with a work environment that is both safe and productive. ∎

# VI References

1. MED-LINE, TOX-LINE, National Library of Medicine, DHHS, PHS (Bethesda, MD: National Institute of Health, 1992).

2. Bourcier, D.R., "Comments on the AIA Composite Task Group Health Hazards Study" (paper presented at the National Center for Advanced Technologies and American Institute for Aeronautics and Astronautics Symposium on Key Technologies for the Year 2000, Washington, D.C., December 1991).

3. U.S. Department of Defense, *Conference on Occupational Health Aspects of Composites* Vol. 1 and 2 (Washington, D.C.: GPO, March 1989, Pub. No. AAMRL-TR-89-008), Executive Summary 61, Proceedings, 410.

4. *Applied Industrial Hygiene: Special Issue on Health Aspects of Composite Materials*, American Conference on Governmental Industrial Hygienists, (December 1989).

5. Luca, J., "Aerospace Industries Association Composites Health and Safety Study" (paper presented at American Conference on Governmental Industrial Hygienists Conference on Advanced Composites, San Diego, Calif., 3 March 1991).

6. Cleghorn, R., "Utilization of Computer Data Bases to Evaluate Industry Experience with Composite Materials in the Aerospace Industry" (paper presented at AIHCE, May 1991).

7. Borgstedt, H. and C. H. Hine, "Toxicity, Hazards and Safe Handling," in *Epoxy Resins: Chemistry and Technology* (New York: 1988).

8. *Safe Handling of Advanced Composites Materials*, Suppliers of Advanced Composite Materials Association, 2nd ed. (Arlington, Va.: 1991), 52.

9. Fregert, S., "Contact Dermatitis from Epoxy Resin Systems," in *Occupational and Industrial Dermatology*, 2nd ed. (Chicago: Yearbook Medical Publishers, Inc., 1987), 341-345.

10. Hine, C., et al., "Epoxy Compounds," in *Patty's Industrial Hygiene and Toxicology* 2A, eds. Clayton and Clayton (New York: John Wiley and Sons, 1982), 2141-2158.

11. Kowalska, M., "Carbon Fiber Reinforced Epoxy Prepregs and Composites-Health Risk Aspects," *SAMPE Quarterly*, January 1982, 13-19.

12. Bourcier, D. R., "Exposure Evaluation of Composite Materials With Emphasis on Cured Composite Dust," *Applied Industrial Hygiene: Special Issue on Health Aspects of Composite Materials* (American Conference on Governmental Industrial Hygienists, December 1989), 40-46.

13. Lutchel, D. L., "Carbon/Graphite Toxicology," in *Fiber Toxicology*, ed. D. Warheit, (New York: Academic Press, 1993), 493-521.

14. Kwan, J. K., "Health Hazard Evaluation of the Postcuring Phase of Graphite Composite Operations at the Lawrence Livermore National Laboratory, Livermore, Calif." (Ph.D. thesis, UCRL-LR-104684. NTIS, Springfield, Va., 1990).

15. Malten, K. E., "Old and New, Mainly Occupational Dermatological Problems in the Production and Processing of Plastics," in *Occupational and Industrial Dermatology*, 2nd ed. (Chicago: Yearbook Medical Publishers, Inc., 1987), 290-340.

16. *IARC Monographs on the Evaluation of the Carcinogenic Risk of Chemicals to Humans: Some Industrial Chemicals and Dyestuffs* 29 (WHO, International Agency for Research on Cancer, 1982), 203-212.

17. Bruze, M., "Contact Dermatitis from Phenol-Formaldehyde Resins," in *Occupational and Industrial Dermatology*, 2nd ed. (Chicago: Yearbook Medical Publishers, Inc., 1987), 430-435.

18. Bruze, M., Persson, L., Trulson, L., and Zimmerson, E., "Demonstration of Contact Sensitizers in Resins and Products Based on Phenol-formaldehyde," *Contact Dermatitis* 14: (1986), 146-154.

19. *Documentation of the Threshold Limit Values and Biological Exposure Indices*, 5th ed., American Conference of Governmental Industrial Hygienists (Cincinnati: 1988).

20. *Criteria for a Recommended Standard, Occupational Exposure to Phenol*, (Washington, D.C.: National Institute of Occupational Safety and Health, 1976, Doc. #76-196), 23-69.

21. Finkel, A. J., ed., *Hamilton and Hardy's Industrial Toxicology*, 4th ed. (New York: John Wright-PSG, Inc., 1983), 270-272.

22. Proctor, N. H., Hughes, J. H., *Chemical Hazards of the Workplace* (Philadelphia: J. B. Lippincott, 1978), 225-226.

23. Key, M. M., Konzon, J. L., and Devitt, G. E., "Polyester Resins," in *Encyclopedia of Occupational Health and Safety* Vol. 2 (1983) 1760-1762.

24. Zuskin, E., Saric, M., and Bouhuys, A., "Airway Responsiveness in Workers Processing Polyester Resins," *Journal Occupational Medicine* 21, no. 12 (1979) 825-827.

25. "The Halogens and the Non-Metals Boron and Silicone," *Patty's Industrial Hygiene and Toxicology*, 2B (19(1), 3039-41).

26. MDA Final Rule, 29 CFR 1910 Section 1050 (General Industry) and 29 CFR 1926 Section 60 (Construction), 10 August 1992.

# DERMAL EXPOSURE:

- ASSESSING THE HAZARD

- EMERGING REGULATORY ISSUES

Kevin Cummins
Senior Industrial Hygienist
OSHA Health Response Team
Salt Lake City, UT.

# WHY IS SKIN EXPOSURE IGNORED?

- Problem doesn't exist, or magnitude of problem overestimated

- Lack of tangible evidence of exposure

- Little historical evidence indicative of problem

- No solution

# IS SKIN EXPOSURE A PROBLEM?

- Dermatitis

- Skin Absorption Compared to Lung

- Reviews of Literature

# DERMATITIS

- Second leading cause of Occupational Illness[1]

- 11% of Working Adults, or 13.7 million, experienced dermatitis. 2.8% specifically cited chemicals[2]

- 25% of all occupational illnesses are skin exposures[3]

[1]    1989 BLS Statistics

[2]    1988 Occupational Health Supplement to the National Health Interview Survey

[3]    "PPE for General Industry; Final Rule", Federal Register, April 6, 1994, pp. 16334-16364.

# SKIN VS LUNG ABSORPTION

## COMPARE:

## AMOUNT ABSORBED VIA SKIN EXPOSURE

- Amount Absorbed = (Surface Exposed in $cm^2$) x ( Absorption rate in $mg/cm^2/hr$) x (Time Exposed in hrs)

## TO:

## AMOUNT ABSORBED BY THE LUNG

- Amount absorbed = (Concentration in air in $mg/m^3$) x (Breathing Rate in $m^3/hr$.) x ( Time Exposed in hrs.)

# GLYCOL ETHERS
## (2-ethoxyethanol and 2-ethoxyethyl acetate)

Amount absorbed by skin $= (900 \text{ cm}^2)$
$(0.8 \text{ mg/cm}^2/\text{hour}^1)(8 \text{ hours})$

$$= 5760 \text{ mg.}$$

Amount absorbed from Air at TLV $= 18$
$\text{mg/m}^3 \times 10 \text{ m}^3$

$$= 180 \text{ mg.}$$

Dose to the skin exceeds the TLV dose by a factor of 32 times!

[1]  Recommended BEI, **Appl. Occup. Envir. Hyg.** 8(5), May 1993.

C-2

# ACRYLAMIDE

Amount absorbed by skin = (900 cm$^2$) (1 mg/cm$^2$/hour$^1$)(8 hours)

= 7200 mg.

Amount absorbed from Air at TLV = 0.038 mg/m$^3$ x 10 m$^3$

=0.38 mg

Dose to the skin exceeds the PEL dose by a factor of 19,000 times!

1   Absorption rate for DMF, Bergerova, **Appl. Occup. Envir. Hyg.** 4(8) 1989.

# FACTORS WHICH AFFECT SKIN ABSORPTION

- OCCLUSION

- TEMPERATURE

- PRESSURE

- PRESENCE OF OTHER SOLVENTS

- AMOUNT OF EXPOSED SKIN

- CONDITION OF SKIN

# EXAMPLES OF SKIN EXPOSURE

PBC'S in Transformers (Lees, Corn, and Breysse, **AIHA**, 49(3) 257-264 (1987):

"The author's conclude that exposure by the dermal route (i.e. skin absorption) is considerable (especially when compared to respiratory exposures), whatever the job task."

Toluene and Xylene from autobody work (Daniell, Stebbins, Kalman, O'Donnell, and Horstman, **AIHA**, 53, (1992) pp. 124-129.):

"Air sampling will substantially underestimate a worker's total solvent dose in the setting of moderate or high skin exposure. "

# EXAMPLES CONTD.

**Polynuclear Aromatics (PNA's) among Coke Oven Workers** (VanRooij, Bodelier-Bade, and Jongeneelen, **Br. J. Ind. Med.,** 1993, 50, 623-632) :

Pyrene: avg. 75% (range 28%-95%) of total dose via skin

Benzoapyrene: avg. 51% (range 8%-92%) of total dose via skin

"Our results indicate that preventive measures to reduce exposure to PAHs should be focused more on the reduction of dermal contamination with PAHs than on the reduction of the inhaled dose."

# EXAMPLES CONTD.

Toluene Diisocyanate (TDI) ( Karol, Hauth, Riley, and Magren, **Tox.& Appl. Pharm.**, 58, 221-230, (1981):

"...1 drop (50uL) 100% TDI applied to the skin in the absence of any adjuvant caused antibody production in 100% of animals and pulmonary sensitization in approximately 30-40% of animals".

Occupational Chemical Exposures in an Academic Medical Center (Weaver, McDiarmid, Guidera, Humphrey, and Schaefer, **JOM**, 35, (1993), pp. 701-706.:

"A total of 253 exposures occurred during a 3 years period....Exposure by the dermal route was most common (37.9%)."

# GLOVE PERMEATION IN SEMICONDUCTOR INDUSTRY[1]

- GLYCOL ETHERS EXPOSURES POSSIBLY LINKED TO EXCESS SPONTANEOUS ABORTIONS

- RE-USE OF GLOVES RESULTED IN RAPID BREAKTHROUGH

- PERMEATION RATES OF GLYCOL MIXTURES GREATER THAN PREDICTED FROM PURE COMPONENTS

1  Zellers, et al, AIHA, 53, (1992), pp. 105-116.

# REVISIONS TO THE PPE STANDARD

- ## 1910.138 HAND PROTECTION

(a):     (General requirements) Employer shall require use "appropriate hand protection when employees' hands are exposed."

(b):     (Selection)  Employers shall base selection on "an evaluation of the performance characteristics of the hand protection relative to the task(s)  to be performed, conditions present, duration of use, and the hazards and potential hazards identified."

# WHAT MEANS SHOULD BE USED TO ASSESS SKIN EXPOSURE AND THE EFFECTIVENESS OF PPE?

- MONITOR SURFACE CONTAMINATION

- MONITOR SKIN EXPOSURE

- BIOLOGICAL MONITORING

- ## SAFETY AND HEALTH PROGRAM STANDARD

Emphasis will be shifted to the employer to enforce Safety and Health

- ## EXPOSURE ASSESSMENT STANDARD

Items being considered as acceptable means of ensuring that exposures are minimized:

Skin exposure Monitoring

Biological Monitoring

# WHAT CAN WE EXPECT?  (or at least:)
# WHAT CAN WE HOPE FOR?

A  future in which OSHA  stops being simply a policeman (albeit one who was rarely present) ...

To a future in which responsibility lies with the employer.  OSHA's role may very well be one of an auditor, rather than an enforcer in this new OSHA.

# SO WHAT DO <u>WE</u> DO ABOUT IT?

- Provide testimony in support of these changes

- Provide examples of successful programs for controlling skin exposure.

file:skintlk.kc

Slide 1: Title

Slide 2: Why is skin exposure ignored?

Why is skin exposure ignored. Let's first explore some possible answers to this question, before further discussing this issue.

## Problem doesn't exist, or magnitude of problem overestimated

Obviously, if this the case then we shouldn't dwell on the issue. Although, I believe that skin exposure is a significant problem, we cannot expect action on this matter until we have convinced ourselves and others of the extent and magnitude of the problem. Later on I'll present some evidence to indicate that it is a problem, but for now let's assume that the problem is real. What other reasons could explain the lack of inaction?

## Lack of tangible evidence

We human beings are rather simple creatures. We seem to deal effectively with tangible problems, but are less responsive to problems with which we have not had direct experience. Skin exposure to toxic chemicals which are not strong irritants may be like this. Because we cannot smell, taste, see, or feel them, we do not perceive that there is a problem, despite the fact that absorption of significant levels of chemical through the skin may be occurring.

## Little historical evidence indicative of problem

Industrial hygiene has traditionally focused on air exposures. Obviously, this was because many classic forms of occupational illnesses occurred via exposure to the lung. Silicosis and asbestosis are two classic examples which come to mind. However, even a historical review brings to mind the story of Percival Potts who recognized scrotal cancer as an occupational illness of chimney sweeps caused principally, if not entirely, by skin exposure to carcinogenic polynuclear aromatics contained in the chimney soot. Thus even history is not devoid of some evidence that skin exposure is a problem.

## No solution

This response is the opposite of the first one. If our perception of the problem is that there are no solutions, then it is understandable that we might choose to ignore the problem. Our fear of the unknown may has cause us not to act on the problem because if appears to be insurmountable. Thus it seems important for us to really answer the question: Is skin exposure a problem?

Slide 3: Is skin exposure a problem?

What evidence is there to support the contention that skin exposure is a significant problem? Let's examine these three potential areas to determine the magnitude of the problem.

Slide 4: Dermatitis

## Dermatitis

First of all there is the obvious one, dermatitis. Estimates of the extent of dermatitis in the workforce vary greatly. Prior to the recognition of ergonomic problems, dermatitis was recognized as the leading reported occupational illness. In a 1988 Occupational Health Supplement to the National Health Interview Survey it is reported that of 11% of working adults (3.7 million workers) surveyed experienced dermatitis. 3.1 million cases, or 2.8% attributed their exposures to the workplace. Higher estimates of the magnitude of the problem were reported to OSHA on the hearings regarding revisions of the PPE standard. In this testimony it was reported that occupational skin disease accounted for 25% of all reported cases of occupational illnesses. Additionally, BLS statistics for the construction industry indicate that 37% of all reported occupational illnesses from 1973 -1984 were dermatitis.

Slide 5: Skin Absorption Compared to Lung

## Skin Absorption Compared to Lung

For chemicals which may not cause dermatitis but which might be systemic poisons, then comparing the potential amount of chemicals absorbed via skin contact with the amount absorbed through the lung is instructive. For the case of skin exposure we will assume that the hands are exposed to a pure or "neat" solution of the chemical for eight hours. For the lung exposure we will use the allowable air exposure level and assume that the average worker breathes 10 m3 of air in an eight hour shift.

Let's apply these formulas to a chemical which has gotten a lot of attention lately, ethylene glycol:

Slide: Glycol Ethers

Let's consider another example, in this case a chemical which is recognized as a potent skin absorber and a neurotoxin, acrylamide.

Slide : Acrylamide

Obviously, by comparison to the allowable body dose, it seems evident that skin exposure is not to be ignored. But aren't we "stacking the deck" to represent the worst case for skin absorption? Afterall the absorption rates shown above are for hands immersed in a neat (pure) solution of the substance. In the real world, workers don't submerge hands in chemicals for 8 hours a day, however they certainly do "submerge" their bodies in air which may be over the PEL.

This is true, but I think a couple of things should be pointed out before we assume that the skin values are gross overestimates of the problem.

Slide: Factors which affect skin absorption

Occlusion: Skin protected by a glove becomes hydrated, this process is called occlusion an is known to enhance the absorbitivity by a factor of 10.

Temperature: Increased surface temperature of skin enhances absorption..

Pressure: The pressure exerted while gloved significantly enhances absorption.

Presence of other solvents: Many solvents enhance the rate of absorption. (e.g.s glycol ethers)

Amount of exposed skin: The amount and type of skin exposed will obviously influence the absorption rates. Many areas of the body have a thinner stratum corneum, which increases the absorption rate.

Condition of skin: Damaged skin no longer provides a barrier to the absorption process.


Finally a number of studies have confirmed the importance of skin absorption:

Slide: Examples of Skin Exposure

And there are further examples of potential problems in this area:

Slide: More Evidence

This study demonstrates that diisocyanates upon skin contact can induce hypersensitivity. The last example in a medical setting further indicates the wide-spread nature of the problem.

Thus it seems evident that not only do estimates of the potential for skin exposure support the need for more attention in this matter, studies of exposed workers for PCB's, diisocyanates, PNA's, solvents, in occupations ranging from steel mills to hospitals demonstrate that skin exposure is a problem! SO THE ANSWER OBVIOUSLY IS SIMPLY PPE!

Wrong, O learned one! Permeation rates through gloves and protective clothing can be so rapid, such that with occlusion, absorption can even be enhanced. What is really needed is **assessment of the effectiveness of PPE.** The need for this is very evident in the semiconductor industry.

Slide: Semiconductor industry

Obviously this is not a work environment in which air exposures work routine operations are significant. Yet despite low air exposures, excess spontaneous abortions have been observed. The focus has been on the glycol ethers used in the photoresist process. Re-use of gloves and the effects of other solvents greatly reduced the breakthrough times for most gloves used in this industry.

Thus it seems obvious that it is essential that the effectiveness, ( or the applicability) of PPE be verified. In this area, I am proud to say that OSHA has acted:

Slide: Revisions to the PPE Standard

The language of this standard strongly suggests that the employer must make some determinations regarding the <u>potential for skin exposure</u> and also some <u>determinations that the selected PPE is effective</u>.

Slide: What means should be used to assess the effectiveness of PPE?

IS THIS SOME "PIE IN THE SKY" IDEA?

Maybe not. In fact OSHA is drafting several "building block" standards which may have an impact on how skin exposure is assessed in the future:

Slide: Safety and Health and Exposure Assessment Standards

## SAFETY AND HEALTH PROGRAM STANDARD

This standard will **require** that employer develop their own safety and health program. The emphasis (or burden depending upon your perspective) will be on the employer to provide a safe and healthful worker. This is a shift away from the current emphasis on complying with OSHA standards.

## EXPOSURE ASSESSMENT STANDARD

The intent of this standard is to specify for the employer methods to assess worker exposures. Hopefully, the emphasis will be exposure assessment methods which truly characterize worker exposure, rather than simply focusing on air exposures.

Items being considered in this standard:

Skin exposure

Biological Monitoring

Slide: What can we expect?

WHAT CAN WE EXPECT? or at least: WHAT CAN WE HOPE FOR?

A future in which OSHA shifts being a policeman (albeit one you was rarely present because of the limited numbers of compliance officers) ...

To a future in which responsibility lies with the employer. OSHA's role may very well be one of an auditor, rather than an enforcer in this new OSHA.

SO WHAT DO WE DO ABOUT IT?

The we includes concerned occupational health specialist and industrial hygienist from both the private and the public sector.

Provide testimony/input on several key pieces of proposed OSHA legislation.

# MISHAP RISK CONTROL FOR
# ADVANCED AEROSPACE/COMPOSITE MATERIALS

1Lt John M. Olson, US Air Force
USAF Advanced Composites Program Office
McClellan Air Force Base, CA

## ABSTRACT

Although advanced aerospace materials and advanced composites provide outstanding performance, they also present several unique post-mishap environmental, safety, and health concerns. The purpose of this paper is to provide information on some of the unique hazards and concerns associated with these materials when damaged by fire, explosion, or high-energy impact. Additionally, recommended procedures and precautions are addressed as they pertain to all phases of a composite aircraft mishap response, including fire-fighting, investigation, recovery, clean-up, and material disposal. Due to the infinite variability of mishap scenarios, the guidelines are general in nature and not application-specific. The goal of this project is to provide factual and realistic information which can be used to develop consistent and effective procedures and policies to minimize the potential environmental, safety, and health impacts of a composite aircraft mishap response effort.

## DEFINITIONS

Composite: A physical combination of two or more materials.
Examples: Fiberglass (Glass/Epoxy, Glass/Polyester)
Advanced Composite: A Composite Material made with high strength/high stiffness reinforcement (i.e. fibers) in a matrix (i.e. resin).
Examples: Graphite/Epoxy, Kevlar/Epoxy, Quartz/Cyanate Ester, Boron/Epoxy
Advanced Aerospace Material: A highly specialized material fulfilling unique aerospace construction, environment or performance requirements.
Examples: Radar Absorbent Material (RAM), Beryllium, Depleted Uranium

Advanced Composites are distinguished from traditional Composites by their increased relative performance, cost, complexity, and mishap hazard potential. It is absolutely essential that a clear distinction be made between Advanced Composites and Advanced Aerospace Materials.

## SCOPE

This report will focus on the hazards and risks associated with exposure to a significant release of damaged *Advanced* Composite/Aerospace Material. Specific emphasis is placed upon carbon/graphite reinforcement and polymer matrix (thermoplastic and thermoset) advanced composites. Other specific advanced aerospace material issues, including beryllium, Radar Absorbent Material (RAM), and depleted uranium, are lightly addressed.

## INTRODUCTION

Advanced composite materials are pressing the envelope of technology by providing design flexibility and superior performance advantages for both military and civilian aerospace vehicles. Distinguished by high-strength, high-stiffness, low weight, and corrosion resistance, these materials are responsible for significant gains in speed, range, payload, agility, efficiency, and low observability. Not only are advanced composites being used on almost every major new aerospace vehicle, including the B-2 Stealth bomber, F-22 Advanced Tactical Fighter, Delta Clipper launch vehicle, and Boeing 777, but they are also used as repairs and modifications on existing systems as well.

Applications have steadily progressed from early minor control surface applications to recent use in secondary and primary structure. However, the inherent diversity of advanced composites/aerospace materials, underscored by the varied chemical mixtures, constituent materials, processing methods, application environments, and mishap scenarios, has limited our understanding of these materials in a mishap event. In the past, a sharply focused emphasis upon performance has been the driver behind technological advancements in materials and applications that have outpaced our ability to fully understand and support them. Society is no longer willing to accept the benefits of technology without careful observation of the human and environmental effects, both on a short- and long-term scale. Tremendous liability, skyrocketing health and disability costs, increased environmental responsibility, and loss potential concerns in this area make risk control absolutely essential.

In their cured or final form, advanced materials/composites are *generally* considered safe, inert, and biologically benign; however, when damaged by fire, explosion, and/or high-energy impact in a mishap, these materials can present environmental, safety, and health hazards that need to be dealt with appropriately. The material hazards are dependent upon the type, amount,

damage extent, and mishap scenario. In all cases, concentrations drive the level of risk.

## BACKGROUND

The relative "infancy" of advanced composite materials combined with the lack of detailed mishap information have contributed to the current level of understanding and often times, misunderstanding, of composite mishaps. Early aircraft fire and crash studies on advanced composites such as the Air Force CORKER program (1975) and HAVE NAME program (JTCG/HN 1 May 81) have incorrectly led to several *fallacies* concerning mishap hazards, including:

- •Release of material will cause widespread electrical blackout.
- •Dispersed composite material is biologically malignant and should be treated like asbestos.
- •Large concentrations of particulates can be carried very long distances downwind in the smoke plume.
- •Fractured composites are all deadly razor sharp
- •Extreme protection is always required

In fact, these claims have proven to be over-reactive or inaccurate by new research and experience. Although on-going research has often been inconclusive, evidence shows that burned or exploded advanced composites DO cause personnel health and safety problems IF they are not properly protected. Although generally conflicting in nature or narrowly focused, all of the health studies recommend caution and state that unknown health hazards do exist. It should be emphasized that advanced composites are comprised of a complex mixture of materials whose composition, concentration, and toxicity may be unknown, especially in a synergistic mishap environment. For this reason, a high degree of precaution with conservative protection is recommended until the hazard exposures can be characterized for an "optimal" response.

## DISCUSSION

A hazard is defined as "a condition or changing set of circumstances that presents a potential for injury, illness, or property damage." Likewise, it can be described as "the potential or inherent characteristics of an activity, condition, or circumstance which can produce adverse or harmful consequences." In this light, the hazards associated with mishap damaged advanced composites/aerospace materials need to be addressed with a risk control mindset. Essentially, risk control is the process of minimizing

accidental and other extraordinary losses by anticipating and preventing unplanned events. It emphasizes the complexities of exposures and encompasses broad areas of risk, which are indicative of a mishap scene. Additionally, risk control is based on the control of exposures through knowledge and preparation. It is both a pre- and post-loss effort. With this fundamental basis intact, the specific hazards can be addressed and minimized.

Damage to advanced composites materials caused by fire, explosion, and/or high-energy impact in a mishap presents unique environmental, safety, and health hazards. In typical aircraft fires of 1000 to 2000°C, organic matrix materials, or polymers, burn off around 400°C, creating toxic combustion or pyrolysis products and liberating the reinforcement, or fibers. Depending on the fiber, the reinforcement dynamics can vary. Glass or aramid fibers tend to melt under extreme heat, whereas carbon or graphite fibers are oxidized by the heat, thereby altering their size, shape, porosity, and other characteristics. The intense thermal and mechanical forces in a mishap generally cause "explosive" fracture or debonding and degradation of advanced composite structures. While absorbing this energy, the reinforcement, usually stiff and strong, may be broken into particulate fibers, turned to dust, or protruding from the vehicle structure. Because of their stiffness, carbon fibers can readily penetrate the skin. Boron fibers can penetrate bone. Furthermore, the absorbed and adsorbed pyrolysis and combustion products (assumed toxic) on activated, oxidized fibers can be an important injection or inhalation hazard. These types of wounds readily inject the toxins into the body. This phenomenon could be especially critical in mishap scenarios where bloodborne pathogens may be present on damaged debris. In all cases, the type, amount, and extent of damage to advanced composites drive the level of health hazard because concentrations are key.

Coupled with heat, shock, and fragmentation, several different types of damage occur. The effects can range from a simple reduction in strength on one end of the spectrum, to a loss of Low Observable (LO) performance, delamination, debonding, charring, melting, burning, and vaporization at the other extreme. Although advnanced composite/aerospace materials represent only one of the many hazards associated with an aerospace mishap (fuel, weapons, metals), they do merit increased awareness because of their hazard potential and persistence. Exposures to the potentially harmful vapors, gases, composite particulates, and airborne fibers generated in a composite mishap need to be controlled because of the symbiotic effect of the dispersion forces and complex chemical mixtures.

110

Exposure routes for the safety and health hazards of damaged advanced composites/aerospace materials include absorption (contact), inhalation, injection, and ingestion. The toxicology of respirable particulates (3-5 microns) and the disease-producing potential associated with them is a function of: 1) the dose or amount of particulates in the lung; 2) the physical dimensions of deposited particulates; and 3) the particulate durability (lifetime) in the lung. Fire-exposed carbon fibers tend to break into shorter lengths and split into smaller diameters, thereby affecting the aspect ratio. In turn, this increases the probability for respiration and ease of transport. Dry and windy conditions at a mishap site increase dispersion of liberated particulates. Whether inhaled or injected, advanced composites (because of their stiffness) are not easily removed or expelled efficiently. This is especially true for brittle, oxidized fibers. Potential health and environmental effects from damaged advanced composites include dermal and respiratory problems, toxic products, contamination, and, in the case of advanced aerospace materials, radiation. Exposure of unprotected personnel may lead to acute or chronic respiratory and dermal problems. Mechanical injection or cuts are the most common skin hazard, although sensitization (local and systemic) can occur. Off-gassing, toxic products in the smoke plume, smoldering debris, and airborne fire-damaged particulates are the primary respiratory hazards. Examples of combustion products include: Hydrogen cyanide, sulfur and silicon dioxide, formaldehyde, hydrogen fluoride, ammonia, hydrochloric acid, hydrogen sulfide, isocyanates, halogenated compounds and aromatics.

Mishaps involving advanced composites that are electrically conductive (i.e. graphite or carbon fiber) may present electrical shorting or arcing problems if very high concentrations exist (usually at the immediate mishap site only). This may result in electrical equipment degradation or failure, including communication interference, although this is rare. Tests have shown that widespread electrical failure due to environmental release and plume dissipation is highly unlikely, except for the immediate mishap site. Despite the low probability of failure, the risk is always present. Carbon fibers are also influenced by the presence of electrostatic fields, causing them to settle in high voltage areas and reduce the local dielectric properties of free air. This may cause equipment malfunction or failure.

Given the existing and projected increases in advanced composites usage for aerospace applications, realistic policies and procedures that focus on minimizing the safety and health hazards of advanced materials are needed. As the knowledge base grows and the mishaps are characterized, the procedures can be situationally optimized in terms of cost and performance while still maintaining a safe public environment.

Based upon the basic hazards already know to exist, and the fact that there are still unknown risks, personnel safety and health precautions are necessary. Administrative controls, including adequate personal protective equipment (PPE) and worker safety practices need to be immediately implemented because the field environment is not conducive to engineering controls. Risk control biased towards conservative measures is essential.

The major issues currently affecting mishap response for damaged advanced composites are:
1. Fiber dispersion and re-dispersion
    - Including an understanding of the mishap dynamics, effective
    response procedures and holddown material (fixant) suitability
2. Synergistic material and combustion effects
    - The combined effects of varied materials and their damage extent
3. Concentrations and compatibility
    - Exposure limits and necessary protection measures, also includes
    equipment, procedural, and suppression agent compatibility issues
4. Adsorbed and absorbed pyrolysis products
    - The impact and extent of the toxin hazard
5. Site and equipment contamination
    - Including the type and extent of contamination
6. Clean-up and disposal complications (Haz-Mat)
    - Evaluate decontamination methods and determine proper disposal
    methods and classifications of the waste debris
7. Peripheral Issues (Bloodborne Pathogens)
    - The potential for multiple injections of Hepatitis B and HIV caused
    by infected remains on damaged advanced composites

These issues are compounded by non-existent or inconsistent material, medical, fire/combustion, environmental, disposal, and operational information. The solution lies in continued research, testing, and the application of experience to provide a knowledge base from which operational guidance may be based.

Because aircraft crashes occur under a diverse assortment of weather and terrain conditions, with widely varying degrees of airframe destruction, a universally applicable set of risk control precautions is not practical. The complex and often times unknown hazards, diverse locations, and infinite variables of a mishap involving advanced composites require conservative protective measures. This includes all phases of a mishap response ranging from first response and firefighting, to investigation, clean-up, recovery, and disposal. A complete "Cradle-to-Grave" mentality must be adopted.

Firefighters (first responders) are considered the primary response group and are subjected to the greatest material hazards; however, they are the best protected in all but the most extreme cases with Self Contained Breathing Apparatus (SCBA) and their bunker or proximity suits. Protection should be worn until the composite fires have been completely extinguished, cooled to a temperature of 300°F (149°C), and no intense smoldering exists. The potential exposure to composite mishap hazards may be more severe for secondary exposure groups, including all of the subsequent response operations, than for initial fire fighting activities because of the duration of exposure and reduced levels of protection. In any case. the hazards exposures are minimal if Personal Protective Equipment (PPE) and proper procedures are used, including:

<u>Advanced Composite Mishap Response PPE Guidelines</u>
    A.  Burning or Smoldering Composites
          1.  Self Contained Breathing Apparatus (SCBA)
          2.  Full protective clothing (NFPA 1971/76)
          3.  Do NOT use rubber gloves
    B.  Broken or Splintered Composites (Post-Fire or Explosion)
          1.  Full-face respirator w/dual cartridge filters: High Efficiency Particulate Air(HEPA) and organic dust/mist
          2.  Coated, hooded Tyvek disposable suit with booties
          3.  Leather work gloves (outer)
          4.  Nitrile rubber gloves (inner) [No surgical gloves]
          5.  Hard-soled work boots (Steel toe/shank are best)
    C.  Peripheral Area Composite Exposure
          1.  Long-sleeve work clothing
          2.  HEPA filtered respirator
          3.  Adequate eye protection (Goggles, or safety glasses)
          4.  Leather work gloves (outer)
          5.  Nitrile rubber gloves (inner)
          6.  Hard-soled work boots (Steel toe/shank are best)

All affected personnel need to know both the hazards and the proper response for mishap risk control. This makes coordination and communication among all groups absolutely essential. Likewise, knowledge and training, accompanied by common sense and good judgment, is key. In order to maximize response effectiveness and minimize hazard exposures, risk control must be exercised using the most current and factual information obtained from all sources, including the military, government, private, industry, academic, and international sectors. This must then be universally applied in operational guidance and constantly updated to reflect revised knowledge.

113

# MISHAP RISK CONTROL GUIDELINES

The following guidelines are recommended:

1. First Responder(s) [Firefighters] shall conduct an initial survey for:
    a. Signs of fire damaged composites
    b. Presence of loose/airborne fibers and particulate
    c. Prevailing weather conditions/wind direction
    d. Degree of site exposed to fire/impact/explosions
    e. Local/proximal equipment/asset damage and hazards
    f. Exposed personnel

2. Establish control at site.

3. Evacuate areas in the immediate vicinity of the mishap site affected by direct and dense fallout from the fire/explosion generated smoke plume, along with easily mobile and critical equipment. Alter/move aircraft and flight operations exposed to the immediate fallout area. Restrict all unprotected personnel from assembling downwind of the site.

4. Extinguish fire and cool composites to below 300° F (149° C). ONLY fire fighters equipped with self-contained breathing apparatus (SCBA) are authorized in the immediate vicinity of a burning/smoldering mishap site until the fire chief declares the area fire safe. If possible, care should be taken to avoid high-pressure water break-up and dispersal of composite materials.

5. No ground or flight operations are to be permitted within 500 feet above ground level (AGL) of the site and 1,000 feet horizontally.

6. Cordon off the mishap site and establish a single entry/exit point. Only sufficiently protected individuals are authorized in the immediate mishap site and peripheral area (contamination reduction zone). The peripheral area is designated in a coordinated effort by the fire chief and bio-environmental engineer and /or the on-scene commander. As a guide, the peripheral area should be defined as more than 25 feet away from damaged composite parts, although it may vary depending upon environmental conditions (rain, dry, high winds, remote site, etc.).

7. If personnel other than those at the accident site have been directly and significantly exposed to material and smoke hazards, the medical staff will be consulted for evaluation and tracking. Advise the otherwise unthreatened populace in affected or fallout areas of precautions.

8. Access to the crash site to conduct a more thorough survey will be coordinated with the Incident Commander (IC).

a. Identify specific aircraft hazards by inspection and consulting with crew chiefs or weapons system manager, reference documents, contractor, or aircraft specialists. Indicate composites and other hazardous materials to response personnel.

b. Minimize airborne particulates/fibers by avoiding excessive disturbance of the dust by walking, working, or moving materials at the crash site to minimize airborne particulate fibers and dust.

9. Entry/exit from the Entry Control Point (ECP) will be monitored. The following guidelines apply:

a When exiting the crash site, personnel should use High Efficiency Particulate Air (HEPA) filtered vacuums, if available, to remove advanced composite contaminates from their outer clothing, work gloves boots, headgear, and equipment. If unavailable, efforts must be made to wipe or brush off as much contamination as possible.

b. Clean sites (i.e., tent or trailer) for donning/removal of PPE should be set up as practical.

c. No eating, drinking, or smoking is permitted within the contamination reduction or exclusion zone of the crash site, or as other wise determined by the on-scene commander. Personnel must be advised to wash hands, forearms, and face prior to eating, drinking or smoking.

d. Wrap and seal contaminated protective clothing and dispose of properly.

e. Personnel should shower (in cool water) prior to going off-duty to preclude injury from loose fibers. Portable showers may need to be provided for this.

f. When practical, remove contaminated outer garments of victims/response personnel at the scene to protect the medical staff. Advise the local medical staff of any ill effects believed to be related to exposure to the advanced composite materials. All contaminated footwear should be

cleaned to limit the spread of debris in the area and inside support vehicle. Symptoms of effects include, but are not limited to:

(1) Respiratory tract irritation and reduced respiratory capacity
(2) Eye irritation
(3) Skin irritation, sensitization, rashes or infections

Material safety data sheet (MSDS) information should be made available to qualified personnel. Security restrictions may require additional control measures during emergencies.

## CONTAINMENT

10. Secure burned/mobile composite fragments and loose ash/particulate residue with:
a. Plastic
b. Firefighting agent
c. Fixant material
d. Tent

Carefully wrap the coated parts and/or material with plastic sheet/film or place in a plastic bag that is minimum of 0.006 inches (6 mils) thick. Generic garbage bags are generally inadequate unless several are used as plies.

NOTE: Fire fighting equipment should be available during fixant/stripper application, aircraft break-up and recovery.

CAUTION: Fire must be completely out and the composites cooled to below 300° F (149° C).

11. Consult specific aircraft authority and the investigators before applying fixant. Safety concerns may override any delayed application. Two types of fixants are used: one for burned composites and debris, and the other for land surfaces. Fixant is usually not needed for open terrain and improved surfaces (concrete or asphalt) unless high concentrations exist.

a. Obtain a fixant or "hold-down" solution, such as Polyacrylic acid (PAA) or acrylic floor wax and water. Light oil is not recommended because it may become an aerosol and collect on equipment, hamper material investigations, and present a health hazard. Generic acrylic floor wax, available at a wide variety of stores, should be mixed in a 10:1 water to wax ratio, although this may vary.

b. Apply (preferably spray) a heavy coating of the fixant solution to all burned composite materials and to areas containing scattered/settled composite debris. Completely coat the material until wet to ensure the particulate fiber/dust is immobilized. Allow the coating to dry.

NOTE: Strippability of the fixant coating is required where coatings are applied to debris that must later undergo microscopic analysis by incident investigators. Care must be exercised in the use of the stripping solutions since they can react with some materials and the process of stripping may damage the parts. PAA may be removed by a dilute solution of household ammonia (about 1% by volume of ammonium hydroxide in water) or trisodium phosphate (approximately one 8 ounce cup trisodium phosphate per 2 gallons of water).

12. If deemed necessary, agricultural soil tackifiers may be used to hold materials on sand or soil. Most solutions can be sprayed onto the ground at a rate of 0.5 gal/sq. yd.

13. Improved hard surfaces (i.e. concrete, asphalt) should be vacuumed (with an electrically protected vacuum). The effluent should be collected via plastic or burlap coated trenches or drainage ditches. Sweeping operations should be avoided as they disseminates the particulate debris.

14. Immediately flush/clean fixate-application equipment with a dilute solvent to avoid clogging.

15. Pad all sharp projections from damaged composite parts to prevent accidental injuries.

NOTE: The entire impact or accident site must be diked to prevent run off of AFFF fire fighting agent (to avoid additional clean-up and fines).

16. Fire fighting vehicles and equipment must be decontaminated at the accident site by washing with water or use of vacuums.

CLEAN-UP AND DISPOSAL CONCERNS
17. Conduct material disposal according to local, state, federal, and international guidelines. The nearest DoD, government, or private environmental management office should be contacted for relevant disposal procedures for the advanced composite parts/materials which do not require accident investigation evaluation, repair, or are not needed. Ensure the parts are released before disposal is authorized.

117

18. Place hazardous waste material in containers and disposed of appropriately as hazardous waste. If possible, a HEPA vacuum should be used to clean-up the local area. All crash debris, vacuum bags, coverall, gloves, and any other contaminated materials should be properly disposed and labeled appropriately with the following: "Composite Waste. Do Not Incinerate. Do Not Sell For Scrap. Composite Waste".

19. For open terrain mishap areas, the appropriate soil and surface restoration will be completed.

20. If aircraft were subjected to the smoke and debris of the immediately affected area, the following should be undertaken:
    a. Vacuum the air intakes with an electrically protected vacuum cleaner.
    b. For internally ingested smoke, visually and electronically inspect all compartments for debris and vacuum thoroughly.
    c. Prior to flying, perform electrical checks and engine run-up.

21. For significantly affected structures and equipment:

    a. Thoroughly clean all antenna insulators, exposed transfer bushings, circuit breakers, etc. Inspect air intakes and outlets for signs of smoke or debris and decontaminate, if necessary.

22. Continue to monitor affected personnel, equipment, and mishap site.

## CONCLUSIONS

Advanced composites/aerospace materials are the driving force behind the materials enhancements in speed, range, payload, and performance of the worlds most technologically advanced aerospace vehicles. Yet, when damaged by fire, explosion, or high-energy impact, these materials pose unique environmental, safety, and health hazards in all phases of a mishap response. As the usage of these materials steadily increases and the application mediums proliferate, it is absolutely essential to know, understand, and respond appropriately to the hazards they present. The variability in weather, terrain, location, type, amount, and damage extent of mishaps make universal risk control protection and procedures essential. The bottom line is to protect people, property, and the environment with a realistic and optimal mishap response. Knowledge and training are the fundamental cornerstones of employing realistic, although conservative, personal protection and procedures. Risk Control is THE solution.

# REFERENCES

"A Composite Picture." *Safety and Health.* NOV 1991. p. 38-41.

*A Composite System Approach to Aircraft Cabin Fire Safety.* NASA Technical Memorandum. APR 1987.

*Advanced Composite Repair Guide.* NOR 82-60. Prepared by Northrup Corporation, Aircraft Division, for USAF Wright Aeronautical Laboratories, Wright-Patterson AFB, OH: MAR 1982.

"Aircraft Fire fighting Procedures for Composite Materials." US Navy/Marine Corp Training Film. #112769. Naval Education and Training Support Center, Atlantic. Norfolk VA: 1993.

Bickers, Charles. "Danger: Toxic Aircraft." *Jane's Defence Weekly.* 19 OCT 1991.

Brauer, Roger L. *Safety and Health for Engineers.* Van Nostrand-Rheinhold, New York, NY:1990.

*Composite Aircraft Mishap Safety and Health Guidelines.* Project Engineer: Capt. Keller. USAF Advanced Composites Program Office, McClellan AFB, CA; 18 JUN 1992.

*Composite Aircraft Mishap Safety and Health Guidelines.* ASCC ADV PUB 25/XX. Air Standardization Coordinating Committee, Washington, DC: 16 SEP 1992.

*Composite Material Protective Equipment and Waste Disposal.* Memo from 650 MED GP/SGB to 411 TS/CC, Edwards AFB, CA 14 OCT 1992.

*Composite Materials Applications.* Air Force Wright Laboratory Manufacturing Technology Directorate, WL/MTA: NOV 1992.

Conference on Advanced Composites, 5-7 MAR 91. Proceedings. San Diego, CA: 1992.

Conference on Occupational Health Aspects of Advanced Composite Technology in the Aerospace Industry, 5-9 FEB 89. AAMRL-TR-89-008. Vol I. Executive Summary. Wright-Patterson AFB, OH: MAR 1989.

Conference on Occupational Health Aspects of Advanced Composite Technology in the Aerospace Industry, 5-9 FEB 89. AAMRL-TR-89-008. Vol II. Proceedings. Wright-Patterson AFB, OH: MAR 1989.

DARCOM/NMC/AFLC/AFSC Commanders Joint Technical Coordinating Group on HAVE NAME (JTCG/HN). *HAVE NAME Guide for Protection of Electrical Equipment from Carbon Fibers .* MAY 1978.

Faeder, Edward J. and Paul E. Gurba. "Health Effects in the Aerospace Workplace - Some Concerns." SME Conference Proceedings: Composites in Manufacturing 9. Dearborn, MI: 15-18 JAN 1990.

*Fire Performance and Suppressibility of Composite Materials.* Hughes SBIR Phase II Report HAI 92-107i DRAFT. 15 DEC 1992.

*Fire Safety Aspects of Polymeric Materials. Volume 6. Aircraft: Civil and Military.* Report by the National Materials Advisory Board of the National Academy of Sciences. 1977.

Fisher, Karen J. "Is Fire a Barrier to Shipboard Composites?" *Advanced Composites.* Vol. 8, No. 3: MAY/JUNE 1993.

*General Advanced Composite Repair Processes Manual.* USAF TO 1-1-690. McClellan AFB, CA: 1 AUG 1990.

Hetcko, John. "Disposal of Advanced Composite Materials." Defense Division, Brunswick Corporation. Lincoln, Nebraska.

Hubbell, M. Patricia. "Hazard Communication and Composites." McDonnell Douglas Space Systems Company. A3-315-12-1. Huntington Beach, CA 92647

*Mishap Response for Advanced Composites.* US Air Force Film. 46th Test Wing Audio-Visual Services, Eglin AFB, FL. Sep 1994.

Naval Safety Center. *Accident Investigation and Cleanup of Aircraft Containing Carbon/Graphite Composite Material Safety Advisory.* Unclassified Telex N03750. From NAS Norfolk, VA: 20 Aug 1993.

Olson, John M. *Aerospace Advanced Composites Interim Technical Mishap Guide.* USAF HQ AFCESA/DF. Mar 22, 1994.

Olson, John M. "Composite Aircraft Mishaps: High Tech Hazards? Part I. *Flying Safety Magazine.* Vol 49, No. 11. Nov 1993.

Olson, John M. "Composite Aircraft Mishaps: High Tech Hazards? Part II. *Flying Safety Magazine.* Vol 49, No. 12. Dec 1993.

Olson, John M. *Mishap Risk Control Guidelines for Advanced Aerospace Materials: Environmental, Safety, and Health Concerns fro Advanced Composites.* Oct 28, 1993. USAF Advanced Composites Program Office, McClellan AFB, CA.

Olson, John M. *Safety, Health, and Environmental Hazards Associated with Composites: A Complete Analysis.* Nov 15, 1992.

"Position Paper on the Corker Program." Oklahoma City Air Logistics Center, 16 FEB 93.

*Revised HAVE NAME Protection Manual.* MP 81-266 MITRE MTR 4654. A.S. Marqulies and D.M. Zasada, Eds. June 1981.

Risk Analysis Program Office at Langley Research Center. *Risk to the Public From Carbon Fibers Released in Civil Aircraft Accidents.* NASA SP-448. Washington DC: 1980.

*Risk to the Public From Carbon Fibers Released in Civil Aircraft Accidents.* NASA SP-448, Washington, DC: 1980.

*Safe Handling of Advanced Composite Materials.* 2nd Ed.SACMA, Arlington, VA: July 1991.

*Summary of Medical Evaluation of Boeing Employees Working With Composite Materials Who Have Filed Workers Compensation Claims for Illness.* Seattle Medical Care, Association of Independent Practitioners. Seattle, WA:

# Sampling and Analytical Methods for Aromatic Amines (MDA Replacements)

James C. Peterson

Pacific Toxicology Laboratories

1545 Pontius Ave.

Los Angeles, CA 90025

# Tools for Monitoring Exposure

### Air monitoring
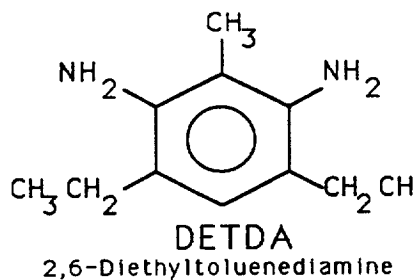
- Exposure by inhalation route

### Surface monitoring

- Dermal exposure

### Biological monitoring
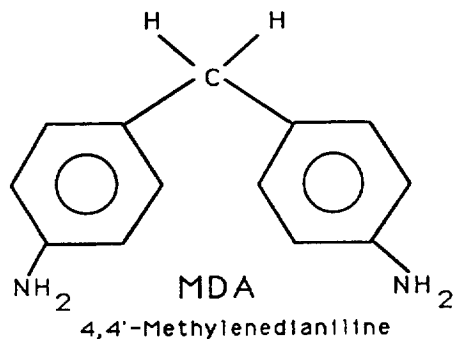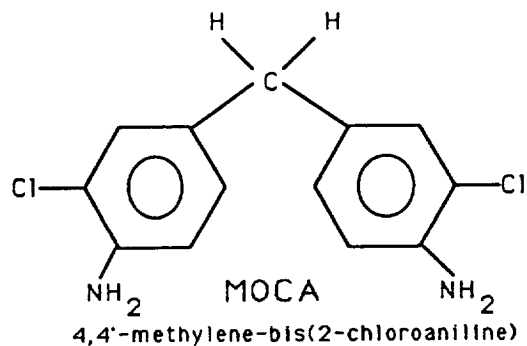
- Exposure by all routes

-Inhalation

-Dermal

-Ingestion

# Major Urine Metabolites
# of Aromatic Amines

| | |
|---|---|
| **Benzidine** | **Hydroxy-, mono- and diacetyl-benzidine (+ N- glucuronides)** |
| **MOCA** | **(+ N-glucuronide)** |
| **MDA** | **mono-acetyl MDA (+ N-glucuronide)** |
| **TDA** | **mono- and diacetyl TDA** |

# Comparison of Aromatic Amine
# Structures



Benzidine

MOCA
4,4'-methylene-bis(2-chloroaniline)

MDA
4,4'-Methylenedianiline

DETDA
2,6-Diethyltoluenediamine
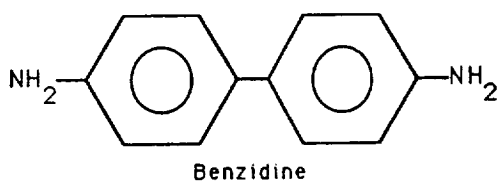
# Air Monitoring

- Indicates level of potential exposure by inhalation

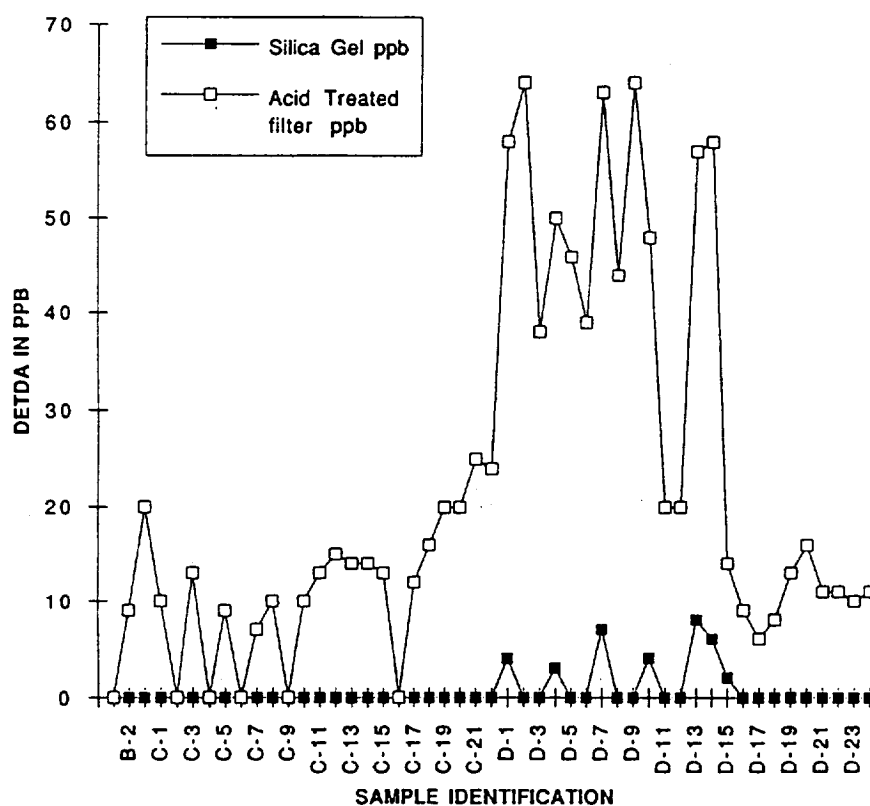- Does not monitor exposure by other routes

- Currently no proposed airborne limit (TLV or PEL) for DETDA

- Currently no NIOSH analytical method for DETDA (Ethyl Corp. has method)

## Comparison of Silica Gel Sorbent Tubes with Acid-Treated Fiber Filters DETDA in Air (Personal Samples)

# Surface Monitoring
# Wipe Testing

- Use to identify potential sources of dermal exposure

- Tests the effectiveness of decontamination procedures

- Can be used to test the effectiveness of personal protective gear

- Spot tests are non-specific. All primary amines will respond to some degree

- Lab analysis necessary for identification

- Does not necessarily correlate with actual exposure

# Biological Monitoring

- All routes of exposure are monitored

- Level of physical activity is reflected in the measurement

- Tests the effectiveness of personal protective equipment

- Assumptions are made to set exposure limits

124

# Biological Monitoring
# Single ring aromatic primary amines
# DETDA, TDA, PPD

Collection

End of shift urine

Handling/storage

No preservatives

Freeze

Shipment

Overnight delivery

# Analysis of Aromatic Amines in Urine

- Base hydrolysis- converts metabolites back to parent compound

- Solvent extraction- high solvent to urine ratio

- Derivatize amine with heptafluorobutyryl chloride

- Analyze by GC/MS in the negative chemical ionization mode

# Fire Hazard Considerations for Composites in Vehicle Design

Rex B. Gordon, P.E.

## ABSTRACT

Military ground vehicles fires are a significant cause of system loss, equipment damage, and crew injury in both combat and non-combat situations. During combat, the abi:.ty to successfully fight an internal fire, without losing fighting and mobility capabilities, is often the key to crew survival and mission success. In addition to enemy hits in combat, vehicle fires are initiated by electrical system failures, fuel line leaks, munitions mishaps and improper personnel actions. If not controlled, such fires can spread to other areas of the vehicle, causing extensive damage and the potential for personnel injury and death. The inherent fire safety characteristics (i.e. ignitability, flame spread and decomposition products) of polymerics located within internal compartments of these vehicles play a major roll in determining rather a newly started fire becomes a fizzle or a catastrophe.

This paper addresses a systems approach to assuring optimum vehicle fire safety during the design phase of complex vehicle systems utilizing extensive uses of composites, plastics and related materials. It provides practical means for defining the potential fire hazard risks during a conceptual design phase, and criteria for the selection of composite materials based on its fire safety characteristics.

## THE FIRE SAFETY DILEMMA

Ground combat vehicle designers find many potential advantages in selecting composites and other polymeric materials in place of traditional metals. These include enhanced crew protection from external ballistic hits in addition to reduced weight and manufacturing costs advantages. However, such usage may inadvertently create additional fire safety related hazard risks which need to be properly managed during the design process.

Today, most U.S..Army and Marine ground combat vehicles are equipped with electronic infra-red (IR) hydrocarbon fuel fire detection and fuel-mist fireball explosion suppression systems. During live-fire testing, these automatic fire suppression systems (AFSS) have been able to detect a growing fuel mist fireball resulting from a shaped charge penetration of a diesel fuel tank, and release pressurized Halon 1301 agent, in a manner that often suppresses the fireball in less than a quarter of a second - quick enough to prevent serious burns on exposed skin of passengers and crew of the vehicle. Although essential in crew protection from the penetrated fuel cell / fuel mist fireball scenario, these AFSS units are not fully optimized for other, more frequent fire scenarios such as accidental fuel line leakage in engine and crew heater locations. In addition, when used to extinguish a fire, high concentrations of acid gases are formed from the decomposition of the Halon agent. These vapors are very

irritating and toxic, and must be evacuated quickly, to provide survivable breathing air for crew members and troops unable to quickly leave the vehicle.

Army Safety Center reports indicate that during the 10 year period 1974 -1984, some 213 non-combat tracked vehicle fires occurred, resulting in 2 fatal and 30 serious injuries. The material losses were estimated at 12.7 million (1984 dollars)  Army safety investigators have indicated that these reported accidents represented perhaps only a fourth or less of the actual (i.e. reported and unreported) fire incidents occurring in the field. Sampling of the accident data base subsequent to the 1984 report indicates that the frequency and cost impact of these non-combat fires are increasing as more sophisticated and expensive vehicles are entering the inventory.  A non-combat vehicle fire incident occurring in South West Asia, involving multiple parked vehicles, accounted for equipment damage which was estimated to be  some 4 to 5 times that reported during the entire ten year period of 1974-1984.  From the data reviewed, non-combat fire continue to constitute a significant safety concern, in fielded tracked vehicles.

In the opinion of this author, the proper utilization of the systems engineering approach in the area of an integrated passive and active fire safety is the most cost effective approach for improving fire safety in new or modified ground combat vehicles.  It is suggested that  this goal should receive a higher priority for development funding in this time of ever reduced combat vehicle resources.  Vehicles which are able to avoid severe damage due to onboard fires, for their entire military life, are available for essential unit training to engage in critical combat when called upon. It is generally agreed that crews that have confidence in the safety features of their vehicles typically perform better in hazardous situations. Trained troop and crews are valuable combat assets which must be protected from accidental injury where ever feasible.

In view of these factors, it would be expected that combat vehicle developers would have an increased interest to improve fire safety through inherent design (passive) and in the research and development of improved AFSS that do not relay on the use of environmentally harmful Halon, a chemical which has been ordered to be phased out of use by DoD policy.  Unfortunately, Army activities having primary technical expertise in this area have been limited in effectiveness due to shortage of funding earmarked for this area.  The limited research conducted in the passive fire safety area have not been initiated under a long range systematic plan, but primarily to address a limited specific one time issue for a specific project.. Consequently, there is only very limited data available for formulating detailed design oriented fire safety criteria which can be provided to the designer, even if such action were  to be given priority by the system developer.

Traditionally, ground combat vehicle designs have emphasized mobility, offensive firepower, hit avoidance and armor protection, rather than behind armor / fire safety characteristics, during conceptual design phases.  This weighting in system design priorities is consistent with the typical overall mission objectives as defined by the using activity when a new or improved weapon system is being developed.  Although safety and crew survivability is often given a high weighting in a list of desirable objectives that the design is to provide, there are usually limited "hard" requirements that accompany this general statement of desirability. Thus, in practice, design

development teams often find they must compromise on the "softer" safety related design requirements (i.e. minimize hazards to crew) in order to satisfy the more readily quantifiable hard requirements (i.e. speed, range, time on target, etc.)

What then are ways to resolve this dilemma? The author suggests that a more focused attention to the systems engineering aspects in this area is the best solution. Certain new vehicle development activities have incorporated such efforts as an integrated aspect of those analyses and technical trade-offs typically occurring as part of the design process. This approach involve system oriented fire risk assessments for defining effective design approaches, material selection criteria and effective fire safety requirements for integrated passive and active of fire safety for new and modified vehicles In its more effective implementation, this approach includes: (1) the conceptual layout of the various vehicle compartments so that ammunition, liquid fuel tanks and lines are separated from crew areas, (2) selection of the optimum fire detection / suppression system for each compartment, based on the significant fire scenarios applicable for al l life cycle phases, and (3) the selection of materials to be incorporated into the vehicle design with fire safety considerations a paramount consideration.

The remainder of this paper will be primarily oriented toward this last noted systems engineering fire safety approach, i.e. the proper selection of fire safe, non-metallic materials in vehicle design activities.


## COMPOSITES, PLASTICS AND VEHICLE FIRE SAFETY

Traditional fuel sources for vehicle fires include heated fuel and hydraulic fluids, electrical motors and wiring, on-board munitions, personal gear and other stored combustibles. As their application increases, polymers will become a significant addition to this listing of potential fire related fuel sources. Plastic components and composite material systems, comprised of high strength fibers in organic resin matrices are finding increasing acceptance as viable solutions to demands for improved battlefield performance. Vehicle development efforts are now focusing on hulls and turrets made primarily of composites. Such vehicles can provide significant weight savings, as well as improved ballistic protection, reduced radar signature, and other desirable survivability characteristics.

Given sufficient oxygen and heat input, most organic polymers will burn more readily than metal Since full avoidance of fire risk concerns is not feasible, intelligent trade-offs between safety, utility, and costs are necessary during the material selection process of the design phase of a project.. It is primarily when polymers are applied in an enclosed environment, where the increased fuel loading is provided in a small inhabited spaces, does the fire safety issue become acute. In addition to ground combat vehicles, such acute fire safety concerns exist in certain buildings, submarines, manned space craft, ships, rapid transit vehicles, and aircraft. Lessons learned from bad experiences and successful design approaches in these other acute fire safety buildings and systems should be utilized be those assigned fire safety responsibility in the developmental phases of a new or modified ground combat vehicles - if potential fire safety risks to be cost effectively controlled.

As previously noted, the most effective approach to fire safety during vehicle design to address this issue in a total systems (i.e. an integrated passive and active fire safety approach) rather than as separate, unrelated elements. The selection of a non-metallic material needs to suitably consider the fire safety aspects of the material, but this consideration needs to influenced by the size, shape location and adjacent ignition potentials of the compartment in which it is to be used in the vehicle.


## FIRE SAFETY CONSIDERATIONS IN MATERIAL SELECTION.

When addressing the fire safety concerns presented from the introduction of a new polymer into a vehicle or component design, the typical approach taken by material experts (and / or Military Specifications) is to specify one or more standard laboratory flammability test method to be performed on a designated sample of the candidate material. It is obviously less expensive and quicker to specify and conduct sample size testing, rather than conduct a full scale vehicle fire testing. The fire safety concern is related to the appropriateness of this type testing to actual hazard reduction during vehicle operations when human lives are at risk.

Most standard flammability test methods involve repeatable, small scale material sample testing in a laboratory apparatus designed to reduce potential environmental variables. A typical flammability test involves preparing a strip of material sample in a prescribed orientation (horizontal, vertical or at an angle), placing a controlled heat source at one end for a specified time and noting the burn length, duration, and melting characteristics of the sample. In some test methods, (i.e. the UL 94 series) the accept reject criteria is included, but in most ASTM test methods this is an open issue, which must be specified by some one for the specific application.

Although repeatable and fairly inexpensive, there is a serious shortcoming of these types of test methods. They are not able to fully predict or describe with certainty the burning characteristics of plastics products under actual fire conditions in the vehicle The size, location, ratio of exposed surface, and relation to adjacent fuels and fire threats are systems issues that need to be addressed during the material selection process. . A key factors in this area is the energy feedback issue. In the combustion of a polymeric material, the thermal energy feedback from any adjacent fire or other high temperature source can result in pyrolysis of the material surface to provide a continuing supply of gaseous fuel to the flame.

Ambient temperature sample testing may not adequately address this thermal feedback risk issue. In actual fire scenarios, the rate of burning is directly related to the magnitude of this energy feedback and the intensity of combustion. In the typical small scale test method (such as the UL 94 series), most of the energy of combustion is dissipated in the rising convective plume and through radiation to the cool surroundings. In a real fire, on the other hand, energy exchange between adjacent fuel surfaces and radiation from the heated surroundings greatly increases the energy feedback and the intensity of combustion.

Another concern in evaluating small scale flammability testing results is the interrelated safety issue of the decomposition products. These issues include reduced visibility due to smoke (hamper safe vehicle operations and exiting hazard area) and the health hazard issues. There are many references in the fire safety literature that relate these combustion product risk factors as the leading cause of injury and fatalities in fires involving polymerics

To overcome this inherent shortcoming, activities concerned with establishing specific fire safety material criteria for a given application are tending toward testing methods that provide a radiant flux input, combined with combustion product evaluations. Another key factor is the utilization of full scale fire scenario testing results to better evaluate the effectiveness of the small scale acceptance criteria selection criteria.

A revision to the Federal Aviation Administration (FAA) air worthiness standards for materials used in aircraft interiors (14 CFR 25.853) provides a good illustration in an application somewhat related to fire safety issues associated with ground combat vehicles. In this example, the selection of an improved flammability test method was made from correlation studies of data from candidate material testing and full scale fire testing. Studies of actual aircraft fire incidents indicated that a post crash landing fuel fire located external to an opening in the aircraft passenger cabin provided the most likely severe fire accident scenario.

Full scale testing of alternate composite interior surface materials (partitions, sidewalls, stowage bins) was conducted in a C-133 wide body crew compartment converted for fire testing use. A large fuel fire was initiated external to the cabin and cameras monitored that reaction of the composite test panels. It was found that the different composite materials presented significant differences in both delay times to flash-over and toxic gas levels. This was not as evident from the normal laboratory burn rate testing results.

Experimentation showed that the best correlation between actual full scale fire testing findings and laboratory testing methods was through use of a modified version of the Ohio State Univ. (OSU) rate of heat release apparatus used in ASTM E 906, Test Method for Heat and Visible Smoke Release Rates for Materials and Products. This is basically a flow through device that measures the heat release rate produced as a function of time by a material subjected to a preset level of radiant heat flux. A significant lessons learned in this activity was the desirability of utilizing results of even limited the full scale testing, when selecting sample testing methods and pass-fail criteria..

# FIRE SAFETY PRINCIPLES IN MATERIAL SELECTION

To help satisfy client requests for fire safety guidelines in the selection of polymeric material being considered for application into combat vehicles, the author has formulated the following basic principles in this specific area of concern:

1.  The complex interactions between real life vehicle fire scenarios, the specific application of a given material, and fire safety characteristics of the vehicle design dictate that material selection criteria in this area cannot be treated solely in a cookbook manor, but rather by professional prescription, based on systems oriented hazard risk analyses. The common design engineering practice of noting some *mil spec* reference on the drawing, - in anticipation that it will provide adequate flammability criteria requirements, without further analysis, should not be allowed by program management.

2.  Fire safety criteria must carefully address the necessary balance between essential performance characteristics (i.e. mechanical loads, durability, etc.) producibility, and flammability. This balance needs to consider the potential product liability risks inherent with the design process (primarily assumed by a private contractor preparing the design) and combat mission requirements of the military customer. Resolution of the often severe conflicts occurring between these two concerns, should involve representative of all parties involved with clear documentation on the technical (not just cost) rationale used.

3.  Fire safety criteria formulated for use in material selection during design must be based, to the degree feasible, on the best possible estimate of the most severe credible fire accident scenarios applicable for both combat and non-combat situations. This evaluation is to consider (and influence where possible) all aspects of both the active as well as passive fire hazard reduction provisions of the vehicle system, The material selection criteria thus established should include suitable rationale as to how the criteria is oriented to minimizing the specific risks identified in the worst case fire accident scenario assessments.

4.  To reduce the costs associated with performing the fire safety assessments, selected generic material selection criteria should be defined which differentiate between low, mid and high hazard risk applications. The low risk applications can use less extensive small scale tests than the high risk applications. For each type of vehicle system, some standard categories material selection criteria can be established to expedite the design process One example of this "category by hazard risk of the material application in the system" approach is as follows:

_**Low Risk Applications**_ - The polymeric material, when assembled into the vehicle, will have **no** exposed surface which will be

a. located in any occupied compartment with a total surface area over 5 cm$^2$, or

b. subject to thermal flux environment (from maintenance process. equipment, combat threat, or accidental mishap ) which could heat surface to over 500 degrees F., or

c. used to cover electrical wires subject to carrying <30 volts, or otherwise presents more than a low fire safety risk due to some unusual application consideration...

_**Moderate Risk Applications**_ - The polymeric material, when assembled into the vehicle, will have **no** exposed surface which will be:

a. located in any occupied compartment with a total surface area over 500 cm$^2$, or,

b. subject to a thermal flux environment (from maintenance process. equipment, combat threat, or accidental mishap ) which could heat surface to over 1000 degrees F., or

c. used to cover electrical wires subject to carrying <140 volts, or otherwise more than a moderate fire safety risk due to some unusual application consideration..

_**High Risk Application**_ -The polymeric material, when assembled into the vehicle, will present potential fire risks which exceed those defined as low or moderate, or has significant uncertain fire risk considerations which preclude proper assessment without further research and testing. .

5. To date, the only end product use oriented material selection fire safety criteria directly applicable to ground combat vehicles is found in MIL-STD-1180(AT) "Safety Standards for Military Ground Vehicles" dated July 1976. This references Federal Motor Vehicle Safety Standard (FMVSS) No. 302. "Flammability of Interior Materials". This was issued by the DOT in 1975 to provide a minimum standard for interior materials used in passenger vehicles. It was based on a scenario in which a seat cover fire was initiated by a dropped cigarette, and all passengers exit the vehicle within a minute or less. The test will pass a material sample strip, which when held horizontal in a holder, and contacted with a flame at one end, burns no more than 4 inches a minute. It is suggested that this criteria be considered only as an initial screening test requirement, and for low risk applications.

## FIRE SAFETY TESTING GUIDELINES AND CRITERIA

With a suitable risk category system established, it is then feasible to define some basic material testing procedures and evaluation guidelines for each risk category. Using the example risk categories noted above the following is one proposed approach:

1. Material testing for fire safety acceptance, are to be performed in accordance with an established fire safety plan, that considers the findings of a vehicle oriented fire risk assessment. Screening test results for selection of polymeric materials shall be evaluated based on fire safety risk categories and how close the samples used for the testing are representative of the actual polymeric item when assembled in the vehicle:

2. Other than for _low risk_ applications, materials being considered for use inside the crew compartment are to be evaluated, using existing data, for potential of toxic gas generation upon combustion in worst-case operating scenarios environments. To the extent feasible, materials should be selected which have the least potential health hazard characteristics, using ASTM E-800 as a guide. Where a trade-off between alternate material candidates is involved, weighting should be given to ignition and low flame spread, over smoke and toxic gas characteristics. This weighting approach is based on the fact that since most all plastics release some smoke and toxic decomposition products, the bast way to control these hazards is to reduce the potential for the material to ignite and burn.

3. Material samples or coupons used for fire safety testing should be as representative as feasible of the end use configuration. This includes any surface finishes, thickness, bonding to other materials, configuration orientations, etc. The test plan (as noted above) should always define the detailed description and source of all needed test specimen samples. Where feasible, the manufactured components should be utilized as the source of test samples, rather than a vendor supplied specimen.

4. The following fire safety testing and evaluation criteria developed by the author for a client company's use in this area is summarized below to serve as an example format. The values selected for the accept criteria were adapted from Federal Transit Administration's "Recommended Fire Safety Practices for Transit Bus and Van Materials Selection",. (This document provides one of the most directly related, government agency published fire safety selection criteria, to combat vehicle applications):

| FIRE RISK CATEGORY | TEST METHOD | ACCEPT CRITERIA |
|---|---|---|
| LOW | FMVSS 302 | PASS |
| MODERATE | UL94 OR ASTM 635<br><br>ASTM E-2863<br><br>ASTM E-662 | V-1 OR EQUIVALENT<br><br>LOI .21 AT 25° C<br><br><200 DS (100 sec)<br><400 Ds (240 sec) |
| HIGH | ASTM E-162<br><br>ASTM E-2863<br><br>ASTM E-662<br><br>UL 746A (IF MATERIAL IS USED AS ELECTRICAL WIRE / COMPONENT PROTECTION) | <35 FLAME SPREAD INDEX<br><br>LOI .>27 AT 25° C<br><br><100 DS (100 sec)<br><200 Ds (240 sec)<br><br>PARA 24,25,42, OR 43 AS APPLICABLE |

5. The above criteria is an interim guide - developed for use when an immediate design decision is needed. It is recommended that those in the military and industry having fire safety responsibilities for combat vehicle development continue to evaluate the material selection criteria issue through a formal joint DoD / Industry working committee. This committee should be the focal point for summarizing lessons-learned information from existing fire accident reports, and establishing requirements for additional full scale testing in the combat vehicle area to provide better benchmarks for validating any proposed laboratory level sample test accept / reject criteria points. This committee should also have provisions for establishing a database of fire safety testing results by material formulation, so that this information can be used by other making similar material selection trade-offs. In time the data collected from both full scale and laboratory scale testing of polymeric materials being considered for combat vehicle usage could organized in a systematic manor, which would lead to a more standardized and universally applied testing criteria established within the combat vehicle development community - than now exists..

# Potential Errors in
# Respirable Fiber Measurements of Dusts
# from Composite Manufacturing

**Edmund A. Merriman**
Product Steward,
DuPont Advanced Fibers Systems

**Joseph F. Viskocil**
Certified Industrial Hygienist
DuPont Haskell Laboratory for
Toxicology and Industrial Medicine

---

# Introduction

- Need Validated Measure of Airborne Respirable Fibers in Composite Plants
- Composite Dusts Have Few Fibers, Much Particulate
- Size, Shape, Conductivity, Density of Non Asbestos Fibers Vary
- Regulators Question Use of Asbestos Methods
- Aim: Validate NIOSH 7400 for Para-Aramids
- Surveying Para-Aramid Fibril Exposures in Composite Workplaces
- Significant for Composite Dust Research

# Overview

- Introduction

- Standard Fiber Counting Method – NIOSH 7400

- Valid for Studying Composite Dusts?

- Sources of Errors

- Potential Magnitude of Errors

- Significance for Composite Workplace Surveys

- Continuing Studies

# NIOSH 7400

- Designed for Asbestos – Straight, Dense, Rod-Like Fibers

- Draw 2 Liters/Min Workplace Air Through 25mm Diameter Filter

- Filter Segment Mounted on Slide, Cleared to Show Particles

- Respirable Sized Fibers Counted Microscopically for Airborne Fiber Concentration
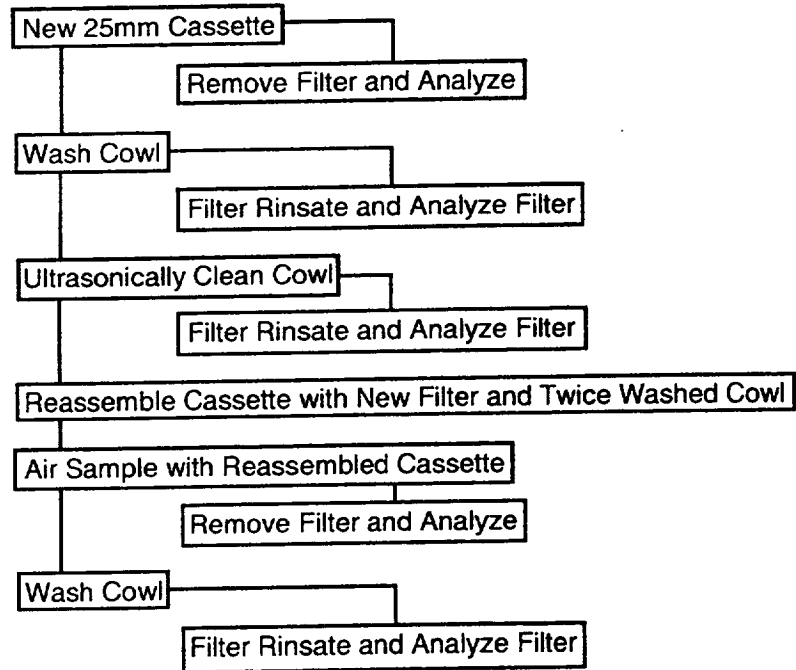
- Statistically Designed, But Highly Variable (Cv = 40%)

# Validity of NIOSH 7400 for Para-Aramids

• Lower Density (1.45 vs. 2.6g/cc)

• Complex Shape – Branched, Ribbon-Like, Curled

• Electrostatically Negative, Easily Charged

• More Likely to Agglomerate

# Potential Sources of Air Sampling Error

• Cassette Cowls Could Contribute Non-Aramid Fibrils
  - Known to Contain Fibrils of Countable Size
  - Would Give Positive Bias – Measurements Too High

• Cassette Cowls Could Capture Incoming Fibrils
  - Higher Fiber Charge and Shape Might
    Favor Adhesion
  - Would Give Negative Bias –
    Measurements Too Low

• Laboratory Tests Designed to Measure
  Potential for Both

# Cowl Study Test Method

New 25mm Cassette

Remove Filter and Analyze

Wash Cowl

Filter Rinsate and Analyze Filter

Ultrasonically Clean Cowl

Filter Rinsate and Analyze Filter

Reassemble Cassette with New Filter and Twice Washed Cowl

Air Sample with Reassembled Cassette

Remove Filter and Analyze

Wash Cowl

Filter Rinsate and Analyze Filter

---

# Cowl Rinsing Test Results

## (Fibers Per Field)

|                                      | Cassettes A avg/med | Cassettes B avg/med | Cassettes C avg/med |
|--------------------------------------|---------------------|---------------------|---------------------|
| From 1st Wash                        | 1.80                | 1.30                | 0.80                |
|                                      | 0.36                | 0.90                | 0.17                |
| From 2nd Wash (After Ultrasonic)     | 2.15                | 3.61                | 1.14                |
|                                      | 1.23                | 1.70                | 0.39                |

**Conclusion:**
- Ultrasonic Rinsing Needed to Clean Cowls
- Levels Equivalent to >1 Fiber/cc in a 1-hr Test

(10 Cassettes Per Set)

# Percent of Sampled Fibrils Caught by Cowl

## Ranked by Total Fibrils

| % Fibrils on Cowl | Filter f/cc | % Fibrils on Cowl | Filter f/cc |
|---|---|---|---|
| 315 | 0.005 | 84 | 0.095 |
| 4975 | 0.005 | 7 | 0.374 |
| 3932 | 0.005 | 16 | 0.309 |
| 2546 | 0.005 | 13 | 0.779 |
| 219 | 0.006 | 7 | 0.831 |
| 883 | 0.015 | 28 | 0.609 |
| 91 | 0.058 | 11 | 0.769 |
| 13 | 0.170 | 4 | 6.030 |

**Conclusion**: Fibrils Trapped on Cowl More Significant at Lower Airborn Fibril Concentration

# Average Respirable Fiber Counts from Fabricating Para-Aramid Composites

| Composites Fabrication Operations | Personal f/cc | Area f/cc | Samples P | A |
|---|---|---|---|---|
| Prepreg Cutting & Laying Up | 0.02 | — | 20 | — |
| Molding | 0.01 | 0.01 | 11 | 2 |
| Trimming, Drilling | 0.03 | 0.01 | 33 | 13 |
| Sandblasting | 0.02 | 0.01 | 4 | 3 |
| Reworking | 0.02 | 0.02 | 5 | 3 |
| Waterjet Cutting | 0.03 | 1.88 | 1 | 2 |
| Maximum (Between Work and Hood) | 0.25 | | | |
| Field Blanks | | 0.007 | 97 Samples | |

**Conclusion**: Para-Aramid Fibril Exposures Well Below 2 f/cc Limit

# Significance of Errors for Workplace Monitoring

- Cowl Contributions Can Be Significant at Low Fiber Counts

    - For Research on Fiber Dust, Cowls Must Be Washed

    - Field Blanks Indicate Few of Many Cowl Fibers Reach Filter

- Cowl-Captured P-Aramid Fibrils Significant Only at Low Levels

    - Insignificant Near DuPont Acceptable Exposure Limit (>2 f/cc)

    - Could Slightly Alter Levels Typical of Composite Shops

- No Apparent Effect of Humidity, Though Expected

- NIOSH 7400, Method B Remains Acceptable Monitoring Method

# Research Program Continuation

- Examine for Size Bias in Captured Fibrils

- Measure Aerodynamic Diameter of Kevlar® Fibrils

    - Use for Inhalation Deposition Modeling

- Characterize Fibrils and Dust from Composite Operations (with AIA/SACMA ?)

# Biotransformation of an Uncured Composite Material

Clement J. Welsh[1,2,3], Michael J. Glass[1,2], Brian Cheslack[1], Robert Pryor[1], Duan K. Tran[1], and Gail Bowers-Irons[1]

[1]EXTRA Research, Inc.
2274 South 1300 East
Suite G8235
Salt Lake City, UT 84106

and

[2]Center for Environmental Technology
2201 MEB
University of Utah
Salt Lake City, UT 84112

[3] Corresponding author: Center for Environmental Technology
2201 MEB, University of Utah, Salt Lake City, UT 84112

## ABSTRACT

The feasibility of biologically degrading prepreg wastes was studied. The work was conducted with the intention of obtaining baseline data that would facilitate the achievement of two long-range goals. Those goals are; 1) the biological remediation of the hazardous components in the prepreg wastes, and 2) providing the potential for recycling the prepreg waste fibers. The experiments examined a prepreg that employs an bismaleimide resin system. Initial results demonstrated an obvious deterioration of the prepreg material when incubated with several bacterial strains. The most active cultures were identified as a mixture of <u>Bacillus cereus</u>. and <u>Pseudomonas sp.</u> Gas chromatographic analyses of the total organic components from the prepreg material revealed seven primary compounds in the resin mixture. Biotransformation studies, using the complete prepreg material, demonstrated an obvious loss of all seven organic compounds. Gas chromatography-mass spectrometry analyses resulted in structure assignments for the two primary components of the resin. Both were analogs of Bisphenol A; one being bismaleimide, the other being Bisphenol A containing a diglycidyl moiety. The "diglycidyl analog" was purified using thin-layer chromatography and the biotransformation of this compound (at 27 ug/ml bacterial culture) was monitored. After a seven-day incubation, approximately 40 % of the organic compound was biotransformed. These results demonstrate the biotransformation of the prepreg resin and indicate that biological remediation of prepreg wastes is feasible.

# INTRODUCTION

Disposal of industrial wastes is an issue that encompasses both environmental and economic concerns. The traditional means of disposal by land filling wastes is becoming more restricted due to the limitation of reasonable landfill sites and the potential for release or leaching of toxic materials from the burial sites. Alternate protocols for waste disposal, such as incineration, have also come under scrutiny, and the expense associated with incineration has increased substantially. Modern waste disposal problems require solutions that address not only the environmental concerns, but also provide answers that are economically viable.

Microbial remediation systems represent a potential means for reducing and/or eliminating the hazard associated with a variety of industrial wastes and accidental spills. Notable applications of such bioremediation systems are aimed at hydrocarbon and halogenated organic wastes (1-9); however inorganics have also been targeted (2). With the anticipation of tighter restrictions on waste disposal, microbes that can remediate wastes hold great promise. An attractive aspect of the microbial systems is the ability to manipulate metabolic capabilities of bacterial cultures. These techniques include forced selection and genetic manipulations using modern molecular biology. Collectively, these laboratory procedures present the possibility of developing a variety of microbial processes or products to address given waste problems (2,9-11). Development of a microbial system targeted to a particular waste stream and installation of the processes at the waste generation site increases the potential value of such remediation systems.

The primary aim of the work described in this communication was to determine the feasibility of developing a microbial system for biologically degrading the resins used in composite materials. The investigations targeted an uncured bismaleimide prepreg material. The work was guided by the long-range goal of developing a microbial remediation system for the prepreg wastes produced during molding and manufacturing processes. The results presented in this communication demonstrate that biotransformation of organic components in a prepreg resin mixture can be accomplished. Furthermore, the results suggest that biologically degrading the resins may render the fiberous materials reusable.

# METHODS AND MATERIALS

**Solvents and Materials.** All solvents were "reagent" or "HPLC" grade and were purchased from Mallinckrodt (Paris, KY) or EM Science (Gibbonstown, NJ). Thin-layer chromatography (TLC) plates (silica gel G) were supplied by Analtech (Wilmington, DE). Medium for bacterial culture was purchased from Difco (Detroit, MI). Bismaleimide (4,4'-Bis(maleimidodiphenyl)methane; CAS # 1376-54-5) was purchased from Lancaster Synthesis, Eastgate, England. The prepreg material is a bismaleimide resin-graphite composite manufactured by BASF/Narmco, and was supplied as an uncured prepreg sheet. The prepreg material was stored at -20° C prior to use.

**Prepreg Extractions** The prepreg material was routinely extracted using 2 ml water and 2 ml ethyl acetate in an 8 ml glass vial (teflon-lined caps) with vigorous mixing on a vortex mixer (60 sec). The vials were centrifuged to break phases and the upper organic layer was removed and saved. The remaining prepreg material and the aqueous phase were re-extracted with a second 2 ml of ethyl acetate. The two ethyl acetate extracts were pooled and the solvent was evaporated at room temperature. For tests designed to evaluate the extraction system, the residual prepreg material left after the first two ethyl acetate extractions was extracted a third time. This third extraction was achieved by adding 2 ml of methanol and 2 ml of chloroform to complete the aqueous vs. organic extraction described by Bligh and Dyer (12).

**Bacterial Culture and Identification.** The prepreg materials were placed into 500 ml flasks containing TGY media (5.0 g/L Tryptone, 2.5 g/L Yeast Extract, 1.0 g/L Dextrose, pH 7.2) with various cultures of organisms. The cultures were incubated at room temperature (25°C) with constant shaking (~200 rpm). After visual inspection for apparent changes in the prepreg materials, portions of

active cultures (100 μl) were plated on TGY agar (1.5% agar) plates and incubated at room temperature, 30° C, or 37° C. Unique colony types were restreaked on TGY plates until the pure bacterial strains were isolated. The strains were then characterized by standard biochemical procedures (13,14). These tests included, Gram reaction, oxidase reaction, motility, flagellar staining, and carbohydrate utilization as described in the "Results".

**Leaching Experiments.** Experiments designed to investigate the leaching characteristics of the prepreg material were performed using 2.5 g of the prepreg (in ~1 cm$^2$ pieces) in 250 ml of water (500 ml flasks) shaken at ~200 rpm. At various time points, small aliquots of the aqueous portion of the mixtures were removed and extracted with ethyl acetate as described above. The organic extracts were evaporated to dryness and the residue was analyzed using quantitative gas chromatography (described below).

**Analyses of Prepreg Components.** The ethyl acetate extractable material was concentrated by evaporating the solvent and the dried residue was resuspended in known volumes of either ethyl acetate or chloroform. For thin-layer chromatographic (TLC) resolution of the ethyl acetate-extractable materials, a solvent system of hexane/chloroform/ethyl acetate/acetic acid (30/10/5/5; v/v/v/v) (TLC System 1) was used. Subsequent recovery of the resolved compounds permitted recovery of "TLC fractions". This TLC-fractionation was achieved by scraping specific areas of the silica gel off of the plate, eluting the compounds from the silica gel with chloroform or chloroform/methanol (1/1; v/v), and evaporating the solvent. Exposure to iodine vapor or acid charring (15,16) was used for visualization of resolved compounds on the TLC plates.

TLC with a solvent system of hexane/chloroform/ethyl acetate/acetic acid (30/5/1/1; v/v/v/v) (TLC System 2) was used to purify a component of the resin mixture. In this system GC Peak 4 (see Figure 2 for GC peak number assignments) migrates to an R$_f$ of ~0.65 and is well resolved from other components of the resin

mixture. The resolved Peak 4 band was scraped from the TLC plate, and eluted from the silica gel using chloroform. The chloroform was evaporated at room temperature and the residue was used for further analyses. Subsequent GC analysis (see below) of the purified Peak 4 component showed the purity was > 96 %.

Gas chromatography (GC) analyses used a Hewlett Packard 5890 gas chromatograph fitted with a HP-1 (methyl silicone gum; Hewlett Packard) capillary column (5 m; x 0.53 mm x 2.65 um film thickness) and fitted to a flame ionization detector. Resin components were routinely resolved using a temperature program of: $150^{\circ}$ C for 2 min, then increasing the oven temperature at a rate of $15^{\circ}$ C/min to $295^{\circ}$ C. Quantative analyses were performed using a "solvent flush" injection technique that routinely provided peak area sample means (n=3) with standard deviations that were less that 2.5 % of the mean. Gas chromatography-mass spectrometry analyses were performed with a Hewlett Packard 5890 GC interfaced to a model 5971 mass selective detector. Compounds were resolved on a DB-5 capillary column (Hewlett Packard; 30 m; x 0.23 mm). All spectra were collected at 70 eV.

## RESULTS

**Initial Characterization and Extraction of the Prepreg Material.** Initial tests, using 1 $cm^2$ sections of the prepreg material in 8 ml glass vials, were conducted to examine the behavior of the prepreg resins in various organic solvents. These tests showed that the prepreg material readily released materials to ethyl acetate, chloroform and methylene chloride. When exposed to these solvents, the prepreg materials "melt" leaving a disorganized lump of fibers in the vial. Less polar solvents, such as hexane, showed a reduced ability to pull materials out of the prepreg. When dry, the ethyl acetate-extracted resin was a viscous, amber colored material.

Tests studying the capability of ethyl acetate to provide quantitative extractions were performed using comparisons of the residues collected with the usual protocol of two repeated extractions vs. the usual extraction protocol that was followed by extraction with a different organic vs aqueous extraction system described by Bligh and Dyer (12). The resin material collected after the usual protocol vs. the thrice extracted material were evaluated, using quantitative GC of Peak 4 (see Figure 2 below for GC Peak assignments). These analyses indicated that 95.3 ±5.7 % (n = 3) of the recovered material was collected with the routine protocol that employed two ethyl acetate extractions. Subsequent testing examined the ability of the ethyl acetate to extract the prepreg resin from a bioreactor mixture. These tests employed 2 ml of bacterial culture ($OD_{595} \geq 1.0$) and approximately 132 mg of the prepreg material (in 8 ml vials; n=4). Extraction of prepreg only "controls", as well as prepreg+bacteria "test cases" was followed by quantitative GC analyses. These tests showed that >96 % of the resin collected from the control samples was collected from the prepreg+bacteria samples. Further analyses, using purified Peak 4 (see Figure 2 for peak numbering), showed that the extraction protocol provided a quantitative recovery of the purified Peak 4 component from concentrated bacterial pellets. When comparing the ug Peak 4 recovered vs. ug Peak 4/vial, the results revealed a quantitative extraction when using 100-25 ug Peak 4/vial (Peak 4 plus water "control"; $y = 0.032+0.022x$; $r^2 = 0.992$; Peak 4 plus water plus bacteria "test case"; $y = 0.087+0.021x$; $r^2 = 0.996$; recoveries were all > 95 % of control). Additional examinations, using gravimetric analyses, found that the ethyl acetate-extractable materials represented 28.7 ± 2.8 % (n = 4) of the total prepreg mass. These results demonstrate that the ethyl acetate extraction can provide a quantitative recovery of the resin in the presence of bacteria, and that the extractable resin represents approximately 28 % of the prepreg mass.

**Initial Exposure of Prepreg to Bioreactor Conditions.**
Experiments to examine the possibility of microbial transformation were conducted using 500 ml flasks containing approximately 250 g

149

of the prepreg material (2.5 cm x 2.5 cm squares) and various proprietary bacterial cultures. Abiotic cultures ("negative controls"), were employed to monitor the the possibilty of breakdown due solely to mechanical agitation. After shaking at room temperature for approximately 2 weeks, the prepreg material placed in several of the microbial cultures showed obvious signs of degradation. This visible degradation was characterized by an "unraveling" on the fibrous components that gave the previously smooth-surfaced prepreg sample a frayed appearance. After 55 days of exposure to the bacterial activity in one of the initial bioreactors, the composite fibers exsited as a jumbled lump from which the fiberous materials could be easily pulled apart.

A sample of the frayed prepreg fibers was removed from the 55-day bioreactor, rinsed 3 times in water, dried, and weighed. A mass of the parent prepreg material, similar to that of the frayed biodegraded prepreg material, was also collected. Each of the "equal mass" samples were extracted with ethyl acetate. The ethyl acetate-extractable material from both the "parent" and "biodegraded" samples were air dried and resuspended in ethyl acetate. The volume of ethyl acetate was manipulated to achieve equivalent concentrations of prepreg material/ml of solvent based on the dry weight of the prepreg samples used in the extractions. Equal volumes of the ethyl acetate extracts were spotted on a TLC plate and resolved (TLC System 1). Figure 1 illustrates the resulting chromatogram and demonstrates obvious loss of organic materials from the prepreg material collected from the bioreactor. Subsequent GC analysis of the same samples also showed a dramatic loss of materials in the prepreg sample exposed to the bacterial activity (Figure 2). The major peaks of the gas chromatogram were "numbered", according to relative retention times, as illustrated in Figure 2. Collectively, these TLC and GC investigations indicate a loss of organics from the biologically treated prepreg material. The results also suggest that a component of the resin mixture, observed as Peak 4 in the gas chromatogram and at ~$R_f$ of 0.65 on TLC, is more resistant to degradation than are the other resin compounds.

150

**Characterization of Bacterial Cultures.** Bacterial growth, as assayed by turbidity and microscopic observation, was observed after several days incubation in the cultures containing the prepreg materials. In an attempt to ensure recovery and identify all the organisms contained in the original cultures, several different media bases (agar solidified medias) were used for isolation of the organisms. Two different colony types were consistantly isolated from the cultures, and these isolates were tested for substrate utilization. The results of theses tests are listed in Table 1, and indicate that one of the isolates was *Bacillus cereus* and that the other was a *Pseudomonus sp.*

**Leaching of Prepreg Resin Components.** In an attempt to ascertain the disposition of the resisn components, experiments investigated the solubility of the prepreg resin components when subjected to an aqueous environment. These experiments revealed that many components of the resin mixture could leach out of the prepreg when exposed to an aqueous environment. Figure 3 presents the GC data obtained from the leaching experiments, and clearly shows that certain resin components are readily soluble in water. The data also demonstrate that specific components apparently leach at different rates relative to other resin components. Under the conditions used, leaching of GC peaks 1, 2, 4, and 7 are obvious (Figure 3). Only insignificant levels or trace levels of the other components were found in the leachate (data not shown). The data show an obvious release of components to the water after only 60 min in the aqueous environment (Figure 3). The leaching of Peaks 1 and 4 increased throughout the time period monitored by the experiment. Peaks 2 and 7 leached for approximately 10-24 hrs. However, after the 24 hr time point, the levels of Peaks 2 and 7 decreased. This result suggests that, over time, Peaks 2 and 7 degrade in the aqueous environment. The levels of Peak 4 remained relatively constant from the 24 hr time point for up to 14 days. The results showing that the levels of Peaks 1 and 4 increased over the time course of the experiment (Figure 3) indicate that these components are stable in water.

Because of the results that indicated biotransformation as well as leaching of materials from the prepreg samples, we examined the ability of the bacteria to "sequester" the leached resin components. Using a theoretical bioreactor environment, these experiments examined samples from a bioreactor (approximately 20 days) that were centrifuged to provide a bacterial pellet as well as an aqueous portion of the sample. The bacterial pellets were washed twice with water and each of the pellet and the aqueous samples were extracted with ethyl acetate. Subsequent GC analyses of those ethyl acetate extracts showed that approximately 50 % of the recovered resin material (primarily GC Peak 4) was found associated with the

bacterial pellet. The remainder was found in the aqueous supernatant. These results indicate that a substantial portion of the leached resin material is closely associated with the bacterial cells, and also suggests that this solubolized portion of the resin material exists as a "cell associated substrate".

Collectively, the results thus far indicate that the resin components can leach into water, that certain resin components are labile in water while others are relatively stable, that the leached components can be closely associated with bacterial cells, and that exposure to bacterial action results in a loss of the parent resin components. At this point it is reasonable to suspect that the loss of the labile components from the bioreactor samples may be due to the inherent instability of those components. However, the more stable compounds (GC Peaks 1 and 4) may be lost from the bioreactor mixture as a result of the biotransformation/biodegradation activities of the culture.

**Characterization of Prepreg Resin Components.** TLC fractionation of the resin mixture provided five crude fractions defined by $R_f$ as follows: Fraction A, $R_f$ = 0.0-0.12; Fraction B, $R_f$ = 0.12-0.25; Fraction C, $R_f$ = 0.25-0.55; Fraction D, $R_f$ = 0.55-0.75 and Fraction E $R_f$ = 0.75-front. Subsequent GC of each of the TLC fractions revealed chromatographic behaviors listed in Table 2. These findings indicated that the two primary components observed in the gas chromatograms (Peaks 4 and 7) possessed very different "polarities" as defined by the specific TLC system used to resolve the components.

To elucidate the structures of the resin components, the ethyl acetate-extractable material was subjected to GC-MS analyses. This work provided data that permitted structure assignments for the two predominant components of the parent resin material (GC Peaks 4 and 7). Based on the GC-MS data, resin components were assigned structures as follows: Peak 4; Benzene, 1,1'-(methylethylidiene)bis[4-

153

(2-propenyloxy)-; and Peak 7; 4,4'-Bis(maleimidoiphenyl)methane. The mass spectral data and the supporting chromatographic information that define and corroborate the structure assignments are presented in Table 2.

Given the structure assignments derived from the GC-MS data, the mass of the resin represented by the gas chromatograms of Peaks 4 (weighed after bulk purification by TLC) and 7 (from a commercial source) was calculated from quantitative GC analyses. These tests found the following GC detector responses: Peak 4 = 2.5 x10$^6$ integration units/ug; ~26 % of the mass of the parent resin mixture; ~7.5 % of the total mass of the parent prepreg, and Peak 7 = 1.1 x10$^6$ integration units/ug; ~29 % of the mass of the total parent resin; ~8.4 % of the total mass of the prepreg material.

The initial degradation studies and the subsequent chromatography and structure elucidation indicate that, of the resin components, GC Peak 4, (Benzene, 1,1'-(methylethylidiene)bis[4-(2-propenyloxy)-), is the most recalcitrant to the biotransformation activities. Therefore, with the intention of testing the most "resistant" of the potential resin substrates, Peak 4 was purified using preparative TLC (TLC System 2), and then used as a substrate in subsequent biotransformation studies. The purified peak 4 was weighed, resuspended in chloroform, aliquots were added to 8 ml vials, and the solvent was evaporated. A mixed culture of *Bacillus* and *Pseudomonus* (333 ug dry weight/ml) was added to the vial to give a total volume of 2 ml and a Peak 4 concentration of 27 ug/ml. The vials were incubated at room temperature for 7 days. After the 7 day test period, the entire sample was extracted with ethyl acetate. The solvent was evaporated and the quantity of Peak 4 in the residue was assessed using GC. Figure 4 illustrates the findings of this experiment and provides comparisons with "time 0" and "sterile aqueous" controls run in parallel. The results of this experiment clearly show a 38 % loss of the Peak 4 component from the bioreactor (27 ug vs. 16.7 ug; Figure 3), and thus demonstrate the biotransformation of the Peak 4.

154

# DISCUSSION

The analytical data demonstrates that the prepreg resin material is composed of a variety of components. The two most prominent compounds were identified as Benzene, 1,1'-(methylethylidiene)bis[4-(2-propenyloxy)-; (GC Peak 4) and 4,4'-Bis(maleimidoiphenyl)methane (GC Peak 7). Collectively these two compounds represent approximately 55 % of the total ethyl acetate extractable material or approximately 15 % of the total mass of the prepreg material.

The investigative studies revealed several characteristics of the prepreg resin components. These include: 1) the resin components can leach into water; 2) certain resin components are labile in water while others are relatively stable, 3) the Benzene, 1,1'-(methylethylidiene)bis[4-(2-propenyloxy)- (GC Peak 4) is apparently the most resistant to biotransformation, and 4) the biotransformation of the resin mixture as well as purified Benzene, 1,1'-(methylethylidiene)bis[4-(2-propenyloxy)- is possible.

The Benzene, 1,1'-(methylethylidiene)bis[4-(2-propenyloxy)- was identified based on the mass spectral characteristics. All spectral aspects of this resin component, including fragment ion pattern and isotope peaks are consistent with the structural assignment given. Furthermore, the TLC and GC chromatographic behavior is consistent with the assigned structure. However it should be noted that the isometric configurations presented (Figure 3) are "likely" but that other isomers are possible. The spectra of "minor peaks" in the ethyl acetate extract (GC Peaks 1, 3 and 5) suggest the presence of such isomers. The identity of the 4,4'-Bis(maleimidoiphenyl)methane was determined with GC-MS and TLC of the resin material and was confirmed by comparisons with a commercial standard.

155

From the TLC (Figure 1) and the GC (Figure 2) studies, Benzene, 1,1'-(methylethylidiene)bis[4-(2-propenyloxy)- is the resin component that is most resistant to biotransformation. However, when purified and subjected to the activities of the proprietary bacterial culture, the substrate was biologically transformed. Finding a 38 % reduction in the Benzene, 1,1'-(methylethylidiene)bis[4-(2-propenyloxy)- after a 7 day incubation indicated that even the most resistant resin component could be biotransformed.

While not a primary objective of these initial studies, observations of the biotransformed fibers were made at various intervals. These observations suggested that the prepreg resins were being removed from the composite fibers. In the original cultures that showed potential for biotransformation (55 days in the bioreactor; see Figures 1 and 2) the residual fibers appeared to be free of the resin, the fibers were present in the bioreactors as lumps of disorganized fiber, and the fiberous lumps could be dissociated with minimal swirling in water and teasing. We have interpreted these findings as an indication that, when exposed to the bioreactor conditions, the resins can be removed from the prepreg fibers, and that it may be possible to use a biotreatment process to clean the resins from waste prepreg materials. Such a process could render the fibers reusable. Definitive results showing the recycleability of the fibers will require further work, and will quite likely depend on the particular fiber and manufacturing processes.

Many investigations have been conducted with the intention of using biodegradation processes to treat polymeric wastes. Although researchers have generally found the development of microbial remediation systems for treatment of industrial and natural polymeric wastes to be a frustrating endeavor, there are some encouraging results. Biodegradation of polymeric materials such as specific plastics, cellulose and lignins have been studied, and under various laboratory conditions, biodegredation has been reported (17-19). In a previous study we have found evidence of a microbial transformation of paint waste components (20). While this work did

not specifically document the degradation of the paint polymer, it did indicate a microbial activity against specific, unidentified, components in the paint mixture. These results are encouraging when considering that they represent initial attempts to degrade a recalcitrant polymeric material in complex mixtures, In addition, the results have lead to conclusions that biotransformations have occured.

An advantage of the strategies that target bioremedation of prepreg waste materials is the possibility of working with the unpolymerized resins, and thus avoiding subsequent treatment of the polymeric matrix that is designed to resist microbial activity. Toward this end it should also be noted that investigators are working on the development of polymers that are more susceptible to attack by microbial enzymes. These polymers are designed to possess the desired physical properties, but also contain specific biodegradable sites (19).

We are presently involved in studies to determine the optimal reaction conditions for complete biodegradation of the prepreg resin material. Concurrent investigations are studying the metabolic pathways involved in the biotransformations. These studies will include investigations of the relative toxicity of the resin components in the bacterial culture, and will determine if the resins can be used as a sole carbon source. Collectively, this work is expected to provide the baseline data needed to build bioreactors that will remediate the resin components of the prepreg materials, and will allow for the routine burial of the waste prepregs and/or recovery of the fibrous components.

# Bibliography

1. Kobayashi, H., and Rittmann, B. E. (1982) Microbial removal of hazardous organic compounds. Envir Sci. Technol., 16:170A183A.

2. Stroo, H. (1992) Biotechnology and hazardous waste treatment. J. Environ. Qual., 21:167-175.

3. Fiorenza, S., Dutson, K. L., and Ward, C. H. (1991) Decision making-Is bioremediation a viable option? J. Hazard. Mat. 28:171-183.

4. Chaudhry, G. R., and Chapalamadugu, S. (1991). Biodegradation of halogenated organic compounds. Microbiol. Rev. 55, 59-79.

5. Clarke, P. H. (1984). The evolution of degradative pathways, p11-27. D. T. Gibson (ed.), Microbial degradation of organic compounds. Marcel Dekker, New York.

6. Clarke, P. H. and Slater, J. H. (1986). Evolution of enzyme structure and function in *Pseudomonas*, p71-144. J. R. Sokatch (ed.), The bacteria, vol. 10. Academic Press, new York.

7. Dagley, S. (1971). Catabolism of aromatic compounds by microorganisms. Adv. Microb. Physiol. 6, 1-46.

8. Wheelis, M. L. (1975). The energetics of dissimilarity pathways in *Pseudomonas*. Annu. Rev. Microbiol. 29, 505-524.

9. Watkinson, R. J., and Morgan, P. (1990) Physiology of aliphatic hydrocarbon-degrading microorganisms. Biodegradation. 1:79-92.

10. Deretic, V., Konyecsni, W. M.,Mohr, C. D., Martin, D. W., and Hibler, N. S. (1989) common denominators of promoter control in *Pseudomonas* and other bacteria. Bio/technology. 7:1249-1254.

11. Bollag, J. (1992) decontaminating soils with enzymes. environ. Sci. Technol. 26:1876-1881.

12. Bligh, E.G. and Dyer, W.J. (1959) J. Bichem. Physiol. 37: 911-917.

13. Bergeys Manuel of Systematic Bacteriology (1984). ed. J. G. Holt, Williams and Wilkins, Baltimore.

14. Smilbert, R. M., and Krieg, N. R. (1981). General characterization. Manual of methods for general bacteriology, American Society for Microbiology, Washington, D. C. ed. Gerhart, P., Murray, R. G. E., Costilow, R. N.., Nester, E. W.,Krieg, W. A., and Phillips, G. B. 409-443.

15. Welsh, C.J. and K. Schmeichel (1993) Improved method for thin-layer chromatographic resolution of the major classes of phospholipids. J. Liquid Chromatog. 16:1819--1831.

16. Welsh, C.J. and K. Schmeichel (1991) Assays for investigations of signal transduction mechanisms involving phospholipase D: Mass measurements of phosphatidate, phosphatidylethanol, and diacylglycerol in cultured cells. Anal. Biochem. 192:281-292.

17. Palmisano, A. C., and Pettigrew, C. A. (1992) Biodegradability of Plastics. BioSci. 42:680-685.

18. Field, J. A., Jong, E.D., Feijoo-Costa, G., and de Bont,J. A. M. (1993) screening for lignolytic fungi applicable to the biodegradation of xenobiotics. TibTECH. 11:44-47.

19. Huang, S. J., Bell, J. P., Knox, J. R., atwood, H., Bansleben, D., Bititto, M., Borghard, T., Chapin,T., Lehong, K. W., Natarjan, K., Nepumuceno, J., Roy, T., Soboslai, J., shoemaker, N. (1976) design, synthesis and degradation of polymers susceptable to hydrolysis by proteolytic enzymes. In: Proceedings of the third international biodegradation symposium, J. M. Sharpley and A. M. Kaplan, Eds. Applied Science Publishers, Ltd. London.

20. Glass, M.J., C.J. Welsh, B.C. Cheslack, R.J. Pryor, D.T. Tran, and G. Bowers-Irons. (1994) Biodegredation of PMB-paint waste by *Pseudomonas*. (manuscript submitted).

## Figure Legends

**Figure 1.** **Thin-layer Chromatography of Resin Recovered from a Parent and Biotransformed Bismaleimide Prepreg.** Ethyl acetate extractable resin materials were resolved by thin-layer chromatography using hexane/chloroform/ethyl acetate/acetic acid (30/10/5/5; v/v/v/v). Equivalent masses of the "parent" and the "biotransformed" (55 days in a bioreactor) prepreg samples were extracted, the solvent was evaporated to dryness, the residue was redissolved in 500 ul of ethyl acetate, and 10 ul were applied to each lane. After resolution of the resin components, the solvent was evaporated from the plate and the compounds visualized after spraying with acid and charring.

**Figure 2.** **Gas Chromatography of Resin recovered from a Parent and Biotransformed Bismaleinide Prepreg.** The "parent" and "biotransformed" samples were the same samples used for the chromatography in Figure 1. Chromatographic resolutions were achieved on a methyl silicone gum capillary column (5 m; x 0.53 mm x 2.65 um film thickness) coupled to a flame ionization detector. The temperature program was: $150^\circ$ C for 2 min, then increase the temperature at a rate of $15^\circ$ C/min to $295^\circ$ C. The chromatographic peaks of interest are numbered according to relative retention times.

**Figure 3.** **Leaching of Resin Components from a Bismaleimide Prepreg.** Leaching characteristics of the prepreg material were determined using 2.5 g of the prepreg in 500 ml flasks, containing 250 ml of water, that were shaken at ~200 rpm. At the given time points, aliquots of the aqueous portion of the mixtures were removed and extracted with ethyl acetate. The organic extracts were evaporated to dryness and the residues were analyzed with quantitative gas chromatography.

**Figure 4.** **Biotransformation of Benzene, 1,1'-(methylethylidiene)bis[4-(2propenyloxy)-.** The substrate, Benzene, 1,1'-(methylethylidiene)bis[4-(2propenyloxy)-,(27 ug/ml) was incubated with a mixed bacterial culture (333 ug dry weight/ml) at 25° C for 7 days. The entire culture was extracted and the level of substrate was assessed by quantitative gas chromatography as described under "Methods and Materials". Data points are the means ± SD of triplicate determinations. t-Tests showed no statistical difference between "time zero" and "negative control", however the "time zero" and the "biotransformed" samples were statistically different at $P < 0.001$.

## Table 1. Biochemical and Growth Analyses for Bacterial Characterization.

| Parameter | *Pseudomonas sp.* | *Bacillus cereus* |
|---|---|---|
| Colony Morphology | smooth, yellow | large, white |
| Gram Stain | - | + |
| Motility | +<br>polar flagella | - |
| Cell Morphology | rods | rods |
| An/Aerobic | aerobe | facultative anaerobe |
| Spores | - | + |
| Oxidase | + | - |
| Catalase | + | + |
| Urease | + | + |
| Arginine Dihydrolase | - | + |
| Gelatinase | - | + |
| Denitrification | - | ND |
| Fluorescent Pigments | + | ND |
| Utilization of: | | |
| Glucose | + | + |
| Lactose | - | - |
| Mannose | + | - |
| Arabinose | + | - |
| Xylose | + | - |
| Cellulose | - | - |
| Citrate | + | + |
| Maltose | - | ND |

+ = growth and/or acid production, - = no growth or acid production
ND = not determined

**Table 2. Characterization of the Prepreg Resin Components.**

| TLC Fraction (Rf) | GC Peaks (retention time) | Structure Assignment | Key Mass Spectral Ions |
|---|---|---|---|
| A (0.0-0.12) | none found | | |
| B (0.12-0.25) | Peak 2 (11.8 min) | unknown | |
| | Peak 7 (18.9 min) | 4,4'-Bis(maleimidoi phenyl)methane[a] | 358 (M+), 329, 261 |
| C (0.25-0.55) | none found | | |
| D (0.55-0.75) | Peak 1 (11.5 min) | possible isomer of Peak 4 | 308 (M+), 293, 253 |
| | Peak 4 (12.8 min) | Benzene, 1,1'-(methyl ethlyidiene)bis [4-(2-propenyloxy)-[b] | 308 (M+), 293, 159 |
| E (0.75-1.0) | Peak 3 (12.5 min) | possible isomer of Peak 4 | 308 (M+), 293, 159 |
| | Peak 5 (13.5 min) | Possible isomer of Peak 4 | 308 (M+), 293 |
| | Peak 6 (13.8 min) | unknown | 348 (M+), 329, 266 |

a   CAS #13676-54-5
b   CAS # 3739-67-1

163

PARENT

BIOTRANSFORMED

FIGURE 1

FIGURE 2

parent

biotransformed
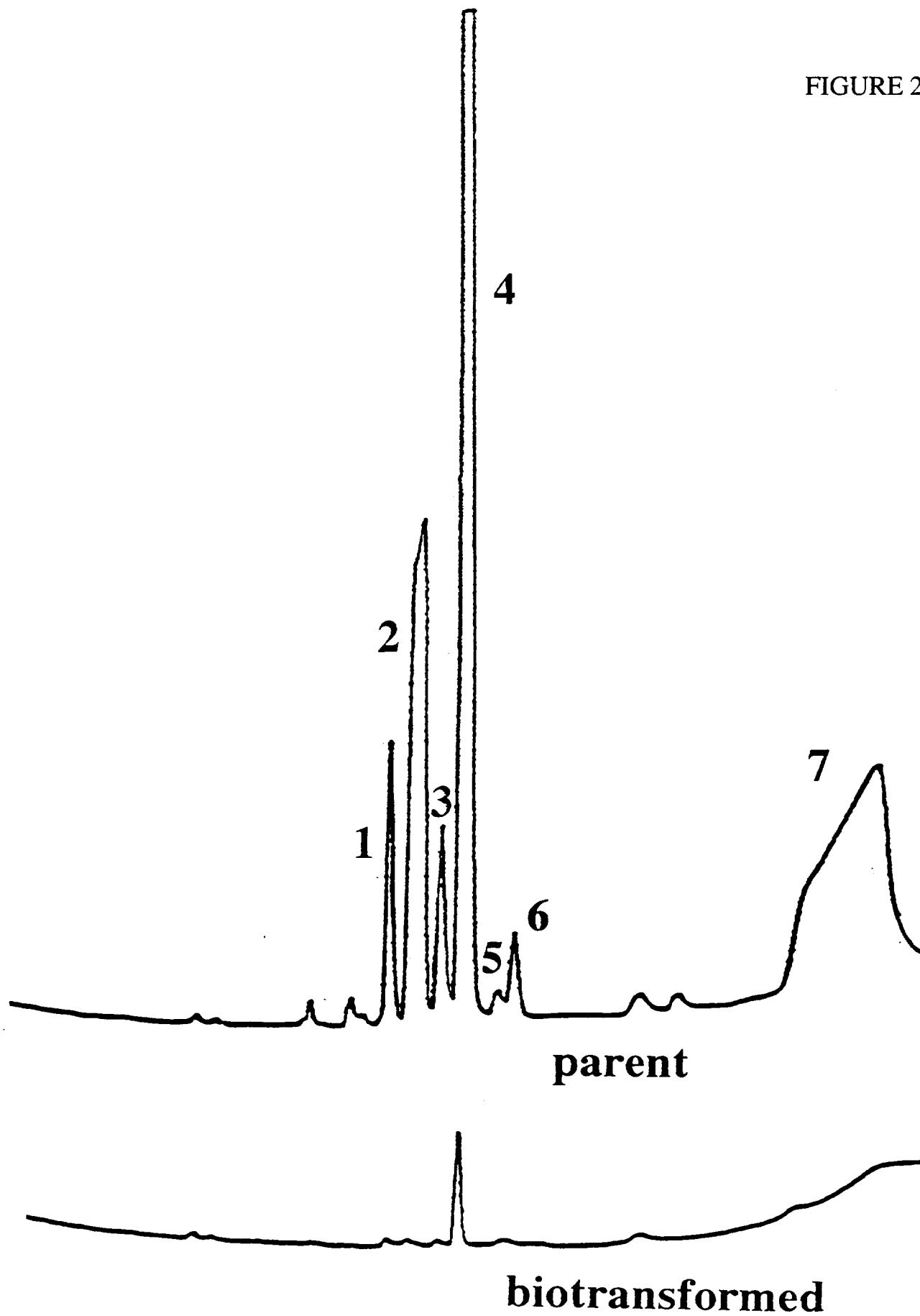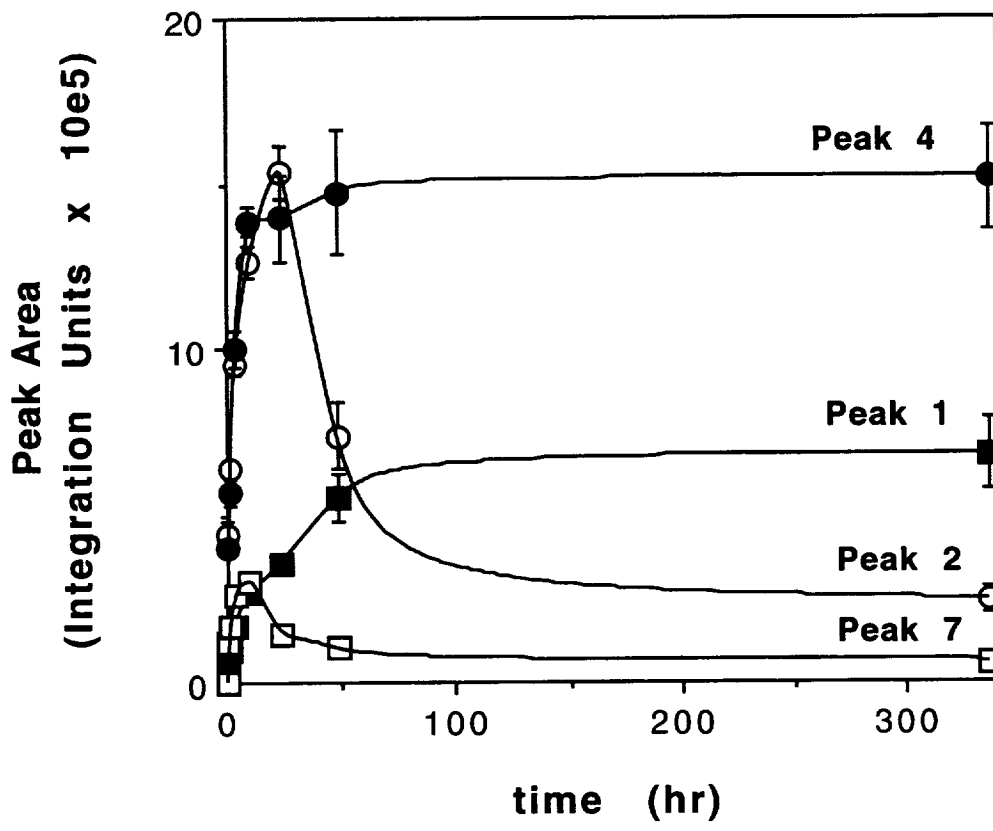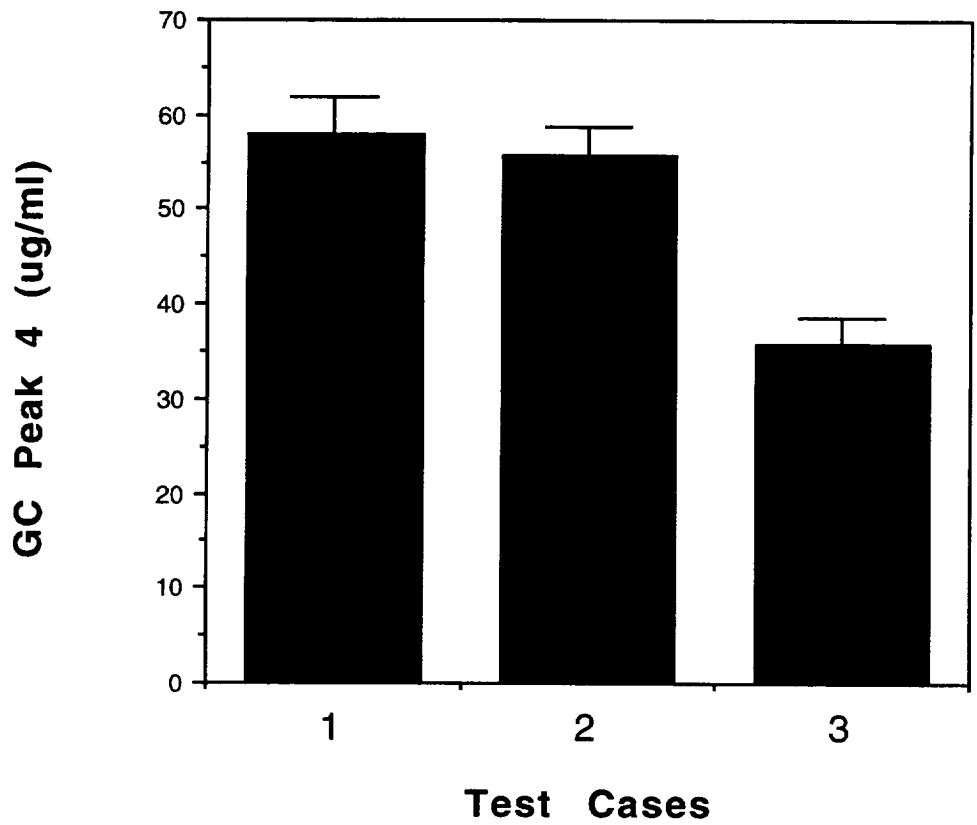
FIGURE 3

FIGURE 4

# Hazardous Waste Determinations for Partially Cured Prepreg Composite Materials
## *Roark Doubt, Boeing*

Hazardous Waste Characterization of Partially-Cured Prepreg

### *Issues to be Addressed at Boeing Defense and Space Sites*

- Free up limited hazardous waste landfill resources
  Verify designation of waste stream

- Reduce hazardous waste disposal costs at Puget Sound facilities

  Investigate methods of reducing costs

  Substitutes for materials that designate as Dangerous Waste

  Treatment by generator for Dangerous Waste materials that cannot be substituted

Hazardous Waste Characterization of Partially-Cured Prepreg

### *Composite Waste at Puget Sound Defense and Space Group Sites*

| Boeing Waste Description | Formulators Description | Disposition of Waste | Rel. Cost[a] |
|---|---|---|---|
| Uncured - frozen - on roll Scrap due to time and temp expiration or program reduction | B Stage | WSDW - conservative disposition - send to secured Landfill | 19 |
| Partially-cured - exposed to ambient Scrap primarily hand trim | B+ and C Stage | Non hazardous - disposed of conservatively in secured landfill | 17 |
| Fully-cured -processed through heat cycle | Cured | Non-hazardous - disposed in municipal landfill (waiver required by County) | 1 |

a Cost based on 1991 estimate, presented as multiple of disposal costs for fully-cured composite

Hazardous Waste Characterization of Partially-Cured Prepreg

---

*Waste Designation Background*

---

- RCRA Designation Criteria

    D001 - Ignitability
    D002 - Corrosivity
    D003 - Reactivity
    List for Toxicity

- WDOE Designation - Same as above plus (173-303-100)

    Toxicity
        Book Designation
        Bioassay

    Persistence
        Halogenated Hydrocarbon
        Polycyclic Aromatic Hydrocarbons

    Carcinogenicity
        WAC List

---

Hazardous Waste Characterization of Partially-Cured Prepreg

---

*Waste Designation Background (continued)*

---

- Washington State Toxicity Designation

    Book designation
        Available data
        Constituents - MSDS
        Toxicity - SAX

        Equivalent Concentration determination (for mixtures)
            EC(%) = X% + A%/10 + B%/100 + C%/1000 + D%/10,000
            (where X,A,,B,C& D are Toxic Categories)

        Chart (WAC 173-303-9906)

    Testing
        Bioassay
            - 100 ppm - EHW
            - 1000 ppm - DW

---

**WAC 173-303-9906   Toxic dangerous waste mixtures graph.**

## WAC 173-303-9906 :  Toxic Dangerous Waste Criteria Graph
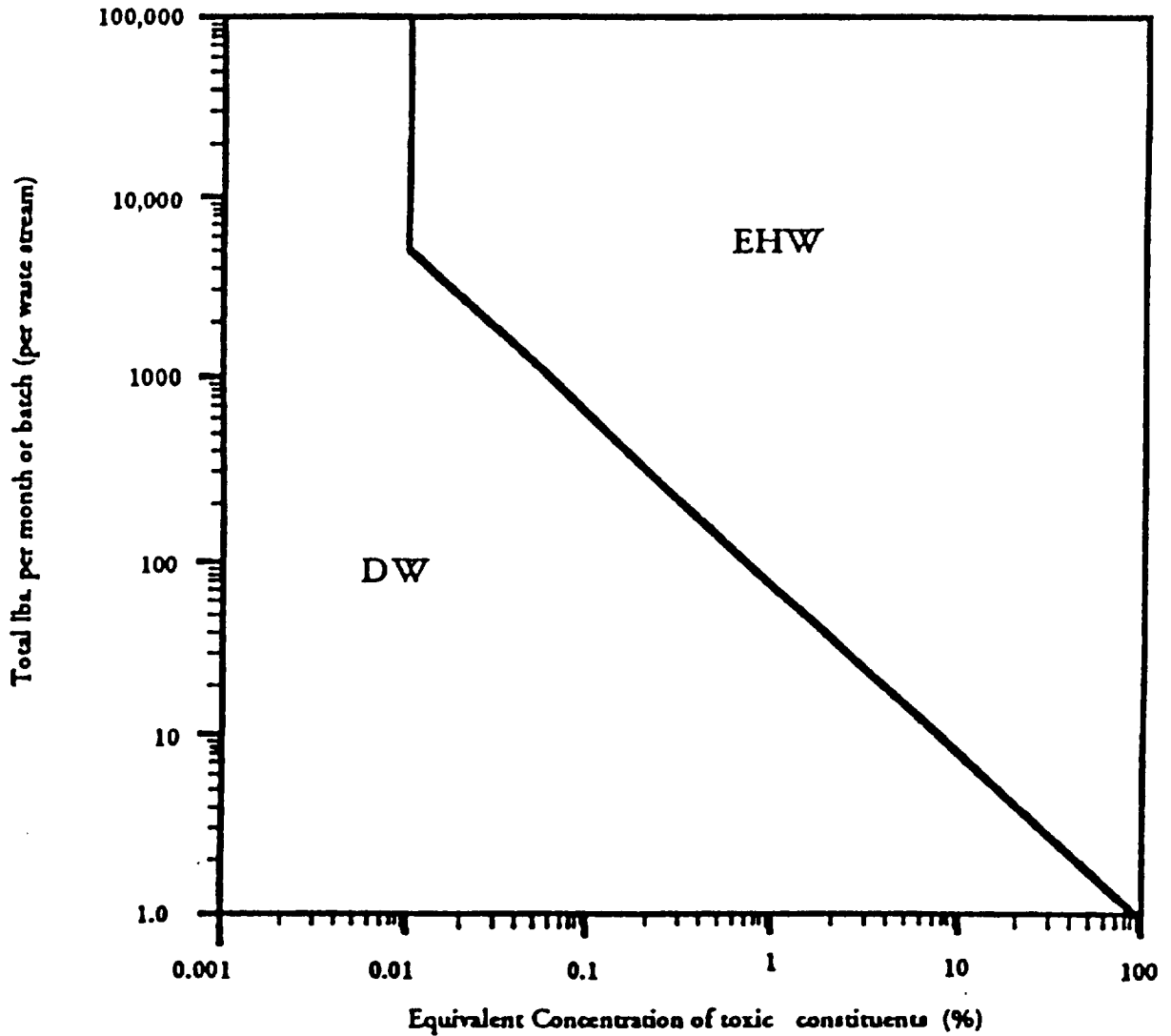
Hazardous Waste Characterization of Partially-Cured Prepreg

***Sample Conditions and Preparation***

- Choose representative material from each category

- Representative of waste
    at point of generation - 7 days (quazi-arbitrary)

- Preparation of sample
    Eliminate potential physical affects to aquatic life, i.e. fibers, dust

Hazardous Waste Characterization of Partially-Cured Prepreg

***Experimental Methods for Hazardous Waste Characterization Using Fish Bioassay***

- Sample Preparation- rotary agitation method

    -Sample placed in 1000 ml extraction vessel

    -Add 200 ml of extraction water (solution) to the extractor bottle

    -Mix on rotary agitation apparatus for six hours

    -Rinse all loose material from the flask into test fish tank
    and place bottle into tank so that it is laying on its side and filled with water

    -Chemical criteria for test water must be met and water monitored throughout test

- Fish Selection

    -Test Species: Rainbow Trout (Oncorhynchus mykis), all of the same age

    -Water Temp in Tanks: 12° C ±1

    -Fish Acclimation Required: 14 days on-site prior to testing

___

**Experimental Methods for Hazardous Waste Characterization**
**Using Fish Bioassay (continued)**

___

• Test Procedure

    - 30 fish total per test, 10 fish per tank using 3 tanks

    - 96 hour test, determine fish mortality at 24 hours intervals

    - Positive and negative control tanks required

    - EHW = > 10 deaths at 96 hr, at 100 mg/l, (>33.3% mortality)

    - DW = > 11 deaths at 96 hr. at 1000 mg/l, (>37% mortality)

___

Hazardous Waste Characterization of Partially-Cured Prepreg

___

**Results**

___

• Fish mortality varied across prepreg samples

• Relatively wide range of test results

    -DW testing ranged from 0 to 100 percent mortality
    -EHW testing resulted in all 0 mortalities

• Increased mortality noted with elevated resin/fiber ratio

___

## Fish Bioassy Results for Epoxy-Based Composites

| Sample # | Fabric | Curing Agent | Test Results[a] DW | EHW |
|----------|--------|--------------|------|-----|
| 1. | Film Adhesive (graphite/glass scrim) | Aromatic amine[b] | F (100)[c] | P (0) |
| 2. | Graphite | Aromatic amine | P (10) | NT |
| 3. | Graphite | Aromatic amine[b] | P (0) | P (0) |
| 4. | Fiberglass | NA (BF$_3$)[d] | P (30)[c] | P (0) |
| 5. | Nickel-coated Graphite | Aromatic amine[b] | P (0) | NT |
| 6. | Graphite | Aliphatic amine | F (100) | P (0) |
| 7. | Fiberglass | NA (Antimony oxide)[de] | P (0) | NT |

[a] Pass (P) or Fail (F) and percent mortality ( ) in test fish per WDOE 80-12 Test Procedure; DW, Dangerous Waste; EHW, Extremely Hazardous Waste; NT, not tested
[b] Identical base resin system
[c] Retest resulted in identical results
[d] NA, information not available, specific additive noted ( )
[e] This system is 250 ° F cure, all others are 350° F

## Conclusions

- Differences in potency of materials exisits within specific types of resin systems and possibly among materials meeting the same performance specifications

- Contribution of pretest leacheate vs 96 hour test leachaete to potency is not known

- Relative conc. of resin in composite may be factor in potency determinations

- Based on results of bioassay test, estimation of potency of new or untested materials based on resin or fiber system is not feasible

## Actions Taken

- TSCA Reporting , Section 8 (e)

- WDOE

  Update generator notification

  Notify factory and Environmental Services of changes in waste management requirements

  Segregation
  Collection
  Disposal

## Future Research

- Verify results consistent within matrix category

- Determine cost of segregation

- Methods of screening in coming materials

  Test prior to production approval

  Correlation of waste designation based on constituents (preferred to extensive testing)

# CHEMICAL RECYCLING OF SCRAP COMPOSITES

## Ronald E. Allred and Richard M. Salas
## Adherent Technologies
## 9621 Camino del Sol NE
## Albuquerque, NM 87111

## ABSTRACT

There are no well-developed technologies for recycling composite materials other than grinding to produce fillers. New approaches are needed to reclaim these valuable resources. Chemical or tertiary recycling, conversion of polymers into low molecular weight hydrocarbons for reuse as chemicals or fuels, is emerging as the most practical means for obtaining value from waste plastics and composites. Adherent Technologies is exploring a low-temperature catalytic process for recycling plastics and composites. Laboratory results show that all types of plastics, thermosets as well as thermoplastics, can be converted in high yields to valuable hydrocarbon products. This novel catalytic process runs at 200°C, conversion times are rapid, the process is closed and, thus, nonpolluting, and no highly toxic gas or liquid products have been observed so no negative environmental impact will result from its implementation. Tests on reclamation of composite materials show that epoxy, imide, and engineering thermoplastic matrices can be converted to low molecular weight hydrocarbons leaving behind the reinforcing fibers for reuse as composite reinforcements in secondary, lower-performance applications. Chemical recycling is also a means to dispose of sensitive or classified organic materials without incineration and provides a means to eliminate or reduce mixed hazardous wastes containing organic materials.

## INTRODUCTION

Fiber-reinforced composite materials offer high strength and stiffness, low weight, corrosion and fatigue resistance, and tailorability of properties to the structural designer. This unique combination of properties are used to increase the performance profile of military and civilian aircraft and vehicles, and the composite material content of these systems is increasing dramatically as each new generation is introduced. Recent additions to the Air Force inventory, the B-2, F117A, and F-22 (under development), are approaching the definition of "all composite aircraft" [1]. Increasing composites use in military and space

systems is expected to continue far into the next century [2,3] as is their use in commercial applications such as aircraft, recreation, and infrastructure components.

The vast majority of composites used today and projected for the future are polymer based. Most of those composites use thermosetting (crosslinked) polymers such as epoxies, phenolics, bismaleimides, polyesters, cyanate esters, and polyimides. Engineering thermoplastic matrix composites are beginning to be introduced and should see increased use in the future. Once a thermoset part is cured, it cannot be changed. Production parts with delaminations, high void content, or lack of dimensional control must be scrapped. Uncured or prepreg materials are also scrapped in large quantities from cutting losses and expiration of shelf life. There is currently no process available for recycling these materials, so they are landfilled with little regard for environmental effects or considerations for reuse.

The majority of high-performance composites have been developed to be temperature-resistant, stable structures. Their intractable nature makes them even more difficult to recycle or reuse than commodity plastics because of their cross-linked or thermally stable structures. Primary recycling (reuse in equivalent performance applications) of these materials is certainly unlikely, even with engineering thermoplastic-matrix composites. Thermoset-matrix composites cannot be changed once molded to shape because of their cross-linked chemical structure. Thermoplastic-matrix composites can be reformed; however, the severe processing conditions and ply orientation control required in high-performance applications make it unlikely that primary recycling will be applicable to most of those materials.

Secondary recycling (reuse in lower performance applications) approaches can be envisioned for both thermoset and thermoplastic composites. The majority of work on composites recycling that has appeared in the literature is concerned with grinding, chipping, or flaking the composite into suitable size to be used as filler in new molded composite parts [4,5]. Usually, the composite is ground into a fine powder with this approach. While that approach may be satisfactory for automotive sheet molding compounds, which are mostly filler to begin with, it will not provide the full value from the expensive fibers and resins used in high performance composites that may be achievable using other recycling processes. Other processes such as acid digestion or incineration in the case of glass-reinforced composites could be used to reclaim the fibers from some systems [6]. Those approaches generally appear impractical from an environmental point of view. Acid digestion uses harsh chemicals and conditions and creates a hydrocarbon/acid mixture that will require further processing. Incineration (quaternary recycling) is an option for carbon- and aramid-reinforced composites, but destroys what are valuable materials in the process and can be a source of pollution.

178

Chemical recycling [7,8] appears to be the most economical recycling method for high performance composites. A chemical recycling process separates the polymer from the valuable fibers as low molecular weight hydrocarbons. The fibers may then be reused as molding compounds, and the hydrocarbons reused as chemicals or fuels. Initial laboratory feasibility studies on chemical recycling of a variety of common consumer plastics, composites, and other organic materials show that this recycling process has the potential to economically recycle all types of polymer matrix composite materials. Results from those feasibility studies on composite materials are given in the following sections.

## EXPERIMENTAL PROCEDURES

The composite chemical recycling studies were conducted in a prototype continuous feed reactor shown schematically in Figure 1. Catalyst composition and process parameters are proprietary and are not covered in this paper. Each composite feedstock was converted using an identical set-up and amount of catalyst. Gas samples were collected in gas sampling tubes.

Conversion products were analyzed using gas chromatography/mass spectroscopy following the procedure specified in EPA Method 8270 for semivolatile analysis. The conversion products were dissolved in methylene chloride before introduction into the gas chromatograph. Elution peaks were analyzed by mass spectroscopy and identified by matching with a library of · 50,000 compounds.
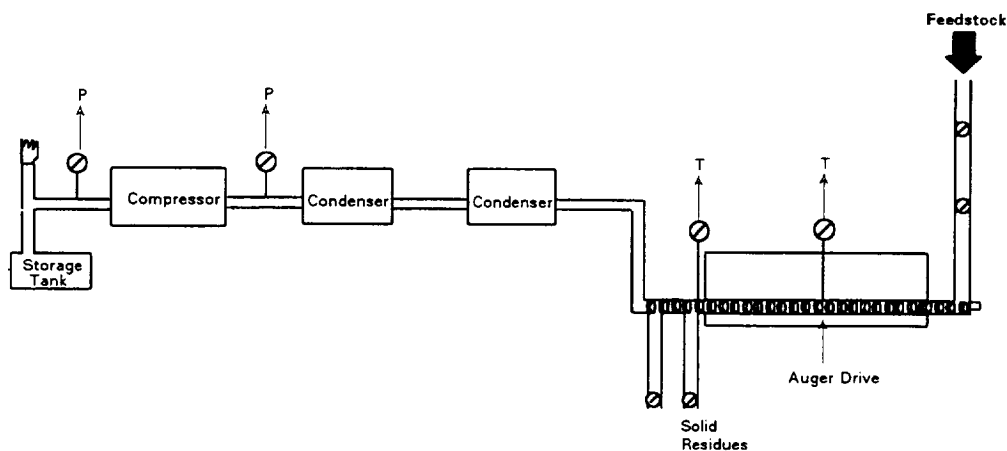


*Figure 1. Schematic Tertiary Plastics Recycling System*

## RESULTS AND DISCUSSION

Two types of epoxy matrix laminates were studied with the low-temperature catalytic conversion process. The first composite was a sample of boron-

reinforced epoxy from an F-15 tail rudder. Samples from the tail rudder skin were pried from the honeycomb core and most of the paint removed before the conversion process. The F-15 boron/epoxy was converted in four minutes leaving 56 weight percent of fiber and glass scrim cloth residue. Separate weights were not obtained for the boron and glass. The epoxy appeared to be completely removed from the composite laminates leaving behind only fibers. The boron fibers were a loose unorganized mass. No evidence of epoxy could be found upon microscopic examination of the fibers.

The chemical composition of the composite used in the F-15 empennage structure has been published by the Air Force [9]. The composition and chemical structures in the Boron/Avco 5505 (now Textron) are given in Figure 2. Major conversion products (>4%) from the F-15 boron/epoxy sample and their chemical structures are given in Figure 3.

## Analysis of Avco 5505

| Composition | | Weight Percent |
|---|---|---|
| Boron Fibers | | 60.1 |
| Fiberglass Scrim Cloth | | 4.1 |
| Resin Matrix        phr<br>  Ciba ECN 1280   70.0<br>  Ciba 0510   30.0<br>  Diglycidyl Ether Bisphenol A   3.0<br>  Dicyandiamide   5.4<br>  Crosslinked Elastomer   ? | } | 35.8 |



glycidyl ether of a cresol formaldehyde novolac
(CIBA ECN 1280)

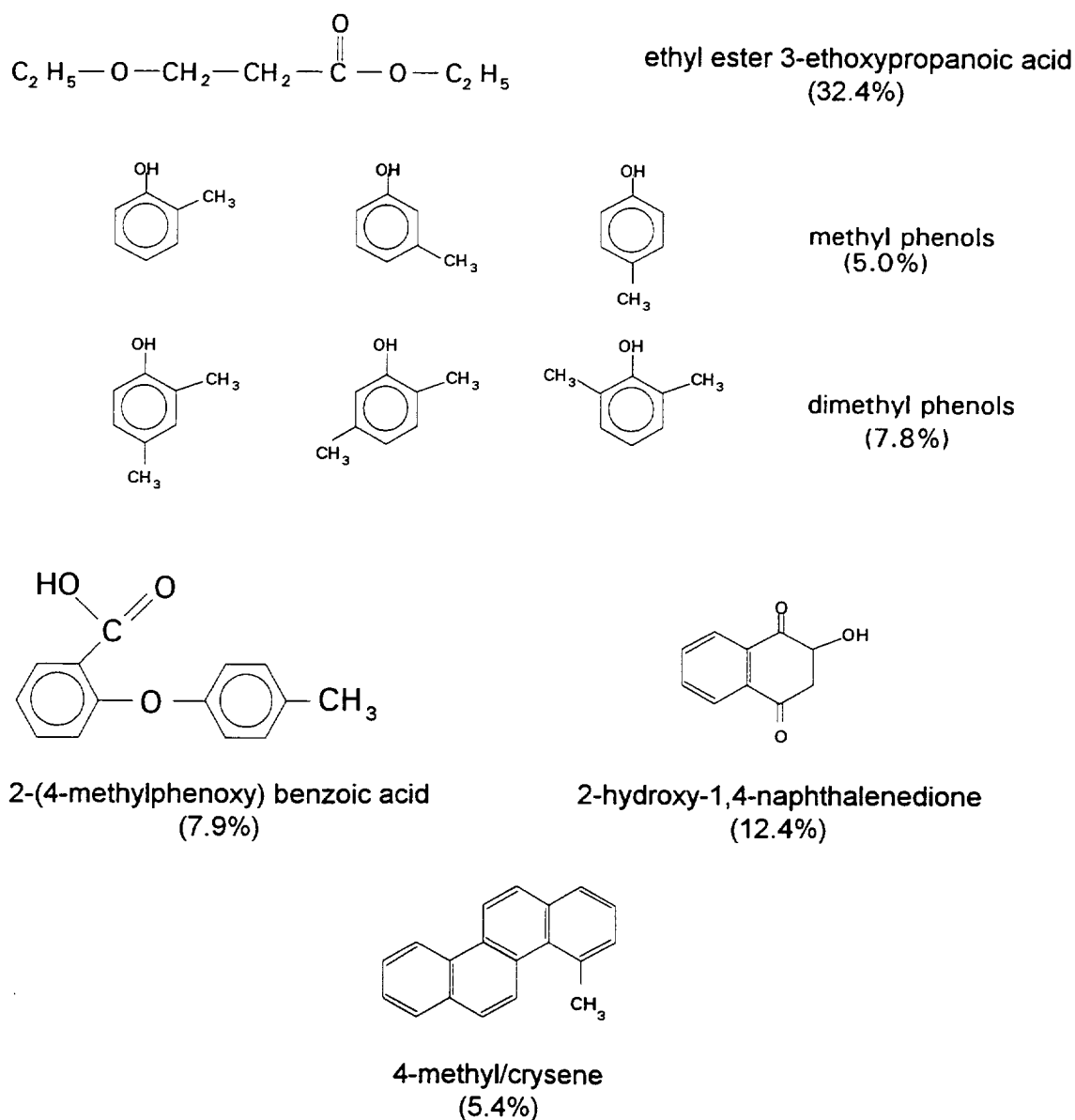n, n-diglycidyl-p-aminophenylglycidyl eth
(ERL 0510, TGPAP)
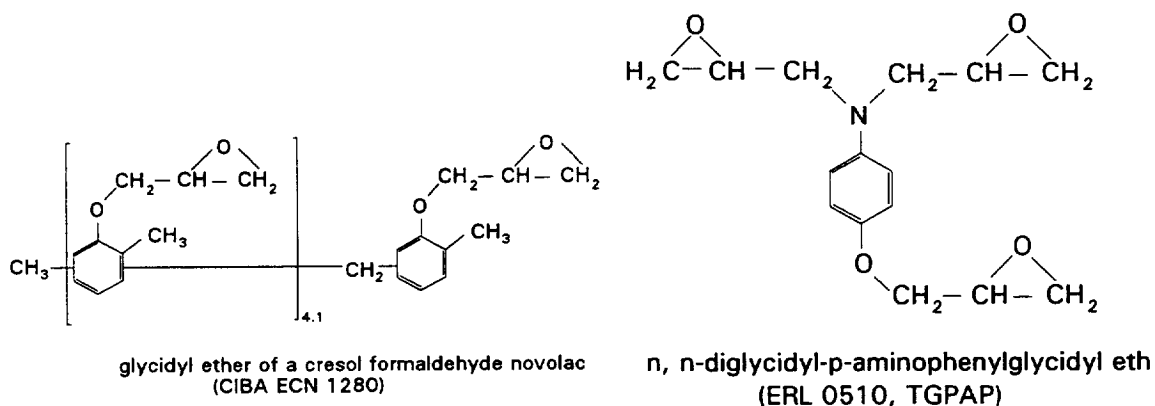
*Figure 2. Composition of Avco 5505 Boron/Epoxy Used in F-15 Tail Rudder [9]*

180

Comparison of the major conversion products from the boron/epoxy F-15 rudder (Figure 3) and the starting epoxide structure shown in Figure 2 shows that the conversion process scissions the methylene and ether linkages to form valuable low molecular weight hydrocarbons from what was an intractable cross-linked epoxy. A high concentration of ethyl ester of 3-ethoxy-propenoic acid is seen. This compound was also seen in the conversion products from other epoxies [10] and appears to be a recombination product from the glycidyl groups found in all epoxy resins.



$C_2 H_5$—O—$CH_2$—$CH_2$—C(=O)—O—$C_2 H_5$

ethyl ester 3-ethoxypropanoic acid
(32.4%)

methyl phenols
(5.0%)

dimethyl phenols
(7.8%)

2-(4-methylphenoxy) benzoic acid
(7.9%)

2-hydroxy-1,4-naphthalenedione
(12.4%)

4-methyl/crysene
(5.4%)

*Figure 3. Chemical Structures of F-15 Boron/5505 Epoxy Major Conversion Products*

The second epoxy matrix laminate studied was a unidirectional 24-ply carbon fiber-reinforced system from Hexcel Corporation designated F584. The carbon/F584 conversion reaction was complete after 4.5 minutes. The remaining carbon fibers represented 69 weight percent of the original composite. No other residues were observed. On a volume basis, 69 weight percent carbon fibers corresponds to 61 volume percent, which is the normal fiber volume range for this type of composite.

The carbon fibers remained as single-ply sheets that could easily be spread apart. In that form, the carbon fibers are readily reusable as reinforcements for molding compounds. Major conversion components of the F584 epoxy system are given in Figure 4.



aniline
(5.4%)

4-methylbenzeneamine'
(5.1%)

3-phenoxy benzaldehyde
(17.4%)

4,4'-diamino-1,1'-biphenyl
(8.3%)

$$C_2H_5-O-CH_2-CH_2-\overset{\overset{\text{O}}{\|}}{C}-O-C_2H_5$$

ethyl ester 3-ethoxypropanoic acid
(34.8%)
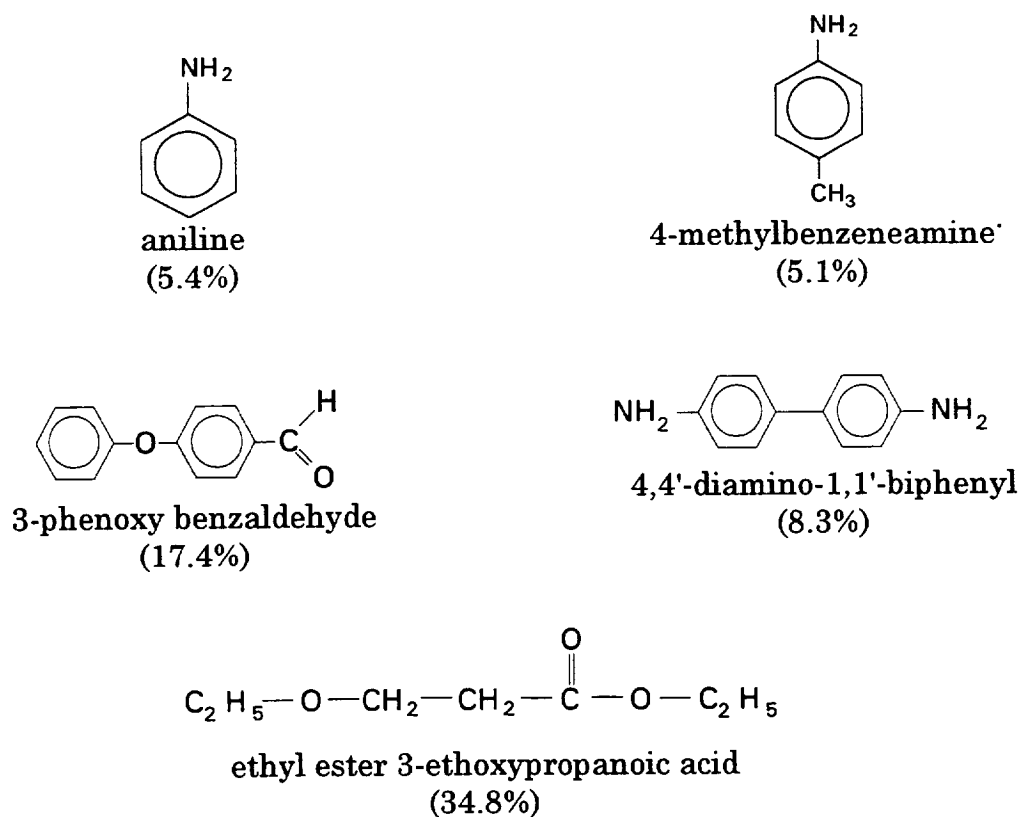
*Figure 4. Conversion Products from F584 Epoxy*

The starting epoxy components in the Hexcel F584 matrix system are proprietary and unknown to the authors. Examination of the major products for the F584 epoxy (Figure 4) shows that there are several aromatic amine compounds (aniline, methyl aniline, diamino biphenyl), which likely indicates that this epoxy is an aromatic amine-cured system.

182

Analysis of the gas fraction given off from carbon/F584 epoxy conversion showed 98.4% propylene. Propylene likely comes from the glycidyl groups that have been scissioned from the ether linkages during conversion.
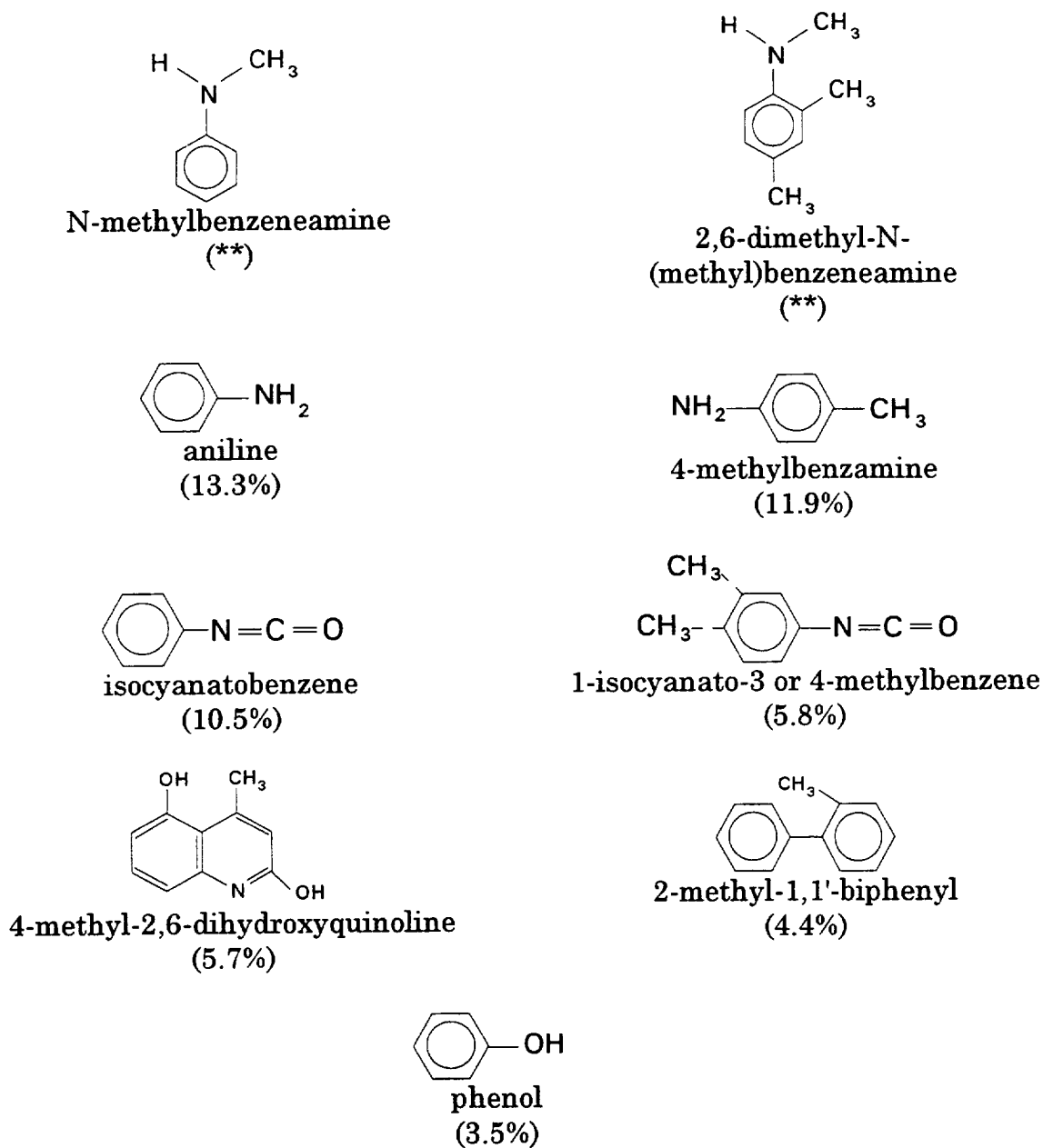
The third composite studied is a high-temperature polyimide matrix system. Polyimide and bismaleimide matrix composite materials are preferred for high-temperature applications near engine ducts and for future aircraft such as the high-speed civil transport. The most common polyimide matrix system in use is PMR-15, which is formed by a condensation reaction between the dimethyl ester of 3,3',4,4'-benzophenonetetracarboxylic acid, 4,4'-methylenedianiline, and the monomethyl ester of 5-norbornene-2,3-dicarboxylic acid [11]. The resultant structure is shown in Figure 5.
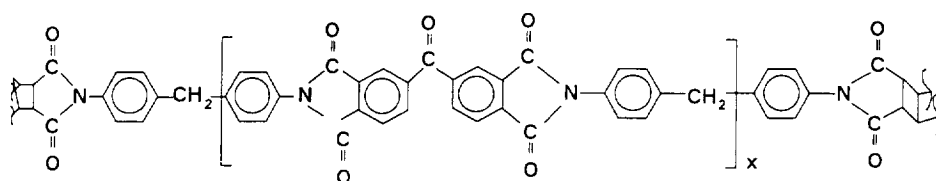


*Figure 5. Chemical Structure of Cured PMR-15 Polyimide*

The carbon/PMR-15 composite was converted only very slowly. A yellow gas evolved three minutes into the reaction. After 20 minutes, enough tar coated the reaction vessel to take an analysis sample, but the composite was not completely broken down. The persistence of the PMR-15 is a further demonstration of the high thermal stability of these materials. Analytical results for the PMR-15 conversion products are shown in Figure 6.

Comparison of the product structures shown in Figure 6 with the PMR-15 structure (Figure 5) reveals that the catalytic conversion reaction is scissioning the imide rings to make a variety of substituted phenyl compounds and recombination structures. This is an encouraging result and may indicate that even these very stable polymer structures can be broken down completely if the conversion process parameters are optimized.

N-methylbenzeneamine
(**)

2,6-dimethyl-N-
(methyl)benzeneamine
(**)

aniline
(13.3%)

4-methylbenzamine
(11.9%)

isocyanatobenzene
(10.5%)

1-isocyanato-3 or 4-methylbenzene
(5.8%)

4-methyl-2,6-dihydroxyquinoline
(5.7%)

2-methyl-1,1'-biphenyl
(4.4%)

phenol
(3.5%)

**Combined total is 28.6%.

*Figure 6. Chemical Structures of PMR-15 Conversion Products*

The last example is an engineering thermoplastic matrix composite:
polyetheretherketone (PEEK) reinforced with carbon fibers. Analysis of the
clear liquid evolved from the carbon/PEEK sample and the structure of PEEK
are given in Figure 7. Ninety-nine percent of the liquid conversion products
from PEEK are phenol and hydroquinone. These are two common and valuable

organic compounds. Producing these compounds in such high yields and purities will likely result in good economics for recycling of PEEK matrix waste components.
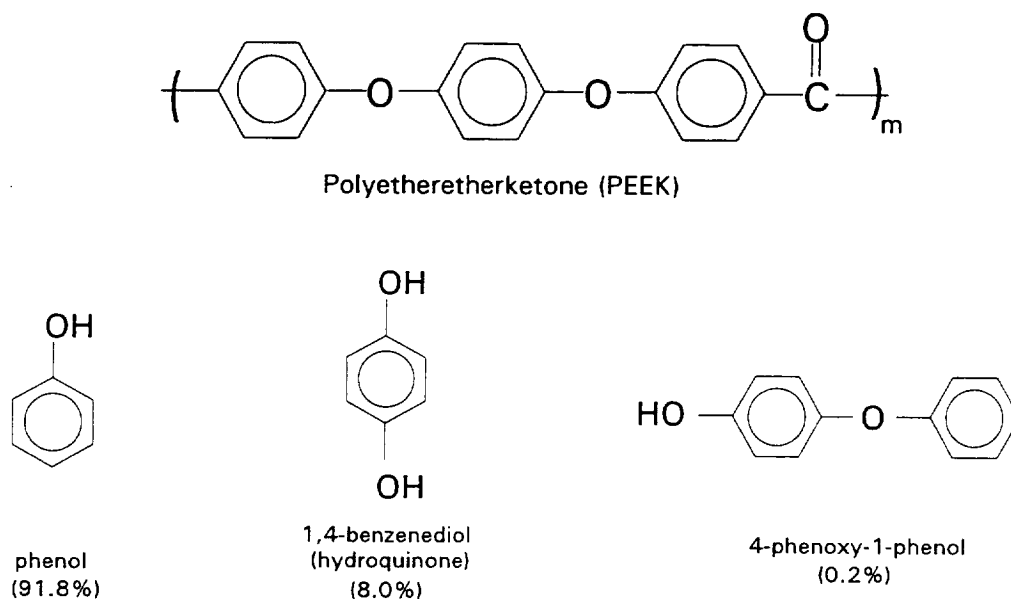


Figure 7. Chemical Structure of PEEK and its Conversion Products

## PROCESS ECONOMICS

The economics of low-temperature, catalytic conversion of high performance composites is difficult to assess accurately at this early stage of development. There are numerous unknowns such as gathering and transportation costs for the waste, volumes of waste available, and markets for the conversion products and reclaimed fibers. Nevertheless, it is beneficial to ignore these unknowns and perform an elementary economics analysis to show the economic viability of the tertiary recycling process.

A 10-ton/day unit operated 330 days per year can recycle 6.6 million pounds of composite or about 15% of current DoD production. Such a plant could be expected to be highly profitable if the hydrocarbons were sold at a price equivalent to that of crude oil and the carbon fibers were sold for use in molding compounds at $2.00 per pound, which is equivalent to the cost of buying virgin glass with the superior properties of carbon fibers.

Assumptions: ❖ Fiber yield          0.6 @ $2.00/pound

❖ Resin yield          0.4 @ $0.08/pound

❖ 10 ton/day capacity

❖ 330 days/year

Projected Revenues:

Fibers (3.96 x $10^6$ lb @ $2.00)          $7,920,000.00

Hydrocarbons (2.64 x $10^6$ lb @ $0.08)          $ _211,200.00_

Total          $8,131,200.00

Operating Expenses:

$1,500,000 plant operation

$_660,000_ shredding operation ($0.10 per pound)

$2,160,000

Gross Profit: $5,971,200

Capital Requirements: $6-8,000,000 (reactor, shredder, site preparation)

*Figure 8. Carbon/Epoxy Composite Recycling Economics Projection*

## CONCLUSIONS

The low-temperature catalytic conversion process under development has been shown to be extremely versatile for breaking down all types of organic materials into low molecular weight hydrocarbons for reuse. Even high thermal stability thermosetting polymers have been converted to valuable low molecular weight organic compounds without producing any highly toxic byproducts. By

removing the polymer from the composite mixture, the expensive reinforcing fibers are recovered in a form that allows their economical reuse in molding compounds. This versatile process may be used to solve many current and future solid and hazardous waste problems with organic-based materials. Because the conversion process is totally closed, no adverse environmental effects are produced. In addition, a preliminary economic analysis shows that recovery of valuable hydrocarbons and fibers from these wastes could be highly profitable.

## ACKNOWLEDGMENTS

## REFERENCES

[1]    V.P. McConnell, "An Investment in Peace: The Advanced Tactical Fighter," *Advanced Composites*, July/Aug 1990, pp. 27-32.

[2]    V.P. McConnell, "Progress Report: Composites in Spacecraft," *Advanced Composites*, July/Aug 1991, pp. 26-34.

[3]    V.P. McConnell, "Next Decade Defense: Less Is More," *Advanced Composites*, Jan/Feb 1993, pp. 18-28.

[4]    "Recycling in Action", *Reinforced Plastics*, February 1992, pp. 32-33.

[5]    "Recycled SMC Now in Appearance Parts," *Plastics Technology*, October 1993, p. 94.

[6]    R. E. Allred and N. H. Hall, "Volume Fraction Determination of Kevlar 49/Epoxy Composites," *J. Poly. Sci. Eng.*, Vol. 19, October 1979, pp. 907-909.

[7]    R. D. Leaversuch, "Chemical Recycling Brings Real Versatility to Solid-waste Management," *Modern Plastics*, July 1991, pp. 40-43.

[8]    P. Mapleston, "Chemical Recycling May Be an Option to Meet Mandated Reclaim Levels," *Modern Plastics*, November 1993, pp. 58-61.

[9]    D. K. Hadad, J. S. Fritzen, and C. A. May, "Exploratory Development of Chemical Quality Assurance and Composition of Epoxy Formulations," Air Force Materials Laboratory Technical Report, AFML-TR-77-0217, January 1978.

[10]   R. E. Allred and R. M. Salas, "Recycling Process for Aircraft Plastics and Composites," AT-93-5133-FR-001, Final Report submitted by Adherent Technologies to the Environics Directorate, Tyndall AFB, FL, December 10, 1993.

[11]   T. T. Serafini, P. Delvigs, and G. R. Lightsey, "Thermally Stable Polyimides from Solutions of Monomer Reactants," *J. Appl. Polymer Sci.*, Vol. 16, No. 4, 1972, pp. 905-906.

# OFFGASSING TEST METHODOLOGY FOR COMPOSITE MATERIALS

by
Dale A. Scheer
McDonnell Douglas Aerospace

## ABSTRACT

A significant increase in the use of composite materials has occurred during the past 20 years. Associated with this increased use is the potential for employees to be exposed to offgassing components from composite systems. Various components in composite systems, particularly residual solvents, call offgas under various conditions. The potential for offgassing to occur increases as a composite material is heated under either during cure or during lay-up operations. Various techniques can be employed to evaluate the offgassing characteristics of a composite system. A joint effort between AIA and SACMA resulted in the drafting of a proposed test method for evaluating the offgassing potential of composite materials. The purpose of testing composite materials for offgassing is to provide the industrial hygienist with information which can be used to assess the safety of the workplace. This paper outlines the proposed test method and presents round robin testing data associated with the test method. Also in this presentation if a discussion of classes of compounds which require specialized sampling techniques.

SPEAKER:
Dale A. Scheer
McDonnell Douglas Aerospace
Analytical Chemical Laboratory
Dept. 257, Box 516
St. Louis, MO 63166
(314) 234-9807

### Biographical Sketch

Dale Scheer is currently a principal technical specialist with McDonnell Douglas Aerospace in St. Louis. He received a Bachelors Degree in Chemistry from the University of Missouri in 1980. For the past ten years he has worked in the area of gas chromatography/mass spectrometry. Much of his work at McDonnell Douglas has focused on the identification of offgassing components resulting from various manufacturing processes. Mr. Scheer is currently coordinating the efforts of the SACMA/AIA Offgassing/Combustion Products Task Force. This task force is developing a test method to evaluate the offgassing characteristics of composite materials.

# Process Emission Initiatives by the Society of the Plastics Industry, Inc.

Joseph McDermott
Composites Services Corporation

# Outline of Contents

# I. Relevance of plastics industry research to aerospace composites
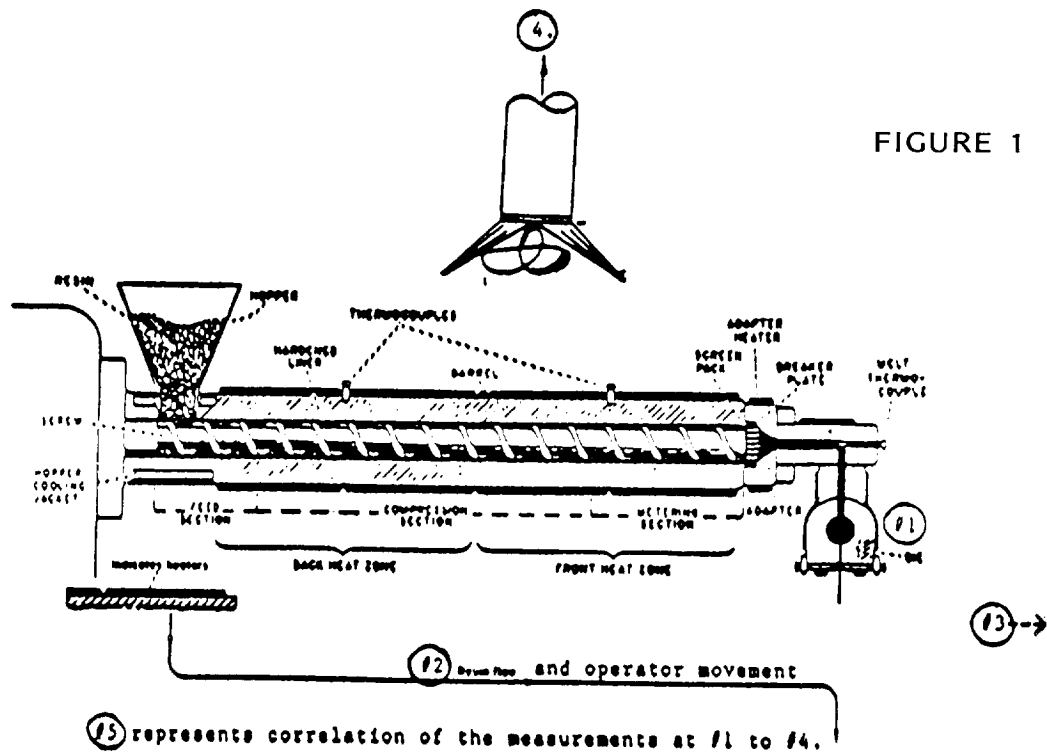
At first view, plastics process emissions research may not seem to have much bearing on outgassing considerations relative to (advanced) composite materials, as discussed by other speakers in this session. We believe several parallel issues and cross-currents are of mutual interest, however, and that different perspectives among the audience will identify these for themselves. At the very least, many within the aerospace industry and NASA use plastics and fiberglass articles in non-structural roles. Familiarity with topically-driven research in those areas may prove useful within readers' organizations.

Figure 1 illustrates topics of concern to plastic processors in the context of "off-gassing" as that term is used on the shop floor. Compliance requirements range from observation of OSHA's Hazard Communications Standard, through TSCA, various industrial hygiene standards, to EPA's environmental regulations.

Today's summary is concerned only with the effort to quantify volatile organic compound (VOC) emissions within the meaning of Title I of the Clean Air Act, and the effort to characterize and quantify hazardous air pollutants (HAPs) within the meaning of Title III.

FIGURE 1

|  | Compliance pressure | Status | Research requirement | Other need | Priority |
|---|---|---|---|---|---|
| 1. Thermal degradation products | HCS Prop. 65 TSCA | Not yet widely affecting processors | Not within scope of OHEIC: too varied, specific | Management educational information | Moderate |
| 2. Operator exposure | OSHA 1910.1000 Part 6 b) rules | Current enforcement | NIOSH methods exist and accepted | Briefing from available sources | Moderate |
| 3. Industrial area sample | Supplemental; STELs (?) | Occasional use | Not evident-adaptable from NIOSH, EPA | General guidance, case study examples | Low |
| 4. Environmental emission | SIPs, Clean Air Act. Local ordinances. | Current problem for bsns formation. In future, more widespread. | EPA methods published, some may not apply. | Case method workshops on state usages. CAA compliance newsletter. | High for current applicants; will be high for many others later. |
| 5. Correlations | Exclusions, exemptions, threshold determinations | A developing concern. techniques of high interest for post 1994. | Data and ratio gathering first. Testing later to fill gaps. | Validations: e.g., "low ppm at work station—no environmental emissions." | Moderate to 1994; High in '94-98 period |

# II. Impact of Clean Air Act Amendment Requirements

A new regime of Federal air quality laws are to be implemented this fall and early in 1995 by the states. Over 34,000 facilities which use chemical compounds will eventually be affected. Some local air pollution control districts have already begun to notify stationary sources of new filing requirements. There will be considerable variation between local requirements. Many manufacturers previously exempt from air pollution permits will now need to conduct measurements or otherwise secure data to determine how their state's rules apply to their facility. Even small air pollution sources will need to do considerable research to document that their activities are below the threshold of regulation.

The Society of the Plastics Industry (SPI) activities have concentrated on Titles I, III, and V of the Act. Title I, among other subjects, regulates volatile organic compound (VOC) emissions depending on a metropolitan area's ozone attainment status. Title III proposes regulation for 189 specific air toxics, listed as "hazardous air pollutants" (HAPs). Some HAPs are ozone precursors, and therefore potentially regulated under VOC provisions in Title I, as well as the HAP provisions of Title III. Styrene is an example. Title V of the Act describes minimum criteria for the states' air permit programs. Because of the unprecedented complexity of the permit process, SPI is very active with compliance alerts and as a guidance source on Title V.

In particular, students of the CAAA are following states' efforts to provide certain sources with means to "opt out" of the full Title V Permit process. This option is available to sources which are classified as "major" by their theoretical "potential to emit" but in fact have a much smaller release of tons per year of air pollutant.

Such sources can accept a "Federally-enforceable" (sometimes "FESOP") limitation such as a rule limiting volume of materials usage, a ceiling on their operating hours, or some other measurable limitation.

The intermittent or batch process nature of polymer composites production suggests that such "FESOPs" may be viable for many aerospace component producers. Others may need to identify MACT -- Maximum Achievable Control Technology -- for their process and build or retrofit their facility accordingly.

A full analysis of the CAAA, particularly MACT analyses, is beyond the scope of this presentation. But it was foreseen as early as 1989 that processors would need more refined tools simply to identify and quantify environmental emissions from their facilities, even before translating this information to permit applications and prior to considering process controls.

Unlike traditional permit programs, Title V puts the burden on the applicant -- not the regulatory agency -- to specify all applicable requirements, and to show how control strategies will be implemented and compliance will be proven. In addition to all applicable air-quality regulations (including those promulgated but not yet in effect), permit applications must describe products and processes produced at a site, and identify fuels and raw materials, pollution-control and monitoring devices, and data-collection procedures.

# III. Scope of the Society of the Plastics Industry, Inc. activities

The Society of the Plastics Industry, Inc. (SPI) is the major national trade association for the U.S. plastics industry. SPI is comprised of more than 2000 member companies, representing approximately 75% of the dollar volume of plastics sales in the United States. SPI is organized to provide general "core" services which benefit all segments of the industry. But, reflecting the diversity of the use of plastics, it also operates units or committees organized along materials, process, or market lines. These committees include resin manufacturers, distributors, machinery manufacturers, plastics processors, model makers and other industry-related companies and individuals. Founded in 1937, SPI serves as the "voice" of the plastics industry.

## A. Thermoplastic process emissions

### 1. University of Lowell research

Research was commissioned in 1991 by the Society of the Plastics Industry's (SPI) Occupational Health and Environmental Issues Committee (OHEIC) at the University of Lowell, Massachusetts. The objectives of this work were several: to establish a protocol for identifying and quantifying polymer off-gasses, and to ascertain whether there were constant ratios between off-gasses at the work station and emitted pollutants from the facility. The study is in the literature, as a poster paper given at the 1993 meeting of the American Industrial Hygiene Association: "Thermal Emission Identification of Organic Vapors Generated During Plastic Processes," C.W. Lu, R. Moure-Eraso, M.J. Ellenbecker, Department of Work

Environment; N.R. Schott, J.C. Huang, Department of Plastics Engineering Department, University of Massachusetts at Lowell, Lowell, MA 01864.

Organic vapors, and in some cases benzene soluble particulate (BSP) and total particulate, were sampled from the hot melt industrial processing of plastic and analyzed to measure vapor and particulate emissions. Organic vapor samples were collected on charcoal tubes and analyzed using gas chromatography/mass spectrometry. Four plastic processes were studied using industrial size machinery: injection molding, extrusion strand, extrusion sheet, and thermoforming. Nine organic vapor samples were taken six inches from the melted plastic output. Five particulate samples and five BSP samples were taken. Organic vapor samples were 2 to 6 liters, and particulate and BSP were 60 to 150 liters.

In the processing of medium-impact polystyrene, for example, nine major organic compounds were found, i.e., 1) benzene, 2) toluene, 3) acetophenone, 4) styrene, 5) benzaldehyde, 6) ethyl benzene, 7) alpha methyl styrene, 8) isopropyl benzene, 9) $C_{16}H_{12}$ isomer.

Percentages of organic compounds emitted were calculated by dividing the amount of each component by the total mass of all collected emissions. Emissions were detected for each plastic process cited above. The emissions actually sampled were a fraction of the total emitted since the conditions of industrial production preclude the stoichiometric capturing of all emissions at steady state. The focus of the study was the emissions generated by plastics processing at industrial operating temperatures. Emissions from additives or purging operations were beyond the scope of this study.

Essentially, this research effort became confused by the diversity of objectives, the discrepancy of interest between analytical chemists and industrial hygienists, and disagreement between the academic and industrial participants on how to simulate industrial production. The work was therefore useful in revealing the complexity of the off-gassing issue. It set the stage for more appropriately-controlled research elsewhere.

## 2. Polymer processing research at Battelle Institute

The unsuccessful work at Lowell moved supplier members of SPI's OHEIC to refine objectives and separate into task groups based on materials composition. Through proprietary research experience it was determined that facilities and expertise exists at the Battelle organization, Columbus, Ohio. Thus far polycarbonate, acrylonitrile butadiene styrene (ABS), and polyethylene resin systems have been evaluated. Nylon, polypropylene, and additional task groups are forming in line to have analysis performed through this facility, using appropriate variants of the basic protocol.

The fume generation facility at Battelle is used to generate and capture fumes produced during the processing of resins and composite resin systems. This facility was specifically designed to perform safety evaluations of fumes produced

during plastic processing under controlled conditions which model industrial practice.

The program consisted of the following two phases: 1) development and validation of a fume sample collection and analysis method, and 2) collection and analysis of fumes emitted from selected production processes. The experimental design was developed by Battelle.

A method was developed which used stainless steel canisters treated by the Summa passivating process to collect the VOCs in fumes generated, for example, from the extrusion of ABS resins. The canister samples were analyzed concurrently by a gas chromatography system equipped with parallel flame ionization detection (FID) and mass selective detection (MSD). A similar method was successfully used in past studies characterizing aircraft engine emissions for the U.S. Air Force. (Aircraft Emissions Characterization from selected engines, Reports ESL TR 87-27 and 87-63 Tyndall AFB, Florida, March 1988. Available through NTIS.)

The characterization of process off-gasses in the Battelle research is comprehensive. Table I illustrates the range of compounds identified during the extrusion of ABS. Despite its complexity, the value of the work at Battelle is proving very practical for plastics processors. The research has documented that, in common production, 180 micrograms of VOC emission are generated for every gram of representative compound. In other words, a processor of 1 million pounds of ABS annually will emit only 180 pounds of VOCs, well below the threshold of regulation even in severe non-attainment zones. As to characterization, ethylbenzene was the largest component of the VOCs, with an emissions rate of 50 micrograms per gram of ABS.

The data indicates that a facility will process a great deal of this family of resin to reach any of the thresholds. A typical high-volume plastics processor, finding emission rates in the part-per-million range, will calculate to less than a ton of annual VOC emissions in this particular scenario.

Polyolefin manufacturers now have followed the ABS lead to calculate emissions rates, while Dow Chemical has calculated polystyrene emissions independently. Suppliers who have done such research are at a competitive advantage when they can supply emission rate data to processors applying for Clean Air Act permits.

## 3. Revision of EPA Manual AP-42

SPI OHEIC's research was given new impetus by a contract let from EPA's Office of Air Quality Planning and Standards in 1993. EPA selected contractor MRI Inc. to review the existing AP-42 Manual's chapter on plastics process emissions and propose a "Development of Test Strategies for Polymer Processing Emission Factors" if any gaps in the existing emission factor guidance were found.

SPI was dismayed to learn that EPA even tentatively considered using the 1985 AP-42 in the context of the Clean Air Act Amendments. The chapter in question is very faulty, based on lost references or a cursory and outdated study performed

198

# TABLE 1

## TARGET ANALYTES AND TENTATIVELY IDENTIFIED COMPOUNDS FOUND IN PHASE 1 AND 2 FUME (CANISTER) SAMPLES

| Peak Number | Compound Name |
|---|---|
| 1* | 1,3-Butadiene |
| 2* | Acrylonitrile |
| 3* | 4-Vinyl-1-Cyclohexene |
| 4* | Ethylbenzene |
| 5 | m and p-Xylene |
| 6* | Styrene |
| 7 | o-Xylene |
| 8* | Isopropylbenzene |
| 9 | Benzaldehyde |
| 10* | n-Propylbenzene |
| 11* | Methyl styrene |
| 12 | 1-Methyl-2-isopropylbenzene |
| 13* | Acetophenone |
| 14 | p-Ethylstyrene |
| 15 | 1-Methylene-4-isopropylene cyclohexane |
| 16* | 2-Phenyl-1-propanol |

\* Target analytes

in 1978 by a research organization which no longer exists. Moreover, MRI's subsequent report repeated unrealistically high emission factors, in the range of 2.1% to 7.5% by weight, for thermoplastics. And, it proposed using pyrolysis with gas chromatography/mass spectroscopy as a laboratory simulation of polymer processing. Thermogravimetric Analysis (TGA) technique was proposed as appropriate to conclude process emission evaluations. SPI believes this approach is seriously deficient for the purpose intended.

- Pyrolysis GC/MS provides for a brutal destruction of the polymer and does not reflect the changes in the polymer which occur during actual processing. GC/MS may provide data, but we suspect it is very different from what is seen in industrial processing. Relative surface area is likely to be much smaller and the hot air exposure time may be much shorter. Additionally, pyrolysis GC/MS would provide no shear of the polymer and potentially high oxygen levels versus high shear and low oxygen levels in, for example, an extruder.

- Typically, TGA methods involve heating the polymer sample from ambient to high temperatures at a fairly slow rate (e.g., 10°C/min). To achieve simulated polyethylene (PE) processing temperatures (e.g., 260°), a residence time of more than 20 minutes would be required. Normal PE processing residence times are on the order of seconds to a few minutes.

- The TGA measures only overall weight loss. If coupled with FTIR the data would give general qualitative identification of emissions. TGA should be used only to identify substances of potential interest.

- The TGA method is designed to measure weight loss at percentage levels versus traditional trapping industrial hygiene equipment which can routinely measure to ppm levels. Analysis of the trapped components also can be compound-specific.

- The TGA method may not duplicate actual atmospheric conditions during processing. Most thermal processing steps result in very low levels of entrained air. TGA analyses run under an inert atmosphere (e.g., nitrogen) may underestimate the emissions, while analyses run under an oxidative atmosphere (air or oxygen) would overestimate them. Researchers have commented on TGA data's showing "creation of matter."

SPI believes these methods are suitable, at best, for qualitative identification of process emission compounds. They cannot generate quantitative emission factors. For this phase of the technology, SPI recommends conducting pilot scale tests using conceptual emissions models. The development of such models to a reliable level, however, will arise from successive pilot studies, not laboratory research. In the final assessment of emissions, the information must be checked in actual plant situations.

Polymer structure (molecular weight, its distribution, degree of unsaturation, and catalyst residuals) will affect emission types and levels. In addition SPI processors have assembled a shopping list of variables affecting a given facility's emissions:

- humidity
- available air volume
- air movement
- mold release used
- condition of process equipment
- aerosol content
- additive content
- filter media
- polymers processed at adjacent equipment

- polymers structure
- molecular weight
- branching
- other reactive gas present
- its own volume/other gas' volume
- cleaning solvent present
- vapor pressure
- thermal history
- comonomer type and level
- compound purity

# B. Reinforced plastics/composites process emissions

## 1. Pultrusion

Pultrusion processing of unsaturated polyester reinforced with continuous glass fiber is potentially a significant styrene emission source, to the extent that the glass passes through an open resin bath on its way to the shaping tool. Research by the Pultrusion Industry Council, a unit of SPI's Composites Institute has demonstrated that emissions at this work station are directly proportional to warm, unrestricted, airflow over wet surfaces. Re-engineering measures to minimize this feature of uncontrolled process emissions are relatively obvious in concept. The Council has recently joined with the SMC/BMC Environmental Committee described below to have an environmental engineering firm document MACT for the pultrusion process.

## 2. SMC/BMC emissions studies

The processing of sheet molding compound (SMC) and bulk molding compound (BMC) would appear at first glance to rank low as an emission source relative to other fiberglass composites manufacturing methods. Both prepreg-like materials are processed by closed molding methods, i.e. in compression presses or by injection molding. The mixing process, however, in which the resins are combined with fillers, pigments and other additives to make the "B-staged" molding compound can be a significant emissions source. SMC/BMC operations also tend to process relatively large amounts of material, since their major market by far is the automotive and light truck sector. Within the Composites Institute of SPI, an active SMC Environmental Subcommittee has shared within its membership the results of in-house emissions evaluation at members' own facilities. This group has also awarded a contract recently to an independent environmental engineering firm to perform an analysis of "Maximum Available Control Technology" (MACT) for their category of operation.

It might be mentioned here that SMC/BMC compounders and molders are high-volume users of VOC-generating cleaning solvents. While substitute cleaners are on the market, these do not appear capable of replacing aggressive solvents needed to clean molds and equipment where the contamination is out of line-of-sight or inaccessible to pressure cleaning. Recently a National Emission Standard for Hazardous Air Pollutants (NESHAP) has been published describing MACT for the aerospace industry using such cleaners. The technologies specified appear to have transfer value to other industries.

### 3. "Open molding" processing: CFA styrene emissions protocol

Another research project should be brought to your attention, if for no other reason than its appearance in future databases as a "composites" study. The research has additional relevance to the polymer composites audience in the event interest groups wish to undertake emissions testing which will be submitted to EPA. The agency has high interest in monitoring the quality of such research, and cannot be counted on to accept it outright. In fact, it is possible that industry or academic-initiated research, when intended to establish a protocol, may not be acceptable to EPA if it does not follow EPA's Quality Assurance procedures.

This test method development program is initiated by the Composites Fabricators Association. CFA is the trade association, with over 700 member companies, which serves the interests of small manufacturers who typically process unsaturated polyester or epoxy vinyl ester resins reinforced with glass fibers. (More of these companies are beginning to handle "advanced" materials, and certain advanced composites molders have joined CFA for its small-business program benefits.) CFA fabricators normally supply the recreational boating industry, the automotive and heavy truck aftermarkets, and both the residential and architectural construction industries. They are present as suppliers to general aviation, and as builders of prototypes and short-run orders for the commercial aircraft market as well.

CFA's program is driven by current state regulators' demands for Reasonably Available Control Technology (RACT) assessments. Also, the development of the Clean Air Act Amendment (CAAA) regulations, and in particular the Maximum Available Control Technology (MACT) standards for the reinforced plastic composites industry, will require definitive baseline data on styrene emissions from the open molding process.

The purpose of the CFA/EPA study is to measure styrene emissions from polyester resin spray application, polyester gel coat spray application and resin hand batch application. The accurate characterization of styrene emissions from this project will establish a background for subsequent studies, which will explore emissions reduction methods. Faulty conclusions from this study may lead to incorrect methods of addressing emissions reduction in subsequent studies. Therefore, a comprehensive Quality Assurance Plan will be in effect to support the testing program.

202

Investigations of available literature reveal that styrene emissions testing which has been done in the field presents an erratic and unacceptable range of results, which may be due to the uncontrolled environments in which the studies were conducted. This study will control environmental variables in order to isolate baseline emissions from the process.

### The Process and Test Facility

The open molding application methods included in this experiment are polyester resin spray application, polyester gel coat spray application and polyester resin hand batch application. The testing will be carried out at the Dow Chemical Composites Laboratory in Freeport, Texas. The test area is a 10' X 14" exhaust hood. Natural draft openings (NDO's) are arranged in accordance with EPA Method 204. See attached Sketch No. 1.

Airflow in the temporary enclosure will be maintained at 1500 cfm and ambient air temperature will maintained at 70°F. Sampling ports will be located in the exhaust duct. A three-sided mold of 30 ft$^2$ will be located in the center of the test enclosure at a height of 1 ft. above the ground.

The design of this experiment is intended to fulfill the requirements of a USEPA Category II Quality Assurance Project Plan (QAPP). The purpose of the Category II QA Project Plan is to present the data generated to the USEPA in an acceptable and standard format, in addition to maintaining a high confidence level in the development and handling of data.

This program is planned with a pretrial to verify the design of the experiment and to debug the emissions measurement procedures. Some of the details of the experiment may be altered as a result of the pretrial, however the basic protocol will remain the same.

Preliminary results are expected about November 1. The experiments and development of the procedure are likely to be discussed in both an EPA Control Technology Guideline, and in a monograph for the Air and Waste Management Association proceedings.

Emissions measurements will be made using both active and passive sampling. A Varian 3700 gas chromatograph, equipped with a flame ionization detector will be used. Passive dosimeter badges will be used in conjunction with the active sampling of the GC. These 3M brand passive dosimeters will be analyzed by the Dow Industrial Hygiene Services laboratory. Mass balance calculations will be made using all material input weights, minus cured test panel weight.
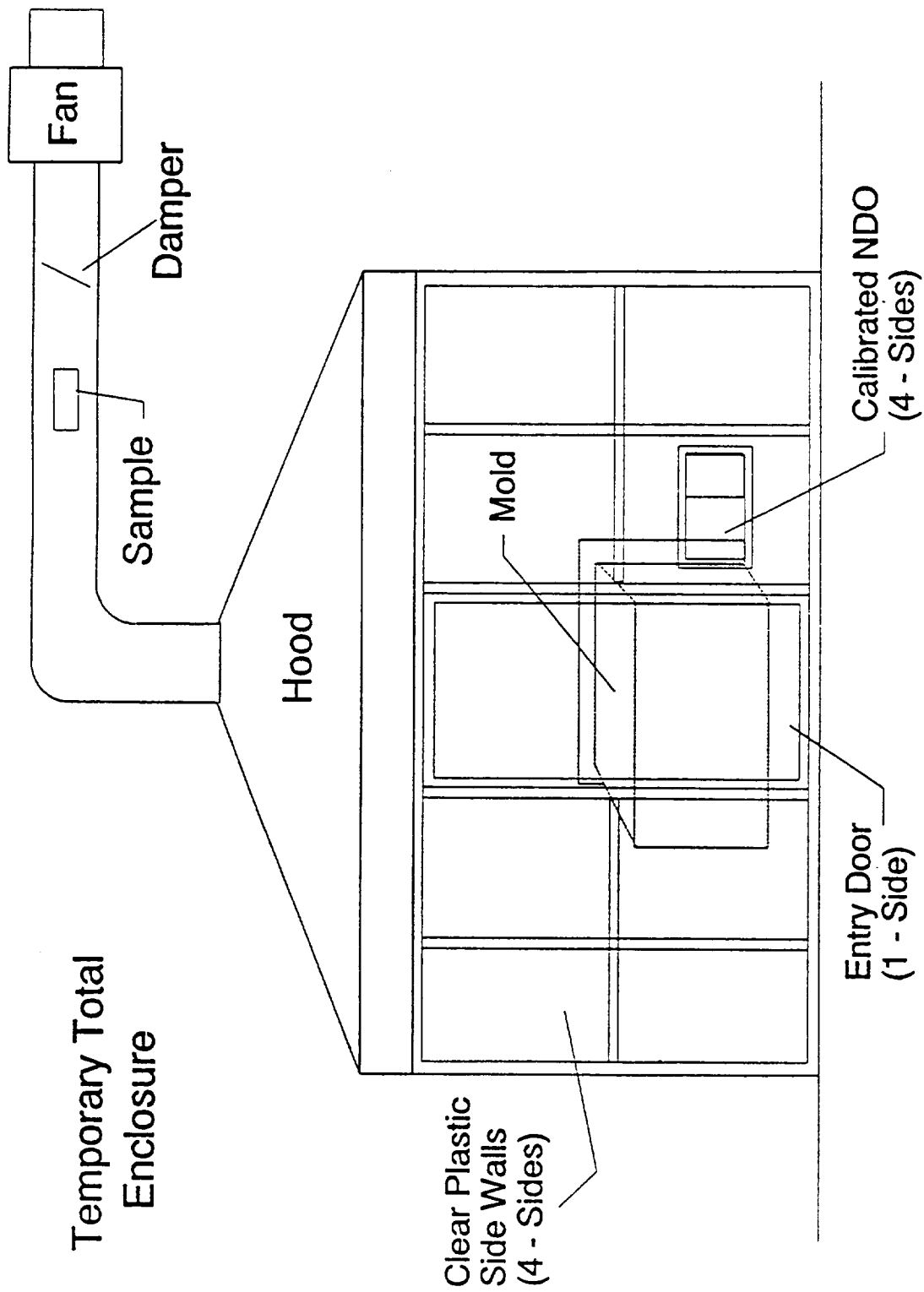
### Statement of Project Objectives

The project objective is to measure baseline styrene emissions from the open molding process. Air temperature and air flow will be held constant throughout the modified Taguchi experiments, to reduce environmental influences on emissions. The process will include resin spray application, gel coat spray application and resin hand batch application. The methods, materials and equipment used will represent a typical set of parameters

commonly found in the FRP composites industry. In the Phase I study no attempt will be made to reduce styrene emissions.

## Thermoset resin emissions

For survey completeness, it may be mentioned that the Epoxy Resin Systems Group of the SPI is developing information to establish a MACT NESHAP for liquid epoxy wet strength resins. At this time the scope of this research is the assessment of air toxics from the resin production facilities. It remains to be seen whether this activity will generate information useful to prepreggers and molding/fabrication users of epoxy compounds and prepregs.

Temporary Total Enclosure

Fan

Damper

Sample

Hood

Clear Plastic Side Walls (4 - Sides)

Mold

Entry Door (1 - Side)

Calibrated NDO (4 - Sides)

SKETCH No. 1

11A

# IV. Utility of SPI research for advanced polymer composites audience

Users of chemical compounds, including wet resins and advanced polymer composite prepregs, may be regulated under various provisions of the Clean Air Act Amendments of 1990. Resin producers are normally familiar with the intricacies of air pollution permit requirements, but small compounders, prepreg manufacturers and contract molders, and the polymer composite production shops of aerospace OEMs, will need to evaluate whether they are in the regulated community. This determination, and the generation of environmental emissions data for permit applications, is not easily completed. The numerous variables inherent in producing composite articles make it difficult for suppliers to provide users with useful emission factors valid for specific operating scenarios.

Research by polymer suppliers through their national trade association, SPI and its several operating units, has begun to sort out the complexities of production analysis. SPI has demonstrated that laboratory analysis by familiar analytical chemistry methods is not appropriate either for the identification or quantification of environmental air emissions from industrial processes which use polymer materials. SPI recommends well-designed process simulations, at as full a scale as possible to actual production conditions, and then verification of pilot-scale results under production conditions specific to the operator's practice.

EPA and the State Implementation Plans (SIPs) it approves will not necessarily accept industry-generated emission data from non-standard research demonstrations. Trade or industry-specific coalitions should work with EPA's

research offices at Research Triangle Park, NC to pre-quality such experiments. This step, while time-consuming, will facilitate adoption of industry evaluations into EPA Control Technology Guidelines in the case of VOC control, and NESHAPs in cases where MACT demonstration is required.

Aerospace end-users of composites who do not themselves manufacture these goods have a stake in monitoring their sources of supply to determine that they are prepared to generate data for all permits which will be required.

# OUTGASSING CONSIDERATIONS FOR COMPOSITES
## IN SPACE APPLICATIONS

By

Petar Arsenovic and Huai-Pu Chu
Goddard Space Flight Center
Greenbelt, MD 20771

## ABSTRACT

Composites have been increasingly used in the construction of spacecraft. However, unlike metals, composites must be used with particular discrection in space applications because of their outgassing properties. For example, the outgas materials may cause serious contamination problems and affect the performance of delicate instruments. This paper presents an overview of the testing procedure and acceptance criteria for outgassing selection of spacecraft materials. Since composites can contain and absorb moisture which will outgas in space as water vapor, the test results of moisture absorption and desorption of a composite material are discussed also.

## INTRODUCTION

The design of modern spacecraft has posed evermore stringent demands on materials. Advanced composites with unique properties have shown great promise to meet such demands. For example, composites have been selected for spacecraft structures, optical benches and instruments due to their high modulus, high strength and dimensional stability. Numerous successful applications of composites in spacecraft have been summarized in Reference 1.

However, it is important to note that certain composite materials may be disqualified for space applications because of their outgassing characteristics even though they do have other desirable properties. Thermoset and thermoplastic materials tend to be outgassers, especially at increased temperatures or in vacuum. They may emit gases and water vapors which would deposit, for instance, on lenses, mirrors and other parts of optical instruments and advsersely affect their performance. Therefore, all composites should be tested for outgassing before they are selected for use in spacecraft in order to prevent contamination. This paper presents a general discussion on outgassing, and summarizes the results of a recent study on moisture absorption and desorption of a composite, which is closely associated with the outgassing problem.

## OUTGASSING

### Test Method

The ASTM Standard E595-90 (Ref. 2) is commonly used for conducting outgassing tests for space applications. Briefly, the test utilizes a "microvolatile condensable system" which mainly consists of isolated sample chambers and collector chambers. Samples are heated to 125 $^{\circ}$C for 24 hours in a vacuum jar to accelerate the outgassing process. Also, testing the materials in vacuum is compatible with their use in space environment. The outgas products in each sample chamber travel through a hole to a corresponding collector chamber, wherein a portion of the outgas products will condense on a collector plate which is maintained at 25 $^{\circ}$C. Test results are determined from the condensed materials and the total amount of outgas from the samples. After testing in vacuum, the samples may be kept in 50% relative humidity at 25 $^{\circ}$C for 24 hours for an optional test to determine the amount of water reabsorbed by each sample. It is termed as water vapor regained (WVR) and expressed as a percentage of sample mass before the test. Because of the micro-quantities involved in the tests all procedures detailed in the ASTM Standard should be followed closely so as to obtain consistent and accurate results.

### Acceptance Criteria

Referring to the above, the mass of condensate on the collector plate is calculated as a percentage of the mass of the original sample; and this is the collected volatile condensible material (CVCM). Also, the total mass of material outgassed from the sample is determined by measuring the sample before and after the test. The total mass loss (TML) due to outgassing is expressed as a percentage of the initial sample mass. In general, materials which have CVCM $\leq$ 0.10% and TML $\leq$ 1.00% as specified in ASTM E595-90 are acceptable for space applications.

### Outgassing Data

Goddard Space Flight Center (GSFC) has extensive experience in the study of outgassing properties of materials for spacecraft applications. A wealth of GSFC test data has been made available to the space industry through a series of NASA publications over a period of some 20 years. The latest is NASA Reference Publication 1124, Revision 3, which includes GSFC outgassing data on many materials generated through July 1993 (Ref. 3). The data are also available through the Materials and Processing Technical Information Service (MAPTIS) data bank in Marshall Space flight Center,

Huntsville, Al. There are other sources of outgassing data, but they may not always conform to ASTM Standard E595-90.

Materials Selection

Although the outgassing data from Reference 3 or other sources can greatly facilitate the selection of materials for use in spacecraft, such test data should still be examined for each application to make sure that they are suitable for the particular functions and design requirements of the spacecraft. For example, the data may become questionable if a composite material is to be used at a temperature below 25 $^\circ$C, because the CVCM is determined from outgassing products that are condensable only at or above 25 $^\circ$C in the ASTM Standard test.

Sometimes outgassing data from different sources on one composite material may disagree with each other although they all have used the same ASTM Standard test method. This is quite possible for a number of reasons. For example, if the samples were taken from different batches with some slight variations in the manufacturing process they could have different outgassing properties; and this could happen even though the variations were all within the producer's specifications. For this reason, after a composite is selected for space application, it is still necessary to perform outgassing test on each batch of the material for quality conrol purposes.

In case a selected composite has all the preferred properties for a particular application except for outgassing, a thermal-vacuum treatment may be used to remove its outgassing materials. Also, some modifications in materials processing, such as a suitable change in the cure cycle, may bring about enough improvement in the outgassing property. If no method could sufficiently reduce its outgassing the composite should be replaced by an alternate material, or it may be used with some shielding or venting devices to protect the instruments from outgassing contamination.

**MOISTURE**

Experimental Procedure

The material tested was T50/ERL1962 graphite - epoxy coupons. For moisture absorption, twelve samples were thoroughly baked out at 90 $^\circ$C for 120 hours and then placed in different environments with respect to humidity in groups of three. The mass of each coupon was measured periodically over time at each humidity level with a high precision Ohaus analytical microbalance having a readability to 0.00001 grams. The coupons were exposed to 21%, 38%, 65%, and 100% relative humidity at 25 $^\circ$C.

Moisture desorption testing was accomplished by first preconditioning a set of graphite – epoxy coupons at 80 °C in an environment of 100% humidity for a period of 670 hours to ensure that the specimens were fully saturated with water. Following this, a Cahn vacuum balance was used to record the mass loss over time of the samples under a vacuum of $10^{-5}$ Torr at temperatures of 40, 60, and 90 °C.

## Results and Discussion

Moisture Absorption

Experimental data on moisture absorption are summarized in Figure 1. The vertical coordinate represents the average mass gains of specimans in three tests in each of the four differet relative humidity levels. The mass gain is defined as the measured increase in mass of a specimen during exposure to controlled humidity and expressed as a percentage of the initial mass of the dry specimen. Figure 1 shows that moisture absorption started with high rates which decreased quickly in low humidity and gradually in high humidity. Each curve appears to level off eventually toward a point of saturation which is dependent on the relative humidity.

It is interesting to note that the mass gain versus time curves become linear in log-log coordinates with approximately the same slope as shown in Figure 2. Therefore, an empirical equation can be established for the tested composite as

$$M = kt^{0.33} \qquad (1)$$

where   M = mass gain, %
        t = time, h

The quantity k is a function of relative humidity and is equal to the mass gain at unit time. Figure 3 shows that a plot of log H versus log k is linear. Thus,

$$k = (H/1238.40)^{0.85} \qquad (2)$$

where H is the relative humidity. After substitution into Equation 1, the overall moisture absorption behavoir can be described by

$$M = (H/1238.40)^{0.85} t^{0.33} \qquad (3)$$

This equation is simple and accurate, and represents the experimental data quite well, as seen in Figure 1.

Test data for moisture desorption are presented in Figure 4. The vertical coordinate represents the mass loss which is expressed as a percentage of the initial mass of the specimens after preconditioning in 100% relative humidity. Figure 4 shows that moisture desorption started with high rates which decreased quickly at high temperature and gradually at low temperature. The curves appear to level off eventually to a point when the coupons would be completely dry. It is interesting to note that the maximum mass loss is about the same magnitude of the mass gain shown in Figure 1. This indicates that all the moisture absorbed in the composite could outgas as water vapor in vacuum.

The moisture desorption data can be analyzed by a diffusion model (Ref. 4) as follows:

$$m = m_t[1-\exp(-7.3(t/t_c)^{0.75})] \qquad (4)$$

Where
$m$ = mass loss, %
$m_t$ = total change in mass, %
$t$ = time, h
$t_c$ = characteristic time, h

The change in mass, i.e. mass loss, is related to the "characteristic" time, which is in turn a function of the diffusion parameters. Thus

$$t_c = x^2/(D_o\exp[-Q/RT]) \qquad (5)$$

Where
$x$ = thickness of the material
$D_o$ = diffusion constant frequency factor
$Q$ = activation energy
$R$ = gas constant
$T$ = absolute temperature

Based on the test data, the activation energy associated with the diffusion process is determined as $Q=8.5$ KCal/Mol. The total change in mass $m_t$ is a parameter which is determined as $m_t = -1.2\%$ by its best fit to the experimental data using Equation 4. The number $m_t$ is given a negative sign to account for moisture desorption. A value of $D_o = 0.85$ in$^2$/hr is used. This value is also determined by the best fit to the data and is typical for an epoxy compound of this type (Ref. 5). The $t_c$ values are calculated for the three test temperatures as follows:

| T ($^o$K) | $t_c$ (hours) |
|-----------|---------------|
| 313       | 402           |
| 333       | 175           |
| 363       | 62            |

Figure 4 shows that there is a good agreement between Equation 4 and the experimental data.


## SUMMARY

The testing procedure and acceptance criteria for outgassing selection of materials to be used in spacecraft has been reviewed. Outgassing testing should be conducted according to ASTM Standard E 595-90. In general, materials with CVCM $\leq$ 0.10 % and TML $\leq$ 1.00 % are acceptable for space applications.

Test data on a composite material T50/ERL1962 are presented over time at various relative humidity levels at room temperature for moisture absorption, and under vacuum at several temperatures for moisture desorption (outgassing). The data can be accurately represented by simple equations which are useful for materials characterization.

## REFERENCES

1.    V. P. McConnell, " Progress Report: Composites in Space", Advanced Composites, July/August 1991, p.26

2.    ASTM Standard E 595-90, Standard Test Method for Total Mass Loss and Collected Volatile Condensable Materials from Outgassing in a Vacuum Environment, Annual Book of ASTM Standards, Vol. 15.03, American Society for Testing and Materials, 1992

3.    W. A. Campbell, Jr., and J. J. Scialdone, "Outgassing Data for Selecting Spacecraft Materials", NASA Reference Publication 1124, Revision 3, September 1993

4.    G. S. Springer, "Environmental Effects, Section 16 in Composite Design, 4th Edition, Edited by S. W. Tsai", Think Composites, 1988

5.    C. Barrett, W. Nix, and A. Tetelman, "The Principles of Engineering Materials", Prentice Hall, 1973, p. 155

6
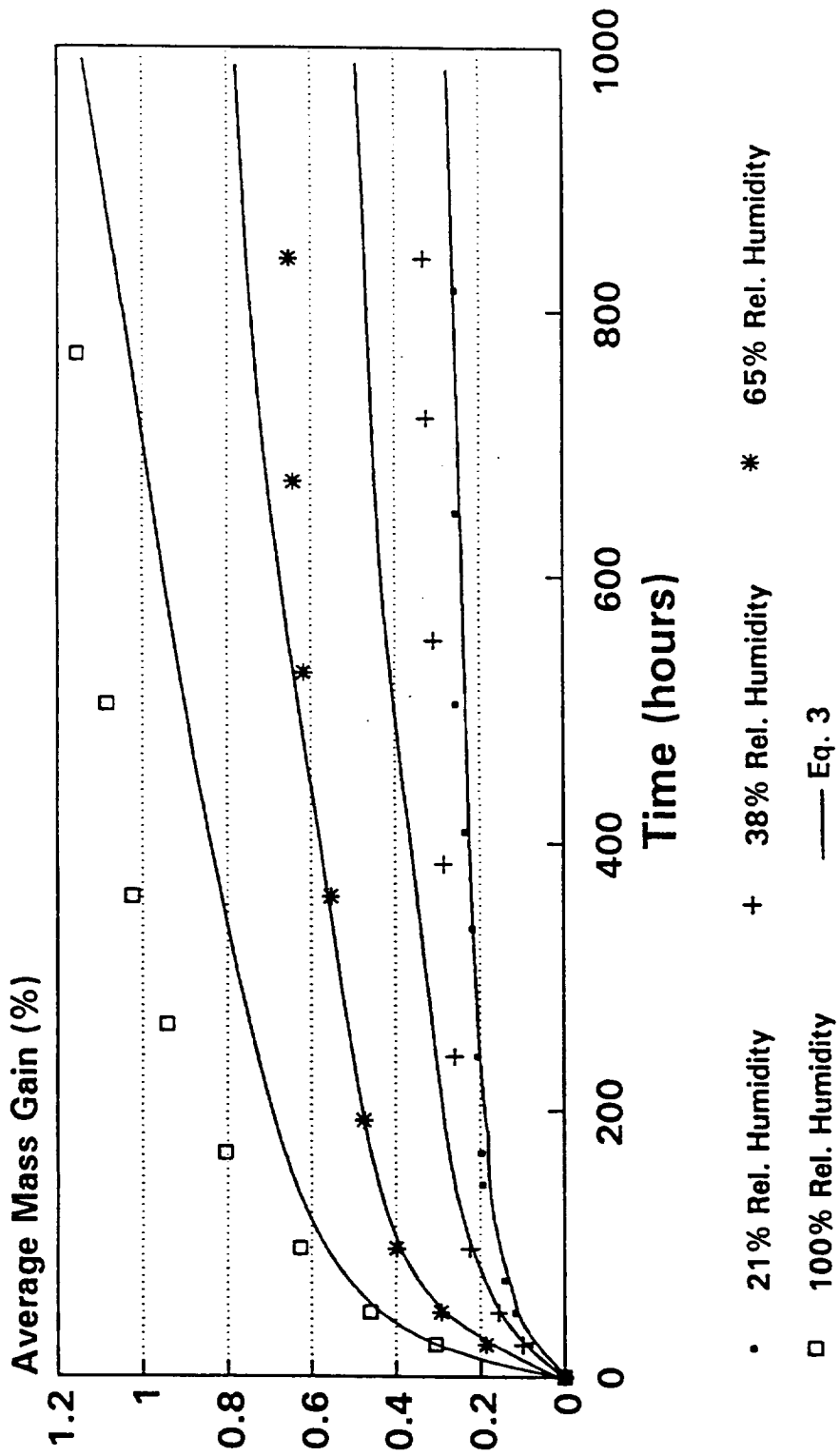
Fig. 1: Moisture absorption of
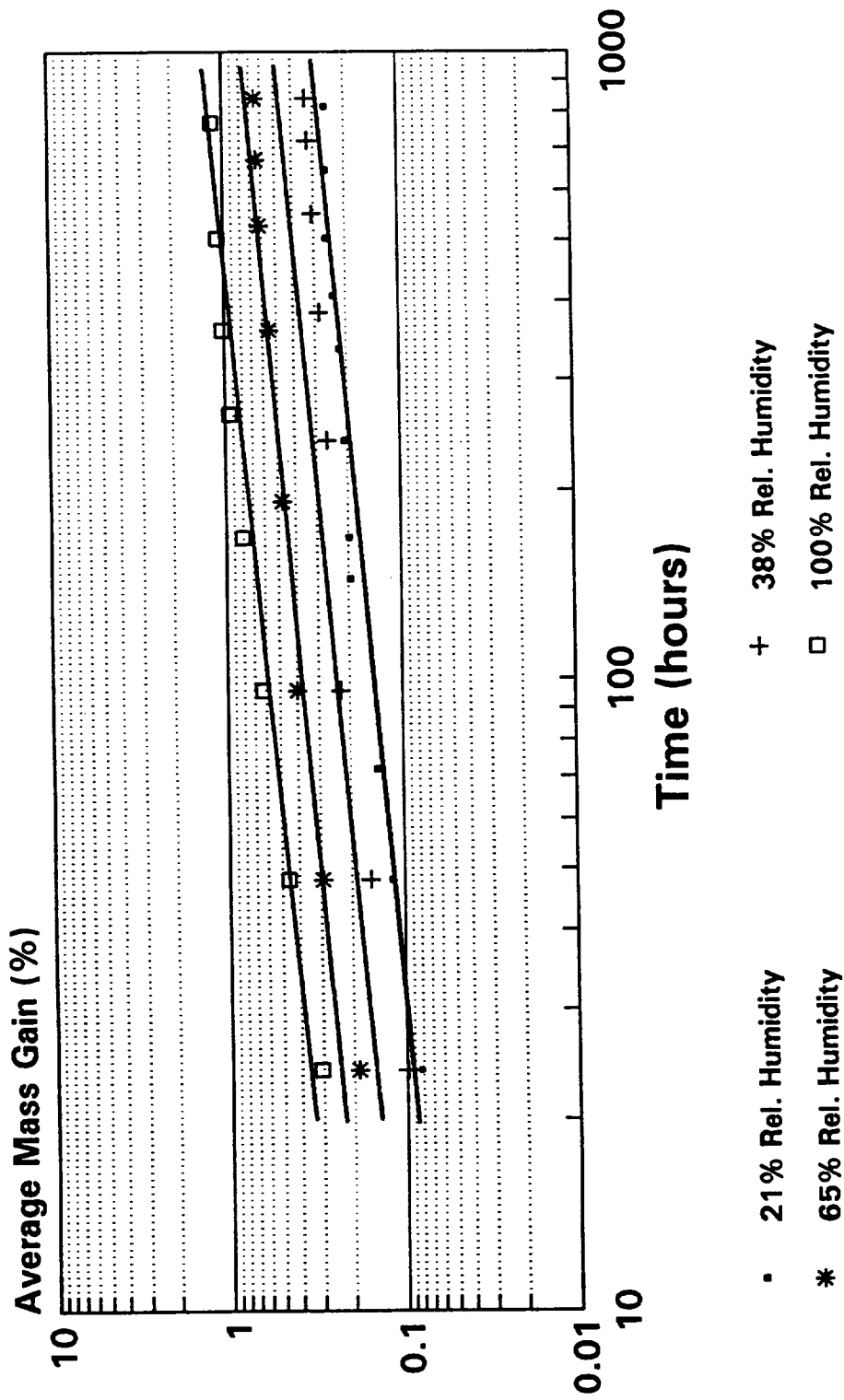T50/ERL1962 at four relative
humidity levels

Fig. 2: Log-Log plot of moisture
absorption data on T50/ERL1962

- 21% Rel. Humidity    + 38% Rel. Humidity
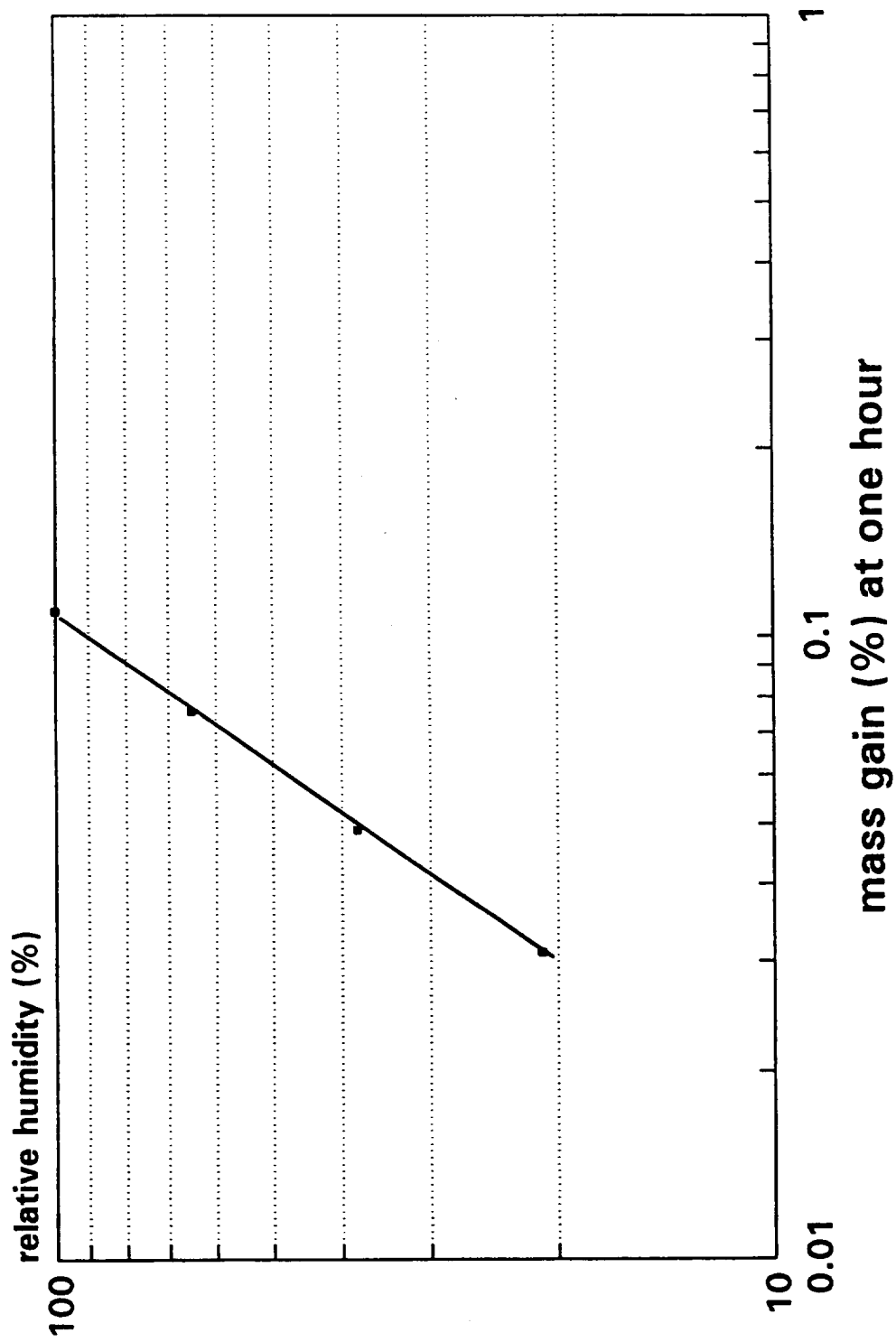* 65% Rel. Humidity    □ 100% Rel. Humidity

216

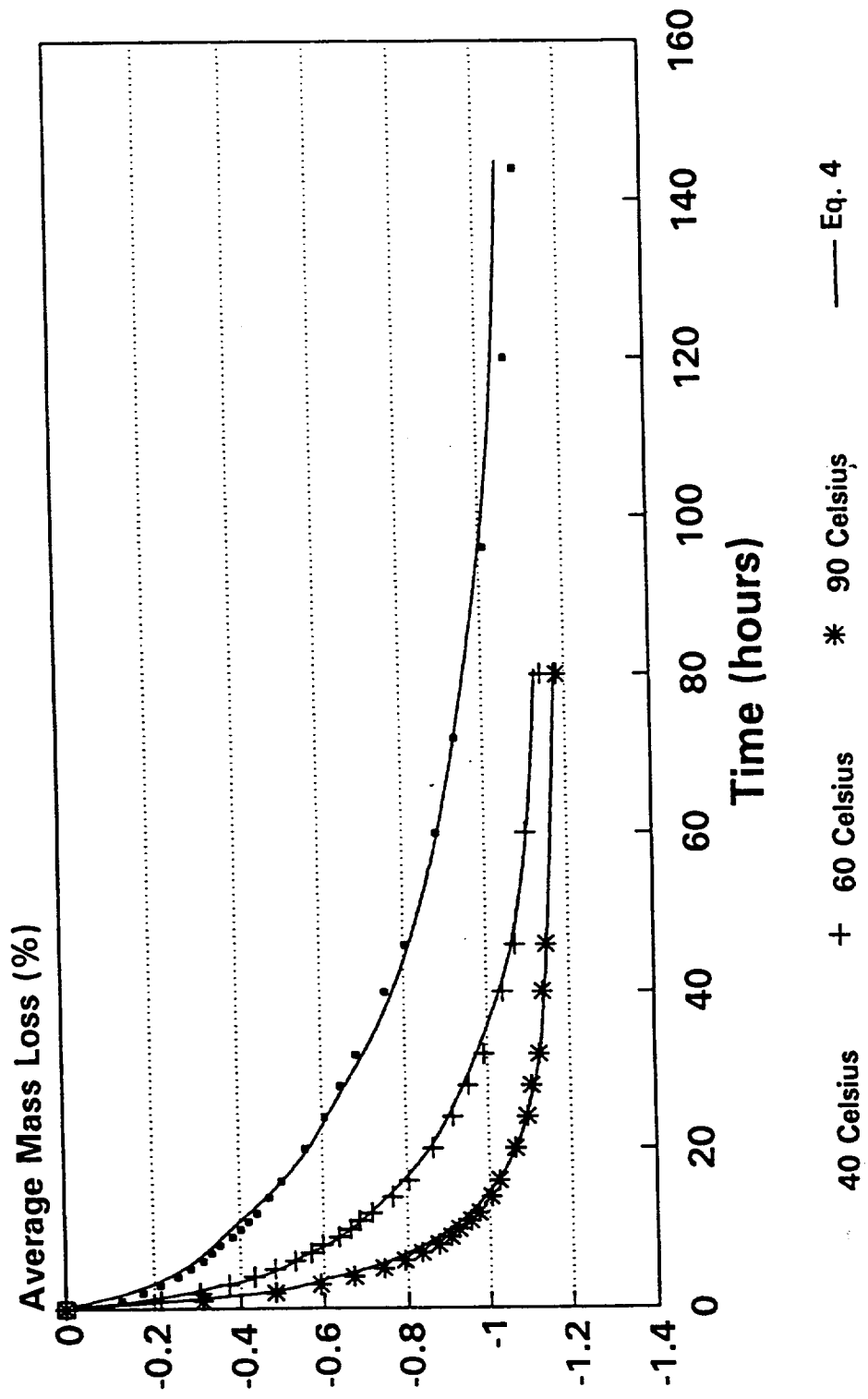Fig. 3: Moisture absorption data on
T50/ERL 1962 at unit time

Fig. 4: Moisture desorption of
T50/ERL1962 at 3 temperatures

# MODELING AEROSOL EMISSIONS FROM THE COMBUSTION OF COMPOSITE MATERIALS

J.A. Roop, D. J. Caldwell, and K. J. Kuhlmann
Air Force Institute of Technology, Wright-Patterson Air Force Base, Ohio 45433-7400, U.S.
Army Medical Research Detachment, and ManTech Environmental, Inc.

The use of advanced composite materials (ACM) in the B-2 bomber, composite armored vehicle, and F-22 advanced tactical fighter has rekindled interest concerning the health risks of burned or burning ACM. The objective of this work was to determine smoke production from burning ACM and its toxicity. A commercial version of the UPITT II combustion toxicity method developed at the University of Pittsburgh, and subsequently refined through a US Army-funded basic research project, was used to establish controlled combustion conditions which were selected to evaluate real-world exposure scenarios. Production and yield of toxic species varied with the combustion conditions. Previous work with this method showed that the combustion conditions directly influenced the toxicity of the decomposition products from a variety of materials.

## INTRODUCTION

Introduced in the 1960s, advanced composite materials (ACM) are expected to compose 40-60 percent of future airframes. Figure 1 illustrates the increased use of ACM in US Air Force aircraft. During the 1990s, several events focused attention on the human and environmental consequences resulting from fabrication and incidental combustion of ACM. In addition, although the fibers and epoxy resins of advanced composites appear to be safe in their original state, the chemical transformation to a hazardous substance during combustion is not well characterized. These resins, such as epoxies, polymides, phenolics, thermosets, and thermoplastics, may release potentially lethal gases, vapors, or particles into the atmosphere when burned.
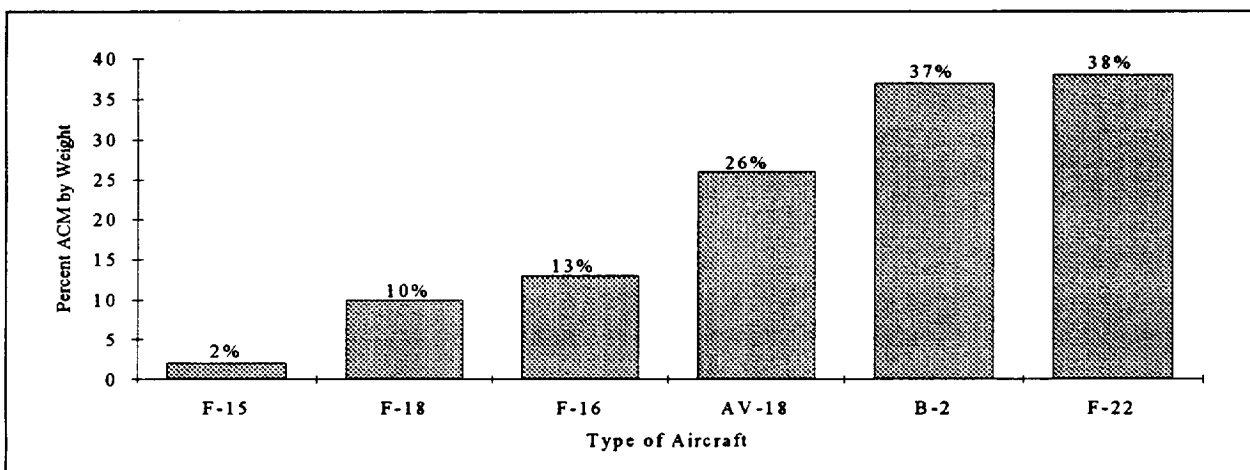


Figure 1  Percent of Aircraft by Weight

As the use of composites increase, so do the potential risks to the environment and those exposed to the smoke and combustion gases during aircraft mishaps. The objective of this work was to determine smoke production from burning ACM and predict its toxicity.

The apparatus used to establish controlled combustion conditions is a commercially available version of the cone heater combustion module of the UPITT II method developed at the University of Pittsburgh. Previous work with this method showed that the combustion conditions directly influenced the toxicity of the decomposition products from a variety of materials. Not only will the toxic potency of the thermal decomposition products be determined, but the time to toxic effect will also be obtained over a variety of combustion conditions selected to enable evaluation of real-world exposure scenarios.

Development of test methods to evaluate smoke from burning materials has been an aspect of fire science which has received much attention. Two approaches exist, the first is the analytical approach which attempts to predict smoke toxicity based on the toxicity of each component found in the smoke. The major drawback of this approach is that limited information exists for only a few chemicals while many unknown chemicals are typically generated during combustion of most materials. Even when the major toxicants in a combustion atmosphere can be identified, the possibility of biological interactions between these chemicals would render any prediction of toxicity speculative. For these reasons the second approach, the bioassay, is preferred. The use of animals is necessary in combustion toxicity tests of materials to detect the presence not only of unusual or uncommon toxicants but also of biological interactions between common gases. All currently used test methods, including the UPITT II method, share lethality as the common endpoint of toxicity and typically determine the $LC_{50}$ for a material. We have incorporated alternate endpoints (such as incapacitation) into the UPITT II method. Thus, we not only measure toxic potency in terms of smoke concentration, but also determine the time to effect, be it lethality, incapacitation, or any other selected endpoint. This research will result in the selection of safer materials for new and existing weapons systems.

## DESCRIPTION OF EXPERIMENT

### Materials
A carbon fiber/modified bismaleimide resin advanced composite material (approximate 2:1 ratio by weight) was used in these studies. Specimens were 108 mm square by 2.5 mm thick with a mass of $53.90 \pm 0.36$ g.

### Combustion Module
A commercial version of the UPITT II combustion toxicity apparatus (1) was used to establish controlled combustion conditions selected to evaluate real-world exposure scenarios. For these experiments the heat flux (Q) was set at 38, 44 57, or 84 kW/m$^2$; the airflow was maintained at 19, 28, 35, or 41 L/min. The time to ignition ($T_{ign}$), duration of flaming ($T_{Fl}$), and mass loss rate ($\dot{m}$) were determined as previously described (1) except that a 10-minute period was used instead of a 30-minute period. The smoke concentration (SC) was calculated by dividing the mass loss rate by the airflow through the apparatus.

*Combustion Product Identification*

A Perkin-Elmer Model 1600 FT-IR spectrometer was used to obtain transmission spectra of the filtered smoke produced by the burning specimen. The major toxic species were qualitatively identified from these spectra.

## RESULTS

Results from experiments conducted under flaming conditions are presented in Table 1. The $T_{ign}$ decreased as Q increased, while the mass loss rate increased with increasing Q (2). Table 1 represents the time to ignition, and mass loss rate for $0.01m^2$ ACM specimens irradiated for 10 minutes.

Table 1 Preliminary Experiment Results

| Q kW/m$^2$ | $T_{ign}$ seconds | m g/min |
|---|---|---|
| 38 | 255 | 1.2 |
| 44 | 60 | 1.2 |
| 57 | 35 | 1.5 |
| 84 | 15 | 1.7 |

Consolidated results of the coupon burn experiments find that the average mass loss of the ACM is 29.1%. Further review of the results from these controlled experiments suggest that, at constant air flow, the mass loss rate increases with heat flux. The graphical representation of these data points and regression line are found in Figure 2. Conversely, Figure 3 demonstrates that, at constant heat flux, the mass loss rate is not significantly related to increasing air flow.

Figure 2  Coupon Mass Loss at Constant Air Flow



Figure 3  Coupon Mass Loss at Constant Heat Flux

The composition of the smoke and properties of the aerosol particles was evaluated. Initial results find the smoke is composed of phenol groups, aniline groups, carbon monoxide, and carbon dioxide. Major spectrum peaks from a representative FT-IR spectrum of smoke from an experiment conducted at 50 kW/m$^2$ are identified in Table 2.

Table 2. Peak identification from representative FT-IR spectrum.

| CM-1 | Height | Identity |
|------|--------|----------|
| 3708 | 17.64 | Aniline |
| 3628 | 19.23 | Aniline |
| 3596 | 25.35 | Aniline |
| 3566 | 53.31 | Aniline |
| 3324 | 53.36 | Phenol |
| 2510 | 81.09 | Carbon Dioxide |
| 2174 | 50.68 | Carbon Monoxide |
| 2116 | 56.36 | Carbon Monoxide |
| 1526 | 10.45 | Aniline |
| 1304 | 29.53 | Aniline |
| 1164 | 47.28 | Phenol |
| 1138 | 53.65 | Phenol |
| 730 | 10.25 | Phenol |

Two samples were analyzed by GC/MS with the results summarized below in Table 3. The quantitative figures were obtained by using the Response Factor = 1 approximation as specified in the CLP Statement of Work. A vapor aliquot was collected using a cold trap. The collection conditions were two runs at 30L/min for 10 minutes. The following compounds were qualified:

Table 3 Quantification of Identified Compounds

| Identified Compound | Soln Conc (µg/ml) | Air Conc (µg/m³) |
|---|---|---|
| Aniline | 342.4 | 0.57 |
| Phenol | 961.8 | 1.60 |
| 4-methylphenol (o-cresol) | 63.7 | 0.11 |
| 2-methylphenol (p-cresol) | 74.7 | 0.12 |
| 3-methyl-1-isocyanobenzene | 5.9 | 0.01 |
| quinoline | 24.9 | 0.04 |
| Biphenyl | 6.8 | 0.01 |
| Diphenyl Ether (diphenyl oxide) | 114.0 | 0.19 |

The aerosol particle density ($\rho_p$) was determined using standard laboratory practice and found to be 0.29 mg/mL. The air samples, analyzed by electron microscopy identified a range of aerosol diameters from 0.5 to 1.5 µm. Given this density and the observed range of particle diameters the gravitational settling velocity ranged from $6.5 \times 10^{-6}$ to $3.8 \times 10^{-4}$ m/sec. Due to this small velocity, the aerosol emissions were found to have no significant affect on the downwind concentrations.

Approximately 1.4g of the soot was extracted with 50:50 Methylene Chloride:Acetone solution. It was apparent, upon examination of the injection port liner, that many of the extracted compounds were not suitable for analysis by GC/MS, as there was obvious evidence of pyrolysis and deposition in the liner. The major compounds identified are shown in Table 4 below.

Table 4 Identification and Quantitation of Major Compounds Extracted from Soot

| Identified Compound | Soln Conc (µg/ml) | Conc in Soot (µg/Kg) |
|---|---|---|
| Aniline | 215.5 | 2994.4 |
| phenol | 156.5 | 2174.6 |
| 2- and 3-methylaniline | 45.0 | 1204.0 |
| quinoline | 250.2 | 3476.3 |
| 5-methylquinoline | 86.4 | 1200.3 |
| Diphenylether | 75.8 | 1053.6 |
| 2-methoxyethoxybenzene | 119.7 | 1662.7 |
| 1,2-dihydro-2,2,4-trimethylquinoline | 159.2 | 2212.3 |
| 1-isocyanonaphthalene | 158.9 | 2208.2 |
| dibenzofuran | 97.6 | 1356.7 |
| 1-Isocyanonaphthalene | 119.6 | 1661.5 |
| Anthracene | 122.2 | 1698.1 |
| N-Hydroxymethylcarbazole | 92.5 | 1285.1 |
| Fluoranthene | 93.3 | 2129.6 |

From experience, the quantification is probably low. Several other comments need to be made. As these identifications were made by mass spectroscopy, it is quite probable that some of the isomers may be some other isomer. That is one of the weaknesses of the technique. There were a number of PAH peaks in the soot extract which were of too low an intensity to characterize properly, and were not included in the above. Additionally, as mentioned above, there are probably a considerable number of compounds which either did not extract in the first place or did not make it out of the GC injection port. The key point is that many of these compounds are known carcinogens.

## DISCUSSION

### ACM Emission Rate

The primary objective of these combustion experiments was to obtain a mass loss rate for the ACM. However, one significant limitation to this study is the lack of research on the heat transfer properties of composite materials. Therefore, we assume that the flame spread characteristics demonstrated by this bench-scale combustion equipment accurately simulates those of a full-scale aircraft. The results, under controlled heat flux and air flow conditions, identified a linear relationship between the mass loss rate and the area of the burning composite.

Multi-variable linear regression of the mass loss rate data with the sample coupon area was preferred. The equation for the regression line is found below in Equation 1-1. The regression results provide a linear equation ($R^2 = 0.99$) that allows accurate prediction of an emission rate for a full-scale aircraft.

$$\dot{m} = \beta_1 (Area) + \beta_2 (HeatFlux) - 0.01 \tag{1-1}$$
$$\text{where:}$$
$$\beta_1 = 1.98$$
$$\beta_2 = 1.86 \times 10^{-4}$$

These findings enable regression analysis of a linear equation for the emission rate given constant heat flux, air flow, and area conditions. Aerosol properties were identified which enabled calculation of the gravitational settling velocity. This, in turn, will serve to better estimate the downwind plume characteristics. The combined results allow for accurately modeling the smoke and aerosol smoke plume generated during the combustion of composite material aircraft.

### Thermogravimetric Analysis

The way heat was applied to the samples in the thermogravimetric analyzer was a little different than that in the larger unit. The TGA uses a cup design, with the sample in the center of a small furnace. It wasn't possible to shield the sample during the heatup cycle from the heat, as is possible in the UPITT II apparatus. Despite this difference, and the much smaller sample size, the weight loss measured by the two units was quite similar. During the first two to three minutes,

the sample lost approximately 25% of its weight. What happened in the TGA after this is a direct result of the differences between the TGA and the larger burn unit. The TGA has the capability to heat in a nitrogen atmosphere or in air. The atmosphere made a significant difference in the weight loss characteristics.

*Burns in Nitrogen:* After the initial weight loss due to the polymer pyrolysis, the weight stabilized at a little over 75% of the initial weight, and stayed there for the rest of the thirty minute test run. There was no significant change with extended time.

*Burns in Air:* The specimen mass never stabilized after the initial pyrolysis mass loss (due to the polymer resin loss). The mass loss curve changed with temperature, the slope of which increased as temperatures increased. Given enough time, the graphite fibers completely disappeared, i.e., at 950°C all mass is lost within 15 minutes, while at 650°C the time required increased to 60 minutes.

We suspect that the graphite fiber was being "eroded" by the oxygen in the air. Unpublished work on diamond showed a molecular surface effect (R. Langford, personal communication). Apparently, when the material is given enough energy (heated), the impact of an oxygen molecule is enough to pull off a carbon atom and form $CO_2$ or $CO$. This is supported by infrared spectroscopy data, which show evolution of these gases until the weight goes to zero.

*Modeling the Plume Corridor*

The Industrial Source Complex Short Term 2 (ISCST2) Model results were was used to identify deposition values, downwind concentrations, and plot the potential plume concentration corridor. These results provide a review of the modeling scenarios described below. Following the scenario are figures that portray the ISC plume corridor concentration results in a plan view or contour plot, and a 3-Dimensional surface plot. Given the very unstable conditions in Scenario 1, Figure 4 suggests a small area of potential contamination, but a large concentration. Further review indicates a maximum concentration of 1400 $\mu g/m^3$ occurring approximately 500 m downwind from the source. A significant difference in the plume area is identified in Figure 6 where the maximum concentration is 1300 $\mu g/m^3$ at 400 m downwind of the source. This should be expected due to the changing meteorological conditions used in the scenario

226

The following describes the parameters for Scenario 1:

- JP-4 Pool Fire Centerline Temperature: 873.5 °C
- Emission Rate: 870.98 g/sec
- Stability Class: A
- Wind Speed: 5 m/sec
- Release Height: 0
- Effective Stack Height: 972 m
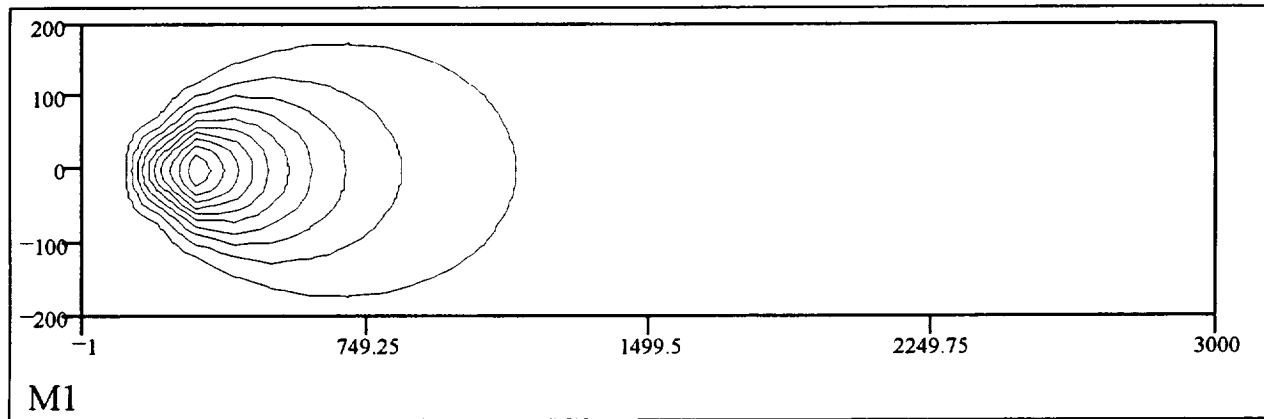- Model: Particle Deposition over a 1 and 3 hour period.



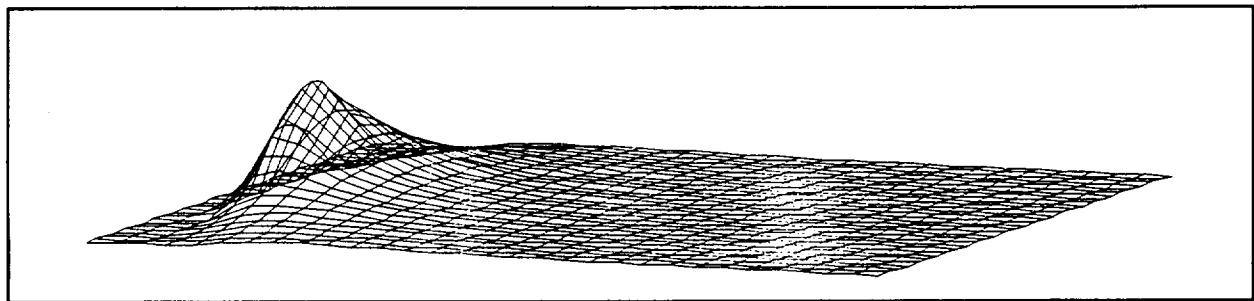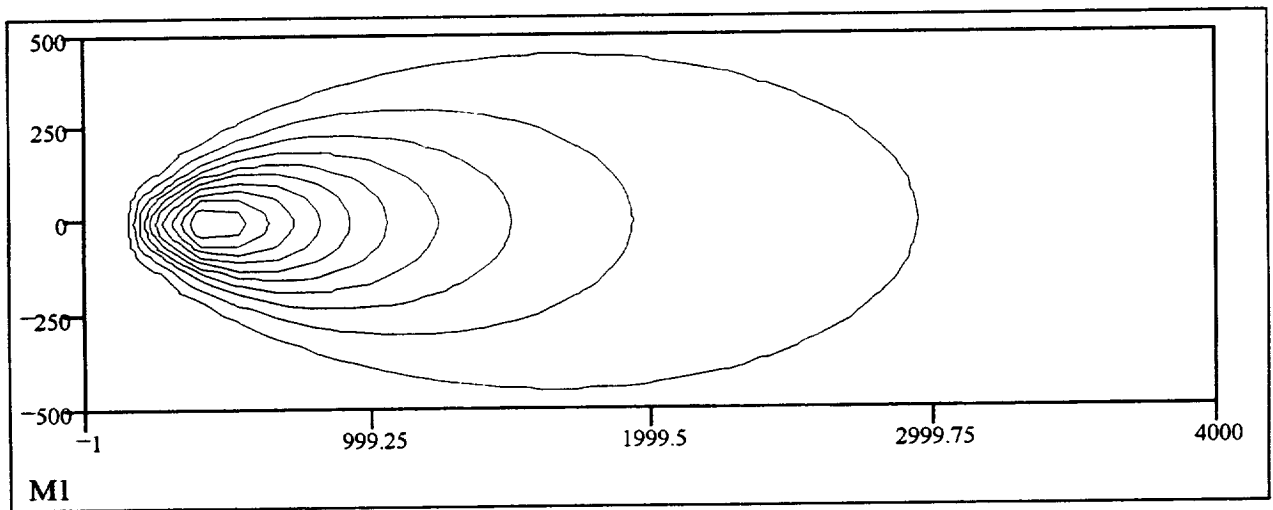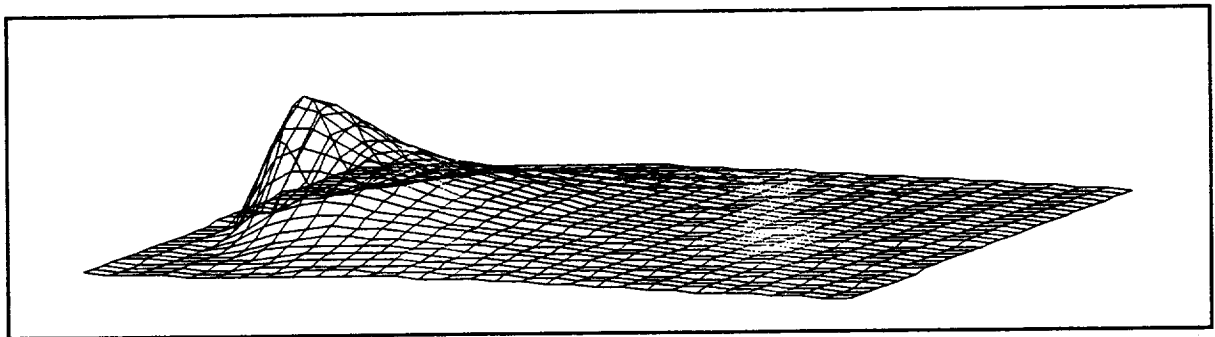Figure 4  A Contour Plot of Plume Corridor for Scenario 1



Figure 4.5  A 3-Dimensional Surface Plot of Plume Corridor for Scenario 1

The following describes the parameters for Scenario 2:

- JP-4 Pool Fire Centerline Temperature: 873.5 °C
- Emission Rate: 870.98 g/sec
- Stability Class: Varying
- Wind Speed: Varying
- Release Height: 0
- Model: Particle Concentrations over a 1 and 3 hour period.



Figure 4.6  A Contour Plot of the Plume Corridor for Scenario 2



Figure 4.7  A 3-Dimensional Plot of the Plume Corridor for Scenario 2

The previous plots suggest that the ACM plume corridor is extremely dependent upon the atmospheric conditions at the time of the mishap. The concentrations will be higher with a nominal plume spread on a turbulent day, whereas the converse will occur during a calm day.

*Other Observations from the TGA runs*

Once the resin was pyrolysed off the fiber matrix, the fibers separated and puffed to several times the original volume and lost any cohesion or tendency to group together. After a burn where the graphite was not completely consumed, there was a considerable difficulty getting fibers out of every nook and cranny of the instrument. This phenomenon happened whether the burn was in nitrogen or air.

This leads to a couple of speculations. In general, even after a long burn, the fibers remain visible and therefore not respirable. It is, however, possible that some are being eroded to the point where they could be respirable. At this point, the answer is unknown, however, there are clear hazards associated with what is known to be contained in the soot particles and that these present the greater hazard to life and property than does the physical shape (i.e., particle or fiber).

The fibers are extremely fluffy, and potentially electrically conductive. They could travel a significant distance in a mild breeze, and have the potential to short out everything from computers to power lines. It is probably critical that measures be taken in fighting a fire involving these materials to reduce dust and aerosols.

## CONCLUSIONS

Smoke production and yield of toxic species varied with the combustion conditions. This finding is consistent with previous work with this method which showed that the combustion conditions directly influenced the yield and toxicity of smoke produced by a variety of materials (3).

Although no animal exposures were performed during this preliminary series of experiments, an estimate of the potential toxicity of the smoke can be made based on the analytical results and the smoke yield from the burning ACM.

Future work will incorporate animal exposures to determine the toxic potency of the smoke and evaluate alternate non-lethal endpoints such as incapacitation. We can not only measure toxic potency in terms of smoke concentration, but also determine the time to effect, i.e. lethality or incapacitation. This approach will result in the selection of safer advanced composite materials for new and existing weapons systems.

## REFERENCES

1. D. J. Caldwell and Y. C. Alarie, *J. Fire Science*, 8, 23-62 (1990).

2. J. A. Roop, *Modeling Aerosol Dispersion from Combustion of Advanced Composite Materials During an Aircraft Mishap*, Master's Degree Thesis (AFIT/GEEM/ENV/94S-21), Air Force Institute of Technology (1994)

3. D. J. Caldwell and Y. C. Alarie, *J. Fire Science*, **9**, 470-518 (1991).

# AQUEOUS ALTERNATIVES FOR METAL AND COMPOSITE CLEANING

by

JoAnn Quitmeyer
Senior Research Associate
W.R.Grace & Co.-Conn.
55 Hayden Avenue
Lexington, MA 02173
617-861-6600

# The Problem

For many years the metalworking industry has cleaned metal and composite substrates with chlorinated solvents. Recently, however, health and disposal related environmental concerns have increased regarding chlorinated solvents, including 1,1,1-trichloroethane, trichloroethylene, methylene chloride, or Freon[1]. World leaders have instituted a production ban of certain ozone depleting chlorofluorocarbons (CFC's) by 1996.

The Occupational Safety and Health Administration (OSHA) has instituted worker vapor exposure limitations for virtually all of the solvents used in solvent-based cleaners. In addition, the United States Environmental Protection Agency (EPA) has defined nearly all solvent-based cleaners as "hazardous". Cradle to grave waste responsibility is another reason manufacturers are trying to replace chlorinated solvents in their cleaning processes.

Because of these factors, there now is a world wide effort to reduce and/or eliminate the use of chlorinated solvents for industrial cleaning.

Waterbased cleaners are among the alternatives being offered to the industry. New technology alkaline cleaners are now available that can be used instead of chlorinated solvents in many cleaning processes. These waterbased cleaners reduce the release of volatile organic compounds (VOC's) by as much as 99 percent. (The definition and method of calculation of VOC's now varies from region to region.) Hazardous waste generation can also be significantly reduced or eliminated with new aqueous technology. This in turn can ease worker exposure restrictions and positively impact the environment.

### TABLE 1
### PHYSICAL PROPERTIES OF VAPOR CLEANERS

| Parameter | A | B | C | D |
|---|---|---|---|---|
| Boiling Point (°C) | 39.8 | 74.1 | 86.9 | 121 |
| Boiling Point (°F) | 104 | 165 | 189 | 250 |
| Specific Gravity | 1.316 | 1.322 | 1.456 | 1.613 |
| Flash Point (TOC) °C | none | none | none | none |
| Vapor Pressure,mm | 340 | 90 | 59 | 13 |
| Volatile Organics (VOC) #/gallon | 10.98 | 10.92 | 12.11 | 13.47 |
| Surface Tension (dynes/cm) | 28 | 28 | 28 | 28 |

CODE: A= Methylene Chloride    C= Perchloroethylene (PERC)
        B= Trichloroethane (TCA)    D= Trichloroethylene (TCE)

The use of aqueous products can also eliminate or reduce the annual reporting required[2] under SARA Title III, Section 313 ( Toxic Chemical Release Reporting: Community Right-To-Know) because these aqueous cleaners contain little or no ( less than 5%) chemicals currently

listed in Section 313. Standard degreasing solvents such as perchloroethylene, methylene chloride, trichloroethylene, and Freon presently require reporting under Section 313 when used in quantities of 10,000 pounds or greater annually.

Tables 1 and 2 compare the physical and chemical properties of waterbased cleaners versus chlorinated solvents.

### TABLE 2
### PHYSICAL PROPERTIES OF AQUEOUS CLEANERS

| Parameter | A | B | C | D |
|---|---|---|---|---|
| Boiling Point (°C) | 100 | 100 | 100 | 100 |
| Boiling Point (°F) | 212 | 212 | 212 | 212 |
| Specific Gravity | 1.02 | 1.07 | 1.07 | 1.02 |
| Flash Point (TOC)°C | none | none | none | none |
| Vapor Pressure, mmHg | 29 | 23 | 23 | 18 |
| Volatile Organics (VOC) #/gallon | 0.2 | 0.0 | 0.0 | 0.5 |
| Surface Tension (dynes/cm) | 29 | 29 | 33 | 32 |
| pH, 100% | 11.5 | 13.0 | 13.0 | 7.8 |
| pH, 10% | 10.5 | 12.0 | 11.7 | 7.1 |

## Cleaning Process Defined

Cleaning is defined as *"the removal of soil or unwanted matter from a surface"*.[3] There are a wide variety of cleaning processes to choose from depending on the nature of the soil, the substrate involved and the degree of cleanliness required.

Cleaning of metal and composite substrates can be accomplished in several ways: 1) by using mechanical action such as wiping, brushing or spraying; 2) by solubilizing the soil; 3) by chemically reacting the soil through saponification or chelation; or 4) by lifting the soil through surface action and detergency. Often a combination of mechanisms is employed.

## Solvent Degreasing

Vapor degreasing[4] has been a traditional means to clean industrial components. During this cleaning process vapors from a boiling solvent condense on the cooler part, flushing off oily soils. The soils are then dissolved in the solvent. This cleaning action continues until the part warms up enough to stop the condensation from occurring. At this time the cleaning process is complete whether the parts are clean or not, generally within ten minutes. The part is then removed from the degreaser tank clean and dry. A spray wand may be used to remove particulate soils not readily removed by the vapors.

Chlorinated solvents most frequently used for vapor degreasing include: 1,1,1-trichloroethane (TCA), trichloroethylene (TCE), perchloroethylene (PERC) and methylene chloride. Freon is also used, especially by the electronics industry.

Vapor degreasing is an effective method for removing organic soils such as oil-based cutting oils, greases, petrolatums and high-melt waxes. It is less effective in removing inorganic soils like fingerprints, water salts and road film. Aerospace, electronics and automotive industries have typically employed vapor degreasing methods for cleaning.

Once a hydrocarbon solvent has been used for degreasing purposes, it must be redistilled in order for it to be reused. This can require a significant capital equipment expense. More often than not, the resulting sludge and/or used solvent is discarded and treated as hazardous waste.

Some waterbased cleaners contain non-chlorinated solvents as part of the package. These semi-aqueous emulsion cleaners contain hydrocarbon solvents and emulsifiers. Since they contain non-volatile residues, water rinsing is generally required. These emulsion cleaners work by solubilizing and/or emulsifying the soils and dispersing them throughout the bath. As the semi-aqueous cleaner is used, the entire bath becomes contaminated. The entire bath, including the water and any water rinses, must be treated as hydrocarbon waste. Again, the waste generator is legally responsible for that waste "from cradle to grave".

## New Technology Aqueous Cleaners

Using new technology, waterbased cleaners are now being developed to replace chlorinated solvents for cleaning metal and composite substrates. These new cleaners, specifically designed for long bath life, are aqueous solutions containing water conditioners, corrosion inhibitors, varying amounts of alkalinity builders and a careful selection of organic surfactants. These ingredients are specially selected for desired foaming, wetting (surface tension) and soil removal properties.

This new technology includes cleaners designed to be self-cleaning. When the cleaner has a greater affinity for the part surface than the soil does, it undercuts the soil. The soil is then released from the part surface. Light oils float while heavier soils such as chlorinated paraffins and particulates settle to the bottom. This way, the cleaning bath can be skimmed and filtered to remove both light and heavy soils. Cleaner concentrate is then added as required to maintain recommended parameters and cleaning continues. Only the contaminants skimmed or filtered from the bath need be hauled away as waste; the liquid can be recycled indefinitely. Shop dirts, cutting oils, fingerprints, grease, carbon, low-melt waxes and road soils can all be readily removed with the new aqueous cleaners. Additionally, by adding heat and/or some mechanical action, these aqueous cleaners can also be used to remove petrolatums and high-melt waxes.

## In-Use Comparisons

Cleaning tests conducted on a wide variety of soils shows comparable cleaning efficiency with aqueous chemistry and chlorinated solvents. Every hydrocarbon solvent tested dissolved the soils. Aqueous cleaners either emulsified, saponified or rejected the soils depending on the chemistry of the cleaner and soil involved. Overall, most of the soils tested were removed by one or more aqueous cleaner within the ten minute time frame typical for vapor degreasing.

Chlorinated solvents did not remove ink, solder paste and candle wax from metal or composite substrates. Mechanical action was required to remove these soils with aqueous chemistry.

Extraction with boiling water and/or hydrocarbon solvents has shown improved cleaning efficiency with aqueous technology versus TCA when measured by ion chromatography, ICP and FTIR methods. Surface examination using X-Ray Photoelectron Spectroscopy (XPS) and Scanning Electron Microscopy (SEM) verify these findings.



**FIGURE 1.**
**Traditional Vapor Degreaser**

XPS showed no evidence of offgassing[5] on parts cleaned with aqueous cleaners when exposed to a vacuum at $10^{-8}$ TORR on either rinsed or unrinsed parts. Rinsing does, however, enhance the aesthetics of the part.

Aqueous cleaners are also used to clean composite surfaces prior to bonding. Bond strength can be measured by Lap Shear Testing. In one study[6], the TCA control had 778 psi Shear Strength versus an aqueous alkaline cleaner with 1239 psi. Other tests used to qualify bonding performance include Double Plate Tensile (DPT) and Peel Tests.

It is a well know fact[7] that many composite materials absorb water during fabrication, therefore offgassing can occur for prolonged periods of time depending on the vent path, amount of water absorbed and temperature of the material. The manufacturer of sensitive parts must determine whether exposure to aqueous environments can be tolerated.
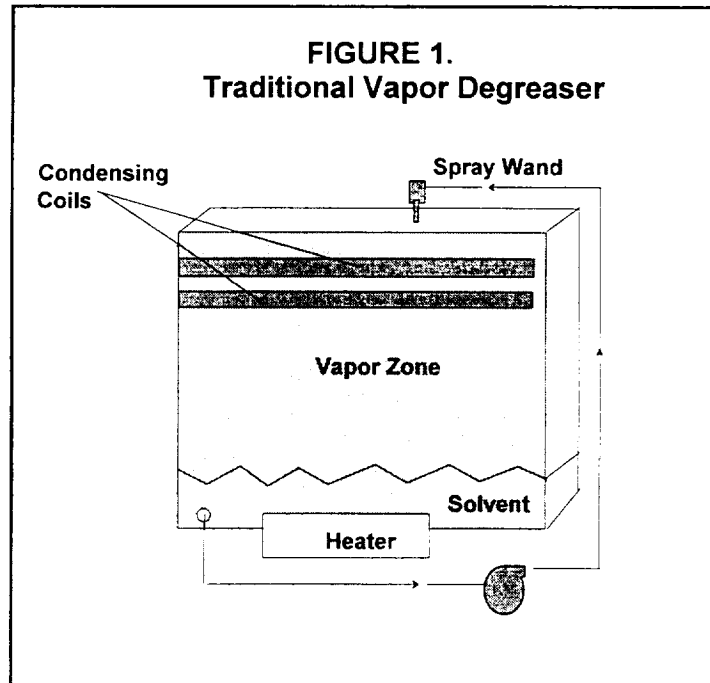
## Applying the Findings

Since these waterbased cleaners have little or no volatile components, with the exception of water, cleaning cannot take place in the vapor phase. Instead, the parts must be immersed in, or sprayed with, the cleaner. Though parts are wet after processing, they can easily be dried with heat, forced air or other means appropriate to the substrate and configuration involved.

Keeping environmental regulations in mind, the manufacturer should select cleaning products that remove the majority of soils at a concentration, temperature and time frame compatible with production needs. To minimize waste, the cleaner selected should have a long or indefinite tank life. Ideally the bath should be filtered periodically to remove contaminants and deionized water should be used for makeup to prevent the buildup of water solids in the bath. Cascading rinses should be used whenever possible with the freshest water in the final stage. Attempts should be made to match the cascade rate to the evaporative loss due to heat. Once again, since the bath need not be dumped, waste is minimized. This in turn translates into reduced costs to the environment and to the company.

## Field Testing

Aqueous cleaners have already replaced vapor degreasers in many industries. Making the change has enabled users to eliminate process stages and reduce waste significantly-- in some cases up to 80 percent. Modification of existing equipment as shown in Figures 1 and 2, enables users to convert to aqueous technology without major capital equipment expense.



**FIGURE 2.**
**Modified Vapor Degreaser**
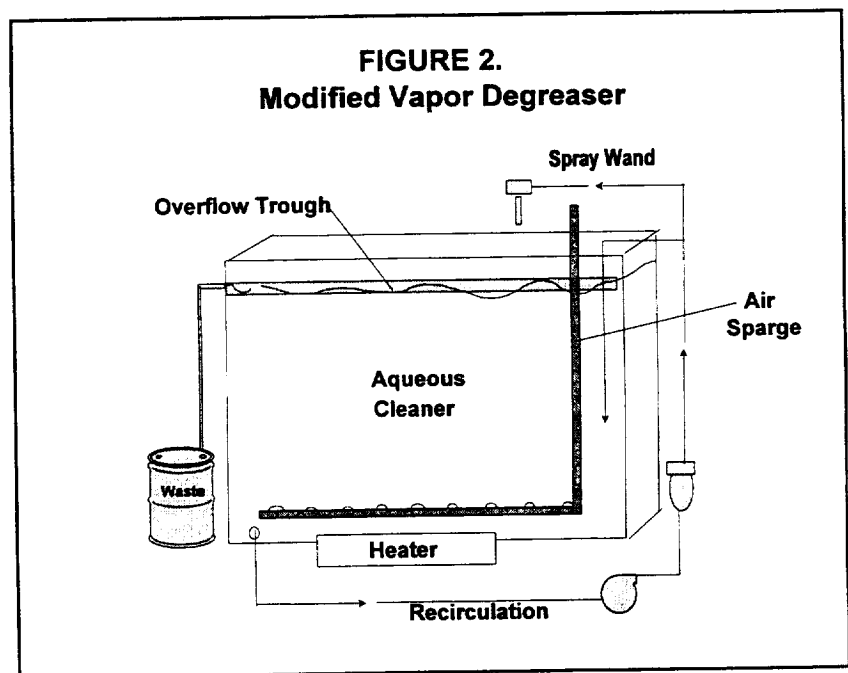
A major aerospace manufacturer successfully replaced 1,1,1-trichloroethane with reduced capital expenditures.[7] With slight modifications, the existing vapor degreaser was converted to an 18,000 gallon aqueous immersion bath. The chiller coils were disconnected, the fluid level was raised to allow immersion of parts, and fluid recirculation pumps were added to facilitate agitation. Skimming and filtration were also added to facilitate removal of contaminants. Tank life to date is over three years.

A major manufacturer of flight and non-flight engines has also converted to aqueous technology for the removal of EDM Oil from turbine blades. Five vapor degreaser units have

been modified for use with aqueous technology, thus avoiding major capital equipment expenditures.

The subcontractor for a global manufacturer of high tech audio and visual equipment is in the process of converting an existing vapor degreaser to an aqueous spray system. A fine deionized rinse spray over the tank will enhance part aesthetics without requiring a separate rinse tank. The rinse volume will match evaporative loss to minimize bleed-off requirements. The aqueous product selected was custom formulated to meet this customer's potassium and sodium limitations.

The military and automotive industries also have or are in the process of converting existing equipment to aqueous immersion systems for cleaning a wide variety of metal and composite components. One military facility has documented the cost to convert a vapor degreaser at approximately $5000 including all stainless and PVC parts and labor.

In each of the above case histories, tank life has or could have been extended by fluid filtration. Media filters, centrifuges and skimmers all work well in removing contaminants from aqueous cleaning baths.

In addition to the above applications, aqueous cleaners are successfully being used to clean in-flight airplane components, printed wiring assemblies, advanced composites, fasteners, communications components, computer systems and hydraulic systems in the United States and world wide.


## New Technology for the Future

Many industries are faced with the challenge of finding new technologies to reduce hazardous chemicals, thus reducing the amount of hazardous wastes generated. Industry must share responsibility with courts and governments around the world for a cleaner, safer environment.

With the new waterbased cleaners, waste minimization is real and obtainable today without loss of cleaning effectiveness. In addition, these aqueous cleaners can be recycled to save on product and disposal costs.

# References

[1] Freon is a registered trade name of Dupont

[2] Quitmeyer, J.A., " Aqueous Cleaners Challenge Chlorinated Solvents", *Pollution Engineering,* December, 1991.

[3] Spring, S., *Industrial Cleaning,* Prism Press, Melbourne, Australia, 1974, p. 1.

[4] Johnson, J.C., "Vapor Degreasing," *Metal Finishing Guidebook Directory 1987,* Metals and Plastics Publications, Inc., Hackensack, NJ, 1987, p. 103.

[5] Dauphin, J., Dunn, B.D., Judd, M.D., Levadow, F., " AEROSPACE...Materials for Space Application", *Metals and Materials,* July 1991, p. 430.

[6] Harrison, A.C., Marlow, M.E., and Levi, L.D. , *Evaluation of Environmentally Acceptable Cleaners As Replacements for Methyl Ethyl Ketone and 1,1,1-Trichloroethane in Solid Rocket Motor Production and Maintenance Applications,* Aerojet Propulsion Division, Sacramento, CA, July 1992.

[7] Hanson, P.A., *Operational Strategies for Contamination Control of Composite Materials,* Science Applications International Corp., Glendora, CA 91740.

[8] Quitmeyer, J.A., *Modification of Vapor Degreasing Equipment For Aqueous Cleaner Applications,* W.R.Grace & Co.-Conn., Lexington, MA 02173, November 1993.
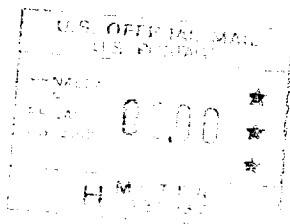
# REPORT DOCUMENTATION PAGE

| 1. AGENCY USE ONLY (Leave blank) | 2. REPORT DATE<br>October 1994 | 3. REPORT TYPE AND DATES COVERED<br>Conference Publication |
|---|---|---|

**4. TITLE AND SUBTITLE**

Joint Conference on Environmental, Safety, and Health Considerations—
Composite Materials in the Aerospace Industry

**5. FUNDING NUMBERS**

313

**6. AUTHOR(S)**

Compiled by: Huai-Pu Chu

**7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)**

Goddard Space Flight Center
Greenbelt, Maryland 20771

**8. PERFORMING ORGANIZATION REPORT NUMBER**

95B00035

**9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)**

National Aeronautics and Space Administration
Washington, D.C. 20546-0001

**10. SPONSORING/MONITORING AGENCY REPORT NUMBER**

CP-3289

**11. SUPPLEMENTARY NOTES**

This conference was co-sponsored by The Aerospace Industries Association, Suppliers of Advanced Composite Materials Association, and the National Aeronautics and Space Administration.

**12a. DISTRIBUTION/AVAILABILITY STATEMENT**

Unclassified-Unlimited
Subject Category: 24
Report is available from the NASA Center for AeroSpace Information,
800 Elkridge Landing Road, Linthicum Heights, MD 21090; (301-621-0390.

**12b. DISTRIBUTION CODE**

**13. ABSTRACT (Maximum 200 words)**

The Aerospace Industries Association, Suppliers of Advanced Composite Materials Association, and the National Aeronautics and Space Administration co-sponsored a conference on "Environmental, Safety, and Health Considerations—Composite Materials in the Aerospace Industry." The conference was held in Mesa, Arizona, on October 20-21, 1994. Seventeen papers were presented in four sessions including general information, safety, waste, and emissions from composites. Topics range from product stewardship, best work practice, biotransformation of uncured composite materials, to hazardous waste determination and offgassing of composite materials.

**14. SUBJECT TERMS**

composite materials, safety, emissions, hazardous waste, offgassing, environmental

**15. NUMBER OF PAGES**
240

**16. PRICE CODE**

| 17. SECURITY CLASSIFICATION OF REPORT | 18. SECURITY CLASSIFICATION OF THIS PAGE | 19. SECURITY CLASSIFICATION OF ABSTRACT | 20. LIMITATION OF ABSTRACT |
|---|---|---|---|
| Unclassified | Unclassified | Unclassified | Unlimited |