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ADHESIVE BONDING OF NICKEL AND NICKEL-BASE ALLOYS

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

Prepared Under the Supervision of the
Research Branch, Redstone Scientific Information Center
Directorate of Research and Development
U. S. Army Missile Command
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NASA

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

ABSTRACT

This report covers the state of the art of adhesive bonding of nickel and its alloys. Typical joint designs, surface preparation procedures, and environmental factors are described as they influence choice among the available adhesives and processing techniques. Both organic and inorganic adhesives are considered.

*Principal Investigators, Battelle Memorial Institute,
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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.

This report deals with the adhesive bonding of nickel and nickel-base alloys, and is oriented toward the interests of the designer and the manufacturing engineer. The processing incident to adhesive bonding, the types of adhesives used for bonding nickel-base alloys, and the available test results on adhesive-bonded nickel-base alloys are included in the report.

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 visits with the following organizations and individuals:

Floyd H. Bair
Materials Laboratory
Wright-Patterson Air Force Base,
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TABLE OF CONTENTS

	Page
SUMMARY	1
INTRODUCTION	1
Nickel-Base Alloys	4
Advantages of Adhesive Bonding	7
Disadvantages of Adhesive Bonding	11
GENERAL COMMENTS ON ADHESIVE BONDING OF METALS	14
Adhesion Mechanisms	14
Differential Dimensional Changes	15
Use of Solvent Carriers	17
BONDING NICKEL-BASE ALLOYS WITH ORGANIC ADHESIVES	17
Designing the Joint	17
Preparing the Adherend Surfaces	21
Step 1. Degrease	25
Step 2. Acid Etch or Alkaline Clean	25
Step 3. Rinse	25
Step 4. Dry	26
Step 5. Condition Surface	26
Steps 6 and 7. Rinse and Dry	26
Step 8. Prime or Bond	26
Reported Surface Preparation Procedures for Bonding Nickel-Base Alloys	
With Organic Adhesives	29
Compromises	29
Tests for Proper Surface Preparation	30
Selecting the Organic Adhesive	30
Adhesive Tests	31
Adhesive Specifications	33
Physical Forms of Adhesives	35
Working and Storage Requirements	35
Service Conditions	36
High Temperature	36
Cryogenic Temperatures	38

TABLE OF CONTENTS
(Continued)

	Page
Radiation	42
Applying the Adhesive	44
Tooling and Fixturing – Joint Assembly	44
Curing	45
Novel Curing Techniques	47
Cleaning the Cured Joint	50
Testing and Inspection	50
Adhesive Evaluation	50
Tooling Evaluation	50
Destructive Testing	51
Nondestructive Testing	51
 BONDING NICKEL-BASE ALLOYS WITH INORGANIC ADHESIVES	52
Surface Preparation of Adherends	52
Inorganic Adhesives	54
Applying the Inorganic Adhesive	56
Maturing	57
Finishing the Joing	57
Tooling and Fixturing	58
 CONCLUSIONS AND RECOMMENDATIONS	59
Adhesion	59
Adhesives Development	60
Processing	60
Service Behavior	61
 REFERENCES	62

LIST OF ILLUSTRATIONS

Figure	Title	Page
1.	Schematic Diagram of Operations Performed in Adhesive Bonding	3
2.	Peel and Cleavage Stresses in Adhesive-Bonded Joints	16
3.	Variations in Stresses in Tensile-Loaded Simple Lap Joint	18
4.	Some Designs for Joints in Flat Plates	19
5.	Corner-Joint Designs	20
6.	Sheet-Metal and Panel-Edge Joint Designs	20
7.	Tee-Joint Designs	20
8.	Designs for Cylindrical Joints	20
9.	Butt-Joint Designs	22
10.	Peel-Resistant Designs for Flexible Members	22
11.	Joint Designs for Hat-Section Skin-And-Stringer Construction	22
12.	Honeycomb-Panel Edge Designs	23
13.	Circumferential Joint in Large Honeycomb Cylinder	23
14.	Generalized Flow Chart of Adherend Surface-Preparation Processes	24
15.	Configuration of Simple Lap Tensile-Shear Test Specimen	32
16.	Configuration of Panel and Individual Tee-Peel Test Specimen	32

LIST OF ILLUSTRATIONS
(Continued)

Figure	Title	Page
17.	Adherend Block and Testing Arrangement for Pi-Tension Test	33
18.	Temperature Dependence of Short-Time Tensile-Shear Strengths of Various Classes of Adhesives	36
19.	Effect of Time at Temperature on Tensile-Shear Strengths of Joints Bonded With Various Adhesives	37
20.	Effect of Time, Temperature, and Exposure in Air or in Nitrogen on Tensile-Shear Strength of Joints Bonded With an Epoxy-Phenolic Adhesive	38
21.	Effects of Time at Temperature on Tensile-Shear Strengths of Polybenzimidazole- and Polyimide-Based Adhesives	39
22.	Tensile-Shear Strengths of Adhesive Systems for Cryogenic Service as a Function of Temperature	41
23.	Tensile-Shear Strengths of Modified Phenolic Adhesives at Cryogenic Temperatures	41
24.	Tensile-Shear Strength Versus Radiation Dosage	43
25.	Methods for Curing Adhesive-Bonded Assemblies	46
26.	End of Flap Fabricated Using Electrically Curing Adhesive, Showing Copper Buses Attached to Heating Wires	48
27.	End of Flap With Leads Attached to Buses Ready for Curing	49
28.	Tensile Shear Strength Versus Testing Temperature of Ceramic-René 41 Adhesive Combinations	54

LIST OF ILLUSTRATIONS
(Continued)

Figure	Title	Page
29.	Tensile-Shear Strength Versus Testing Temperature of Ceramic-René 41 Adhesive Joints	55
30.	Typical Ceramic Adhesive Bonding Vacuum Pressure Fixture	58

LIST OF TABLES

Table	Title	Page
I.	Compositions and Mechanical Properties of Nickel and Alloys of Nickel	5
II.	Compositions and Mechanical Properties of Annealed Nickel-Copper Alloys (Monels)	6
III.	Compositions and Mechanical Properties of Complex Nickel-Base Alloys	9
IV.	Surface Preparation Procedures for Stainless Steels Prior to Bonding With Organic Adhesives	27
V.	Adhesive Specifications	34
VI.	MIL-A-5090 Tensile-Shear Requirements	35
VII.	Effect of Glue-Line Thickness on Tee-Peel Strength of a Nitrile-Phenolic Adhesive With Radiation Exposures	44

TECHNICAL MEMORANDUM X-53428

ADHESIVE BONDING OF NICKEL AND NICKEL-BASE ALLOYS

SUMMARY

Nickel and nickel-base alloys can be successfully adhesive bonded using presently available techniques and adhesives. Relatively little work has been done on adhesive bonding of nickel-base alloys, however, because most nickel-base alloys are used at temperatures above the present maximum service temperatures of organic adhesives or under corrosive conditions. Inorganic adhesives of sufficient ductility and low enough maturing temperatures have not been developed to compete effectively with brazing and welding for joining high-temperature structures. As the maximum service temperatures of new organic adhesives continue to increase, production applications of adhesive bonding to nickel-base alloys should become more attractive. Since the principles of adhesive bonding are generally similar for all metals, the information contained in this report is expected to be useful for such anticipated applications, as well as for the occasional specialized applications that may be presently encountered.

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.

INTRODUCTION

Adhesive bonding, the various forms of welding, brazing, and soldering, and mechanical fastening, comprise the available methods for joining of materials. All five of these methods have long been in

use because each joining method has particular advantages that are responsible for its continued use. Each method has its drawbacks. For example, welding can result in the lightest joints; mechanical fastening usually results in the heaviest joints. On the other hand, welded joints are permanent, whereas mechanically fastened joints can easily be taken apart. 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 with relative freedom not only to join dissimilar metals, but to join metals to wood, ceramics, and plastics as well.

Many other comparisons could be made among the different joining processes, but those given above 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 nickel and nickel-base alloys.

The steps necessary to make an adhesive bond are shown in Figure 1. The surfaces to be joined, usually referred to as the adherends, must be properly cleaned and conditioned. The conditioning may involve application of an electrolytic 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 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 this 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. For critical adhesive joints, non-destructive testing is employed, following which the joint may be painted.

When inorganic adhesives are used, the bonding procedure differs somewhat. Since inorganic metal-bonding adhesives are not generally available commercially, it is necessary to prepare the adhesives from

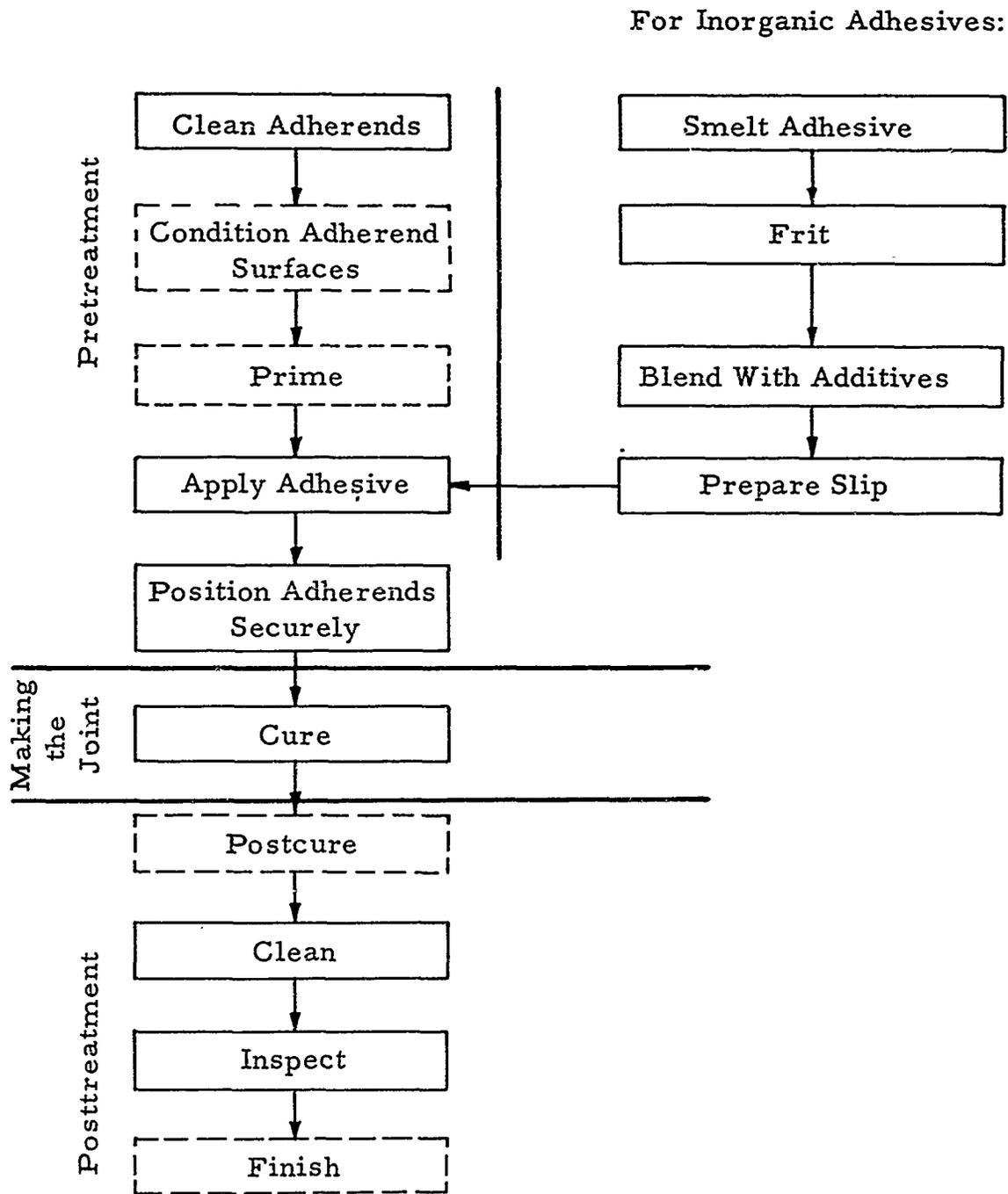


FIGURE 1. SCHEMATIC DIAGRAM OF OPERATIONS PERFORMED IN ADHESIVE BONDING

Dashed boxes indicate steps not always performed.

raw materials. These are typically inorganic chemicals similar to those used in glass manufacture. The proper mixture of raw materials is fused or smelted at a temperature that may be as high as 4500 F. The molten melt is then poured into water. This quenching operation, referred to as fritting, rapidly cools the adhesive and results in the formation of a coarse powder or frit. The frit may be blended with additives prior to use. These additives may be metal or metal-oxide powders, which are added to improve the bond strength, or they may be materials added to stabilize the water suspension, or slip, the form in which the adhesive is to be ultimately applied. After the additives have been mixed with the frit, they are blended in a milling operation, during which the particle sizes are reduced. When the desired range and distribution of particle sizes has been attained, as evidenced by screening analysis, water is mixed with the powder to form the slip. The slip is then ready for application to the adherends. The remaining steps in the bonding process with inorganic adhesives are similar to those using organic adhesives, except that the curing step is referred to as maturing. Maturing temperatures are typically much higher than curing temperatures of organic adhesives.

The increasing interest in adhesive bonding as a practical means of joining of metals is attested to by 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), which have appeared during the last several years. The reader is referred to these publications for a general background in metal-to-metal adhesive bonding. The bulk of the metal-adhesive-bonding work done in this country has been on aluminum, and the largest volume of literature is concerned with bonding of various aluminum alloys. The B-58 bomber made extensive use of adhesively bonded honeycomb panels, but the major material used was precipitation-hardenable stainless steel. Stainless steels of the 300 series have also been adhesively bonded with organic adhesives. Almost all of the development work on inorganic (ceramic) adhesives has been done using precipitation-hardening stainless steel adherends.

NICKEL-BASE ALLOYS

Nickel is used commercially in pure form and in a wide variety of alloys in which it is the major constituent. Elemental nickel in several degrees of purity (Table I) is used in the chemical and electronics industries. Nickel-copper alloys, the Monels (Table II), are used in applications where corrosion resistance at room and slightly elevated temperatures is required. The more complex nickel-base alloys

TABLE I. COMPOSITIONS AND MECHANICAL PROPERTIES OF NICKEL AND ALLOYS OF NICKEL

Nickel Alloy(a)	Nominal Chemical Composition(b), per cent										Room Temperature Properties(c)		
	Ni	Co	Fe	Mg	Mn	Cu	W	Ti	C	Si	Tensile Strength, ksi	Yield	Elongation, per cent
270	99.97	--	--	--	--	--	--	--	--	--	52	15-30	55
200	99.5	--	--	--	--	--	--	0.06	--	--	55-80	40-100	55-40
201	99.5	--	--	--	--	--	--	0.01	--	--	65-110	21	35-10
205	99.5	--	--	0.04	--	--	0.02	0.06	--	--	60-100	35-90	55-40
220 and 225	99.5	--	--	0.04	--	--	0.02	0.06	--	--	65-110	40-100	35-10
230	99.5	--	--	0.06	--	--	0.003	0.09	--	--	60-70	18-22	47
233	99.5	--	--	0.07	--	--	0.003	0.09	--	--	65-110	40-100	35-10
212	98	--	--	--	2	--	--	0.10	--	--	60-70	18-22	47
TD Nickel	98	--	--	--	--	--	--	--	--	--	65-110	40-100	35-10
202	95.5	--	--	0.03	--	--	3.8	0.03	--	--	76	28	43
204	95.2	4.5	--	--	--	--	--	0.03	--	--	62-90	50-80	25-23
211	95	--	--	--	4.75	--	--	0.10	--	--	*	*	*
210	95.6	--	0.5	--	0.9	0.5	--	0.8	1.6	86	34	40	
213	95	--	0.5	--	0.8	0.5	--	1.5	1.6	45-60	20-30	30-15	
305	91.5	--	0.5	--	0.9	0.5	--	0.8	6	*	*	*	

(a) Designations of Huntington Alloy Products Division, International Nickel Company. (Ref. 8)

(b) Elements present when not used as alloying materials: manganese, trace to 0.20; iron, trace to 0.10; sulfur, trace to 0.008; silicon, trace to 0.2; and copper, trace to 0.05.

(c) Asterisks denote the data are unavailable.

TABLE II. COMPOSITIONS AND MECHANICAL PROPERTIES OF ANNEALED
NICKEL-COPPER ALLOYS (MONELS)

Monel Alloy (a)	Usual Form (b)	Nominal Chemical Composition, per cent					Room Temperature Properties (c)		
		Ni	Cu	Si	C	Others	Tensile Strength, ksi	Yield	Elongation, per cent
406	W	84	13	--	0.12	--	*	*	*
R405	W	66	31.5	--	0.18	--	70-85	25-40	50-35
400	W	66	31.5	--	0.12	--	70-85	25-40	50-35
410	C	66	30.5	1.6	0.2	--	65-90	32-40	45-25
505	C	64	29	4	--	--	110-145	80-115	45-25
506	C	64	30	3.2	0.10	--	100-130	60-80	25-10
507	C	64	30.5	2.7	0.55	--	90-115	60-80	20-10
411	C	62	32.5	1.6	0.2	Cb 1.3	*	*	*
402	W	58	40	--	0.12	--	60-85	23-40	50-35
403	W	57.5	40	--	0.12	Mn 1.8	60-85	23-40	50-35
404	W	55	44	--	0.06	--	67	25	47
<u>Work Hardenable</u>									
<u>Age Hardenable</u>									
K500	W	65	29.5	--	0.15	Ti 0.6 - Al 3.0	90-110	40-60	45-25
501	W	65	29.5	--	0.23	Ti 0.6 - Al 3.0	90-110	40-60	45-25

(a) Designations of Huntington Alloy Products Division, International Nickel Company. (Ref. 8)

(b) W = wrought products

C = castings.

(c) Asterisks denote that data are unavailable.

(Table III) are intended for use at high temperatures, usually in the range between 1000 and 2000 F.

The amount of adhesive bonding that has been done on nickel and nickel-base alloys is relatively small in comparison with the amount done on other metals. The reasons for this are apparent in the light of the nature of the applications for nickel-base alloys. Nickel chemical-processing equipment is appropriately welded, soldered, or mechanically fastened. Many electronic applications use nickel under high-vacuum conditions and at high temperature, where welding is dictated as the joining method. In highly corrosive environments where the Monels are used, adhesives seldom possess the necessary chemical stability. The service temperatures of the nickel-base high-temperature alloys are beyond the capability of present-day organic adhesives. If possible, welding is the preferred joining method for these alloys, in order to take maximum advantage of the temperature resistance of the alloys, although brazing is also used.

A few adhesive-bonding studies have been carried out using nickel alloys, and enough work has been done to show that they can be bonded using conventional procedures for organic-adhesive bonding and techniques developed for inorganic-adhesive bonding of stainless steels.

ADVANTAGES OF ADHESIVE BONDING

Although most of the adhesive-bonding technology has been developed for aluminum and steels, the techniques can be applied to nickel-base alloys as well. Before beginning the study of adhesive bonding of nickel, 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 made with organic adhesives, when properly designed and fabricated have shown lap-shear tensile strengths at room temperature ranging up to 7000 psi, and in some cases fracture includes pieces of metal pulled from the surface at the bond plane. Not only do the tensile strengths of adhesive-bonded joints compare favorably with riveted and spot-welded joints, 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. A smooth exterior surface is an absolute requirement for such applications as high-speed aircraft. There are many other applications where smooth contours contribute to the pleasing appearance of a product.

Since organic 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 direct metallic connection can be made between the adherends. If the primary purpose of a joint is for electrical insulation, however, 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, such as paper and metal foil. Both mechanical fastening and welding become difficult for thin material. Freedom from high-intensity or sudden mechanical loading during the making of an adhesive-bonded joint is also an advantage when joining brittle materials.

TABLE III. COMPOSITIONS AND MECHANICAL PROPERTIES OF COMPLEX NICKEL-BASE ALLOYS

Name of Alloy(a)	Nominal Chemical Composition, per cent										Room Temperature Properties(b)						
	Ni	Co	Fe	Cr	Mo	W	Ta	Cb	Ti	Al	B	C	Usual Form(c)	Condition(d)	Strength, ksi Tensile(e)	Yield	Elongation, per cent
D979	45	-	27	15	4	4	-	-	3	1	0.01	0.05	W	STA	204b	146	15
René 62	48	-	22	15	9	-	-	2.3	2.5	1.2	0.01	0.08	W	STA	195f	134	14
Inconel Alloy 718	53	-	18	19	3	-	-	5.2	0.8	0.6	-	0.04	W	STA	205	160	7
DCM	60	-	12	14	5.3	-	-	-	3.4	4.3	0.08	0.05	C	STA	145	120	10
Hastelloy R-235	63	-	10	16	5.5	-	-	-	2.5	2.0	-	0.16	W	STA	140	115	5
GMR 235	63	-	10	16	5.3	-	-	-	2	3	0.07	0.15	C	AC	166b	100	32
Nimonic 80 A	70	-	5	20	-	-	-	-	2.3	1.3	-	0.10	W	STA	155	87	39
Inconel Alloy 721	72	-	7.2	16	-	-	-	-	3	-	-	0.04	W	Ann	115	50	50
Inconel Alloy 751	73	-	6.8	15	-	-	-	1	2.5	1.2	-	0.04	W	STA	180	120	25
Nimonic 75	73	-	5	20	-	-	-	-	0.4	-	-	0.15	W	*	*	*	*
Inconel Alloy X750	73	-	6.8	15	-	-	-	0.85	2.5	0.8	-	0.04	W	ST	96-103	60	50
Inconel Alloy X722	74	-	7	15	-	-	-	-	2.4	0.6	-	0.04	W	STA	160	92	22
Inconel Alloy 713 C	74	-	1	11	4.5	-	-	2	0.7	6	-	0.12	C	STA	188	138	18
Inconel Alloy 702	80	-	0.4	15	-	-	-	-	0.7	3.4	-	0.04	W	AC	165b	99	31
Nichrotung 1	61	10	-	12	-	8	-	-	4	4	0.05	0.10	C	STA	145	85	38
Nimonic 100	57	20	-	11	5	-	-	-	1.5	5	-	0.02	W	AC	130	120	5
Nimonic 90	58	18	-	20	-	-	-	-	1.4	1.4	-	0.10	W	STA	181	101	39
Waspaloy	56	14	1	19	4.3	-	-	-	3	1.3	0.01	0.05	W	STA	166	101	39
Astroloy	56	15	-	15	5.8	-	-	-	3.5	4.4	0.03	0.10	W	STA	180	115	28
René 41	55	10	1	19	10	-	-	-	3.2	1.7	0.01	0.10	W	STA	180-205	145-155	5-15
M252	55	10	2	19	10	-	-	-	2.5	0.8	-	0.15	W	STA	185*	148	9
Unitemp 1753	53	7	9	16	1.6	8.4	-	-	3	1.9	-	0.22	W	STA	206b	154	14
Udimet 700	52	18	0.8	15	5.1	-	-	-	3	4.3	-	0.12	W	STA	180	122	20
Udimet 500	50	19	2	19	4	-	-	-	2.9	2.9	0.01	0.12	W	STA	123	61	55
Nimonic 95	49	20	5	20	-	-	-	-	3.1	1.9	-	0.15	W	STA	195	135	20
B & B	48	25	-	15	6	-	-	-	2.7	3.2	0.5	0.05	W	STA	204	140	17
S.E.L. No. 1	48	27	-	15	4	-	-	-	2	4	-	0.13	W	*	*	*	*
Inconel 700	46	29	0.7	15	3.8	-	-	-	2	3	-	0.12	W	*	*	*	*
J1570	28	39	2	20	-	6	-	-	4	-	-	0.2	W	STA	171	104	25
J1650	27	36	-	19	-	12	2	-	3.8	-	-	0.02	W	STA	145b	88	16
M203	25	36	-	1.5	20	-	12	-	2.2	0.8	-	0.07	W	STA	174	116	9
M205	26	37	1.5	19	-	12	-	1.2	-	2.8	-	0.15	C	*	*	*	*
M204	25	41	1.5	19	-	12	-	1.2	-	-	-	0.22	C	*	*	*	*
X50	20	42	2.5	23	12	-	-	-	-	-	-	0.76	C	*	*	*	*
V36	20	43	3	25	4	2	-	2	-	-	-	0.3	W	ST	146	83	19.5
S816	20	43	3	20	4	4	-	4	-	Mn 1.2	-	0.4	W	ST	140	67	35
HS30	16	53	-	24	6	-	-	-	-	-	-	0.4	C	Aged	120	95	3
HS36	10	55	-	19	-	15	-	-	-	-	-	0.4	C	AC	90-115	85-105	3-8
														Aged	115-135	100-115	0 5-3

TABLE III. (Continued)

Name of Alloy(a)	Nominal Chemical Composition, per cent										Usual Form(c)	Condition(d)	Room Temperature Properties(b)		
	Ni	Co	Fe	Cr	Mo	W	Ta	Cb	Ti	Al			B	C	Tensile(e) Yield
HS31	10	56	-	25	-	8	-	-	-	-	-	0.5	113	80	8
ML1700	-	59	-	25	-	15	-	-	-	-	0.4	0.2	128	112	2
HS21	3	62	-	27	5	-	-	-	-	-	0.01	0.25	*	*	*
W1-52	-	65	-	21	-	11	-	-	-	-	-	0.45	124	110	2
HS23	2	66	-	24	-	6	-	-	-	-	-	0.4	119	89	-
Refractaloy 26	37	20	18	18	3	-	-	2.9	0.2	-	-	0.05	111	86	9
NI55	20	20	32	21	3	2.5	1	-	-	-	-	0.15	132	121	3
S590	20	20	27	20	4	4	-	-	-	-	-	0.43	170	100	18
Refractaloy 80	20	30	14	20	10	5	-	-	-	-	-	0.10	117f	71	30
Refractaloy 70	20	30	15	20	8	4	-	-	-	-	-	0.05	111b	54	57
Elgiloy(f)	15	40	16	20	7	-	-	-	-	-	-	0.15	*	*	*
Incoloy Alloy 800 32	-	46	-	21	-	-	-	-	-	-	-	0.04	100	84	3
Incoloy Alloy 895 36	-	55	-	8	0.5	-	-	-	-	-	-	0.12	83	57	8
Incoloy Alloy 810 32	-	46	-	21	-	-	-	-	-	-	-	0.25	132	87	3
Incoloy Alloy 801 32	-	45	-	21	-	-	-	1	-	-	-	0.04	160	est	-
Incoloy Alloy 901 43	-	34	-	14	6	-	-	2.5	0.25	-	-	0.05	185	129	17
Incoloy Alloy 825 43	-	30	-	22	3	-	-	1	0.15	-	-	0.03	75-100	30-50	50-30
Incoloy Alloy 804 44	-	26	-	29	-	-	-	0.4	0.25	-	-	0.06	100-150	75-125	30-10
Hastelloy X	48	-	19	22	9	1	-	-	-	-	-	0.15	*	*	*
Hastelloy F	48	-	16	22	7	1	0.5	2	-	-	-	0.05	90	40	36
NA-22H	48	-	18	27	-	6	-	-	-	-	-	0.5	166s	107	23
Hastelloy C	55	-	6	16	17	4	-	-	-	-	-	0.08	175b	130	-
Inconel Alloy 625 61	-	3	22	9	-	-	-	4	-	-	-	0.05	85-105	35-65	50-30
Inconel Alloy 604 74	-	7	16	-	-	-	-	2	-	-	-	0.04	104p	49	46
Inconel Alloy 600 76	-	7	16	-	-	-	-	-	-	-	-	0.04	108b	51	50

(a) Alloy designations normally used for identification are shown. Licensees may use somewhat similar designations.

(b) Asterisks denote that data are unavailable.

(c) W - wrought products
C - castings.

(d) Ann - annealed.

STA - solution treated and aged by heat treatment

ST - solution treated by heat treatment

AC - as-cast

CD - cold drawn.

(e) b - bar; f - forging; P - plate; s - sheet.

(f) Elgiloy also contains 2Mn and 0.04Be.

Although butt-welded joints are the lightest possible type of construction, adhesive-bonded joints nevertheless may offer considerable weight and size advantage over mechanical fastening in cases where parts are small, thin, or light, or 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 in this instance is contained within the wing by 100 per cent sealing of structural joints.

Following curing of the organic-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. Oxidation which occurred on adherend surfaces during maturing of inorganic adhesives may have to be removed.

The curing temperatures required for most organic 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. However, in the case of inorganic adhesives and some organic adhesives for high-temperature service, curing temperatures may be high enough to cause alteration of the metallurgical structure of the adherends.

When the entire cost of making a joint is completely accounted for, adhesive bonding may be found to be 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.

DISADVANTAGES OF ADHESIVE BONDING

As with any process, there are certain limitations and drawbacks to adhesive bonding. These include:

- (1) Limited service conditions
- (2) Residual stresses

- (3) Accurate joint fitup required
- (4) High standard of cleanliness
- (5) Subject to weathering, solvent, and moisture attack
- (6) Curing time required 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. 28), 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 temperature increases. The stresses arise partly 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 fitup tolerance than some plants are accustomed to using.

Any but the most rudimentary joining process requires at least some treatment of the surface prior to making the joint, even if it is only removal of the burr around a drilled hole. 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. Some of the ceramic adhesives are also attacked by moisture. 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 100 different curing agents for epoxy resins on the market today, many under trade names that give no indication of their composition. There is no substitute for knowledge and testing experience at this point.

Use of any organic material in enclosed or hermetically sealed devices should be 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 with contact fidelity in small electrical relays from deposits 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 with organic adhesives is the most radiation sensitive of the joining processes. Ceramic adhesives, on the other hand, are among the least sensitive materials to radiation.

With the present state of the art, inorganic adhesives do not possess the advantages previously cited to the same extent that organic

adhesives do. The highest mechanical strengths obtained using inorganic adhesives are considerably higher than the highest strengths that have been obtained with organic adhesives. Inorganic adhesives tend to be brittle, however, and possess little damping capability. Inorganic adhesives intended for metal bonding may contain metal powders that may provide electrically conductive paths. The higher density of inorganic adhesives and the necessity to maintain bond-line thicknesses in excess of approximately 0.010 inch to avoid joint starvation are unfavorable for weight reduction. High maturing temperatures required with inorganic adhesives may cause metallurgical damage to the adherends, although it is sometimes possible to combine the adhesive maturing treatment with the adherend heat treatment. Not enough inorganic-adhesive bonding has been done to make an accurate estimate of its economics relative to other joining methods.

On the other hand, inorganic adhesives in comparison with organic adhesives are: (1) usable at higher temperatures, (2) require less elaborate adherend preparation, (3) not as sensitive to weathering, solvent, and moisture attack, (4) outgas less in service, and (5) more radiation-resistant.

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. However, 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 which are particularly important in metal-to-metal adhesive bonding will be mentioned briefly.

ADHESION MECHANISMS

Any adhesive, to be effective, must wet the adherend surface. Although the forces of adhesion of organic materials to metal surfaces

are not clearly understood, it is known that these are short-range forces with respect to the molecular dimensions. Therefore, presence of foreign substances that do not permit the close approach of the adhesive molecules to the metal surface is likely to result in poor bonding.

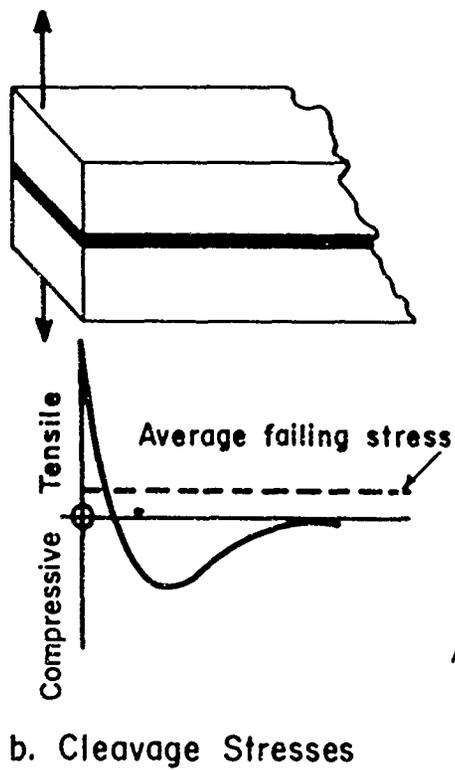
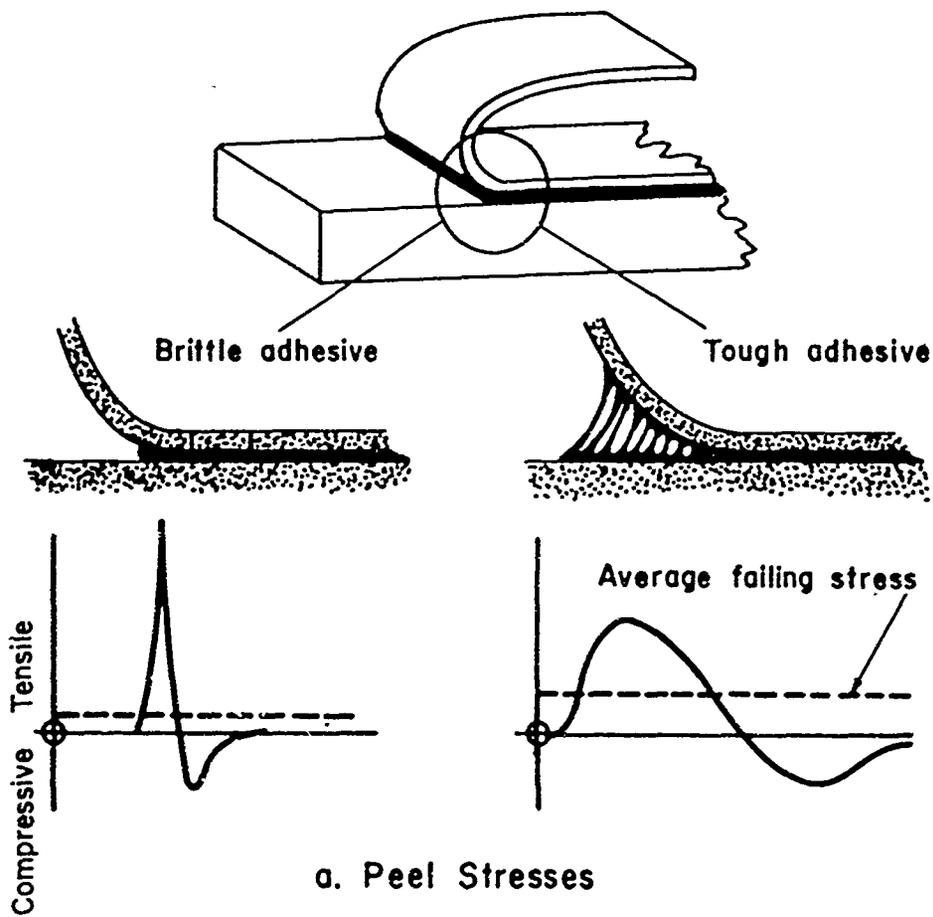
In the case of inorganic adhesives, the bonding mechanism appears to involve transport of adherend ions into the adhesive as well as transport of metal ions from the adhesive into the surface layer on the adherend. Adherends to be bonded with inorganic adhesives are often deliberately oxidized prior to bonding in order to provide a surface oxide coating that will be wetted and mutually soluble with the adhesive.

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 fairly frequent occurrence during the developmental stage of an adhesive-bonding application, particularly when the bond area is large. 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 to the service temperature, which may result in immediate and spontaneous failure of the bond.

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

Adhesives intended for use with metals are often complex mixtures of an 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 to accommodate to the internal stresses in the joint and to resist failure by peeling than a hard or brittle one (Figure 2).



A-51269

FIGURE 2. PEEL AND CLEAVAGE STRESSES IN ADHESIVE-BONDED JOINTS (REF. 29)

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 such porous materials 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 may result 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 the most widely used metal adhesives, such as the epoxies and phenolics, contain little or no solvent. Phenolics do liberate water on curing, however, and joints bonded with them should be vented and securely clamped.

Inorganic adhesives, regardless of the method of application, will generally contain some water. Heating rates must be controlled to allow this water to escape slowly. Adherends must be rigidly fixed to prevent any movement during water evolution.

BONDING NICKEL-BASE ALLOYS WITH ORGANIC ADHESIVES

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 recent survey report (Ref. 30) presents a critical review of the present knowledge in this area. For purposes of this report, 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 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.

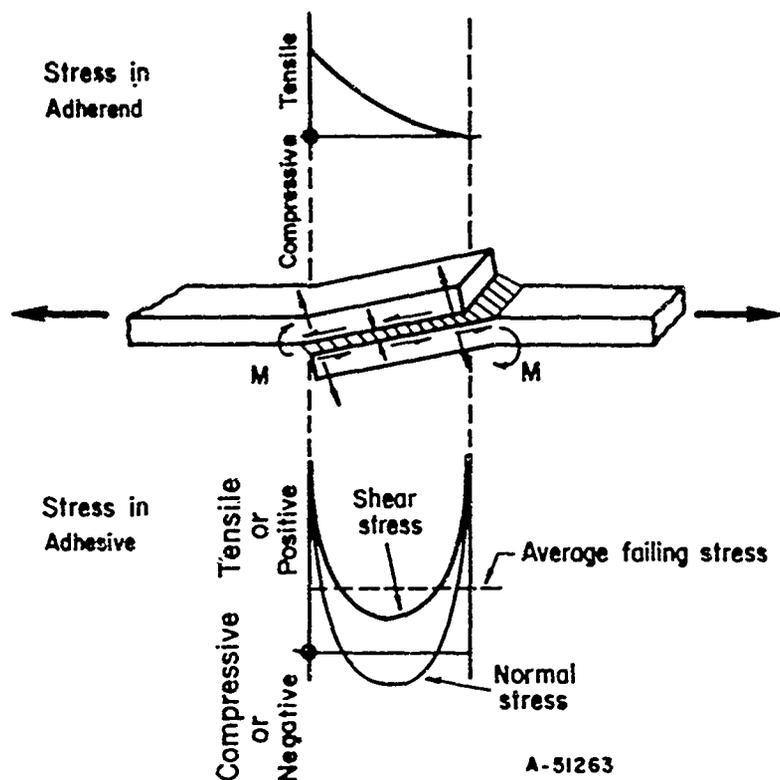


FIGURE 3. VARIATIONS IN STRESSES IN TENSILE-LOADED SIMPLE LAP JOINT

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, or by sizing one adherend to fit within the other. 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 having 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).

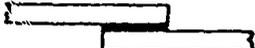
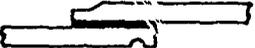
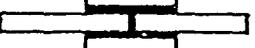
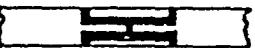
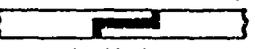
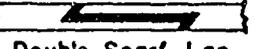
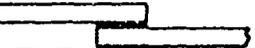
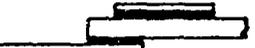
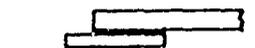
	Unsatisfactory
Butt	
	Good, practical
Lap	
	Very good, usually practical
Beveled Lap	
	Good, usually practical
Relieved Lap	
	Very good, usually practical
Scarf	
	Good, practical
Joggle Lap	
	Fair, sometimes desirable
Strap	
	Good, sometimes desirable
Double Strap	
	Good, expensive machining
Recessed Double Strap	
	Very good, difficult production
Beveled Double Strap	
	Good, requires machining
Half Lap	
	Good, requires machining
Double Scarf Lap	
	Good, difficult to balance load
Double Lap	
	Good, difficult production
Reinforced Lap	
	Good, difficult production
Intermediate Lap	

FIGURE 4. SOME DESIGNS FOR JOINTS IN FLAT PLATES (REFS. 19, 29, 24)

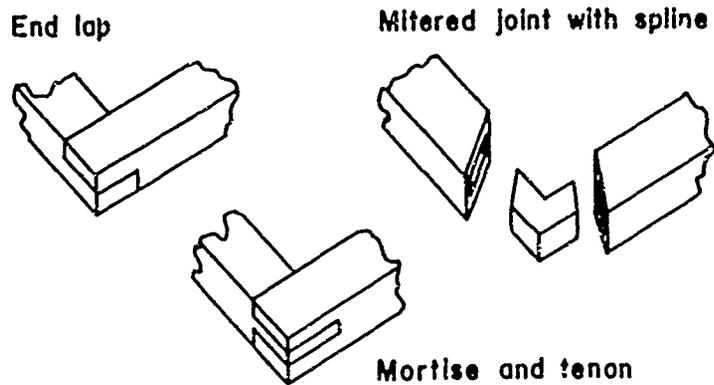


FIGURE 5. CORNER-JOINT DESIGNS (REF. 24)

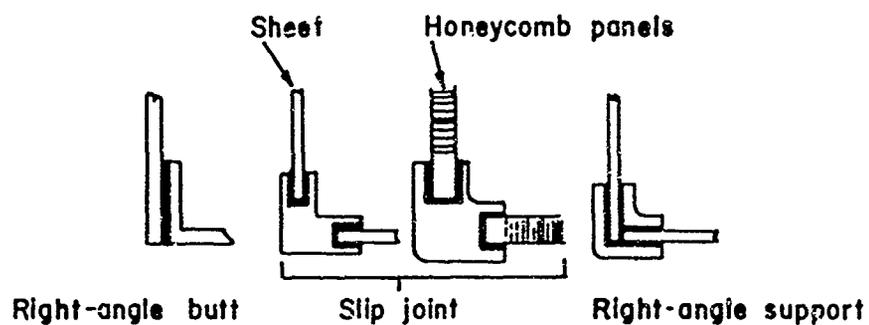


FIGURE 6. SHEET-METAL AND PANEL-EDGE JOINT DESIGNS (REF. 24)

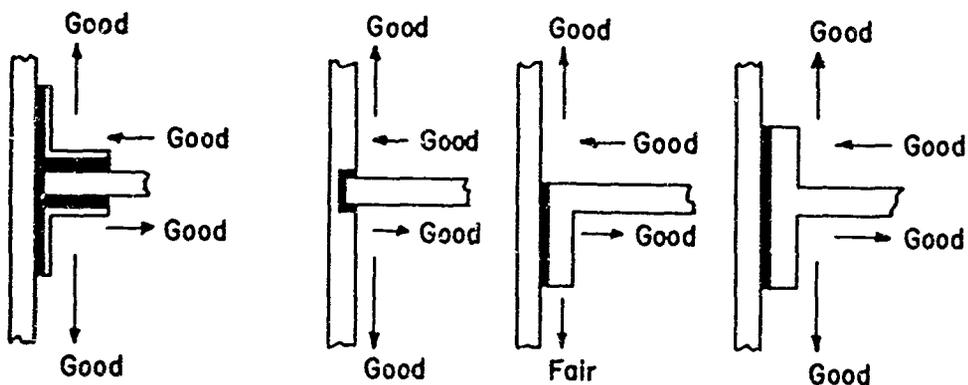


FIGURE 7. TEE-JOINT DESIGNS (REF. 24)

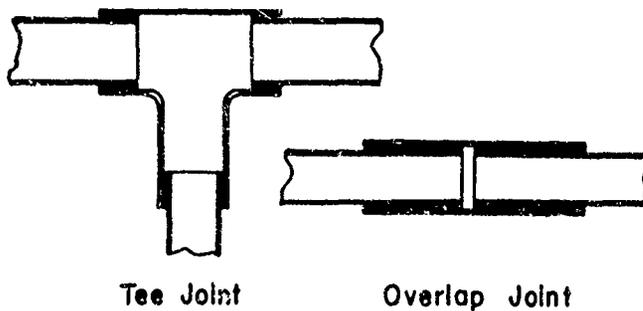


FIGURE 8. DESIGNS FOR CYLINDRICAL JOINTS (REF. 24)

In adhesively bonded skin-and-stringer panels the designer has considerable control over lateral stiffness of the joints 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 organic and inorganic 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. 31). Figure 12 shows some typical edge-closure configurations that have been used with adhesively bonded honeycomb panels. A typical panel joint that has been used with titanium-faced aluminum honeycomb, but which could be used equally well with nickel-base alloys, is shown in Figure 13.

When using some of the stronger adhesives with thin-metal adherends in the metallurgically soft condition, 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 that has a higher yield point (Ref. 34), to use a larger overlap, or to make the adherend thicker.

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.

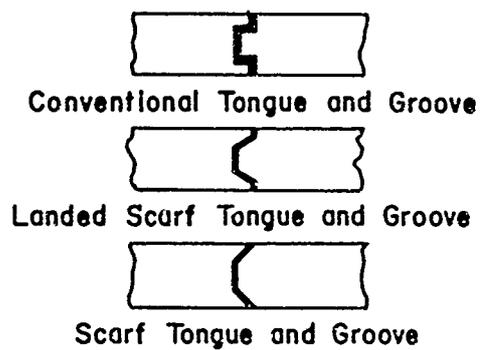


FIGURE 9. BUTT-JOINT DESIGNS (REF. 24)

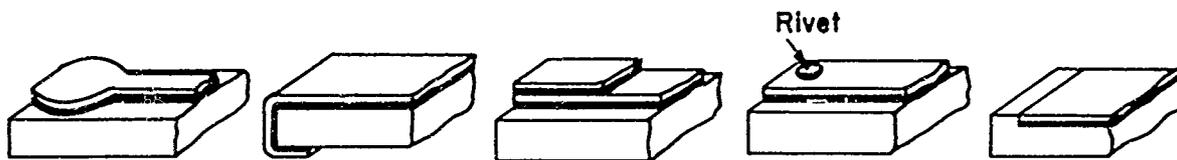


FIGURE 10. PEEL-RESISTANT DESIGNS FOR FLEXIBLE MEMBERS (REF. 29)

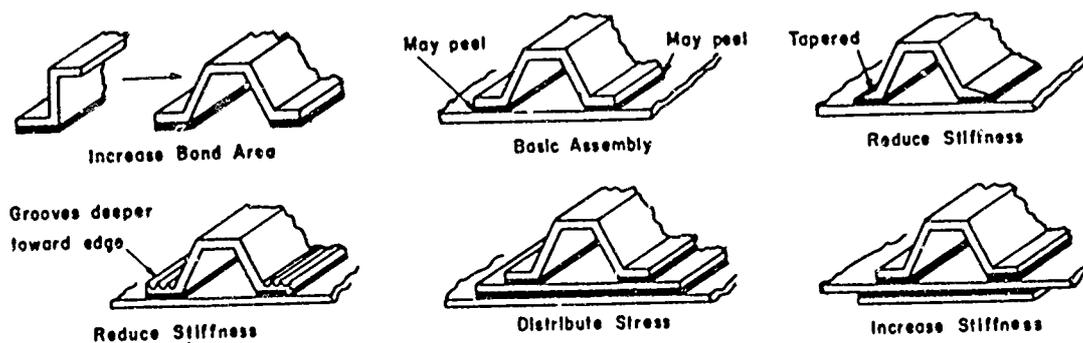


FIGURE 11. JOINT DESIGNS FOR HAT-SECTION SKIN-AND-STRINGER CONSTRUCTION (REF. 19)

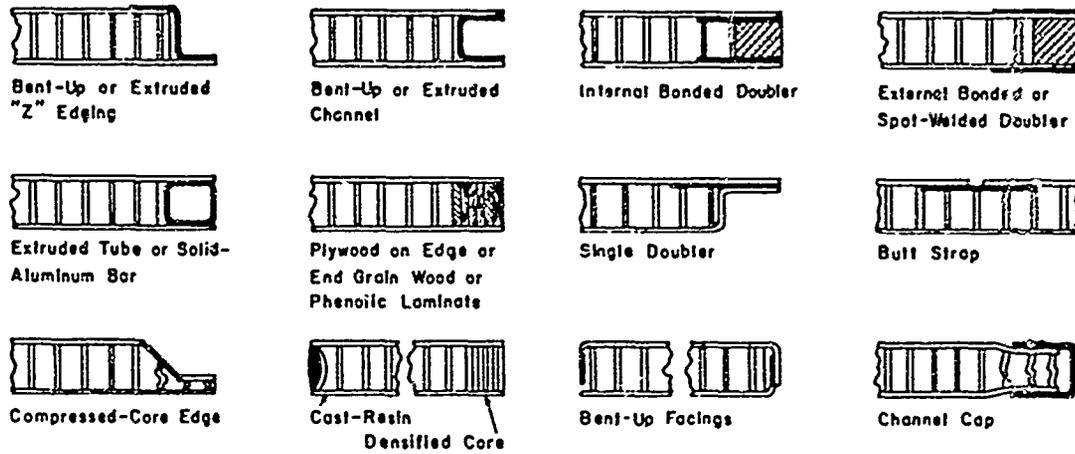


FIGURE 12. HONEYCOMB-PANEL EDGE DESIGNS (REF. 32)

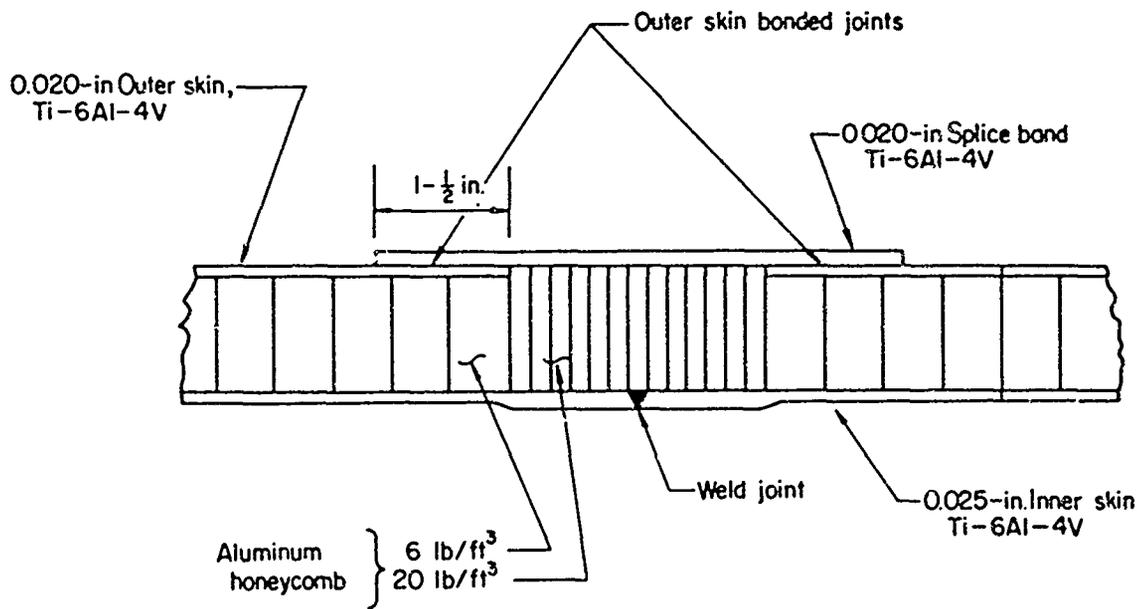


FIGURE 13. CIRCUMFERENTIAL JOINT IN LARGE HONEYCOMB CYLINDER (REF. 33)

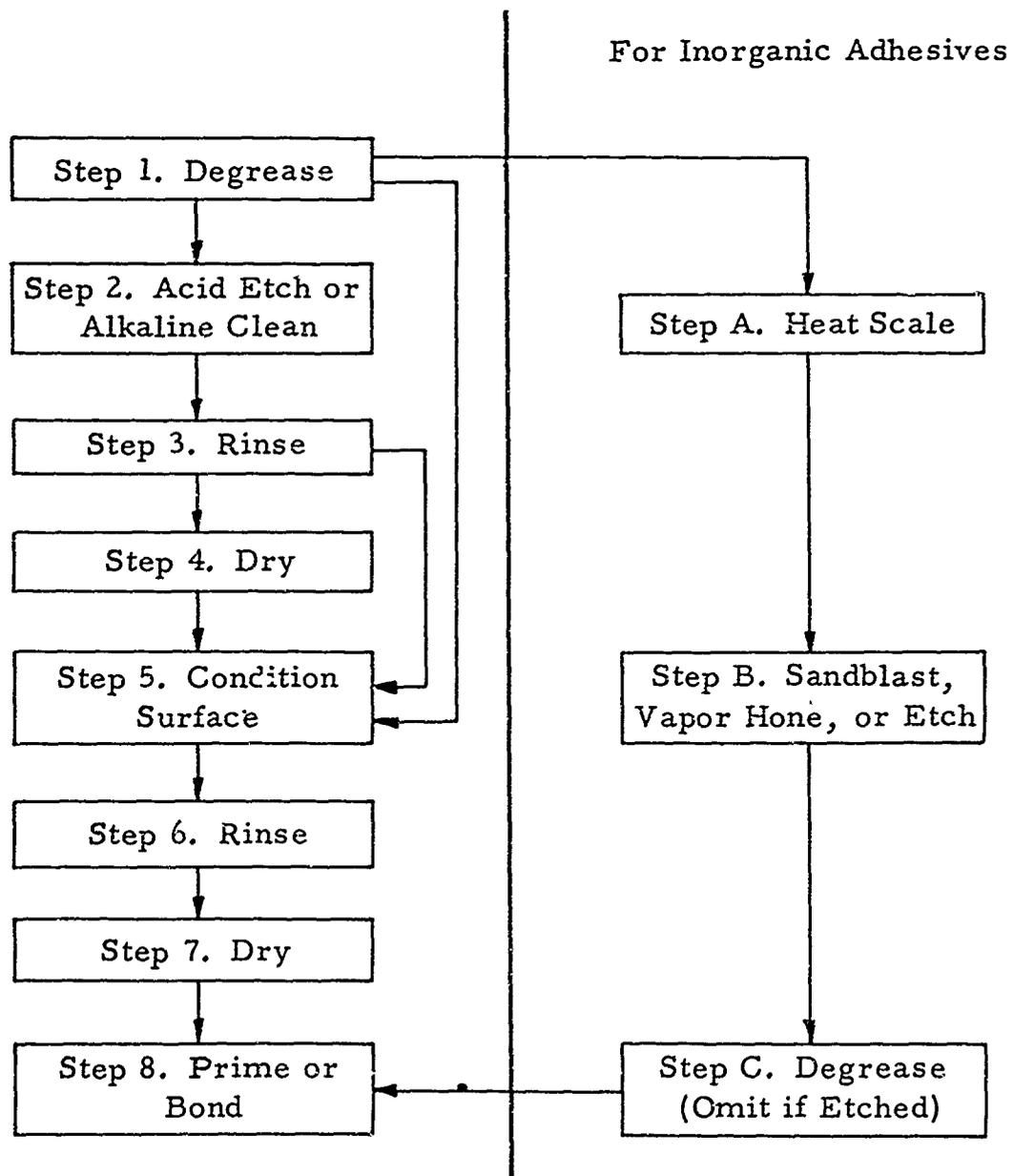


FIGURE 14. GENERALIZED FLOW CHART OF ADHEREND SURFACE-PREPARATION PROCESSES

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

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. 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 adherend. 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 cleaning solutions used are proprietary, and manufacturers' instructions should be followed concerning their use. For large parts which require the wipe-on process, mechanical abrasion with an abrasive pad or fine-grit paper has been substituted for this step in the procedure (Ref. 33).

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. 35) 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, long-term strength retention 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. The impurity levels in tap water, even from a single source,

are not subjected to long-term control and may be responsible for apparently random time periods during which bond strengths produced are below specification. The objective of any rinsing procedure is the complete removal of the etching or cleaning solution as indicated by neutrality of the effluent rinse water (pH = 7). Presence of 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 should be done in air as clean, still, and dust free as possible, or drying can be forced using a clean, warm air blast.

Step 5. Condition Surface. In the surface-conditioning step, a corrosion film of controlled chemical composition and thickness is deliberately formed on the adherend surface. Typically, the films used are complex mixtures of phosphates, fluorides, chromates, sulfates, or 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. For example, copper and brass should be bonded immediately after cleaning. Bonding of aluminum can be delayed a half hour after cleaning. For titanium, an elapsed time no greater than 8 hours between cleaning and bonding is recommended. Stainless steel can be successfully bonded days after cleaning. Maximum allowable times

TABLE IV. SURFACE PREPARATION PROCEDURES FOR STAINLESS STEELS PRIOR TO BONDING WITH

Procedure	Process Step					Surface Condition
	Degrease	Clean/Etch	Rinse	Dry	Surface Condition	
A(Ref. 37)	--	--	--	--	10 wt % H ₂ SO ₄ 10 wt % oxalic acid 80 wt % H ₂ O Temp 60-95 C Time 30-10 min	Co.
B(Ref. 37)	--	--	--	--	46 wt % HCl 2 wt % H ₂ O ₂ 10 wt % formalin 42 wt % H ₂ O Temp 60 C Time 10 min	Col
C(Ref. 37)	--	--	--	--	81 vol % HCl 91 vol % H ₂ O Temp 20 C Time 15 min	Colr
D(Ref. 38)	Trichloroethylene 10 min at RT or vapor degrease 10 min at 180-190 F	--	--	--	<u>A</u> 94.4 wt % H ₂ O 2.0 wt % Na ₂ SiO ₃ (meta) 3.6 wt % Triton X200 or <u>B</u> 96.6 vol % H ₂ SO ₄ 3.4 vol % saturated Na ₂ Cr ₂ O ₇ solution Temp 150-160 F Time 15 min	Tap Derr 18
E(Ref. 3)	MEK; TCE	55 parts/wt Na ₂ SiO ₃ (meta) 35 parts/wt tetra sodium pyrophosphate 5 parts/wt Nacconal NR 15 parts/wt NaOH 2400 parts/wt H ₂ O Temp 165-185 F Time 5-10 min	10 vol % HCl 90 vol % H ₂ O	--	100 parts/wt H ₂ O 40 parts/wt H ₂ SO ₄ 0.5 parts/wt Nacconal NR Temp 150-160 F Time 5-10 min H ₂ O rinse 100 parts/wt H ₂ O 20 parts/wt HNO ₃ 2.5 parts/wt HF RT Time 5-10 min	Tap Distri s s 17 5
F(Ref. 3)	MEK; TCE	--	--	--	25 parts/wt hexa- methylene tetramine 100 parts/wt H ₂ O 10 parts/wt HCl 5 parts/wt 30 per cent H ₂ O ₂ Temp 150-160 F Time 5-10 min	Tap v Distri
G(Ref. 3)	MEK; TCE	--	--	--	80 parts/wt HCl 8 parts/wt H ₃ PO ₄ 4 parts/wt HF Temp 180-190 F Time 1-2 min	Tap v Distri

A

PREPARATION PROCEDURES FOR STAINLESS STEELS PRIOR TO BONDING WITH ORGANIC ADHESIVES

Clean/Etch	Process Step			Rinse	Dry
	Rinse	Dry	Surface Condition		
--	--	--	10 wt % H ₂ SO ₄ 10 wt % oxalic acid 80 wt % H ₂ O Temp 60-95 C Time 30-40 min	Cold H ₂ O	--
--	--	--	46 wt % HCl 2 wt % H ₂ O ₂ 10 wt % formalin 42 wt % H ₂ O Temp 60 C Time 10 min	Cold H ₂ O	--
--	--	--	81 vol % HCl 91 vol % H ₂ O Temp 20 C Time 15 min	Cold H ₂ O	--
--	--	--	A 94.4 wt % H ₂ O 2.0 wt % Na ₂ SiO ₃ (meta) 3.6 wt % Triton X200 or B 96.6 vol % H ₂ SO ₄ 3.4 vol % saturated Na ₂ Cr ₂ O ₇ solution Temp 150-160 F Time 15 min	Tap water 180-200 F Demineralized water 180-200 F or RT	Air; even if RT rinse; <200 F
parts/wt Na ₂ SiO ₃ (meta) parts/wt tetra sodium pyrophosphate parts/wt Nacconal NR parts/wt NaOH parts/wt H ₂ O 165-185 F 5-10 min	10 vol % HCl 90 vol % H ₂ O	--	100 parts/wt H ₂ O 40 parts/wt H ₂ SO ₄ 0.5 parts/wt Nacconal NR Temp 150-160 F Time 5-10 min H ₂ O rinse 100 parts/wt H ₂ O 20 parts/wt HNO ₃ 2.5 parts/wt HF RT Time 5-10 min	Tap water Distilled water spray	Oven 10-15 min 200 F
--	--	--	25 parts/wt hexa- methylene tetramine 100 parts/wt H ₂ O 10 parts/wt HCl 5 parts/wt 30 per cent H ₂ O ₂ Temp 150-160 F Time 5-10 min	Tap water Distilled water spray	Oven 10-15 min 200 F
--	--	--	80 parts/wt HCl 8 parts/wt H ₃ PO ₄ 4 parts/wt HF Temp 180-190 F Time 1-2 min	Tap water Distilled water spray	Oven 10-15 min 200 F

B

between cleaning and bonding have not been determined for nickel-base alloys, but they should be comparable to those for stainless steels. The longer the time, however, the more likelihood of organic contamination from handling, from airborne mists, or from 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 surfaces should be primed according to the adhesive manufacturer's directions and the parts 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 for Bonding Nickel-Base Alloys With Organic Adhesives. Not enough experimental work has been reported on the bonding of nickel-base alloys with organic adhesives for any standardized or optimum surface-preparation procedure to have been agreed upon. In the absence of information to the contrary, it is assumed that the procedures used for stainless steels will give at least satisfactory results with nickel-base alloys. The Minnesota Mining and Manufacturing Company has used a relatively simple treatment with stainless steel consisting of vapor honing followed by a trichloroethylene rinse (Ref. 36). Some other treatments for stainless steels preparatory to bonding with organic adhesives are summarized in Table IV. Meckelburg, Schlothauer, and Neumann (Ref. 37) studied a variety of surface-preparation processes for stainless steels and reported that the three identified in the table as A, B, and C resulted in the highest tensile-shear-strength adhesive bonds. They also noted, however, that sandblasting or simply degreasing in carbon tetrachloride gave almost equivalent results. Guttman (Ref. 3) lists four procedures (D through G) for stainless steels, the first also recommended by Lindsay (Ref. 38) (D).

Compromises. Relaxing of the surface-preparation requirements must be done cautiously, because some very subtle factors may cause an unexpected loss of bond strength. Bikerman (Ref. 2) suggests that surfaces may 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, instead of the other way around.

Tests for Proper Surface Preparation. The so-called water-break 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, 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 which 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 water-break test merely shows whether the surface energy of the metal (which may still be coated with a hydrophilic 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. A satisfactory waterbreak test is at best a necessary, but not a sufficient, requirement for high bond strengths.

SELECTING THE ORGANIC ADHESIVE

Because of the large number of organic compounds, 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, each of the many different curing agents for epoxy resins 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 detailed information concerning adhesive compositions is usually proprietary with the adhesive manufacturer. For these reasons, 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 might be high sensitivity of one adhesive to alkalinity of a poorly rinsed adherend surface, while another adhesive may be relatively

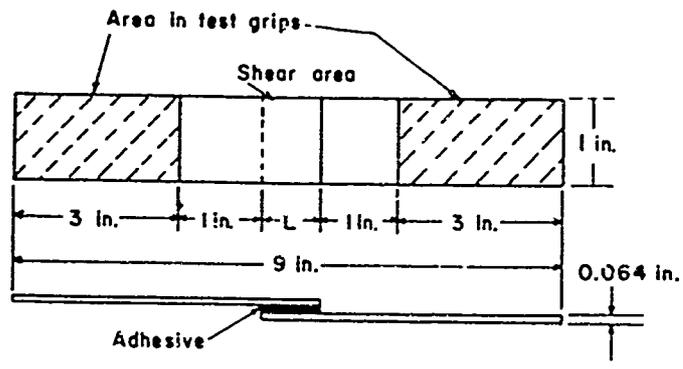
unaffected. Two or three promising adhesives should therefore be tried for a new application if there is any uncertainty of results.

The only adhesives known to have been used for adhesive bonding of nickel-base alloys 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 or melted. They tend to char when overheated. Chemically, the change during curing consists of the formation of crosslinkages 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. Organic adhesives known to have been used to bond nickel and nickel-base alloys have all been of the epoxy type (Ref. 3).

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. '39), 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 test 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, one specimen for which 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 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 from the rest of the cover sheets using a fly cutter. They are then bonded to blocks, and the entire assembly



$$L_{\max} = \frac{Yt}{r} \text{ in.}$$

where Y = adherend yield strength, psi
 t = adherend thickness, in.
 r = 1.5 x estimated adhesive shear strength, psi

L is usually taken as 0.5 in. for metal adherends.

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

From Federal Test Method No. 175.

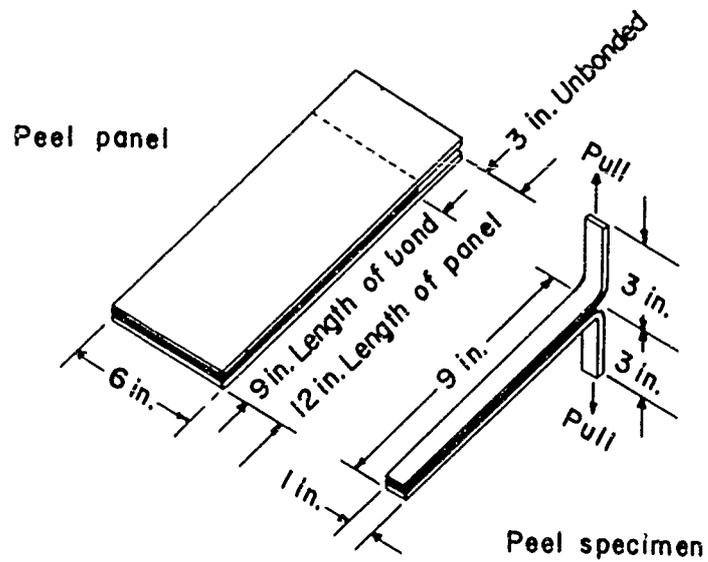


FIGURE 16. CONFIGURATION OF PANEL AND INDIVIDUAL TEE-PEEL TEST SPECIMEN (REF. 40)

is pulled in tension. Results will be influenced by the details of core configuration, so this is a specialized test.

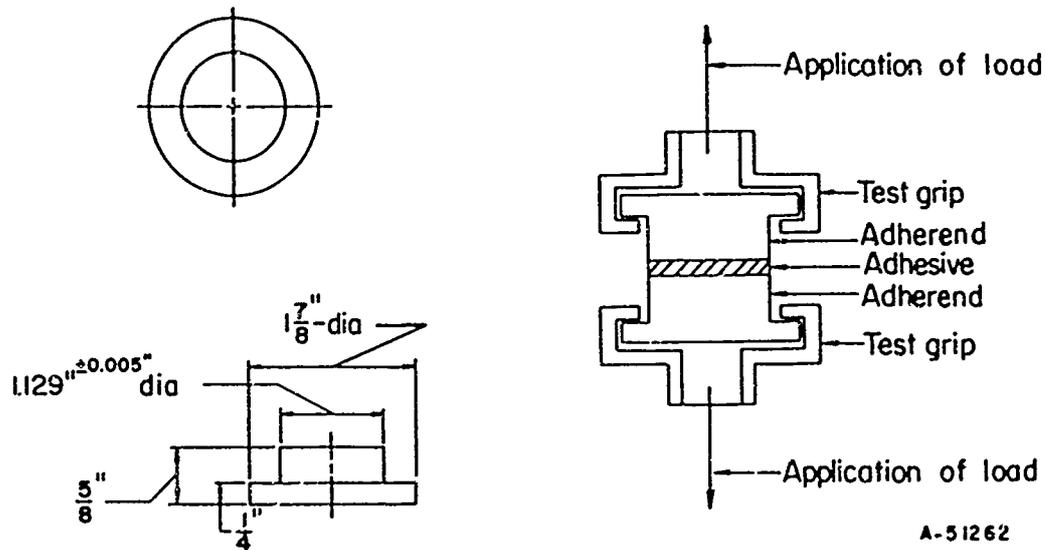


FIGURE 17. ADHEREND BLOCK AND TESTING ARRANGEMENT FOR PI-TENSION TEST

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 3-point and 4-point beams, in flatwise compression, and in edgewise compression, tension, or shear. A detailed study of these tests is beyond the scope of this report, however, some information concerning them will be found in References 13 and 31.

Adhesive Specifications. Guttman (Ref. 3), Katz (Ref. 7), and Licari (Ref. 41), have summarized or reproduced in their entirety the numerous Government, military, and industry-wide specifications relating to adhesive bonding. Table V 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 on tensile-shear strengths measured at temperature. Table VI shows the minimum average strength requirements for qualification by type and class for adhesives under MIL-A-5090.

TABLE V. ADHESIVE SPECIFICATIONS

Specification	Title	Comment
Government Specifications		
Federal Test Method No. 175	Adhesives: Method of Testing	Sampling, inspection, and testing
Military Specifications		
MIL-A-5090	Adhesive: Airframe Structural Metal-to-Metal	See Table VI
MIL-A-25457	Adhesives: Air-Drying, Silicone Rubber	Two-component silicone adhesive for bonding silicone to itself and to aluminum
MIL-A-8623	Adhesives: Epoxy Resin, Metal-to-Metal Structural Bonding	Epoxy adhesives for use up to 200 F. Three classes based on curing temperature
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		
D950-54	Impact Strength Test	
D903-49	Peel or Stripping Strength	
D897-49	Tensile Properties Test	
D1002-53T	Shear Properties, and Tension Loading Metal-to-Metal Tests	

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

Test Conditions	Minimum Average Strength Requirements, psi				
	Type 1		Type 11	Type 111	Type 1V
	Class 1	Class 2			
75F	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. Thicker liquids can be troweled 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 unsupported or supported on a carrier, 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, 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 may be 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 generally inferior to those of heat-cured epoxies, however, unless they are given an elevated-temperature postcure.

One-part epoxies and phenolics generally must be cured at elevated temperatures, although a room-temperature-curing epoxy film adhesive has recently become available. The former are compounded

*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.

mixture of resin and curing agent and have a limited shelf life. Usual shelf life of present commercially available one-part epoxies and phenolic adhesives is 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. The recently developed film adhesive mentioned above has very limited room-temperature working life and is 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. 42).

Service Conditions. No single adhesive is available which 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. Strengths of adhesives, like strengths of metals, decrease with increasing temperature (Figure 18).

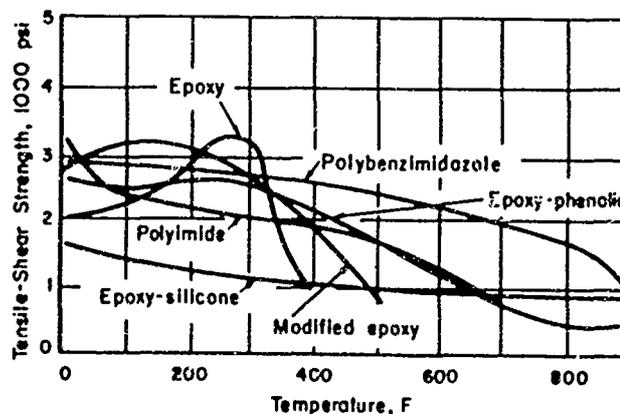


FIGURE 18. TEMPERATURE DEPENDENCE OF SHORT-TIME TENSILE-SHEAR STRENGTHS OF VARIOUS CLASSES OF ADHESIVES (REF. 44)

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.

Several helpful review articles have recently appeared dealing with high-temperature adhesives (Refs. 43, 44, 45). These articles do not refer specifically to nickel or nickel-base alloys. 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 bonds with other adherends will be achieved with nickel bonds. 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 19). Over some ranges of temperature, and depending on curing conditions, bond strength may increase with time for a while (Figure 20). The general trend, however, is towards progressive loss of strength with time, the loss occurring at increasing rate with increasing temperature.

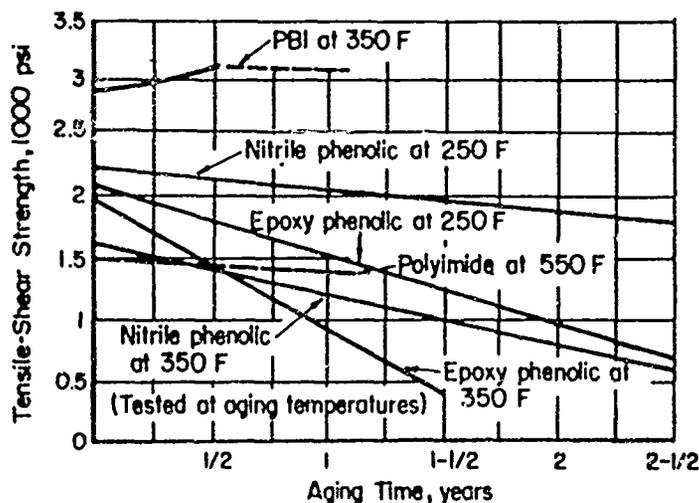


FIGURE 19. EFFECT OF TIME AT TEMPERATURE ON TENSILE-SHEAR STRENGTHS OF JOINTS BONDED WITH VARIOUS ADHESIVES (REF. 44)

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 20 shows the behavior of one adhesive at 600 F in air and in nitrogen, for example.

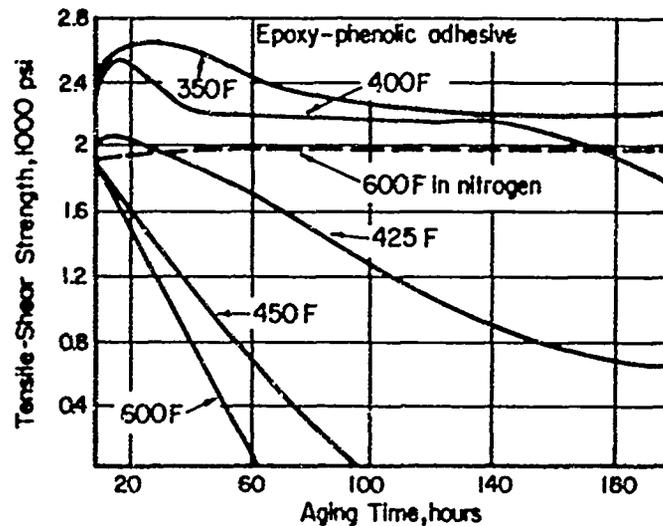
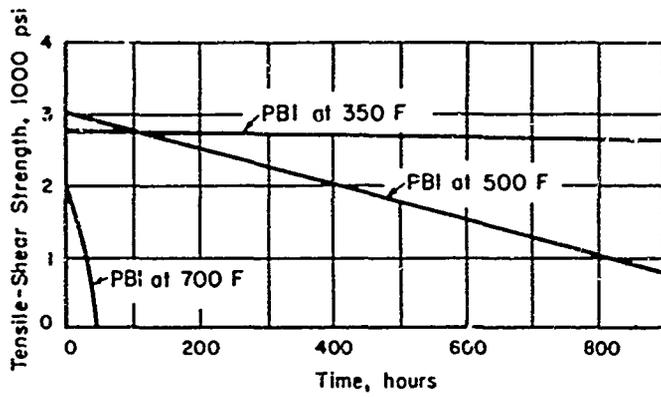


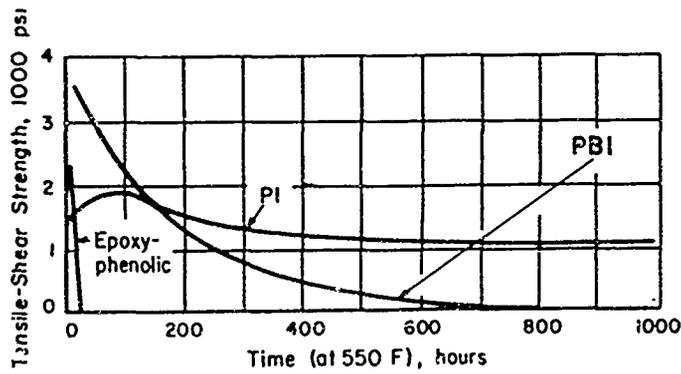
FIGURE 20. EFFECT OF TIME, TEMPERATURE, AND EXPOSURE IN AIR OR IN NITROGEN ON TENSILE-SHEAR STRENGTH OF JOINTS BONDED WITH AN EPOXY-PHENOLIC ADHESIVE (REF. 44)

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. 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 21). It is likely that both types of adhesive will be further developed and will find use for high-temperature applications.

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. 45-50).



a. Polybenzimidazole-Based Adhesive



b. Polyimide-Based Adhesive

FIGURE 21. EFFECTS OF TIME AT TEMPERATURE ON TENSILE-SHEAR STRENGTHS OF POLYBENZIMIDAZOLE- AND POLYIMIDE-BASED ADHESIVES (REF. 44)

Tested at aging temperature.

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. 44) includes adhesives for cryogenic temperature service. Figures 22 and 23, taken from his paper, summarize the tensile shear strengths of different adhesive types and some specific modified phenolic systems. From Figure 22 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 23 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 22 and 23 were taken using adherends other than nickel, and are therefore useful only as a rough guide for nickel-base-alloy bonding.

Recent British experiments (Ref. 51) have been conducted using stainless steel and titanium alloys bonded with epoxy adhesives in which tensile-shear specimens were repeatedly cycled between room temperature and various cryogenic temperatures. After ten complete cycles, the specimens were tested at room temperature. Temperature cycling caused little change in maximum strength but a noticeable increase in strength variation. The investigators noted an embrittling effect of the temperature cycling on the adhesives as evidenced by abrupt failures of cycled specimens during testing. Uncycled specimens pulled apart gradually.

Smith and Susman (Ref. 50) tested three of their developmental cryogenic adhesives using aluminum adherends, after twenty cycles between room temperature and -320 F. They, too, found no significant deterioration of tensile-shear strength following cycling.

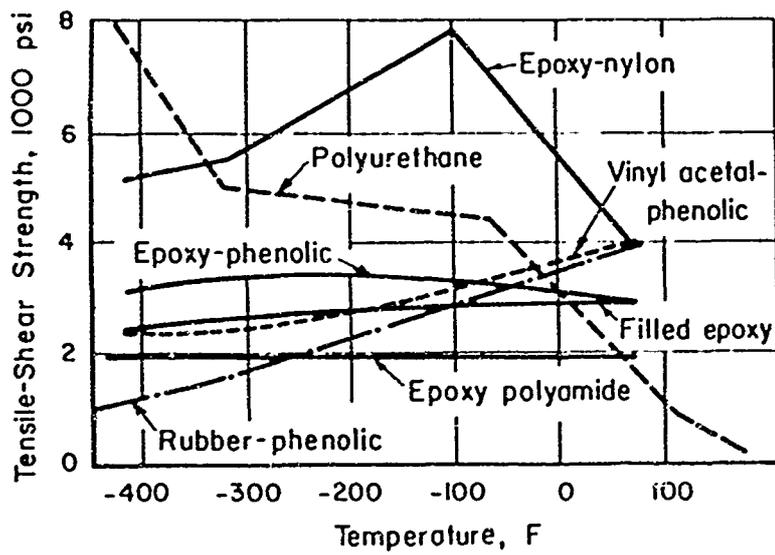


FIGURE 22. TENSILE-SHEAR STRENGTHS OF ADHESIVE SYSTEMS FOR CRYOGENIC SERVICE AS A FUNCTION OF TEMPERATURE (REF. 44)

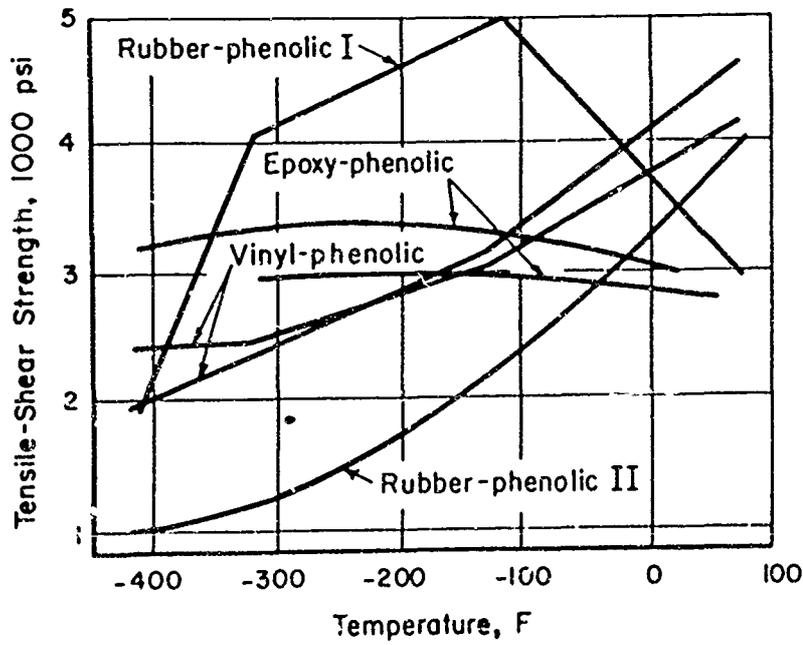


FIGURE 23. TENSILE-SHEAR STRENGTHS OF MODIFIED PHENOLIC ADHESIVES AT CRYOGENIC TEMPERATURES (REF. 44)

Radiation. Kircher and Bowman (Ref. 52) 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 which consider radiation effects on adhesives (Refs. 53-55). 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 in some cases there are constructive chemical reactions 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 nickel-base 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 24, taken from Arlook and Harvey (Ref. 54), 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 was somewhat different.

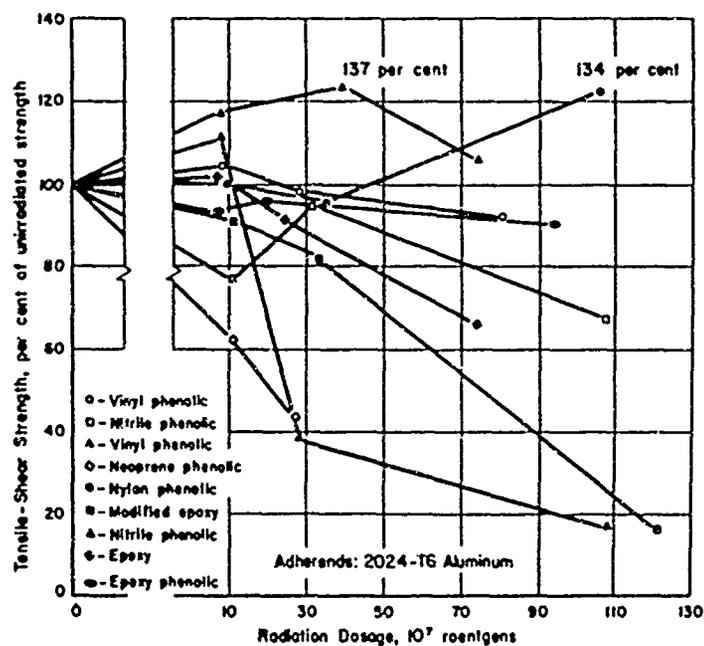


FIGURE 24. TENSILE-SHEAR STRENGTH VERSUS RADIATION DOSAGE (REF. 54)

Specimens tested at room temperature.

McCurdy and Rambosek (Ref. 55), 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 VII). The same investigators report the results of tests made on honeycomb panels using composite film adhesives. In these 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 VII. EFFECT OF GLUE-LINE THICKNESS ON TEE-PEEL STRENGTH OF A NITRILE-PHENOLIC ADHESIVE WITH RADIATION EXPOSURES (REF. 55)

Glue-Line Thickness, mils	Tee-Peel Strength, in-lb/in., At Indicated 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. However, adhesives that can withstand the intense radiation found in the immediate vicinity of nuclear reactors are not presently available.

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, troweling, 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 adherend may be laid on an unheated table and a tacking iron 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 which 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 pounds per square inch. With "100 per cent solids" adhesives, such as the epoxies, such curing pressures are not necessary except in critical work where clamping will be used to control glue-line thickness and alignment. In some cases, parts can be made

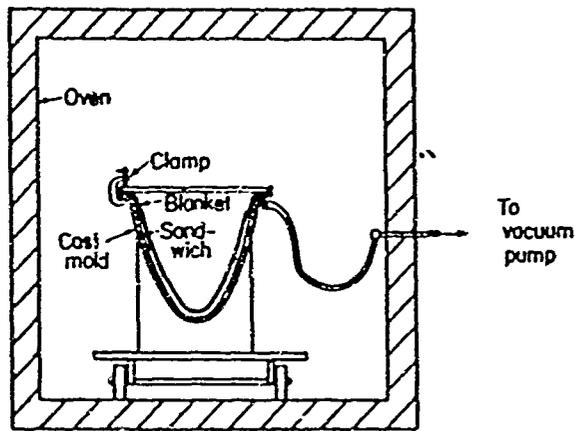
self-aligning and self-clamping by appropriate design. Methods of applying pressure during curing will depend upon the size and shape of the part, the magnitude of the pressure to be applied, and the quantity to be produced. There are several basic methods in use. The simplest method is to make the adherends 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 25a. The vacuum-bag method is limited to pressures below 14 psi, however. Where higher pressures are necessary, the pressure-shell method shown used with a heated mold in Figure 25b can be used. With the pressure-shell method, 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 25a, and, in the same way, the vacuum-bag method could be used with a heated mold.

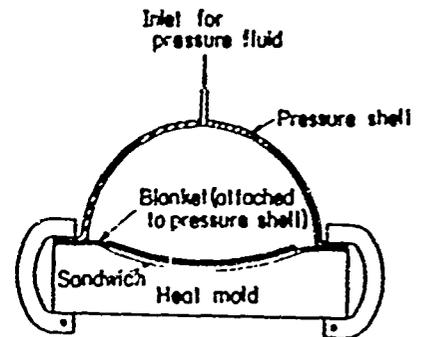
The autoclave method shown in Figure 25c is more elaborate. The part must be sealed into a flexible-blanket assembly vented to atmosphere so that a differential pressure is applied. A hot-inert-gas atmosphere under forced circulation is used in the autoclave. Use of a sheet-metal mold is shown with the 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. However, for such applications as aircraft skins, 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 25d must be used.

CURING

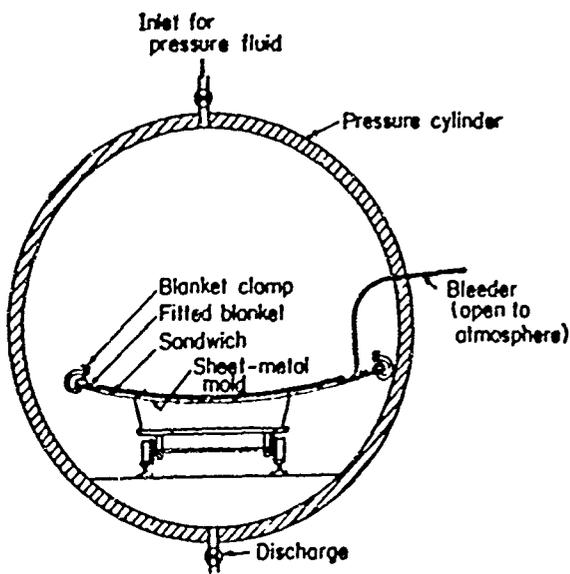
Usually, but not always, the adhesive manufacturer's recommended curing conditions will result in bonds of optimum quality in a given application. Where maximum properties are important, such as for aircraft skin panels, development work by the airframe manufacturer has resulted in complex curing cycles in which heating rates are controlled, and temperatures and pressures are varied during the cure in a precise manner.



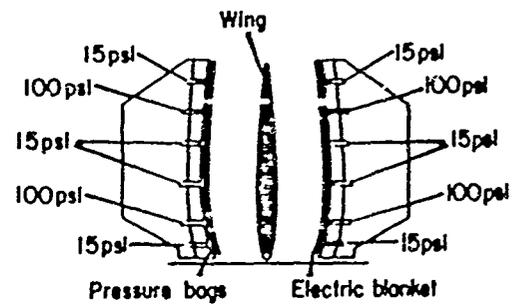
a. Vacuum-Bag Curing



b. Pressure-Shell Curing



c. Autoclave Curing



d. Press Curing

FIGURE 25. METHODS FOR CURING ADHESIVE-BONDED ASSEMBLIES (REF. 31)

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: (1) be certain that the working life has not been exceeded before use, and (2) keep the volume of adhesive small. Considerable heat is often generated during curing.

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

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. 56) 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. 57) 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 26 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 27, 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 commercially available.

Another novel approach to adhesive curing consists of using an exothermic-adhesive-reaction mixture (Ref. 58). The mixture is placed between the surfaces to be bonded and they are then clamped in contact. The parts are then heated to the ignition temperature of the exo-reactant 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 which will cure rapidly.



FIGURE 26. END OF FLAP FABRICATED USING ELECTRICALLY CURING ADHESIVE SHOWING
COPPER BUSES ATTACHED TO HEATING WIRES (REF. 57)



FIGURE 27. END OF FLAP WITH LEADS ATTACHED TO BUSES READY FOR CURING (REF. 57)

CLEANING THE CURED JOINT

Very little cleaning of the organic adhesive-bonded 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. Finally, 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, 39, 40, 59-65, for example), and only a few salient features will be mentioned here.

Adhesive Evaluation. Convair (Ref. 42) 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 which 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 give 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-Meter, the Coindascope, and the Fokker Bond Tester.

At the very least, sonic-bond-testing equipment can detect unbonded regions in adhesive joints. However, if detection of unbonded regions is the only information desired, 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. 66). 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. 67). 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 F₂ and 70 per cent O₂).

BONDING NICKEL-BASE ALLOYS WITH INORGANIC ADHESIVES

Large programs concerned with the development and application of inorganic adhesives were carried out between 1956 and 1962. At the University of Illinois, adhesives were developed for use on 17-7 PH stainless steel, Inconel-X, and Rene 41. Program results for the 17-7 PH have been summarized by Thornton (Ref. 68), and for René 41 by Benzel (Ref. 69). At the Boeing Company, attention was directed particularly toward improvement of the ductility of the Illinois adhesives by the addition of brazing-alloy foils and powders to the adhesive (Ref. 70). At both Boeing and the Aeronca Manufacturing Corporation (Ref. 71), ceramic-adhesive-bonded honeycomb was the desired program objective.

The adherend material used for the bulk of the work on all of these programs was 17-7 PH. On all of the programs, however, some work was done using nickel-base alloys, and it is this portion of these and other programs that will be considered in this report.

SURFACE PREPARATION OF ADHERENDS

Surface-preparation procedures for nickel-base-alloy adherends to be bonded with inorganic adhesives have in some cases been similar to those for adherends to be bonded with organic adhesives. Convair, for example, adapted the following treatment from a stainless steel treatment for an investigation of ceramic-adhesive bonding of René 41: (Ref. 72)

- (1) Remove heat-treat scale by vapor-honing with No. 120 aluminum-oxide grit
- (2) Wipe with methylethyl ketone
- (3) Vapor degrease with stabilized trichloroethylene
- (4) Immerse in the following solution for 4 minutes at 135 F

MF acid*	59.5 grams
(70%) nitric acid	170 milliliters
Tap water to make one liter of solution	

*Proprietary compound of the Wyandotte Chemical Co., Wyandotte, Michigan.

(5) Rinse in running tap water

(6) Immerse in the following solution for 30 minutes at 170 F

Sodium dichromate	113 grams
(96.6%) sulphuric acid	282 grams
Tap water to make one liter of solution	

(7) Rinse in running tap water

(8) Distilled-water spray rinse

(9) Dry at 160 F for 20 minutes.

The more usual surface treatments consist of sandblasting (used by the University of Illinois), heat scaling plus sandblasting, or heat scaling plus etching. If sandblasting is used, it may be followed by a solvent rinse to remove metal dust and abrasive particles.

Aeronca used heat-scaling conditions of 1000 F and 30 minutes on 17-7 PH stainless steel. After air cooling, the adherend was etched in a bath of the following composition to remove the scale:

20 vol % HNO ₃ (63%)
4 vol % HF (70%)
Balance H ₂ O

Etching was done at 150 to 160 F for from 5 to 7 minutes, using the minimum time necessary to remove the scale.

The adherend was then rinsed 5 minutes in cold water, wiped to remove smut, washed, and rinsed an additional 5 minutes.

The adherend was then neutralized in a solution of 0.16 oz/gal borax and 0.48 oz/gal soda ash in water at 125 to 130 F for 30 minutes. Following a 10-min cold-water rinse, the adherend was air dried under forced ventilation. Similar procedures were apparently used by Aeronca for Inconel-X and René 41 adherends.

Boeing used the following surface-preparation treatment on René 41:

- (1) Vapor degrease in trichloroethylene for 3 minutes
- (2) Immerse for 10 minutes in an alkaline solution containing 5 to 12 oz/gal of Oakite 61 at 170 to 190 F
- (3) Rinse for 3 minutes in hot or cold water.

INORGANIC ADHESIVES

Although some experiments were carried out with air-drying cements, silicates, and crystallizable glass adhesives, glassy phase materials were found to be superior metal adhesives. Beginning with the UI 1067 frit having the following raw-material composition:

<u>Parts by Weight</u>	
SiO ₂	38.0
B ₂ O ₃	57.0
Na ₂ O	5.0

Benzel cites results obtained in bonding René 41 with adhesives consisting of mixtures of 60 parts frit to 40 parts of metal powder. Tensile-shear-test results are shown in Figure 28. Addition of

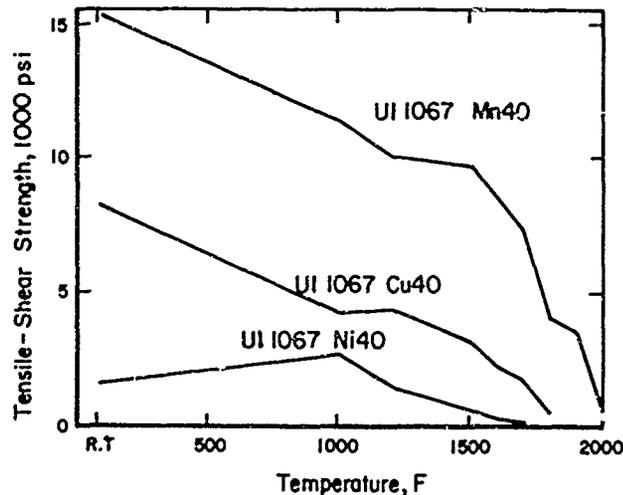


FIGURE 28. TENSILE SHEAR STRENGTH VERSUS TESTING TEMPERATURE OF CERAMIC-RENÉ 41 ADHESIVE COMBINATIONS (REF. 69)

manganese powder gave strengths much superior to additions of copper or nickel powders.

Boeing's best results on René 41 were obtained using an A418 frit composed of:

Parts by Weight

Quartz	94
BaCO ₃	141
Boric acid	29
CaCO ₃	16
ZnO	13
Calcined Al ₂ O ₃	2
Milled zircon	9

with an Alloy 62 (16Ni-16Co-1B-67Mn) brazing-powder interlayer.

Figure 29 shows statistically obtained curves of tensile-shear strengths of the joints obtained, but there was considerable scatter in the individual test points.

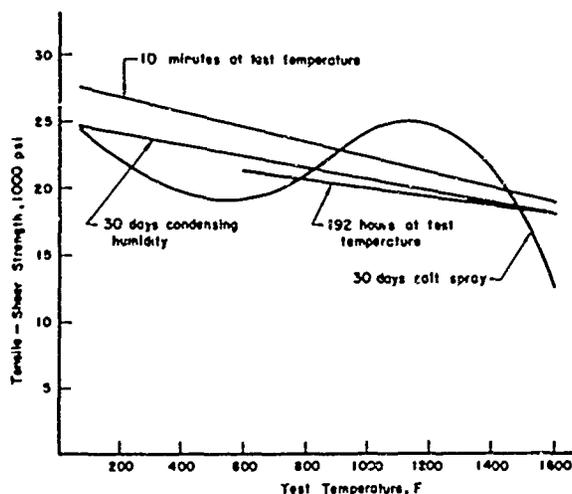


FIGURE 29. TENSILE-SHEAR STRENGTH VERSUS TESTING TEMPERATURE OF CERAMIC-RENÉ 41 ADHESIVE JOINTS (REF. 70)

René 41 was bonded at Aeronca using three adhesives: the A418 frit mentioned above and two compositions designated ACA 100-22 and ACA 100-23, the raw material formulations for which were:

	<u>ACA 100-22,</u> <u>parts by weight</u>	<u>ACA 100-23,</u> <u>parts by weight</u>
Quartz	24.5	23.9
NaNO ₃	8.8	8.6
H ₃ BO ₃	65.3	64.8
NiO	1.4	1.4
Cr ₂ O ₃	--	1.3

Tensile-shear strengths, presumably at room temperature, of the joints made on René 41 adherends were as follows:

<u>Adhesive</u>	<u>Tensile-Shear</u> <u>Strength, psi</u>
A418	1330
ACA 100-22	1780
ACA 100-23	1630

These strengths are quite low in comparison with those reported in Figures 28 and 29. Inconel-X specimens bonded with the same adhesives all failed on removal from the firing furnace. These results show the effectiveness of manganese or high-manganese brazing alloy in improving tensile-shear strength.

APPLYING THE INORGANIC ADHESIVE

Inorganic adhesives are applied to the adherend surfaces as water suspensions (though other suspension media might be used). These suspensions, or slips, should be prepared immediately before use, since they tend to deteriorate on standing longer than a few hours. Presumably this deterioration is by particle agglomeration. The stability and flow properties of slips are critically dependent upon the acidity or alkalinity of the medium. The reader should consult recent textbooks in the field of ceramic engineering for further information.

Slips may be applied to an adherend surface by immersing the adherend in the slip or by spraying the slip onto the adherend. If immersion is used, the slip must be wiped off all surfaces where it is not desired. If spraying is used, considerable skill is necessary to apply a uniform layer.

After the slip has been applied to the surface, it must be allowed to dry before the adherends are placed in registry. The drying

process must not be hurried, or the cake or bisque, as it is called, may form shrinkage cracks.

Thickness of the adhesive in the finished bond may be controlled by using a spacer layer of metal screen in a manner analogous to the use of glass cloth in organic adhesive bonds.

MATURING

The firing temperature that must be used for any ceramic adhesive will depend upon its composition. The firing cycles used for the adhesives mentioned earlier that were used with René 41 were:

Adhesive	Temperature, F	Time, min
UI 1067 Mn40 (University of Illinois)	2200	10
A418/Alloy 62 (Boeing)	2050	20
A418 (Aeronca)	2150	12
ACA 100-22 (Aeronca)	2150	12
ACA 100-23 (Aeronca)	2150	12

The adhesives in the Aeronca program were prefired as follows:

Adhesive	Temperature, F	Time, min
A418	1900-1950	3
ACA 100-22	1750	3
ACA 100-23	1750	3

The firing cycle also served as the solution treatment for the René 41.

FINISHING THE JOINT

Firing of ceramic bodies is preferably done in an oxidizing atmosphere in order to avoid the occurrence of reduction reactions at the surface of the body. This is also true for ceramic adhesives, which means that scale will be formed on the free surfaces of the adherends. If the scale is objectionable it can be removed by one or another of the conventional scale-removal techniques, such as pickling, sandblasting, vapor honing, or machining.

TOOLING AND FIXTURING

Tooling and fixturing for bonding with inorganic adhesives is similar to that used with organic adhesives, with due allowance for the higher temperatures involved. Since inorganic adhesives have not been used commercially in production of large parts, elaborate tooling, such as exists for organic-adhesive-bonded aircraft parts, has not been built. Large autoclaves and electric blankets are clearly impractical for the temperatures required with inorganic adhesives. Furnaces are required, although quartz heat lamps have been successfully used as well. Figure 30 shows a cross section drawing of Aeronca's fixture for making honeycomb panels. It is analogous to fixtures used in fabricating such panels by organic-adhesive bonding or by brazing.

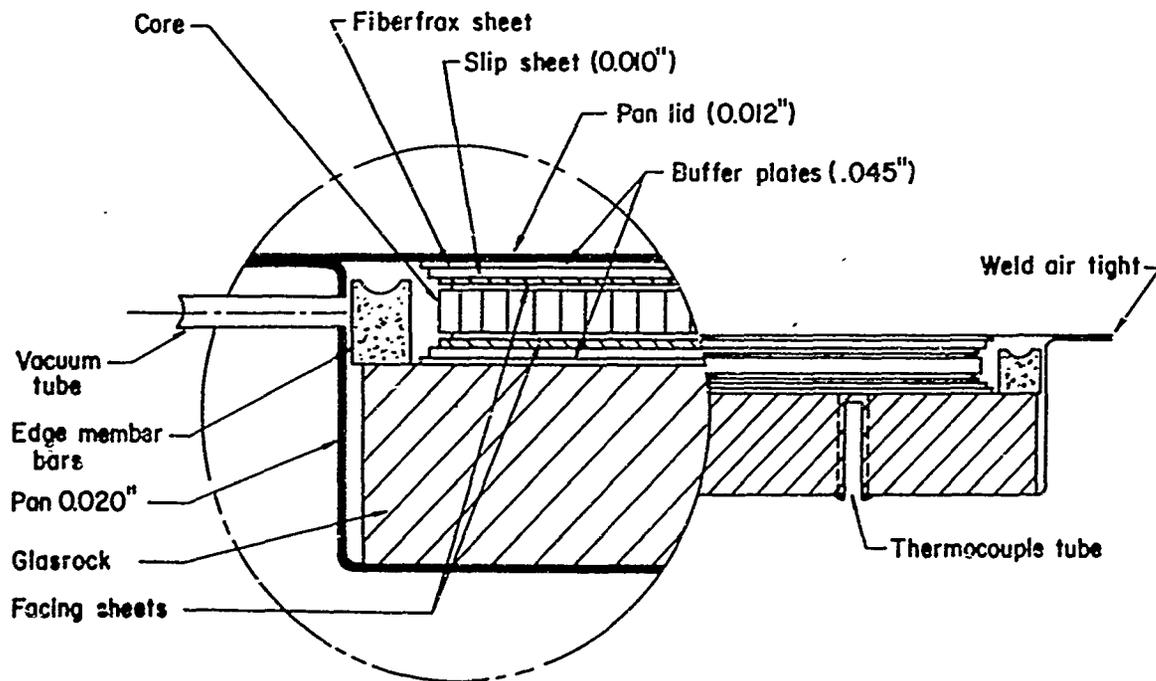


FIGURE 30. TYPICAL CERAMIC ADHESIVE BONDING VACUUM PRESSURE FIXTURE (REF. 71)

CONCLUSIONS AND RECOMMENDATIONS

The problems encountered in adhesive bonding of nickel and nickel-base alloys are those associated with adhesive bonding in general. The problem areas will be discussed under four headings: adhesion, adhesives development, processing, and service behavior. The field of adhesive bonding is an active one, and work on most of these problems is already under way.

ADHESION

Despite research extending over a number of years, puzzling questions remain concerning the forces of adhesion. Calculations made using present knowledge of the long-range molecular forces indicate that adhesion should occur much more generally and between a far wider range of materials than it does. While it is fortunate for the functioning of civilization that this is the case, our inability to predict in detail the occurrence and nonoccurrence of adhesion indicates a lack of knowledge. The study of surfaces by such techniques as field ion-emission microscopy and low-energy electron diffraction can be expected to give useful insight into numerous surface phenomena including adhesion, but investigations of surfaces are always difficult. Properties of the two-dimensional surfaces themselves must be carefully distinguished from bulk properties of the underlying solid or liquid.

A related problem area is the understanding of the role of surface films in adhesion. With the advent of high-vacuum technology, oxide films and layers of adsorbed gases were identified as being responsible in many cases for the prevention of adhesion between solid surfaces. Adhesion occurred when these films were evaporated in vacuum, with disastrous results in the case of bearings, for example. In more normal atmospheres, however, these naturally occurring films are always present. It is often necessary to deliberately apply other films to surfaces in order to obtain corrosion resistance or a pleasing appearance. As has been pointed out in this report, the surface-preparation procedures of metal surfaces for adhesive bonding leave reaction products in the form of films. It is probably a safe statement that in most cases an adhesive molecule is not aware of the nature of the metallic adherend, but bonds to the surface film, the composition of which is only indirectly related to the adherend-alloy

composition. Surface treatments for adherends have been empirically arrived at, and there is almost no systematic understanding of the desirable compositions, thicknesses, and morphologies of adherend surface films for optimum adhesive-bond properties. Furthermore, the authors know of no fundamental work presently under way in this area. In some ways, investigation of surface films is even more difficult than that of clean surfaces, because distinctions must be drawn between the bulk and surface effects of both the film and the underlying substrate. It is likely, however, that some of the understanding gained from the study of extremely thin vacuum-deposited and electroplated films for electronic applications could be useful in understanding the effects of films on adhesion.

ADHESIVES DEVELOPMENT

The tailoring of adhesive molecules for particular applications is a very active field of development, and it is difficult to point out any areas that are not already receiving attention from competent chemists. The need for organic adhesives capable of service at higher temperatures is a continuing urgent need. The heterocyclic adhesives presently being developed are promising high-temperature adhesives as well as being good room-temperature adhesives. They also have superior radiation resistance compared to many other organic compounds, which is desirable. For low-temperature service, the polyurethanes are apparently going to be satisfactory for liquid-hydrogen temperatures, but their serviceability at even lower temperatures - liquid helium and on towards absolute zero - has yet to be demonstrated. From the temperature-strength dependence of the polyurethanes down to -423 F, however, one would predict that they will be satisfactory at even lower temperatures.

Inorganic adhesives, if they can be designed having increased ductility, good bond strength, and reasonable maturing temperatures, would find application in high-temperature structures. Considerable research has been done, however, without having achieved these goals.

PROCESSING

From the manufacturing viewpoint, adhesive systems are desired that are easily applied, tolerant of shortcomings in adherend preparation, cure at room temperature or with only a short, moderate-temperature curing cycle, non-toxic, and inexpensive. These ideal goals appear to be incompatible to some extent with the desired performance of adhesives. For example, it is difficult to visualize

an adhesive capable of high-temperature service that does not also require a relatively high curing temperature. Nevertheless, these goals of manufacturability should be kept in mind by those engaged in adhesive development.

Novel methods of handling, applying, and curing adhesives that enable the bonding process to be reliably accomplished in the field will be welcomed. The internally heated film adhesives and the room-temperature-curing epoxy film recently introduced are useful contributions in this area. The chemically blocked adhesives, such as the newly marketed silicone sealants, are another example. Work needs to be done on mechanically blocked adhesive preparations, in which the hardeners are encapsulated in frangible membranes and distributed throughout the resin. Activation is accomplished in such systems by mechanical rupture of the membranes. Suitable membrane materials capable of withstanding the chemical action of resins and hardeners are needed.

SERVICE BEHAVIOR

More understanding needs to be gained of the interaction effects of combined environmental factors, such as temperature, humidity, stress, and time, on the useful life of adhesive-bonded joints. Testing procedures need to be developed and standardized for combined-factor testing.

Nondestructive-testing techniques capable of determining as-welded bond strength and of considerable sophistication have been developed for examination of adhesive bonds. Further refinement of these techniques or the development of others to enable the detection of in-service or postexposure loss of bond strength would be desirable.

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This document has also been reviewed and approved for technical accuracy.



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