# Advanced Composite Material Manufacturing Operations

## Safety and Health

## Work Practice Observations and Recommendations

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**Environmental, Safety & Health Committee**
**Composites Task Group**

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# AIA COMPOSITES SURVEY

## Aerospace Industries Association (AIA)

- Newspaper articles on adverse health effects of composites in 1988

- Aerospace Industries Association wanted more information

- HR Council tasked Safety & Health Committee to study

- Task Group formed in 1988

## AIA COMPOSITES SURVEY

AIA Composites Task Group Actions

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

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

- MSDSs categorized by composite type (1000 usable MSDSs)

- 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

Results/Findings

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

The Aerospace Industries Association (AIA) recognizes the following member companies who contributed data to the AIA Composites Task Group survey:

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

AIA also recognizes individual contributions made by member company representatives of the Environmental, Safety & Health Committee who compiled this report:

| | |
|---|---|
| Robert Cleghorn | General Dynamics Corporation |
| Jackie Luca | Northrop Grumman Corporation |
| Denis Bourcier | The Boeing Company |

AIA appreciates the efforts of the AIA Office Communications in the development of this report. Tracy Stuckrath deserves special recognition and thanks.

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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


| Section | Title | Page |
|---|---|---|
| I | Introduction | 7 |
| II | Information Resources | 9 |
| | A. Toxicological Review | 9 |
| | B. Member Company Experience Survey | 9 |
| | C. Task Group Interaction With Other Organizations | 9 |
| III | Scope of Survey | 11 |
| | A. Composite Materials Reviewed | 11 |
| | B. Manufacturing Operations Reviewed | 11 |
| | C. Toxicological Review | 11 |
| | D. Industry Experience Survey | 11 |
| | 1) Phase I | 11 |
| | 2) Phase II | 12 |
| | 3) Phase III | 12 |
| | E. Work Practice Recommendations | 12 |
| IV | Results/Recommendations | 13 |
| | A. Exposure Routes | 13 |
| | 1) Ingestion | 13 |
| | 2) Inhalation | 13 |
| | 3) Dermal | 13 |
| | B. Work Practice Recommendations | 13 |
| | 1) Engineering/Personal Protective Equipment Controls | 13 |
| | (a) Barrier Creams | 14 |
| | (b) Coveralls/Smocks | 14 |
| | (c) Gloves | 14 |
| | (d) Respirators | 15 |
| | (e) Ventilation | 15 |
| | 2) Composite-Specific Observations/Recommendations | 16 |
| | (a) Epoxy Resin Systems | 17 |
| | (b) Polyimide Resin Systems | 19 |
| | (c) Phenolic Resin Systems | 20 |
| | (d) Polyester Resin Systems | 21 |
| | (e) Silicone Resin Systems | 22 |
| | (f) Aliphatic Amine Curing Agents | 23 |
| | (g) Aromatic Amine Curing Agents | 24 |
| | (h) Thermoplastics | 25 |
| | 3) Operation-Specific Observations/Recommendations | 26 |
| | (a) Assembly | 26 |
| | (b) Bagging | 27 |
| | (c) Curing | 27 |
| | (d) Kitting | 27 |
| | (e) Wet Lay-Up | 27 |
| | (f) Pre-Preg Lay-Up | 27 |
| | (g) Rework | 28 |
| | (h) Sand/Machine/Trim | 28 |
| | (i) Research & Development | 28 |
| | (j) Tooling | 29 |
| | C. Information Needs | 29 |
| | 1) Toxicology of Raw Materials | 29 |
| | 2) Occupational Exposure Monitoring | 29 |
| | 3) Medical Surveillance | 30 |
| | 4) Hazard Communication | 30 |
| V | Conclusion | 31 |
| VI | References | 32 |

# 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]. ■

# 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.

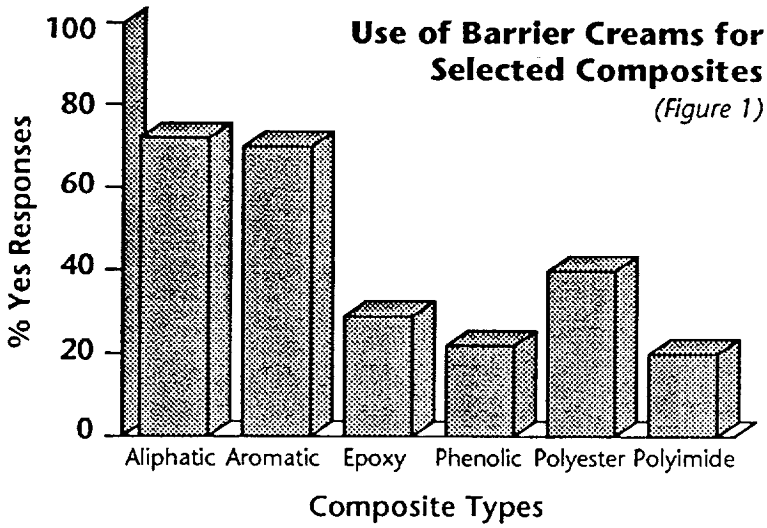
Dermal dose can be estimated by biological monitoring, controlling for inhalation exposure. The ability of a material to be available for absorption through the skin can be estimated by wipe samples taken from the surface of skin and gloves, or from workplace surfaces where skin contact is likely. The 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

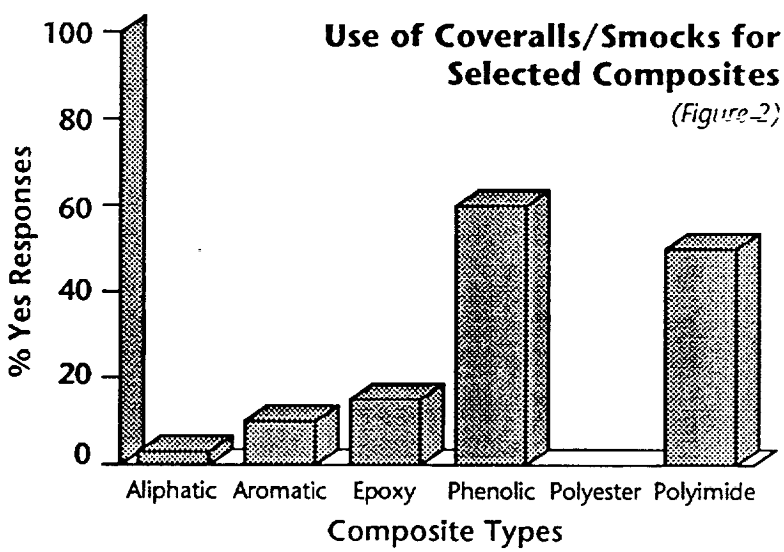
This section discusses work practice recommendations that were compiled with input from the toxicological review and the industry-wide user experience survey. These recommendations are provided only as guidelines and should be treated accordingly. As control technologies continue to improve and additional 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)*




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

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.

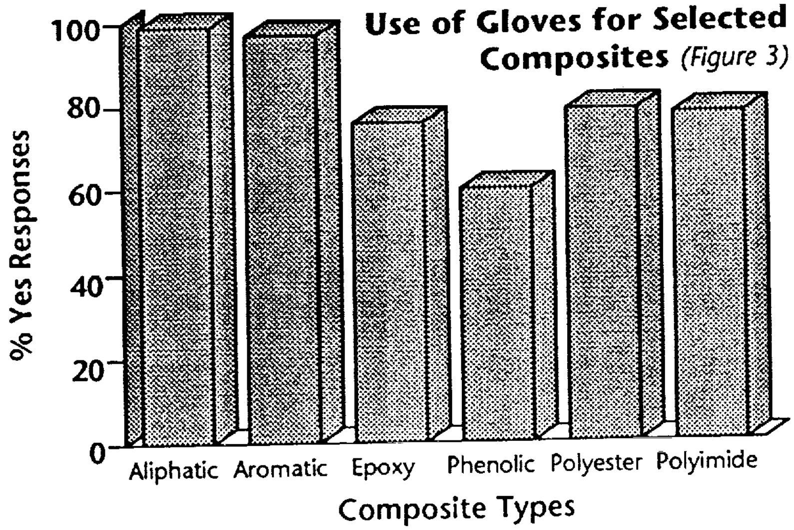
**(b) Coveralls/Smocks**

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.

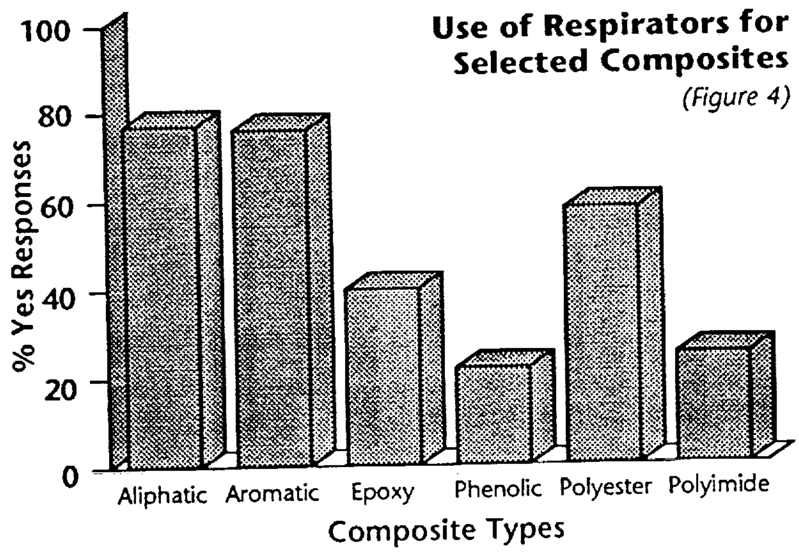
**(c) Gloves**

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

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 recommended, 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.

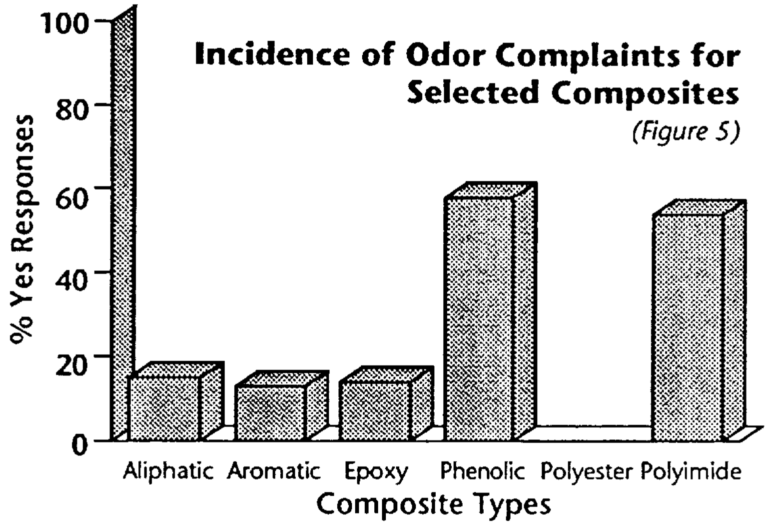
Air-supplied respirators are recommended when spraying composite materials in areas where there is direct exposure to sprayed material or when good booth ventilation is not available. Figure 4 illustrates responses from the industry-wide survey regarding use of respirators by composite type.

**(e) Ventilation**

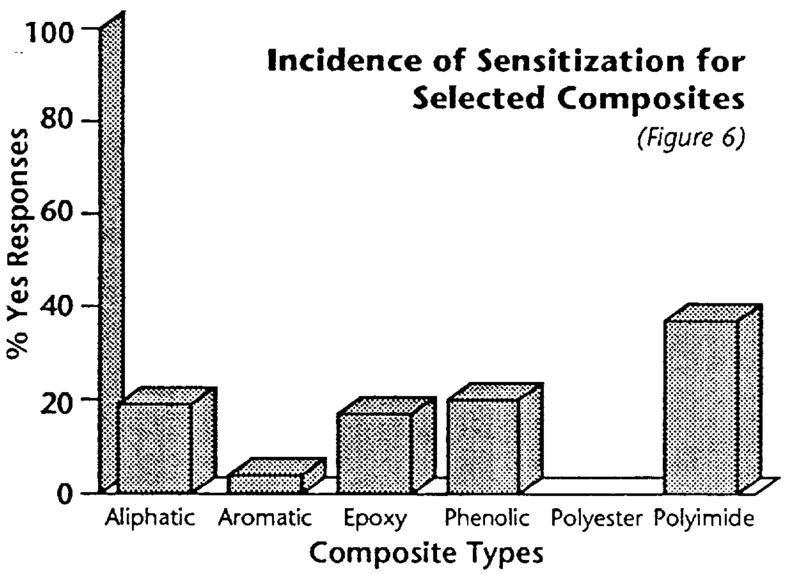
The four primary ventilation controls used in composite manufacturing operations include good general ventilation, local exhaust, downdraft tables, and booth ventilation:

- **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.

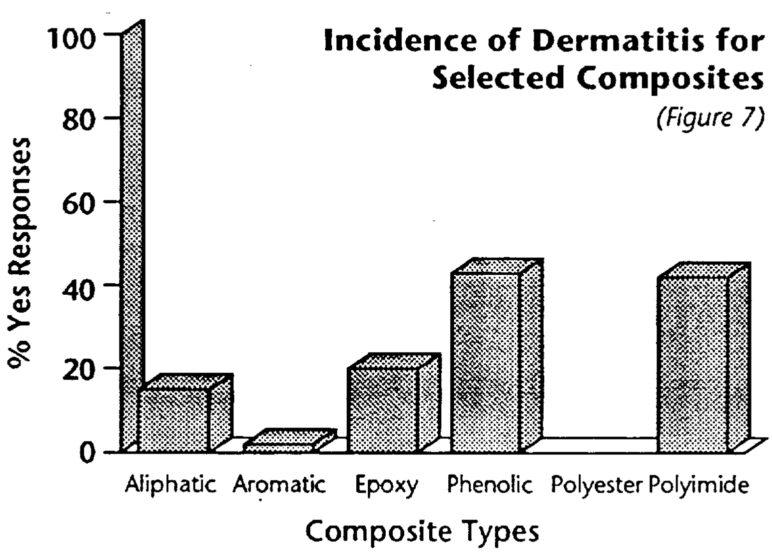
- **Local Exhaust:** High-velocity, low-volume local exhaust ventilation at the point-of-operation is recommended for controlling dusts generated during cutting, drilling, and sanding operations. These dusts cause mechanical and chemical irritation of




**Incidence of Odor Complaints for Selected Composites**
*(Figure 5)*




**Incidence of Sensitization for Selected Composites**
*(Figure 6)*




**Incidence of Dermatitis for Selected Composites**
*(Figure 7)*

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.

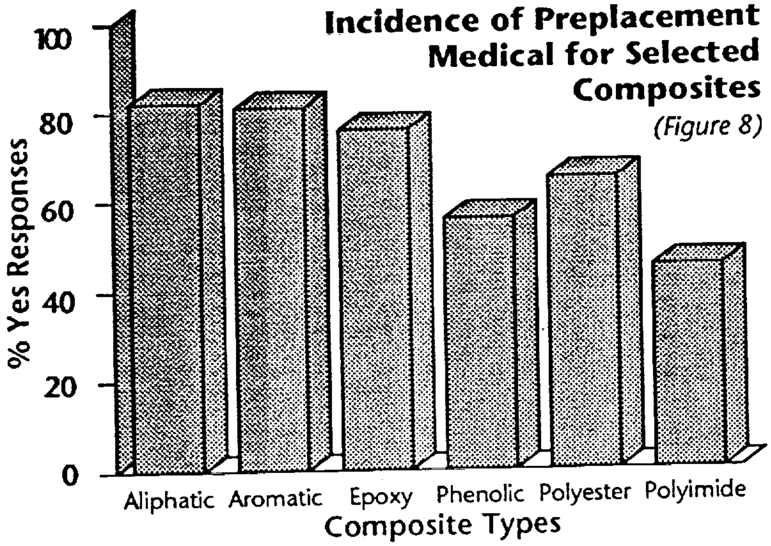
• **Booth Ventilation:** Booth ventilation is recommended when composite materials are being sprayed or when large volumes of volatile materials are being handled. If areas can be isolated where hazardous operations are being performed, it is often more cost-effective to perform the task within the confines of a booth to minimize air handling costs and prevent odors from adversely affecting personnel in adjacent work areas.

### 2) Composite-Specific Observations/ Recommendations

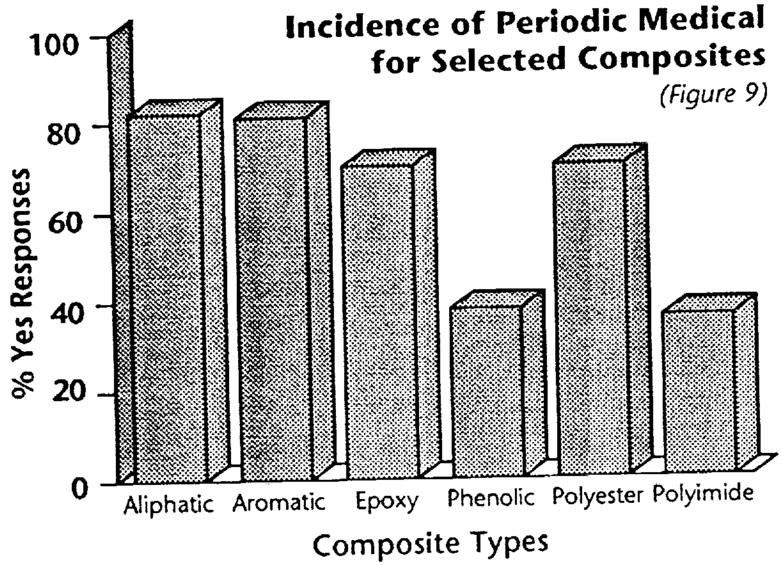
The following is a summary of observations from the user experience survey, including data on odor complaints, incidence of sensitization and dermatitis, and information pertaining to medical surveillance.

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 Periodic Medical for Selected Composites**
*(Figure 9)*

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 epichlorohydrin 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 systemic 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 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 ventilation. 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[8].

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 percent 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.

**Hazards by Manufacturing Operation**

| Operation | Potential Hazards | | | Target Effects | | |
|---|---|---|---|---|---|---|
| | 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)*

### 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 composite 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.

**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 processing 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 composite 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 procedures 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 contamination. 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 established for composite components which are of sufficient toxicity and are readily absorbed dermally.

### 3) Medical Surveillance

Medical monitoring protocols should be established through review of the product hazards combined with information regarding relative exposure levels to which workers are exposed. In many cases, neither of these parameters are known and therefore, the fundamental information needed to establish 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 industry. Additionally, the manufacturers should be encouraged to share toxicology information about chemicals with occupational medicine personnel representing the user industry. Lastly, accurate exposure measurements 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 different 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 materials 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 material 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. ■

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