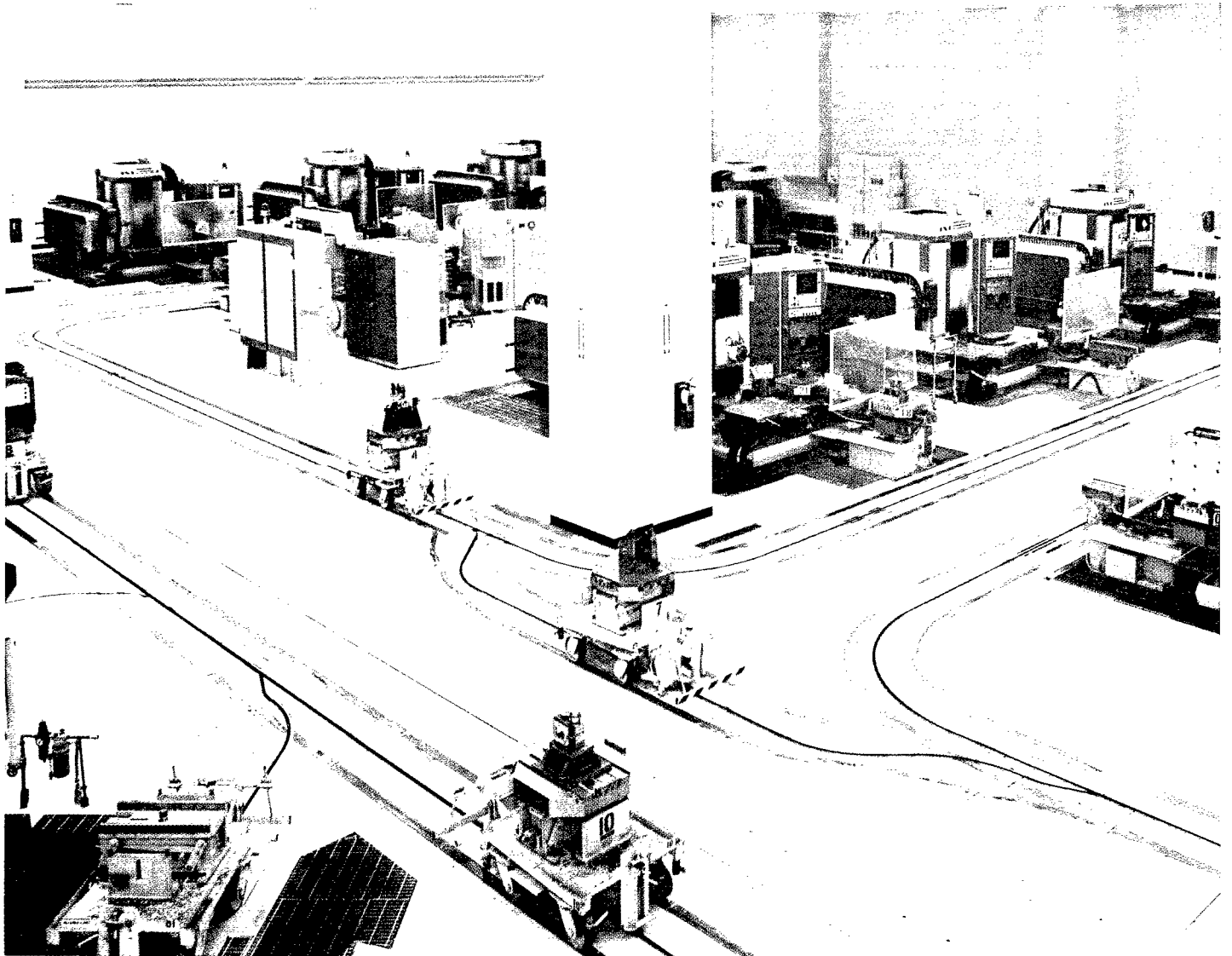


# US Army ManTechJournal

Meeting the Challenge

Volume 10/Number 2/1985

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## Editor

RAYMOND L. FARROW  
U.S. Army Materials & Mechanics Research  
Center  
Watertown, Massachusetts

## Technical Advisor

DAROLD L. GRIFFIN  
Deputy Chief of Staff, Production  
U.S. Army Materiel Command  
Alexandria, Virginia

## Associate Editor

DAVID W. SEITZ  
U.S. Army Materials & Mechanics Research  
Center  
Watertown, Massachusetts

## Assistant Editor

WILLIAM A. SPALSBURY  
Metals & Ceramics Information Center  
Battelle's Columbus Laboratories  
Columbus, Ohio

## Technical Consultants

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U.S. Army Laboratory Command  
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U.S. Army Communications-Electronics  
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# US Army ManTech Journal

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### ABOUT THE COVER:

The flexible manufacturing system in operation reflects a significant step forward by the U.S. Army in its thrust toward implementing more automation in the production base. The contractor, Draper Laboratories, collaborated closely with several defense contractors and prepared a 5-volume handbook and a computerized program for decision making. This approach (shown here) integrates work stations and material transport under control of a host computer. The decision support software assists the system designer and implementer in designing, evaluating, simulating, and operating an FMS. By reducing the risks in implementing these systems, the project has stimulated the introduction of more productive manufacturing systems for producing Army items. It currently is used with manufacturing processes on the Bradley fighting vehicle and the Abrams tank.

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# Comments by the Editor

**C**orrosion has been one of Man's most baneful facts of life as he has progressed into the age of machinery—most of which has been fabricated from materials highly subject to combination with other elements. Corrosion takes many forms besides simple oxidation and now with the wider use of composite materials, degradation of structural properties can result from nearly everything under the sun. However, simple rust still constitutes the bulk of the vast damage incurred regularly in the machinery that society uses, and this also holds true in regard to military equipment. The loss of property from corrosion is staggering and has been estimated in the billions of dollars worldwide each year; but the actual loss is incalculable because of all the attendant unaccounted waste.



RAYMOND L. FARROW

To better inform our readers with the problems facing the U.S. Army because of corrosion, we plan to devote the fourth issue this year of the U.S. Army ManTech Journal to that subject and are soliciting papers to be presented in that publication. The note at the bottom of this page gives the pertinent information for submitting these papers; we hope to have a wide response from our readers to make the issue one containing significant and timely information.

This issue of the Journal contains several items of special note. The first article on ultrasonic bonding describes work that has since been adapted for use on several aircraft now in production, and we plan to present an update on this implementation in the near future.

The second article, on development of a process to manufacture image intensifier tubes, discusses the steps by which the contractor achieved this special capability—a capability long sought by electronics suppliers.

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#### CALL FOR PAPERS

The Fourth Quarter, 1985, issue of the U.S. Army ManTech Journal will be devoted to the subject of CORROSION. The readers of this Journal are invited to submit articles of 4 to 6 pages, with photographs, that document case history corrosion problems and the steps taken to correct or alleviate those problems. A "lessons learned" approach would be useful. Articles should be submitted by September 1, 1985, to:

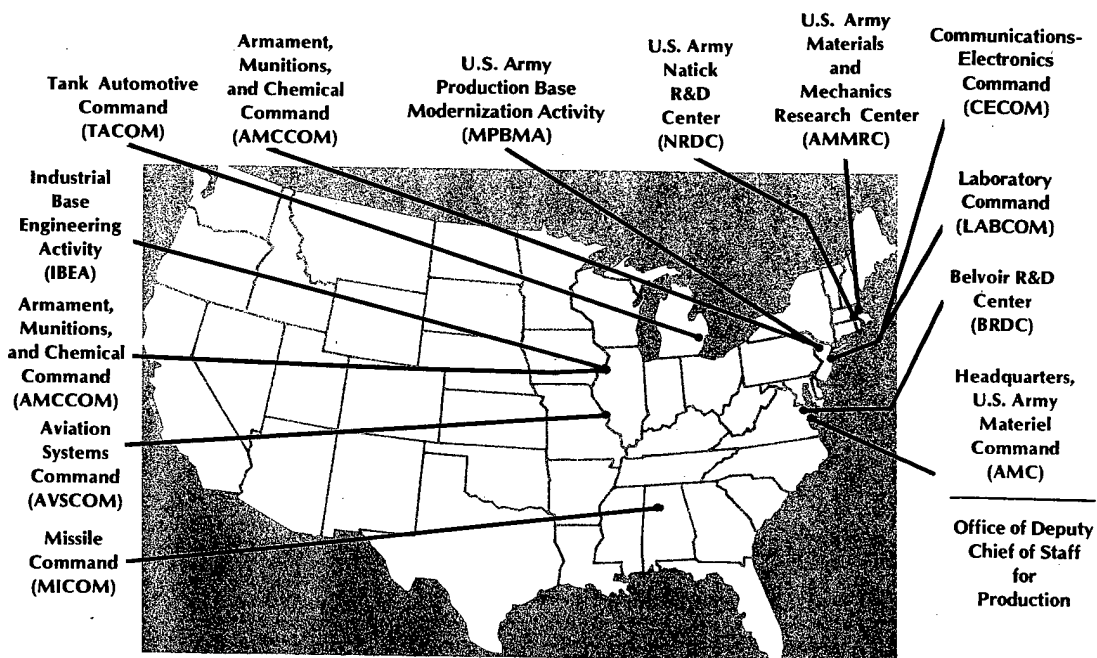
W.A. Spalsbury, Assistant Editor  
U.S. Army ManTech Journal  
Battelle's Columbus Laboratories  
505 King Avenue  
Columbus, Ohio 43201-2693

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The next three articles are part of a series on the characterization of composite materials. The work was conducted by both academic institutions and by industrial firms in a seven-part effort funded by the U.S. Aviation Systems Command through the Army's Materials and Mechanics Research Center. We are presenting reports on three of these phases in this issue—an overview, a treatise on physiochemical characteristics, and one on radiographic considerations. Our next issue of the Journal will present reports on other phases of this work. We hope our readers will find some very useful information in the series on this comprehensive work.

As usual, we also include numerous brief status reports on ongoing projects and will attempt to furnish complete coverage of all other current projects in our next issue.

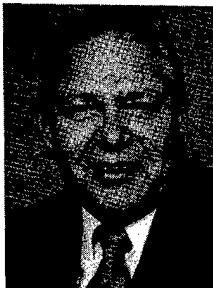
### AMC Manufacturing Methods and Technology Community



## Different Joining Technologies Merged

# Ultrasonic Weld Bonding of Primary Structures

ROBERT L. RODGERS is an Electronic Engineer with the Structures Technology Division, Applied Technology Laboratory, Ft. Eustis, VA. He has been active in materials investigations there for the past nineteen years, following six years of work in weapons systems testing at Newport News Shipbuilding and seven years as resident engineer at Vickers Electronics Products Division of Sperry Rand Corporation. A participant in MTAG activities, Mr. Rodgers is a member of the American Helicopter Society. He received his B.S.E.E. from Washington University, St. Louis, in 1951.



Costly tooling and fixtures required for adhesive bonding, also extreme labor costs and weight disadvantages of riveting, soon may be avoided through use of a new combination of technologies constituting ultrasonic weld bonding. In a manufacturing technology project conducted by Hughes Helicopters for the U.S. Army Aviation Systems Command through the Applied Technology Laboratory, conditional success was achieved; however, continued work will be required in order to make the technology practical for production.

### Accomplishments

This program was a study to develop and optimize an ultrasonic weld bonding procedure for the fabrication of primary structural components for helicopters. This procedure, a combination of ultrasonic welding and adhesive bonding, was developed through a series of coupon tests. Various adhesives and surface treatments were evaluated with regard to their adaptability to ultrasonic weld bonding. Adhesive bond quality and weld quality were evaluated through various T-shear, fatigue, and environmental salt-spray tests. Environmental degradation of the adhesively bonded areas occurred consistently and will need to be resolved.

### Introduction

Hughes Helicopters, Inc., with the assistance of Sono-bond Corporation as a major subcontractor, concluded a study of ultrasonic weld bonding, a new method for fabricating primary structural components for helicopters. This program followed a previously completed ultrasonic welding program involving secondary structures (Reference 1).

The previous program showed that ultrasonic welding could provide a viable, high-strength, low-cost method of fabrication applicable to secondary aircraft structures. The ultrasonic welding procedure was demonstrated to be effective for most aluminum alloys and some titanium

**NOTE:** This manufacturing project, conducted by Hughes Helicopters, Inc., was funded by the U.S. Army Aviation Systems Command's Applied Technology Laboratory under the overall direction of the Office of the Deputy Chief of Staff, Production, U.S. Army Materiel Command (AMC). The AVSCOM Point of Contact for more information is Fred Reed, (314) 263-3079.

alloys. In the welding procedure, the workpiece is clamped in place between the tip and anvil of the spot welder. The various parameters, such as input power and weld time, are set on the frequency converter power unit (see Figure 1). Welding occurs when the tip is made to oscillate in a plane parallel to the weld interface. The oscillating vibratory motion disrupts the oxide layers and other surface film on the mating surfaces, allowing solid-state bonding to occur. The fusion that takes place between mating surfaces occurs without formation of the cast nugget found in normal resistance spot welding.

The weld bonding procedure involves a combination of ultrasonic welding and adhesive bonding. The vibratory motion of the welding tip displaces the adhesive between mating surfaces, allowing welding to occur. The welded assembly is then placed in an oven to cure the adhesive, thus completing the weld bond procedure.

The study to develop a new, reliable, cost-effective manufacturing technique attempted to provide an alternative to adhesive bonding and riveting, the methods currently used to produce structurally sound primary components in the aerospace industry. Adhesive bonding requires costly tooling and fixturing during the assembly process. Riveting requires extensive cost in time and labor, as well as adding a significant amount of weight to an assembled structure. New methods are constantly being investigated in an attempt to provide less costly manufacturing processes. Other programs have studied weld bonding processes using resistance welds (References 2 and 3). In a similar manner, the intent of this program was to use the cost savings provided by ultrasonic welding and to apply it to a weld bonding process. The ultrasonic welds which hold the various subcomponents together, with adhesive in place, eliminate the need for complicated fixturing during the bonding process. The ultrasonic welds would also provide a strong structural backup to the bonded component.

The purpose of this program was to develop and optimize the ultrasonic weld bonding process, and after application to various test components, develop an implementation plan for its application on the Advanced Attack Helicopter (AAH) program. Various adhesives were considered before selecting the unsupported film adhesives for use in the study. A surface condition compatible to both ultrasonic welding and adhesive bonding (a primed and etched surface) was determined and used throughout. Testing consisted of static, fatigue, and accelerated environmental tests of coupons. Sonobond Corporation fabricated the test coupons, which were submitted to Hughes for analysis. Coupon testing revealed problems; with the bond quality between welds and with environmental degradation. Further attempts were made to correct these problems. However, environmental degradation of bond quality continued to occur, reducing weld bond strengths to weld strengths. It appears that the conditions required for bonding and welding may not be compatible enough to provide a sufficiently sound weld bonded part. Also, it seems that present control and

monitoring capabilities may not be adequate for weld bonding purposes. Results of the tests are presented and discussed in this report.

## Discussion

This effort was originally planned as a five-phase program. Phase I involved selection of a structural component and process optimization; this included the selection of adhesive and surface treatments, followed by coupon fabrication and testing. Phase II involved fabrication and tool proofing of a test component. Phase III involved fabrication, test, and evaluation of additional test components. Phase IV involved the development of an implementation plan for incorporation into the Advanced Attack Helicopter Program. Phase V involved the presentation of an industry/government briefing.

Initially, a primary structural AAH component had to be selected based on adaptability of the fabrication process, cost competitiveness, and structural performance. After consideration of several candidates, the wing flap was selected as most suitable. It consisted of several riveted joints and fittings, the bulk of which could be replaced by ultrasonic weld bonding. A major factor in the selection of this component was the minimal interface problems involved in the fit and function check of the item, required in Phase II of the program. After this candidate had been selected, a later design modification of the AAH eliminated the wing flap. After another review of the available candidates, the deck assembly was finally chosen as the most suitable remaining candidate. The assembly is a large component with many riveted attachments which could be assembled by the weld bonding procedure. Due to the impossibility of performing a fit and function test of such a part, those requirements were eliminated. It was decided that the assembly would be fabricated as a subcomponent, rather than as a whole, and would be subjected to localized testing which would provide data indicative of the effect on the total component.

The selected deck assembly was to be fabricated by ultrasonic weld bonding, which involves a combination of ultrasonic welding and adhesive bonding. It is a fabrication procedure intended to provide an easily manufactured, structurally sound part at lower cost. Riveting and adhesive bonding are presently the most common methods of manufacturing primary aircraft structures. However, the costs involved in production time and tooling have encouraged research toward finding alternative methods. Some previous weld bonding studies have used resistance welding (References 2 and 3). This program attempted to use the benefits of ultrasonic welding in the weld bonding process. The various aspects of ultrasonic welding have been examined and documented in studies conducted by Sonobond and Fairchild Republic (References 1 and 4).

In the weld bonding procedure, adhesive is placed between mating surfaces and the part is welded to hold the

adhesive in place. The vibratory action on the welding tip displaces the adhesive between the surfaces, allowing welding to occur at that point. The assembly is then placed in an oven to cure the adhesive which results in the weld bonded component.

The welding machine used during this effort was a standard MH-1540 ultrasonic welder provided by Sono-bond Corporation. The welder was equipped with a 15-kHz transducer rated at 4.2 kilowatts for welding. A frequency converter (power source) was connected to the welder, which controlled input power and weld time (see Figure 1).

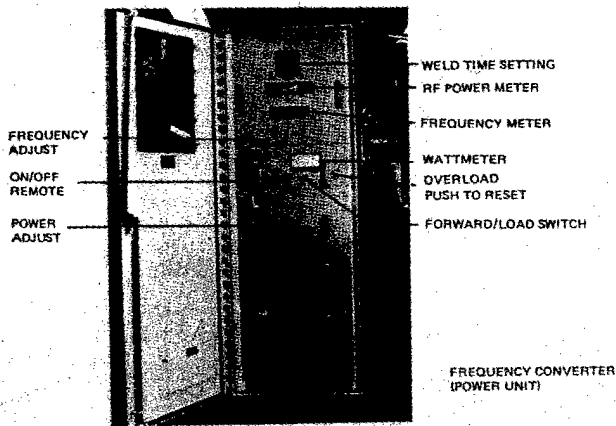
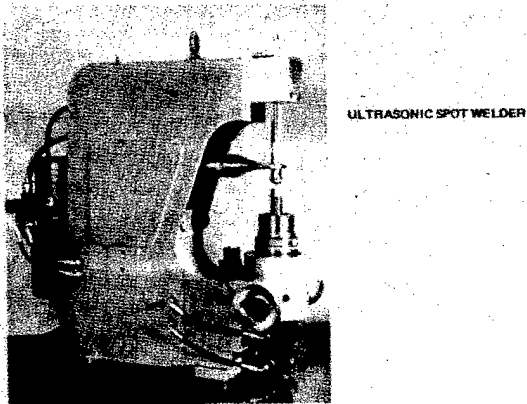


Figure 1

### Primary Goal

The primary concern of this program was to obtain an optimized ultrasonic weld bonding procedure that would provide adequate strength and durability. Various candidate adhesives and surface treatments were originally considered in an attempt to select an adhesive

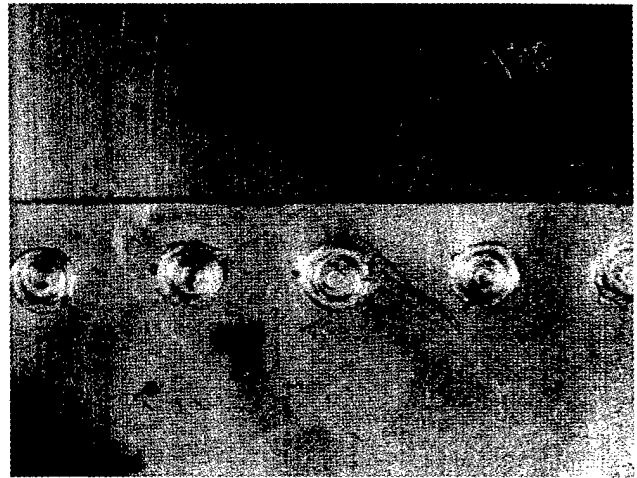


Figure 2

system to be used for the bulk of the test program.

The selected system would have to be compatible with both ultrasonic welding and adhesive bonding. The effect of different surface conditions (etched versus anodized) on ultrasonic welding was evaluated through some tensile shear tests of welded coupons.

Anodized surfaces proved difficult to weld. The optimum surface condition, yielding the highest shear value with the least deviation, occurred with an etched surface using EA 9210 primer. The use of this surface preparation led to the use of the Hysol EA 9628 and American Cyanamid FM 123-2u film adhesives. (Early in the program, it was decided that for ease of handling and application, film adhesives should be used exclusively in this weld bonding effort.)

Using one of the selected adhesive-primer combinations, differences in adhesively bonded strengths due to

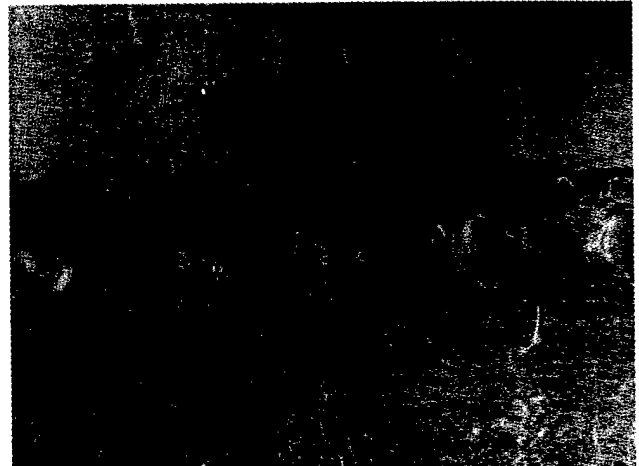


Figure 3

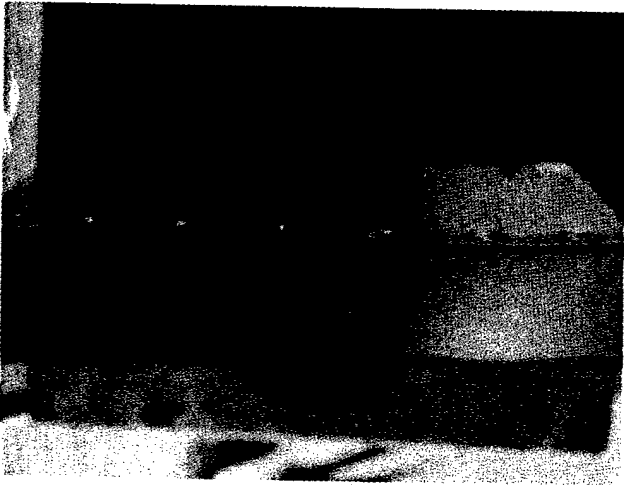


Figure 4

surface conditions (etched versus anodized) were evaluated. Tensile-shear strength (psi) was measured; the evaluation was done using EA 9210 Primer and FM 123-2u Adhesive, 0.030 psf:

- (1) Etched with room temperature cured primer, 3645
- (2) Etched with oven cured (1 hr, 250 F) primer, 4125
- (3) Anodized with oven cured (1 hr, 250 F) primer, 4205.

The data indicated that the use of an etched surface, as opposed to an anodized surface, would not significantly affect adhesively bonded strengths.

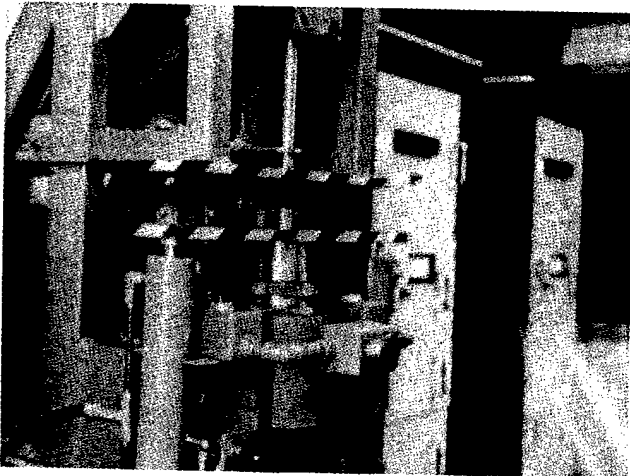


Figure 5

Welding parameters of power, time, and clamping force were also optimized to provide the highest strength. Initial welding of the panels revealed some difficulties with surface deformation and bulging tendencies between welds. These difficulties, which did not occur during normal ultrasonic welding, appear to have been caused by the higher power and clamping force required to weld through the adhesive film layer. To correct these problems, the tip configuration was altered from a series of concentric rings to a spherical tip. A hydraulic clamping fixture was developed and used to eliminate gaps in the bonded area between welds. (See Figures 2 through 6).

Figure 2 illustrates the deep indentations left by the concentric ring tip configuration. Some warping of the panel edge can also be seen. Figure 3 shows the surface condition using the spherical tip configuration. The surface is smoother, with less deformation. Figure 4 is an edge view of the welded interface, clearly exhibiting bulging and deformation. The hydraulic clamping fixture shown in Figure 5 was used to eliminate the bulging problem.

The mating panels were placed between the clamping boards and held in place during welding. Use of the external clamping fixture, along with the spherical tip configuration, resulted in the smooth, uniform, weld bonded assembly shown in Figure 6.

The final optimized weld parameters of power, time, and clamp force required for weld bonding were determined to be 3200 watts, 0.50 second, and 275 psi, respectively.

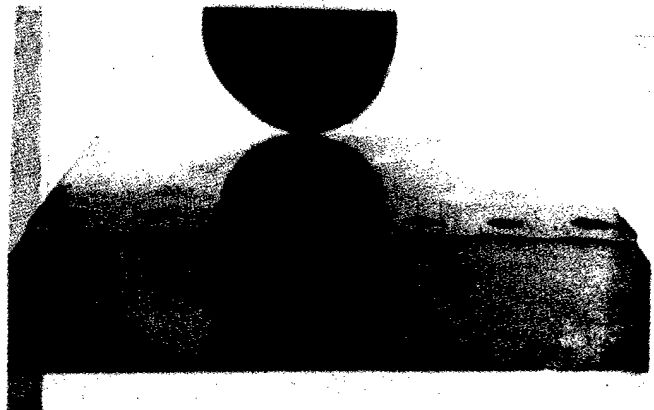


Figure 6

## Test Procedures, Results

After the optimum surface preparation and welding parameters were determined, coupon tests were con-

ducted; the tests examined the adhesive bond quality, the weld quality, and the environmental effects. All of the tests were conducted using 5-inch by 7-inch by 0.040-inch-thick 2024-T3 Alclad aluminum alloy panels which were cut into 1-inch-wide coupons after fabrication. Coupon configurations are shown in Figure 7.

Conditions typical of the weld bond interface, where adhesive remnants exist within the weld zone and bits of clad material are entrapped within the adhesive zone, are illustrated in Figures 8 through 11. The results indicate that ultrasonic weld bonding achieved higher strengths than resistance welds, rivets, or ultrasonic

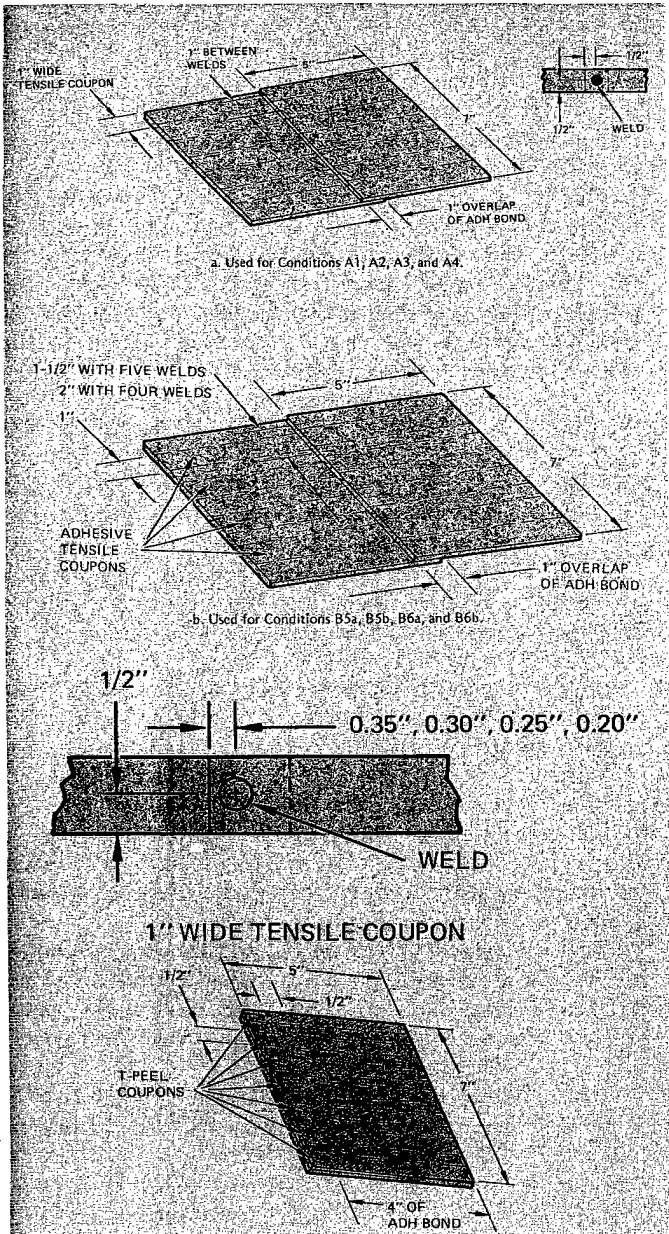


Figure 7

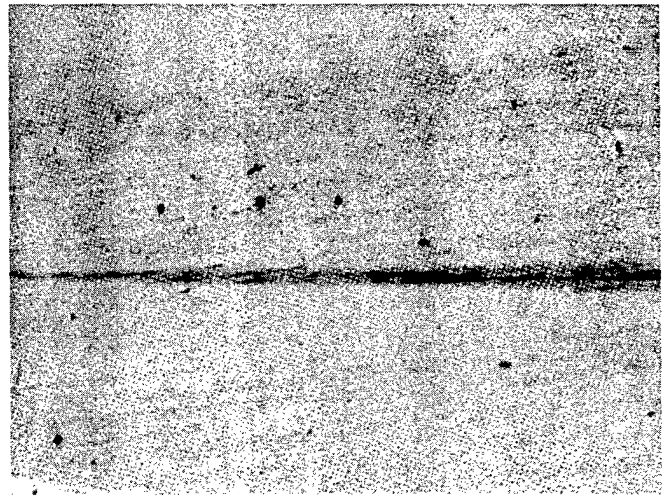


Figure 8

welds when joining comparable sheet thicknesses. However, the adhesive bond in the area between welds was not able to achieve the standard strengths of a normal adhesive bond. In addition, the lack of adequate adhesion resulted in severe degradation in strength when exposed to a salt-spray environment. As a result, weld bond strengths were reduced to that of the ultrasonic weld during environmental tests.

The results of the coupon tests indicated that further work was required to resolve the problems encountered. An extension of the coupon test phase directed toward correction of the problems then was begun. All coupons fabricated in the extended coupon test phase (except for a set of adhesively bonded 0.090-inch panels) were made from 0.040-inch-thick 2024-T3 Alclad aluminum

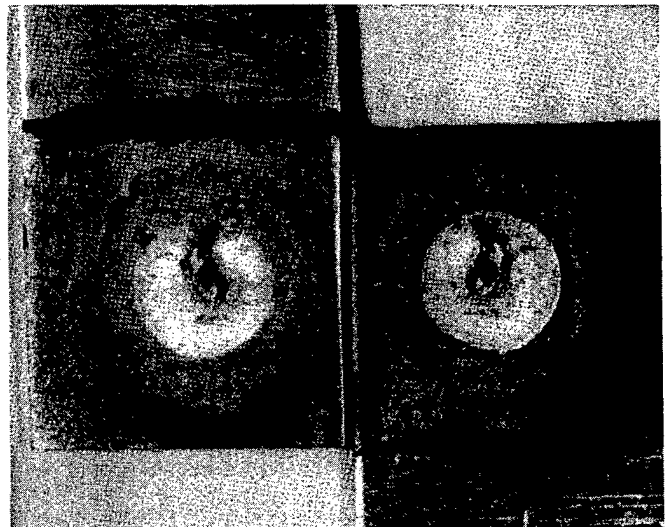


Figure 9



Figure 10

alloy panels. Test coupons used a 0.75-inch overlap (reduced from the 1-inch overlap used in previous tests), in an attempt to insure failure through the bond rather than through the substrate. All tests were conducted using both FM 123-2u and EA 9628 unsupported film adhesives, and results are given in a series of tables in the final report, which can be obtained from the AVS-COM representative.



Figure 11

### Test Conditions Set

The test conditions formulated for the extended coupon tests attempted to identify and correct factors which may have caused undesirable results in the initial tests.

Condition 1 addressed the effect of backing configurations in an effort to reduce peeling and distortion, which may have affected the test results. Condition 2 provided various adhesively bonded conditions for comparative purposes; the anodized and primed condition is normally used by Hughes for adhesive bonding. Bonding with and without pressure was studied to determine its impact, since lack of pressure was suspected to be one cause of insufficient bonding between welds. Condition 3 provided a comparison with the weld bonding results of the initial tests. Condition 4 was to determine whether a cleaner surface would help improve bonding. Conditions 5 through 7 were various approaches for correcting the inadequacy of the bond between welds. Environmental samples from each condition were studied to determine the factors that would help maintain the bond in a salt-spray environment. In addition, a few tests were conducted to determine the effect of certain conditions on fatigue.

The double unbalanced backing configuration tended to give the most satisfactory failure of the bond, without cleavage or distortion. Application of curing pressure resulted in higher bond strengths. The anodized and primed surfaces resulted in the strongest adhesive bonds, and the environmental tests indicate that they were the only ones able to retain strengths.

The T-shear strengths obtained in Conditions 3 through 7 for these weld bonded coupons tend to be higher than the values obtained previously. The shear values obtained for Conditions 5 and 6 appear to be about as good as those for a purely adhesive bond. This may be due to the added pressure (presence of dead load for Condition 5, or thicker film which possibly creates greater pressure in Condition 6). This would be consistent with the finding that higher adhesive bond strengths are obtained with application of pressure during cure.

The environmental samples of all the weld bond conditions resulted in a manner consistent with previous studies. The coupons containing the welds appear to have reduced in strength down to the weld strengths. The coupons between welds continue to fall apart, unable to maintain the bonds and prevent moisture penetration. The environmental coupons between the welds failed in a manner similar to the etched and primed adhesively bonded coupons exposed to the salt spray.

Results of selected fatigue tests indicate that the bonds formed between welds are not as good as those formed through normal adhesive bonding procedures. The coupons tested fell short of required stress levels specified for the adhesives.

After reviewing the results of Conditions 1 through 7, it became apparent that surface condition (anodized rather than etched) was the key factor in obtaining and maintaining good bonding. The following discussion describes each of the various test configurations.

### Condition 1

The effect of different backing configurations was determined using only adhesively bonded coupons. Earlier, an investigation was conducted involving various backing configurations in an attempt to determine one which would result in the least cleavage and the least local deflection. The previous configuration study showed that the highest loads and the least cleavage and deflection occurred for the double unbalanced configuration using a 0.090-inch-thick backing. A comparison study between the double balanced and double unbalanced configurations was repeated, with the effect of cure pressure application and environmental exposure also being determined. Again, the double unbalanced configuration seemed to give better results.

### Condition 2

Using the double unbalanced backing configuration, various adhesive bond comparisons were made. The values of the T-shear specimens adhesively bonded by Sonobond were generally comparable to those obtained by Hughes. The discrepancy involving the double thickness of FM 123-2u adhesive was due to gaps existing between the two layers of adhesive in the Sonobond sample. A set of anodized and primed panels were bonded for comparison with the etched and primed panels. A set of unbacked 0.090-inch panels were also bonded for comparison.

Panels were adhesively bonded under both a dead load and a curing pressure of 35 psi for comparison. Test results indicate that higher adhesive bond strengths are obtained when curing pressure is applied. Generally, whenever the data reflected the opposite, it was due to the occurrence of thinner bond lines under curing pressure. The EA 9628 film appeared less sensitive to the effect of curing pressure.

Environmental samples taken from each situation were exposed to a 10-day salt spray. Results show that the anodized and primed panels were the only ones able to retain strengths after salt-spray exposure. A thin, even bond line is displayed, with good cohesive failure. Coupons that fell apart after the salt spray displayed complete adhesive failure, with separation occurring between the primer and panel. Coupons retaining some strength typically displayed adhesive failure, although some portion of the film remained attached to the mating surface.

### Condition 3

For Conditions 3 through 7, 5-inch by 7-inch panels were weld bonded by Sonobond using both FM 123-2u

and EA 9628 unsupported film adhesives. The weld bonded panel configuration remained the same as in the original coupon phase, except for the use of the 0.75-inch overlap and the 0.090-inch double unbalanced backing system. All conditions were tested for the adhesive bond quality around the weld (1-inch-wide coupons containing the weld) and for the bond quality between welds (1-inch-wide coupons taken between welds). Environmental samples were taken again from each situation for exposure to a 10-day salt spray. Also, selected samples between welds were fatigue tested to determine bond quality.

For Condition 3, the conditions used for the initial coupon fabrication were repeated as a comparison of the 0.75-inch overlap to the 1-inch overlap. The data indicates a significant increase in strengths (+ or - 20%) compared to previous results. This is basically due to less distortion (and less peeling effect) experienced by our present coupon configuration.

### Condition 4

The effect of cleaning the panels with a solvent wipe prior to weld bonding was studied to see if a better bond between welds could be achieved. This procedure did not appear to have much significance. (Conditions 5 through 7 included solvent wiping of panels prior to weld bonding.)

### Condition 5

The effect of applying a small dead load between welds during the cure cycle was studied. This appeared to aid the bond strength between welds.

### Condition 6

A double thickness of film was used to determine its effect on bond qualities. It appears that the thicker film may create greater pressures and reduce voids between welds during the weld sequence, thus resulting in higher bonding strengths.

### Condition 7

Application of a higher external clamping force during welding (through FM 123-2u adhesive) yielded inconclusive results. Studying the bond failure surfaces did not reveal any unusual pattern or explanation. In the case of EA 9628, the increased outside clamping force increased the strength around the weld areas, but it did little to increase strengths between welds.

The data indicates that an anodized surface is important

in resisting environmental degradation. The etched and primed panels all displayed degradation of strength ranging from considerable to complete. However, early attempts to ultrasonically weld through an anodized surface proved futile, thus resulting in weld bonding efforts through an etched and primed surface.

In an effort to allow ease of implementation in conducting the program, typical bath and surface treatments were used. Film (rather than paste) adhesive also was used to provide easy application and implementation.

The consistent environmental degradation of Hughes' weld bonded specimens suggests the use of special baths and surface treatment used by Fairchild/Northrop in their successful resistance weld bond study, which displayed no environmental problems (References 2 and 5). Their preparation involves an anodize (using different voltage and solution), a special cleaning solution, and a special weld bond paste adhesive (Goodrich 1444B).

The thickness of the anodize used by Fairchild/Northrop in their studies is much thinner than Hughes' anodize thickness. Before attempting to apply their procedures (using their materials and solutions), a determination of the effect of anodize thickness on ultrasonic weldability is desired.

It should also be noted that the Fairchild/Northrop resistance weld bonding program used equipment that enabled them to control the entire weld cycle. Controlled use of current and force enabled precise monitoring of weld initiation and expansion. Use of a microprocessor allowed repeatable feedback control on a cycle-by-cycle basis for consistent welding through the treated surfaces.

It appears that present control and monitoring capabilities of the ultrasonic welder may not be adequate for weld bonding purposes. Ultrasonic welding is very sensitive to surface condition. Unless the three critical variables of frequency, power, and force can be controlled and monitored more accurately - and with relative ease, it appears that ultrasonic weld bonding would be difficult to accomplish.

## Conclusions

Results of the initial set of coupon tests indicated that further work was required to improve bonding characteristics of the ultrasonic weld bond operation. An extended coupon test phase was conducted in an attempt to improve the quality of bonding between welds and the environmental durability of the bonds. After studying various conditions, the following conclusions can be drawn:

- The surface conditions for adhesive bonding and ultrasonic welding appear to be incompatible. The anodized surface conducive to adhesive bonding appears to be unweldable. Conversely, the etched

surface conducive to welding is subject to environmental degradation.

- Application of pressure during cure results in higher bond strengths. Use of thicker film (double thickness of 0.006-inch FM 123-2u and double thickness of 0.010-inch EA 9628) appears to provide some added pressure.
- The ultrasonic welding equipment requires greater control and monitoring capabilities regarding frequency, power, and force for weld bonding application.

## Recommendations

Based on the results of this effort, it is recommended that:

- Variations in anodize solutions and thicknesses be studied to determine whether welding can take place through some type of anodized surface.
- Improvements be made on the welding equipment to make it more applicable to weld bonding. Additional equipment to control and monitor the weld sequence should also be used.

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Production Capacity Established

# Image Intensifier Tube Fabrication Successful

KURT VILLHAUER is a Project Engineer currently engaged with development of third generation image intensifier tubes and related components at the Night Vision and Electro-Optics Laboratory, Fort Belvoir, Virginia. He has worked on image intensification projects there for 22 years, developing night fighting optical devices. Among his earlier activities were involvement in development of a passive device in the early '60s which produced no source radiation; also, high gain intensification tubes using microchannel plates and not requiring an infrared source. Mr. Villhauer received his Mechanical Engineering Degree in 1954 from Long Island Technical College, State University of New York.

Photograph

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**P**roducibility was the key objective in a U.S. Army manufacturing technology project that successfully developed the technology to fabricate a new lightweight, high performance goggle tube for use in airborne night vision applications.

During this project for the U.S. Army Electronics Research and Development Command's Night Vision and Electro-Optics Laboratory, Varian Associates developed a process to manufacture high performance third generation image intensifier tube assemblies at the rate of at least five tubes per station per week.

The objective of Varian's program was the qualification and pilot production of high performance third generation image intensifier tubes which had a high sensitivity InGaAs/GaAs/glass photocathode, filmed microchannel plate, and a high-resolution phosphor on a fiber optic inverter output. Tube processing rate requirements were

at least five tubes per station per week. Successful completion of this project was intended to show the producibility of a new lightweight, high performance goggle tube for specific use in airborne applications.

Varian has been actively engaged in research, development, and engineering of photocathodes and third generation image tubes under various contracts with the Night Vision & Electro-Optics Laboratory (NV&EOL) for the past 14 years. These efforts have led to the successful fabrication of third generation wafer intensifier tubes. Despite past advances, however, there still remained work to be done in various areas of the production process. Through the combined efforts of equipment, process, and quality engineering, Varian proposed to increase the yields and ultimately reduce the costs of the 18 mm third generation wafer intensifier tube.

Specific activities that Varian undertook to accomplish the program objectives included analysis of tube ceramic design; analysis of optic glasses; evaluation of screen intagliation; analysis of "brush" vs "spray" as the preferred screening technique; development of four-port batch processing of

**NOTE: This manufacturing project, conducted by Varian Associates, was funded by the U.S. Army Electronics Research and Development Command under the overall direction of the Office of the Deputy Chief of Staff, Production, U.S. Army Materiel Command (AMC). The ERADCOM (LABCOM) Point of Contact for more information is Bob Moore, (202) 394-3812.**

tubes; development of all tube specification test equipment; and integration of a comprehensive quality assurance system into the tube manufacturing process.

### Tube Manufacture

The 18 mm third generation ANVIS-type wafer intensifier incorporates Varian's VLI-238 tube, encapsulated with a power supply (Figure 1). The VLI-238 tube consists of an 18 mm third generation glass-sealed GaAs photocathode, input-filmed, high resolution microchannel plate (MCP) and fiber optic inverter output window with phosphor screen (Figure 2).

The tube incorporates state-of-the-art design and components aimed at improving performance. Among these

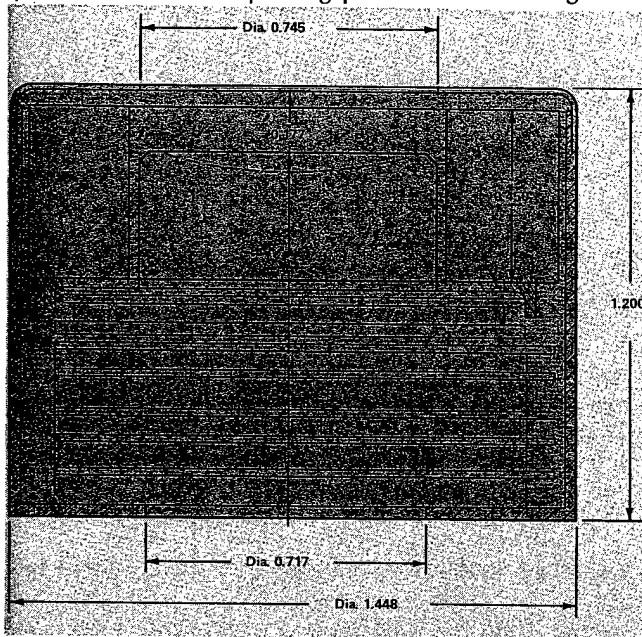


Figure 1

features are reduced size and weight; low noise figure MCP; phosphor screen, high resolution, reduced size and weight fiber optic inverter; and reduced input and output gaps to restrict halo size and to improve resolution.

Other design characteristics include indexing of input and output seals to enable control of both proximity gaps and the condition of critical sealing edges; and tube and process design allowing salvage of the tube body, MCP, and screen assemblies, as warranted.

The basic manufacturing functions used to produce the VLI-238 tube assembly include third generation cathode manufacture; phosphor screen manufacture; MCP fabrication; tube body assembly; exhaust and processing; and finishing and testing. Third generation cathode production process is provided in Figure 3.

### Screen Manufacture

Varian's contract originally required that the fiber optic output phosphor screen be intagliated. Although this requirement later was dropped, early tubes had intagliated screens. Intagliation related objectives included analysis of

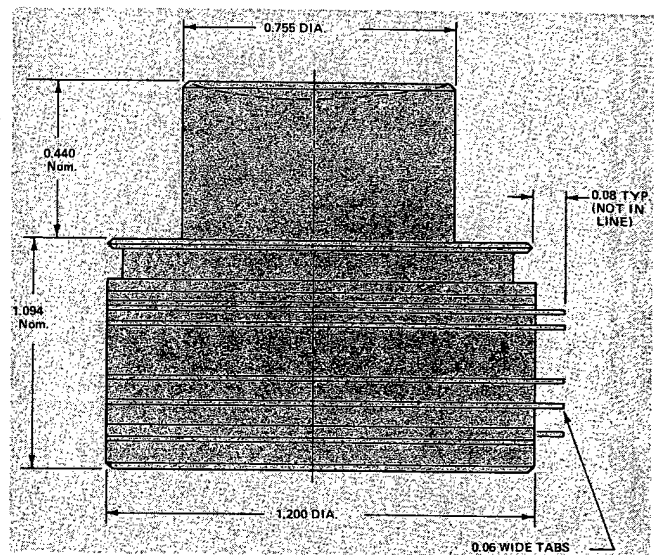


Figure 2

fiber optic types vs the intagliation etch process and analysis of brush vs spray screening techniques and optimization of the technique chosen. The incoming fiber optic inverters were inspected, tested, and sealed to an expansion matched metal flange. The fiber optics then were intagliated by removal of the core glass to a predetermined depth. The fiber optic intagliation process was standardized early in the program. The fiber optic assemblies were intagliated using special Teflon fixtures in an etching solution interspersed with and followed by a water rinse. Varian also designed a fixture to tech the optics in batches of six, and it performed well. The process used for batch etching was the same as that previously standardized for individual optic etching. The optic assemblies then were neutralized and again rinsed in running water.

The intagliation on all the optic assemblies was uniform and approximately 1/2 fiber diameter deep. The process resulted in consistent 1/2-diameter depth intagliation regardless of fiber size or manufacturer.

The intagliated optic assemblies were contact evaporated and the intagliation pits packed with phosphor by means of a forcing process, using a brush technique. This process was

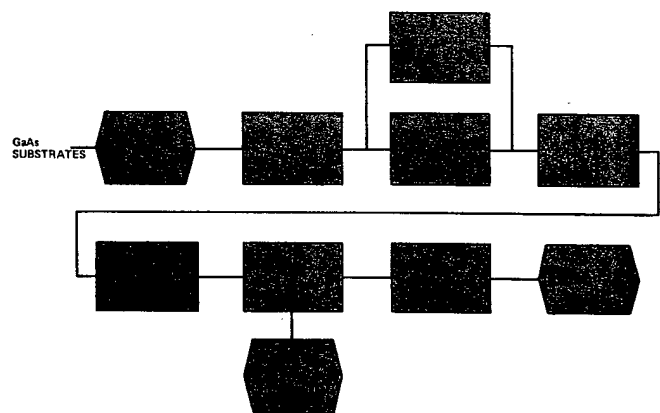


Figure 3

followed by wiping the residual phosphor from the optic surface, leaving only the phosphor particles that were lodged in the etched channels.

By the early part of the second quarter, 100% phosphor coverage was continually achieved, with no unfilled intagliation pits. The 6-micron optics were somewhat easier to phosphor than the 10-micron size, with the packed phosphor exhibiting a slight tendency to pull out of the 10-micron optic pits during the final brushing step, thus requiring exceedingly careful control.

Some small variations in the luminous efficiency of the phosphored intagliated optics were found, and examination of optic rejects showed that the phosphor particles were not in intimate contact with the bottom of the intagliated pits. To alleviate this problem, more careful brushing and closer microscopic inspection procedures during the first phosphoring step were used. The anticipated improvements resulting from these procedures were verified by using UV activation from the external optic face and comparing the emitted light levels with the characteristics of a known phosphored optic. Continued use of these new procedures resulted in improved luminous uniformity of the screens.

The use of brushing vs spraying as screening techniques was analyzed, and it was concluded that brushing was the preferable method. It was found that spraying had a tendency to leave voids in the bottom of the intagliated channel and that, with sprayed phosphor packing, the top particles tended to pull off during the wiping operation.

### Rework Time-Consuming

Optimization of the intagliation etch and screen processes showed that the fiber optic processing produced consistent results, with little or no difference in optic luminous efficiency. Testing showed that the adherence of aluminum on the phosphor particles as well as phosphor-to-glass bonding characteristics were comparable to standard brushed optics. The phosphoring process was optimized to produce an intagliated screen of slightly lower efficiency than the standard brushed screen but well within the limits of the power supply capabilities.

To evaluate the effectiveness of the intagliated screen, a tube was built which had half of the A.O. 10-micron screen area intagliated and half not intagliated. The reduction in phosphor efficiency on the intagliated half of the screen was apparent, and no improvement in performance was observed. Both halves of the screen showed a limiting resolution of 35 lp/mm, and the MTF curves were essentially identical. A second tube with a Galileo 6-micron half-intagliated screen was also constructed that, upon comparative analysis, showed results similar to the first.

The main problem with intagliation was that, during each resork, the optics were not simply washed off, given a light polish, and rephosphored. Each reject optic needed to be cleaned off, the contact removed, and the bare optic face ground and polished to remove the intagliation pits. After this, the optic had to be recycled through the

entire process. Since this was a more time-consuming process and the recycling of the reject became lengthier as well, the ramifications in a production environment became evident. A larger than normal inventory of fiber optic output had to be carried and the finished screen produced had to be a rugged, high-quality component with the potential to be salvaged and reused.

### Microchannel Plate (MCP) Manufacture

Although MCPs were a purchased component manufactured elsewhere within Varian, it is useful to identify the MCP manufacturing processes that particularly impacted tube performance requirements. Fabrication includes three steps not normally used in conventional MCP manufacture:

- Input funnelling during chemical processing
- Input coating with high secondary emission materials
- Input hermetic seal to reduce ion feedback.

While the input funnelling and high secondary emission input coating have minimal impact on MCP yield, the input hermetic seal filming has a substantial effect on yield. Varian uses evaporated silicon dioxide as this seal. Production of high performance MCPs requires that the film be thick enough to stop heavy, damaging ions and remain continuous, yet thin enough to allow high transmission of cathode electrons at typical strike voltages. The film must also have a sufficiently narrow spread in thickness so that its charge voltage under high light conditions is sufficiently controlled to insure simultaneous passage of bright source damage and high light level resolution specifications. Hermetic seal filming consists of lacquer film deposition, silicon dioxide evaporation, and lacquer bake.

### Body Assembly

The tube body is an all metal-ceramic assembly with the metal parts made of composite, insulator of ceramic, and all braze joints made of copper braze wafers.

Starting with clean parts and metallized ceramics, the body is stacked on a body brazing jig. This jig indexes critical metal parts off their IDs, and sliding nylon retainers are moved into position to OD jig the ceramics. The jig is then tightened, capturing the body stack in its desired format, the nylon retainers are slid back, and the assembly is removed from the base and placed on a boat for hydrogen brazing. After brazing, the body is removed from the fixture, all braze joints are visually inspected for quality, and the body is leak checked to verify vacuum integrity. Critical body measurements are made at this time, including (1) overall body length; (2) position of MCP output land with respect to cathode indexing land on the input seal dagger; and (3) position of the MCP input ring with respect to the output ring.

Next, the body is cleaned, fired with ultrapure hydrogen, and indium is placed into the body output flange to provide the output seal. After indium fill, the body has getter

installed and is loaded into the spot knock jar for vacuum bake. While in the spot knock jar, a high voltage is placed across all ceramics to clean up potential arcing points and/or potential leakage problems. The bodies are removed from the spot knock jar, and, after a final inspection, are complete and ready for processing.

The major program objectives in the body assembly area were to optimize the tube body design vs body processing steps and to analyze the grooved anode ceramic design.

The tube body design underwent several modifications, including changes to the MCP output ring geometry, the proximity gap dimensions, and the tube case. In addition, changes to the anode ceramic and to processing prior to indium fill were investigated but proved to be unnecessary to fulfill requirements.

A problem with MCP contact led to modification of the MCP output ring geometry. Initial investigation into the problem revealed high ohmic contact resistance between MCP and contact spacer, and the spacers were modified to provide "dimples," which were placed with the extruded side toward the MCP surface. The dimple design did not appear to remedy the situation, and further study showed that the problem appeared to be associated with the unmetallized glass surface of the MCP riding up on the corner of the MCP output ring. The problem was resolved through modification of the output ring geometry. In another MCP-related effort, the MCP centering land was raised to a higher level to ensure MCP centering.

The proximity gap measurements in the tube were relaxed to eliminate some problems that hampered efforts to build tubes free of emission points. The input spacing was increased, as was the output spacing.

To provide better control over leakage, an investigation was made into the possibility of replacing the smooth anode ceramic with a circumferentially ID-grooved ceramic. From preliminary evaluations of the performance for each design, it was concluded that both designs were fully acceptable to meet contract requirements, and design selection at any given time was subsequently based on availability. Data generated later in the program suggested that the grooved ceramics might be a source of long-term leaks, and the use of these ceramics was ultimately dropped.

At the onset of the program, the use of ion plating before indium fill was contemplated as a means to enhance retardation of dendrite formation. Evaluation of this technique early into the contract, however, indicated that the use of nickel plating would provide an adequate barrier to dendrite growth.

### Exhaust/Processing

All of Varian's third generation wafer tubes are fabricated using a "semi-EPIC" process. With this method, the cathode is heat cleaned and activated with cesium and oxygen in a separate chamber and then transferred for final sealing to the tube chamber.

The major steps in the processing and sealing cycle of a third generation wafer tube are as follows:

- Load tube body and cathode

- Bake and cool
- Microchannel plate and phosphor screen scrub
- Photocathode preparation (includes heat clean)
- Cathode activation
- Seal and unload.

The major program goals in the exhaust/processing area included analyzing the batch processing for the optimum number of ports; debugging the batch system; establishing a processing schedule for the multiport system; correlating tube processing vs initial photocathode response, noise figure, operational life, EBI, and thermal stability; and optimizing tube processing vs overall performance.

### Finish and Test

The final assembly and testing of the intensifier tube and assembly uses standard processes and techniques. The major program accomplishment in this area was the development and installation of equipment for the performance of acceptance tests. In the finish and test area, the tube is mechanically inspected and the preliminary photocathode sensitivity is measured. After being rinsed in freon, the tube is taped to prevent breakdown across the ceramic, and flying leads are attached and taped over.

A remeasurement is made of photocathode sensitivity, and the tube is turned on to inspect for general image quality and ion barrier film quality. The incoming power supply is inspected visually and mechanically. Following a 24-hour burn-in at elevated temperatures, the power supply is checked for automatic brightness control, output regulation, and input current performance. After possible grind and polish of the external cathode surface, the external surfaces of the ceramics are grit-blasted with high purity alumina. The power supply and tube are cleaned and primed, the tube is sprayed with RTV, and the power supply leads are soldered to the tube connections.

The tube and power supply assembly is aligned electro-optically, and plotted into the case with RTV under vacuum conditions to avoid air inclusion. The backing plate is set into place to complete the assembly and it then goes through "A", "B", "C", and "D" acceptance testing.

### Engineering: Equipment, Process, and Quality

Program efforts in equipment engineering centered on refinements to Varian's four-port batch processing system, designing new fixturing, and development and installation of test equipment needed for specification testing of tubes under this contract.

The four-port system, developed as a result of an ongoing in-house batch processing improvement program, was used for exhaust and processing in a fully loaded condition in the program. Although processing results were unsatisfactory, the problems were a function of cathode substrate cleaning, cesiation, and heat cleaning rather than anything pertaining to the station design.

Several improvements to the system were subsequently introduced, including forced heater block cooling to reduce processing time, double transfer arms to improve component manipulation procedures within the vacuum system, and better current-sensing techniques during cathode activation. The system performed adequately until late in the program, when 11 tubes were lost on the exhaust stations due to failures with the heater block, cathode transfer arm, and sealing ram subassemblies. All three subassemblies were redesigned and retrofitted onto the exhaust stations.

Process engineering is key to the manufacture of a third generation image tube, and exhaust/cathode activation processing is its most critical area. Exhaust and cathode processing is most critical as it impacts thermal stability and reliability. Cathode processing-related defects that affected yield included blemishes, nonspecification uniformity, and cathode scuffs, water marks and stains. These problems were met by adding new inline cathode checks and by improving existing inline cathode inspection.

Various steps were taken to improve tube yield through changes in MCP processing. These changes included the use of pretest fixtures to evaluate MCPs for film quality and persistence characteristics. Other measures taken to improve film quality included identification of residual lacquer at the edge of pinholes in the film as a source of contamination during the tube vacuum processing cycle; this contamination caused difficulty in obtaining adequate photoresponse in our finished tubes. The problem was addressed by moving to higher lacquer bakeoff temperatures.

MCP processing changes also included:

- An 8-hour vacuum bake for each MCP used in a tube prior to its final film quality test
- Development of more reliable lacquers
- Development of more refined lacquering techniques
- Institution of better control in the film evaporation process
- Increasing the dead voltage specification for film acceptance, to ensure adequate strength through tube processing
- Redesign of the alignment on the MCP output flange to solve a problem with MCP glow.

The major problems in exhaust processing and cathode activations relate to the electron scrub, cesiation, and activation schedules as they affect photoresponse, equivalent brightness input (EBI), thermal stability, high brightness resolution, low damage under bright source, and resistance to reliability tests.

The quality engineering program included integrating a comprehensive quality assurance system into the tube manufacturing process, and accomplished the following program goals:

- Establishment of incoming inspection procedures for tube parts and materials.
- Establishment of manufacturing line quality control procedures and tests. In-process inspection procedures were developed for the complete manufacturing operation, and a fulltime quality assurance inspector was installed on the manufacturing line.
- Establishment of a quality feedback system for correlation of the various tube performance characteristics with the pertinent manufacturing station.
- Establishment of routine calibration schedules and procedures for production equipment; the Varian test equipment calibration system was reviewed for compliance with the requirements of military specification MIL-C-45662. Calibration of light sources was handled by the NV&EOL quality assurance group, while Varian's Metrology Laboratory performed calibration of electronic and mechanical equipment.
- Implementation of QA material review procedures.
- Implementation of military specification MIL-Q-9858 for tube production.

## Quality Assurance Monitored

The Night Vision and Electro-Optics Laboratory conducted an audit of quality assurance operations midway during the program. This audit resulted in recommendations for quality assurance review of manufacturing process documentation to ensure comprehensiveness, clarity, and detailing of rework schedules and parts traceability. These recommendations were incorporated into the quality assurance program.

A number of changes were implemented in ANV operations final assembly relative to additional recommendations by the Night Vision and Electro-Optics Laboratory. These changes included:

- Establishment of complete incoming inspection for both electrical and mechanical characteristics for all power supplies
- Obtaining of special power supplies having 600V clamp voltages
- Installation of incandescent light cabinets for storage of tubes and power supplies
- Specification of the final procedures for matching the power supply to the tube
- Instituting the following procedures in the potting area: a bench check of sprayed tubes, inspecting for coverage, particles, bubbles, and inclusions; a bench check of the primer; recording the date of

RTV-catalyst mixture formulation to ensure that useful life has not expired;

- Performing quality audits of the process steps for each manufacturing area. After the initial performance of these audits, they subsequently were carried out by quality assurance staff on a continuing basis.

Quality assurance staff also monitored acceptance testing of the Engineering Samples and Pilot Run tubes and submitted the test data and reports to the Night Vision and Electro-Optics Laboratory

### Varian's Conclusions

Varian's accomplishments in this program may be summarized as (1) having developed a tube design that can be

built, (2) having developed the manufacturing equipment to build that tube to adequate throughput, and (3) having developed and documented the processes which allow that tube to be built at high yield and with the capability of surviving anticipated environments. The tube design was confirmed through the engineering sample phase of the program, with 12 tubes delivered with this program and many more delivered during the engineering design contract.

Concurrent with these efforts, a batch system was analyzed and optimized at four ports, a size that minimizes equipment and facility costs while insuring ten tubes per station per week. This manufacturing capability was verified, and corresponding manufacturing capabilities were developed in the screen, body, and test manufacturing areas.

Details of these achievements are listed in Figure 4.

#### Manufacturing

- \* Met delivery requirements for 12 Engineering Samples, 5 Confirmatory Samples, and 15 Pilot Run tubes.

#### Exhaust/Processing

- \* Optimized the 4-port batch design.
- \* Analyzed optimum number of ports for batch system while insuring 10 tubes per station per week.
- \* Established processing schedules for batch system.
- \* Performed studies correlating tube processing vs:
  - Photocathode response
  - Noise figure
  - Operational life
  - EBI
  - Thermal stability
- \* Optimized tube processing vs overall tube performance

#### Finish/Test

- \* Designed, developed, and installed equipment for 24 acceptance tests.

#### Fiber Optic Screen Fabrication

- \* Analyzed fiber optic types vs intagliation etch process.
- \* Optimized screening technique.

#### Tube Body Assembly

- \* Optimized tube body design vs body processing steps.

#### Quality Assurance

- \* Established a complete set of incoming inspection procedures for tube parts and materials.
- \* Set up complete incoming inspection for both electrical and mechanical characteristics for all power supplies.
- \* Established in-process inspection procedures for the complete manufacturing operation.
- \* Established continuing quality audits of the process steps for each manufacturing area.
- \* Implemented QA material review procedures.
- \* Implemented MIL-Q-9858 to tube production.
- \* Documented all manufacturing process specifications.

Figure 4

# Composite Characterization Techniques: Overview

DAVID H. KAEUBLE is Director of Arroyo Computer Center, Thousand Oaks, California, where he is a consultant and developer of computer aided design and computer aided manufacturing (CAD-CAM) models using chemical analysis. Mr. Kaelble was with Rockwell International Science Center for 15 years, where he was Manager of polymer and composite research; he previously was with 3M for 15 years in polymer research. A member of the American Chemical Society, he recently authored a new book, "Computer-Aided Design of Polymers and Composites", Marcel Dekker, Publisher, New York, 1985. A revolutionary monograph, it presents six interlinked computer based design models for polymer chemistry and composite performance. He has an international reputation in the fields of polymers, composites, adhesion, and adhesives.



DR. RICHARD J. SHUFORD is a Supervisory Materials Engineer in the Composites Development Division of the Organic Materials Laboratory. He received his B.S. in Chemistry from Stetson University and his Ph.D. from Southern Illinois University. He joined AMMRC in 1971, serving the first three years as a 1st Lieutenant in the U.S. Army. His current research interests include preparation and characterization of fibers and composites, characterization and application of piezoelectric polymers, and development of non-destructive evaluation techniques for composites.

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Advanced composite materials technology has undergone a fundamental transition in the last decade and is now implemented in a wide range of large scale primary structures ranging from composite helicopter rotor blades to composite cargo bay doors for Space Shuttle orbiter. Part of this technology development for composite reliability is a highly organized advancement in the methods and management of characterization methodologies. These characterization methodologies can be listed in the approximate order of their implementation as follows:

1. Chemical Quality Assurance Testing
2. Processability Testing
3. Cure Monitoring and Management
4. Nondestructive Evaluation (NDE)
5. Performance and Proof Testing
6. Durability Analysis and Service Life Prediction.

This overview will discuss the detailed characterization methods in the context of the management concept for implementing the specific tests.

Chemical analysis, nondestructive evaluation, and environmental fatigue testing of composites generate

three classes of information on composite reliability which need to be integrated in a reliability analysis. The rapid evolution of computer aided design and manufacturing (CAD/CAM) places new emphasis on automated monitoring and feedback control during both the manufacture and service usage of composite materials. The idealized feedback control signal from a nondestructive evaluation monitoring system is a structural margin of safety indicator. Computer models for composite durability and environmental fatigue presently contain margin of safety predictions. A major challenge for characterization methodologies is the development of practical structural margin of safety monitoring systems which operate in the structure during manufacture and service.

**NOTE:** This manufacturing project, conducted by Rockwell International Science Center thru AMMRC was funded by the U.S. Army Aviation Systems Command under the overall direction of the Office of the Deputy Chief of Staff, Production U.S. Army Materiel Command (AMC). The AVSCOM Point of Contact for more information is Jon Pratcher or Fred Reed, (314) 263-3079.

## The Beginning

Characterization begins with materials selection and continues through manufacture and use of a composite material. The logic flow chart of Figure 1 shows a typical predictive design methodology which begins on the left with system definition and ends on the right with an accept or reject decision for the manufactured part. The logic flow of Figure 1 shows that materials selection occurs as an early step in component design. Requirements for materials improvement are also shown to be closely linked to component design, life prediction, and materials selection. Physical property data on commercial polymers is extensively tabulated but is generally limited to performance and proof test data developed under ASTM or DIN standard methods. For example, one publisher systematically compares over 16,000 polymeric materials including adhesives, plastics, foams, films, sheets and laminates, and composite prepregs. This discussion is specifically addressed to fiber reinforced composite characterization and covers the full range of special topics from initial quality acceptance of prepreg constituents to durability analysis and service life prediction of the reinforced composite structure. A recent encyclopedic review provides a comprehensive presentation of commercially available fiber reinforced prepregs and cured laminates with extensive compilations and ranking of performance and proof test properties of composites.

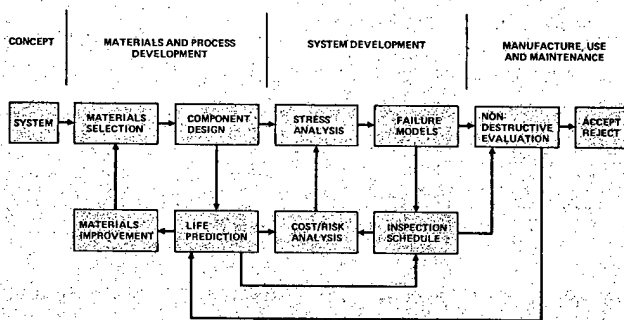


Figure 1

The classification and methods listing of Table 1 includes thirteen test methods for chemical quality assurance, processability, and cure monitoring.

The concepts of characterization have been reviewed in several general references. One presents the general principles of polymer chemistry and introduces the essential definitions of polymer physical chemistry measurement which are essential to this discussion. Another develops and combines the subject of chemistry, adhesion, and polymer rheology into models of composite response which are essential to this discussion. The proceedings of several recent American Chemical Society symposiums review the state of progress in resins for aerospace and physical characterization methods. The specific effects of service environments on composite materials has been recently reviewed in an AGARD conference, and this report adequately assesses the current status of proof testing and service life prediction.

1. Chemical Quality Assurance
  1. HPLC (high performance liquid chromatography)
  2. GC/MS (gas chromatography/mass spectroscopy)
  3. FTIR (Fourier transform infrared spectroscopy)
  4. NMR (nuclear magnetic resonance spectroscopy)
  5. Elemental analysis
  6. Surface analysis
2. Processability Testing
  1. DSC (differential scanning calorimetry)
  2. TMA (thermal mechanical analysis)
  3. DMA (dynamic mechanical analysis)
  4. TGA (thermal gravimetric analysis)
  5. SEA (surface energy analysis)
3. Cure Monitoring and Management
  1. Temperature/Pressure/Vacuum
  2. AC Dielectrometry
  3. DC Conductivity
  4. Acoustic Emission
4. Nondestructive Evaluation
  1. US (ultrasonic) immersion C-scan reflector plate
  2. US immersion C-scan through transmission
  3. US contact through transmission
  4. US contact pulse-echo
  5. Fokker bond tester
  6. 210 sonic bond tester
  7. Soudicator
  8. Harmonic bond tester
  9. Neutron radiography
  10. Low KV X-ray
  11. Coin tap test
  12. Acoustic emission
  13. Thermography
5. Surface Nondestructive Evaluation (NDE)
  1. Ellipsometry
  2. Surface Potential Difference (SPD)
  3. Photoelectron Emission (PEE)
  4. Surface Remission Photometry (SRP)
6. Performance and Proof Testing

Table 1

## Polymer States and Transitions

It is useful to define five potential physical states for components of polymer composites:

Vapor (v) — involving volatile or condensible components, generally of low molecular weight;

Liquid (l) — involving the flow state where interchain entanglements or crosslinks do not inhibit macromolecular motion;

Rubber (r) — involving free motion of polymer segments with superposed restriction of macromolecular motion by interchain entanglements and crosslinks;

Glass (g) — involving the formation of an amorphous solid state with restricted rotational motion of short chain segments;

Crystalline (c) — involving the first-order transition to a crystalline solid state with restricted rotational and vibrational motion of short chain segments.

In discussing thermal or rheological transitions from one to another of these five states there is often a confusion as to both the type of transition and time direction

of transition from initial to final state. We will adopt a nomenclature which details both the type and direction of transition.

During curing is is often shown that the path of cure involves changes from liquid to rubber to glass to rubber. A detailed time-temperature-transformation-state diagram illustrates these multiple transitions and the potential value of the above definitions.

### Characterization Diagrammed

A brief pictorial review of polymer characterization is shown in Figures 2-5, which clarifies the interrelations between these numerous test methods.

The upper view of Figure 2 shows the chemical degree of polymerization (left ordinate) versus degree of cure (abscissa). The polymer is soluble up to the gel point. The breadth of the molecular weight distribution is measured by the ration of weight to number average molecular weight, which is termed the heterogeneity index of molecular weights. At the gel point the weight average molecular weight, which describes the larger molecules of the polymer, approaches infinity. Further increase of the degree of cure beyond this gel point causes a rapid rise in the insoluble fraction termed gel formed by the crosslinking of these large molecules. At complete cure the gel fraction should constitute the bulk of the polymer with negligible unreacted low molecular polymer.

The curves in lower Figure 2 outline the characteristic changes in rheological states of liquid flow, rubber, and glass which shift the flow temperature and glass tempera-

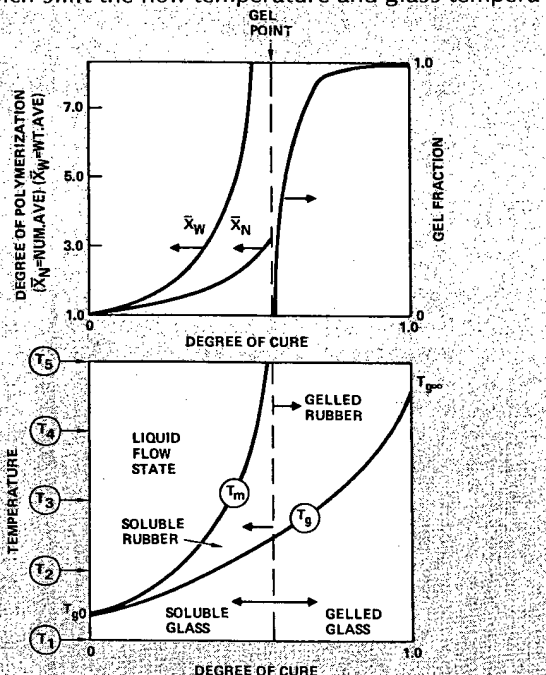


Figure 2

ture with degree of cure. The lower limit of the liquid flow state extends down to the monomeric glass temperature. The uncured resin does not possess a rubbery state at zero degree of cure. With increasing degree of cure, the lower curves of Figure 2 show the appearance of a soluble rubbery state which separates the flow state from the soluble glass state. The transition between flow and rubbery state rises to the limits of thermal stability as the degree of cure approaches the gel point. In cure processing, the elimination of bubbles, entrapped air, and unwetted interface by manipulation of pressure and vacuum must all be accomplished in the flow state and prior to gelation. The gelled polymer has an infinite viscosity and will not flow. At a degree of cure beyond the gel point only the gelled rubber and gelled glass states exist. The right margin of lower Figure 2 identifies five scan temperatures for isothermal monitoring of the degree of cure.

The curves of lower Figure 2 show that the glass transition rises with degree of cure to a final value for the fully cured polymer of infinite molecular weight. This shift in transition temperature with degree of cure is the fundamental change in properties which produces the structural stiffness and strength for the cured polymer.

### Cure State Not An Effect

The idealized isothermal dynamic mechanical monitoring of the degree of cure for the degree of cure for the five temperatures is shown in Figure 3. The lowest temperature is below the monomeric glass temperature and therefore monitors the glass state throughout cure. The upper curve plots the nearly constant value of the glass state storage modulus and shows that cure state does not influence this property. The remaining curves show

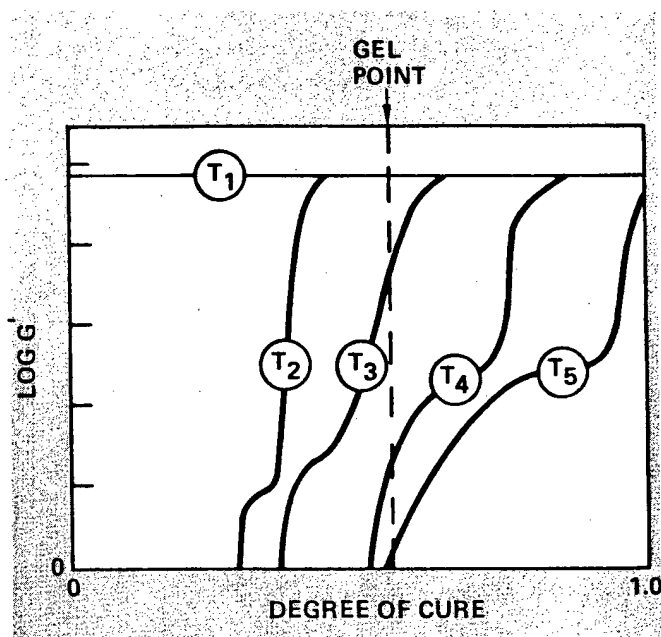


Figure 3

the characteristic rise in log of the glass state storage modulus to the glass state value as the increasing degree of cure first raises melt temperature and then glass transition temperature through the constant monitoring temperatures. In the flow state where, for example,  $T_2$  is greater than melt temperature, the expected value of glass state storage modulus, which measures the elastic energy of dynamic deformation, should be zero.

The upper view of Figure 4 sketches the expected form of the tensile stress versus strain curves. The stress is represented as the true stress of the deformed cross-section. The area beneath the related curves of nominal stress (of the undeformed area) versus strain defines the unnotched fracture energy per unit volume shown by the temperature curve. The lower curve is typical of many structural polymers which display maximum toughness near the glass transition temperature. The temperature

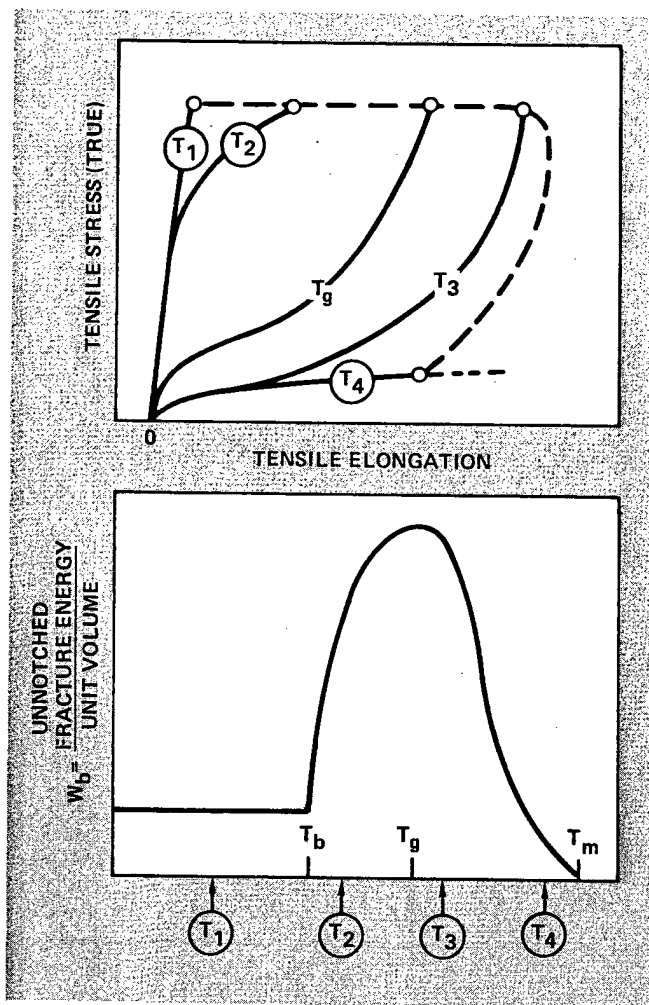


Figure 4

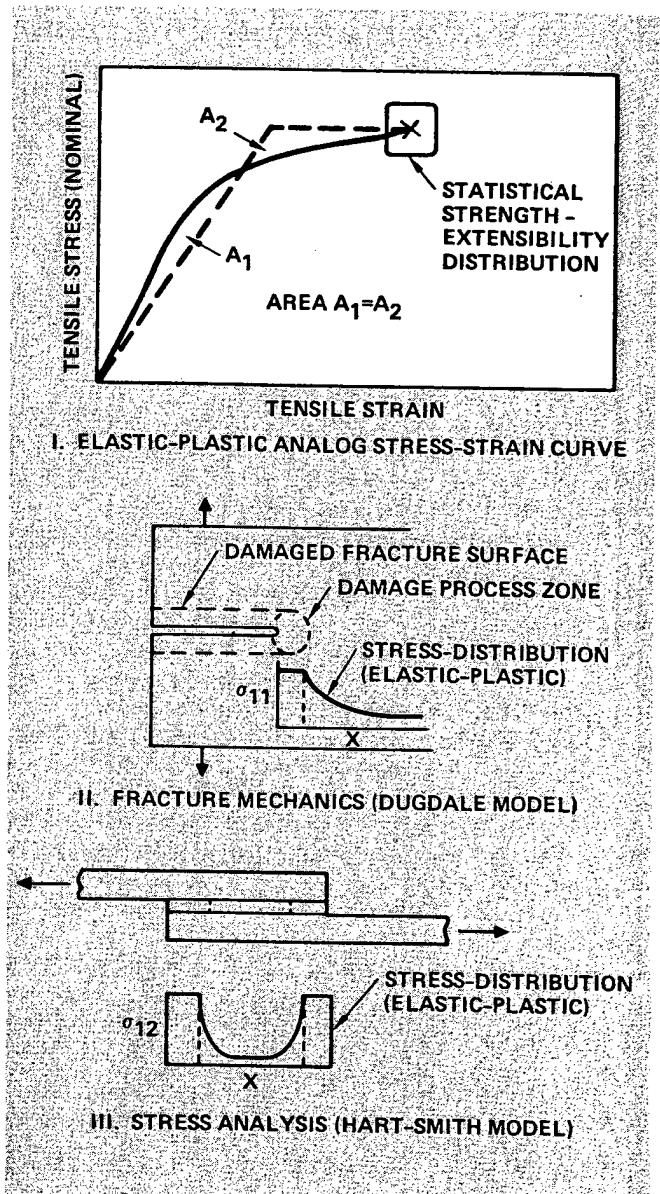


Figure 5

span of high fracture toughness is one of the distinct features of engineering thermosets such as epoxy resins and thermoplastics such as the polycarbonates.

The stress strain curves of upper Figure 4 show the typical shapes shown by engineering plastics. At the glass transition temperature or higher temperature the upward curvature reflects chain orientation effects which in some polymers are quite pronounced. At the highest temperature,  $T_4$ , failure is caused by a tensile cold drawing which is characteristic of filamentary orientation of cavities at crack tips in fracture mechanics specimens.

The upper curve of Figure 5 illustrates an elastic-plastic analog curve which is fit to an experimentally measured polymer stress versus strain response. The analog (dashed) curve has the same curve area, since Area 1 = Area 2 and the same strength and extensibility end point

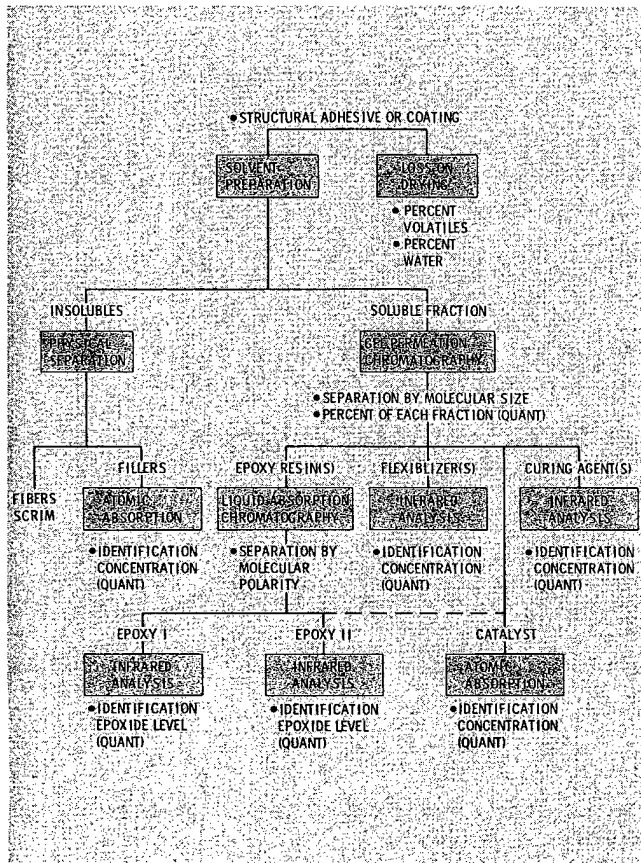


Figure 6

as measured by repetitive testing and statistical analysis. For fracture mechanics analysis for crack growth, this elastic-plastic analog is introduced into the Dugdale model shown in the middle view of Figure 5. For stress analysis, this elastic-plastic analog is introduced into typical Hart-Smith models for adhesive joints design as shown in lower Figure 5.

### CHEMICAL QUALITY ASSURANCE

One essential objective in chemical quality assurance testing is verifying the lot-to-lot reproducibility of material constituents in composite preregs. Each prepreg chemistry may require a complete development of a chemical quality assurance program. The flow chart for chemical analysis illustrated in Figure 6 involves a sequence of chemical separations combined with quantitative chemical analysis of each of the separated components. The flow chart of Figure 7 was developed for analysis of selected types of 350 F (177 C) service ceiling epoxy matrix composite preregs and adhesives. Chemical characterization programs for composite preregs are reported which implement a similar approach of successive molecular separation followed by quantitative chemical analysis. The separation methodologies implemented in the analysis of epoxies depends largely upon solvolytic separation by HPLC combined with infrared spectroscopy and elemental analysis. Quite a different approach has been

the one of chemically analysing fully cured PMR-15 polyimide-graphite composites by use of thermo-oxidative degradation combined with Fourier transform IR and NMR analysis of degradation products.

Several recent reports describe and demonstrate interdisciplinary approaches for composite characterization which incorporate chemical characterization, adhesion criteria, and composite durability analysis in a unified characterization scheme. These early attempts to integrate chemical quality assurance into a general composites durability evaluation follows the strategy suggested by Figure 1. A recent special issue of the journal "Polymer Composites" presents a collection of papers which summarize the central position of chemical characterization in the U.S. Army composite materials research program.

What follows are brief summaries and descriptive references to the chemical quality assurance test methods listed in Table 1.

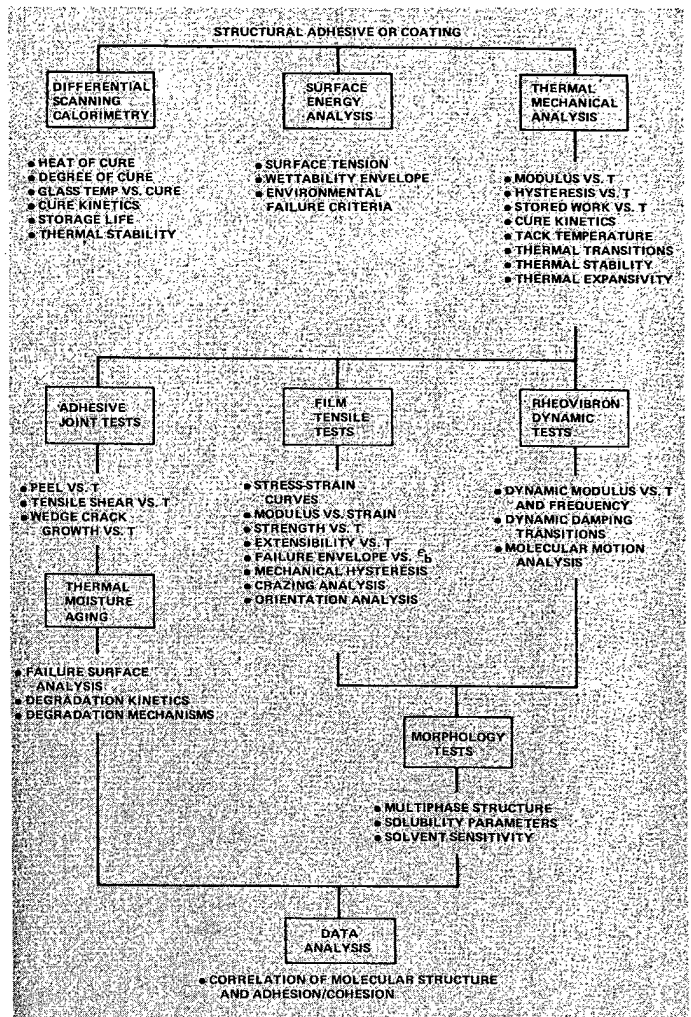


Figure 7

### HPLC (High Performance Liquid Chromatography)

**Advantages:** Quick separations; very high resolution; easily performed; very small sample size; largely automated.

**Limitations:** Requires high-resolution column and high-pressure pump; instruments are expensive; extensive experience required; limited to soluble materials.

### GC/MS (Gas Chromatography/Mass Spectroscopy)

**Advantages:** Direct chemical separation and analysis of insoluble and crosslinked polymers; profile of gas chromatographic peaks for mass spectrum analysis.

**Limitations:** Expensive.

### FTIR (Fourier Transform Infrared Spectroscopy)

**Advantages:** High resolution, rapid scanning of the IR spectrum; computer assisted; versatility.

**Limitations:** Few limitations; its versatility is a continuing challenge to the analyst.

### Nuclear Magnetic Resonance

**Advantages:** Defining of short range stereochemical structure; defining of tacticity, comonomer sequence, cis-trans isomerism, branching and cross-linking; high resolution.

**Limitations:** Still under development; not amenable to routine use.

### Elemental Analysis

**Advantages:** Identifying of the organic chemistry of composite materials; automated; highly sensitive; useful in detecting organometallic catalysts which modify the processability of thermosetting resins.

**Limitations:** No direct information on molecular structure; must be supplemented by other analysis.

### Surface Chemistry Analysis

#### Wettability, SEA via Scanning

**Advantages:** Measures fiber circumference; estimates surface roughness, concentrations; indirectly measures surface energies and environmental durability.

**Limitations:** Sensitive to swelling; liquids analysis complicated; gives no direct chemical information.

### SEM plus EDAX

**Advantages:** High resolution; great depth of focus; low magnification; can bypass metal coatings.

**Limitations:** Requires high vacuum; may cause charging; signal from thin coatings too weak for analysis.

### ESCA Method

**Advantages:** Small sampling depth; X-ray does not damage the surface; coating thickness can be evaluated.

**Limitations:** Requires high vacuum; depth profiling restricted.

### ASTM Adhesion Tests

**Advantages:** Gives direct measure of apparent bond strength; durability.

**Limitations:** Measures a system response; no direct chemical information.

### FTIR, Internal Reflection & ATR

**Advantages:** Little sample preparation; direct chemical identification; extended data processing; rapid multi-scans; isolates chemistry of thin coatings.

**Limitations:** Penetration depth; absorption bands enhanced.

### Optical Microscopy

**Advantages:** Little sample preparation; records color and birefringence; can scan large areas.

**Limitations:** Low resolution, limited depth of focus; does not resolve curved surfaces nor show evenly distributed coatings; no chemical information.

### Secondary Ion Mass Spectroscopy

**Advantages:** Small sampling depth; potentially broad range of secondary ions.

**Limitations:** High vacuum; degradation and pyrolysis; nonoperative on polymeric fibers.

### *Laser Raman Spectroscopy Mass Analysis*

**Advantages:** Analysis of a small fiber area possible to map surface; small sample volume.

**Limitations:** High vacuum; disintegration of the fiber.

### *MOLLA or Raman Microscopy*

**Advantages:** Small area; does not require high vacuum.

**Limitations:** Requires strong Raman scatterers in coating and weak scatterers in fiber.

## PROCESSABILITY TESTING

Laboratory tests for composite processability are designed to determine how a sample performs during a simulated manufacturing cure cycle. In general, these tests use small quantities of material, are fully instrumented, and are operated by programmed scanning of temperature at constant scan rate. The function of processability testing is to define the kinetics of curing, the limits of thermal stability, and the optimum cure cycle which leads to high performance and durability. Very often, procedures of chemical analysis such as outlined in Figure 6 are implemented to verify thermal analysis data and to define the chemical mechanisms of curing. Composite matrix polymers are commonly classified in terms of their temperature range of cure processing or the service ceiling temperature for environmental stability. The earlier discussion of Figures 2-5 has already introduced the multiple changes induced in thermal and rheological response as a consequence of curing. Considering the complexity of curing processes it is not surprising that logic flow diagrams such as shown in Figure 7 have been developed to better integrate processability testing with evaluation of composite performance and durability.

The upper portion of Figure 7 describes two forms of thermal analysis, DSC (differential scanning calorimetry) and TMA (thermal mechanical analysis), as central components of processability testing. These combined tests characterize the degree of cure and the effect of cure on the melt temperature and glass temperature as shown by the lower view of Figure 2. The function of processability testing is to find the optimum processing "window", which is a combination of processing times, temperatures, and pressures that consolidate, form by flow, and chemically cure the composite laminate. These processability studies should always be accompanied by relevant chemical analysis.

The processing of laminates and fiber reinforced composites inevitably involves interface bonding during

the process cycle. The utilization of wettability tests and surface energy analysis (SEA) is a subject well developed in the field of adhesive bonding but still largely overlooked in fibrous composite process evaluation. Rather extensive interface integrity studies sponsored by the Army Composites Research Program and the Air Force Materials Laboratory strongly support the implementation of SEA in conjunction with thermal analysis. SEA involves the testing of solid surface wettability by contact angle measurements with a selected set of test liquids. The analysis which accompanies SEA testing gives predictions of bonding ability and bond durability of the composite interface.

Brief descriptions of the commonly used processability test methods are presented in terms of advantages and limitations.

### Differential Thermal Analysis (DTA)

**Advantages:** Measures the temperature difference between sample and reference under programmed thermal scan; high sensitivity, wide range of high temperature and pressure, small sample size, and measurement simplicity.

**Limitations:** Calibrations and data processing required.

### Differential Scanning Calorimetry (DSC)

**Advantages:** Directly measures the rate of heat release; quantitative measure of heat of reaction and heat capacity directly measures thermal state of cure, cure kinetics, and cure effects on glass transition.

**Limitation:** Less sensitive and more limited temperature and pressure ranges than DTA.

### Thermal Mechanical Analysis (TMA)

**Advantages:** Measures thermal expansion; high displacement sensitivity.

**Limitations:** Physical limitations of precision measurement.

### Thermal Gravimetric Analysis (TGA)

**Advantages:** Measures weight changes; detects chemical reactions which change sample weight; high precision and sensitivity.

**Limitations:** Weight change measurement needs additional modes of characterization.

### Surface Energy Analysis (SEA)

**Advantages:** Tests for bonding ability; automatic measure of advancing and receding contact angle on fibers; adhesive bonding and interface durability parameters can be calculated.

**Limitations:** Limited to continuous surfaces; high micro-roughness introduces contact angle hysteresis.

### Dynamic Mechanical Analysis (DMA)

**Advantages:** Isolates the storage and loss components of rheological response; applicable to unsupported or supported polymer; highly sensitive to both flow and glass transitions at all states of cure.

**Limitations:** Multiple DMA required; requires concurrent chemical analysis.

### CURE MONITORING AND MANAGEMENT

This section is concerned with feasible methods for direct in situ monitoring of cure during press or autoclave molding processes typical of composite production. The related subject of cure management is the utilization of the cure monitor in a closed loop control of the production cure process through the program time (t) versus cure temperature (T), external pressure (P), and internal degassing vacuum (V) imposed on the curing part. Information for "real time" management of this (t-T-P-V) program for production process control can be derived from three sources:

1. Prior chemical analysis
2. Prior processability testing
3. Current cure monitor data from within the curing part.

The U.S. Army Composites Research Program provides extensive documentation of the combined utilization of the above three approaches to cure management of epoxy-glass and epoxy-graphite composites. In these Army studies of matrix resins, prepregs, and composites, the minimum chemical analysis includes high performance liquid chromatography and Fourier transform infrared spectroscopy, used both individually and jointly as quality assurance tests to verify chemical reproducibility. The minimum processability testing is by differential scanning calorimetry to verify the reproducibility of the curing kinetics. The characteristics of the epoxy resins which can be determined by these prior tests are degree of cure, aging of prepreg, effect of cure conditions on the oxidative stability of the resin, products of degradation

attack, and effect of processing on the resin chemistry. This information can be exploited to optimize the cure cycle to accommodate variability in resin chemical composition and prepreg aging.

Four methodologies of cure monitoring are listed in Table 1. The first is augmented by the other three:

### AC Dielectrometry

**Advantages:** Close relations exist between AC dielectrometry and DMA response; commercial instrumentation is available for measurement.

**Limitations:** Changes in spacing between electrodes can modify the dielectric output; increasing the number of prepreg plies between electrodes lowers measurement reliability.

### DC Resistance

**Advantages:** Very simple electrical circuit; resistance variations correlate.

**Limitations:** No physical model correlating DC resistance and rheology is available.

### Acoustic Emission

**Advantages:** Acoustic emission sensors provide direct information on microcracking processes.

**Limitations:** This method is new and needs further development.

In principal, the sensors for all three of the above cure monitors could remain in the cured part for utilization in nondestructive evaluation (NDE) in service.

### NONDESTRUCTIVE EVALUATION (NDE)

By adopting new modes of computer controlled three dimensional scanning, the ultrasonic response of parts with complex surface curvatures can be automatically mapped for flaws.

Normally, no nondestructive testing method presently employed can detect poor adhesion resulting in low bond strength. However, new methods provide a viable reliability and durability test methodology for adhesive bonded structures.

One study forms one of the most detailed assessments of conventional NDE methods for large area inspection of critical bond-line flaws in laminated structures.

## Characteristics of Standard Methods

### Ultrasonic NDE

**Advantages:** Uses pulsed ultra sound; both contact and immersion techniques employed.

**Limitations:** Suffers from destructive wave interference.

### Fokker Bondtester

**Advantages:** Operates on the principle of resonance impedance; can detect porosity; measures both amplitude and frequency shift.

**Limitations:** Low spatial resolution; must be manually scanned.

### NDT — 210 Bondtester

**Advantages:** Operation similar to Fokker bondtester.

**Limitations:** Restricted in interpretation.

### Shurtronics Harmonic Bondtester

**Advantages:** Does not require a liquid couplant.

**Limitations:** Limited to metallic structures.

### Neutron Radiography

**Advantages:** Particularly useful when bonding components are not X-ray opaque; can be used to detect voids and porosity.

**Limitations:** Requires radiographic facility.

### X-ray Radiography

**Advantages:** Maximum contrast; effective for complex geometries difficult to inspect ultrasonically; can be used to detect water intrusion.

**Limitations:** Requires X-ray opaque materials as adhesive and matrix components.

### Coin Tap Test

**Advantages:** Useful in locating large voids and disbonds; applicable for metal-metal or thin skin-honeycomb assemblies.

**Limitations:** Limited to the outer ply disbonds; method is subjective and may yield variation in test results.

### Acoustic Emission (Dunegan-301)

**Advantages:** Detects wet interface corrosion delamination.

**Limitations:** Detector transducer must be placed over the corroded area.

### Thermography

**Advantages:** Locates stress concentrations or structural defects.

**Limitations:** Requires physical interpretation; not applicable to metal skin laminates.

### SURFACE NDE

Standard NDE methods reviewed are not capable of defining poor interface quality which may lower the durability of a laminated composite structure. A new and rapidly developing area of surface NDE has recently emerged to fill this important gap in standard NDE methodology. Surface NDE methods in general are modifications of the tools of surface characterization to permit automation, rapid surface property mapping, and computerized data storage and processing. The objective of surface NDE is to perform a final inspection of surfaces to be bonded and to make accept-reject decisions on whether the surface will form a reliable, durable bonded joint or whether rejection and recycling through surface treatment is required.

Surface NDE falls into direct methods which identify the nature of the surface contaminant and indirect methods which identify contaminants through a surface property change. Of the several indirect surface NDE measurements, the following four methods have complementary advantages and limitations.

### Ellipsometry

**Advantages:** Noncontacting and nondestructive; automated and developed for rapid computer controlled surface mapping.

**Limitations:** Sensitivity is limited by difference in refractive index.

### Surface Potential Difference (SPD)

**Advantages:** Noncontacting and nondestructive; commercial instruments are available and computerized surface mapping has been developed.

**NOTE:** This article and the two following are part of a series of comprehensive investigations into the characterization of composite materials. The work was funded by the U.S. Army and conducted by both prime contractors and academic institutions. The other parts of the series will be presented in the next issue of the U.S. Army ManTech Journal.

**Limitations:** Requires other measurements to make a physical interpretation of data.

### Photoelectron Emission (PEE)

**Advantages:** Sensitive to both substrate and surface properties; extremely sensitive to thickness effects.

**Limitations:** Requires intense ultraviolet light source.

### Surface Remission Photometry (SRP)

**Advantages:** Permits surface spectral analysis; influence of surface roughness is small.

**Limitations:** Requires use of a light integrating sphere and twin beam optics.

The combination of surface NDE and surface chemical analysis promises to provide a valid approach to reliability and durability analysis of structural adhesive bonding. At the moment, surface NDE is an emerging technology which needs further development and integration of measurement and analysis methodologies to provide quantitative reliability and durability predictions.

## PERFORMANCE AND PROOF TESTING

Performance and proof testing of composite reliability by standard ASTM methods involves a group of 47 test methods. These ASTM test methods fall into six categories of response:

1. Processing
2. Mechanical Properties
3. Thermal Properties
4. Electrical Properties
5. Optical Properties
6. Environmental Properties.

The great importance of these ASTM performance and proof tests very largely relates to the fact they are commonly accepted and utilized, thus providing a common fund of characterization data. Experience shows that ASTM tests used alone are an expensive and generally inadequate means of testing for composite reliability and durability. On the other hand, extensive quantitative characterization without ASTM testing provides a data base without a general technology reference. A full understanding of the stress and environment dependent glass temperature and flow temperature is essential in terms of performance and proof test conditions. The utilization of standard ASTM tests to establish the iso-

thermal stress-strain-time response is essential to fully define the mechanical responses.

## IMPORTANCE OF CHARACTERIZATION

In lieu of a detailed summary and personal conclusion relative to this overview of characterization techniques, an overview questionnaire on chemical characterization of composite reliability was conducted. It is evident from the questionnaire response that cure monitoring and management are of high importance to the investigators and that chemical characterization has already developed a more mature status. It is anticipated that these fields of investigation will be readily incorporated into a general life prediction program such as outlined by the flow chart of Figure 8.

The descending flow chart of Figure 8 is an outline of composite material interactions under UV radiation, hydrothermal cycling, and mechanical loading which leads to property changes, damage mechanisms, and results in diminished reliability and durability. The types of chemical, physical, and mechanical tests which accompany the several stages of degradation are listed on the right side of Figure 8. While still in an early development stage, a general laminate life prediction program which combines measurement and analysis appears to form an important avenue for future research. An important subject presented as a central issue in lower Figure 8 is chemical corrosion degradation within the composite system. While this subject has only recently received detailed attention in composite life studies, it appears to warrant increased attention in life prediction modelling.

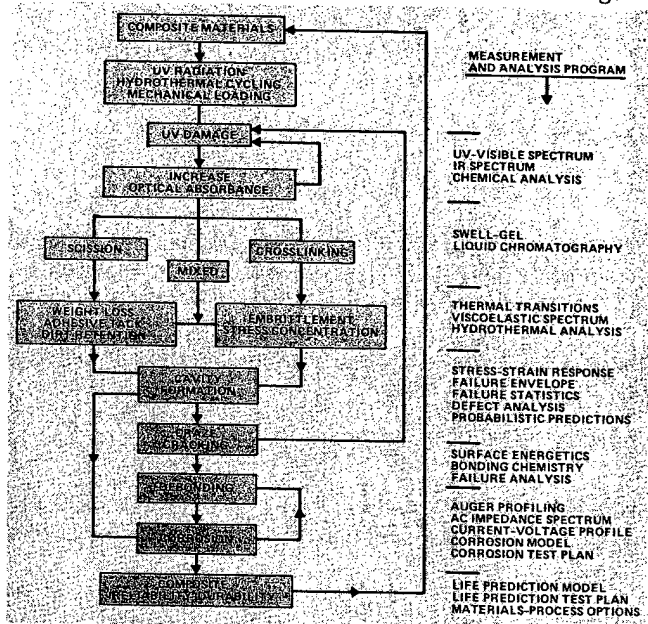


Figure 8

## Controlling the Curing Process

# Composite Characterization Techniques: Physiochemical

JACK L. KOENIG is Professor of Macromolecular Science and Physical Chemistry, Case Western Reserve University, where he also serves as Director of the Nuclear Magnetic Resonance, Molecular Spectroscopy, and Materials Research laboratories. Dr. Koenig has been Program Director, Solid State Chemistry and Polymer Science Division of Materials Research, National Science Foundation, and has conducted plastic research chemistry for DuPont Company. He is a member of the American Physical Society, Coblentz Society, Society of Applied Spectroscopy, and Sigma Xi. Dr. Koenig received his Ph.D. in Physical Chemistry from the University of Nebraska in 1959 after receiving his M.S. there in 1957. He earlier had received a B.A. in Chemistry and Mathematics from Yankton College.



Dr. Richard J. Shuford, Composites Development Division, Organic Materials Laboratory, AMMRC, served as monitor of the multiple studies on Composite Characterization.

The physical, chemical, and ultimate mechanical properties of high performance glass fiber reinforced-composites are dependent on the degree of cure and structure of epoxy matrices. Therefore, a knowledge of curing process and composition of epoxy matrices is essential for relating the properties of composites to the extent of the reaction and for optimizing their performance. Several methods have been developed to characterize and control the curing of epoxy matrices; these methods include spectroscopy, differential scanning calorimetry, dielectric analysis, and dynamic mechanical tests. These methods can be used to characterize the curing process during or after the fabrication of the cured epoxy matrices to justify reproducibility, reliability, and durability. A combination of these methods provides a powerful technique to analyze and control the quality of epoxy matrices in fiber-reinforced composites. The sensitivity, advantages, and selectivity of these techniques are reviewed and discussed in this article.

### Epoxy Resin Selection Criteria

There are three major types of epoxy resins of commercial significance: (a) epichlorohydrin-bisphenol A (conventional), (b) epoxy novolak, and (c) epoxidized polyolefin resins. The most commonly used curing agents are anhydrides and amines. Miscellaneous modifications of epoxy systems are used to meet the specific performance requirements. In order to optimize performance, several factors must be considered in choosing the epoxy resin for suitable composite matrices. These factors are based

**NOTE:** This manufacturing project that was conducted by Case Western Reserve University thru AMMRC was funded by the U.S. Army Aviation Systems Command under the overall direction of the Office of the Deputy Chief of Staff, Production, U.S. Army Materiel Command (AMC). The AVSCOM Point of Contact for more information is Jon Pratcher or Fred Reed, (314) 263-3079.

on the following considerations: (1) processing requirements, (2) economic preference, and (3) mechanical performance.

Processing requirements involve viscosity considerations (rheological behaviors of epoxy resins), high or low temperature cure, etc. One of the ways of decreasing the viscosity of an epoxy resin is to add a diluent. Reactive diluents are liquid materials which have lower viscosity than the epoxy resin and are assimilated into the resin network during cure. Nonreactive diluents comprise materials which don't contain epoxide groups, but which are completely sorbed in the cured epoxy resin network. Nonreactive diluents usually may be removed by solvent extraction.

Inhomogeneities observed in cured epoxy resins appear to be related to the effectiveness of mixing the reactants. Dynamic mixing has improved impact strength by as much as 58%. The effect of mixing on homogeneity by using an electrical field to induce mixing of viscous fluids of different conductivity was studied and was shown to significantly increase the ultimate tensile strength of epoxy resins.

Another processing requirement is concerned with the temperature of cure. For advanced fiber composites, the difference in thermal expansion coefficients between the fiber and the epoxy matrices during the high-temperature cure cycle creates a very serious problem, such as visible delamination or fiber microbuckling. On the other hand, the commonly used room temperature cured epoxy resins have some disadvantages, such as poor mechanical properties; also, the working life is too short to be used in composite processing.

In one particular study, specific amine and the pure diglycidyl ether of bisphenol A were used to fabricate polyether amine-cured epoxy matrices. In spite of good flexibility and toughness, this resin system has fairly well balanced mechanical properties. It can be room-temperature cured and presents no problem in filament winding — which requires a good epoxy resin of low viscosity and long working life.

### Economics A Sometimes Factor

For economic considerations, sometimes it is necessary to consider energy savings as well as increases in productivity. Then, a fast-curing epoxy system is required. Accelerators have been developed that provide greater than a six-fold advantage over tertiary amines in anhydride cured epoxies. It should be emphasized that the properties obtained with a short cure (2 hours) are the same as those properties previously requiring 12-24 hours for the curing process with conventional accelerators. Generally, the lower the temperature, the slower the reaction. On the other hand, the higher the temperature, the greater the risk of degradation. For production consideration, the optimum condition is the shortest cure time which will still assure a resin matrix with the desired properties.

A current problem with epoxy resin systems used in continuous fiber reinforced composites is their shelf life.

Once the resin is mixed, it must be used immediately or stored at low temperatures in the form of a prepreg. Prepregs typically must be stored at -18 C, where they are estimated to remain stable for six months. The ideal system from a storage point of view would be a prepreg which is stable at room temperature in the B-stage and which retains its tack and drape. Currently, no such ideal system exists. However, a resin system which is cured with a sterically hindered amine is stable at room temperature in the B-stage in a glassy state. Upon mixing at room temperature, the primary amine hydrogens react to form a linear polymer. The secondary amine hydrogens do not react at room temperature because they are much less reactive due to the steric hindrance of the nearby methyl groups. The epoxy resin does not form a three-dimensional structure until the secondary amine hydrogens react upon additional heating.

### Field Use/Repair

The growing use of composite materials in commercial and military equipment has led to concern over field repair or patching of damaged composites. Field level repair has some unique materials requirements in terms of storage and curing characteristics. Since the presence of freezer storage space is not guaranteed, the resin used in the composite patch would necessarily require room-temperature stability. Also, since cure facilities are very limited, the resin system must be curable at low temperatures and times (150 C for one hour).

### Heat Resistance Requirements

Heat resistance is another requirement of the epoxy matrix. Several methods have been pursued to improve the Heat-Deflection-Temperature (thermal mechanical properties). It has been shown that cured epoxy resins based on Bisphenol S have a considerable increase in heat resistance over those based on Bisphenol A. The increased heat resistance results from the replacement of the isopropylidene group in Bisphenol A with the more thermally stable sulfone group. The increased heat resistance results from the replacement of the isopropylidene group in bisphenol A with the more thermally stable sulfone group. The increased heat resistance is indicated by the resistance to heat aging and to heat deformation as well as retention of strength at elevated temperature. The enhanced thermal properties of sulfone epoxy are achieved in a different way from that of the epoxy novolacs, which results from an increase in the crosslinking density. Another way of improving the high temperature performance is to add a rigid structure in the backbone of epoxy resins. Polyimides have good high temperature performance and the epoxy resins possess many desirable properties of the aromatic polyimide if it contains the phthalimides moiety.

The primary role of epoxy matrices is to transfer stress from the fiber to the finished composites. Currently prevailing epoxy resins are designed for glass fiber composites. Since graphite fibers have a higher modulus

than glass fiber, it is important to use high strength matrices to maximize the efficient transfer of the fiber strength to the composites.

### Calorimetric Analysis

The processing of epoxy resins (such as curing/cross-linking) involves the exposure of these materials to various levels of heat treatment. The physical and mechanical performance and the quality of the cured articles are largely determined by the extent of cure, the control of temperature distribution, and the rate of temperature rise during processing. Moreover, temperature variations during cure — which determine the degree of cure in an epoxy resin system — depend to a large extent not only on the heat of the reaction but also on the specific heat and the thermal conductivity of the material at different stages of the cure cycle. These parameters can be characterized by differential scanning calorimetry and are essential for optimizing product quality and processing condition considering the heat transfer.

Differential scanning calorimetry measures the difference in the rates of heat absorption or evolution by a sample with respect to an inert reference as the temperature is raised at a constant rate. Differential thermal analysis measures the differential temperature caused by heat changes in the sample. Differential scanning calorimetry can be used to characterize the curing reaction of epoxy resins in the presence of fillers or without them. The basic assumption made is that the heat of reaction is proportional to the extent of the reaction. Moreover, it is also assumed that the specific heat of the material either stays constant or varies linearly with scanning temperature during a scan while both the temperature and degree of cure change simultaneously. These assumptions are valid for simple reactions, but not obviously valid for the complicated crosslinking reactions which occur in the cure of epoxy resin.

There are three ways of measuring the extent of curing in epoxy resin. This can be achieved by (1) isothermal operation, (2) analysis of thermograms with different scan rates, or (3) scans on partly cured resins. For isothermal operation (because a short time is needed for the samples and the test cell to heat up to the desired temperature), the beginning portion of the exotherm is lost. Therefore, isothermal scans become unreliable for very fast cures. This problem can be solved by analysis of thermograms with different scan rates.

At low temperature the isothermal method gives reliable results, while the scan method gives insufficient data from which to construct a reliable curve. For fast cure or when the curing temperature is very high, the thermograms with different scan rates must be used. The third method is to scan only partly cured resins. Each partly cured sample is scanned and the area of the thermogram gives the residual heat of reaction. This method becomes useful when the rate of heat evolution is too small for isothermal detection.

### Two Interrelated Methods

On the other hand, characterization of the kinetics of epoxy resin curing reactions is not only essential for a better understanding of structure-property relationships but also is required for determining the time-temperature dependence of the degree of cure. Differential scanning calorimetry has been used by several workers both to monitor the state of cure and to determine the kinetic parameters of cure of epoxy resins in isothermal and dynamic modes. There are two interrelated methods for analyzing these curves of crosslinking reaction of epoxy resins. The first method utilizes a single thermogram to evaluate the kinetic parameters, such as activation energy, kinetic order of reaction, and the total heat of reaction, by detailed differential-integral analysis of the thermogram. The second method uses the multiple scan, obtained at various rates of heating.

Most research on the cure kinetics of epoxy resin systems was without fillers, and very little information has been reported on epoxy systems containing fillers. It does appear that the carbon black fillers affect kinetic rate constants through the Arrhenius frequency factor, whereas the surface-treated silicas influence the kinetic rate constants through the activation energy.

The most serious problem with differential scanning calorimetry is the requirement of an accurate knowledge of the baseline. The baselines are always taken at locations preceding and following the exotherm. However, the baselines should take into account the change in heat capacity of the cured resin compared to starting materials.

Compared with differential scanning calorimetry, differential thermal analysis is seldom used in the study of epoxy resins. It was shown that there is a good correlation between the gelation time and the temperature corresponding to the peak of the exotherm on these curves. The method permitted a rapid and sufficiently accurate estimate of gelation time of epoxy resin in a broad temperature range. Isothermal differential scanning calorimetry provides the heat output as a function of time, representing directly the rate of the reaction. However, the information provided by this method gives us little insight into the chemical mechanism of the curing process and the chemistry of cure.

### Dynamic Mechanical Tests

One of the most important factors affecting the processing of the epoxy resins is gelation. When gelation begins, the viscosity of the system rises exponentially and has a remarkable effect on the processing such as injection molding or autoclaving. A typical method for determining time to gelation is by a standard ASTM test, which is based on steady-state viscosity. A schematic representation for the cure behavior of an epoxy system is shown in Figure 1.

Steady-state viscosity measurements only characterize the liquid state. Characterization of the rubbery and

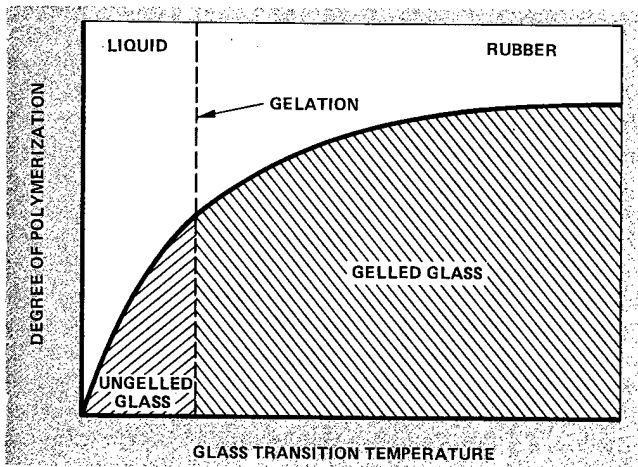


Figure 1

glassy states can be made with dynamic mechanical techniques.

Torsional braid analysis, a dynamic mechanical technique involving an adaptation of the torsional pendulum with a freehanging composite specimen, consists of a multifilamented glass braid and the epoxy system. With this technique, we can measure the change in rigidity and damping in the reacting system throughout the cure and study transitions during cure, cure kinetics, and activation energy.

Two physical transitions are usually observable with torsional braid analysis as cure proceeds isothermally. The first — gelation — corresponds to a transition from linear or branched molecules to an infinite network. The second — vitrification — corresponds to a transition from a rubbery to a glassy state. Each of these phenomena is accompanied by an increase in rigidity and by a maximum in mechanical damping. There exist two critical isothermal temperatures. These are the maximum glass transition temperature and the glass transition temperature at its gel point. This information is related to the rheological changes which occur during the complete cure of the epoxy resin and is useful in composite processing. Figure 2 shows a typical torsional braid analysis interpretation.

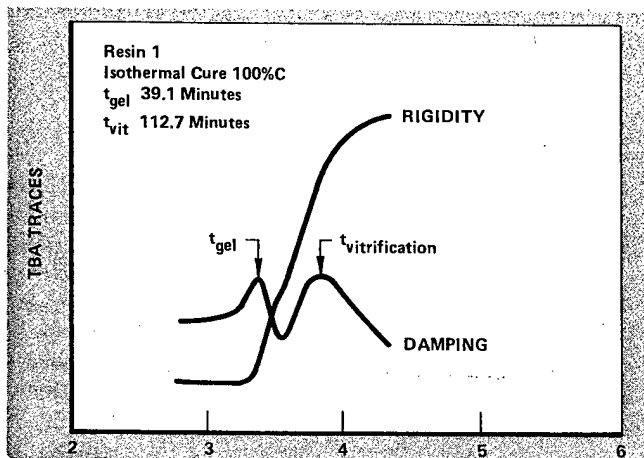


Figure 2

A number of studies have been reported on the curing behavior of epoxy resins employing torsional braid analysis. Quite a few of the studies were concerned with mixture of fiber and epoxy. Torsional braid analysis was used to study the prepreg material consisting of epoxy resin on glass fiber, carbon fiber, or aramid fiber, and measured gelation and vitrification times as a function of temperature. The study has shown that substantially all of the information concerning the curing behavior of epoxy resins which has been obtained by torsional braid analysis, can also be obtained on the prepreg material directly. The only difference is a marked weakening of the gelation mechanical damping peak in the prepreg material. In spite of its weak intensity, the gel points still can be constructed very accurately to determine the activation energy by plotting an Arrhenius equation over a wide range of temperature. It is obvious that the filler does not affect the behavior significantly, nor does it interfere with the results under study.

### Other Useful Techniques

In addition to torsional braid analysis, there are other similar techniques. Dynamic spring analysis was used to study the curing behavior of two commercially formulated epoxy resins. It was demonstrated that this supported viscoelastic technique is suitable for the determination of the onset of gelation, but the method is not useful for studying later stages of reaction when the resins become more rigid.

Torsional impregnated cloth analysis has some advantages over torsional braid analysis. Its frequency of measurement is constant, and the frequency can also be varied to study the frequency effect on transition. In torsional braid analysis, the resin impregnated braid is set in free oscillatory motion and its damping decay characteristic is recorded. On the other hand, in torsional impregnated cloth analysis, the cloth undergoes an oscillatory strain at a fixed frequency and the resultant torque is analyzed by a frequency response analyser to give both the in-phase and out-of-phase component amplitudes. The results obtained from torsional impregnated cloth analysis are not absolute values, and have the advantage over the torsional braid analysis in that the frequency of measurement is constant.

A viscoelastic tester was used to perform the dynamic test. Since a disadvantage of this kind of dynamic mechanical approach is that gelation is not clearly observed, a method was developed for determining the gel time of epoxy resins from dynamic viscoelastic data, which is based on the crossover of the dynamic storage and loss moduli measured during isothermal curing.

Another application of dynamic mechanical test is for the characterization of cured composites. The useful information obtained is the glass transition temperature. The most interesting observation is the appearance of an additional damping peak above the glass transition temperature of the matrix resin. Also, as the fiber direction is changed from transverse to longitudinal, the transition region broadens and the change in frequency

over this temperature range exhibits a maximum at intermediate angles. This phenomenon is associated with the unique resin layer in the interface; the structure of this interfacial region is different.

Dynamic mechanical tests can be used to detect gelation and vitrification that are the key parameters which describe the curing behavior. They are useful in prepreg technology and composite processing. However, dynamic mechanical tests cannot provide the necessary information about the curing chemistry and curing mechanism.

## Spectroscopy

Infrared spectroscopy long has been recognized as a powerful tool for monitoring the curing process and characterizing the cured epoxy composites. It is based on the absorption of radiation in the infrared frequency range due to the molecular vibrations of the functional groups contained in the polymer chain. Prior to Fourier transform infrared, infrared spectroscopy was carried out using a dispersive instrument utilizing prisms or gratings to geometrically disperse the infrared radiation. Using a scanning mechanism, the dispersed radiation is passed over a slit system which isolates the frequency range falling on the detector. In this manner, the spectrum — that is, the energy transmitted through a sample as a function of frequency — is obtained. This infrared method is highly limited in sensitivity because most of the available energy is being thrown away; i.e., does not fall on the open slits. For polymer analysis, where the bands are generally broad and weak, this energy limitation is particularly severe. Hence, to improve the sensitivity of infrared spectroscopy, Fourier transform infrared was developed, which allows the examination of all of the transmitted energy all of the time.

## Fourier Transform IR Spectroscopy

Fourier transform spectroscopy uses the Michelson interferometer rather than the conventional grating instruments. The Michelson interferometer has two mutually perpendicular arms. One arm of the interferometer contains a stationary, plane mirror; the other arm contains a movable mirror. Bisecting the two arms is a beam-splitter which splits the source beam into two equal beams. These two light beams travel down their respective arms of the interferometer and are reflected back to the beam splitter and on to the detector. The two reunited beams will interfere constructively or destructively, depending on the relationship between their path difference and the wavelengths of light. When the movable mirror and the stationary mirror are positioned the same distance from the beam splitter in their respective arms of the interferometer, the paths of the light beams are identical.

Under these conditions all wavelengths of the radiation striking the beam splitter after reflection add coherently to produce a maximum flux at the detector and generate what is known as the center burst. As the movable mirror is displaced from this point, the path length in that arm

of the interferometer is changed. This difference in path length causes each wavelength of source radiation to destructively interfere with itself at the beam splitter. The resulting flux at the detector, which is the sum of the fluxes for each of the individual wavelengths, rapidly decreases with mirror displacement. By sampling the flux at the detector, one obtains an interferogram. An infrared detector and AC amplifier converts this flux into an electrical signal. For highest accuracy in the digitized signal, the maximum intensity in an interferogram should match as closely as possible the maximum input voltage of the analog/digital converter.

The advantages of Fourier transform infrared over grating infrared arises from several sources. For measurements taken at equal resolution and for equal measurement time with the same detector and optical throughput, the signal-to-noise of spectra will be  $M$  times greater than on a grating instrument where  $M$  is the number of resolution elements being examined during the measurement. Another advantage comes from the fact that the frequencies of the instrument are internally calibrated by a laser, whereas a conventional infrared instrument exhibits drift when changes in alignment occur. This advantage is particularly useful for coaddition of spectra to signal average, since the frequency accuracy is a requirement in this case. For the absorbance subtraction technique to be useful for epoxy resins examined over a period of time such as months or years, long-term frequency accuracy must be maintained. Applications such as quality control and long-term aging and weathering require the reproducibility of the frequency that can be achieved by a Fourier transform infrared instrument over the long term.

The overall simplicity of this instrument compared to a dispersive type is also an advantage. For example, a single instrument can be easily converted to study the near, mid or far-infrared frequency regions, whereas with the dispersive method three totally different instruments are required. To improve resolution with a Fourier transform infrared instrument, the basic design is only slightly modified, while for a dispersive instrument different optical components are required.

## Quantitative Infrared Measurements

Quantitative infrared methods are based on the Beer-Lambert Law. The analysis of any multicomponent resin or composite is greatly facilitated if the spectrum of that material may be expressed by a linear combination of a finite set of pure component spectra. The entire process may be separated into three steps: (1) calculation of the number of species present, (2) identification of each of those species, and (3) a suitable fitting of the spectra of those species to the spectra of composites. The factor analysis method is useful in determining the number of spectroscopically distinguishable components in the composites.

## Factor Analysis of Mixture

Factor analysis is based upon expressing a property as a linear sum of terms called factors; the technique has found wide application to a variety of multidimensional problems. It has been applied to infrared and Raman spectra and most recently to Fourier transform infrared spectra.

There are two basic assumptions in factor analysis. First, the individual spectra of the components are not linear combinations of those of the other components; and second, the concentration of one or more species cannot be expressed as a constant ratio of another species. It is the different relative concentrations of the components in the mixtures that provides the additional information necessary to deconvolute the spectra.

What factor analysis allows initially is a determination of the number of components in the mixtures required to reproduce the absorbance or data matrix. In factor analysis, we find the rank of the matrix, which can be interpreted as being equal to the number of absorbing components.

## Least Squares Analysis

Since the set of pure component spectra determined are linearly independent, they may be unambiguously fitted by a least squares criterion to the spectrum of the composite. The least squares algorithm is derived from the criterion of minimization of the sum of squared differences between the experimental and the fitted spectra. The algorithm employed is a simple linear regression model for gamma spectra. The least squares coefficients as derived are useful in determining proper scaling factors for absorbance subtraction techniques in Fourier transform infrared. If the pure component spectra are properly scaled, then the least squares coefficients yield the correct volume fractions (or weight or mole fractions, if desired) for a composite consisting of any mixture of those components. If the quality of the least squares fit within random error, then a statistical error analysis may be performed to determine confidence intervals for each least squares coefficient.

## Absorbance Subtraction

One of the spectral processing operations most widely used in polymer analysis is the digital subtraction of absorbance spectra to reveal or emphasize subtle differences between two samples or a sample and a reference material. Spectral subtraction with Fourier transform infrared is a powerful method of extracting structural information about components of composite spectra. When the epoxy resin is examined before and after a chemical or physical treatment, and the original spectrum is subtracted from the final spectrum, positive absorbances reflect the structures that are formed during the treatment and negative absorbances reflect the loss of structure. The advantage of Fourier transform infrared

difference spectra lies in the ability to compensate for difference in thicknesses of the two solid samples. This balance of thicknesses allows small spectral difference to be associated with structural changes and not be outweighed by the difference in the amount of sample in the beams. Additionally, with properly compensated thickness, the differences in absorbances can be magnified through computer scale expansion to reveal small details of the spectral differences.

## Sampling Techniques Important

Transmission spectroscopy, diffuse reflectance spectroscopy, and internal reflection spectroscopy can be used to characterize the epoxy resin in composites.

The optics of the sampling chamber of commercial Fourier transform infrared instruments are the same as the traditional dispersive instruments, so the accessories which are generally available commercially can be used. The main difference between the two types of instrumental optics is that the beam is round and larger at the focus for Fourier transform infrared. Thus, some of the sampling accessories may block some of the beam energy in these analyses. When energy is a limiting factor, the accessories can be modified to accommodate the larger beam.

In internal reflection spectroscopy, the sample is in optical contact with another material (e.g., a prism). The prism is optically denser than the sample and the incoming light forms a standing wave pattern at the interface within the dense prism medium, whereas in the rare medium the amplitude of the electric field falls off exponentially with the distance from the phase boundary. If the rare medium exhibits absorption, the penetrating wave becomes attenuated. The resulting energy loss in the reflected wave is referred to as attenuated total reflection. When multiple reflections are used to increase the sensitivity, the technique is often called multiple internal reflection. Thus, qualitatively, an internal reflection spectroscopy spectrum resembles a transmission spectrum. There are two adverse effects arising from the wavelength dependence of internal reflection spectroscopy. First, the long wavelength side of an absorption band tends to be distorted; second, bands of longer wavelengths appear relatively stronger. With Fourier transform infrared spectrometers, one does not achieve the same improvement in internal reflection spectroscopy as in transmission, compared to dispersion instruments because these attenuated total reflection attachments have not been redesigned for the larger, round beam. However, the signal averaging capability and speed have increased the utility of internal reflection spectroscopy for polymers, particularly for surface studies. In internal reflection spectroscopy, the infrared beam penetrates the surface of the composite between a few tenths of a micron to a few microns, depending on the type of reflection plate, and angle of incidence, and the wavelength of the infrared beam. The depth of beam penetration can be reduced by placing a thin barrier film between

the trapezoidal reflection plate and the epoxy resin under study. The optimum method to determine the optical constants of a sample from a pair of independent reflectivity measurements at each frequency appears to be to determine the total reflectance at two polarizations at the same incidence angle.

Another important sampling technique is diffuse reflectance measurements. When light is directed onto a sample it may either be transmitted or reflected. Hence, one can obtain the spectra by either transmission or reflection. Since some of the light is absorbed and the remainder is reflected, study of the diffuse reflected light can be used to measure the amount absorbed. However, the low efficiency of this diffuse reflectance process makes it extremely difficult to measure, and it was speculated that infrared diffuse reflectance measurements would be futile. Initially, an integrating sphere was used to capture all of the reflected light, but more recently improved diffuse reflectance cells have been designed which allow the measurement of diffuse reflectance spectra using Fourier transform infrared instrumentation.

The requirement for reflectance to be diffuse is that the intensity of reflected light is isotropic, but for a solid sample both scattering and absorption occur, and since the scattered radiation is angularly distributed, it is by no means isotropic. However, with a large number of particles, as is found in a powder, an isotropic scattering distribution can be achieved so the emerging light will still be diffuse.

The principal problem with diffuse reflectance is that the specular component of the reflected radiation — that which does not penetrate the sample — is measured along with the diffuse reflected light which penetrates the sample. Generally, the change in specular reflection with frequency is small except in regions of strong absorption bands, where the anomalous dispersion leads to reststrahlen bands in the specular reflection spectrum. When the reststrahlen bands are observed, the absorption bands can appear inverted at their center. This effect makes quantitative measurements on samples with strong absorptivity very difficult.

For powdered samples, diffuse reflectance offers considerable advantage, particularly since no sample preparation is required which could change the morphology of the sample.

### IR Studies of Epoxy Resin Curing

The studies of epoxy resin curing with infrared spectroscopy are based on the absorption intensity of the epoxy, anhydride, and hydroxyl functional groups. In other cases the near-infrared spectra of the epoxy functional group is used. Since the glass fiber has a strong absorption in the mid-infrared region, it is very difficult to measure the spectra of epoxy matrices with dispersive spectrometers for glass fiber-reinforced composites. A new method of separating the epoxy resin from the cured fiberglass-epoxy composites is based on the concept of

differential floatation, which involves the separation of two materials of different specific gravity with a liquid of three differently prepared specimens of the same lot of prepreg composite were compared and the results demonstrate the feasibility of this approach for cured composites. The low signal-to-noise resolution limit and the time of scanning the entire spectrum with a dispersive instrument limits the application of conventional infrared to the study of reaction with short half-lives. Since Fourier transform infrared can solve this kind of problem with rapid scanning, this technique demonstrated by studying the kinetics of a sterically hindered amine-cured epoxy resin system. Variation in epoxide absorbance caused by differences in specimen thickness can be eliminated by normalizing the epoxide peak height to an internal reference peak.

Near infrared was used to study the curing reaction of epoxy resins and demonstrated the advantages of this technique, which is very sensitive due to the fact that the epoxide group has a strong overtone absorption frequency in the near infrared region.

### Quality Control of Epoxy Matrices

Fiber reinforced composite structures have gained a significant position as materials of construction for the aerospace industry and transportation industry. It thus follows that large expenditures of funds and human lives are dependent on the reliability of these products. An important step in gaining confidence is an product is knowing that the starting prepreg has the same chemical formulation and that each lot of material has been processed in the same manner.

A general and convenient method was developed for determining the initial resin composition and, simultaneously, the extent of crosslinking of epoxy matrices. This technique can be used as a quality control method to determine that the starting prepreg has the same chemical formulations and that each lot has been processed in the same manner.

Figure 3 shows the results of the factor analysis of crosslinked epoxy/anhydride resins in the 2000-1400

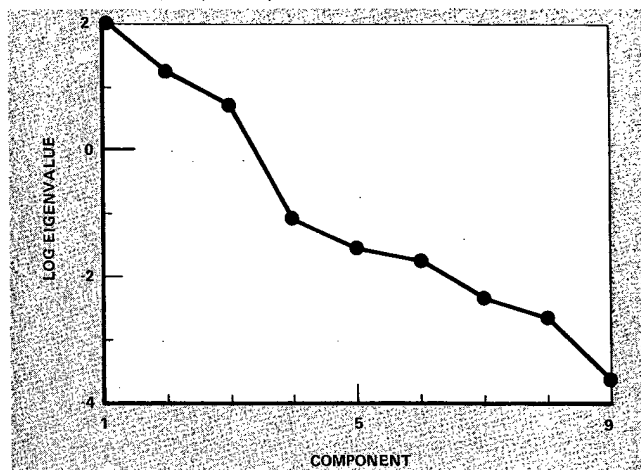


Figure 3

cm<sup>-1</sup> region. The plot of logeigenvalue in descending order reveals a break in magnitude between the third and fourth eigenvalue. As indicated, the number of these larger eigenvalues is equal to the number of components in the system. Therefore, the spectrum of the cross-linked epoxy matrix may be approximated by a linear combination of only three linearly independent component spectra.

The three spectra chosen to represent the components were that of pure NMA, pure Epon 828, and a difference spectrum characteristic of the crosslinking reaction. The difference spectrum was calculated by subtracting the spectrum of a stoichiometric mixture of NMA and Epon 828 crosslinked for 37 min at 80 C from the spectrum of the same reactant mixture crosslinked for 83 minutes at 80 C. The procedure is illustrated in Figure 4. Figure 5 shows the absorbance spectra employed for the analysis of the crosslinked epoxy matrix. A boxcar function is included as a fourth component in the least squares analysis of the resin in order to prevent errors in the background level from affecting the accuracy of the least squares coefficients. The spectrum of S-glass, also shown in Figure 5, is included as a fifth component in the least squares curve-fit analysis for S-glass reinforced composites. After performing the least squares curve fitting, the quality of the fit between the experimental resin spectrum and the least squares fitted spectrum is illustrated in Figure 6, the least square coefficient corresponding to the difference spectrum is a measure of the extent of crosslinking, and the coefficients corresponding to the pure NMA and pure epoxy are a measure of the amount of reactants.

Figure 7 shows the factor analysis of glass fiber-reinforced epoxy composite. Since there is no obvious separa-

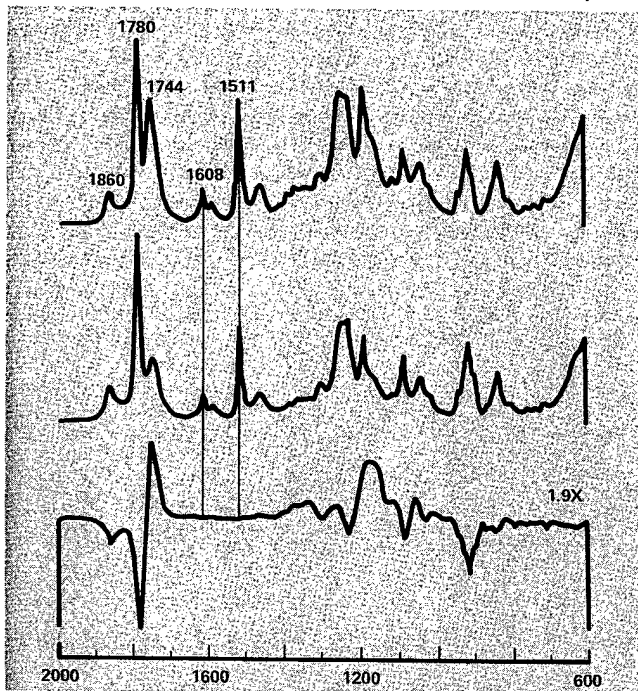


Figure 4

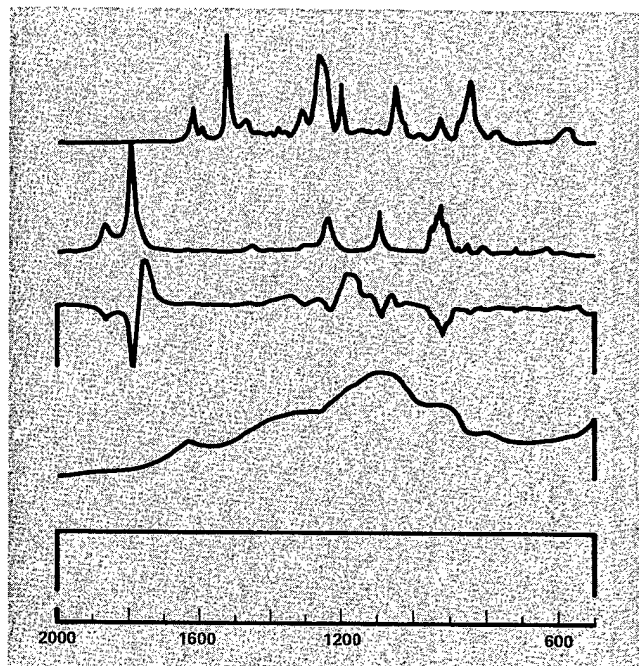


Figure 5

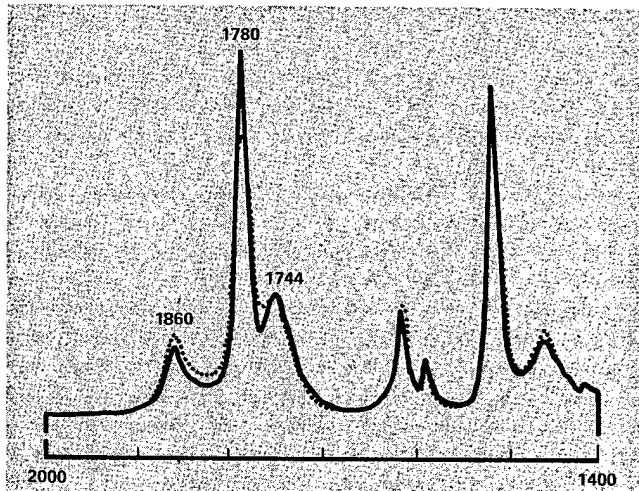


Figure 6

tion between the nonzero and error eigenvalues, it is an arbitrary decision to determine the number of components that contribute to the composite spectrum. Figure 8 shows a least square curve fitting of five component spectra to the spectrum of a composite. As can be seen, the fitted curve and the experimental result coincide satisfactorily.

The least squares analysis of epoxy matrix yields reproducible information with an accuracy limited by several spectroscopic problems. A source of error comes from sample preparation limitations. The wedge effect occurs from nonuniformity in the infrared path length through the sample; that results in the deviation from the Beer law and causes a weakening of the stronger absorption bands in highly absorbing materials.

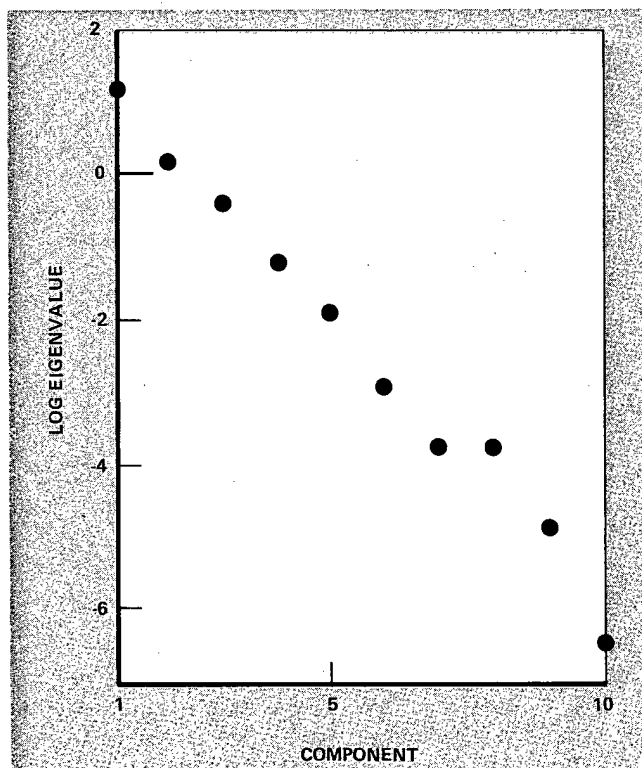


Figure 7

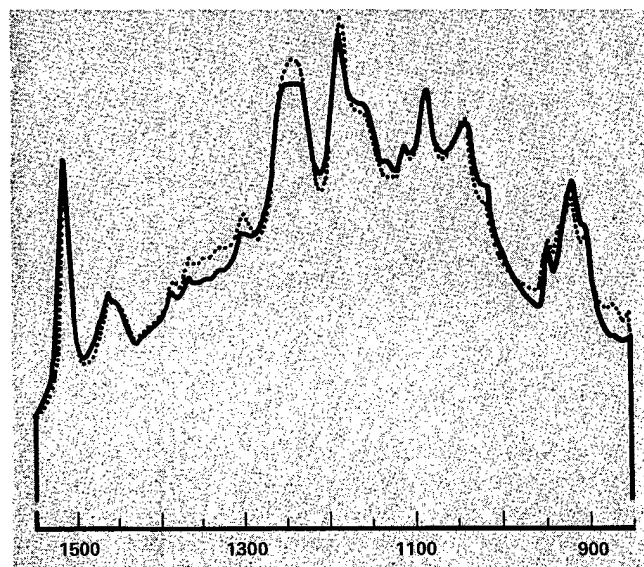


Figure 8

### IR Studies of Resin Degradation

Another important application of infrared spectroscopy in characterization of cured epoxy composites is to determine the effect of in-service exposure conditions (degradation, hydrolysis, weathering, aging) on composites. The surface of a glass fiber-reinforced epoxy composite is degraded rapidly upon outdoor exposure unless it is protected by an ultraviolet absorber or a paint. The

degradation phenomena are difficult to study due to the uncertainty in epoxy resin composition and the intractable nature of the cured composite that prevent the use of conventional techniques of polymer analysis. Although differential scanning calorimetry can be used to evaluate the thermal stability of epoxy composites, it only gives an estimate of thermal stability and cannot provide enough information to interpret the degradation process.

Several techniques, such as gas chromatography, chemical analysis, and mass spectroscopy, have been developed to study the degradation phenomena. These methods are based on the analysis of the degradation products related to the original polymer. However, these methods are complicated, since the degradation of material at high temperature may cause rearrangement of the degradation fragments, or other reactions. Therefore, degradation product analysis may lead to a false degradation mechanism.

Another study showed Fourier transform infrared capable of identifying irreversible chemical effects of moisture on an anhydride-cured epoxy resin. Exposure of a crosslinked epoxy film to 80 C liquid water environment caused a hydrolysis of the unreacted anhydride groups (approximately 5% of the initial anhydrides) to diacids. This effect, dominant during the early stages of moisture exposure, is illustrated in Figure 9. The decrease in anhydride concentration is indicated by intensity decrease of NMA vibrations at 1860, 1080  $\text{cm}^{-1}$ . Figure 9 also shows the effect of long-term exposure of the same epoxy film to 80 C liquid water. The short-term effect is hydrolysis and leaching of unreacted NMA molecules; the longer term effect rules out matrix hydrolysis and may be due to subtle structural changes such as perfection of the H bonding of polar groups.

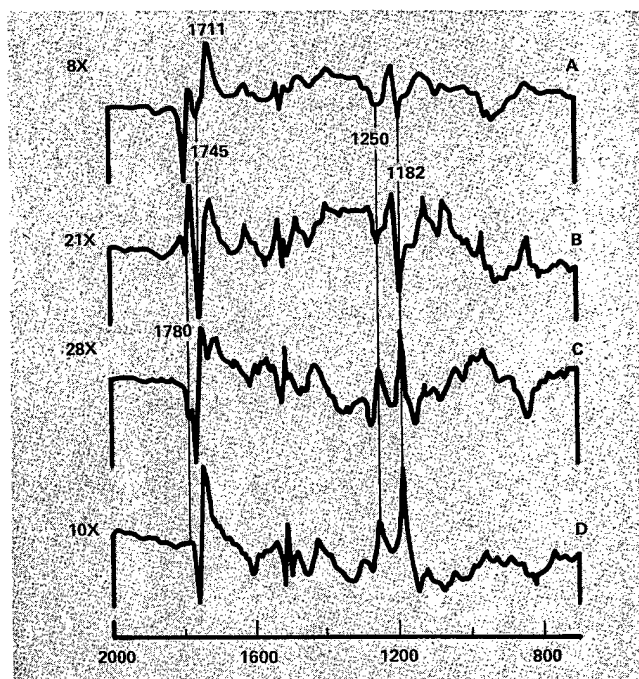


Figure 9

## Raman Spectroscopy Use

Since the advent of laser, Raman spectroscopy has become an important analytical tool in polymer research. Raman scattering occurs for those vibrational motions which produce a polarization or distortion of the electron charge of the chemical bonds. Thus, the stretching motion of a homonuclear diatomic molecule is active in the Raman effect. The Raman effect provides more information about the nonpolar portions of the molecules, while the infrared effect yields information about the polar portions of the molecule. Due to the complementary nature of the two types of spectroscopy, they should both be used whenever possible, since Raman spectroscopy enhances the effectiveness of infrared for solving chemical structure problems and vice versa.

The Raman effect is a light scattering rather than a light transmission process, so the transparency, size, and shape of the samples are relatively unimportant. Thus, one can run large samples or extremely small samples with comparative ease. Filled polymer composites present difficulty for infrared investigations, since the fillers such as glass, clay, and silica are strong infrared absorbers that block the infrared spectrum of the polymer. These particulate fillers (glass, silica) are poor scatterers, so the Raman spectrum of the polymer is obtainable without removal of the filler.

## Dielectric Analysis

Dielectric analysis is based on measuring the ability of the dipole in a system to align with an oscillating electric field. In aligning the dipoles, a certain amount of energy is utilized. By subjecting an epoxy system to the oscillating field, information about the viscous and elastic properties can be obtained.

A typical dielectric analysis is shown in Figure 10, where capacitance, dissipation factor, and temperature are plotted as a function of time.

The dissipation factor curve is related to the curing of the epoxy matrix. The lefthand peak of the curve corresponds to the softening and flow of the resin system. The righthand peak is associated with the setting of the matrix. The portion between the peaks shows low dissipation

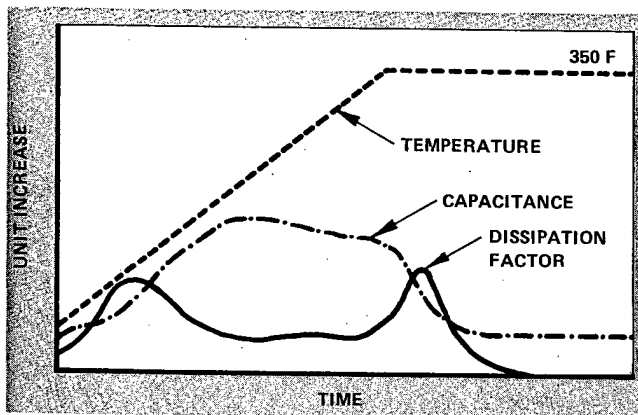


Figure 10

since the epoxy resin displays a less viscous behavior. This is the region where process changes such as the application of pressure for consolidation of the laminates are performed.

Examples of the use of dielectrometry in the study of composites demonstrate the feasibility of using dielectric analysis as a means of monitoring and controlling cure of epoxy composites in autoclave molding. The mechanical properties are correlated with the variables on the dissipation factor profiles.

Another method related to dielectric changes when an epoxy cures is an electric monitoring technique based on the charge-flow transistor, which resembles a conventional metal-oxide-semiconductor-field-effect transistor, but with a portion of the metal gate replaced by the epoxy resin under study. The dramatic change in the shape of the electrical signal during cure can be related to corresponding changes in both the real and imaginary parts of the dielectric constant and can be used for monitoring curing. A typical signal output is shown in Figure 11.

The instrumentation in dielectric analysis is simple, and since the peaks in the curve which result from relaxation phenomena (associated with softening and gelation of epoxy resin) are frequency dependent, these peaks do not define the point in time when softening or gelation occur. Therefore, one should be careful to interpret the dielectric analysis.

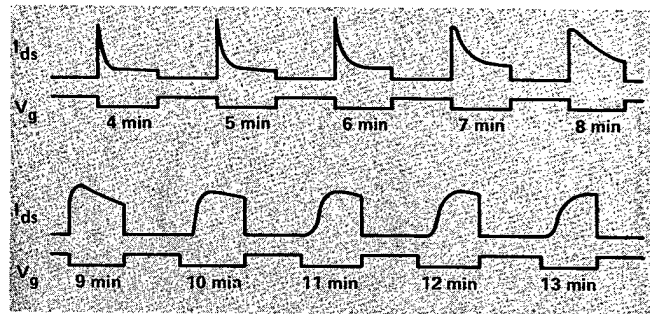


Figure 11

## Combination the Best Bet

Several methods have been reviewed for characterization of the epoxy matrix in glass fiber-reinforced composites. For example, torsional braid analysis and dielectric analysis yield the rheological changes during curing that are useful in composite processing. Differential scanning calorimetry gives the extent of cure on the assumption that it is proportional to the heat of reaction, but this assumption is invalid for complicated crosslinking reaction. While infrared spectroscopy is very useful, in studying the mechanism of cure and extent of cure, Fourier transform infrared is an ideal tool for investigating the degradation behavior of composites and controlling the quality of epoxy matrices in fiber-reinforced composites. No method provides all the necessary answers, but a combination of these techniques constitutes a powerful method in the study of composites.

Quality Accurately Gaged

# Composite Characterization Techniques: Radiography

**R**adiography is perhaps the most commonly known method of nondestructive examination, its origins dating back to the early 1920's. Using the penetration and absorptive properties of gamma or X-radiation to impart an image of the item under examination onto radiographic film, radiographic inspection has become a standard technique for inspecting modern industrial and advanced composite materials.

Another type of radiation imaging—neutron radiography—has been developed recently and improved for use in numerous specialized applications. Due to its inherent differences in processing, techniques, and applications, neutron radiography will be treated separately.

Earlier uses of radiography were limited to the examination of metallic items such as welds, castings, forgings, and various other metal parts to reveal imperfections (voids, inclusions, density variations, and other fabrication irregularities). Radiography is now applied to a wider range of materials comprising metallics, nonmetallics, and composites to insure the integrity of components for industrial and military needs, aircraft elements, aerospace components, and numerous other applications. In composite materials, radiography is used to detect and identify such defects as void content (porosity), unpolymerized resins, irregular matrix content, fiber-matrix unbonds, interlaminar unbonds, foreign inclusions, fiber

FRANK P. ALBERTI is a Registered Professional Engineer in Massachusetts, a certified Radiographer, and an Associate Professor of Engineering at the University of Lowell. Dr. Alberti received his Ph.D. from the University of New Hampshire in 1975 in Applied Mechanics/Random Vibrations and has published papers on stationary and nonstationary vibrations of plate and beam structures subject to various random excitations. His research activities include destructive and nondestructive testing of composite materials at Lowell and has participated in a number of research projects for the Army Mechanics and Materials Research Center. These involved NDT techniques, used alone or in combination, for various materials, including flaw detections and material property determinations. He presently is investigating the use of ultrasonic techniques in determining the physical properties of concrete and other highway materials.

Photograph  
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Dr. Richard J. Shuford, Composites Development Division, Organic Materials Laboratory, AMMRC, served as monitor of the multiple studies on Composite Characterization.

**NOTE:** This manufacturing project, conducted by The University of Lowell thru AMMRC was funded by the U.S. Army Aviation Systems Command under the overall direction of the Office of the Deputy Chief of Staff, Production, U.S. Army Materiel Command (AMC). The AVSCOM Point of Contact for more information is Jonathan Pratcher or Fred Reed, (314) 263-3079.

and laminate misalignments, fiber breaks, and moisture content.

### Distinctive Properties

The following is a list of some of the properties and characteristics of gamma and X-rays and is included together with Figure 1, which shows a basic radiographic setup, as an introductory aid toward the understanding of their processes and effects.

1. Invisible electromagnetic radiation
2. Can penetrate matter
3. Absorption dependent on material density and thickness
4. Travel in straight lines at 186,000 mi/sec
5. Produce photochemical effects in photographic emulsions
6. Ionize gases through which they pass
7. Unaffected by electrical or magnetic fields
8. Liberate photoelectrons
9. Cause some substances to fluoresce
10. Damage or destroy living tissue.

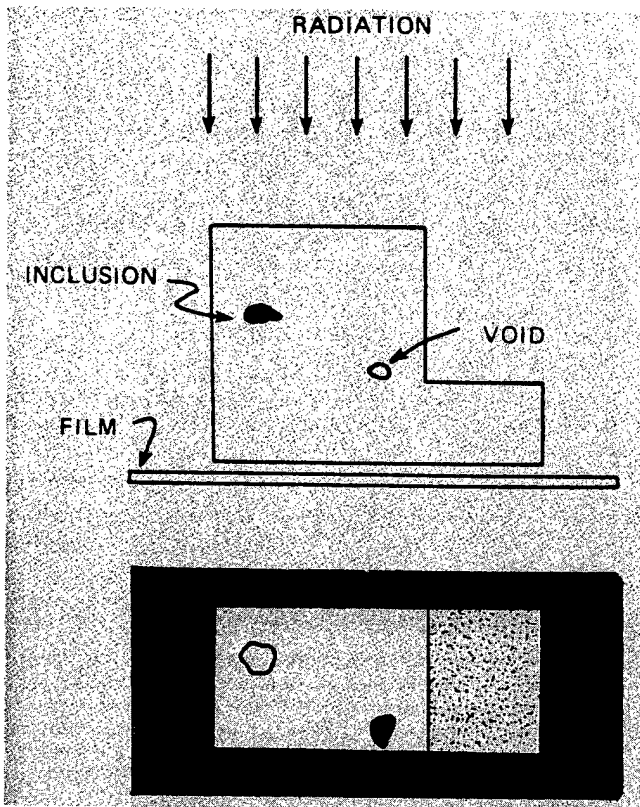


Figure 1

The production of a quality radiograph requires not only the selection of an appropriate radiation source, but also thorough understanding and control of the geometric, spatial, equipment, material, and film variables involved. In addition, proper film development techniques are necessary to produce a readable radiograph prior to the final steps of film interpretation and item evaluation.

This article reviews the procedures, variables, and techniques for producing a quality radiograph and relates them to past and ongoing research that is aimed at improving the radiographic technique as a nondestructive evaluation method; composite material investigations are emphasized. In particular, it includes discussions of state-of-the-art techniques such as microradiography, stereoradiography, and neutron radiography. Fluoroscopy is discussed along with recent developments in filmless techniques of radiographic imaging, electronic image enhancement, and use of opaque additives and penetrants.

### RADIATION SOURCES

#### X-Rays

In a typical high vacuum X-ray tube, an incandescent filament at the negative cathode electrode releases or "boils off" electrons as it is heated. These electrons are made to accelerate across the tube by a voltage difference applied across the electrodes (see Figure 2). X-rays are produced by these bombarding electrons as they undergo deceleration while moving into the positive anode target material. The X-rays or photons (energy packets) emitted comprise a range or spectrum of intensities similar to that shown in Figure 3, the characteristic peaks shown being dependent upon the type of anode target material. This characteristic radiation is of specific wave-

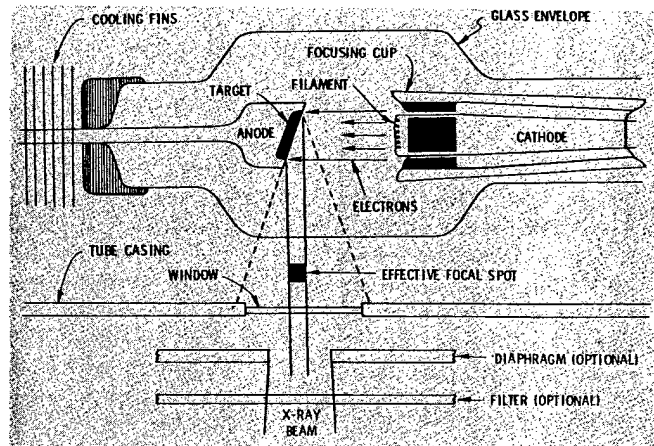


Figure 2

length and small energy content and can be neglected in considering the effects of X-radiation. What is important to recognize is that X-rays reaching an item under investigation comprise a spectrum of intensities with a range of wavelengths. The high-energy (short wavelength) rays have greater penetrating ability and are termed hard X-rays. The lower energy (long wavelength) rays have little penetrating power and are more easily scattered within the item material. These are called soft X-rays.

Since X-ray intensity is dependent upon the energy (or velocity) of the electrons bombarding the anode target, an increase in voltage across the X-ray tube will produce more short wavelength X-rays (see Figure 4). This is important to the radiographer, since it indicates that X-ray penetrating ability is increased as tube voltage is increased. That is, higher voltages produce more short-wavelength penetrating rays. However, the relationship is not linear, and no general analytical expression exists which can describe the relationship between voltage increase and X-ray penetrating ability. Such a relationship, if desired, would have to be experimentally derived for each particular X-ray tube. It is not necessary, however, to do this in order to produce a quality radiograph.

## Gamma Rays

Gamma rays are produced when the nuclei of radioactive isotopes disintegrate. An isotope is dissimilar to its parent element in that it has a different atomic weight due to a different number of neutrons. The number of protons, or atomic number, is the same. Isotopes with

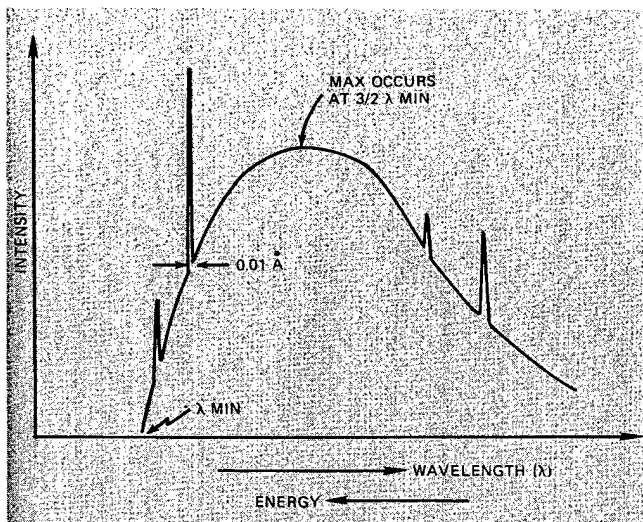


Figure 3

excessive neutron differences are inherently unstable and release energy in the form of gamma rays, alpha particles, and beta particles as they disintegrate. Of these, the penetrating powers of alpha and beta particles are negligible, and only the gamma rays are useful in radiography.

While some natural elements such as radium are inherently unstable and radioactive, man-made radioactive isotopes can be created. Cobalt 60, thulium 170, and iridium 192 are isotopes used in radiography and are created by bombarding their parent elements with neutrons. A second method of creating an artificial radioactive isotope is through a by-product of nuclear fission. Cesium 137 is an example of this process. The number assigned to each of these isotopes denotes its mass number and distinguishes it from its parent element and other isotopes of the same element.

Since gamma rays are available only at discrete energy levels, the radiation quality (hardness) cannot be varied as is the case with X-rays. If softer, less penetrating gamma rays are required, another isotope such as iridium 192 would have to be selected. Iridium 192 emits radiation principally at 0.31, 0.47, and 0.60 MeV, which corresponds to wavelengths from 0.04 to 0.02 angstroms (higher energies producing shorter wavelength rays). It is roughly comparable in penetrating power to a 600-kV X-ray machine and is used to radiograph medium weight metals from 0.25 to 3.0 inches in thickness.

## MAKING A RADIOGRAPH

A radiographic image is imparted onto film in much the same manner as a shadow is cast from a light source past an object onto a flat surface; that is, a radiograph is essentially a shadow graph. The important difference between a shadow and a radiograph is that, in radiography, the radiation penetrates and passes through the object, thereby creating not only a peripheral outline, but also an image of the internal structure of the object. In so doing, radiation is differentially absorbed and scattered, causing variations in film density (blackness) and image clarity. The radiographer seeks to optimize the readability of a radiograph by controlling the distribution of film density and creating a clearly defined image. In order to do this, he must have a thorough understanding of some basic concepts of image formulation and a basic knowledge of some of the factors relating object and film radiation effects to image quality.

## Geometric Factors

In establishing the optimum radiographic setup, it is important to understand the effects of the spatial arrange-

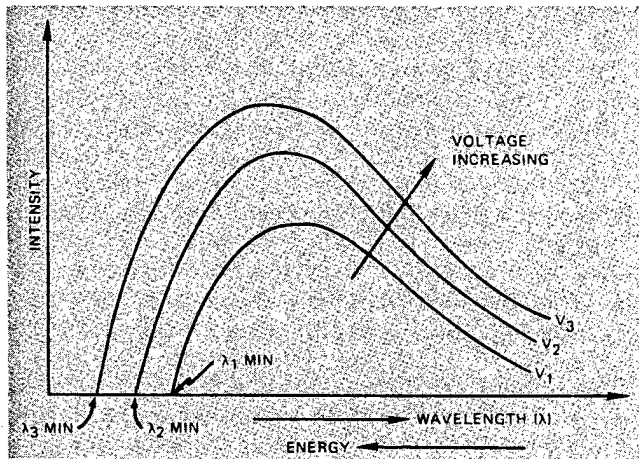


Figure 4

ment of the object, source, and film, as well as the effects of source size. Minimizing the object-to-film distance improves image sharpness by reducing shadows, and it also minimizes object enlargement. Image sharpness is also improved by maximizing the source-to-object distance. In general, therefore, the object should be in intimate contact with the film, unless prohibited by the shape of the object, and the source should be as far as possible from the film.

### Object Effects

As radiation penetrates an object, part of it is absorbed, some is scattered, and the remainder passes through unobstructed. The undeviated, primary radiation reaching the film forms the object image, and it is this differential absorption-transmission effect which causes variations in film blackening and makes radiography possible. Scattered secondary radiation also reaches the film, but it is not image forming and serves only to fog a radiograph. This is a problem which radiographers must acknowledge and control as much as possible.

The amount of primary radiation reaching the film depends in part upon the level of radiation energy and can be controlled either by varying the voltage at the X-ray tube or by selecting a proper gamma ray source. As was discussed earlier, both higher voltage X-rays and gamma ray sources of high discrete energy levels produce more penetrating radiation. The amount of radiation absorbed depends, as expected, upon the thickness and density of the object (Figure 1). Moreover, for industrial metallic materials, absorption also depends on the internal atomic structure of the object material. The influence of atomic number and material composition on radiation absorption

is known to be more important than either thickness or density for these particular materials. This effect, while complex, has received thorough investigation in empirically determined radiograph equivalence factors.

### Scattered Radiation

When electromagnetic radiation penetrates an object, much of it passes through, but a large part of it is either absorbed or scattered as it comes in contact with the atoms of the material. The problem of scattering is a phenomenon of both X-rays and gamma rays.

In the radiography of composites, which are comprised of low and medium density materials, scattered radiation forms a high percentage of the total radiation reaching the film. This is due to the nature of the soft, low voltage radiation used to radiograph these materials, which is inherently less penetrating and more subject to scatter. However, if higher, more penetrating voltages were used, excessive overall film density could occur, resulting in reduced contrast and a radiograph unreadable in terms of flaw detection. Scatter is, therefore, a major problem when radiographing composites. In general, this presents a paradox for the radiographer, since, as we have seen, low voltages are desirable for improving subject contrast, but lead to fogging of the image due to scatter, which, in turn, reduces subject contrast. However, some commonly used methods of reducing the effects of scattered radiation in radiographs of industrial metallic materials can be applied to the radiography of composites.

Another source of scattered radiation, side scatter (as shown in Figure 5), is reflected from walls or objects adjacent to the specimen or from portions of the specimen itself. Again, specimen outline is blurred by this type of scatter. One measure of the harmful image effects of scatter can be obtained by comparing the dimensions

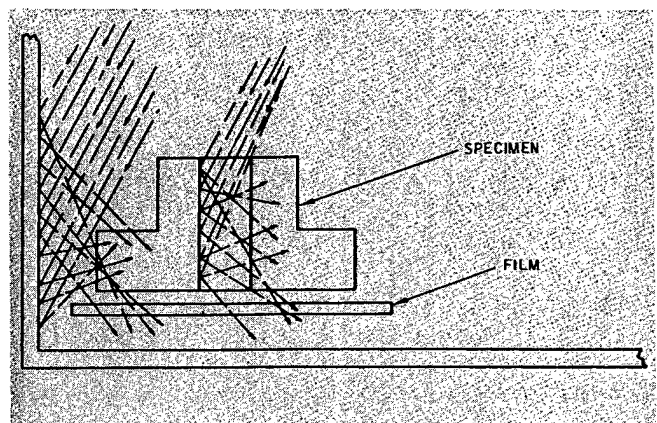


Figure 5

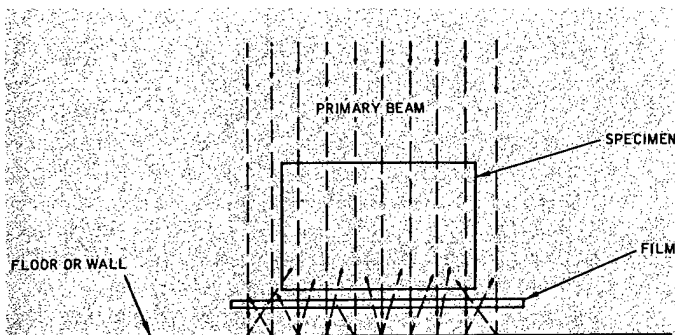


Figure 6

of the object itself with the dimensions of the radiographed image.

An additional source of scatter arises from objects such as floors, benches, or tables beneath the specimen (see Figure 6). This type of scatter usually occurs only when the film and specimen are not in contact with a supporting surface.

Another more indirect form of scatter occurs when the film holder or cassette extends beyond the edges of the specimen. As the cassette receives primary radiation, it becomes a source of scatter which can encroach upon the outline of the object image. This effect on image quality is termed "undercut" and can best be eliminated by using heavy density masking material.

### Film Effects

Radiographic film is constructed of a base sheet of transparent cellulose material which is coated on one or both sides with a special gelatin emulsion containing microscopic silver halide salt crystals (primarily silver bromide). The emulsion is approximately 0.001 inch thick on either side of the base sheet. As X-, gamma, or visible light rays reach the emulsion, the silver halide grains become sensitized and metallic silver is formed within the crystal. This is referred to as the latent image, since a

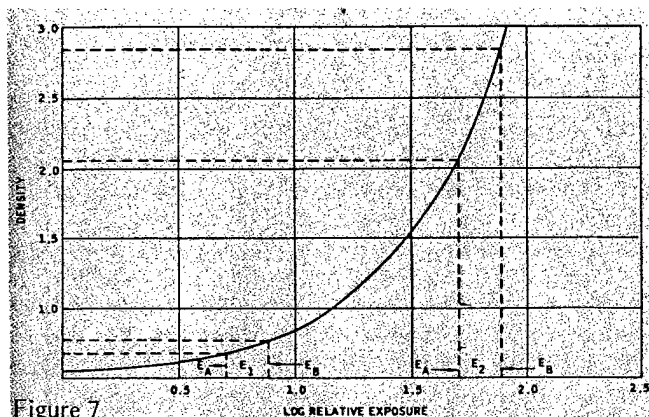


Figure 7

subsequent development process is necessary to bring forth the final visible image.

Of particular importance to the radiographer is the capability of a particular type of film for detecting and recording film density differences in adjacent areas of a specimen (due to flaws, voids, inclusions, thickness, and matrix material density variations). It is this film density difference, or film contrast, which aids the human eye in distinguishing small imperfections. The ASTM defines film contrast as "a qualitative expression of the slope or steepness of the characteristic curve of a film; that property of a photographic material which is related to the magnitude of the density difference resulting from a given exposure difference."

The importance of film contrast for detection ability is demonstrated by Figure 7, which indicates the film density differences recorded at two portions of a specimen. We see that the film density difference, or film contrast, is far greater at a high exposure and that the presence of a flaw can thus be detected much more clearly. Moreover, at a low exposure, the film contrast may be so small as to approach the lower limit of the eye's ability to detect tonal differences. The radiographer thus can make most use of inherent film contrast capabilities by exposing the film to the highest densities readable with available illumination. In addition, if we recall that overall radiographic contrast is a combination of both film and subject contrast, we can think of film as a contrast amplifier. In general, a quality readable radiograph can best be produced by using the lowest voltage necessary for specimen penetration, together with an exposure sufficient to produce high, readable densities. This will yield good subject and film contrasts and provide optimum detection ability.

### EXPOSURE FORMULATION

Since there are many variables involved which must all be optimized for each investigation, the radiographer must rely upon data provided by film manufacturers and isotope suppliers, as well as data recorded from his own past experiences. This information is generally presented in the form of charts, graphs, and tables, including film characteristic curves, radiographic equivalence factor tables, X-ray and gamma-ray exposure charts, and dated decay curves for gamma isotopes.

When a radiographer sets out to produce a radiograph for a particular material specimen, he selects an appropriate radiation source, type of film, a reasonable source-to-film distance, and decides whether or not to use radiographic screens. Then, knowing the specimen thickness (or average thickness for a specimen of complex shape) and selecting a density level as required for high film contrast, he can use an X-ray exposure chart (or gamma

ray exposure chart and isotope decay curve) prepared for the specific conditions selected to arrive at his preliminary settings. The radiographer uses the exposure chart prepared under conditions which most closely approximate those of his ongoing investigation, adjusting the preliminary settings obtained to account for the differences. In the case of X-radiography, the exposure chart allows him to choose kilovoltage, amperage, and time settings. For gamma radiography, with a value of source strength obtained from the isotope decay curve, he must simply calculate an exposure time using the exposure factor obtained from the gamma ray exposure chart. Therefore, once a series of exposure charts and isotope decay curves has been established for the specific X-ray machine and gamma isotopes to be used, it is a simple matter to select preliminary exposure settings.

The preceding discussion has illustrated the procedures and data available to the radiographer for investigation of specimens of commonly encountered industrial metal materials. Radiographic investigation of composite materials, while similar in overall setup and approach, has required the radiographer to refine and extend his capabilities to meet the challenges posed by these new materials. Since composites usually are comprised of low-density materials, composite structures are generally radiographed at very low voltages—on the order of 20-100 kV (depending upon thickness, film, source-to-film distance, etc.). As discussed earlier, this type of soft radiation causes the film to be exposed predominantly to scattered radiation, and it is the control of this scatter which poses particular difficulties for the radiographer.

### Scatter Control

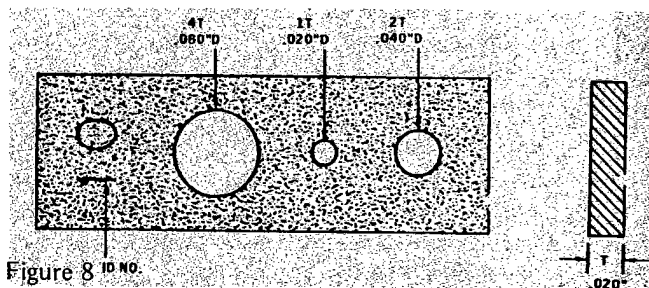
For most industrial material investigations, a number of techniques and auxiliary items have been developed to aid the radiographer in controlling scatter and improving image quality. These methods and items include high-density material filters, collimators, cones, diaphragms, and masking material, as well as the use of a variety of screen types including lead, fluorescent, and a combination of these. Since these items and techniques have been developed for investigation of higher density materials and higher energy radiation, they usually offer very little control of scatter caused by the soft radiation used for composites. Since composites generally are radiographed with relatively soft radiation, filters would have the effect of completely blocking out this soft radiation.

### Penetrators, Radiographic Sensitivity

The attainment of a minimum acceptable image quality level is a necessary part of any code or specification

governing the acceptance or rejection of an item. For this reason, extensive work has been carried out in industrial radiography to establish methods for measuring radiographic image quality as a check on the adequacy of the radiographic technique. This has led to the adoption of standard items commonly referred to as penetrators and image quality indicators. The ASTM defines a penetrator as a device employed to obtain evidence on a radiograph that the technique used is satisfactory.

The penetrator method consists of placing the penetrator, which contains carefully prepared defect indicators (the holes shown in Figure 8), onto the source side of the specimen under investigation and proceeding with the exposure process. The penetrator thickness and hole sizes are standardized to indicate a certain level of image quality. It thus serves as a built-in defect of known thickness and known diameter. In this way, the ability to detect desired density, penetrator outline, and defect size from the radiographed penetrator image is an assurance that adequate imaging has occurred. This method is quite successful for industrial metal material investigations, but it is not adequate for determining image quality in composite material investigations, due to the complexity of composite material composition and the type of defects associated with common composite materials.



## COMPOSITE MATERIAL INVESTIGATIONS

### Typical Applications

By far the most widely used radiographic technique for the inspection of composite materials is the straightforward radiographic method, as previously described. It has been shown that the density on a radiograph depends upon the relative absorption of radiation by the material or defects in its path. In composite material investigations, the radiographer has had to deal with a vast spectrum of reinforcement and matrix material systems, together with a number of associated types of defects. In particular, some of the defect considerations investigated with radiography include: bond evaluations, curing effects, damage considerations, flaw content and growth,

voids, failure mechanisms, fatigue behavior, fiber characteristics and fiber breaks, fracture characteristics, moisture effects, physical properties, resin content, and thermal effects. The need for detection of these types of defects and the general nature of composite systems has brought about a number of advancements in the traditional, straightforward radiographic technique, and has spurred the development of some new and promising techniques.

### Microradiography

The microradiography technique is particularly suited to obtaining images of thin specimens of low density; for this reason, it is being used more and more extensively for composite material investigations. The detail and radiographic quality obtained with a successful application of this technique can be extremely good. However, there are some difficulties which must be considered when employing a low energy X-ray method such as this.

One difficulty, depending upon the thickness of the specimen and the source-to-film distance used, is that exposure times can be very long—three hours or more. This exposure time could be reduced by decreasing the source-to-film distance to a minimum (which is an advantage of having a very small focal spot), but the specimen area intercepted by the radiation beam would also be reduced. Also, in the low kilovoltage range, the inverse square law normally governing radiation intensity is violated due to the absorption of these low energy X-rays by the air. Moreover, the film cassette material also plays a part in radiation absorption and should be of minimum thickness and density. Many radiographers use plastic or paper film holders reinforced with tape and a thin lead backed screen.

### Computerized Image Enhancement

While visual inspection and interpretation continues to be the most widely used technique for defect detection, the increasing need for more rapid and more accurate acceptance/rejection decisions has spurred the development of automatic, computer-based image enhancement and analysis systems.

Radiographic images were examined on a television monitor under various degrees of magnification and enhancement. The enhancement was accomplished by generating a video signal whose amplitude was proportional to the rate of change of image density. Points, lines, edges, and other density variations that were faintly registered in the original image were thus rendered in sharp relief.

Overall, the video system proved to be a valuable tool

for the examination of radiographs. Over 100 samples of radiographs were examined and interpreted with the aid of the enhancer. Each was found to contain some detail that was either missed or difficult to see without enhancement.

Automatic computer-based signal processing techniques improved the interpretation and evaluation of NDT data in two important ways. First, the data was enhanced to accentuate details which would otherwise not be apparent to the observer and, second, the enhanced data was automatically evaluated by the computer and the item was accepted or rejected on the basis of a predetermined defect size criterion without relying exclusively on the subjective interpretation of an inspector.

Several new and innovative signal processing techniques for image data enhancement and restoration were combined to provide an automatic computer-based method for measuring voids on radiographs of graphite/epoxy composite structures. The techniques employed included high-pass filtering, low-pass filtering (smoothing), thresholding, requantization, and contrast stretching to produce a binary image from a radiograph. Then the computer evaluated the binary image, counted voids, measured them, and either accepted or rejected the item.

Once an optimum quality radiograph had been obtained, the image enhancement system began its automatic analysis. The first step was to scan the radiograph with a TV camera. The resulting video output was digitized by a converter and the digitized image was stored in the computer memory as a 512 x 512 pixel (picture element) array—each pixel quantized to one of 512 gray shades (from black at 0 to white at 511). The radiograph thus was converted into a form that the computer could manipulate and analyze.

In the final step, the flaw sizes (adjacent areas of white defect group locations) were measured by the computer and a report was printed out. The report listed the number of flaws falling within specified flaw size ranges. The results were compared against predetermined specifications, and the specimen was either accepted or rejected by the computer. The radiographer simply positioned the film on the light table under the TV camera and instructed the computer where to search. Control then reverted to the computer, and the analysis of the film was done automatically.

The results of recently completed work suggest several potential advantages of image processing:

- Greater operator convenience and less fatigue
- Less time between the discovery of an anomaly and initiation of corrective action
- Decreased direct inspection cost

- Fewer rejects at later stages of production run.

The greatest disadvantage is the increased cost of the equipment.

### Stereoradiography

In order to determine the depth of a flaw within a specimen, a number of stereo methods have been devised. These methods involve the making of a pair of radiographs of the same specimen, but with the tube head either shifted laterally or rotated with respect to the perpendicular to the film plane. These radiographs then are examined simultaneously and, with suitable markers placed on the specimen surfaces, the depth location of the defect within the specimen can be determined.

In one of these methods, commonly termed stereoradiography, two radiographs are made from two positions of the X-ray tube separated by a nominal inter-eye distance. The radiographs then are viewed with a stereoscope, a device which permits the left eye to see only the left eye position radiograph and the right eye to see only the radiograph made in the right eye position. With this viewing technique, the brain causes the image to be seen in its correct 3-dimensional spatial relationship, as with normal vision, and defects are seen to stand out. This method, however, does not readily afford an actual depth measurement of a defect.

With another technique, termed double-exposure or parallax method, an actual depth measurement can be made. A double-exposure method was used to measure the depth location of boron filament defects in a metal matrix composite. In order to obtain clear filament definition, a narrow-beam microradiographic technique was used to make a stereographic pair of radiographs taken at known offset angles to the titanium-boron specimens. Using the measured shift of a known marker location, the depth of the defect was calculated by triangulation.

From the results obtained, the authors calculated the defect depth to be 0.009 inch. The composite had been fabricated using four layers of 4-mil boron filaments alternately sandwiched between five 0.0008-in.-thick titanium alloy sheets. After diffusion bonding, the composite thickness was 0.045 in., which gives a nominal thickness of 0.009 in. for each layer; thus, the defect was located in the first filament layer under the X-ray entry surface.

### Opaque Additive Enhancement

In early work, significant improvements were made in image quality and sensitivity by impregnating subject

materials with contrasting liquids to increase image definition of voids and small cracks in graphite and to provide clearer weave patterns in composite materials.

The radiography of graphite presents certain difficulties; at X-ray energies where differential absorption is greatest, graphite, because of its low atomic number, is more effective as a scatterer than as an absorber of radiation. Therefore, the processes of scatter and absorption occur at the same time and are in conflict. This difficulty becomes even more pronounced as the graphite shapes become more complex.

Radiographic images of graphite rocket nozzle inserts, nose tips, nose cones, etc., often are unclear and lack sharpness around the edges. To overcome this problem, one approach taken was to impregnate the materials with a solution of a higher atomic number compound so that differential absorption of the X-rays would improve the contrast on the resultant radiograph and greater resolution of the structure of the material would be obtained. Tetrabromomethane was selected for this work.

In a graphite-epoxy composite investigation, experimental results established that this modified X-ray technique using tetrabromomethane as an opaque additive can be very helpful in enhancing the radiographic image and in assessing the damage growth zone surrounding discontinuities in fibrous composite laminates. The method is efficient and can be economically applied in real time for stress concentration studies in composites. In addition, it was found that this technique can be used simultaneously with an acoustic emission monitoring technique for residual serviceability evaluation of composite components.

### Neutron Radiography

Neutron radiography, like X- or gamma radiography, depends upon the differential absorption of neutrons by the specimen material. However, while X-rays interact with the atomic orbiting electrons, neutrons interact with the atom's nucleus. There is no well ordered relationship between neutron absorption and scattering coefficients and material atomic number as there is for X-rays (where absorption and scatter generally increase with atomic number).

Neutrons, particularly those with low velocities (thermal neutrons), exhibit a random variation of absorption from element to element. The range of absorption coefficients for neutrons is 0.03 to 90, considerably exceeding that for X-rays (0.13 to 4.0), which allows for greater flexibility and excellent contrast in neutron radiographs. Furthermore, elements with adjacent atomic numbers may have widely different neutron absorption coefficients, and some low atomic number elements (such as hydrogen)

NOTE: Dr. Alberti was principal investigator on the compilation of a comprehensive index on composite characterization which is available from the Organic Materials Laboratory at the U. S. Army Materials and Mechanics Research Center, (617)923-5572.

can attenuate neutrons much more strongly than some high atomic number elements (such as lead).

Thus, thicker sections of high atomic number materials can be radiographed with neutrons in a much shorter time than with X- or gamma rays. Also, neutron radiographs can exhibit a sharp contrast between elements which have similar absorption coefficients for X- or gamma rays but quite different ones for neutrons, such as boron and carbon, cadmium and barium.

Unfortunately, however, since neutrons are uncharged particles, they exhibit negligible direct photographic effects on film, and neutron energy must be somehow converted to produce a radiographic image. Two techniques using converter foils are presently employed to accomplish this. The first technique is direct exposure wherein the film is sandwiched between two layers of foil (gadolinium, rhodium, indium, or cadmium) and exposed. The foils become radioactive when exposed to the neutrons and emit beta or gamma radiation which in turn exposes the film to produce an image. The second technique is a transfer exposure method wherein the converter foil alone is exposed to the neutron radiation passing through the specimen. The radioactive foil then is placed in intimate contact with the film for sufficient time to expose the film and produce an image.

The most common source of neutrons for neutron radiography is a nuclear reactor which provides a horizontal beam of thermal neutrons of high intensities but limited to only a few inches in diameter. This permits short exposure times but may require numerous radiographs for imaging large objects. Neutron beams which do not spread significantly and which contain few gamma rays are desirable for promoting high resolution in the radiographic image.

While neutron radiography is most frequently used when X- or gamma ray techniques are unable to perform a desired inspection task, it is also considered a useful complement to those techniques. For example, hydrogen pockets within a metal container are readily detected by neutron radiography. Other applications include the inspection of brazed joints, tires, printed circuits, and the location of core materials in investment castings.

Neutron radiography is being explored as an inspection tool for numerous composite materials (such as boron fiber-aluminum, boron-epoxy, or bonded honeycomb structures). Neutron radiography is also being used together with X-radiography to inspect fiber-reinforced plastic composites, with resin voids being detected by the neutrons and fiber orientation by the X-rays. Bondline defects in certain adhesively bonded composite/metal structures have also been accurately and reliably inspected by neutron radiography.

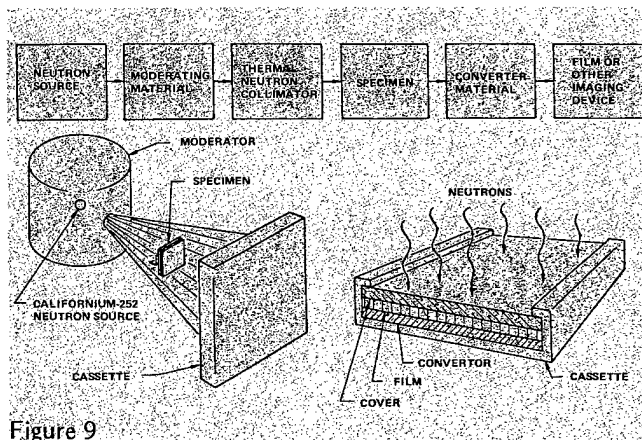


Figure 9

### A Case History

Neutron radiography was used to inspect the structural integrity of adhesive bondlines between a laminated aluminum alloy skin and the rib/spar in an airframe wing box. The laminated skin consisted of three 0.063-inch aluminum layers bonded to each other and to the rib/spar with 0.005-in. epoxy adhesive. The hydrogen content of organic materials, such as epoxy adhesives, typically ranges from 8 to 12 percent. It is readily evident, therefore, that even very thin bondlines can be easily imaged using neutron radiography. Furthermore, the neutron radiography technique is not troubled by discontinuities, such as those occurring at bondline overlap edges, as are acoustic and ultrasonic techniques. This is particularly important because of the nature of the stresses in the bonded joint. The edges should be the area of most effective inspection.

Neutron radiographic inspection was performed using a 2.8-mg californium-252 source. A 0.001-in.-thick vapor-deposited gadolinium metal film was used as a converter (see Figure 9). In addition to neutron radiographic inspection, each critical bondline between the laminated skin and rib/spar was tested for strength in order to correlate observed void fractions and strength predictions. Radiographs were made of all the specimen assemblies and bondline voids were clearly visible in all cases. However, it was obvious that the gadolinium oxide image enhancer significantly improved the contrast whenever used.

From the data obtained, the authors concluded that the value of neutron radiography for assessing the serviceability of this type of laminated structure had been clearly demonstrated. They also concluded that the use of gadolinium oxide as an image enhancer greatly improves radiographic contrast and is effective for rapid inspection and strength prediction of adhesively bonded joints.

# Brief Status Reports

**Project 4001.** Non-corrosive composite assemblies for tactical vehicles. Contract award is expected. For more information, contact Ed Borto, TACOM, (313) 574-8709.

**Project 4008. Composite Drive Shafts.** The procurement request and determination and findings have been processed and are currently in the procurement division. For more information, contact Ed Borto, TACOM, (313) 574-8709.

**Project 4042. Flexible Manufacturing Technology Integration.** This work is being conducted at NBS. A robot along with end effector and basic fixturing elements have been set up. For more information, contact Ed Borto, TACOM, (313) 574-8709.

**Project 4575. Laser Welding Techniques for Military Vehicles.** Deoxidants have proved successful, showing, sound porosity free welds obtained with Cor-weld 70 tubular metal electronic. For more information, contact Ed Borto, TACOM, (313) 574-8709.

**Project 5005. Computer-Aided Design for Cold Forged Gears (Phase II).** 20 Spur gears and 20 helical gears were produced. Technology aspects of process were established. Dimensions, microstructure, hardness distribution and surface quality are progressing. Gears are being

finished to all drawing requirements. For more information, contact Ed Borto, TACOM, (313) 574-8709.

**Project 5019. Storage Battery Low Maintenance.** This project is completed. Testing work was carried out at YPG, CRTC and in the laboratories. A final report on the ZHL tactical vehicle low maintenance battery has been prepared. For more information, contact Ed Borto, TACOM, (313) 574-8709.

**Project 1089. Integral Rocket Motor Composite Attachments.** Design, fabrication and delivery has been completed for eight of ten subscale (20 in) pressure vessels. The preparation of an interim technical report is underway. For more information, contact Bobby Austin, MICOM, (205) 876-2147.

**Project 1089. Integral Rocket Motor Composite Attachments.** The technical effort for this last phase of the project was begun in 1985. For more information, contact Bobby Austin, MICOM, (205) 876-2147.

**Project 1095. Automatic Sealing of Hybrid Packages (CAM).** A technical data package was worked on. A contractor will develop a hybrid package sealing system that will use computer control and automation to weld or solder and make fine and

gross leak tests on various package configurations. For more information, contact Bobby Austin, MICOM, (205) 876-2147.

**Project 1109. Robotized Wire Harness Assembly System.** All major equipment has been received by the contractor and is being integrated into the final configuration. Software development is progressing well in each of the subsystem areas. The laser marker has been installed and checked out. For more information, contact Bobby Austin, MICOM, (205) 876-2147.

**Project 3749. Hydraulic Rotary Actuators.** A hydraulic simulator has been fabricated and used to test an actuator under mission profile loads for 300 hours. For more information, contact Ed Borto, TACOM, (313) 574-8709.

**Project 3749. Hydraulic Rotary Actuators.** Simulator completed and under test for 300 hours. For more information, contact Ed Borto, TACOM, (313) 574-8709.

**Project 3010. Hybrid Modulator for Pulsed Impatt Millimeter Wave Sources.** A slimmed down version of the composite oscillator, modulator and circulator block structure was fabricated and tested. A modulator repackaging effort and circulator change will be attempted to gain more space 1 AW MLRS requirements. For more information, contact Bob

Moore, ERADCOM, (202)  
394-3812.

**Project 3011. Indium-Phosphide Gunn Devices.** Varian modified doping profile, tightened control of thin indium phosphide starting material and obtained rigorous control of epitaxial processing to build good 56 and 94 GHz diodes. Yield was raised 10 times to 50 percent. Varian gave a 2 Mu. No-cost extension. For more information, contact Bob Moore, ERADCOM, (202) 394-3812.

**Project 3501. Third Generation Photocathode on Fiber Optic Faceplate.** ITT cannot make 3rd generation photocathodes into tubes that meet minimum sensitivity specifications. Fiberoptic and gallium ARS faceplates crack due to diffusion coefficient of expansion. Because of TCE and low output, project engineer wants to go to glass faceplates or diffusion to glass. For more information, contact Bob Moore, ERADCOM, (202) 394-3812.

**Project 5010. Bonded Grid Electron Gun.** Varian had improved 50 percent yields of boron nitride blanks received from subcontractor. Sufficient blanks are available for both engineering and confirmatory samples Bonded grid gun number 2 was fabricated with redesigned material pattern. For more information, contact Bob Moore, ERADCOM, (202) 394-3812.

**Project 5019. Laser-Cut Substrates for Microwave Tubes.** A 3 month, no cost contract extension was used to change the high leakage samarium cobalt magnet design to an Alnico V7 design. The two S-band and two C-band IBCFA tube deliverables are retained at Northrup for the production capability demonstration. For more information, contact Bob Moore, ERADCOM, (202) 394-3812.

**Project 3050. Epitaxy of III-V Semiconductor Photodetectors.** RCA, Quebec, obtained improved alumina substrates from RCA Burlington and with new jigging and rapid soldering joined delicate III-V detectors to thick film circuitry on the substrates. Epoxy was eliminated. For more information, contact Al Feddeler, CECOM, (201) 535-4926.

**Project 3054. Production Methods for Multi-Layer Folded Circuits.** Hughes instituted changes in subcontractors rigid-flex circuit board specifications to eliminate plated-through-hole (PTH) cracking. Flexible layer delamination and polyimide adhesive outgassing. Yield has been increased to 50 percent. For more information, contact Al Feddeler, CECOM, (201) 535-4926.

**Project 3056. Electroluminescent Numeric Modules.** Rockwell Collins continued efforts to resolve electroluminescent layer uniformity and thin film conductor

etching problems. Improvements in deposition procedures and clean room techniques have improved DMD panel quality. Two engineering samples were received. For more information, contact Al Feddeler, CECOM, (201) 535-4926.

**Project 1066. Semiadditive Single and Multilayer Circuitry.** Contract not yet awarded. Contractor will use electrolytic additive and semiadditive techniques that are not etch dependent to produce 2 mil lines and 2 mil spaces on multilayer printed circuit boards. For more information, contact Bobby Austin, MICOM, (205) 876-2147.

**Project 1075. Electronics Computer Aided Manufacturing (ECAM).** Boeing submitted a draft final report which is being reviewed. Boeing reviewed cable and harness manufacturing capabilities and future product mix and developed a "test bed" concept. Computer integrated manufacturing guidelines were started. For more information, contact Bobby Austin, MICOM, (205) 876-2147.

**Project 1076. Automatic Recognition of Chips.** Kulicke and Soffa improved SPAR robot deceleration by changing 0 axis bumpers. New power detect board was assembled and testing started. Host/axis serial communication code debugging was completed. Automatic hybrid die bonder

diagnostics is continuing. For more information, contact Bobby Austin, MICOM, (205) 876-2147.

**Project 3073. Tactical Graphics Display Panel.** GTE is still having breaks in TFEL panel indium tin oxide (ITO) layers and is unable to fabricate a perfect panel. Hermetic seal was improved with an optimum frit material that matches expansion of glass panel. For more information, contact Al Feddeler, CECOM, (201) 535-4926.

**Project 1060. Electrical Test and Screening of Chips.** A prototype system has been fabricated and will have an industry demonstration. A TDP for the inspection system will be a deliverable with final documentation. For more information, contact Bobby Austin, MICOM, (205) 876-2147.

**Project 3057. High stability vibration resistant quartz crystals.** FEI corrected flatpack sealing problems with preform gold/tin gaskets. Parallel gap welding was enhanced by a new fixture which reduced electrode pressure and shock. Cut quartz crystals were chemically polished to frequency and successfully tested. For more information, contact Al Feddeler, CECOM, (201) 535-4926.

**Project 3068. Increase Producibility of Varactors and PIN Diodes.** Studies of M/A-COM have shown that GAAS varactors with

breakdown of -25 V and high capacitance cannot be fabricated. The lower capacitance diodes have no problems. The silicon PIN diodes are in double stud packages. 100 PIN diodes are delivered. Low capacitance varactors are awaiting package selection. Silicon may be used for the high capacitance ones. A polysilicon layer is being added to the PIN design to eliminate shorting. The third engineering sample is being fabricated. For more information, contact Al Feddeler, CECOM, (201) 535-4926.

**Project 5041. Millimeter Wave Mixers and Arrays.** Ten 94 GHZ mixer units had already been delivered to ET and DL. The delivery of 30 mixer units at 60 GHZ was delayed because the Alpha MMW devices group moved from Woburn to Metochen. For more information, contact Bob Moore, ERADCOM, (202) 394-3812.

**Project 3115-17. Dynamic Electrical Measurement Standards.** The necessary STDS and software were identified for the in-system calibration of the PII SCTS. The scope of work is presently being developed for the out-of-system calibration of the PII SCTS. For more information, contact Ken Magnant, TMDE, (205) 876-1850.

**Project 6350-2446. Blacklight Video Inspection System.** This project was successfully completed.

A black light video borescope was developed that produces clear shape images of cracks in 105 MM, 120 MM, and 155 MM cannon tubes. The technical report has been completed. For more information, contact John Gassner, AMMRC, (617) 923-5521.

**Project 6350-2642. Advanced Penetrating Radiation Techniques for Product Evaluation.** The evaluation of the gamma-gauging equipment was completed. A negative finding concerning the applicability of equipment is contained in the final technical report which is being reviewed and coordination within AMMRC. For more information, contact John Gassner, AMMRC, (617) 923-5521.

**Project 5071. TECOM Production Test Methodology Engineering Measures.** All four subtasks have been completed. The final report for 5071-90, toxic gas analysis by gas chromatography has not been prepared. For more information, contact William Deaver, TECOM, (301) 278-3677.

**Project 7187. Powder Metallurgy Gears for Helicopter Applications.** Contract not awarded. Revision of the request to eliminate work not essential to the effort. The best and final offers are expected to lower the cost closer to the estimated cost. For more information, contact Fred Reed, AVSCOM, (314) 263-3079.