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ADHESIVE BONDING OF TITANIUM AND ITS ALLOYS

R.E. Keith, R.E. Monroe, D.C. Martin

Prepared Under the Supervision of the
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ADHESIVE BONDING OF TITANIUM AND ITS ALLOYS

By

R. E. Keith, R. E. Monroe, and D. C. Martin*

ABSTRACT

This report covers the state of the art of adhesive bonding of titanium and its alloys and is oriented toward the interests of the designer and the manufacturing engineer. In it are described typical joint designs, surface preparation procedures, types of adhesives used for bonding, environmental factors as they influence choice among available adhesives, processing techniques, representative applications of adhesive bonding, and available test results on adhesive-bonded titanium alloys.

*Principal Investigators, Battelle Memorial Institute, Contract DA-01-021-AMC-11651(Z).

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Prepared for

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In Cooperation with

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PREFACE

This report is one of a series of state-of-the-art reports being prepared by Battelle Memorial Institute, Columbus, Ohio, under Contract DA-01-021-AMC-11651(Z), in the general field of materials fabrication.

The intensive literature search carried out in connection with preparation of this report began with the year 1957, since TML Report No. 104, issued in mid-1958 by the organization that is now the Defense Metals Information Center, covered the adhesive bonding of titanium up to that time. Pre-1957 references are included where appropriate.

In accumulating the information necessary to prepare this report, the following sources within Battelle were searched for the period from 1957 to the present:

Main Library
Slavic Library
Chemistry Library
Defense Metals Information Center
Atomic Energy Commission Library

Outside Battelle, the following information centers were searched:

Redstone Scientific Information Center
Defense Documentation Center
Plastics Technical Evaluation Center

In addition to the literature search, personal contacts were made by telephone or visit with the following organizations and individuals:

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ADHESIVE BONDING OF TITANIUM AND ITS ALLOYS

SUMMARY

Titanium alloys can be successfully adhesive bonded using presently available techniques and adhesives. The preparation of the metal surfaces prior to bonding has a marked effect on the strength and quality of the joints obtained. Particular attention must be given to metal surface preparation for joints intended to be used at elevated temperatures or at cryogenic temperatures.

For successful production of quantities of adhesive bonded assemblies having uniformly high mechanical properties, careful inspection and quality control procedures are essential throughout the manufacturing process. Continual monitoring of adhesive characteristics, compositions of surface preparation solutions, adjustment of processing equipment, accuracy of process control instruments, and testing of joints is essential.

Adhesive bonded titanium structures of considerable size and complexity have been successfully produced.

Attention is directed to some recent developments in adhesive bonding technology that can be applied to titanium alloys.

INTRODUCTION

Adhesive bonding, the various forms of welding, brazing, soldering, and mechanical fastening comprise the available methods for joining of materials. All five of these methods have been in use since antiquity, yet new joining problems continue to appear that require fresh solutions. The joining of titanium is one of these problems.

Titanium alloys have been competitive structural materials since only about 1954. Since 1954, almost the entire technology of titanium has had to be developed. Titanium alloys have been successfully joined by all of the above joining methods. Most titanium joining has been by welding and mechanical fastening, a somewhat lesser amount by adhesive bonding, and only a small amount by brazing and soldering.

Each joining method has its particular advantages, which are responsible for its continued use. Each method has its drawbacks. For example, the lightest joints can be produced by welding; mechanically fastened joints are usually the heaviest. On the other hand, welded joints are permanent, whereas mechanically fastened joints can be taken apart easily. Welded joints are usually made at high temperatures, at or near the melting point of the metal. Adhesive bonding may require no external heating at all. The range of dissimilar metals that can be joined by welding is severely limited. Adhesive bonding can be used relatively freely not only to join dissimilar metals, but to join metals to ceramics and plastics as well.

Many other comparisons among the different joining processes could be made, but these are illustrative of the considerations that result in one method being chosen over the others to make a joint for a given application. This report deals specifically with adhesive bonding as applied to titanium alloys.

All joining processes can be broken down into three steps — preparation, making the joint, and posttreatment of the joint — but the steps become meaningful only as they are further subdivided for a particular process. Figure 1 shows the steps necessary to make an adhesive bond. The surfaces to be joined, usually referred to as the adherends, must be properly cleaned and conditioned. The conditioning may involve application of an electroplate or a chemical conversion coating, and may be followed by application of a primer adhesive in a volatile solvent. The substance used to form the bond, known as the glue or the adhesive, is placed on the area to be bonded. The adherends are placed in the desired relative position, both adherends being in contact with the adhesive, and some means of maintaining them in this relationship is provided. Time is allowed for the adhesive to cure, or harden, during which period many adhesives require the application of external heating. After the cure, the adhesive, now a solid, is hopefully uniformly distributed as a film several thousandths of an inch thick between the adherend surfaces. When viewed in cross section, the plane of adhesive has the appearance of a thin line, referred to as the glue line. The joint is now complete, although for some applications a second curing cycle, or postcure, is desirable. Posttreatment of the joint may include removal of any excess adhesive that has oozed out of the bond area.

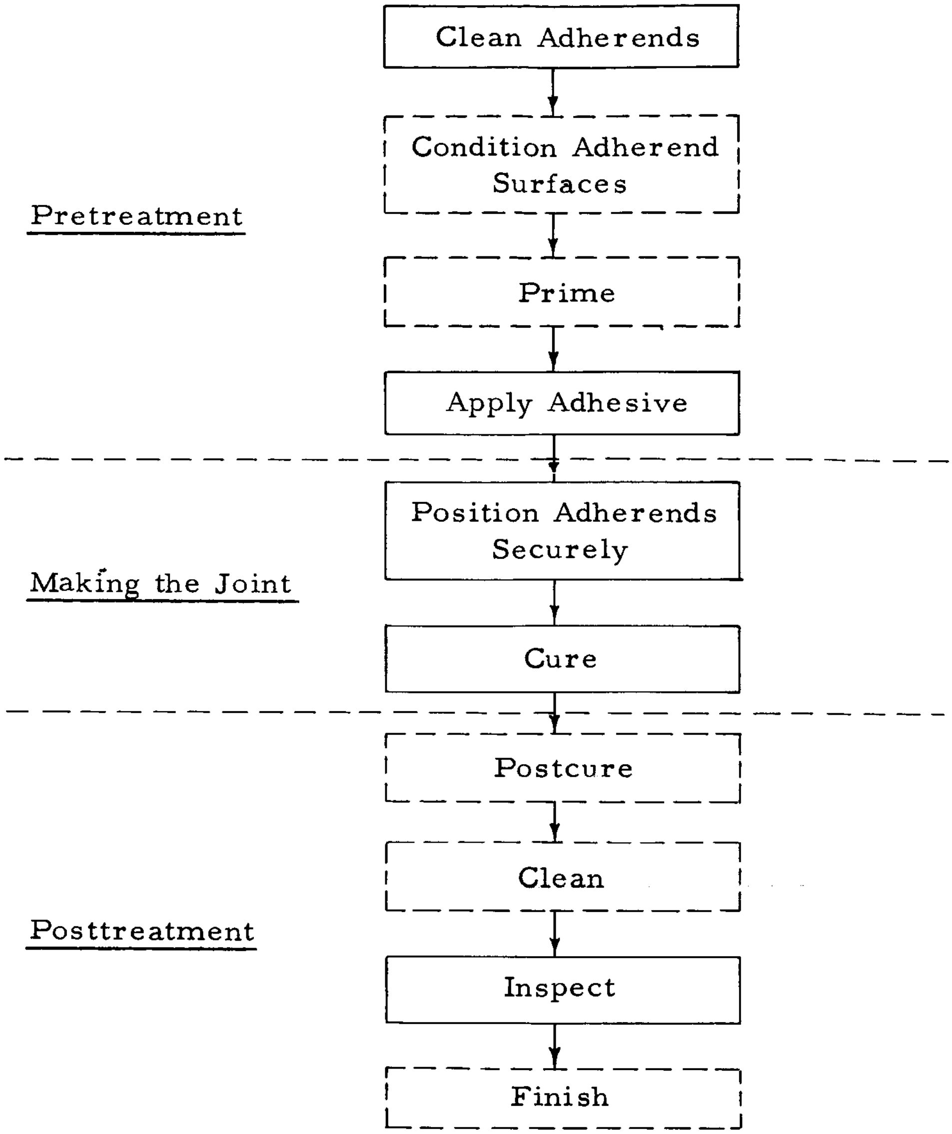


FIGURE 1. SCHEMATIC DIAGRAM OF OPERATIONS PERFORMED IN ADHESIVE BONDING

Dashed-line boxes indicate steps not always performed.

For critical adhesive joints nondestructive testing is employed, following which the joint may be painted.

The large number of books and handbooks (Refs. 1-7), bibliographies (Refs. 8-11), symposia transactions (Refs. 12-18), and summary articles (Refs. 19-27) that have appeared during the last several years attests to the increasing interest in adhesive bonding as a practical means of joining of metals. The reader is referred to these publications for a general background in metal-to-metal adhesive bonding.

During World War II, the British pioneered in the use of synthetic adhesives for primary structural joints in aircraft. Experience gained with wooden aircraft such as the Mosquito light bomber was sufficiently encouraging that the adhesive-bonding technique has been adapted to making wood-to-metal and metal-to-metal joints in numerous European and American military and commercial aircraft (Refs. 12,13). Similar applications are being made in Soviet aircraft construction (Ref. 14). Although this work is important for the present report because it shows the extent to which the adhesive-bonding technology has been developed, the metal bonded in all of the reported applications in Europe to date has been aluminum. It is also true that the bulk of the metal adhesive bonding work done in this country has been on aluminum, and the largest body of literature is concerned with bonding of various aluminum alloys. The B-58 bomber made extensive use of adhesively bonded honeycomb panels (Ref. 28), but the major material used was precipitation-hardenable stainless steel. Recent aircraft in which titanium was extensively used, notably the YF-12A, made use of riveted rather than adhesive-bonded construction.

ADVANTAGES OF ADHESIVE BONDING

Although most of the adhesive-bonding technology has been developed for aluminum and steels, the techniques can be largely applied to titanium as well. Before beginning the discussion of adhesive bonding of titanium, it is appropriate to review briefly the advantages and disadvantages of the adhesive-bonding process itself. Knowledge concerning adhesive bonding is not yet as widespread throughout industry as is knowledge of such other joining techniques as riveting, welding, and brazing.

Advantages of adhesive bonding include:

(1) Mechanical strength
(2) Mechanical damping
(3) Smooth external appearance
(4) Electrical insulation
(5) Capable of joining dissimilar materials
(6) Usable with thin or brittle materials
(7) Possible weight and size reduction
(8) Combined sealing and structural function
(9) Minimum finishing required
(10) No thermal damage to metals
(11) May be least expensive joining method.

Adhesive-bonded joints, when properly designed and fabricated, have shown lap shear tensile strengths at room temperature ranging up to 7000 psi, and in some cases fracture is accompanied by pulling pieces of metal from the surface at the bond plane. Not only do the tensile strengths of adhesive-bonded joints compare favorably with riveting and spot welding, but adhesive-bonded joints are often superior under cyclic loading conditions. They distribute the load more uniformly across the joint than is possible with rivets or spot welds.

The high damping capacity of organic adhesives relative to metals is advantageous in reducing sensitivity of a structure to vibrational loading and contributes to the lowering of noise level.

Smooth, unbroken lines are obtainable by adhesive bonding. The maintenance of a smooth exterior surface is an absolute requirement on a high-speed aircraft. There are many other applications in which smooth lines contribute to the pleasing appearance of a product.

Since adhesives are electrical insulators, they serve to isolate structural members that are joined by adhesive bonding. In cases where electrical isolation is not desired, a limited electrical conductivity can be provided in the adhesive, or provision can be made for direct metallic connection between the adherends at some point. The ability of a thin adhesive joint to withstand voltage is limited. If the primary purpose of a joint is for electrical insulation, superior insulators are available, and the joint must be designed to provide sufficient insulator path length to avoid electrical leakage.

The electrical insulating properties of adhesives make possible the joining of dissimilar metals with much reduced danger from galvanic corrosion. This characteristic gives a designer increased freedom in materials selection.

Adhesive-bonded joints can be made easily with very thin materials, and adhesive bonding is in fact the standard method of making paper-backed foils. Mechanical fastening and welding both become difficult for material thicknesses below about 0.040 inch. Freedom from high-intensity or sudden mechanical loading during the making of an adhesive-bonded joint is also an advantage when joining brittle materials.

Although adhesive-bonded joints must take second place to butt-welded joints as the lightest possible type of construction, adhesive bonding, nevertheless, may offer considerable weight and size advantage over mechanical fastening in cases where parts are small, thin, or light, and would otherwise have to be joined with large numbers of fasteners.

Certain adhesives, notably the elastomers and elastomer-phenolic blends, are frequently used as sealants as well as structural adhesives. One example of their use for this purpose is in the so-called "wet wing" type of aircraft construction, in which no separate fuel tank is used, the fuel being contained within the wing by 100 per cent sealing of structural joints.

Following curing of the adhesive-bonded joint, there is little or no further work necessary. It may be desirable to remove any small amount of adhesive that extends beyond the joint, but this is easily accomplished. Most joints are put in service without further attention after curing.

The curing temperatures required for most adhesives are below the temperature range that will cause alteration of the metallurgical structure of the common metals. In an adhesive-bonded joint there is nothing corresponding to the heat-affected zone of a weld. In the case of adhesives for high-temperature service, however, curing temperatures are sometimes high enough to cause metallurgical damage in heat-treated aluminum and magnesium.

When the entire cost of making a joint is completely accounted for, adhesive bonding is frequently less expensive than other methods of joining. Such factors as capital costs associated with tooling and fixturing, special joint preparation, bond area coverage per unit volume of adhesive, finishing, and the associated labor costs must be considered. These costs must be balanced against all corresponding costs for other joining methods, and a priori estimates as to relative costs are frequently mistaken.

DISADVANTAGES OF ADHESIVE BONDING

There are certain limitations and drawbacks to adhesive bonding. These include:

(1) Limited service conditions
(2) Residual stresses
(3) Requires accurate joint fitup
(4) Requires high standard of cleanliness
(5) Subject to weathering, solvent, and moisture attack
(6) Requires curing time to develop maximum properties
(7) Adhesive may react with the material being joined
(8) Adhesive may outgas
(9) Adhesive may degrade under radiation.

The upper service-temperature limit that a good epoxy or phenolic adhesive can withstand for an indefinite time is usually given as about 350 F. Although adhesives are available that will withstand several hundred hours at 500 F, and some recent Russian work reports tests made at temperatures up to 1832 F (Ref. 29), allowable service time at high temperatures for adhesive-bonded joints is limited.

The presence of residual stresses in an adhesive-bonded joint becomes an increasingly serious problem as curing temperatures increase. The stresses arise because of differential thermal expansion between the adhesive and the adherend. Typically the thermal expansion coefficient of the adhesive is greater than that of the metal adherend, so the adhesive layer is put in tension as the joint cools following curing. Unlike the residual stresses resulting from welding, these residual stresses cannot readily be annealed out. They can be minimized, however, by using a thicker glue line, by altering the adhesive composition to make it more resilient, and by postcuring.

Clearance between adherends to be adhesively joined should be uniform and usually somewhere between 0.005 and 0.010 inch. This is a more accurate fit-up tolerance than many plants are accustomed to using.

Any joining process requires at least some treatment of the surface prior to making the joint. In welding, this surface is obtained by melting away the surface layers of metal. In brazing and soldering, surface films are removed by fluxing. In adhesive bonding, where neither of these methods can be used as presently practiced, adherend surfaces must be pretreated and kept clean until bonded. The difficulty of accomplishing the necessary surface treatment depends upon the accustomed standards within a particular plant or industry, and often it represents no major changes from practices already in use for preparing a surface to be painted.

Care must be exercised in the choice of an adhesive for a given application, since there is danger of degradation of the adhesive by its environment. Thermoplastic adhesives, in particular, are subject to attack by solvents. Cyanoacrylates are moisture sensitive. Intelligent choice among the many available adhesives can minimize the dangers from the service environment.

In some manufacturing operations, the curing time for an adhesive-bonded joint presents a problem. Typically, this time ranges from a few minutes to several hours. During this period, the adherends must be fixtured so that there is no relative motion between them. There are possibilities of reducing the magnitude of this disadvantage. In some cases the parts can be designed so as to be self-registering, for example. In some applications, the adhesive cure is accomplished at the same time the paint is baked on.

Care must be taken in the selection of adhesives, fillers, extenders, and curing agents to avoid compounds that will corrode the adherends. For example, amine-cured adhesives are corrosive to copper-base alloys. The magnitude of the problem can be appreciated when it is realized that there are over one hundred different curing agents for epoxy resins on the market today, many under trademarks that give no indication of their composition. There is no substitute for knowledge and testing experience at this point.

Any organic material in enclosed or hermetically sealed devices should be used with caution, since sufficient vapor may be given off from the organic material during and after curing to impair the function of the device. Considerable difficulty has been encountered in the past in small electrical relays from deposits formed on contacts traceable to volatile components and decomposition products from organic materials.

While all materials are damaged by radiation, rates of accumulation of damage to the relatively delicate molecules of organic materials are greater than for metals exposed to the same radiation. Adhesive bonding is the most radiation sensitive of the joining processes.

To summarize, adhesive bonding is a joining process that has unique advantages. It supplements other joining techniques and, when full advantage is taken of the design opportunities offered by adhesive bonding, it may supplant the more traditional metal-joining processes in a surprising number of applications. Failure to allow for the limitations and peculiar characteristics of adhesives can lead to unsatisfactory results.

GENERAL COMMENTS ON ADHESIVE BONDING OF METALS

It is beyond the scope of this report to go into detail concerning adhesion theory. The reader is referred to the general references cited earlier for information on the subject. In this section, some principles that are particularly important in metal-to-metal adhesive bonding will be mentioned briefly.

DIFFERENTIAL DIMENSIONAL CHANGES

Thermal expansion coefficients of adhesives as a class of materials are higher than those of metals. As has been mentioned previously, the mismatch in thermal expansion coefficients can cause residual stresses in the joint with temperature changes. An adhesive bond will tend to be under internal stress on cooling after the cure, the adhesive tending to be in tension. If there has been shrinkage of the adhesive during the cure, the tensile stress in the adhesive will be further increased in the completed joint. Delayed room-temperature failure of joints due to these residual stresses is a frequent occurrence during the developmental stage of an adhesive-bonding application. This problem can usually be solved by adjustment of the curing cycle. If the joint is intended for service below room temperature, even greater stresses will develop during cooling, which may result in immediate and spontaneous failure of the bond.

One method sometimes used to reduce the thermal-expansion mismatch is to fill the adhesive with metal powder, preferably of the metal being bonded. This is done at the peril of causing loss of adhesion, however.

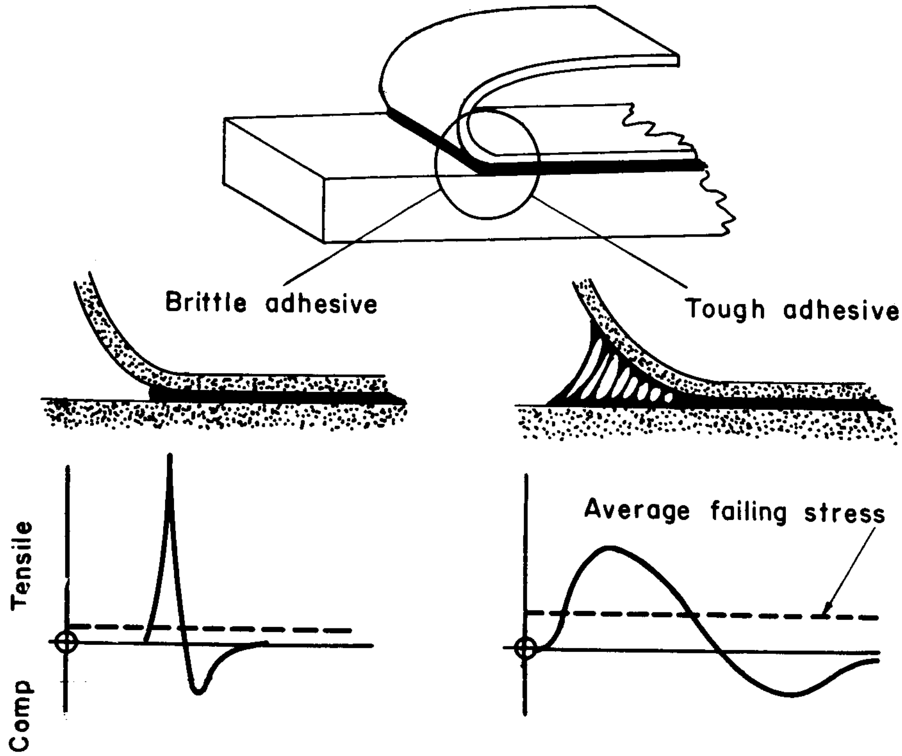
Adhesives intended for use with metals are often complex mixtures of a base epoxy or phenolic resin blended with an elastomer, such as nitrile rubber, or a thermoplastic, such as nylon.. The purpose of these latter materials is to increase the resiliency of the adhesive. A resilient adhesive is better able than a hard or brittle one to accommodate to the internal stresses in the joint and to resist failure by peeling (Figure 2).

USE OF SOLVENT CARRIERS

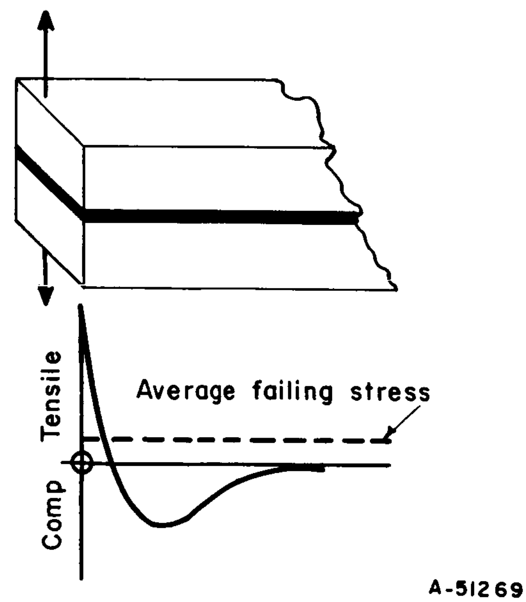
Adhesives intended for use in the bonding of metals, ceramics, and glasses usually contain only small amounts of the solvents or other volatile materials that are commonly found in adhesives intended for use with porous materials such as wood, concrete, paper, and leather. The inability of solvents, if used, to escape from between nonporous surfaces leads to greatly extended cure times and results in ~~porous bonds~~. Primers for metal joints do contain solvents, but it is intended that these solvents be allowed to evaporate before the bonding operation is carried out. Adhesives containing solvents can be used with metals if they are coated and left apart until most of the solvent has evaporated, but most widely used metal adhesives, such as the epoxies and phenolics, contain little or no solvent.

DETAILS OF ADHESIVE BONDING OF TITANIUM

The Titanium Metallurgical Laboratory report on adhesive bonding of titanium by Pattee, Faulkner, and Rieppel (Ref. 31), published in June, 1958, was taken as the starting point for the present report. It summarized the state of the art as of the end of 1957. Since the issuance of that report, considerable information on adhesive bonding of titanium has appeared in the literature. Most of the results reported, however, are of work done prior to about 1958. There is a hiatus of reported data, which extends from that date up to the present time, that reflects the cutback in the Government sponsorship of titanium development. With the increased interest in titanium as a leading candidate material for construction of high-speed aircraft, it is understood that airframe manufacturers and adhesive vendors have resumed adhesive-bonding studies. The results of these studies



a. Peel Stresses



b. Cleavage Stresses

FIGURE 2. PEEL AND CLEAVAGE STRESSES IN ADHESIVE-BONDED JOINTS

After Rider (Ref. 30).

are at this time proprietary, however, and are thus not available for inclusion in this report.

DESIGNING THE JOINT

Since the best strength properties of adhesives are typically those obtained under shear loading, lap joints are the preferred type where possible. The detailed stress analysis of an adhesive-bonded joint is difficult, partly because of the nonlinear stress-strain characteristics of adhesives. Stress analyses have been made, however, and a very recent survey report (Ref. 32) presents a critical review of the present knowledge in this area. For the present discussion, it is sufficient to point out that stresses are not uniformly distributed across an adhesive joint. Stress concentrations occur at the free edges of the glue line, as shown in Figure 3. If the adherends are thin enough to bend as shown in Figure 3, the stress concentrations in the plane

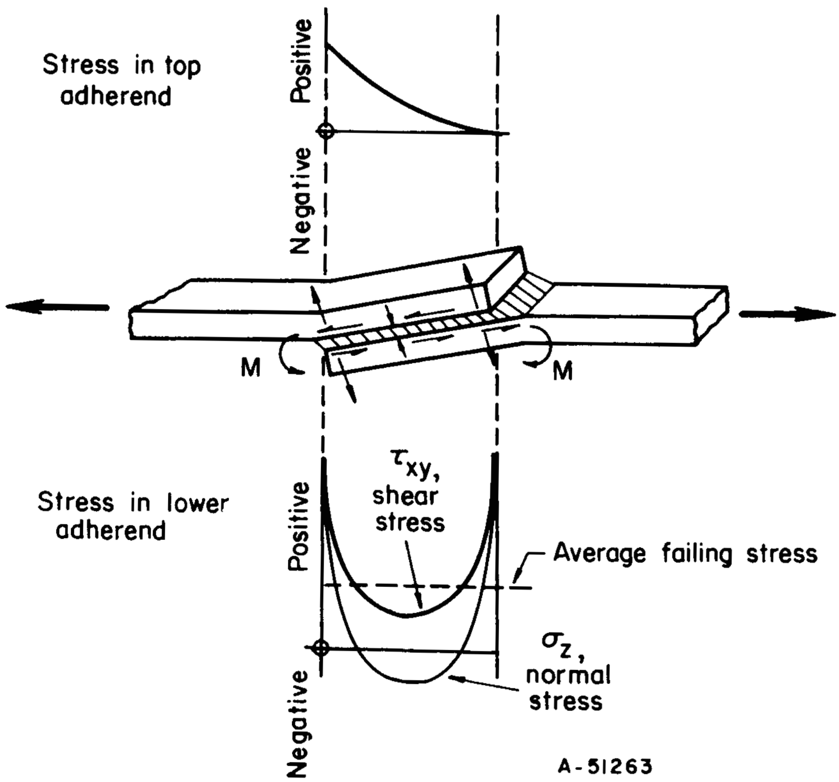


FIGURE 3. VARIATIONS IN STRESSES IN TENSILE-LOADED SIMPLE LAP JOINT

of the adhesive are accompanied by appearance of a tensile stress in the free edges of the adhesive in a direction normal to the glue line, causing a tendency toward peeling. A compilation of the numerous designs developed for adhesive bonded lap joints is shown in Figure 4. Selection among these joint designs is a compromise between strength and joint preparation cost. Similar principles of placing the glue line in shear can be applied in the design of other types of joints. Figure 5 shows some corner-joint designs. Sheet-metal corner joints usually require a third component, which may be a formed, machined or extruded part (Figure 6). Tee joints (Figure 7) can be variously designed, depending upon the type of loading to be encountered. Cylindrical joints in hollow components should be designed using sleeves around the bond area, as in Figure 8. In those cases where a butt joint must be made in thick materials, edges should be prepared so that a shearing component exists along at least part of the glue line, as shown in Figure 9. Similarly prepared faces with radial symmetry can be used when bonding solid rods. Thin strips of bonded metal that are likely to peel in flexure loading can be secured in several ways (Figure 10).

Turning to more complex structures, the designer has considerable control over lateral stiffness of the joints in adhesively bonded skin-and-stringer panels through the use of doublers and changes in details of the stringer cross sections, as shown in Figure 11.

Honeycomb panel construction is becoming increasingly important as a lightweight, stiff structural configuration. Such panels have been fabricated from wood, plastics, light metals, and ceramics by adhesive bonding, brazing, welding, and diffusion bonding. The Armed Forces Supply Center has published a comprehensive handbook which covers details of adhesive bonding of honeycomb (Ref. 33). Figure 12 shows some typical edge closure configurations that have been used with adhesively bonded honeycomb panels. A panel joint that has been used with titanium-faced honeycomb is shown in Figure 13.

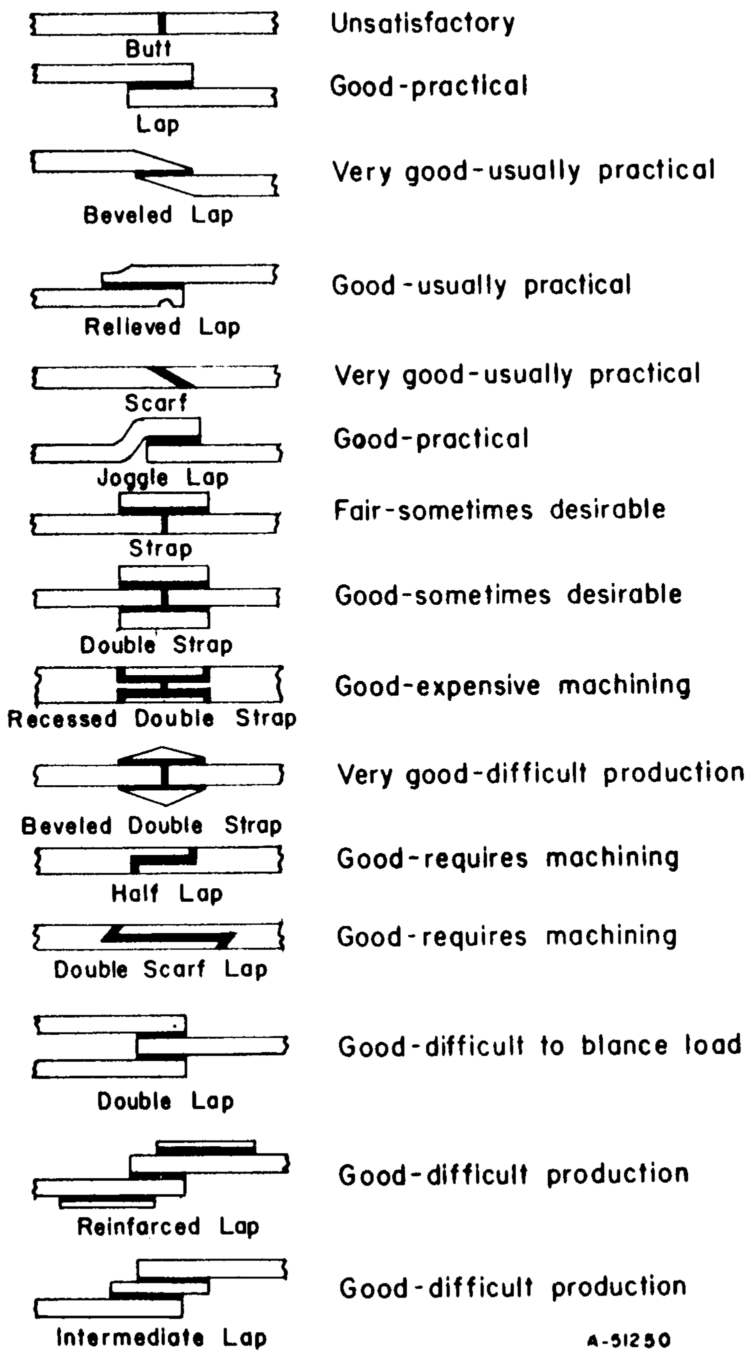


FIGURE 4. SOME DESIGNS FOR JOINTS IN FLAT PLATES

After Reinhart and Callomon (Ref. 19), Rider (Ref. 30), and Hause (Ref. 24).

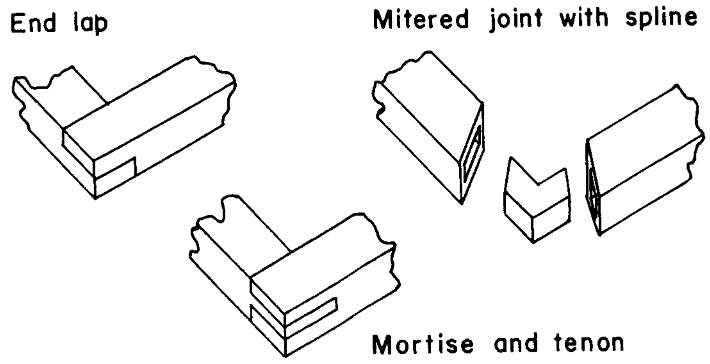


FIGURE 5. CORNER-JOINT DESIGNS

After Hause (Ref. 24).

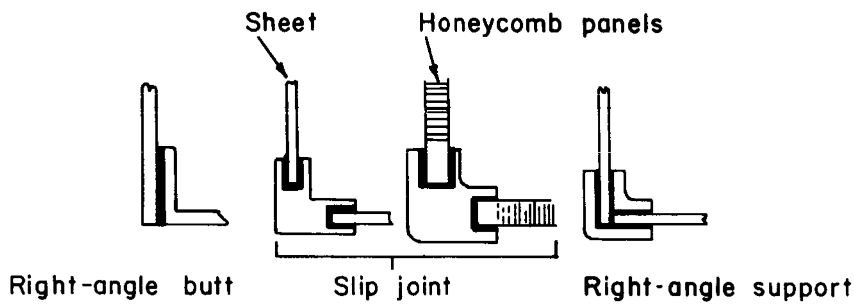


FIGURE 6. SHEET-METAL AND PANEL-EDGE-JOINT DESIGNS

After Hause (Ref. 24).

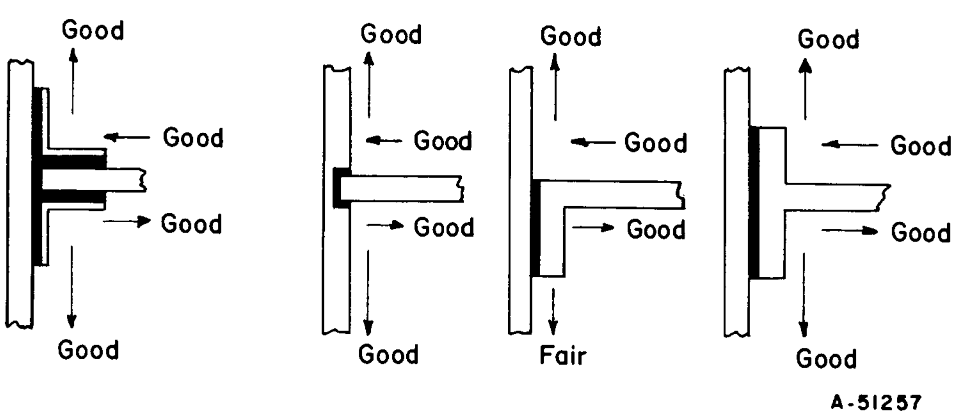


FIGURE 7. TEE-JOINT DESIGNS

Partly after Hause (Ref. 24).

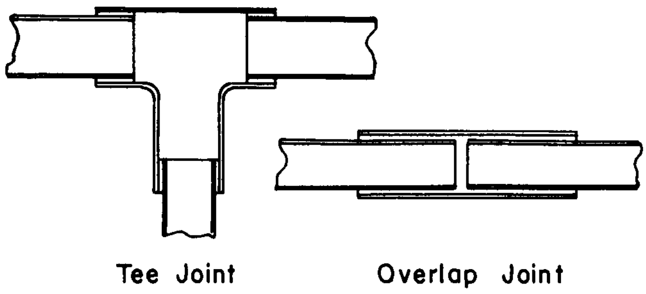


FIGURE 8. DESIGNS FOR CYLINDRICAL JOINTS

After Hause (Ref. 24).

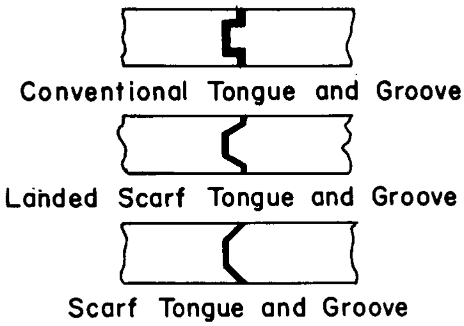


FIGURE 9. BUTT-JOINT DESIGNS

After Hause (Ref. 24).

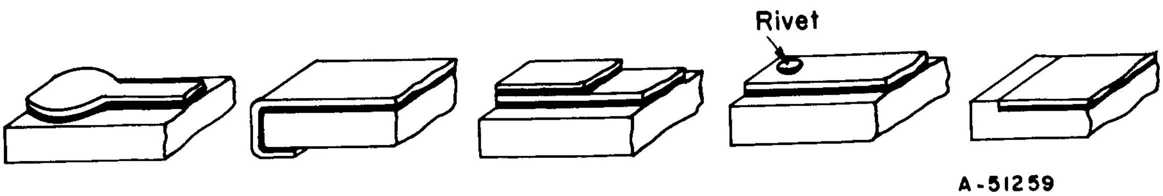


FIGURE 10. PEEL-RESISTANT DESIGNS FOR FLEXIBLE MEMBERS

After Rider (Ref. 30).

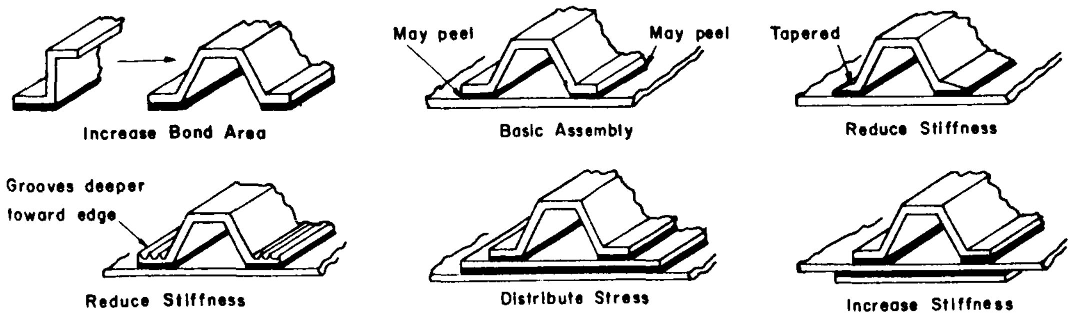


FIGURE 11. JOINT DESIGNS FOR HAT-SECTION SKIN-AND-STRINGER CONSTRUCTION

After Reinhart and Callomon (Ref. 19).

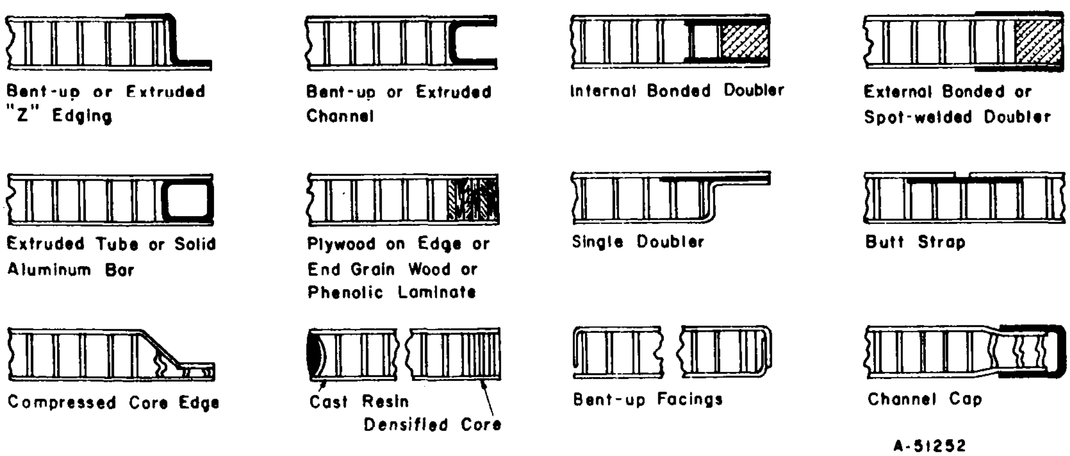


FIGURE 12. HONEYCOMB-PANEL-EDGE DESIGNS

After Pajak (Ref. 34).

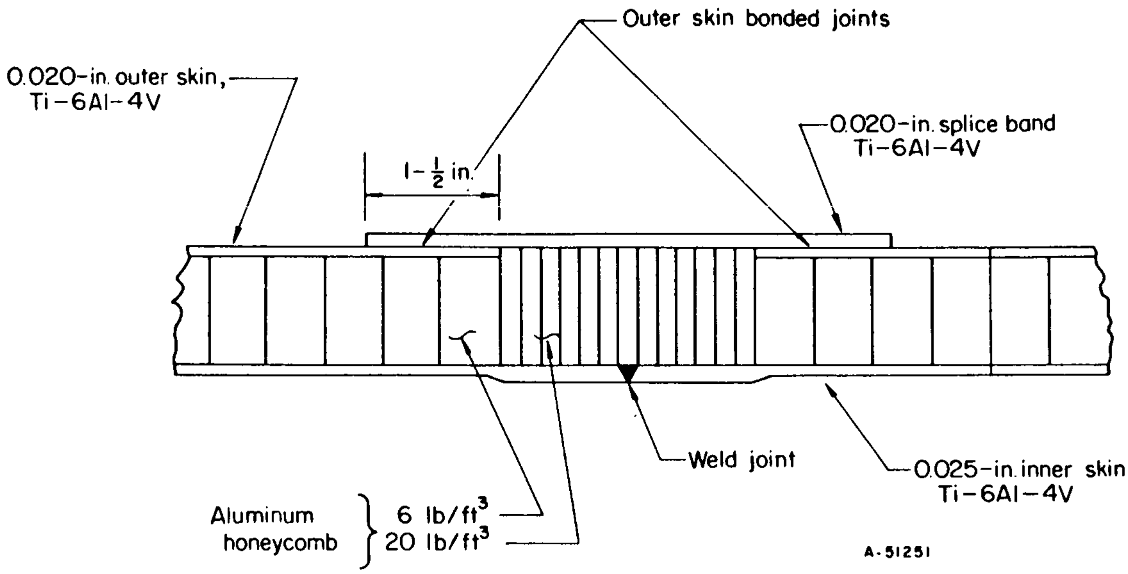


FIGURE 13. CIRCUMFERENTIAL JOINT IN LARGE HONEYCOMB CYLINDER

After Morita (Ref. 35).

When using some of today's stronger adhesives with thin metal adherends in the metallurgically soft condition, including as-annealed Ti-6Al-6V-2Sn, cases have been encountered in which the bond apparently fails adhesively, that is, at the adhesive-adherend interface. Closer examination has revealed that the failure is not a result of poor adhesion, but is caused by mechanical yielding of the metal, with the consequent development of a large shear stress at the interface. The remedy for this type of failure is to change the metal to a heat-treated or cold-worked condition, which has a higher yield point (Ref. 36). Alternatively, a larger overlap can be used in the joint.

PREPARING THE ADHEREND SURFACES

Perhaps the most critical step in achieving a good adhesive bond is the preparation of the surfaces to be joined. Although it is frequently stated that the surfaces must be "clean", what is really meant is that certain types of contamination must not be present. This fact was not appreciated in some of the early work with metal-to-metal adhesive bonding, and many bond failures that were attributed to poor adhesion are now believed to have resulted from the presence of a mechanically weak surface film on the metal.

Figure 14 shows the sequence of operations common to most adherend-preparation processes. Numerous procedures for preparation of titanium alloys were found in the literature, but the principal differences among them are in the compositions of the etching and surface-conditioning reagents.

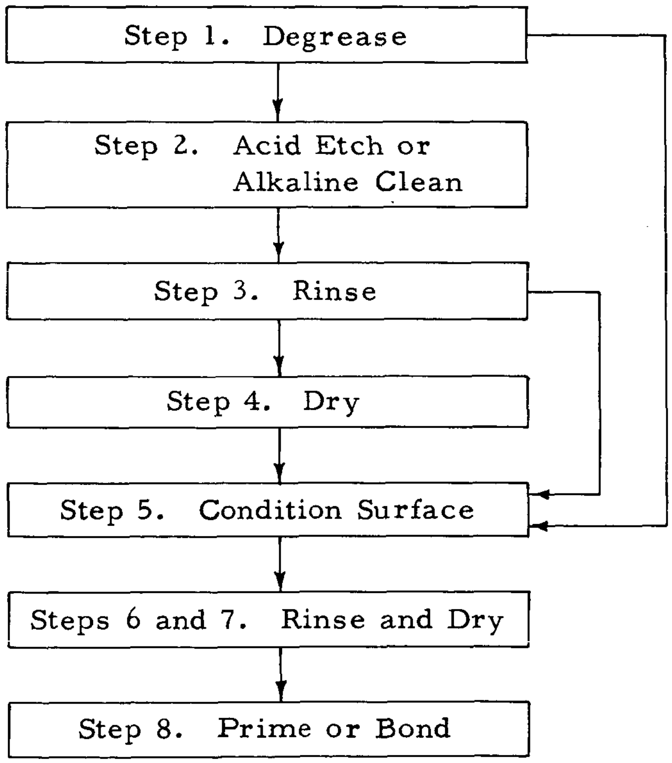


FIGURE 14. FLOW CHART OF SURFACE-PREPARATION PROCESSES FOR ADHESIVE BONDING OF TITANIUM ALLOYS

The following are steps in the surface-treatment process.

Step 1. Degrease. Degreasing is common to all processes, and usually employs a chlorinated solvent such as trichloroethylene. Parts may be immersed, vapor degreased, or swabbed with solvent-moistened cloths. Other solvents, such as acetone, methyl ethyl ketone, carbon tetrachloride, isopropyl alcohol, xylene, toluene, and perchlorethylene, can be used with proper regard for their flammability, toxicity, or cost*.

Vapor-phase degreasing removes contamination by a refluxing action in which the pure solvent vapor condenses on the cold workpiece, dissolves the contaminants capable of solution, and drips off the workpiece. This action ceases when the workpiece reaches the vapor temperature, and it serves no purpose to leave the workpiece in the degreaser for longer times.

When using the solvent-wiping technique, often necessary when the pieces to be bonded are large, it is important to use clean, soap-free cloths, plenty of oil-free solvent, and to wipe the solvent off the surface before it has time to dry.

Step 2. Acid Etch or Alkaline Clean. In some of the reported procedures for preparing titanium, the next step is to remove any visible oxide film or scale by a pickling or acid-etching treatment or to remove any organic material with an alkaline cleaning solution. Whether either of these treatments is necessary depends upon the history of the titanium. They may be omitted for a cold-finished mill product if tests indicate no improvement in adhesive-joint properties from their use. Many of the solutions used are proprietary, and manufacturers' instructions should be followed concerning their use. For large parts on which a wipe-on process is necessary, mechanical abrasion with an abrasive pad or fine-grit paper has been substituted for this step in the procedure (Ref. 35).

Different titanium alloys are attacked by the acid-etching solutions at different rates, alloys containing lower percentages of

*Chlorinated solvents, if incompletely removed from titanium alloys, give rise to stress-corrosion cracking in the vicinity of subsequently made welds. Since welding of titanium is often done in the same plant as adhesive bonding, and is sometimes done on the same parts (see Figure 13), best practice is to avoid the use of chlorinated solvents quickly. Several airframe manufacturers who fabricate titanium alloys no longer permit use of chlorinated solvents.

alloying elements in general being more resistant, so minimum treating times will differ.

In strongly acidic etching solutions, and particularly in sulfuric acid pickling solutions, there can be appreciable hydrogen pickup during treatment. Hydrogen has a deleterious effect on mechanical properties of titanium alloys through formation of a brittle hydride surface layer and is also believed to be a major cause of porosity in welds made in titanium alloys. Experiments reported by Johnson, Sunafrank, Kaarlela, Kastrop, and Slifer (Ref. 37) indicate a hydrogen pickup of 81 ppm by Ti-6Al-4V (0.051-inch sheet) after 1 minute in hot concentrated sulfuric acid. They found a hydrogen pickup of 229 ppm by commercially pure titanium foil (Ti-75A1, 0.002 inch thick) after 30 seconds immersion.

Stough, George, Friedl, Boyd, and Fink (Ref. 38), in their extensive review of descaling and cleaning procedures for titanium, cite evidence that hydrogen pickup in titanium can be held to a small amount by using a pickling solution containing nitric and hydrofluoric acids in the ratio of 10:1 parts by volume of the concentrated acids. At this acid ratio, the metal-removal reaction is

$$3Ti + 4HNO_3 + 12HF \rightarrow 3TiF_4 + 8H_2O + 4NO \quad .$$

If the nitric acid content is allowed to become depleted, however, the reaction changes to

$$2Ti + 6HF \rightarrow 2TiF_3 + 3H_2 \quad ,$$

with hydrogen solution in the metal taking place. The authors caution, however, that the 10:1 acid ratio, which is commonly used as a rule of thumb, was established for Ti-8Mn alloy. They cite some evidence that indicates that Ti-6Al-4V, Ti-5Al-2.5Sn, and commercially pure titanium are relatively insensitive to acid ratio, and that Ti-4Al-4Mn is more sensitive than Ti-8Mn, all in the form of 0.030- to 0.040-inch sheet.

Step 3. Rinse. Opinions differ as to whether water rinses should be hot or cold, tap, demineralized or distilled water, immersion or spray, or whether the hot rinse should precede the cold. Rider (Ref. 39) recommends that electrical conductance of water to be used for a spray rinse be less than 10 micromhos, water for a tank rinse be less than 30 micromhos, and warns that water in many plants contains organic materials. To determine whether tap water in a given locality can be used for rinsing, tests should be made of adhesive bonds made using tap-water-rinsed adherends as compared with similar bonds made using organic-free distilled water. Use of tap-water rinsing is not recommended, however. Tap water contains varying amounts of impurities, chlorine among them, and may be responsible for apparently random time periods during which bond strengths produced are below specification. Whatever the rinsing procedure used, the objective is the complete removal of the etching or cleaning solution as indicated by neutrality of the effluent rinse water (pH = 7). Residual etching or cleaning solutions may cause corrosion of the adherends and may affect the adhesive chemically.

Step 4. Dry. Few processes include this drying step, preferable practice being to proceed directly to the surface-conditioning step following the rinse. If it is necessary to dry the workpiece after Step 3, it can be done in air as clean, still, and dust-free as possible, or drying can be forced using a clean, warm-air blast. If forced drying is used with titanium alloys, the temperature should be limited in order to slow oxide film growth. Maximum drying temperatures recommended by various investigators range from 90 to 200 F.

Step 5. Condition Surface. In the surface-conditioning step, a corrosion film controlled as to chemical composition and thickness is deliberately formed on the adherend surface. Typically, the films used for titanium are complex mixtures of phosphates, fluorides, chromates, sulfates, and nitrates. The composition of the film may be the most important single factor controlling the strength of the adhesive-bonded joint under the desired service conditions. Evidence suggests that some film compositions and thicknesses are markedly superior to others, especially at extremes of service temperatures. No systematic study has been published of the influence on joint properties of film compositions and thicknesses as functions of solution composition, treatment time and temperature, and alloy. The approach has instead been empirical, which is understandable considering the complexity of the relationships and the experimental difficulties in characterizing the films. Until more fundamental information is available, the user must choose among possible surface-conditioning processes on the basis of tests made using his parts bonded and tested under simulated service conditions.

Steps 6 and 7. Rinse and Dry. Statements made under Steps 3 and 4 apply here also.

Step 8. Prime or Bond. Metals differ in the rate at which atmospheric oxygen and moisture will reform a sufficiently thick film on the metal surface so that the value of the surface preparation is lost. With titanium, an elapsed time no greater than 8 hours between cleaning and bonding is recommended. Copper and brass should be bonded immediately after cleaning. Bonding of aluminum can be delayed 1/2 hour after cleaning. Stainless steel can be successfully bonded days after cleaning. The longer this time, however, the greater is the danger of organic contamination from airborne or accidental causes, or of mechanical damage to the surface film. Best practice, therefore, is to bond immediately after surface preparation. If this is not possible, the prepared surface should be primed according to the adhesive manufacturer's directions. The primed parts should then be stored in a clean, dry place, preferably protected by a cover of some sort, until ready for bonding. Handling of cleaned parts should be done only using clean cotton or nylon gloves.

Reported Surface-Preparation Procedures. Table I is a summary of procedures that have been used by various investigators to prepare titanium-alloy surfaces for adhesive bonding. It is difficult to tell how much attention was actually paid to the surface preparation in some of these investigations. Some were limited studies aimed at the evaluation of adhesive systems and one feels that the adherend preparation may have been incidental. Others are recipes presented in survey articles or books. They are presented here without any attempt at evaluation, since no single source was found that attempted to list more than a few procedures, and it was felt that a summary would be of value to anyone undertaking the development or modification of a surface-preparation procedure.

The most extensive study of surface-preparation procedures for adhesive bonding of titanium alloys was made as part of the sandwich-panel-development program at Convair, Ft. Worth, reference to which has been made earlier (Ref. 37). These investigators systematically evaluated 31 procedures all of which, including several anodizing processes, are listed in Table II. The following phosphate-fluoride method was finally selected.

(1) Methyl ethyl ketone wipe

(2) Trichloroethylene vapor degrease

(3) Pickle in the following water solution at room temperature for 30 seconds:

Nitric Acid - 15% by volume of 70% HNO_3 solution
Hydrofluoric Acid - 3% by volume of 50% HF solution

(4) Rinse in tap water at room temperature

(5) Immerse in the following water solution at room temperature for 2 minutes:

Trisodium phosphate - 50 grams/liter of solution
Potassium fluoride - 20 grams/liter of solution
Hydrofluoric acid (50% solution) 26 milliliters/liter of solution

(6) Rinse in tap water at room temperature

(7) Soak in 150 F tap water for 15 minutes

(8) Spray with distilled water and air dry.

It is known that the phosphate-fluoride process gives good results with nitrile-phenolic and epoxy-phenolic adhesives for short-time service up to 600 F and fair results for 100 hours at 500 F. The process, with proprietary modifications, is the standard surface-preparation procedure for adhesive bonding with at least one other airframe manufacturer. The phosphate-fluoride process was developed as a treatment related to high-temperature applications. There is no assurance that it is the optimum, or even a satisfactory, titanium surface treatment for adhesive bonds intended for cryogenic service.

Compromises. The surface-preparation procedures outlined represent the best current practices for attaining the maximum adhesive-bond strengths possible with present adhesives. They should be used for primary structural bonds and in critical applications where loss of life or property would result from bond failure. Where requirements are less stringent, treatments as straightforward as sandblasting or rubbing with abrasive paper have given sufficiently good surfaces for adhesive bonding of titanium. Relaxing of the surface-preparation requirements must be done cautiously, however, because some very subtle factors may cause an unexpected loss of bond strength. Bikerman (Ref. 2) suggests that surfaces may

TABLE I. REPORTED TREATMENTS FOR SURFACE CLEANING AND CONDITIONING OF TITANIUM PREPARATORY TO ADHESIVE BONDING

Source	Process Step						
	Degrease	Clean Etch	Rinse	Dry	Surface Conditioning	Rinse	Dry
Forest Products Laboratory (Ref. 40)	CCL_4	0.3 wt % HNO_3 2.5 wt % HF 97.2 wt % H_2O Temp 20 C Time 15 min	Cold H_2O		5 wt % CrO_3 95 wt % H_2O Temp 60 to 70 C Time 5 min	Cold H_2O	
Narmco (Ref. 41)					9.6 vol % H_2SO_4 3 vol % NaF 1.4 vol % CrO_3 86 vol % H_2O Temp 20 C Time 8 min	Cold H_2O	
Bäder (Ref. 42)		22.5 wt % HNO_3 2.5 wt % HF 75 wt % H_2O Temp 50 C Time 20 min	Cold H_2O				
Homeyer (Ref. 43)		10 wt % HF 90 wt % H_2O Temp 20 C Time 1 min	Cold H_2O		50 vol % HNO_3 50 vol % H_2O Temp 20 C Time 30 min	Cold H_2O	
VLW-Bäder (Ref. 42)		15 vol % HF 30 vol % HNO_3 55 vol % H_2O Temp 20 C Time 1 min	Cold H_2O		27.5 wt % H_2SO_4 7.5 wt % $Na_2Cr_2O_7$ 65 wt % H_2O Temp 60 to 70 C Time 1 min	H_2O	

TABLE I. (Continued)

Source	Process Step						
	Degrease	Clean Etch	Rinse	Dry	Surface Conditioning	Rinse	Dry
Franklin Institute (Ref. 44)	TCE-10 min RT or vapor degrease 10 min 180 to 190 F				(A) 96.6 vol % H_2SO_4 3.4 vol % saturated solution $Na_2Cr_2O_7$ or (B) 94.4 wt % H_2O 2.0 wt % Na_2SiO_3 (meta) 3.6 Triton X200 Temp 155 ± 5 F Time 15 min	Tap H_2O; 180 to 200 F or RT demineralized H_2O; 180 to 200 F or RT	Air or oven <200 F
ASTM (Ref. 45)		42 wt % H_2O 47 wt % HCl 9.2 wt % Formalin 1.8 H_2O_2 Temp 60 to 65.5 C Time 10 min	H_2O		73 wt % H_2O 24 wt % H_2SO_4 3 wt % $Na_2Cr_2O_7$ Temp 60 to 65.5 C Time 5 min	H_2O	<98 C
Matting and Ulmer (Ref. 46)		(A) Conc. KCl or (B) 15 vol % HF Temp (A) 90 to 100 C; (B) RT Time (A) 10 min; (B) 3 min					

TABLE I. (Continued)

Source	Process Step						
	Degrease	Clean Etch	Rinse	Dry	Surface Conditioning	Rinse	Dry
Guttman Method I (Ref. 3)	Acetone, MEK, toluene, TCE, isopropyl alc., xylene				3.3 wt % NaF 1.7 wt % CrO_3 79 wt % H_2O 16 wt % H_2SO_4 Temp RT Time 5 to 10 min	Tap H_2O plus distilled H_2O spray	160 to 180 F 10 to 15 min
Guttman Method II (Ref. 3)		22 vol % HNO_3 3.7 vol % HF 74.3 vol % H_2O Temp 100 to 125 F Time 10 to 15 min	Tap H_2O plus distilled H_2O spray	160 to 180 F 10 to 15 min			
Katz Immersion (Ref. 7)	Alkaline cleaner	52 to 58 vol % HNO_3 2.8 to 2.3 vol % NH_4F Bal H_2O Temp RT Time 4 to 6 min	H_2O		4.5 to 5.5% Na_3PO_4 0.8 to 1.0 % NaF 1.4 to 1.6% HF Bal H_2O Temp RT Time 2 min	(A) H_2O; (B) 15 min in 140 to 150 F H_2O; (C) Demineralized H_2O	<140 F
Katz Manual (Ref. 7)	Sandpaper; TCE or other solvent				4 to 5% Na_3PO_4 1.1 to 1.3 NaF 2.5 to 2.9 HF Bal H_2O Temp Wipe on - RT Time 2 to 3 min	H_2O rinse until neutral	<140 F

TABLE I. (Continued)

Source	Process Step						
	Degrease	Clean Etch	Rinse	Dry	Surface Conditioning	Rinse	Dry
Rider (Ref. 39)		3.0 oz Na metasilicate 1.5 oz tetrasodium pyrophosphate 1.5 oz NaOH 0.5 oz anionic detergent 1 gal H_2O Temp 160 to 180 F Time 10 min	(A) Hot H_2O (B) Cold H_2O		3.4 vol % $Na_2Cr_2O_7$ (saturated solution) 96.6 vol % H_2SO_4 Temp 155 F Time 15 min	Cold H_2O	<200 F
Kempf (Ref. 47)	TCE 10 min				3.5 vol % $Na_2Cr_2O_7$ (saturated solution) 96.5 vol % H_2SO_4 Temp 120 F Time 15 min	(A) H_2O 150 to 160 F (B) Distilled H_2O	80 to 90 F 5 to 10 min
Hertz (Ref. 48)	TCE wipe	46.8 wt % HCl 1.9 wt % H_2O_2 9.5 wt % Formalin 41 wt % H_2O Temp 150 F Time 10 min	(A) Cold tap H_2O; (B) Cold distilled H_2O	Air dry	90.9 wt % H_2SO_4 9.1 wt % $Na_2Cr_2O_7$ Temp 140 to 160 F Time 5 to 10 min	(A) Cold tap H_2O; (B) Cold distilled H_2O	Air dry
Morita Immersion (Ref. 35)	TCE 1 min	Turco 4215-S 5 oz/gal Temp 160 F Time 15 min	Cold H_2O		υ.5% Na_3PO_4 0.9% NaF 1.6% HF Bal H_2O Temp RT Time 2 min	(A) Cold H_2O spray; (B) Hot H_2O 5 min 150 F	Air dry

TABLE I. (Continued)

Source	Process Step						
	Degrease	Clean Etch	Rinse	Dry	Surface Conditioning	Rinse	Dry
Morita Wipe-On (Ref. 35)	MEK wipe	Abrade with pad or wheel			Swab on phosphate solution Temp RT Time 2 min minimum	(A) Wipe with damp cloth; (B) Rinse neutral with demineralized H_2O	Air dry Air dry

Notes: Blank spaces indicate that no information was given in the reference.
MEK - methyl ethyl ketone
TCE - trichloroethylene
RT - room temperature
wt % - weight per cent
vol % - volume per cent
% - per cent, weight or volume not specified.

TABLE II. EVALUATION OF TITANIUM-SURFACE-PREPARATION PROCEDURES FOR ADHESIVE BONDING

After Johnson, Sunafrank, Kaarlele, Kastrop, and Slifer (Ref. 37)

Surface-Preparation Procedure	Adhesive	Tensile Shear Strength, psi at -67 F	75 F	350 F	600 F
(1) Anodize in 15% H_2SO_4	A	2580	1740	2070	1260
	B	3460	3420	860	270
(2) Anodize in 15% H_2SO_4 - 2% CrO_3	A	2780	2060	2170	1140
	B	3220	2750	640	340
(3) Immersion in concentrated H_2SO_4 - $Na_2Cr_2O_7$	A	2200	1590	1600	1170
	B	2960	3250	1160	210
(4) Immersion in 10% HF	A	2090	1790	1800	1090
	B	3040	3580	990	200
(5) No. 4 followed by immersion in H_2SO_4-$Na_2Cr_2O_7$	A	1840	1840	2220	950
	B	2790	2460	510	280
(6) Anodize in 15% H_3PO_4	A	1090	1150	1350	740
	B	1570	2290	660	310
(7) Anodize in buffered fluoride solution	A	970	1250	1350	760
	B	1840	2500	700	320
(8) Anodize in 5% NaOH	A	1670	1340	2340	1030
	B	910	2670	850	280
(9) Anodize in 5% HCO_2H	A	1780	1590	2150	1380
	B	3280	3030	820	350
(10) Immerse in $Na_2B_4O_7$-KF-HF	A	1640	1130	1460	650
	B	1890	2670	930	320
(11) Immerse in Na_3PO_4-KF-HF	A	1730	1410	1890	920
	B	1660	2030	900	220
(12) Immerse in HNO_3-HF	A	1530	1360	1310	660
	B	3740	3890	770	210
(13) Immerse in HCl-H_3PO_4-HF	A	1580	1460	1440	630
	B	2870	2560	540	210
(14) Immerse in hot H_2SO_4	A	2330	2230	2190	880
(15) Immerse in $H_2C_2O_4$-H_2SO_4	A	2040	1700	1780	900
	B	3050	2980	660	300

TABLE II. (Continued)

Surface-Preparation Procedure	Adhesive	Tensile Shear Strength, psi at -67 F	75 F	350 F	600 F
(16) Immerse in Nonic No. 218 - Na_2SiO_3	A	2300	2020	2160	1210
	B	4230	3350	900	290
(17) Same as No. 12 followed by No. 16	A	2600	2030	2420	1020
	B	4190	3430	880	210
(18) Same as No. 14 followed by No. 16	A	2640	2570	2680	1490
	B	4230	3550	940	320
(19) Same as No. 18	A	2550	2600	2420	1440
	B	4440	3680	1070	300
(20) Same as No. 12, followed by No. 11, followed by 75 F - 1-hr tap-water soak	A	--	2840	2680	--
	B	--	2830	869	--
(21) Same as No. 20 without tap-water soak	A	--	1330	--	--
	B	--	3240	--	--
(22) Same as No. 12, followed by No. 11 followed by Sterox CD-Na_2SiO_3 - $Na_2Cr_2O_7$ immersion	A	--	2260	--	--
	B	--	2410	--	--
(23) Same as No. 12, followed by No. 11 followed by NaOH immersion	A	--	1800	--	--
	B	--	3210	--	--
(24) Same as No. 12, followed by NaOH-$Na_2Cr_2O_7$ chelate immersion	A		1790		
	B	--	2380	--	--
(25) Same as No. 12, followed by No. 11 followed by Turco 2623 immersion	A	--	1650	--	--
			3650	--	--
(26) Same as No. 12, followed by No. 11 followed by Triton X-200 - Na_2SiO_3 immersion	A	--	1560	--	--
	B		3440	--	--
(27) Same as No. 20, followed by Nonic No. 218 - Na_2SiO_3 immersion	A	--	3380	--	--
	B	--	3840	--	--

TABLE II. (Continued)

Surface-Preparation Procedure	Adhesive	Tensile Shear Strength, psi at -67 F	75 F	350 F	600 F
(28) Same as No. 27 except a 75 F - 2-hr tap-water soak was used	A	--	3280	--	--
	B	--	3440	--	--
(29) Same as No. 28 - omit Nonic No. 218 - Na_2SiO_3 immersion	A	--	3000	--	--
	B		4220	--	--
(30) Same as No. 27 without water soak	A	--	1370	--	--
	B	--	1440	--	--
(31) Same as No. 29 except 150 F - 15 min tap-water soak used	A	2630	2690	2800	1500
	B	4230	3550	940	320

Note: In all of the above runs with the exception of Number 19, the titanium used was 0.05-inch-thick Ti-6Al-4V alloy in the annealed condition. Also, each room-temperature value represents an average of 6 specimens. The elevated- and low-temperature values each represent an average of 5 specimens. In Run Number 19, the titanium used was Ti-6Al-4V alloy in the heat-treated and aged condition.

Adhesive A is a phenolic-epoxy; Adhesive B is a nitrile-phenolic.

the metal (which may still be coated with an inorganic film) is higher than that of water. It gives no information concerning the strength of any film present and, therefore, is not a test of attainable adhesive-bond strength.

SELECTING THE ADHESIVE

Because of the nature of organic chemistry, it is not surprising to find that there are hundreds of commercially available adhesives. Although these substances fall into a limited number of chemical categories, it is probably safe to say that no two adhesives manufactured by different companies are precisely alike. For example, over one hundred different curing agents for epoxy resins are said to be in use and, to a greater or lesser degree, each curing agent imparts something of its own characteristics to the adhesive. Innumerable variations are possible in details of resin chemistry and blending, and the industry pattern is that such information is usually proprietary with the adhesive manufacturer. Unsatisfactory performance of one manufacturer's adhesive in an application cannot be interpreted as an indication that no adhesive of that class can be used. The unsatisfactory behavior may be due to some detail of the user's bonding process to which another adhesive might not be so sensitive. A good example of this sort of thing might be high sensitivity of one adhesive to alkalinity of a poorly rinsed adherent surface, while another adhesive may be relatively unaffected.

The only adhesives known to have been used for adhesive bonding of titanium belong to the class known as thermosetting adhesives. These adhesives undergo chemical changes during the curing cycle, which render them incapable of being dissolved in the common solvents and of melting. They tend to char when overheated. Chemically, the change during curing consists of the formation of cross linkages between resin molecules to form three-dimensional polymer networks. Thermosetting adhesives are the strongest class of adhesives and the only class worthy of consideration for high-temperature applications. Adhesives known to have been used to bond titanium alloys include the following types:

actually be contaminated by a sandblasting operation if the sand contains organic matter, as is often the case if the sand has not been prebaked. He also cites results by other investigators that show a 50 per cent loss in adhesive-bond strength due to 0.1 microgram of decanoic acid (a material similar to a perspiration film) per square centimeter of adherend surface. Even if the user is experienced in the art of adhesive bonding, when beginning work with a new material, he will probably save time and money in the long run if he will use more elaborate procedures than he believes are necessary and will then work toward their simplification.

New Surface-Preparation Processes. Within the near future, it is expected that some of the proprietary processes recently developed by airframe manufacturers will be made public. These are processes specifically for titanium bonds intended for high-temperature use. At least one of them, the Boeing process, was designed to form a barrier film to prevent oxygen dissolved in the titanium from reaching the adhesive.

A proprietary alkaline cleaner introduced by the Bloomingdale Rubber Division of American Cyanamid appears to be satisfactory for a number of metal adherends, including titanium, and was recommended by personnel of one aerospace company as a versatile one-step surface-preparation process for a variety of metals, including titanium (Ref. 49).

Tests for Proper Surface Preparation. The so-called waterbreak test, which can be used at any stage of the cleaning procedure, is the simplest and most widely used method of determining surface cleanliness. If a drop of distilled water wets the metal surface and spreads out, or if a film of distilled water on the surface does not break up into individual droplets, the surface can be presumed to be free of harmful organic films. A surface that is uniformly wet by distilled water will probably also be wet by the adhesive.

A drop of an organic solvent has sometimes been substituted for the drop of water. This is not a suitable test, since the organic solvent may have the power of dissolving any organic film present and then wetting the surface. Thus, it would not indicate presence of the contaminant.

It should be emphasized that satisfactory wetting of the surface in the waterbreak test merely shows whether the surface energy of

Adhesive Type	Reference
Epoxy	3
Alloyed epoxy	3
Epoxy-silicone	3
Epoxy-phenolic	3,35,44,48,37,50
Epoxy-polysulfide	51
Epoxy-polyamide	48
Epoxy-nylon	48
Modified phenolic	3
Nitrile-phenolic	37,50,52
Vinyl-phenolic	44
Polyester	51
Polyurethane	48

Titanium alloys are compatible with all the commonly available adhesive systems. The strengths of the bonds obtained depend on the particular adhesive used and on the prior surface preparation of the titanium.

Adhesive Tests. In this report, comparisons of bond strengths will be made on the basis of simple overlap tensile-shear tests. Although other types of tests are necessary to evaluate an adhesive completely, and may even be preferable from a theoretical standpoint (Ref. 28), the simple lap joint pulled in tension is easy to make and test and provides meaningful comparative results. Dimensions of the tensile-shear specimen have become generally accepted as set forth in Federal Test Method No. 175, Tentative Standard Method 1033.1-T. A sketch of the specimen is shown in Figure 15. All tensile-shear results mentioned in this report were obtained using specimens having dimensions shown in the sketch unless otherwise noted.

Another type of mechanical test that is sometimes used in adhesive evaluation is the tee-peel test, for which one specimen is shown in Figure 16. This test is not covered by Federal Test Method No. 175. It is apparent that adherend thickness can influence the results of this test, which are reported in terms of strain energy per unit width of specimen, in-lb/in.

A third type of test, referred to as the pi-tension test, is one in which two circular blocks of the adherend metal are bonded with

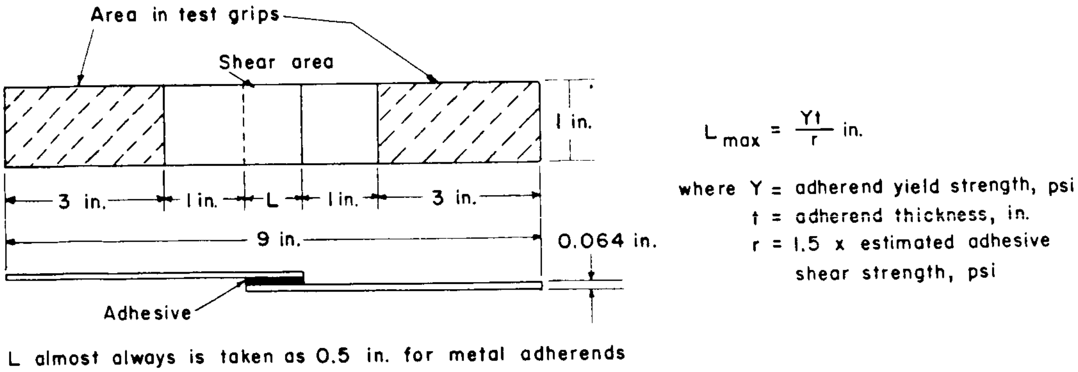


FIGURE 15. CONFIGURATION OF SIMPLE-LAP TENSILE-SHEAR-TEST SPECIMEN

From Federal Test Method No. 175.

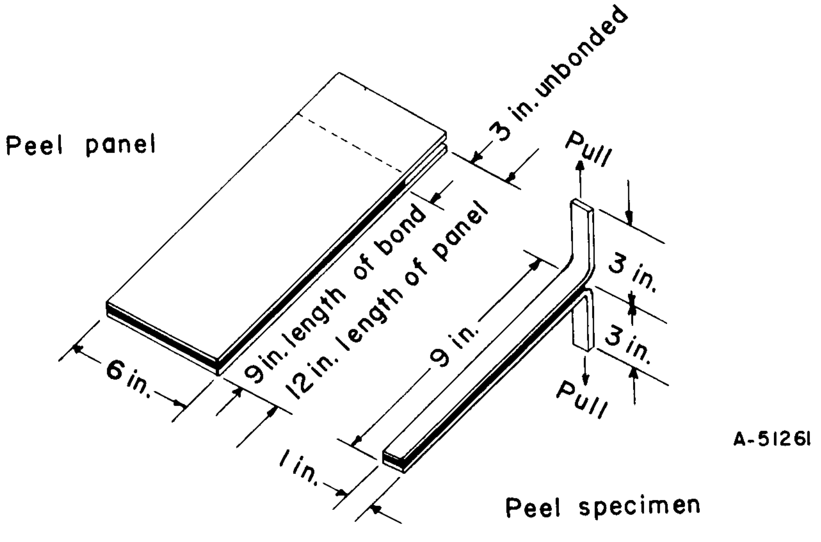


FIGURE 16. CONFIGURATION OF PANEL AND INDIVIDUAL TEE-PEEL-TEST SPECIMEN

From Reference 53.

the adhesive under test and then pulled in tension normal to the bond plane. This test is covered by Federal Test Method No. 175, and sketches of the adherend block and the testing arrangement appear in Figure 17. This test has been adapted for testing adherence of honeycomb-panel cover sheets to core. Circular portions of the cover sheets opposite each other are first isolated by a circular cutter. They are then bonded to blocks, and the entire assembly is pulled in tension. Results will be influenced by the details of core configuration, so this is a specialized test.

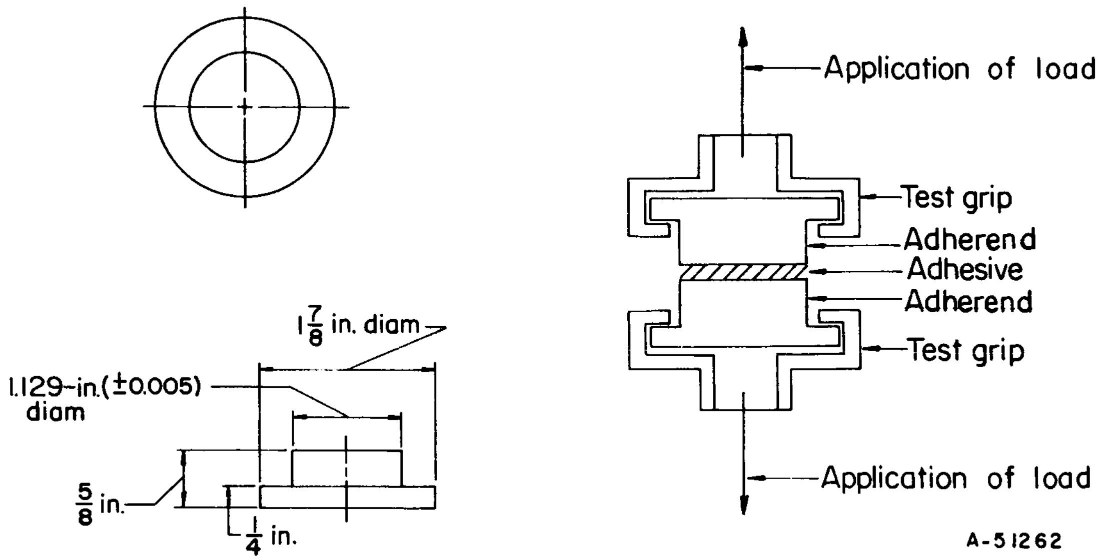


FIGURE 17. ADHEREND BLOCK AND TESTING ARRANGEMENT FOR PI-TENSION TEST

From Federal Test Method No. 175, Method 1011.1.

Other mechanical tests applied to honeycomb include the climbing drum-peel test (covered by Federal Test Method No. 175) and various forms of tests in which honeycomb panels are loaded as three- and four-point beams in flatwise compression and in edgewise compression, tension, or shear. Discussion of these tests is beyond the scope of this report. Some information concerning them will be found in References 13 and 33.

Adhesive Specifications. Guttman (Ref. 3), Katz (Ref. 7), and Licari (Ref. 54) have summarized or reproduced in their

TABLE III. ADHESIVE SPECIFICATIONS

No.	Title	Comment
	Government Specifications	
Federal Test Method, Std. No. 175	Adhesives: Method of Testing	Sampling, inspection, and testing
	Military Specifications	
MIL-A-5090	Adhesive, Airframe Structural Metal-to-Metal	See Table IV
MIL-A-25457	Adhesives: Air-Drying, Silicone Rubber	Two component silicone adhesive for bonding silicone to itself and to Al
MIL-A-8623	Adhesives: Epoxy Resin, Metal-to-Metal Structural Bonding	Epoxy adhesives for use up to 200 F. Three classes based on curing temp
MIL-A-25463	Adhesives: Metallic Sandwich Construction	For bonding metal facings to metal cores for exposure to 500 F
MIL-A-9067	Adhesives: Bonding Process and Inspection Requirements	Processing policies and surface-preparation recommendations
	American Society for Testing Materials	
D1763 (Ref. 9)	Epoxy Resin Specification	Base epoxy resins for formulating. Two grades are specified: Grade 1 - Liquid resin with solvent; Grade 2 - Liquid resin without solvent
D1780 (Ref. 6)	Creep Tests of Metal-to-Metal Adhesives	
D950 (Ref. 6)	Impact-Strength Test	
D903 (Ref. 6)	Peel or Stripping Strength	
D1344 (Ref. 6)	Tensile-Properties Test	
D1002 (Refs. 6, 11)	Shear Properties, and Tension Loading Metal-to-Metal Tests	

entirety the numerous Government, military, and industry-wide specifications relating to adhesive bonding. Table III lists the pertinent numbers, titles, and ranges of application of the specifications dealing with metal-to-metal adhesive bonding. The MIL-A-5090 specification covers structural adhesive bonds intended for elevated-temperature service. It sets up classifications of adhesives based upon tensile-shear strengths measured at temperature. Table IV shows the minimum average strength requirements for qualification by type and class for adhesives under MIL-A-5090.

TABLE IV. MIL-A-5090 TENSILE-SHEAR REQUIREMENTS

Test Conditions	Minimum Average Strength Requirements, psi				
	Type I				
	Class 1	Class 2	Type II	Type III	Type IV
75 F	4500	2500	2250	2250	2250
10 min at 180 F	2500	1250	--	--	--
102 min at 300 F	--	--	2000	2000	2000
192 hr at 300 F	--	--	2000	2000	2000
10 min at 500 F	--	--	--	1850	1850
192 hr at 500 F	--	--	--	--	1000

Physical Forms of Adhesives. Metal-bonding adhesives are most commonly used as liquids, films, or tapes. Thin liquids are applied by spraying, flow coating, or brushing. Thicker liquids can be trowelled or printed. Some of the thicker liquids are thixotropic*, which is an aid in maintaining proper positioning of adherends following adhesive application, but prior to curing.

Adhesive films and tapes, either supported on a carrier or unsupported, are attractive for production operations because of easy control of bond-line thickness and convenience of handling. The form in which the adhesive is used in a particular application will depend upon the joint area to be bonded, the production volume, the types of equipment on hand, and the available forms of the adhesive to be used.

Working and Storage Requirements. Prior to mixing, two-part epoxy adhesives consisting of resin and curing agent, can be stored at room temperature almost indefinitely. Once mixed,

*Thixotropic materials are viscous if allowed to stand undisturbed, but decrease in viscosity temporarily following stirring or other agitation. On standing, they revert to their former gelled state.

however, they have working times of only minutes or hours, depending upon the ratio of resin to curing agent and the specific curing agent used. The adhesives must be applied during the working time or the cure will have progressed to the point that the resins are too stiff to apply. Two-part epoxies have the advantage that they cure at room temperature, thus requiring no curing ovens, autoclaves, or heated presses. Their properties are inferior to those of heat-cured epoxies, however, unless they are given an elevated-temperature postcure.

One-part epoxies and phenolics must be cured at elevated temperatures. They are compounded mixtures of resin and curing agent and have a limited shelf life. Usual shelf lives of present commercially available one-part epoxies and phenolic adhesives are from 6 months to a year at room temperature. Shelf life can be extended if the adhesives can be stored in a freezer or refrigerator. Some recently developed tape adhesives have very limited room-temperature working life and are shipped from the manufacturer to the user under dry-ice refrigeration.

Cans of adhesives and curing agents, once opened, should be used as quickly as possible or tightly reclosed and returned to storage in a cool place. Curing agents should be ordered with, and used with, specific batches of adhesive. Use of adhesives from storage should be on a first in-first out basis, and outdated adhesives should be discarded or should not be used without at least first making bond-strength measurements to insure that they have not deteriorated. Users of large quantities of adhesives make simple quality assurance tests on their adhesives (such as tensile shear and tee peel, for example) at frequent intervals to eliminate the possibility of off-specification adhesives being used in their manufacturing operations (Ref. 52).

<u>Service Conditions</u>. No single adhesive is available that is superior for all service conditions. A user, therefore, makes a selection among possible adhesives on the basis of known or anticipated service conditions for the application.

High Temperature. Much of the current interest in titanium alloys results from their usefulness at moderately elevated temperatures (below 1000 F) encountered in such service applications as jet engines and high-speed airframes. Titanium alloys are now used in continuous service at temperatures up to 400 F, and alloys

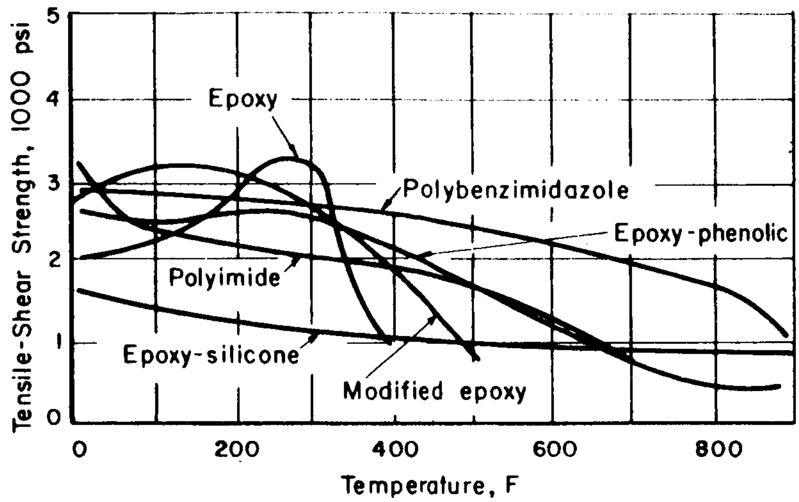


FIGURE 18. TEMPERATURE DEPENDENCE OF SHORT-TIME TENSILE-SHEAR STRENGTHS OF VARIOUS CLASSES OF ADHESIVES

After Kausen (Ref. 56).

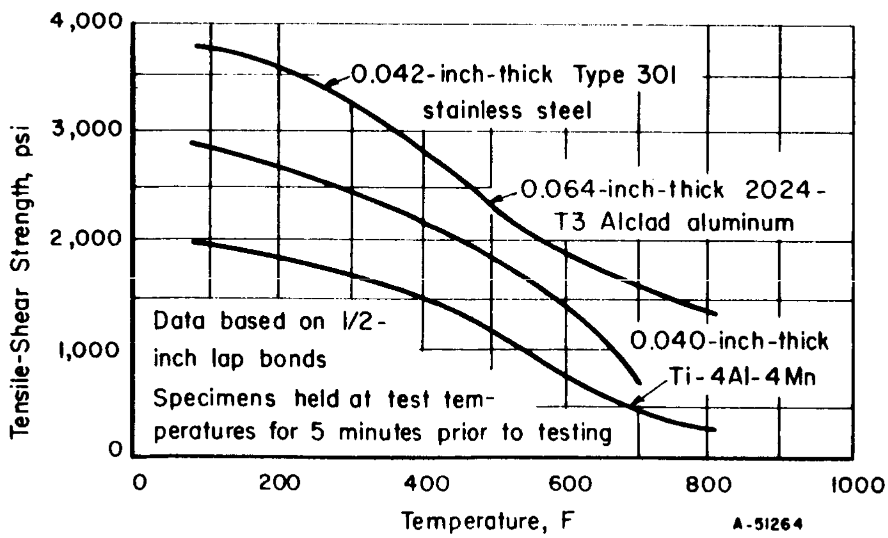


FIGURE 19. TENSILE-SHEAR STRENGTH VERSUS TEMPERATURE FOR AN EPOXY-PHENOLIC ADHESIVE

After Horton and Cowan (Ref. 58).

are available that can be used in long-life structures (1000 to 10,000 hours) between 400 and 1000 F.

Strengths of adhesives, like strengths of metals, decrease with increasing temperature (Figure 18). It is difficult to state precise upper limits for service temperatures of the various types of adhesives. The limiting temperature depends on the anticipated service life, the magnitude and kind of stresses imposed, and the presence or absence of deleterious environmental factors such as oxygen and radiation. Phenolic and epoxy adhesives appear to be limited to temperatures in the vicinity of 350 F for continuous service with titanium, although they can withstand short times at temperatures up to 500 F.

Several helpful review articles have recently appeared dealing with high-temperature adhesives (Refs. 55-57). Although these articles do not refer specifically to titanium, all available titanium alloys can be bonded with the adhesives discussed, so far as is known.

It is generally observed, however, that the same adhesive will give different tensile-shear-strength values when used to bond different adherends. It is therefore dangerous to assume without making tests that a strength value reported for stainless steel bonds will be achieved with titanium bonds. Figure 19 shows a good example (Ref. 56). Note that the strength levels shown are not in order of decreasing elastic modulus. Additional variables influence the bond strength, among them surface treatments and degradation reactions.

At elevated temperatures, strengths of adhesive bonds generally decrease with time (Figure 20). Over some ranges of temperature, and depending on curing conditions, bond strength may increase with time for awhile (Ref. 56) (Figure 21). The general trend, however, is towards progressive loss of strength with time, the loss occurring at increasing rate with increasing temperature.

Figure 22 shows the losses in bond strength encountered with three nitrile-phenolic adhesives when used to bond adherends of Ti-5Al-1.25Fe-2.75Cr alloy (Ref. 37). There was about a 50 per cent loss of strength following 100 hours' exposure at 500 F. The same investigators reported very rapid loss of strength of these and other adhesives when exposed at 600 F.

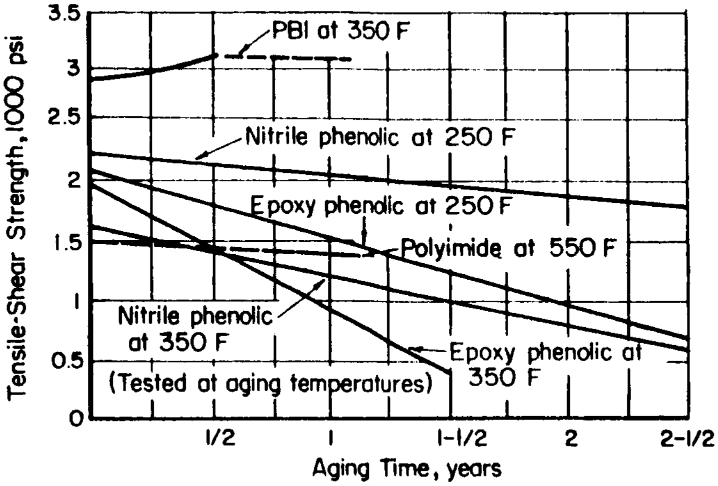


FIGURE 20. EFFECT OF TIME AT TEMPERATURE ON TENSILE-SHEAR STRENGTHS OF JOINTS BONDED WITH VARIOUS ADHESIVES

After Kausen (Ref. 56).

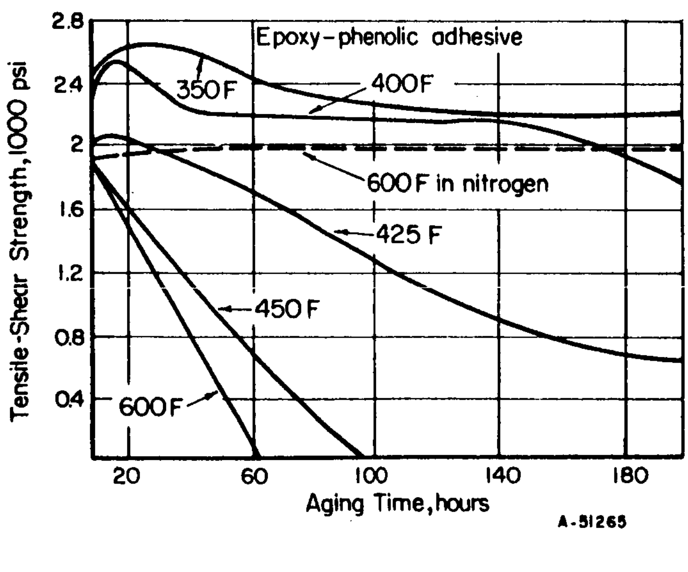


FIGURE 21. EFFECT OF TIME, TEMPERATURE, AND EXPOSURE IN AIR OR IN NITROGEN ON TENSILE-SHEAR STRENGTH OF JOINTS BONDED WITH AN EPOXY-PHENOLIC ADHESIVE

After Kausen (Ref. 56).

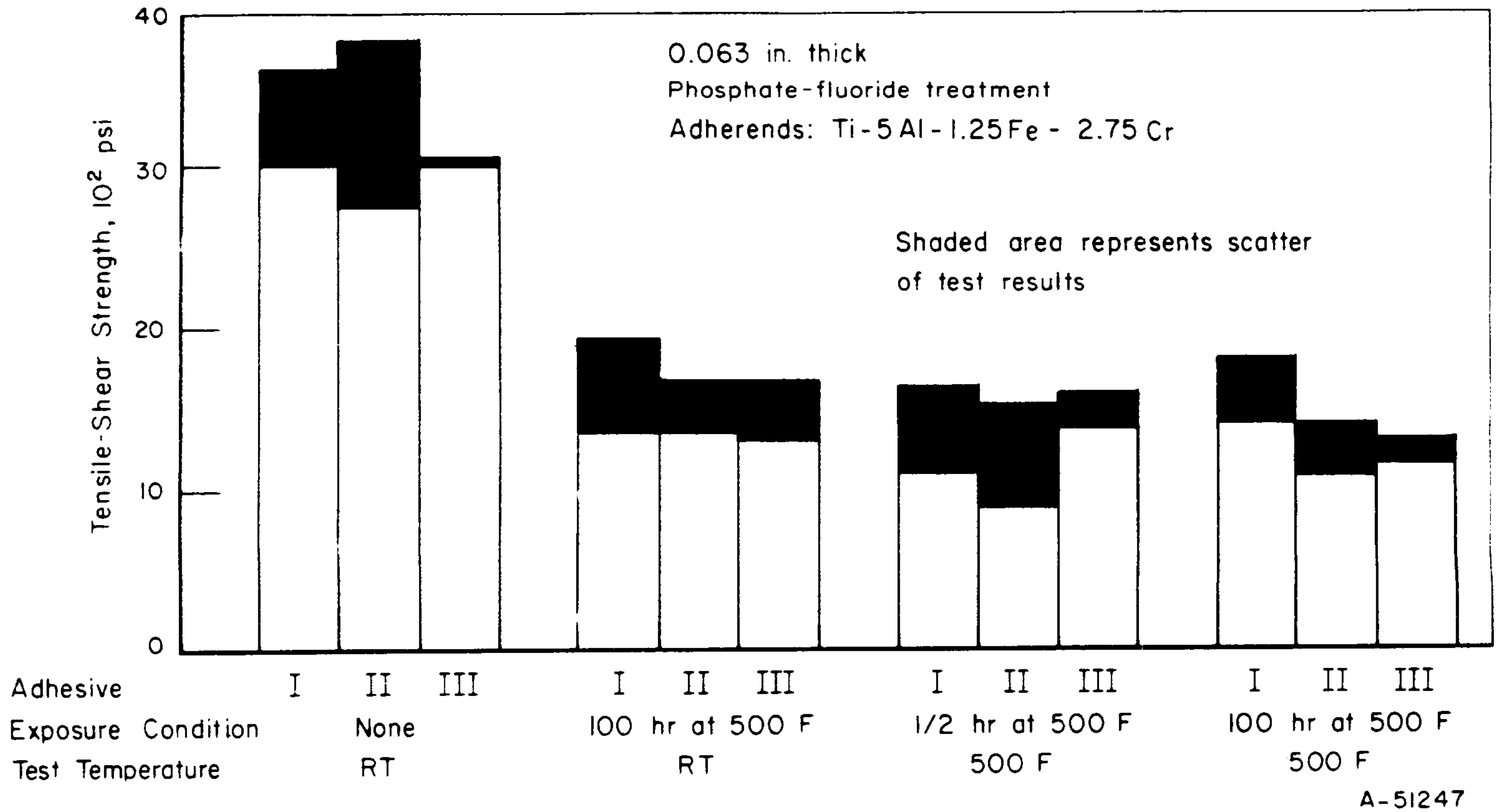


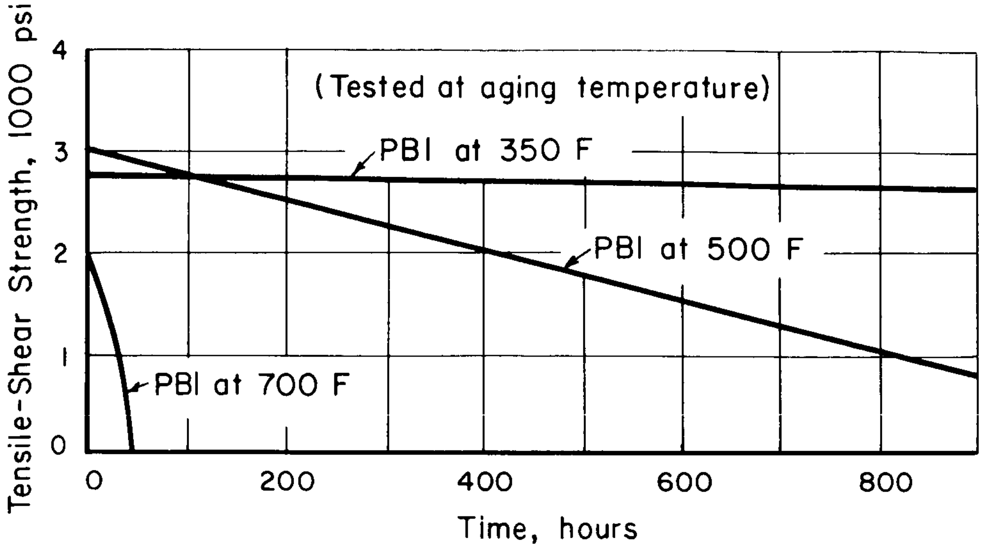
FIGURE 22. EFFECTS OF TEMPERATURE AND TIME OF EXPOSURE IN AIR ON TENSILE-SHEAR STRENGTHS OF ADHESIVE JOINTS USING TITANIUM ADHERENDS AND THREE NITRILE-PHENOLIC ADHESIVES

After Johnson, Sunafrank, Kaarlela, Kastrop, and Slifer (Ref. 37).

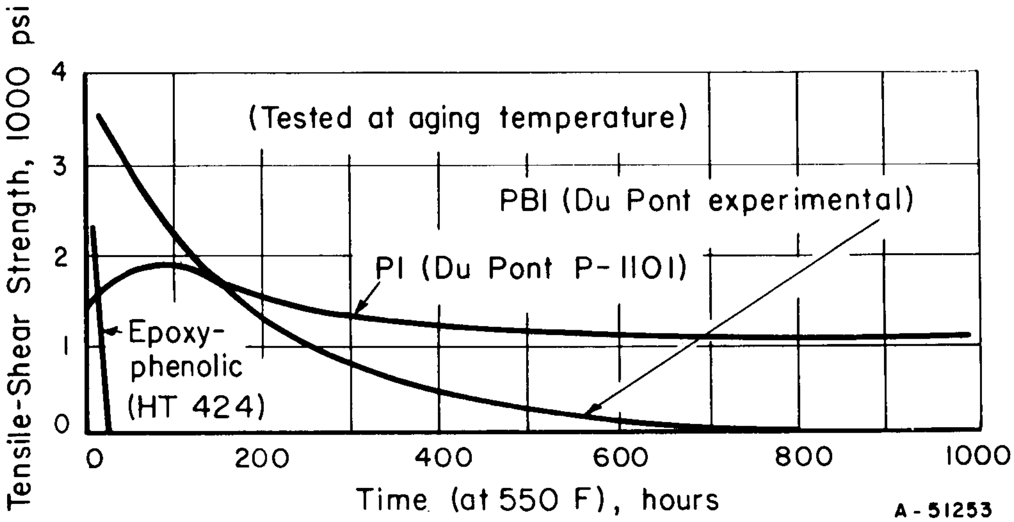
Among the mechanisms by which organic adhesives degrade at high temperatures, oxidation by atmospheric oxygen has been identified as being among the most important. Figure 21 shows the behavior of one adhesive at 600 F in air and in nitrogen, for example. Investigators at the Boeing Company (Ref. 59) have discovered that, in the case of titanium alloys, dissolved oxygen in the titanium is, in effect, pumped to the adhesive bond by the activity gradient resulting from the affinity of the adhesive for oxygen. Oxygen is highly soluble in titanium, the rate of oxygen transport at elevated temperatures is high, and adhesive degradation is accelerated. In Boeing's initial experiments, adhesive systems that had useful lives of from 7000 to 8000 hours at 400 F when used to bond aluminum lasted only 500 hours with titanium. Appearance of the adhesives following 400 F testing was black, and failure was adhesive, indicating contamination from the adherend. Boeing has developed a proprietary surface-preparation process for titanium based upon the principle of creating an oxygen-diffusion barrier at the adherend-adhesive interface. With its use, the useful life of the adhesive bond has been extended to 3000 hours. Titanium alloys being used in Boeing's studies are Ti-6Al-4V and Ti-8Al-1Mo-1V.

New metal-bonding adhesives now on the market, the polybenzimidazoles (PBI) and polyimides (PI), offer promise for service for long times above 350 F and for short times above 500 F in air. It is understood that adhesives of these types are under consideration for adhesive bonding of titanium in the supersonic transport. Figure 18 shows the short-time tensile-shear strength of different classes of adhesives, including PBI and PI types. High-temperature strengths of the present polyimides are not as high as those of the polybenzimidazoles, but their oxidation resistance is better (Figure 23). It is likely that both types of adhesive will be further developed and will find use for high-temperature applications.

Limited data on strengths of adhesive joints of titanium have been reported in the Soviet literature. Chernin and Goroshkova (Ref. 60) report average values of tensile-shear strength ranging from 350 to 1450 psi at temperatures between -76 and +140 F using L-4 epoxy-polyamide adhesive. Ivanova and Sobolevskii (Ref. 61) report room temperature and 662 F tensile-shear strengths of 1080 and 285 psi, respectively, with VC-10-I modified phenolic adhesive. Kardashov (Ref. 6) cites tensile-shear strengths of 600 and 500 psi at room temperature and 798 F using VK-2 organosilicon adhesives. Ivanova and Davidov (Ref. 29) claim higher strengths than Kardashov for VK-2 adhesive at room temperature and 798 F, viz., 950 and



a. Polybenimidazole-Based Adhesive



b. Polyimide-Based Adhesive Compared With a Polybenzimidazole

FIGURE 23. EFFECTS OF TIME AT TEMPERATURE ON TENSILE SHEAR STRENGTHS OF POLYBENZAMIDAZOLE- AND POLYIMIDE-BASED ADHESIVES

After Kausen (Ref. 56).

670 psi. The last investigators also bonded titanium using VK-6 modified organosilicon adhesive and report tensile-shear strengths of 1320 psi at room temperature and 570 psi at 798 F. Kardashov, et al., (Ref. 62) report room-temperature tensile-shear strengths between 2850 and 3270 psi and 392 F strengths between 995 and 1565 psi with titanium adherends using a nitrile-phenolic adhesive blend.

Cryogenic Temperatures. With the development of liquid-fueled rockets utilizing cryogenic propellants and the need to meet service conditions in space, programs have been undertaken to develop adhesive systems capable of retaining strength at extremely low temperatures such as -325 and -423 F, the boiling points of liquid nitrogen and hydrogen, respectively. Several adhesive development evaluation studies have been made at -423 F (Refs. 48,57, 63-66).

The requirements for cryogenic adhesives reflected in retention of strength include: thermal expansion coefficient approximately that of the adherend, resiliency as demonstrated by good peel strength at cryogenic temperatures, low curing shrinkage, high thermal conductivity, and an elastic modulus no greater than that of the adherend. Other desirable characteristics, some of which are of interest only in specific applications, include low specific gravity, long shelf life, short cure time, room-temperature curing without pressure, sufficient flow to fill voids, good impact and vibration resistance, and freedom from reaction with liquid oxygen when mechanically shocked (LOX compatibility).

Kausen's survey (Ref. 56) includes adhesives for cryogenic temperature service. Figures 24 and 25, taken from his paper, summarize the tensile-shear strengths of different adhesive types and some specific modified phenolic systems. From Figure 24 it will be noted that polyurethane and epoxy-nylon adhesives have superior strengths up to around room temperature. As with high-temperature adhesives, however, these data should be applied to specific adherends with caution.

Figure 25 shows more detailed data for specific adhesives of the modified phenolic class. It is interesting to note that the two rubber-phenolic blends had the highest and lowest shear strengths in the group, which emphasizes the fact that adhesives, even of the same type, differ widely in their properties. The data appearing in Figures 24 and 25 were taken using adherends other than titanium and are, therefore, useful only as a rough guide for titanium bonding.

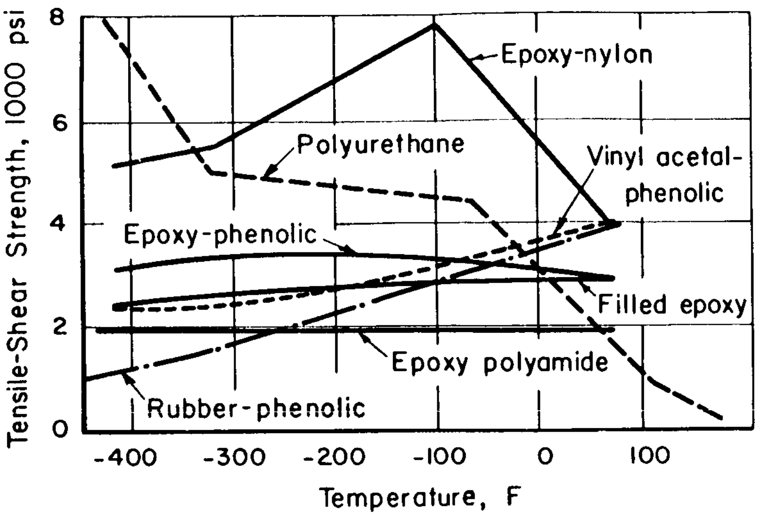


FIGURE 24. TENSILE-SHEAR STRENGTHS OF ADHESIVE SYSTEMS FOR CRYOGENIC SERVICE AS A FUNCTION OF TEMPERATURE

After Kausen (Ref. 56).

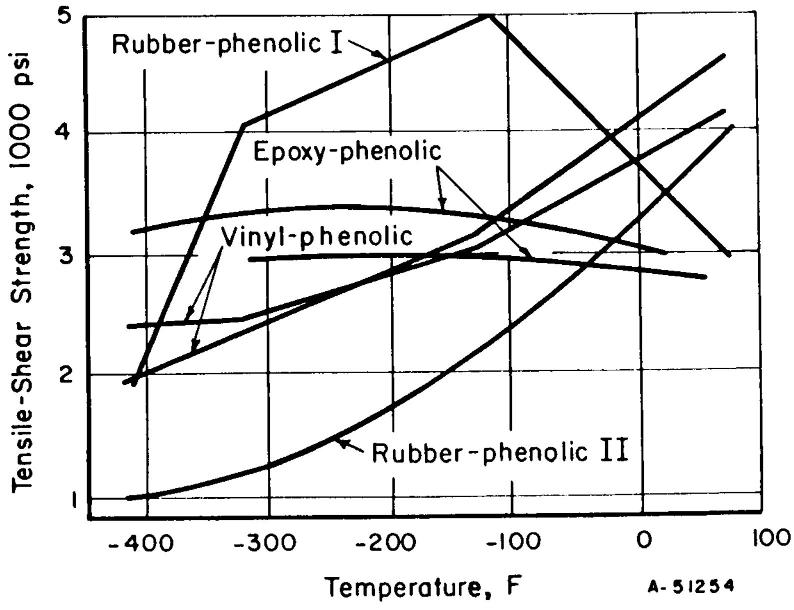


FIGURE 25. TENSILE-SHEAR STRENGTHS OF MODIFIED PHENOLIC ADHESIVES AT CRYOGENIC TEMPERATURES

After Kausen (Ref. 56).

Hertz (Ref. 48) has evaluated several types of adhesives against Ti-8Mn alloy adherends down to -423 F. His tensile-shear data are shown in Figure 26. The surface preparation used is presented in Table I. Epoxy-nylon adhesives had the highest tensile-shear strengths of the adhesives studied.

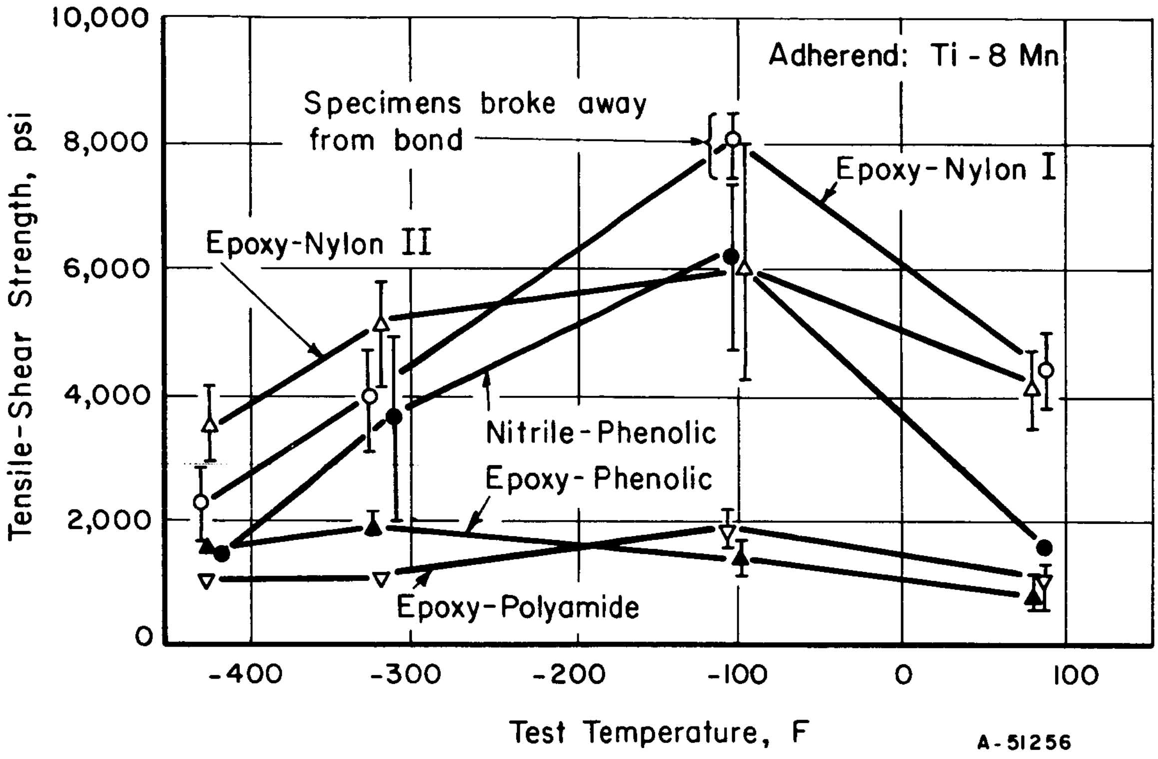


FIGURE 26. TENSILE-SHEAR STRENGTHS OF VARIOUS ADHESIVES USED TO BOND Ti-8Mn ALLOY TESTED AT CRYOGENIC TEMPERATURES

After Hertz (Ref. 48).

Recent British experiments (Ref. 67) have been conducted using two British titanium alloys, 317 and 318A, Ti-5Al-2.5Sn and Ti-6Al-4V, respectively, in which adhesive-bonded tensile-shear specimens were repeatedly cycled between room temperature and various cryogenic temperatures. After ten complete cycles, the specimens were tested at room temperature. The results of temperature cycling on room-temperature tensile-shear strength of titanium bonds (Figure 27) showed little change in maximum strength but a noticeable increase in range. The investigators noted an embrittling effect of the temperature cycling on the adhesives as evidenced by abrupt

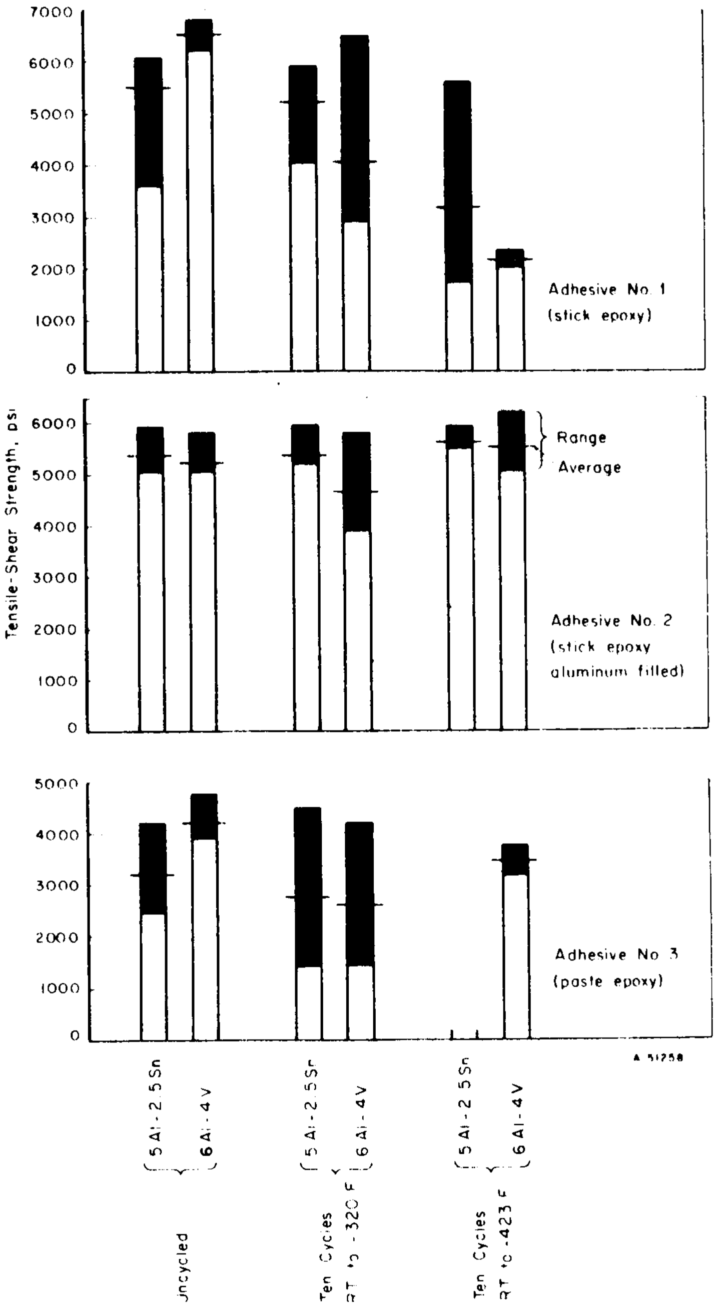


FIGURE 27. EFFECT OF CYCLING TO CRYOGENIC TEMPERATURES ON ROOM-TEMPERATURE TENSILE-SHEAR STRENGTH

Eight specimens per group.

After Arslett and Jeffs (Ref. 67).

failures of cycled specimens during testing. Uncycled specimens pulled apart gradually.

Smith and Susman (Ref. 66) tested three of their developmental cryogenic adhesives using aluminum adherends after 20 cycles between room temperature and -320 F. They, too, found no significant deterioration of tensile-shear strength following cycling. These investigators made a limited number of tensile-shear tests of their adhesives at room temperature and -320 F using Ti-8Mn alloy adherends (Table V).

TABLE V. TENSILE-SHEAR STRENGTHS OF EXPERIMENTAL ADHESIVES FOR CRYOGENIC SERVICE WITH Ti-8Mn ADHERENCES (REF. 66)

	Tensile-Shear Strength, psi[a] Room Temperature	Tensile-Shear Strength, psi[a] -320 F
Adhesive A		
Epoxy-polyamine + nylon	2450	1330
Adhesive B		
Two cementable 1-mil FEP films in epoxy-polyamine matrix	1580	990
Adhesive C		
Adiprene L-100 urethane elastomer cured with Moca	440	4000

Adherend Surface Preparation:

Concentrated HNO_3	30 parts by weight
Concentrated HF	5 parts by weight
Water	100 parts by weight

(a) Average of four specimens.

Radiation. Kircher and Bowman (Ref. 68) have recently summarized the known information on the effects of radiation on materials. Their book, though it does not deal specifically with adhesives, provides a timely and comprehensive view of the field of radiation damage. Several earlier reviews have been published that consider radiation effects on adhesives (Ref. 69-71). Two types of high-radiation environments are visualized as being of principal interest for possible applications of adhesive-bonded structures. These are the radiation fields in space and those in the vicinity of nuclear reactors. Radiation fields in space, so far as is known, consist principally of electrons, protons, and gamma radiation.

Fields in and around reactors consist principally of neutrons, alpha particles, and gamma radiation.

Most organic materials, probably because of the low atomic numbers of their constituent atoms, are affected much the same by the different varieties of radiation. The damage mechanism consists of the transfer of large amounts of energy to electrons within the material by their interaction with the incident radiation, of whatever form. Organic materials, as a class, are sensitive to radiation dosage, and the differences in damage due to differences in type or intensity of radiation are secondary. Aromatic and heterocyclic (ring containing) molecules are generally more radiation resistant than straight-chain polymers. Although there are constructive chemical reactions in some cases due to radiation bombardment, the common form of damage consists of bond rupture due to the high-energy electrons, with consequent loss in molecular weight and decreased mechanical strength and ductility. Organic materials as a class are more radiation sensitive than metals and ceramics. Radiation damage to an adhesive shows up first as a loss of peel strength.

No experimental studies of the effects of radiation on adhesive bonds were found in which titanium adherends had been used. Radiation effects should be relatively independent of adherend, however, except in those cases where the adherend itself becomes radioactive. The adherends, in fact, offer to the adhesive a degree of protection against soft radiation.

Figure 28, taken from Arlook and Harvey (Ref. 70), shows typical behavior of the tensile-shear strength of several adhesives bonded to aluminum adherends with increasing amounts of gamma radiation. Under room-temperature tensile-testing conditions, most of the adhesives showed continued loss of strength with increasing amounts of radiation. One adhesive showed a strength maximum and another showed increasing strength over the entire range of dosage studied. For specimens tested at elevated temperatures following irradiation, the order of ranking of the adhesive strengths are somewhat different.

McCurdy and Rambosek (Ref. 71), using aluminum and stainless steel adherends bonded with a nitrile-phenolic adhesive, report that thick glue lines are less susceptible than thin glue lines to damage from gamma radiation as measured by tee-peel strength (Table VI). The same investigators report the results of tests made on honeycomb panels made using composite film adhesives. In these

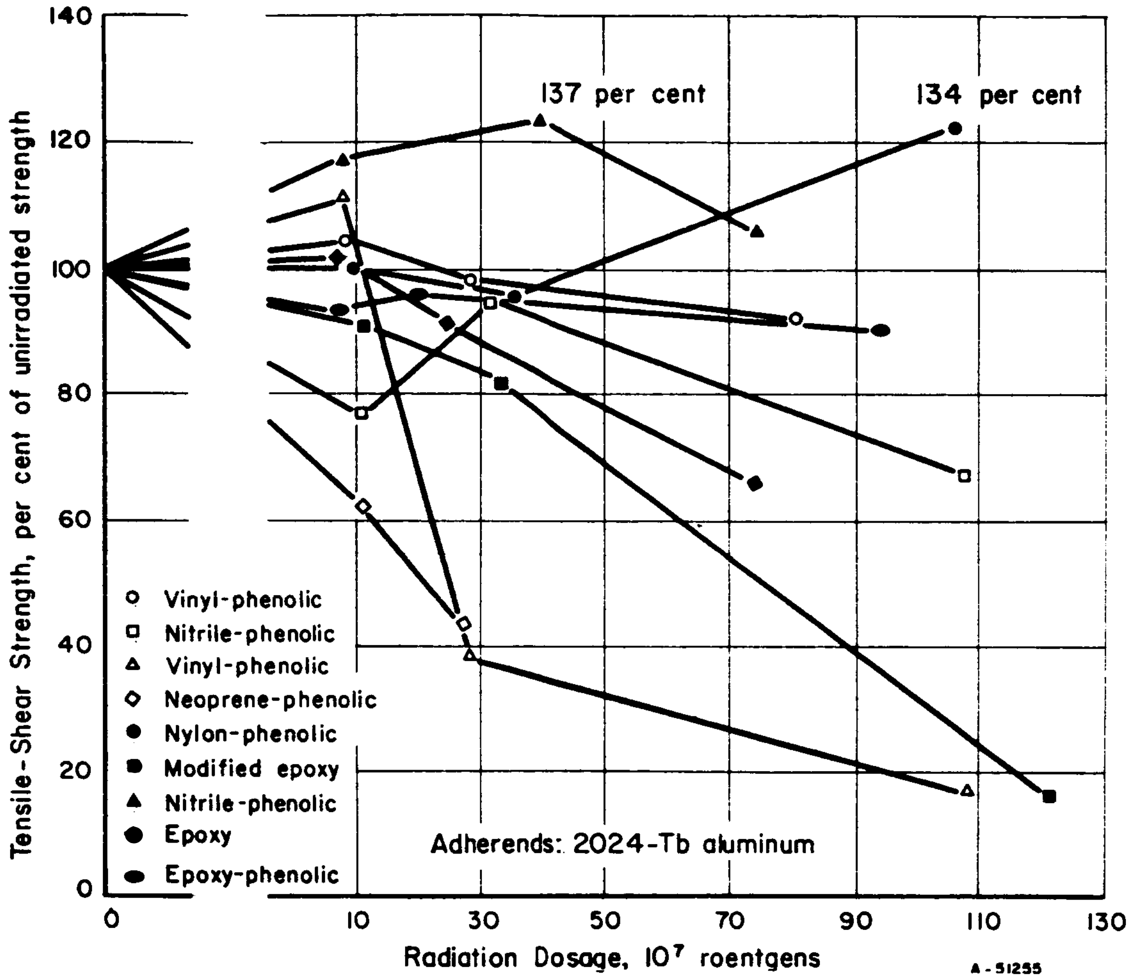


FIGURE 28. TENSILE-SHEAR STRENGTH VERSUS RADIATION DOSAGE; SPECIMENS TESTED AT ROOM TEMPERATURE

After Arlook and Harvey (Ref. 70).

composite adhesives, which are fairly widely used for honeycomb fabrication, a glass-cloth carrier is coated on the face sheet side with a flexible adhesive for peel strength and is coated on the core side with a more rigid adhesive that has better filleting characteristics. Loss of peel strength following irradiation was found to be severe, adhesion failure occurring on the core side.

TABLE VI. EFFECT OF GLUE-LINE THICKNESS ON TEE-PEEL STRENGTH OF A NITRILE-PHENOLIC ADHESIVE WITH RADIATION EXPOSURES

After McCurdy and Rambosek (Ref. 71)

Glue-Line Thickness, mils	Tee-Peel Strength at Indicated Dosage, in-lb/in.				
Radiation Dosage, megarads:	None	100	300	600	900
1.2	10	7	5	3.5	2.5
3.7	14	9	7	4	2.5
10.0	30	20	9	3.7	3.5
16.1	19	14	6	4.5	3.5

The amounts of radiation required to cause serious deterioration of adhesive bonds appear to be such that adhesive bonding can be considered for use in space for missions lasting at least of the order of months. The new heterocyclic adhesives, such as the polybenzimidazoles, should be less radiation sensitive than types heretofore available. Adhesives are not presently available that can withstand the intense radiation found in the immediate vicinity of nuclear reactors, however.

APPLYING THE ADHESIVE

The manner in which adhesives are applied to adherend surfaces will depend upon the form of the adhesive and the production rates desired. Thick liquid adhesives can be applied by roller coating, brushing, trowelling, or dip coating. Thinner liquids can be brushed on, flow coated, or sprayed. Tapes and films can be conveniently hand applied if the adherend is first laid out on a heated table. Alternatively, the table may not be heated and a tacking iron is then used in spots to cause sufficient adhesion of the film to the adherend to hold the adhesive in place. Adhesives in powder or stick forms do not appear to be widely used in this country for metal-to-metal adhesive bonding.

TOOLING AND FIXTURING - JOINT ASSEMBLY

When bonding with adhesives that release water, solvents, or other volatile substances during curing, it is often necessary to clamp the adherends in proper relation to each other with pressures up to several hundred psi. With "100 per cent solids" adhesives, such as the epoxies, such curing pressures are not necessary except that, in critical work, clamping will be used for control of glue-line thickness and alignment. In some cases, parts can be made self-aligning and self-clamping by appropriate design. Methods of applying pressure during curing will depend upon the size and shape of the part, the magnitude of the pressure to be applied, and the quantity to be produced. There are several basic methods in use. The simplest method is to make the adherends self-clamping. Another method is to combine adhesive bonding with another fastening method such as riveting. Dead-weight loading can also be used for parts having simple shapes. For parts having more complex shapes, the vacuum-bag technique can be used as shown in Figure 29a. The vacuum-bag method is limited to pressures below 14 psi, however. Where higher pressures are necessary, the method shown in Figure 29b can be used. With the pressure-shell method, shown used with a heated mold, pressure is limited only by the mechanical design of the confining parts. It could be used equally well with oven curing as shown in Figure 29a and, in the same way, the vacuum-bag method could be used with a heated mold. The autoclave method, as shown in Figure 29c, is more elaborate. The part must be sealed into a flexible blanket assembly vented to atmosphere so that a differential pressure is applied. A hot inert-gas atmosphere under forced circulation is used in the autoclave. Use of a sheet-metal mold is shown with the autoclave. This type of mold can be used if it is not essential to maintain the maximum degree of smoothness on one side of the bonded assembly. For such applications as aircraft skins, however, in which the exterior surface must meet stringent aerodynamic requirements, a rigid mold must be used for the exterior, all tolerance mismatches being taken up on the back side, or interior side, of the panel. For those situations where both surfaces of a bonded assembly must meet smoothness and shape requirements, tolerances of parts to be bonded must be held very closely, and heated presses such as the one shown in Figure 29d must be used.

CURING

Usually, but not always, the adhesive manufacturer's recommended curing conditions will result in bonds of optimum quality in a

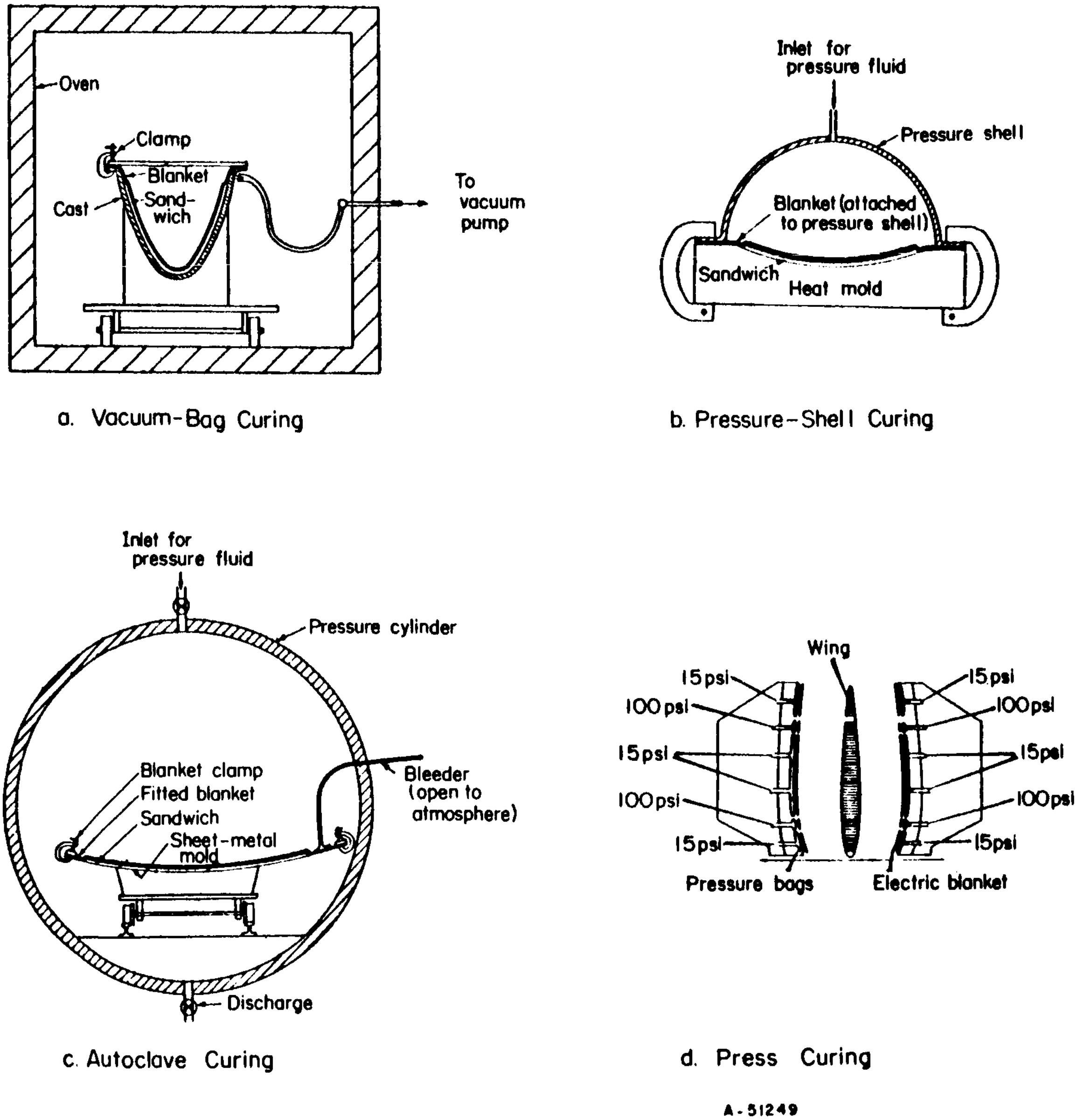


FIGURE 29. METHODS FOR CURING ADHESIVE-BONDED ASSEMBLIES

After Reference 33.

given application. Where maximum properties are important, such as for aircraft skin panels, development work by the airframe manufacturer has resulted in complex curing cycles in which heating rates are controlled, and temperatures and pressures are varied during the cure in a precise manner.

Adhesive systems of the film and liquid types are available that cure at room temperature. Precautions to be observed with this type of adhesive are to be certain that the working life has not been exceeded before use and to keep the volume of adhesive small. Considerable heat is often generated during curing.

Room-temperature-curing adhesives do not usually have strength properties as good as adhesives cured at elevated temperatures. Their strengths can be improved by a postcure heat treatment.

Novel Curing Techniques. Curing can sometimes be accomplished in ways that take advantages of heating done for other reasons. In some automotive applications, the adhesive is cured by the heat applied to dry the body enamel, for example.

Radio-frequency dielectric heating can be used to cure adhesive bonds in which the adherends are insulators, such as wood or plastics. Smith and Susman (Ref. 72) have reported results of the application of direct and alternating electrical potential across a metal-to-metal bond. The direct voltage is to be avoided, since it results in electrolysis of the adhesive, but slight increase over room-temperature-cured strengths resulted from a 700-volt alternating potential (frequency not specified) with an epoxy-polyamide adhesive.

North American Aviation (Ref. 73) has recently developed a film adhesive containing an array of fine high-resistance wires. Current is passed through the wires for a sufficient time to accomplish the cure. Figure 30 shows the end of an aluminum honeycomb wing-flap assembly before bonding by this means. Copper buses to which the wires are attached are visible extending beyond the end of the flap. In Figure 31, electrical connections have been made to the buses. When tested in peel, failure occurred in the rivets used to attach the flap to the testing frame at 750 per cent of design load. The adhesive containing resistance wires is commercailly available.

Another novel approach to adhesive curing consists of using an exothermic adhesive reaction mixture (Ref. 74). The mixture is

FIGURE 30. END OF FLAP FABRICATED USING ELECTRICALLY CURING ADHESIVE, SHOWING COPPER BUSES ATTACHED TO HEATING WIRES

After Tipton, Corson, Steen, Newsome, and Hutchinson (Ref. 73).

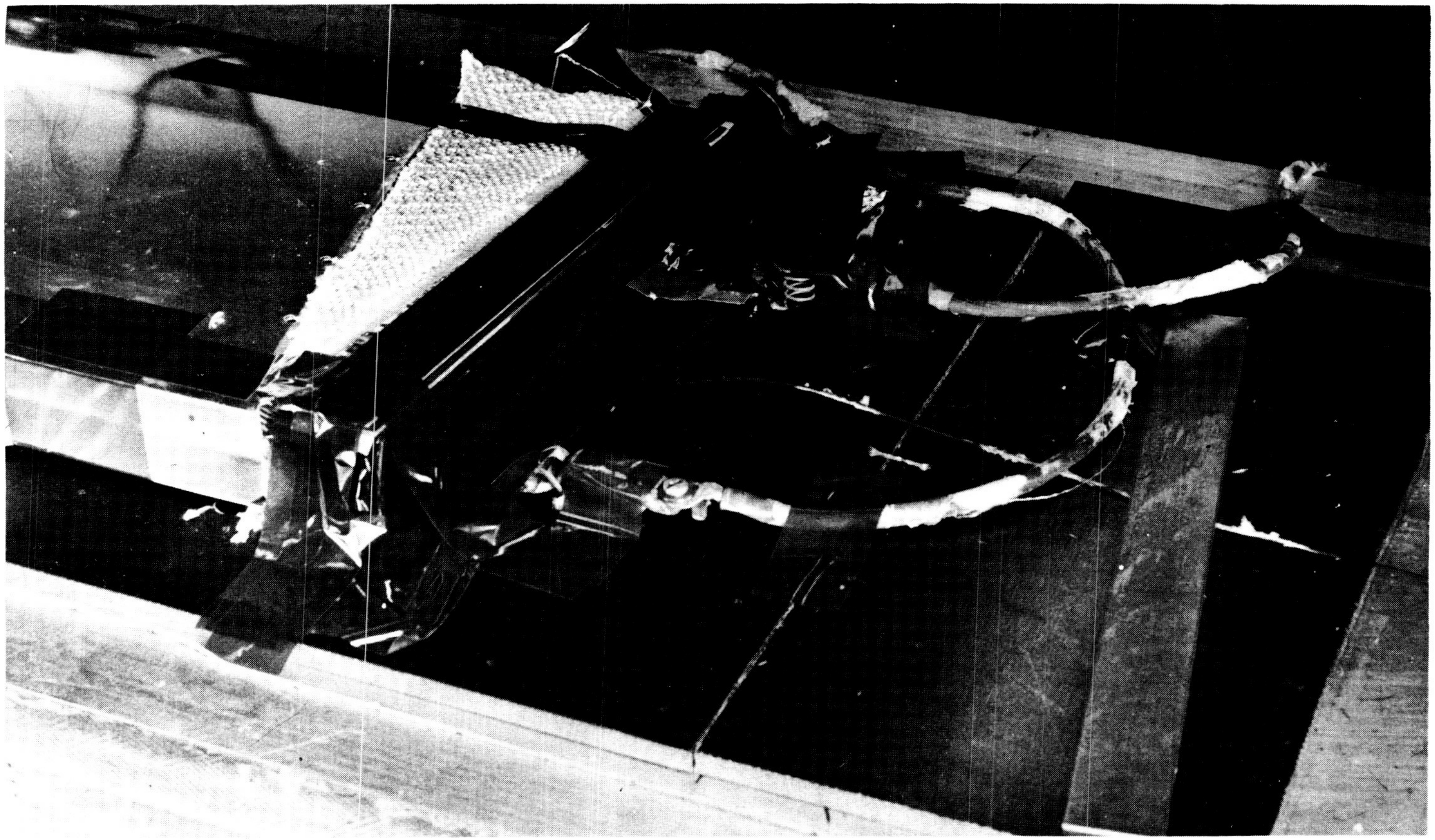


FIGURE 31. END OF FLAP WITH LEADS ATTACHED TO BUSES READY FOR CURING

After Tipton, Corson, Steen, Newsome, and Hutchinson (Ref. 73).

placed between the surfaces to be bonded, which are then clamped in contact. The parts are then heated to the ignition temperature of the exoreactant mixture, whereupon the reaction takes place, and a cured adhesive bond results. It is apparent that the short time at temperature limits the adhesive composition to one that will cure rapidly.

CLEANING THE CURED JOINT

Very little cleaning of the cured joint is usually necessary, and most often none is performed. Any adhesive extruded from the bond line can be removed by scraping or single-point machining.

TESTING AND INSPECTION

The importance of testing, for adhesive acceptance, process control, and outgoing quality assurance, cannot be overstressed. Lot-to-lot variation in adhesives is sometimes significant for critical applications. Adhesives and primers already in-plant must be checked before and during use to be certain that they have not deteriorated with age or improper storage conditions. The adherend-surface-preparation process must be continually monitored, and the curing process controls must be in calibration. Lastly, the bonded parts must be inspected to assure quality. Successful manufacturers of high-integrity adhesive-bonded structures invariably maintain effective testing programs. Some have gone to great lengths to establish their own tests. The literature on adhesive-bond testing is extensive (Refs. 3,28,53,75-81, for example), and only a few salient features will be mentioned here.

Adhesive Evaluation. Convair (Ref. 52) uses the tensile-shear test for incoming batches of adhesive, a peel test for day-to-day checking of adhesive quality and adherent-cleaning efficiency, a beam-compression test if the adhesive is to be used in honeycomb bonding, and a flow- or gel-time test to measure ability of the adhesive to flow and wet the adherend surface. In the case of low-flow adhesives, measurement of compressibility is substituted for the flow test. Filleting strength of adhesives intended for bonding honeycomb is measured by a pi-tension test, in which a circular skin sample is bonded to a core and the skin is then pulled in tension.

Tooling Evaluation. Before bonding tools and fixtures are placed in production, they must be proven by making destructive tests on parts bonded with them. Process equipment and instrumentation must be periodically checked to insure satisfactory operation. On-the-spot inspection during adhesive bonding is necessary to enable adjustment of processing equipment with a minimum scrap loss of product.

Destructive Testing. It is desirable to hold to a minimum any destructive testing that renders the bonded parts unsuitable for service. One way this objective has been met is through the use of small detachable test coupons. Planning for this type of testing must be done at the time the tooling is designed. The specific tests performed will depend upon the nature of the bonded part and its intended service. Use of test coupons does not entirely eliminate the need for some destructive testing of the parts themselves.

Nondestructive Testing. Although some X-ray examination of adhesive-bonded parts has been done, nondestructive tests based on introduction of sonic waves gives more information and are most widely used. Unlike the case of brazed honeycomb, where X-ray is a major inspection tool, adhesive bonds are transparent to X-rays of the energies necessary to penetrate metal cores and face sheets. The test techniques used are adaptations of ultrasonic test methods developed for metals, and may be carried out with the parts immersed in water or dry with only a fluid-coupled transducer. Several types of sonic test equipment are available, among them the Stub-Water, the Coinda-scope, and the Fokker Bond Tester.

At the very least, sonic-bond testing equipment can detect unbonded regions in adhesive joints. If detection of unbonded regions is the only information desired, however, they can also be located by a skilled inspector using a coin or a special light hammer to tap the part. Ultrasonic testers are capable of giving additional information concerning adhesive-bonded joints. Correlations have been made between tester reading and tensile-shear strength, so that as-bonded strengths can be predicted (Ref. 82). Several aerospace manufacturers have worked out these correlations for their particular bonding systems, and they are presently being used in quality control.

An attempt has been made to carry the use of the sonic tester one step further, viz., to detect in-service bond-strength deterioration (Ref. 83). This attempt was not successful. Tester readings did not give consistent correlation with losses in bond strength following exposure to salt spray, boiling water, high temperature, vacuum, gaseous and liquid fluorine, and FLOX (30 per cent F_2 and 70 per cent O_2).

APPLICATION OF ADHESIVE-BONDED TITANIUM ALLOYS

Increasing amounts of titanium alloys are finding application in places where high strength-to-weight ratios, moderate service-temperature resistance, and good corrosion resistance are required. These applications typically fall in the category of aerospace structures.

BOX BEAMS

Under sponsorship of the Air Force (Ref. 50), North American Aviation fabricated and evaluated box beams of titanium and several other metals. Face sheets of the titanium beams were of Ti-6Al-4V. Stringers were of commercially pure titanium. A drawing of the beam construction is shown in Figure 32. Cleaning procedure was a nitric acid-ammonium bifluoride etch, and the statement was made that this treatment was not considered satisfactory. Riveting was used in conjunction with the adhesive bonding to assure proper positioning and to assist the vacuum bag in providing the required pressure. The titanium beams were rated as being more difficult than aluminum from the standpoint of ease of manufacture but less difficult than either adhesive-bonded or brazed 17-7PH stainless steel. Cost of the titanium beams was greater than for the aluminum or adhesive-bonded 17-7PH, but was less than for brazed 17-7PH. The cost ranking of titanium was due to material cost and the fact that forming the corrugated spacers was more difficult than for aluminum.

HELICALLY WRAPPED SOLID ROCKET-MOTOR CASES

The Ingersoll-Kalamazoo Division of the Borg-Warner Corp. conducted an extensive program for the U. S. Army on adhesively bonded solid rocket-motor cases fabricated from high-strength steel and from titanium alloy strip (Ref. 34). The all-beta titanium alloy, Ti-13V-11Cr-3Al, was used at the 175,000 psi strength level. The nitrile-phenolic adhesive used for bonding steel cases was replaced by a nylon-epoxy. Test cylinders 8 and 20 inches in diameter were fabricated. End closures were developed, and cylinders were both hydrotested and static test fired with satisfactory results. Strength-to-density ratios in excess of 1 million inches were achieved. Three designs of end closures were found to be satisfactory. No failures were observed traceable to inherent notch sensitivity or crack-propagation problems with the titanium alloy. The Ti-13V-11Cr-3Al alloy functioned at an equivalent strength-to-density ratio to that of AM-355 (Condition XH) steel strip.

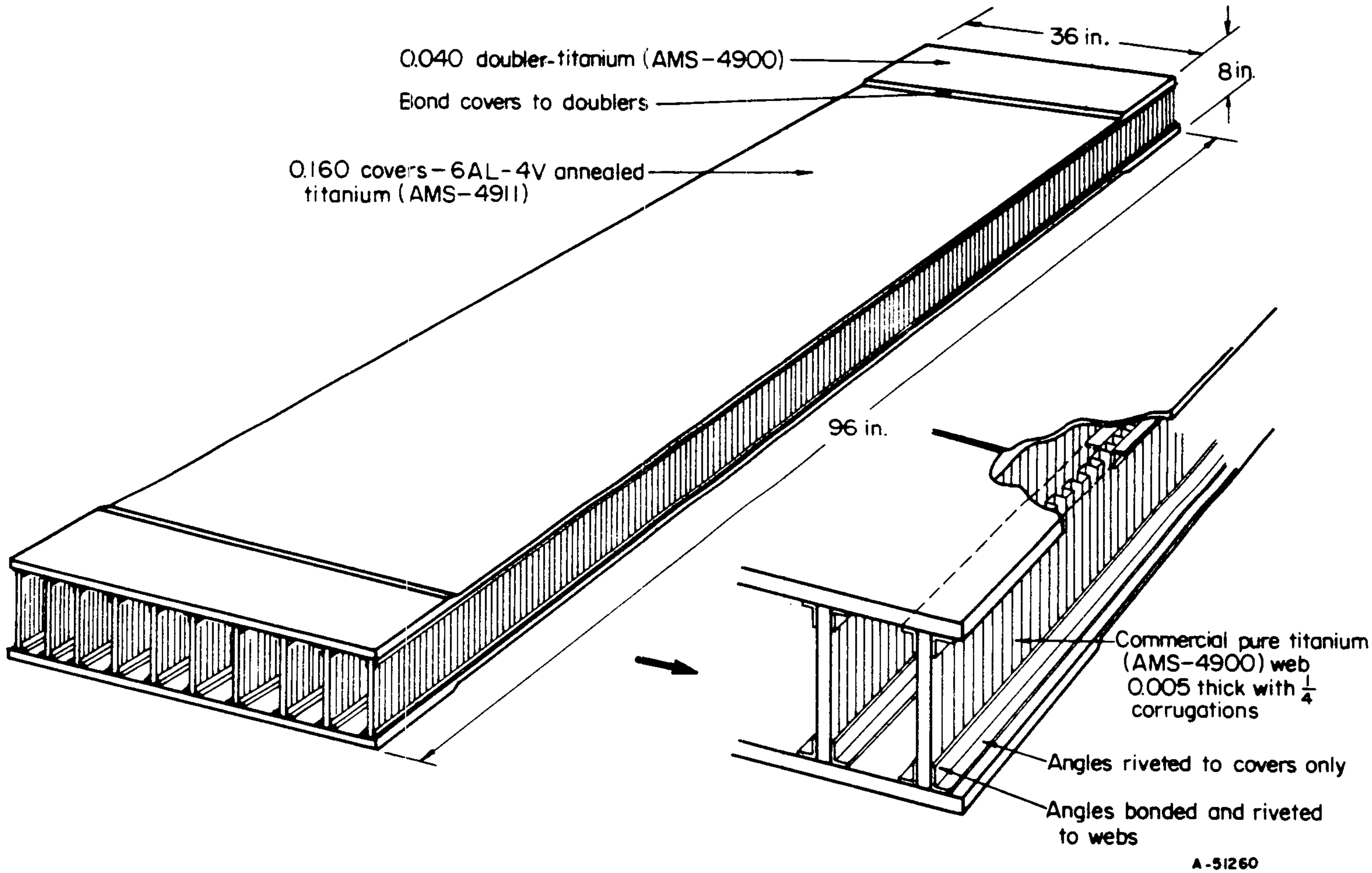


FIGURE 32. ADHESIVE-BONDED TITANIUM BOX BEAM

After Cizek (Ref. 50).

INTEGRAL FUEL TANK

Work at the Air Force Materials Laboratory has recently been reported in which a hydrofluorocarbon adhesive sealant was developed for sealing fuel compartments in wet-wing aircraft construction fabricated from titanium (Ref. 85). Testing performed included adhesion to titanium surfaces, exposure to hydrocarbon fuel and its vapor at temperatures up to 550 F, and elevated-temperature pressurization of joints. Considerable difficulty was initially encountered in obtaining satisfactory adhesion to titanium, and a variety of priming procedures were tried, metal plating of the adherends among them. It was concluded that plating was not a promising surface-preparation method due to difficulties associated with the plating process itself when applied to titanium. Fluorosilicone oil incorporated into the sealant as a plasticizer resulted in much improved adhesion.

HONEYCOMB APPLICATION

A number of applications of adhesively bonded titanium have been in the form of honeycomb panels for primary and secondary structural use. In most of these applications, titanium-alloy face sheets are used, but an aluminum honeycomb core is retained. The aluminum core continues to be used because of economy, lightness, lower interior temperatures than face temperatures, and the fact that the titanium-to-aluminum adhesive bond works well.

Aircraft Skin Panels. The first major effort to develop adhesively bonded titanium sandwich panels was at Convair, Ft. Worth (Ref. 86), and took advantage of experience gained with aluminum and stainless steel panels during the production of the B-58. Two types of panels were fabricated. The first was a 6- by 12-inch panel containing titanium-edge splice slugs, which was intended to be tested in compression (Figure 33). The second type of panel was 21 by 24 inches and contained rows of attachment sockets (Figure 34). The latter panels were intended to be compression tested to determine the effect of internal stiffeners between panel bays. Panels were made successfully, but apparently they were not tested because of termination of the program. Face sheets were of Ti-5Al-1.25Fe-2.75Cr alloy. Core was a 3/16-inch-square cell, 0.003-inch commercially pure titanium foil. Face sheet-to-core bonds were made with a polyvinyl formal-modified epoxy adhesive. Solid titanium parts were bonded with a nitrile-phenolic adhesive.

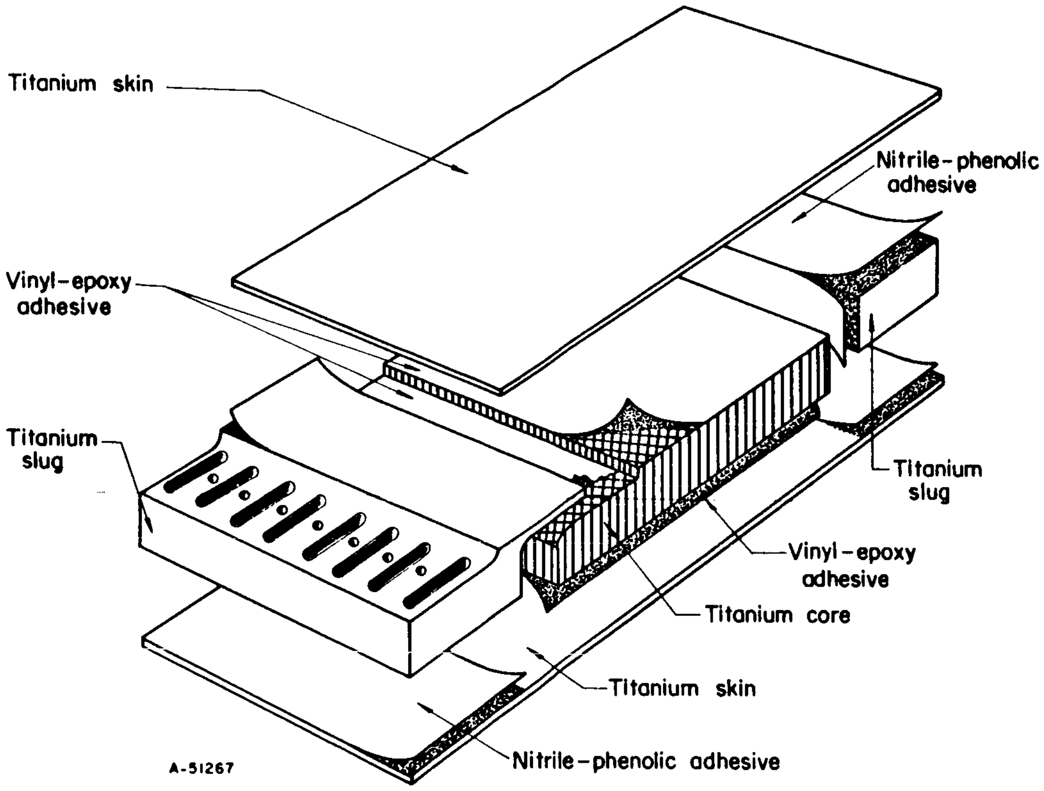


FIGURE 33. CONVAIR ADHESIVE-BONDED TITANIUM PANEL A

After Johnson, Sunafrank, Kaarlela, Kastrop, and Slifer (Ref. 86).

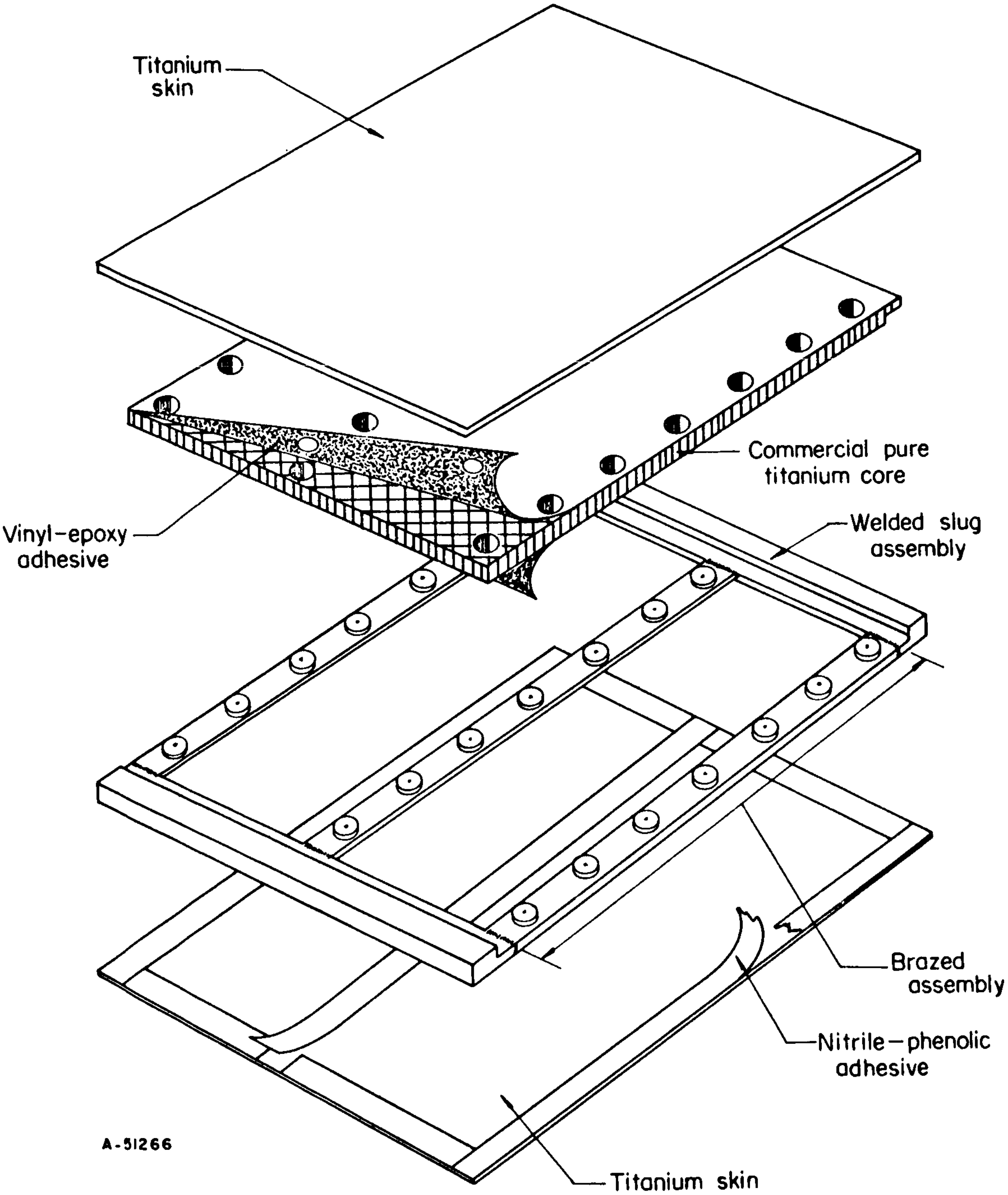


FIGURE 34. CONVAIR ADHESIVE-BONDED TITANIUM PANEL B

After Johnson, Sunafrank, Kaarlela, Kastrop, and Slifer (Ref. 86).

Rear-Wing Fitting. The F-111 interservice fighter has an adhesive-bonded aluminum-cone titanium sandwich panel rear-wing fitting (Ref. 36). A photograph of this panel appears in Figure 35. The purpose of the panel is to provide a load-carrying transition joint of intermediate elastic modulus, between the moduli of aluminum and steel. The panel closures are 0.012-inch-thick titanium Z-member stiffeners. One skin panel, as can be seen, is chemically milled. The adhesive used is a modified epoxy-phenolic.

Titanium Tankage. The Air Force has sponsored a development program with North American Aviation, Inc., that had as its objective the fabrication from titanium of prototype cryogenic tankage for liquid-fueled rocket motors (Ref. 35). A composite honeycomb construction consisting of Ti-6Al-4V face sheets and aluminum honeycomb core was bonded with an epoxy-phenolic film adhesive to form subscale cylindrical tanks. A drawing of the circumferential joint developed for the tanks is shown in Figure 13. At a late stage in the program, it was discovered that the primer used contains a small amount of thermoplastic material and that, if close-out joints were cured at 340 F, the normal curing temperature for the adhesive, there was risk of damaging the existing adhesive bonds in the honeycomb panels. Close-out joints were therefore made using a modified epoxy adhesive and were cured at 200 F.

Variable Air-Inlet Ramp. Because of a corrosion problem due to entrapment of water, North American Aviation found it necessary to substitute titanium face plates for aluminum in an adhesively bonded variable air-inlet ramp on their A3J aircraft. The face sheet surface had to be perforated, as shown in Figure 36, which allowed entry of the water. Both Ti-8Mn and Ti-2Fe-2Cr-2Mo alloys were used for the face plate, and an epoxy-phenolic film adhesive was used to bond to the aluminum core. The ramp consisted of two honeycomb sections, shown in Figures 37 and 38. They were hinged together and lay flat along the top surface of the engine air-inlet duct when in the restricted position. When desired, the ramp could be intruded into the air stream, taking a V-configuration.

Surface preparation of the titanium proved to be the most critical step in the adhesive-bonding process. A four-step procedure consisting of vapor degreasing an acid etch (25 to 35 per cent HNO_3; 2 to 4 per cent HF) was used, followed by fluoride-phosphate coating and a hot-water rinse.

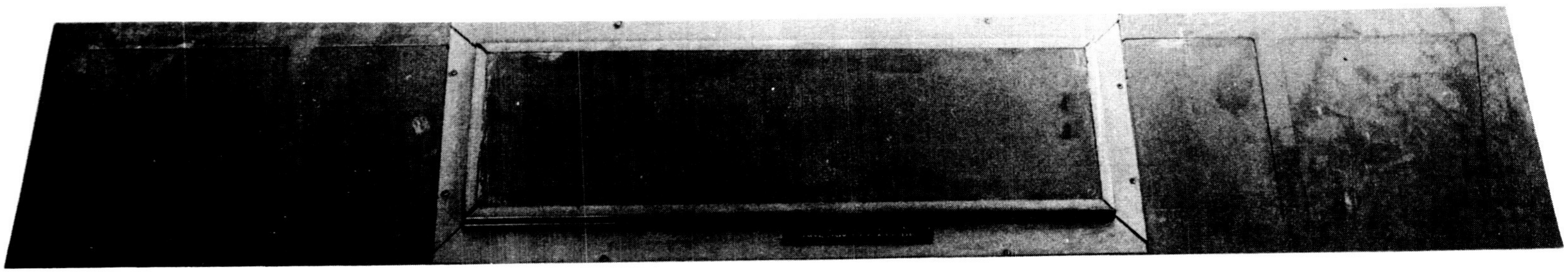


FIGURE 35. ADHESIVE-BONDED TITANIUM SANDWICH PANEL FOR F-111 AIRCRAFT

Courtesy of General Dynamics Corporation.

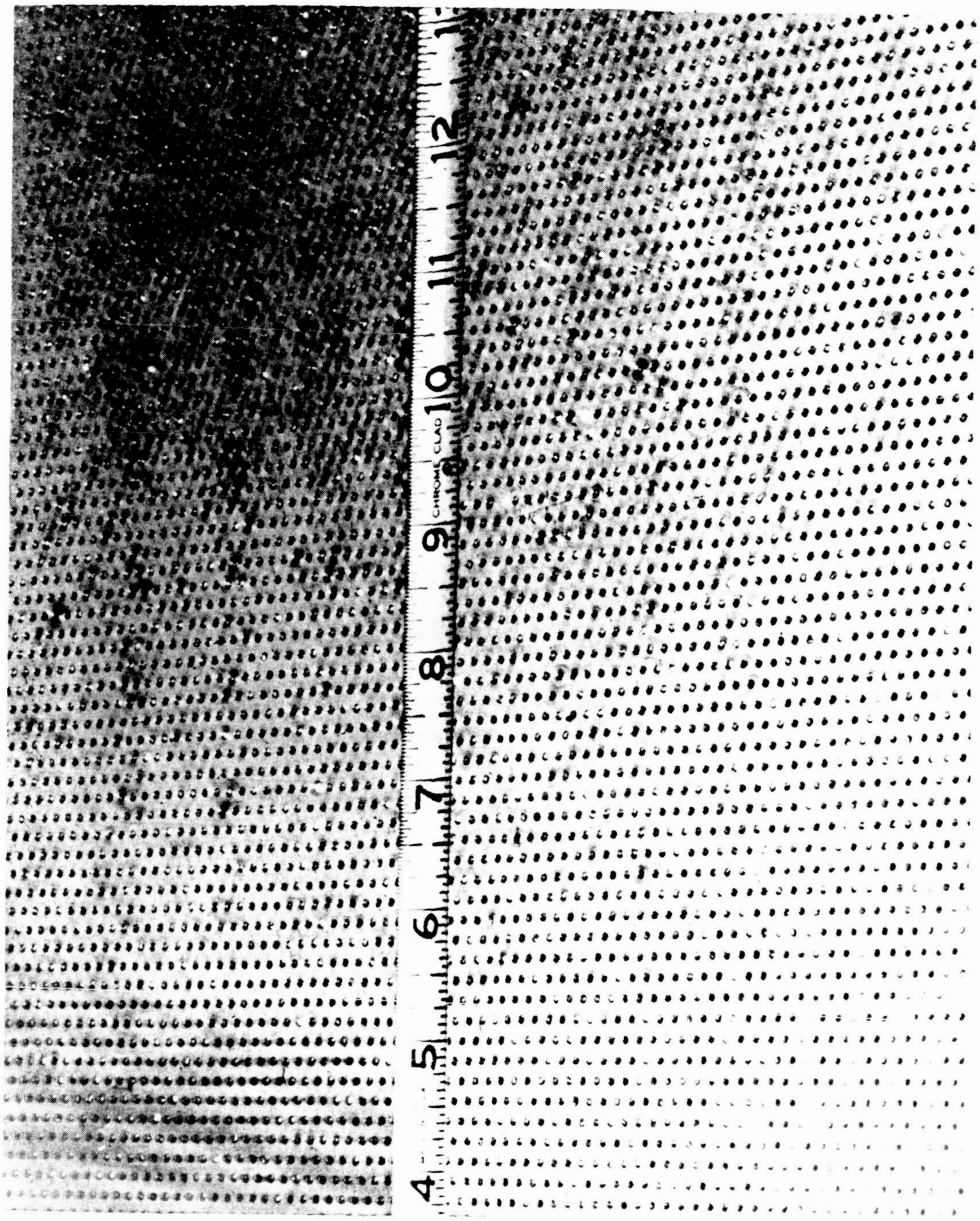


FIGURE 36. VIEW OF A3J INLET RAMP FACE SHEETS SHOWING SOME OF THE THOUSANDS OF HOLES DRILLED IN RAMP AFTER ADHESIVE BONDING

Courtesy North American Aviation, Inc.

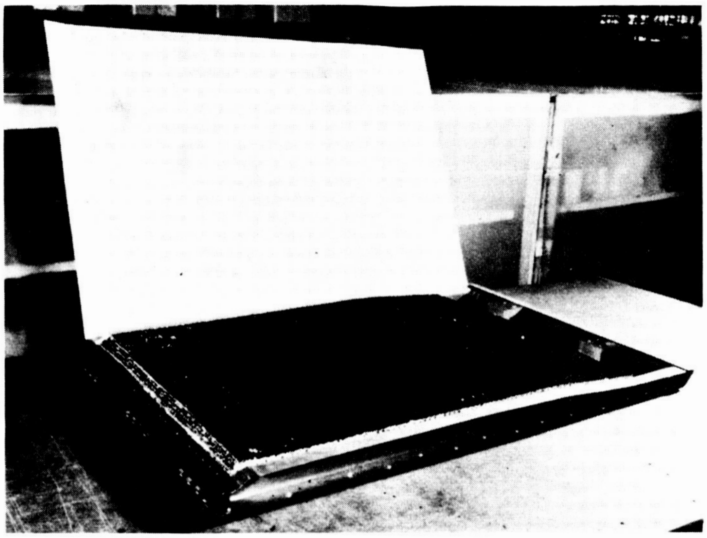


FIGURE 37. SMALLER COMPONENT MAKING UP A3J INLET RAMP

Face sheets and edge members are titanium alloy, core is aluminum alloy.

Courtesy North American Aviation, Inc.

FIGURE 38. LARGER COMPONENT OF A3J INLET RAMP

Honeycomb core has been omitted to show titanium details.

Courtesy North American Aviation, Inc.

Use of the titanium face sheets successfully eliminated the corrosion problem, and service performance of the adhesively bonded structure was satisfactory. The need for the ramp was later eliminated in a redesign, and it is no longer in production.

HYBRID JOINING METHODS

An interesting development that deserves increased attention is the use of adhesive bonding combined with other joining methods. Although no cases of combined joining techniques as applied to titanium alloys have come to the authors' attention, information concerning the techniques is included here because they are applicable to many metals and offer unique structural advantages.

It has already been mentioned that adhesive bonds have high fatigue strengths. It is also well known that spot welds may have disappointingly poor fatigue strength. Three papers (Refs. 87-89) and a book ~~(Ref. 90) have~~ appeared in the Soviet literature describing combined use of adhesive bonding and spot welding, under the name of "adhesive welding" or "glue welding". Fatigue test data presented for lap joints made by combined adhesive bonding and spot welding indicate that their fatigue strengths are increased over the fatigue strengths of joints made by either technique singly. Combining adhesive bonding with spot welding is shown to give improved fatigue strengths over either joining technique used singly (Figures 39 and 40).

The Soviets use two procedures for preparing adhesive-welded lap joints. In the first, the adhesive joint is laid up and the spot welds are made through the uncured adhesive. In the second, the spot welds are made first, following which the liquid adhesive is introduced into the bond area using a dispensing tool similar to a hypodermic syringe.

It might be anticipated that there would be difficulty in spot welding reproducibly through the adhesive. This has proved to be the case in experiments conducted in this country by at least two airframe manufacturers (Refs. 59,91). The alternative process would be slow and subject to considerable variability and would require the use of liquid adhesives on the main assembly line, which at least some manufacturers would prefer to avoid.

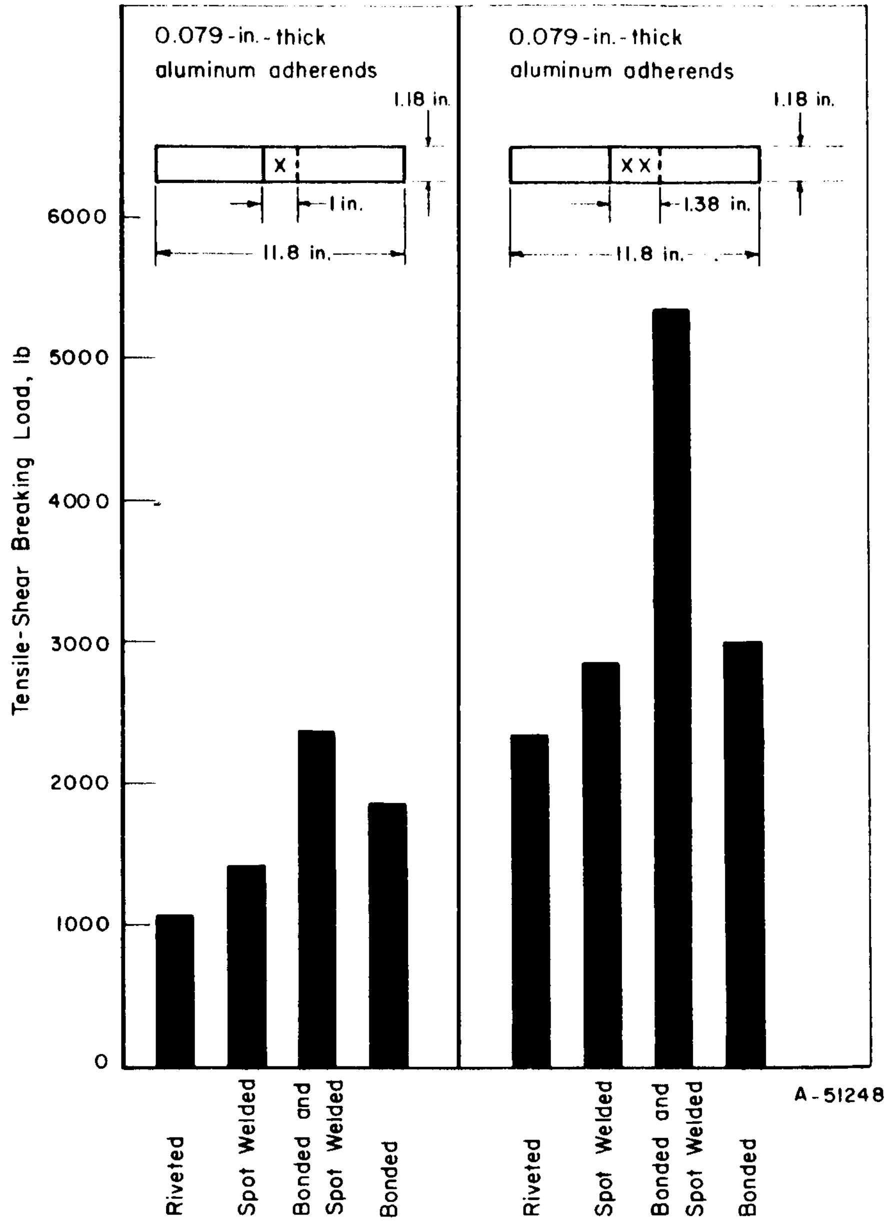


FIGURE 39. STATIC TENSILE-SHEAR STRENGTHS OF RIVETED, SPOT-WELDED, ADHESIVE-BONDED, AND ADHESIVE-BONDED PLUS SPOT-WELDED JOINTS

After Shavyrin (Ref. 88).

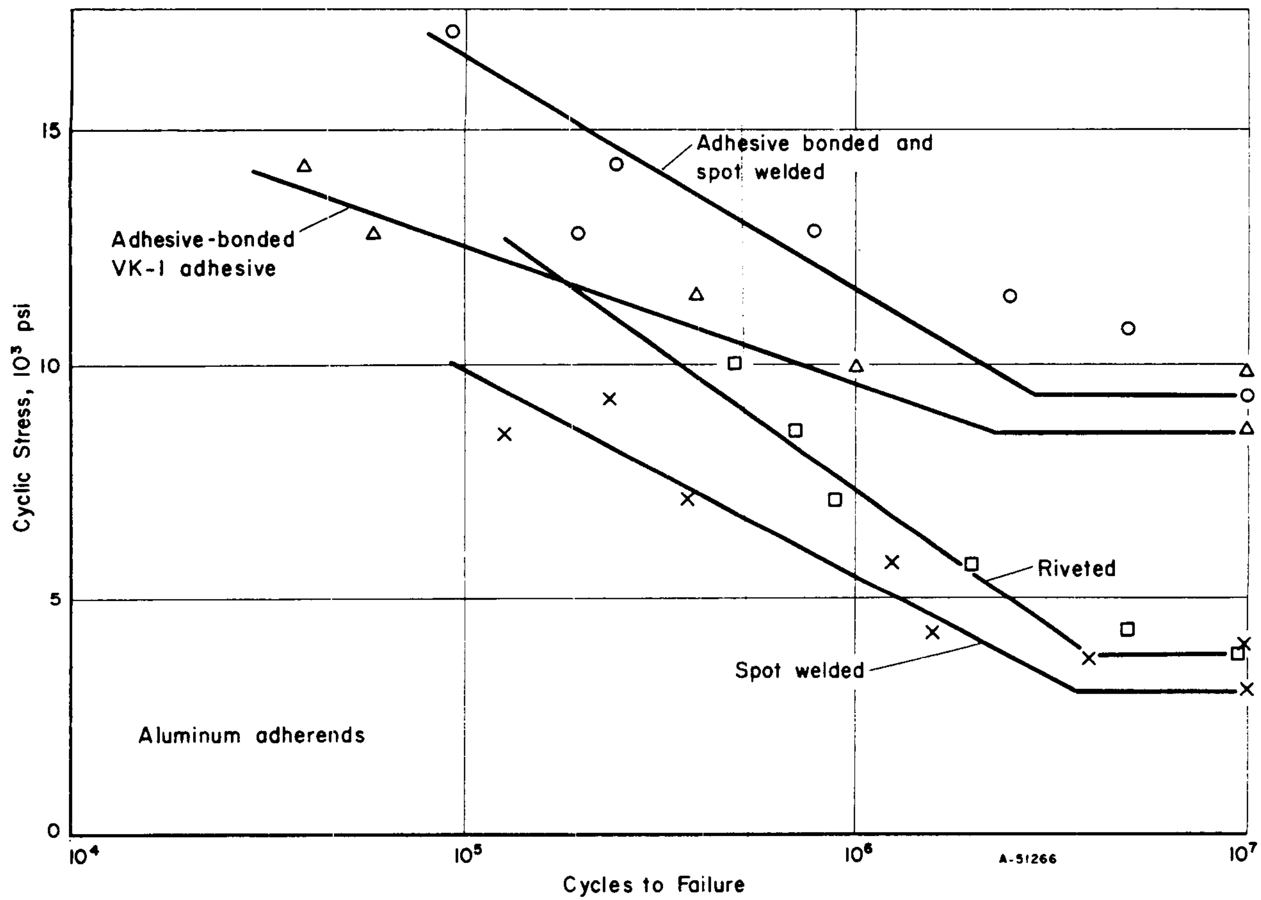


FIGURE 40. FATIGUE STRENGTHS IN SHEAR FOR RIVETED, SPOT-WELDED, ADHESIVE-BONDED, AND ADHESIVE-BONDED PLUS SPOT-WELDED JOINTS

After Shavyrin (Ref. 88).

Combining adhesive bonding with riveting, however, is a fully practicable technique. It is presently being used on the Boeing 727 transport for longitudinal body splices, as shown in Figure 41. Because of the difficulties associated with elevated-temperature curing of bonds in such large structures, a room-temperature-curing epoxy film adhesive is used. It is shipped and stored under refrigeration until required for use.

For tear-stopper doublers, as shown in Figure 42, the same adhesive tape is used. The doublers are bonded to the skin panels before the skin is assembled. A conventional lay-up and vacuum-bagging technique is used for curing the doubler bonds, except that the cure is allowed to take place at room temperature after the bag is evacuated.

Use of combined adhesive bonding and riveting for the longitudinal splices in the Boeing 727 permitted the use of a 0.040-inch-thick aluminum skin. If riveting alone had been used, a 0.050-inch skin would have been required. Test joints have been cycled to design stress for 1,200,000 cycles, following which the rivets have been removed and the adhesive bond given another 1,000,000 cycles without failure (Ref. 59). With the availability of the new 2000 psi room-temperature-curing tape adhesive, the combined use of adhesive bonding and riveting should become a widely used technique, especially for larger structures.

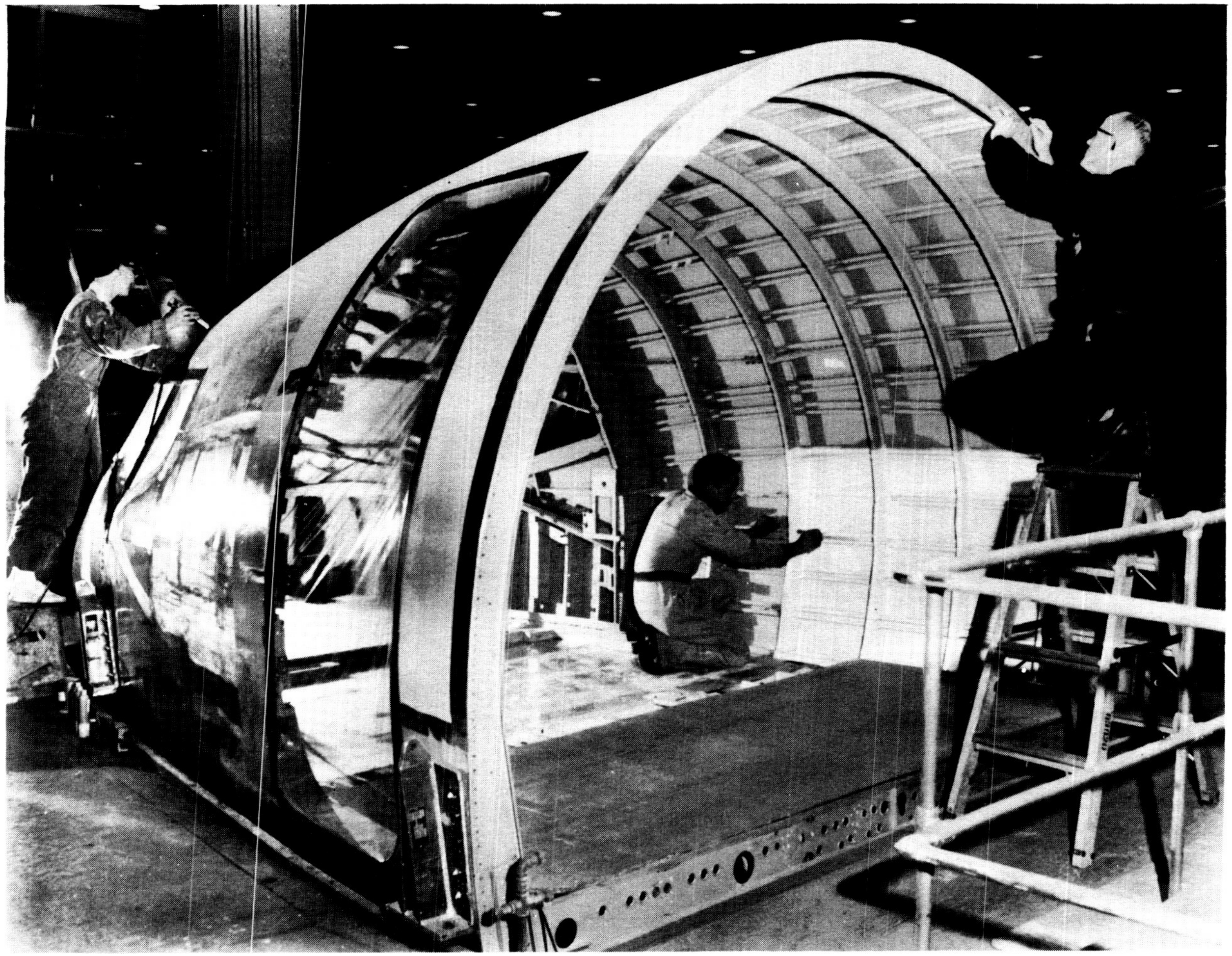


FIGURE 41. LONGITUDINAL BODY SPLICES AND DOUBLERS IN THE BOEING 727 AIRCRAFT BONDED WITH ROOM-TEMPERATURE-CURING EPOXY TAPE ADHESIVE

Technician inside the fuselage is pointing to location of longitudinal body splice.

Courtesy of Boeing Airplane Company.

FIGURE 42. ADHESIVE-BONDED TEAR-STOPPER APPLICATION IN A COMPLETED AIRCRAFT-BODY SECTION
Courtesy of Boeing Airplane Company.

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By R. E. Keith, R. E. Monroe, D. C. Martin

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