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RESEARCH MEMORANDUM

METAL-BONDING ADHESIVES FOR HIGH-TEMPERATURE SERVICE

By John M. Black and R. F. Blomquist

Forest Products Laboratory

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SUMMARY

The results of an investigation made for the purpose of developing a metal-bonding adhesive with improved heat-resistant properties are reported. The most promising results were obtained with a formulation of a phenol resin and an epoxy resin with certain heat stabilizers and catalysts. The formulation has high resistance to aging at 550° F and is particularly promising in tape form for bonding sandwich constructions. An improved straight epoxy-resin adhesive that has superior strength properties at 250° to 300° F compared with any other known epoxy-resin adhesive formulation is also reported.

INTRODUCTION

This report presents one phase of an investigation of experimental adhesive formulations with improved performance and heat-resistant properties for structural bonding of metal to metal in aircraft fabrication which has been conducted at the Forest Products Laboratory under the sponsorship and with the financial assistance of the National Advisory Committee for Aeronautics. Particular attention has been given to the development of adhesives of phenol and epoxy resins that are less sensitive to variations in bonding techniques and that have better strength in joints over the range of -70° to 600° F. Earlier results of this investigation have been reported in references 1 and 2.

Reference 1 described adhesive FPL-710, an adhesive that developed promising shear strength when tested at temperatures up to 600° F and possessed good resistance to aging at temperatures as high as 450° F. The principal limitations of adhesive FPL-710 were that it was somewhat brittle, it possessed marginal bending and fatigue strength and variable performance at 600° F, and the optimum film thickness for bonding (0.002 inch) was too thin for practical use in aircraft. Reference 2 described further work on and development of FPL-710 adhesive. The variable performance in immediate tests at 600° F was improved by post-curing the adhesive and by impregnating it into a glass-mat carrier to form a tape adhesive. The tape adhesive increased the optimum film thickness for bonding to 0.010 inch, which made it more practical in industrial bonding applications. The resistance of adhesive FPL-710 to aging at 550° F was also improved by the addition of certain chelating agents to the adhesive mixture. The tape adhesive, however, was still quite brittle, and low resistance to peel, was somewhat variable in its performance after aging at 550° F, and lacked adequate flow and filleting action to be completely satisfactory for the bonding of honeycomb sandwich construction.

The present report includes additional work on FPL-710 adhesive and covers the development of FPL-878 liquid and tape adhesives and FPL-881, an epoxy-resin adhesive. The FPL-878 adhesives are considered improvements over FPL-710 adhesive in many respects and are particularly promising in tape form for the bonding of heat-resistant sandwich materials. For this investigation a large amount of experimental work was performed in order to determine the most promising components for the adhesives, the optimum proportions of these components, and the optimum conditions under which the resultant formulations could be used. In order to make this report more concise, only the more important trends in the work are discussed and only selected typical data are included to illustrate these trends and to demonstrate properly the performance of the three most promising experimental adhesive formulations designated as FPL-710, FPL-878, and FPL-881.

EXPERIMENTAL PROCEDURE

Since many of the experimental procedures used in individual experiments were typical only of that experiment, such procedures are outlined only briefly in the section entitled "Discussion of Experimental Results." The procedures described herein for preparing the metal for bonding and for conducting the strength tests were common to most of the experiments.

Preparation of Metal for Bonding

The aluminum surfaces were prepared for bonding by immersion for 5 to 10 minutes in a solution of sulfuric acid (10 grams) and sodium dichromate (1 gram) in 30 grams of water at 140° to 160° F. The panels were rinsed in cold running water, then in hot water or steam, and then were air dried.

The stainless-steel surfaces were cleaned by the following methods:

(1) A 10-minute immersion at 190° F in a solution of:

Sodium metasilicate, parts by weight	21
Tetra sodium pyrophosphate, parts by weight	11

Sodium hydroxide, parts by weight	11
Nacconol NR (wetting agent), parts by weight	3.5
Water, parts by weight	910

The panels were rinsed in cold water, then in hot water or steam, and then were air dried.

(2) Cleaning by method (1) followed by a 10-minute immersion at 190° F in a solution of:

Oxalic acid, parts by weight	10
Sulfuric acid (sp. gr., 1.84), parts by weight	10
Water, parts by weight	80

The panels were rinsed in cold water, then in hot water or steam, and then were air dried.

(3) Cleaning by method (1) followed by a 10-minute immersion at 190° F in a solution of:

Hydrofluoric acid (48 percent), parts by volume	15
Sulfuric acid (sp. gr., 1.84), parts by volume	10
Water, parts by volume	25

The panels were rinsed in cold water, then in hot water or steam, and then were air dried.

Test Methods

Specimens of 0.064-inch 2024-T3 (24S-T3) clad aluminum alloy with 0.5-inch overlap, as described in reference 3, were used for the evaluation of bending strength and shear strength. Two lap panels, each 8 inches wide, were bonded for each variable. Each panel was then cut into 7 individual test specimens, and the 14 specimens per variable were then divided into three representative groups. One group of five specimens was tested as a control group at room temperature, another group of five specimens was aged for 200 hours at 550° F and then tested at room temperature, and the final group of four specimens was tested immediately after reaching equilibrium at 600° F.

Lap shear specimens were loaded in self-alining grips at the rate of 300 pounds per 0.5 square inch per minute.[1] Specimens for the bending tests were loaded flatwise at the center as a simple beam with a 1.5-inch span at the rate of 200 pounds per minute, as described in reference 3. The loading block was over the center of the bonded area.

Test temperatures were controlled during heat-aging and testing to within ±3° F of the desired temperature. In tests at elevated temperatures, a period of 3 to 5 minutes was required to heat the specimens from

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[1]This is the slower rate prescribed in reference 4, which preceded reference 3.

room temperature to the test temperatures. In tests made at elevated temperatures and at -70° F, the load was applied as soon as the specimen reached the desired temperature.

In order to get some information on the peel properties of the FPL-878 adhesive in a typical sandwich construction, some limited tests were made. Since no well-standardized peel tests for adhesives have yet been described, an experimental procedure was selected that was currently under study at the Forest Products Laboratory as a part of another project conducted in cooperation with the U. S. Air Forces. For this test, sandwich specimens (3 by 12 inches) of 0.020-inch clad 2024-T3 aluminum faces bonded to 1/2-inch-thick aluminum honeycomb cores (3/16-inch cell, 0.002-inch foil) were tested by peeling over an experimental peel-test apparatus with a 4-inch-diameter drum. The peel-test apparatus was equipped with a movable table and tension spring to maintain movement of the test specimens at the same rate as peeling. A peeling rate of approximately 12 inches per minute was used, and an autographic recording was made of load versus distance peeled.

DISCUSSION OF EXPERIMENTAL RESULTS

FPL-710 Adhesive

Resistance to aging at 550° F.- The effect of several different chelating agents on the resistance of FPL-710 adhesive to aging for 200 hours at 550° F was reported in reference 2. The data presented in this reference indicated that a few of the chelating agents were effective in improving the resistance of the bonds to heat-aging. It was thought that the agents reduced the activity of trace elements, such as copper and iron in the clad-aluminum surface, that could be contributing to the oxidation and deterioration of the adhesive during heat-aging.

This phase of the study was continued and other chelating agents were investigated. In a study of FPL-710 adhesive in methyl ethyl ketone, a quantity of 1 percent chelating agent, based on the weight of the resin solids of adhesive, was employed, and joints were tested at 80° F after aging for 200 hours at 550° F. The results of these tests are shown in the following tabulation:

Chelating agent	Shear strength at 80° F after 200 hours at 550° F, psi
None	670
8-Quinolinol	960
Copper 8-quinolinol	298
n-Propyl gallate	1,074
Gallic acid	820
1-Hydroxy-2 naphthoic acid	486
3-Hydroxy-2 naphthoic acid	414
5-Phenyl salicylic acid	320
Salicylic acid	890
Salicylaldehyde	785
Acetyl-acetone	985
Acetonyl-acetone	965
Aluminum triacetonyl-acetonate	960
Catechol	980
o-Amino-phenol	320
Ethylenediamine	835
Oxalic acid	120
Mucic acid	480
Tartaric acid	320
Copper citrate	480
Triethanolamine titanate	440

Several of the chelate stabilizers were promising for retarding the degradation of the adhesive on aging at elevated temperatures. The n-propyl gallate appeared most effective, but 8-quinolinol, gallic acid, salicylic acid, salicylaldehyde, acetyl-acetone, acetonyl-acetone, aluminum triacetonyl-acetonate, catechol, and ethylenediamine were also quite effective when results were compared with those from the control specimens. Although 8-quinolinol was an effective stabilizer, the copper salt of 8-quinolinol was quite ineffective and actually appeared to contribute to the rate of thermal breakdown of the adhesive.

Subsequent bonding with FPL-710 adhesive formulations containing the better chelate stabilizers shows a definite improvement over the control-specimen bonds in the resistance of the bonds to aging at 550° F. The spread in individual strength values was reduced, but the problem of obtaining consistently high strength bonds remained. In attempting to overcome this limitation, a study was made of many bonding variables and variations in the adhesive formulation. Bonding variables studied included preparation of the metal surface, age of the stock adhesive, age of the thinned adhesive, percentage of hexamethylenetetramine curing agent, time of reflux in preparation of the adhesive, precure and curing conditions, and the type of solvent and thinner employed in the adhesive. The results of these studies showed no definite trend in the reduction of joint-strength variability after heat-aging, with the exception of the type of solvent and thinner. In this study toluene, ethyl acetate, and methyl ethyl ketone were employed, and results showed that ethyl acetate, solvent and thinner reduced the variability of results to a slight degree. The following formula appeared most promising for this adhesive:

Bakelite BV 9700 (phenol resin)[a], g	100
Epon 1007 (epoxy resin)[b], g	20
Ethyl acetate, g	20
Hexamethylenetetramine, g	4
n-propyl gallate, g	0.8

[a]A product of Bakelite Corp., reported to have approximately 60 percent solids in solution form

[b]A solid resin produced by Shell Chemical Corp.

This adhesive formulation was then used for the determination of resistance to salt-spray exposure and for the development of the mat tape.

Salt-spray exposure.- The salt-spray exposure tests of panels bonded with FPL-710 were conducted in accordance with reference 3. The results of salt-spray exposure tests were as follows:

Panel (a)	Shear strength after exposure, psi (b)		Type of failure, percent (c)	
	Average	Range	Adhesion	Cohesion
1592-1-1	2,771	2,665 to 2,970	100	0
1592-1-2	2,951	2,845 to 3,065	99	1
1592-1-3	2,896	2,835 to 3,005	100	0
1592-1-4	2,860	2,700 to 2,930	99	1
1592-1-5	2,893	2,670 to 3,065	100	0
1592-1-6	2,915	2,860 to 3,005	98	2

[a]Five specimens were exposed and tested from each panel.

[b]Average control strength of this group of panels before exposure was 2,440 psi.

[c]Values are estimated averages.

These tests showed that the FPL-710 adhesive bonds had a high degree of resistance to salt-spray exposure and were consistently higher in shear strength than the 2,000 psi required in reference 3.

Development of tape adhesive.- Preliminary tests reported previously indicated that bonds made with FPL-710 adhesive impregnated into glass cloth to form a supported tape adhesive resulted in improved shear strength of lap joints tested immediately at elevated temperatures, such as 600° F. The tape adhesive was also found to be more satisfactory for bonding metal faces to honeycomb core material than the liquid adhesive.

In view of the encouraging results of these preliminary tests, work on methods of making the tape more uniform and freer of volatiles was continued. Various impregnation methods by dipping and spraying were tried in addition to solvent casting of the adhesive onto the mat on sheets of Teflon. The principal problem in each case was to remove the solvent from the adhesive film without overcuring the adhesive and to prevent skinning over the film thus entrapping the solvent and resulting in formation of bubbles. A method of building-up the film thickness by multiple thin coats was most promising but was far too slow and laborious to be practical. In bonding clad-aluminum faces to high-strength phenol-resin-impregnated glass-cloth honeycomb cores, it was observed that the adhesive did not flow and fillet adequately about the edges of the honeycomb to develop a bond strength high enough to fail the core in flexural tests. It seemed desirable to improve the flow of resin during cure to overcome this limitation. An adhesive formulation employing phenol resins with a lower molecular weight and softening point should allow the film to remain fluid at the precure temperature and thus more readily permit the loss of volatiles to occur during precuring. Such a formulation would also have a longer flow life during cure, which would be advantageous. Therefore, the development of FPL-710 composition as a tape adhesive was discontinued in order to concentrate on such a combination of resins.

FPL-878 Adhesive

Although the liquid adhesive FPL-710 described previously had excellent strength properties at temperatures up to 600° F and showed good aging characteristics at 550° F when used to bond aluminum lap joints, it was unsatisfactory for bonding metal faces to honeycomb cores in sandwich construction and for bonding larger areas in metal laminating because of insufficient film thickness, inadequate flow, and inadequate filleting action of the adhesive during the curing cycle. Effective use of a thicker film of the liquid adhesive to get the desired filleting and flow was limited by the problems arising from the additional solvents incorporated in a thicker film.

Further work included the investigation of various phenol resins and epoxy resins that could be substituted into the original FPL-710 formula to improve the flow and the release of solvents during drying of the adhesive. The use of a phenolic resin, Durez 16227, to replace most of the Bakelite BV 9700 improved these properties markedly over the FPL-710 adhesive. The following discussion of the results is a summary of the most important effects of variations in formulation and bonding procedures in the development of adhesive FPL-878.

Effect of composition.- In the initial stages of development, the optimum ratio of phenol resin Durez 16227 to epoxy resin Epon 1007 was determined by dissolving the resins and other components in ethyl acetate to give a solids content of about 70 percent and applying the liquid adhesive by brush to cleaned clad aluminum-alloy surfaces. The following results of tests show how the strength of bonds tested at room temperature and immediately at 600° F was affected by the ratio of the two resins in the adhesive:

Durez 16227, g	Epon 1007, g	Shear strength, psi	
		At 80° F	At 600° F
100	--	1,924	688
100	5	1,650	1,010
100	10	1,706	744
100	20	2,090	774
100	25	2,100	618
100	30	2,236	682
100	40	1,884	202

In a subsequent series of tests evaluating the effect of different epoxy resins, 100 parts by weight of the phenol resin, Durez 16227, were modified with 20 parts by weight of several different epoxy resins in ethyl acetate and the shear strength of the lap joints was determined at room temperature and immediately at 600° F. The results were as follows:

Epoxy resin	Shear strength, psi	
	At 80° F	At 600° F
Epon 1009	1,460	670
Epon 1007	1,790	646
Epon 1001	1,308	452
Epon RN-34	1,204	512
Epon RN-48	1,302	750

Based on the results of these tests, a formulation of 100 parts of Durez 16227 and 20 parts of Epon 1007 was selected for further study. The addition of small amounts of hexamethylenetetramine, which was used as curing agent in FPL-710 to increase bond strength at 600° F, was found to be unnecessary in these formulations. In fact, it actually caused a reduction in the shear strength of bonds tested immediately at 600° F. In an effort to increase the strength of bonds at 600° F, small amounts of Bakelite BV 9700, a phenol resin which cures faster than Durez 16227, were added to the formulation of Durez 16227 and Epon 1007. The shear strength of several of these adhesive formulations when tested immediately at 600° F was as follows:

Durez 16227, g	Epon 1007, g	BV 9700, g	Shear strength, psi	
			At 80° F	At 600° F
100	20	--	1,790	644
100	20	10	1,622	704
100	20	20	1,488	930
100	20	30	1,442	966

The addition of increasing amounts of the phenol resin BV 9700 to the mixture of Durez 16227 and Epon 1007 resin resulted in an increase in bond strength at 600° F. The strength of the bonds at 80° F, however, was decreased, indicating that the adhesive was made more brittle at normal temperatures. The composition of 100 parts of Durez 16227, 20 parts of Epon 1007, and 20 parts of Bakelite BV 9700, which appeared to be the most promising combination and the best compromise in strength properties, was selected for further study in aging tests. This was the basic formulation from which FPL-878 adhesive was derived.

Resistance to aging at 550° F.- A study of the performance of adhesive FPL-878 in clad aluminum lap joints when aged at 550° F for 200 hours showed that a considerable loss in strength may occur as a result of thermal decomposition or degradation of the adhesive. The following results of tests made before and after aging at this condition show that only 16 percent of the initial strength was retained. The bonds were initially cured at 350° F for 60 minutes after a precure of 45 minutes at 270° F.

Heat-exposure conditions		Shear strength at 80° F, psi
Time, hr	Temperature, °F	
None	---	1,488
200	550	240

The addition of 1 percent of n-propyl gallate based on the resin solids of the FPL-878 formulation, which was known to be an effective chelate stabilizer in the FPL-710 adhesive, improved the thermal resistance as follows and showed over 100-percent increase in strength after aging:

Heat-exposure conditions		Shear strength at 80° F, psi
Time, hr	Temperature, °F	
200	550	553

Further study of bonding variables in the use of FPL-878, particularly precure conditions, revealed the possibility of even greater improvements in the resistance of the adhesive to aging for 200 hours at 550° F. In an experiment where the precure of the adhesive was varied from 15 minutes to 45 minutes at 270° F, the strength of bonds after aging was increased as the precure period was shortened. The following data indicate that possibly some component which contributed to greater thermal resistance was lost from the adhesive or was otherwise inactivated during the longer precure periods. At present, an explanation of a mechanism for such a phenomenon is not available.

Precure period at 270° F, min	Shear strength at 80° F after 200 hours at 550° F, psi	
	(a)	(b)
15	952	780
30	665	330
45	553	240

[a]Adhesive contained 1 percent of n-propyl gallate.

[b]Adhesive contained no n-propyl gallate.

The performance of adhesive FPL-878 containing no n-propyl gallate was likewise improved when shorter precure periods were employed. This indicated that the n-propyl gallate was not being destroyed during precure but that some components of resins in the adhesive were adversely affected.

Further study of the effect of varying amounts of n-propyl gallate stabilizer revealed that the amount of n-propyl gallate affected the strength properties of the bonds initially at 80° F and also the immediate strength at 600° F. Increased amounts of n-propyl gallate seemed to have a plasticizing effect on the adhesive and resulted in increased bond strength at 80° F but decreased bond strength at 600° F, as shown in the following data on lap joints that were bonded at 300° F for 60 minutes after a precure period of 30 minutes at 270° F:

Amount of n-propyl gallate, percent	Shear strength, psi, at -	
	80° F	600° F
0	1,930	350
1	1,952	284
3	2,546	174

The addition of certain organic acids to the adhesive formulation with n-propyl gallate increased the rate of cure and increased the joint strength of bonds tested immediately at 600° F. This was considered indicative of more thorough cross-linkage and greater cure. The results of shear tests of lap joints bonded with FPL-878 adhesive, with 1 percent n-propyl gallate and 1 or 2 percent of one of several different organic acids, which were also considered as chelating agents, to accelerate the rate of cure, are shown in the following table. The lap-joint specimens were bonded at 300° F for 60 minutes after a precure of 15 minutes at 270° F.

Acid accelerator	Shear strength, psi, at -			
	80° F (a)	600° F (a)	80° F (b)	600° F (b)
None	2,243	339	952	302
3-Hydroxy-2-naphthoic, 2 percent	2,350	650	1,298	776
1-Hydroxy-2-naphthoic, 2 percent	2,176	894	1,376	866
Salicylic, 2 percent	2,450	720	1,264	724
5-Phenyl salicylic, 2 percent	2,150	624	1,248	764
Benzene sulfonic, 1 percent	2,316	230	1,162	636

[a]Tested immediately at temperature shown

[b]Tested at temperature shown after 200 hours at 550° F.

The most effective of these acid accelerators was 1-hydroxy-2-naphthoic acid. The addition of this acid accelerator to the adhesive formulation which also contained 1 percent of n-propyl gallate produced the most promising heat-resistant adhesive developed during this investigation. This adhesive was designated FPL-878, and its composition, method of preparation, and use are as follows:

Durez 16227 (phenol resin)[a], g	125
Bakelite BV 9700 (phenol resin), g	33
Epon 1007 (epoxy resin), g	20
Ethyl acetate, g	20
1-Hydroxy-2-naphthoic acid, g	2.8
n-Propyl gallate, g	1.4

[a]A product of Durez Plastics and Chemicals, Inc., reported to contain approximately 80 percent solids in solution form.

The adhesive is prepared by dissolving the Epon 1007 resin in the ethyl acetate, to which the remaining components may be added and readily dissolved by warming and thorough mixing. Storage in a closed container at room temperature for a period as long as 3 months has produced no adverse effect either on the use conditions or on the quality of joints made after storage. The approximate solids content of the adhesive is 78 percent.

The following steps in bonding procedure are recommended for most consistent results with FPL-878:

(1) Prepare the metal surfaces for bonding by an effective chemical cleaning method. For bonding aluminum, an immersion in a solution of sulfuric acid and sodium dichromate is recommended. For bonding stainless steel, immersion in a solution of sulfuric acid and oxalic acid appears most effective. These cleaning methods were described in detail in the section entitled "Experimental Procedure."

(2) Thin 10 parts by weight of the adhesive with 10 parts by weight of ethyl acetate. The thinned solution has been used for 2 months without adverse effects. Apply one brush coat to each surface to be bonded. Application by spray or roller has not been studied.

(3) Precure the adhesive film for 15 minutes at 270° F.

(4) Assemble the parts to be bonded and press at 320° F for 1 hour. For optimum strength properties at elevated temperatures, the bond should be postcured for 16 hours at 270° F. Minimum curing and postcuring requirements have not been established.

Bonding of stainless steel.- A limited investigation was made of the liquid adhesive FPL-878 for bonding stainless steel. This work consisted primarily of studying the effect of several methods of preparing the surface for bonding on the strength properties of the bond and the resistance of these bonds to aging for 200 hours at 550° F. The results of lap shear tests of specimens of T302, 1/2 hard, 0.020-inch-thick stainless steel after a precure of 15 minutes at 270° F and an initial cure of 60 minutes at 320° F are shown in the following tabulation:

Method of cleaning (a)	Shear strength, psi, at 80° F	
	Unaged (b)	Aged (c)
Metasilicate-pyrophosphate degrease	1,664	92
Sulfuric acid - oxalic acid	4,292	160
Sulfuric acid - hydrofluoric acid	2,408	0

[a]Methods of preparing stainless steel for bonding are described fully in section entitled "Preparation of Metal for Bonding."

[b]Specimens tested after initial cure only.

[c]Specimens tested after aging for 200 hours at 550° F.

The most effective cleaning method was immersion in a bath consisting of 10 percent each of sulfuric acid and oxalic acid in water. The metal was first degreased in a metasilicate-pyrophosphate bath, then immersed in the acid bath for 10 minutes at 190° F, and then rinsed and air dried. The average strength of these bonds at room temperature initially was 4,292 psi, which far exceeded the highest individual strength of any bonds made between surfaces of clad aluminum alloy. The strength of the bonds after aging at 550° F, however, was very low and much inferior to bonds between surfaces of aluminum made with this adhesive after similar aging. Preparing the metal for bonding with the sulfuric-acid—hydrofluoric-acid treatment had an exceedingly adverse effect on resistance to aging, and the bonds were completely charred and decomposed and had no strength.

In similar tests of stainless-steel joints made with FPL-710 adhesive, initial dry shear strength was 2,190 psi and strength after 200 hours at 550° F was 1,490 psi. Only very light charring was noted when the metal was prepared by using a solution of hydrochloric acid, hydrogen peroxide, and formalin. Several other chemical treatments gave low heat-aging results and showed jet-black charring of the adhesive bond. Generally high degrees of black charring were observed after heat-aging of stainless-steel joints made with FPL-710 and FPL-878, whereas joints on aluminum showed only lightbrown discoloration after aging. This might be expected to be due to a larger degree of physical cracking or crazing of the adhesive film on the stainless steel during aging, thus allowing greater entry of oxygen and resultant oxidation. However, one set of joints on aluminum made with FPL-878 liquid adhesive applied in narrow strips to give a discontinuous glueline so that such oxidation could presumably occur more readily in the aluminum joints did not show abnormal charring or poor aging characteristics as noted for the stainless-steel joints.

These limited tests on stainless steel along with the other work, not reported, on clad aluminum alloy indicate quite definitely that the type of metal and the methods of preparing the metal for bonding have a very marked effect on both the initial shear strength and the strength of the adhesive joints at elevated temperatures and after heat-aging. A more extensive study of metal bonding along these lines is needed to understand the effect of the type of metal and of the preparation of the metal surface on thermal degradation. This information would also be helpful in formulation of more heat-resistant adhesives.

Development of tape adhesive.- The more desirable features of adhesive FPL-878 as compared with FPL-710, such as greater film thickness, greater ease in solvent removal, and improved flow properties, made FPL-878 particularly promising for further study and development into a supported tape adhesive. The development of a tape adhesive was considered to be of special importance since it would make the adhesive more practical and easier to use, both in the laminating of metal and also in the bonding of various face materials to honeycomb cores in sandwich construction.

Since no facilities were available for making unsupported films, preliminary investigations of various glass-fiber cloths and mats for carriers for supported films were undertaken. The best material appeared to be a glass-fiber mat that was approximately 0.010 inch thick and weighed 0.0071 pound per square foot (Owens-Corning Fiberglas Mat S11L). The mat material as a carrier seemed to have better blotting and holding properties than did available cloths, and its use made possible an adhesive tape with greater resin solids per unit area. The cost of the glass mat, approximately 1 cent per square foot, was also considerably less than that of the glass-fiber cloth.

Various methods of impregnating the liquid adhesive FPL-878 into the mat by dipping, spraying, and solvent casting were investigated. A method employing solvent casting on Teflon film was most promising. The procedures for preparing the FPL-878 tape adhesive and for its use are as follows:

The mat tape adhesive is prepared by impregnating the FPL-878 liquid adhesive (not thinned) into a glass-fiber mat or cloth by a solvent-casting method on Teflon film. In this process, the Teflon film is laid on a flat surface, and about one-half the required amount of unthinned liquid adhesive is spread out evenly over the area. The glass mat or cloth is then laid on top of this and worked down through the liquid adhesive. The remainder of the liquid adhesive is then applied to the glass-fabric surface and rolled out evenly with hard-rubber hand rollers. The whole assembly is precured at 270° F for 35 minutes. Immediately after removal from the precuring chamber, the hot liquid-adhesive surface is covered with another film of Teflon, and the film is rolled with hand rollers to force out entrapped air and volatile vapors. After cooling, the Teflon sheets are stripped from the adhesive film and the adhesive tape, which is relatively tack free, is ready for use. The film should be stored between sheets of polyethylene film to prevent the sticking of adjacent film layers on the tape adhesive. The optimum amounts of adhesive impregnation have not been fully established, but an amount to give about 0.10 to 0.15 pound of solids per square foot of tape appears to be necessary to develop the strength of certain high-strength honey cores used in sandwich construction.

The FPL-878 tape may be used under the same bonding conditions as described for the liquid adhesive. In bonding of large areas of laminated metal or sandwich panels, it is recommended that the bonding pressure be released and then restored or the panel breathed three times within the first 6 minutes of the curing period. The same postcure of 16 hours at 270° F is recommended for the tape as for the liquid adhesive to obtain optimum heat-resistant properties.

Although the present form of adhesive FPL-878 tape has excellent flow and filleting properties and appears particularly promising for bonding metal laminates and sandwich materials, it requires an extensive cure and postcure to develop full strength and optimum strength properties at elevated temperatures. Present forms of the glass-mat-base tape also lack the desired resistance to long aging at elevated temperatures. Further developmental work will be required to improve these present limitations.

Bonding of sandwich construction with FPL-878 tape adhesive.- The FPL-878 tape adhesive has been used to bond sandwich-panel specimens of high-strength, glass-cloth honeycomb cores with either clad aluminum or stainless-steel faces in a study to determine the strength properties of the cores in flexural tests at elevated temperatures. This study is part of an Air Force project this laboratory is conducting in cooperation with Wright Air Development Center. The FPL-878 tape adhesive has given consistently higher test results on this type of sandwich specimen at temperatures of 300° to 700° F than has any other experimental or commercial adhesive which was tried for this purpose and has facilitated tests, not previously possible, of new high-strength heat-resistant cores.

Flexural tests of these sandwich specimens have been made at 80°, 300°, 500°, and 700° F, and in some cases actual shear failure of the core was attained. The following results present the highest individually computed shear-strength values attained at the various temperatures in a flexural test of clad aluminum faces bonded to high-strength phenolic-resin-impregnated glass-cloth honeycomb cores:

Test temperature, °F	Computed shear stress in core, psi
80	660 (bond failure)
300	560 (bond failure)
500	420 (bond failure)
700	160 (bond failure)

The average peel strength of 13.7 inch-pounds for an all-aluminum sandwich panel made with FPL-878 tape, as shown in table I, is somewhat lower than that of a similar panel made with a commercial phenol-butyral liquid adhesive (which had a strength of approximately 17 inch-pounds) and much lower than that of a panel bonded with phenol-butyral tape adhesive (strength of approximately 45 inch-pounds). Neither of these commercial adhesives, however, has significant resistance to heat-aging at 550° F or resistance to thermal softening at 450° or 600° F.

<u>Strength properties of FPL-878 bonds</u>.- A summary of the strength properties of aluminum lap joints bonded with FPL-878 liquid and tape adhesives is presented in table I. The strength properties of the liquid form of FPL-878 in the various lap-joint tests were generally superior to the tape modification of FPL-878. Both adhesives were outstanding in immediate shear-strength properties at elevated temperatures and in resistance to creep at 300° F. The liquid adhesive was particularly resistant to long-time aging at elevated temperatures, while the tape adhesive showed a very significant loss in strength when aged at a temperature of 450° F. The bend strength and peel strength of both types of adhesive were low and indicative of the brittle characteristics of the adhesives at room temperature. Neither the liquid nor the tape form showed any loss in strength when immersed in hydrocarbon fluid for 7 days.

In the limited number of long-time strength tests, the lap shear specimens were first loaded to 1,00 psi at 300° F for a period of 200 hours and then the load was increased to 1,500 psi for an additional 200 hours. There was no creep observed by a periodic microscopic observation of a scratch line on the side of the specimen while under load after the total 400-hour loading period. Lap joints that were not given the

16-hour postcure at 270° F, however, failed immediately when the 1,000-pound load was applied at 300° F.

FPL-881 Adhesive

Previous comments have indicated that entrapped volatile solvents in liquid-solution adhesives and in film adhesives prepared from such liquid adhesives are believed to be a major factor in reducing the stability of adhesives at high temperatures. A logical solution to this problem would then appear to be the utilization of some of the newer liquid resins that, because of their reactivity, contain potentially 100 percent solids and can be cured without entrapment of solvents or loss of volatile byproducts. One of these is the liquid epoxy type of resin. Such resins have been investigated previously at the Forest Products Laboratory in metal-bonding adhesive formulations in cooperation with the Navy Bureau of Aeronautics. This investigation indicated that certain highly methylated tertiary amines were promising curing agents for such liquid epoxy resins, without phenol resins, giving reasonably satisfactory metal-to-metal lap joints at 200° and 250° F.

Some further preliminary studies on such formulations were undertaken during the present investigation. Based on certain theoretical reasoning from the results of previous studies, one special amine, pentamethyl diethylene triamine, was selected for trial as a curing agent. Since this was not commercially available, the Union Carbide and Carbon Chemicals Company kindly synthesized this amine for the present work. This amine was used with Epon RN-48 liquid epoxy resin and gave strength values of 3,000 psi at room temperature and as high as 3,400 psi at 250° F in aluminum lap shear specimens when cured at elevated temperatures. The adhesive can be applied as a liquid and pressed immediately at temperatures from room temperature to 300° F, with no previous air-drying or precuring.

In the evaluation of pentamethyl diethylene triamine as a curing agent for epoxy resin Epon RN-48, the amount of the amine was varied to study the relation of the ratio of the number of epoxide groups present in the resin to the number of amino groups present in the amine and their effect on the degree of cure and cross-linkage of the resin, as determined by the shear strength of bonds tested at 250° F. The results of these tests of lap-joint specimens after a cure of 1 hour at 200° F. and a postcure of 1 hour at 300° F were as follows:

Amount of amine, percent (a)	Ratio of epoxide groups per amino group (b)	Shear strength at 250° F, psi (c)
1.90	15.7 to 1	112
2.25	13.3 to 1	400
2.95	10.2 to 1	2,096
3.50	8.7 to 1	2,928
4.00	7.5 to 1	3,358
4.3	7.0 to 1	2,678
5.2	5.6 to 1	1,890
7.8	3.8 to 1	758
9.7	3.1 to 1	578

[a]Percent by weight of pentamethyl diethylene triamine based on weight of epoxy resin Epon RN-48.

[b]Ratio of reactive groups in resin (epoxide) to reactive groups in amine (amino) in adhesive mixtures.

[c]Tested immediately after reaching equilibrium at this temperature.

The data showed that a maximum shear strength at 250° F was attained when 4 percent by weight of the amine was used as a curing agent. This combination of resin and amine apparently resulted in the optimum reaction of the reactive groups present in the mixture and resulted in optimum cross-linkage and thermal stability. Since this combination of amine and resin was most effective, it showed that on the average approximately seven and a half epoxide groups from the resin were reacting with each of the three amino groups in the amine curing agent. This adhesive composition, composed of 100 grams of Epon RN-48 and 4 grams of pentamethyl diethylene triamine, is designated as FPL-881. These results are in close agreement with the mechanism of polymerization and cure of epoxide resins reported by Narracott (ref. 5) who showed, by the characterization of the products of triethylamine and phenylglycidyl ether, that one mono tertiary amine reacts with about eight epoxide groups.

Further study of the formulation FPL-881 with 4 percent of pentamethyl diethylene triamine showed that the adhesive had the following shear-strength properties when tested immediately after reaching equilibrium at temperatures ranging from -70° to 500° F:

Test temperature, °F	Shear strength, psi
-70	3,240
80	3,110
250	2,950
300	1,040
400	570
500	380

A rather abrupt loss in strength was observed in increasing the test temperature from 250° to 300° F, indicating that the adhesive was still somewhat thermoplastic at those conditions. A limited amount of additional work on the effect of ionic polymerization catalysts, such as iodine, and of chelating agents showed only a slight increase in the strength of bonds at 300° F.

This adhesive FPL-881 is believed to have distinctly improved strength properties at elevated temperatures over known conventional epoxy-resin adhesives and is considered to be a very promising approach to the problem of developing metal-bonding adhesives that have better heat resistance.

CONCLUSIONS

Based on extensive experience gained in an investigation of metal-bonding adhesives, the effect of different adhesive components and bonding variables on the performance of adhesives at elevated temperatures may be summarized generally as follows:

(1) The strength of adhesive bonds when tested immediately at elevated temperatures is apparently dependent primarily on the cohesive strength of the adhesive as a result of the polymerization and cross-linkage that occurs during the initial cure of the adhesive.

(2) The resistance of the adhesive to long-time aging at elevated temperatures is dependent in part on the chemical makeup of the resin of which the adhesive is composed.

(3) The resistance of the adhesive to long-time aging at elevated temperatures is also dependent on the conditions employed in the process of bonding. The metal being bonded has a marked effect on the thermal resistance of the adhesive. The method of preparing the metal for bonding and the chemical composition of the metal surface are likewise critical in determining the heat resistance of the bond. The removal of volatiles and solvents from the adhesive film prior to bonding is important. The type of carrier employed in supported tapes also has a marked effect on the performance of the adhesive at elevated temperatures.

(4) Three adhesives with promising heat-resisting characteristics have been described in this report. Adhesive FPL-710, a phenol-epoxy resin formulation, has shown good resistance to thermal softening up to 600° F and to thermal degradation on heat-aging for 200 hours at 550° F in thin gluelines in aluminum-to-aluminum lap shear tests. Adhesive FPL-878, another phenol-epoxy resin formulation, has better flow and filleting properties than FPL-710 and can be made into a tape,

supported on glass-fiber mat, for use in bonding sandwich panels having high heat resistance. This tape adhesive has provided bonds of aluminum and stainless-steel faces to high-strength heat-resistant phenol-resin-impregnated glass-cloth honeycomb cores that are superior in heat resistance at 500° and 700° F to those made with any other currently available adhesive process. Heat-aging resistance of the FPL-878 tape is not so high as for the liquid adhesive in lap joints. This is apparently due to an undesirable action of the glass surface on the resins at 550° F and is one of the most serious present limitations of the FPL-878 tape adhesive. Adhesive FPL-881, composed of a liquid epoxy resin with a special amine curing agent, is a very promising 100-percent-reactive liquid adhesive for metal bonding when cured at 200° F or higher. Without the need of elaborate precuring, it gives very good resistance to thermal softening at 250° F, a major limitation of other straight epoxy-resin adhesives. This FPL-881 adhesive does not have the high resistance to thermal softening at 500° and 600° F noted for the phenol-epoxy resin combinations.

(5) Adhesive formulations that possess outstanding strength properties at elevated temperatures and high resistance to thermal degradation may be excessively brittle at normal and subnormal temperatures. Since there is a definite need for a single adhesive with acceptable strength properties over a wide range of temperatures, further work in the development of such adhesives is highly desirable.

Forest Products Laboratory,
Madison, Wisc., September 25, 1954.

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TABLE I.- AVERAGE STRENGTH PROPERTIES OF ADHESIVE FPL-878 IN VARIOUS TESTS

Test temperature, °F	Type of test (a)	FPL-878 liquid				FPL-878 tape			
		Control (b)	Aged 200 hr at 350° F	Aged 200 hr at 450° F	Aged 200 hr at 550° F	Control (b)	Aged 200 hr at 350° F	Aged 200 hr at 450° F	Aged 200 hr at 550° F
-70	Shear strength, psi	1,840	-----	-----	-----	1,200	-----	---	---
80	Shear strength, psi	2,044	1,674	1,320	1,080	1,540	1,274	120	0
250	Shear strength, psi	3,134	-----	-----	-----	1,634	-----	---	---
350	Shear strength, psi	1,336	2,310	1,162	-----	1,168	1,390	256	---
450	Shear strength, psi	1,298	2,078	1,322	-----	920	1,210	124	---
600	Shear strength, psi	806	958	1,156	866	690	860	80	---
80	7-day immersion in hydrocarbon fluid, psi	2,028	[c]1,704	-----	-----	1,518	[c]1,264	---	---
300	Long-time strength, psi	1,500	-----	-----	-----	1,500	-----	---	---
80	Bend, lb	110	-----	-----	-----	87	-----	---	---
76	Peel, in.-lb	-----	-----	-----	-----	13.7	-----	---	---

[a]All tests except peel tests were made on lap shear specimens of 0.064-inch clad 2024-T3 aluminum alloy with a 0.5-inch lap joint. Tests were conducted in accordance with reference 4. Each value is average of at least five test specimens except long-time strength values which are average of two specimens, and peel test values are averages for four specimens.

[b]All specimens were cured for 60 minutes at 320° F. Control specimens only were postcured for 16 hours at 270° F.

[c]Specimens were aged for 200 hours at 350° F before immersion.

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