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TECHNICAL NOTE 4287

RELATIONSHIP OF METAL SURFACES TO HEAT-AGING PROPERTIES OF ADHESIVE BONDS

By J. M. Black and R. F. Blomquist

Forest Products Laboratory

Washington
September 1958

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RELATIONSHIP OF METAL SURFACES TO HEAT-AGING PROPERTIES OF ADHESIVE BONDS

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SUMMARY

A study was made to determine the probable causes of deterioration of each of several adhesives in bonds to stainless steel at temperatures from 400° to 550° F. Preliminary studies of aluminum surfaces on which ions of metals used in stainless steel were introduced showed that iron was probably catalyzing a thermal deterioration of the adhesive. The resistance of FPL-878 adhesive to thermal deterioration at 550° F on steel was improved significantly by treating the steel surface to be bonded with either zinc or cerium naphthenate and firing at 1,200° F. The addition of manganese dioxide to the adhesive also increased its resistance to thermal deterioration. A study of the thermal-aging properties of five different chemical types of adhesives on stainless steel and aluminum revealed that a phenol-nitrile rubber adhesive was superior to a phenol-epoxy adhesive on steel, but this order was reversed on aluminum. These and other observations indicated probable specific relationships among the chemical structure of the adhesive, the metal adherend, and the resultant thermal stability of bonds after aging at high temperatures.

INTRODUCTION

Adhesive bonds in metals may react in two ways when subjected to elevated temperatures. The adhesive may soften and lose a considerable part of its initial strength merely because of thermal softening. Much of this loss may be regained when the adhesive cools. The adhesive may also permanently lose strength because of thermal aging at elevated temperatures. This loss involves chemical deteriorations that probably have definite rate effects and are irreversible.

The work reported herein has been directed toward establishing probable causes and mechanisms for the erratic and generally unsatisfactory resistance of adhesive bonds on certain metals to thermal aging at temperatures up to 550° F. In previous work (ref. 1) adhesive bonds on certain metals, particularly stainless steel, made with a phenol-epoxy

resin adhesive were shown to have generally low resistance to thermal aging, while bonds of the same adhesive on aluminum were quite high in heat resistance. Low resistance to aging at elevated temperatures has also been observed for a phenol-epoxy resin adhesive in bonds on titanium, brass, copper, and low-carbon steel.

These and similar empirical observations suggested an important dependence of the heat-aging characteristics of an adhesive on the metal surface being bonded. The very marked difference in the performance of the same adhesive on aluminum and stainless steel indicated strongly that certain metal surfaces may have a critical catalytic effect on the deterioration of the organic adhesive. In the work reported in reference 1, the deterioration of bonds on stainless steel was greatly reduced when bonds were aged in nitrogen. Air or oxygen must therefore play an important role in the thermal-degradation mechanism. The adverse behavior at elevated temperatures of several different types of commercial adhesives on stainless steel has also been observed by investigators in the aircraft industry. The work on this project has been restricted mainly to a study of clad aluminum alloy (2024-T3) and stainless steel (type 302) bonded with FPL-878 adhesive. (This is an experimental phenol-epoxy resin adhesive developed for high temperature use by the Forest Products Laboratory in cooperation with the National Advisory Committee for Aeronautics and described in ref. 2.) For background knowledge on some of the metallurgical aspects of surface properties and film composition of stainless steel, the work by Gulbransen and associates (refs. 3 to 6) seemed to give the best insight into what might be happening to the various oxides of iron, chromium, and nickel on the surface of the stainless steel during heat aging. Their work revealed that, at elevated temperatures, the oxides on the surface of iron undergo a number of solid phase oxidation-reduction reactions with transformation from one oxide to another. Diffusion of metal and oxygen ions through the surface lattices also occurs to cause continuation of the oxidation process. The oxidation characteristics of iron become more complicated in the stainless-steel alloys, where diffusion and oxidation of the different metal components may occur to different degrees, depending on surface treatment and conditions of oxidation. Gulbransen also reported that iron showed a very marked gain in weight after oxidation for 2 hours at 400° F, but aluminum showed practically no gain after a similar exposure. Rhodin (ref. 7) in his study of oxide films on 18-8 type stainless steel showed that the percentages of the metals in the oxide film are not the same as the percentages in the alloy. Surface films become enriched with silicon by mild chemical pickling and passivating treatments, while a very marked increase in the chromium content of the film occurs with air oxidation at elevated temperatures. The perferential diffusion of chromium and the oxidation of this chromium was also reported to occur in conditions of limited oxygen supply such as would be expected within adhesive bonds between stainless-steel

plates. The principal metal components of stainless steel, namely, iron, chromium, and nickel, and their oxides are also well recognized as catalysts for a number of organic reactions involving oxidation, hydrogenation, and dehydrogenation (ref. 8). From these chemical considerations of the stainless-steel surface it seems quite likely that the adhesive forms a bridge or bond to a highly reactive metal-oxide surface that could be continually changing in chemical composition at elevated temperatures.

This investigation was carried out at the Forest Products Laboratory under the sponsorship and with the financial assistance of the NACA.

EXPERIMENTAL PROCEDURE

Since many of the procedures used in individual experiments were typical only of that experiment, such procedures are outlined briefly in the section entitled "Discussion of Experimental Results" rather than in this section. Some of the chemical-treating procedures for preparing the metal for bonding and for conducting the strength tests, however, were common to a number of the experiments and are described in this section.

Materials

Metals.- This bonding study was conducted on 0.064-inch 2024-T3 clad aluminum alloy and 0.020-inch type 302 stainless steel that conformed to the specifications given in reference 9. The stainless steel had the following approximate composition by weight: iron, 70 percent; chromium, 18 percent; nickel, 8 percent; manganese, 2 percent; silicon, 1 percent; and traces of copper, molybdenum, carbon, phosphorous, and sulfur.

Adhesives.- The adhesive used most frequently in these studies was FPL-878 (ref. 2) which had the following composition: phenol resin (Durez 16227), 12.5 grams; phenol resin (Bakelite BV 9700), 3.3 grams; epoxy resin (Epon 1007), 2.0 grams; ethyl acetate, 2.0 grams; n-propyl gallate, 0.2 gram; and 1-hydroxy-2-naphthoic acid, 0.2 gram. This formulation was thinned with an equal weight of ethyl acetate before it was spread. The adhesive coat was precured for 30 minutes at 200° F and was then pressed at 320° F for 60 minutes at 50 psi. Previous work with this adhesive indicated that it was one of the most promising structural metal-bonding adhesives for aluminum joints and that these were the best bonding conditions from the standpoint of resistance to both thermal softening and thermal aging.

Four other commercial resins of different chemical types, identified in this report by the letters A, B, C, and D, were also evaluated for resistance to heat-aging in bonds between plates of aluminum and stainless steel. Adhesive A is a high-temperature-setting phenol resin; adhesive B is an uncatalyzed epoxy resin; adhesive C is a high-temperature-setting liquid adhesive composed of phenol resin and nitrile rubber; and adhesive D is a high-temperature-setting silicone resin.

The following conditions, which were considered adequate for good bonds, were used for these adhesives in bonding lap-joint shear specimens:

Adhesive	Precure		Bonding pressure, psi	Curing conditions	
	Temperature, °F	Time, min		Temperature, °F	Time, min
A	200	30	50	320	60
[a]B	---	--	Contact	450	Overnight
C	200	15	250	320	60
D	320	10	200	400	190

[a]Resin and metal heated to 300° F; resin was applied by brush while hot.

Preparation of Metal Surfaces for Bonding

After the surfaces were wiped with methyl ethyl ketone, the following two methods were employed in preparing the metal surfaces for bonding:

(1) Method A: Method A consisted of immersion of the specimen for 10 minutes at 150° F in the following solution: hydrochloric acid (concentrated), 100 grams; hydrogen peroxide (30 percent), 4 grams; formalin (40 percent), 20 grams; and water, 90 grams. The metal was then rinsed in cold tap water and then in distilled water and was then air dried.

(2) Method B: Method B consisted of immersion of the specimen for 5 to 10 minutes at 140° to 160° F in the following solution: sulfuric acid (concentrated), 100 grams; sodium dichromate, 10 grams; and water, 30 grams. The metal was then rinsed in cold tap water and then in distilled water and was then air dried.

Method A was used on stainless steel to produce an active surface, and method A followed by method B, which contained dichromate, was employed to produce a passive surface on steel. Method B was also used for preparing aluminum surfaces. These chemical treatments were considered from previous work (ref. 1) to be the most promising methods for preparing stainless-steel and aluminum surfaces for bonding.

Test Methods

Lap-joint shear specimens with an 0.5-inch overlap were prepared for both the aluminum and stainless-steel surfaces. The specimens were tested at room temperature initially and again at room temperature after aging at elevated temperatures. The lap-shear specimens were loaded until they failed in tension in self-alining grips at the rate of 600 pounds per 0.5 square inch per minute. The type of bond failure in most bonds, as determined by visual examination of the broken specimens, was estimated to be 100-percent failure in cohesion of the adhesive layer. Whenever failure occurred in adhesion to the metal, the average estimated percentage of area of adhesion failure is shown in parentheses following the joint strength values in the various tables throughout the report.

The stainless-steel test specimens were prepared individually by bonding 1- by 2-inch coupons to form a 0.5-inch overlap specimen 1 by 3.5 inches in size. The aluminum test specimens were prepared by bonding 4- by 8-inch pieces into a panel 8 by 7.5 inches in size. Seven 1-inch-wide test specimens were then cut from each test panel. At least five specimens were tested for each test condition. Temperatures during heat aging and when testing at the elevated temperatures were controlled to within $\pm 3^{\circ}$ F in special, electrically heated ovens. Other details of metal preparation, adhesive formulation, bonding, and testing conditions are given for individual experiments in the following section.

DISCUSSION OF EXPERIMENTAL RESULTS

Studies of Adhesive Bonds to Aluminum Surfaces

Earlier experience at the Forest Products Laboratory indicated that aluminum surfaces prepared for bonding using sulfuric acid and sodium dichromate (method B) had very little or no undesirable effect on the thermal deterioration of FPL-878 adhesive. For this reason,

aluminum surfaces were prepared by this process, and other metal ions were deposited on these surfaces to study their effect on the heat-aging properties of the adhesive. In these experiments, the various ions of the metals found in stainless steel, and also other ions, were deposited on the aluminum surface by chemical displacement from a dilute acid solution of the metal salt. This deposition was accomplished by immersion of the clean aluminum metal for 60 minutes at 80° F in a 10-percent nitric acid solution (by weight) in which the metal salt was dissolved. The concentration of the salt was varied from 0.005 to 0.100 mole per liter of solution. After the metal surface was immersed, it was rinsed well with cold tap water and then with distilled water and was air dried before bonding. No chemical characterization of the resultant metal surfaces was attempted. The results of shear tests of bonds on aluminum surfaces containing iron, nickel, chromium, or manganese, the metals present in the stainless steel, and certain other metals are contained in table 1. Tests were conducted initially at room temperature and also at room temperature after aging for 100 hours at 550° F. The data show that ferrous and ferric iron and nickel ions that were deposited from the 0.1-molar solutions lowered the resistance of the adhesive bonds to aging for 100 hours at 550° F. Ferric iron had the greatest adverse effect at this concentration. Chromium and manganese seemed to have no consistent significant effect at the concentrations and conditions employed in the study. The results of these experiments indicate that the iron of the stainless steel was probably the alloying element causing the accelerated deterioration of adhesive FPL-878 at elevated temperatures.

In a further experiment, small amounts of iron were deposited on the cleaned aluminum surfaces (method B) by electrodeposition with a direct current of 3 volts and 0.210 ampere for 2 minutes from a 0.03-molar aqueous solution of ferric chloride at room temperature. From these electrolysis measurements it was calculated that about 0.0012 gram of iron was deposited per square inch of aluminum surface. In the electrodeposition procedure, stainless steel (type 302) was used as the anode, and the aluminum to be bonded was used as the cathode. After the iron was deposited, the surfaces were washed with distilled water, air dried, and then heated to 300° F for 30 minutes. Bonds were then made with FPL-878 adhesive to the iron-modified surface as prepared and to similar surfaces from which the iron had been subsequently removed by a second treatment with a solution of sulfuric acid and sodium dichromate (method B). The following results of tests of these bonds at room temperature, before and after they were aged for 100 hours at 550° F, show conclusively the marked adverse effect of iron on the thermal deterioration of the adhesive:

Surface treatment	Shear strength of specimen, psi	
	No aging	Aged 100 hr at 550° F
(1) Control (method B)	2,210	1,184
(2) Method B plus iron deposit	2,104	0
(3) Same as (2) with iron removed	2,162	1,258

The results obtained with other metals that were introduced on the aluminum surface by chemical displacement are shown in table 1. Several of these metals, particularly silver, zinc, and cerium, improved the resistance of the adhesive to aging at 550° F. The deposition of a relatively thick layer of copper, which was observed from the most dilute solution, resulted in complete loss of joint strength after heat aging. Lesser amounts of copper deposited on the aluminum from the 0.015-molar or higher concentrations showed no adverse effect. Mercury had a very severe adverse effect, whereas cobalt and lead, at the conditions employed, had no well-defined effects. The performance obtained with the various surfaces treated with the different metals was of interest because of the possible correlation of the chemical properties of the metals or the metal oxides, which presumably are formed at the metal surface after very short exposure to air, and the subsequent behavior of the adhesive when exposed to heat. For example, the oxides of zinc and cerium, which improved the resistance of the adhesive to thermal aging, are known to be amphoteric in their chemical properties and also have high thermal stability. Zinc oxide has long been employed as a protective coating for iron (galvanized iron) because it prevents further oxidation and corrosion.

From a general review of metal catalysts for various organic reactions at elevated temperatures (ref. 8), a number of examples were noted that involved the metals included in the present study. Silver and its oxide, for example, are known to be strong oxidizing agents and catalysts for oxidation reactions. Copper and its oxides are catalysts for organic reactions involving dehydrogenation. Chromium, however, is also an excellent catalyst for dehydrogenation, but it showed no adverse effect on adhesive performance. Nickel is usually classified as a catalyst for hydrogenation but may be an active catalyst for dehydrogenation in the presence of promoters such as aluminum oxide. Iron is also a dehydrogenation catalyst. The metals iron, copper, and nickel, which showed the greatest adverse effect on the resistance of the adhesive to aging at 550° F, are all classified as catalysts for the Fischer-Tropsch synthesis of hydrocarbon fuel from carbon monoxide and hydrogen, which involves reactions of hydrogenation, dehydrogenation, and dehydration.

In another reaction described by Emmett (ref. 8), where o-xylene or naphthalene is partially oxidized to phthalic anhydride with a vanadium pentoxide catalyst, complete oxidation will occur if iron oxide is present. This oxidation reaction may more closely resemble the conditions of adhesive deterioration observed in bonds at high temperature in the presence of stainless steel or of iron on aluminum than did any of the catalytic reactions previously cited because of the similarity in aromatic structures of the phenol and epoxy resins and those of naphthalene and xylene.

Studies of Adhesive Bonds to Stainless-Steel Surfaces

The studies of stainless-steel surfaces were directed toward improvement of the rather poor thermal-aging resistance of adhesive bonds to stainless steel. The postulated catalytic effects of iron in the steel were to be reduced by certain surface treatments that could either have a poisoning effect or could tie up the iron to reduce or destroy its catalytic effects. Before such poisoning possibilities were investigated, the effect of several different initial surface treatments for steel on the heat resistance of the resultant FPL-878 bonds was determined. The following data are the results of tests at 80° F on bonds made with FPL-878 on stainless steel that were aged for 50 or 100 hours at 550° F:

Surface treatment	Shear strength of specimen, psi	
	Aged 50 hours	Aged 100 hours
Milled	[a]104-(72)	---
Method A	250	28
Method A plus 2 hours at 450° F	--------	36
Method A plus 2 hours at 900° F	--------	20
Method A plus method B	300	156

[a]Value in parenthesis is average estimated percentage of shear area failing in adhesion to the metal. In all other cases, failure was completely in cohesion of the adhesive layer.

Methods A and B for treating the surfaces are described in the section "Experimental Procedure." The milled surfaces were prepared while the steel was immersed in a bath of the liquid adhesive. This milling procedure was an attempt to produce a fresh surface of metal in immediate contact with the adhesive so that the adhesive could be preferentially adsorbed before any oxygen could come in contact with the surface. Such

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oxygen adsorption would normally be expected to follow a chemical treatment where surfaces are then dried in air.

These precautions to exclude adsorbed oxygen from the surface were not effective in retarding thermal deterioration of the adhesive, which suggests that air or oxygen that is accessible to the periphery of the bonded area may have been a factor in the deterioration of the bonds on stainless steel at elevated temperatures. Since previous studies showed that bonds on aluminum did not deteriorate seriously, however, entry of air at the periphery of the bond during heat aging was not considered to be the major factor contributing to deterioration but rather it was considered that a combination of air or oxygen and the presence of iron instead of aluminum was necessary to cause severe deterioration of the adhesive bond.

A surface treatment involving immersion in a solution of hydrochloric acid, hydrogen peroxide, and formalin (method A) to produce an active surface gave joints that were low in strength after heat aging, and heating the surfaces for 2 hours at either 450° or 900° F in an attempt to passivate the surface by increasing the thickness of the oxide layer was not beneficial. Heating iron surfaces at 900° F was reported by Moreau (ref. 10) and Hickman (ref. 11) to promote the formation of reduced iron oxides such as Fe_3O_4 and FeO, whereas principally Fe_2O_3 existed at or below 450° F. The results of tests of these bonded surfaces, however, showed no marked difference in performance or any increase of thermal resistance over the results of tests on those surfaces that were only air dried.

Stainless-steel surfaces prepared for bonding by method A followed by immersion in a solution of sulfuric acid and sodium dichromate (method B) had the highest strength after aging for 100 hours at 550° F and showed the least amount of visible thermal deterioration of the adhesive bond. This surface was considered to be somewhat more passive in nature than the surface prepared by method A only because of the oxidation effects of the dichromate ion used in method B.

Treatment of stainless steel with metal naphthenates.- In one approach to the problem of deactivating the iron, the stainless-steel surfaces were modified by a firing technique. Other metal ions were introduced on the stainless steel in the form of metal naphthenates, and the steel was then heated at 1,200° F for 15 minutes to remove the organic components. This naphthenate method of depositing ions on stainless-steel surfaces showed promising results in a previous study of thermal deterioration of adhesive bonds conducted in cooperation with the Wright Air Development Center (ref. 1). The treated surfaces were cooled and bonded with FPL-878 adhesive under the usual procedures, and the joints were then aged for 100 hours at 550° F before they were

tested at room temperature. The surfaces were cleaned by method A before the naphthenate was applied.

The results of this work (table 2) showed that zinc- and cerium-treated surfaces were quite superior to all other metal-treated surfaces in reducing adhesive deterioration during heat aging. These results agreed with those obtained on aluminum surfaces that contained either zinc or cerium. Surfaces treated with lithium, nickel, and tin showed slight improvement over the control surface with no naphthenate treatment. Treating the steel surface with either calcium, iron, cadmium, lead, vanadium, or copper caused complete deterioration of the bond during heat aging. These results also showed that, of the elements usually found in stainless steel, enrichment of the surface film with iron by the naphthenate treatment caused complete loss in bond strength, chromium had no significant effect, and nickel appeared to improve the retention of bond strength when heat aged. The elements calcium, cerium, and zirconium, which are known as "long life" elements (ref. 12) that increase the life of electrical resistance wires, were markedly different in their effect. Calcium caused a complete loss in joint strength, zirconium had no effect, and cerium showed a very significant improvement. These elements are thought to increase the life of heating wires by either increasing the adhesion of the protective oxide scale or a specific influence on the formation of simple oxides and spinels in the scale that are thought to have a direct effect on the rates of diffusion of the ions through the scale. Spinels are a group of minerals occurring in octahedrons of great hardness that are usually formed from aluminates or ferrates of the type $M^{++}M_2^{+++}O_4$; M^{++} may be magnesium, zinc, manganous manganese, or ferrous iron, and M^{+++} may be aluminum, chromium, ferric iron, or manganic manganese. A number of the metals studied, such as calcium, cerium, zirconium, vanadium, and manganese, are also known to act as purifiers and scavengers of oxygen in the manufacture of steel, while strontium and barium are used as scavengers in the refining of copper. Magnesium is also an excellent deoxidizer for other metals. Zinc, of course, is well known for its anodic protection of iron against electrolytic corrosion and is also believed to protect iron from thermal-oxidation effects at intermediate temperatures by virtue of the protective oxide layer formed on the surface. Zinc is also soluble in steel and readily diffuses into the metal at the elevated temperatures used in the firing technique.

The particular surface treatment of the steel used before application of the naphthenate solution was also found to influence the effectiveness of the zinc and cerium surfaces. Zinc surfaces were most effective in reducing adhesive deterioration when the stainless steel was first treated by method A followed by method B. Cerium was most effective when the steel surface was cleaned by method A. The results of tests made at room temperature after 100 hours at 550° F to establish these effects are shown in the following tabulation:

Cleaning method	Naphthenate	Shear strength of specimen, psi
Method A	Zinc	380
Method A plus method B	Zinc	536
Method A	Cerium	382
Method A plus method B	Cerium	158

In another study, small amounts of different metal ions were electrodeposited on stainless steel by passing a direct current of 1 to 2 amperes at a potential of 3 volts for 5 minutes through 0.03-molar salt solutions in 10 percent nitric acid, by weight, at room temperature. The metal was then rinsed and heated to 1,200° F for 15 minutes before it was cooled and bonded with FPL-878 adhesive. In the deposition process, a sheet of 18-8 type 302 stainless steel was used as the anode, and a similar piece of stainless steel was used as the cathode. Both electrodes were first cleaned by method A.

The strength values for bonds made to these various surfaces were determined at 80° F after aging for 100 hours at 550° F and are as follow:

Metal salt	Shear strength of specimen, psi
None	50
Zinc chloride	104
Cerous nitrate	154
Aluminum chloride	136
Bismuth subnitrate	24
Copper chloride	0
Silver nitrate	0

Zinc, cerium, and aluminum salts gave the best results, although they gave joint-strength values considerably lower than those obtained when the corresponding naphthenates were fired on the surfaces. Bismuth, which was reported in the literature (ref. 8) as a poison for iron oxidation catalysts, had no marked effect on adhesive deterioration, but copper again caused complete deterioration of the bond. Silver, which had been found to increase the resistance of the adhesive to thermal aging on aluminum, caused complete deterioration of the adhesive when used to modify the stainless-steel surface.

Treatment of the stainless-steel surface with chelating agents.- In this study, it was hypothesized that certain organic compounds could possibly form chelates with the iron at the surface of the steel and that these chelates might be stable compounds which would reduce or prevent the catalytic deterioration of the adhesive when aged at 550° F. To investigate this possibility, the stainless-steel surfaces were cleaned with a solution of hydrochloric acid, formalin, and hydrogen peroxide (method A) and were then immersed for 1 hour in a boiling-water solution containing 5 percent of the selected chelating agents. The surfaces were then rinsed and air dried before they were bonded with FPL-878 adhesive. The results of tests at room temperature after aging at 550° F for 100 hours were as follows:

Chelate	Shear strength of specimen, psi
None	54
1-hydroxy-2-naphthoic acid	196
Quinolinol	0
Salicylic acid	0
Dicyandiamide	274

Some rather significant improvements in joint strength were obtained with 1-hydroxy-2-naphthoic acid and dicyandiamide, although results were not so high as those shown in table 2 for the zinc and cerium naphthenate treatments on steel.

Effect of additives in FPL-878 adhesive when bonding stainless steel.- In this phase of the work on bonds to stainless steel, improvement in the resistance to heat aging was attempted by reducing the possible catalytic effects of iron with certain additives to the adhesive itself instead of the metal surface. These additives were selected because they might have a poisoning or inhibiting effect on iron or because they could also act as oxygen scavengers in the bonded area. The stainless-steel surfaces were first prepared for bonding by method A followed by method B.

A study of 21 different inorganic materials that were added to adhesive FPL-878, in amounts of 5 percent or less, showed several additives that contributed significantly to improved resistance to aging at 550° F (table 3). Most effective of the different compounds studied was manganese dioxide, which increased the joint strength of the bonds after aging for 100 hours from 130 psi (controls) to 566 psi when a concentration of 1.0 percent was used. Aluminum oxide (3 percent)

increased the joint strength to 474 psi, arsenic trioxide (3 percent), to 440 psi, stannous sulfide (1 percent), to 426 psi, and antimony trisulfide (3 percent) increased the joint strength to 416 psi. These results indicated that the sulfur and arsenic compounds, which are poisons that will inhibit the catalytic effects of iron in many organic reactions, were effective in reducing the deterioration of the adhesive bond during heat aging.

There was also an indication that low and intermediate valence forms of several different metals were more effective in improving heat-aging properties than were metals in their completely oxidized state. This was the case for antimony and zinc at 3-percent concentration and for arsenic at both 3- and 5-percent concentration, which suggests that the low valence forms of the metals were able to take up oxygen or unite with the iron in some way to inhibit the catalytic effects of iron. The action of manganese dioxide as an intermediate valence form of manganese may also be as an oxygen scavenger, although this compound is a mild oxidizing agent and is used as a depolarizer in dry cells, where it reacts with liberated hydrogen to form water. The excellent performance of aluminum oxide in these tests was surprising since it is generally considered to be a relatively inert and heat-stable material.

The significant improvement in strength of heat-aged bonds containing addditives at concentrations as low as 5 percent is a further indication that iron acts as a catalyst in the deterioration of the phenol-epoxy resin adhesive in contact with stainless steel at high temperatures.

Effect of adhesive composition in bonds to stainless steel.- All previous work discussed in this report concerned the performance of FPL-878, a phenol-epoxy resin adhesive. The purpose of this phase of the study was to investigate the relationship of chemical composition of other adhesives to their thermal deterioration in bonds to aluminum and stainless steel at various temperatures. A series of bonded aluminum and stainless-steel specimens were prepared with each of several different chemical types of adhesives. The decomposition temperatures of the bonds were then determined by (1) aging the specimens for 50 hours at temperatures from 400° to 550° F and then testing them at room temperature and (2) aging the specimens for various lengths of time at 550° F before testing them at room temperature.

The chemical types of adhesives used are described in the section "Experimental Procedure." It should be noted that some of these adhesives, such as the particular phenol-nitrile rubber and the uncatalyzed epoxy resin, did not produce joints of high strength when loaded initially at elevated temperatures. This study, however, was concerned only with the resistance of such joints to chemical and thermal deterioration when aged in an unstressed condition at elevated temperatures

and then tested at room temperature. The results of this work are presented in table 4 and are also shown graphically in figures 1 to 6. The aluminum surfaces were prepared for bonding by method B, and the stainless-steel surfaces were prepared by method A followed by method B.

The results of these tests point out some very interesting relationships among the chemical type of adhesive, the aging temperature, and the metal adherend. When used with aluminum, adhesive FPL-878, a phenol-epoxy type adhesive, showed practically no difference in joint strength at temperatures from 450° to 550° F after aging for 50 hours (fig. 1). The same adhesive used with stainless steel (fig. 2) decreased significantly in strength with an increase in aging temperature. Phenol-resin adhesive A, when used alone as an adhesive, showed a moderate loss in strength when aged at 550° F on aluminum compared with its performance at 500° F or lower; it showed a very definite loss in strength on stainless steel at temperatures of 450° F and above. Epoxy-resin adhesive B on aluminum had excellent strength after aging for 50 hours at 450° and 500° F but was almost completely deteriorated after 50 hours at 550° F. The same epoxy resin on stainless steel showed an abrupt loss in strength when aged at 500° F and almost complete deterioration at 550° F. Thus, aluminum specimens bonded with a straight phenol- or a straight epoxy-resin adhesive were low in resistance to thermal deterioration when aged at 550° F, but a combination of phenol and epoxy resin, such as FPL-878 adhesive, had high resistance at 550° F. These observations would indicate that there is presumably a weak chemical link in both the phenol and epoxy resins that is readily broken at 550° F. When the two resins are used together, however, this inherent weakness is strengthened by some cross-linking reaction to form a more thermally stable bond. The improved thermal stability of the combined resins over that of the individual component resins is lost, however, when the combination is used to bond stainless steel, which would indicate a specific effect of iron on the deterioration of this type of adhesive.

In figure 1, the strength of bonds made to aluminum with adhesive C, a phenol-nitrile type adhesive, was shown to decrease noticeably with an increase in the aging temperature. Adhesive C on steel (fig. 2) also showed a loss in strength when aged for 50 hours at 500° F, but little or no further loss occurred when the aging temperature was raised to 550° F. This performance would indicate that iron in the steel probably has no important catalytic effect on the deterioration of the phenol-nitrile adhesive and that the nitrile-rubber portion of the adhesive may have a protective influence over the phenol resin.

Adhesive C was believed to contain only a relatively small proportion of phenol resin with the nitrile component. In some further work, 40 and 80 percent by weight of phenol resin A, based on the solids contents of each resin, were therefore added to adhesive C, and bonds made to steel with the new mixture were aged for 50 hours at 550° F before

they were tested at room temperature. The results of tests made at room temperature before and after aging were as follows:

Adhesive	Shear strength of specimen, psi	
	Before aging	After aging
Adhesive C	2,102	1,336
Adhesive C plus 40 percent of adhesive A	2,026	1,392
Adhesive C plus 80 percent of adhesive A	1,864	680

These results indicated that, when larger amounts of phenol resin were present, joint strength after heat aging was considerably lower because the nitrile component was too small to protect the phenol resin.

The performance of silicone adhesive D was much better in bonds on stainless steel (fig. 2) that in bonds on aluminum (fig. 1). The initial strength of bonds on stainless steel (table 4) was also significantly higher than that of bonds on aluminum, which indicated that a higher degree of adhesion was attained on steel than was attained on aluminum. The silicone adhesive on steel (fig. 2) showed an abrupt loss in strength, however, when the aging temperature was increased from 500° to 550° F.

Figures 3 and 4 show the results of tests at room temperature on specimens made with the different adhesives on aluminum and stainless steel that were aged for various periods of time at 550° F. On aluminum, FPL-878 adhesive (phenol-epoxy type) was superior to other types of adhesives, although phenol-resin adhesive A also showed a promising degree of thermal resistance. It was noted that the main change in strength with all adhesives on aluminum was during the first 50 hours of aging, after which the strength tended toward a constant level. On stainless steel, adhesive C (phenol-nitrile rubber) was best in resistance to thermal deterioration at all aging periods (fig. 4). Silicone adhesive D and FPL-878 adhesive retained a strength of 900 psi or more after 16 hours of aging but then decreased markedly in strength after 50 hours of exposure. Phenol-resin A and epoxy-resin B adhesives suffered the greatest losses in initial strength after aging for 16 hours at 550° F. After 100 hours at 550° F, only adhesive C retained any significant strength on stainless steel.

The data shown graphically in figures 5 and 6 indicate the behavior of a phenol-epoxy type adhesive (FPL-878) and a phenol-nitrile rubber adhesive (adhesive C) in bonds on aluminum and stainless steel when aged at elevated temperatures. The phenol-epoxy type adhesive showed high

resistance to thermal deterioration at 550° F on aluminum but low resistance on stainless steel. The phenol-nitrile rubber adhesive, on the other hand, had a high resistance on stainless steel but was low in resistance to thermal deterioration at 550° F on aluminum.

From these observations on adhesives of different chemical types for bonding aluminum and stainless steel, it appears that a very definite relationship must exist between chemical structure of the adhesive and its thermal stability on various metal adherends. Further study in this direction would offer leads towards tailoring special resins and other components for adhesives for use on specific metals when heat aging was expected to be a problem.

Effect of surface preparation and adhesive composition on bonds to stainless steel.- In the final phase of this project, the best metal surface treatments for stainless steel (zinc and cerium naphthenates) and the most promising adhesive additive (1 percent of manganese dioxide) were used in preparing bonds made with a phenol-epoxy type adhesive (FPL-878) and with the phenol-resin—nitrile-rubber type adhesive (adhesive C). The surfaces were initially treated by method A followed by method B before application of the metal naphthenate and heating to 1,200° F for 15 minutes. The following data on tests of bonds at room temperature that were aged for 100 hours at 550° F show the effects on joint strength with changes in surface preparation and adhesive additive:

Adhesive	Naphthenate treatment	Manganese dioxide, percent	Shear strength of specimen at 80° F after 100 hours at 550° F, psi
FPL-878	None	0	130
FPL-878	Zinc	0	536
FPL-878	Cerium	0	158
FPL-878	Zinc	1	658
FPL-878	Cerium	1	552
Adhesive C	None	0	1,020
Adhesive C	Zinc	0	894
Adhesive C	Cerium	0	750
Adhesive C	Zinc	1	470
Adhesive C	Cerium	1	306

These data showed that, as had been previously noted with FPL-878 adhesive (phenol-epoxy type), the zinc naphthenate surface treatment with 1 percent of manganese dioxide added to the adhesive definitely improved the resistance of the adhesive to thermal deterioration at 550° F. For

adhesive C (phenol-resin—nitrile-rubber type), treatment of the surface with these same metal naphthenates lowered the thermal resistance of the adhesive, and addition of manganese dioxide to the adhesive lowered the resistance to aging at 550° F still further. These results further suggest that the effects of metal surfaces and additives on the adhesive are specific for a given chemical type of adhesive.

CONCLUSIONS

The following conclusions derived from this study of the relationship of metal surfaces to the heat-aging properties of adhesive bonds were considered to be the most important and pertinent:

1. The high resistance of adhesive FPL-878 (phenol-epoxy resin type) to thermal deterioration at 550° F was destroyed when either iron or copper was deposited on the aluminum surface before it was bonded. From the performance of iron in these tests, it was concluded that the iron in stainless steel apparently had a catalytic effect on the deterioration of phenol-epoxy resin adhesives at elevated temperatures.

2. The low resistance of adhesive FPL-878 to thermal deterioration at 550° F on stainless steel was improved by applying either zinc or cerium naphthenate to a clean steel surface and firing at 1,200° F to remove organic components. Similar surface treatments with 15 other metal naphthenates resulted in either no marked improvement or complete deterioration of the bond.

3. A surface treatment consisting of immersion of clean stainless-steel surfaces in an aqueous solution of either dicyandiamide or 1-hydroxy-2-naphthoic acid at the boiling point improved the resistance of FPL-878 bonds to thermal aging. The use of several other organic compounds and chelating agents in a similar way was not beneficial.

4. A study in which a number of inorganic compounds were added to adhesive FPL-878 in quantities of less than 5 percent showed several that improved the resistance of the adhesive to thermal aging on stainless steel. Most beneficial of these compounds were manganese dioxide, aluminum oxide, arsenic trioxide, stannous sulfide, and antimony trisulfide. These materials were believed to have catalytically poisoned or inhibited the action of the iron on the adhesive during high-temperature aging.

5. A study to determine the thermal-aging properties of five different chemical types of adhesives in bonds on stainless steel and aluminum showed that a phenol-nitrile rubber type (adhesive C) was superior

to a phenol-epoxy resin type (adhesive FPL-878) on stainless steel, but the phenol-epoxy type was most resistant on aluminum. Silicone resin adhesive D also showed better thermal resistance on steel than on aluminum, whereas the phenol resin and the epoxy resin separately had greater resistance to deterioration on aluminum than on stainless steel.

6. The treatment of stainless-steel surfaces with zinc naphthenate and the addition of 1 percent of manganese dioxide to adhesive FPL-878 increased the strength of the adhesive on stainless steel at 80° F after aging for 100 hours at 550° F from 130 to 658 psi. Similar treatment of the steel and addition of manganese dioxide reduced the thermal-aging properties of the phenol-nitrile adhesive.

Forest Products Laboratory,
Madison, Wis., November 29, 1956.

REFERENCES

1. Black, J. M., and Blomquist, R. F.: A Study of the Deterioration of Adhesives in Metal Bonds at High Temperatures. WADC Tech. Rep. 55-330, U. S. Air Force, Mar. 1956.

2. Black, John M., and Blomquist, R. F.: Metal-Bonding Adhesives for High-Temperature Service. NACA RM 55F08, 1955.

3. Gulbransen, Earl A.: Kinetics and Structural Factors Involved in Oxidation of Metals. Ind. and Eng. Chem., vol. 41, no. 7, July 1949, pp. 1385-1391.

4. Gulbransen, Earl A., and Ruka, Roswell: Kinetics and Mechanism of Solid Phase Reactions in Oxide Films on Pure Iron. Ind. and Eng. Chem., vol. 43, no. 3, Mar. 1951, pp. 697-703.

5. Gulbransen, Earl A., and McMillan, William R.: Oxide Film on Nickel-Chromium Alloys - Crystal Structure Studies. Ind. and Eng. Chem., vol. 45, no. 8, Aug. 1953, pp. 1734-1744.

6. Gulbransen, Earl A., Phelps, R. T., and Hickman, J. W.: Electron Diffraction and Electron Microscope Study of Oxide Films Formed on Metals and Alloys at Moderate Temperatures. Ind. and Eng. Chem., Analytical Ed., vol. 18, June 1946, pp. 391-400.

7. Rhodin, T. N.: Oxide Films on Stainless Steel. Corrosion, vol. 12, no. 3, Mar. 1956, pp. 123-135.

8. Emmett, P. H.: Surface Area Measurements - A New Tool for Studying Contact Catalysts. Advances in Catalysis, vol. I, W. G. Frankenburg, V. I. Komarewsky, and E. K. Rideal, eds., Academic Press, Inc. (New York), 1948.

9. Anon.: Steel, Corrosion-Resistant (18-8), Plate, Sheet and Strip. Military Specification MIL-S-5059A(ASG), Mar. 16, 1953.

10. Moreau, Jean, and Bardolle, Jean: Détermination par diffraction électronique de la constitution der films d'oxydes formér à la surface du fer. Comptes Rendus, t. 240, no. 5, Jan. 31, 1955, pp. 524-526.

11. Hickman, J. W.: Oxide Films Formed on Metals and Binary Alloys. Electron Diffraction Study. A.I.M.E. Tech. Pub. no. 2483, Dec. 1948.

12. Pfeil, L. B.: Metallurgical Aspects of Dry Corrosion. Chem. and Ind., no. 9, Feb. 26, 1955, pp. 208-218.

TABLE 1.- EFFECT OF VARIOUS METAL IONS DEPOSITED BY CHEMICAL DISPLACEMENT ON CLAD ALUMINUM ON SHEAR STRENGTH OF RESULTANT BONDS AFTER AGING AT 550° F

[Metal salts were dissolved in a 10-percent nitric acid solution, and aluminum surfaces were immersed for 60 minutes at 80° F; test specimens were bonded with FPL-878 adhesive under standard conditions described in the section "Experimental Procedure"]

Metal salt	Concentration, mols	Shear strength at 80° F, psi	
		Before aging	After 100 hr at 550° F (a)
None	-----	1,771	935
Manganous chloride	0.005	1,712	1,044
	.015	1,876	930
	.030	1,480	912
	.060	1,860	1,084
	.100	1,322	1,054
Chromic chloride	.005	1,690	890
	.015	1,926	1,194
	.030	1,560	924
	.060	1,832	1,032
	.100	1,622	912
Ferrous chloride	.005	1,716	1,084
	.015	2,026	1,286
	.030	1,926	954
	.060	1,930	820
	.100	1,420	732
Ferric chloride	.005	1,460	962
	.015	2,032	1,044
	.030	1,886	930
	.060	1,796	884-(7)
	.100	1,466	552
Nickel chloride	.005	1,876	1,126
	.015	1,740	1,042
	.030	1,342	866
	.060	1,496	926
	.100	1,606	702

[a]Value in parentheses is average estimated percentage of shear area failing in adhesion to metal. In all other cases, failure was completely in cohesion of adhesive layer.

TABLE 1.- EFFECT OF VARIOUS METAL IONS DEPOSITED BY CHEMICAL DISPLACEMENT ON CLAD ALUMINUM ON SHEAR STRENGTH OF RESULTANT BONDS AFTER AGING AT 550° F - Concluded

Metal salt	Concentration, mols	Shear strength at 80° F, psi	
		Before aging	After 100 hr at 550° F (a)
Zinc chloride	0.005	1,800	1,304
	.015	1,606	1,192
	.030	1,966	1,124
	.060	1,706	1,040
	.100	1,836	1,136
Cupric chloride	.005	1,390	0
	.015	2,200	1,106
	.030	2,156	1,160
	.060	2,266	1,206
	.100	2,000	1,282
Silver nitrate	.005	2,100	1,254
	.015	2,152	1,450
	.030	2,376	1,450
	.060	2,120	1,272
	.100	2,120	1,162
Cerous nitrate	.005	1,732	1,094
	.015	2,040	1,146
	.030	1,890	1,196-(6)
	.060	1,530	966
	.100	1,390	874
Cobaltous chloride	.015	1,880	892-(5)
Mercuric chloride	.015	1,200	0-(100)
Lead nitrate	.015	1,790	886

[a]Values in parentheses are average estimated percentages of shear area failing in adhesion to metal. In all other cases, failure was completely in cohesion of adhesive layer.

TABLE 2.- SHEAR-STRENGTH VALUES FOR LAP SPECIMENS MADE WITH FPL-878 ADHESIVE ON STAINLESS STEEL TREATED WITH VARIOUS NAPHTHENATES AFTER AGING FOR 100 HOURS AT 550° F

[Metal surfaces were cleaned by method A described in section "Experimental Procedure," one coat of naphthenate was applied by brush, and steel was then heated to 1,200° F for 15 minutes before cooling and application of adhesive]

Metal naphthenate	Shear strength at 80° F, psi	
	Before aging (a)	After aging
None	2,470	50
Lithium		110
Strontium		32
Barium		20
Calcium		0
Magnesium		66
Aluminum		50
Manganese		60
Zinc	2,206	380
Chromium		46
Iron		0
Cadmium		0
Cobalt	2,532	28
Nickel	2,064	138
Tin		124
Lead	100-(30)	0
Vanadium		0
Copper	1,280-(60)	0
Cerium		382
Zirconium		44

[a]Values in parentheses are average estimated percentages of shear area failing in adhesion to metal. In all other cases, failure was completely in cohesion of adhesive layer.

TABLE 3.- SHEAR STRENGTH OF FPL-878 ADHESIVE CONTAINING VARYING AMOUNTS OF DIFFERENT INORGANIC MATERIALS ON STAINLESS STEEL WHEN TESTED AT 80° F AFTER 100 HOURS AT 550° F

[Stainless-steel surfaces were prepared for bonding by method A followed by method B, as described in section "Experimental Procedure"]

Material added	Shear strength at 80° F after 100 hr at 550° F, psi				
	0.5 percent additive	1.0 percent additive	2.0 percent additive	3.0 percent additive	5.0 percent additive
None	[a]130	---	---	---	---
Aluminum flake	---	20	---	20	---
Aluminum oxide	---	162	272	474	422
Manganese dioxide	376	566	436	326	---
Zinc dust	---	0	---	218	266
Zinc oxide	---	52	---	0	---
Stannous oxide	---	72	---	372	---
Stannic oxide	---	228	---	306	---
Stannous sulfide	98	426	320	380	---
Cupric oxide	---	226	---	---	---
Cuprous sulfide	---	222	---	176	---
Arsenic trioxide	---	366	---	440	---
Arsenic pentoxide	---	140	---	60	---
Bismuth trioxide	---	304	---	66	---
Antimony trioxide	0	250	---	0	---
Antimony trisulfide	---	328	---	416	---
Antimony pentasulfide	---	0	---	---	---

[a]Control value; no inorganic material was added to adhesive.

TABLE 4.- SHEAR STRENGTH OF DIFFERENT CHEMICAL-TYPE ADHESIVES ON STAINLESS STEEL AND ALUMINUM WHEN TESTED AT 80° F AFTER EXPOSURE TO ELEVATED TEMPERATURES FOR VARIOUS LENGTHS OF TIME

[Bonding conditions for each adhesive are described in the section "Experimental Procedure"]

Metal (a)	Exposure conditions		Shear strength at 80° F, psi (b)				
	Time, hr	Temperature, °F	FPL-878	Adhesive A	Adhesive B	Adhesive C	Adhesive D
Stainless steel (type 302)	24	80 (control)	2144	1764	4390	2102	1418
	50	400	1750	950-(48)	4220-(28)	3220	2060
	50	450	1602	596-(17)	4130-(33)	4510-(28)	1926
	50	500	1028	296-(30)	1424-(10)	1446-(11)	1516
	16	550	944	56	596	1796	1486
	50	550	300	160	196	1336	470
	100	550	130	0	200	1020	38
Aluminum alloy (2024-T3)	24	80 (control)	2210	1224	3890	2250	504
	50	450	1244	958	3520	2944	452
	50	500	1202	1160	3020	1624	186
	50	550	1184	644	105	398	44
	100	550	1184	714	93	308	104
	200	550	826	514	215	254	112

[a]Stainless-steel surfaces were prepared for bonding by method A followed by method B; aluminum surfaces were prepared for bonding by method B; methods A and B described in section "Experimental Procedure."

[b]Values in parentheses are average estimated percentages of shear area failing in adhesion to metal. In all other cases, failure was completely in cohesion of adhesive layer.

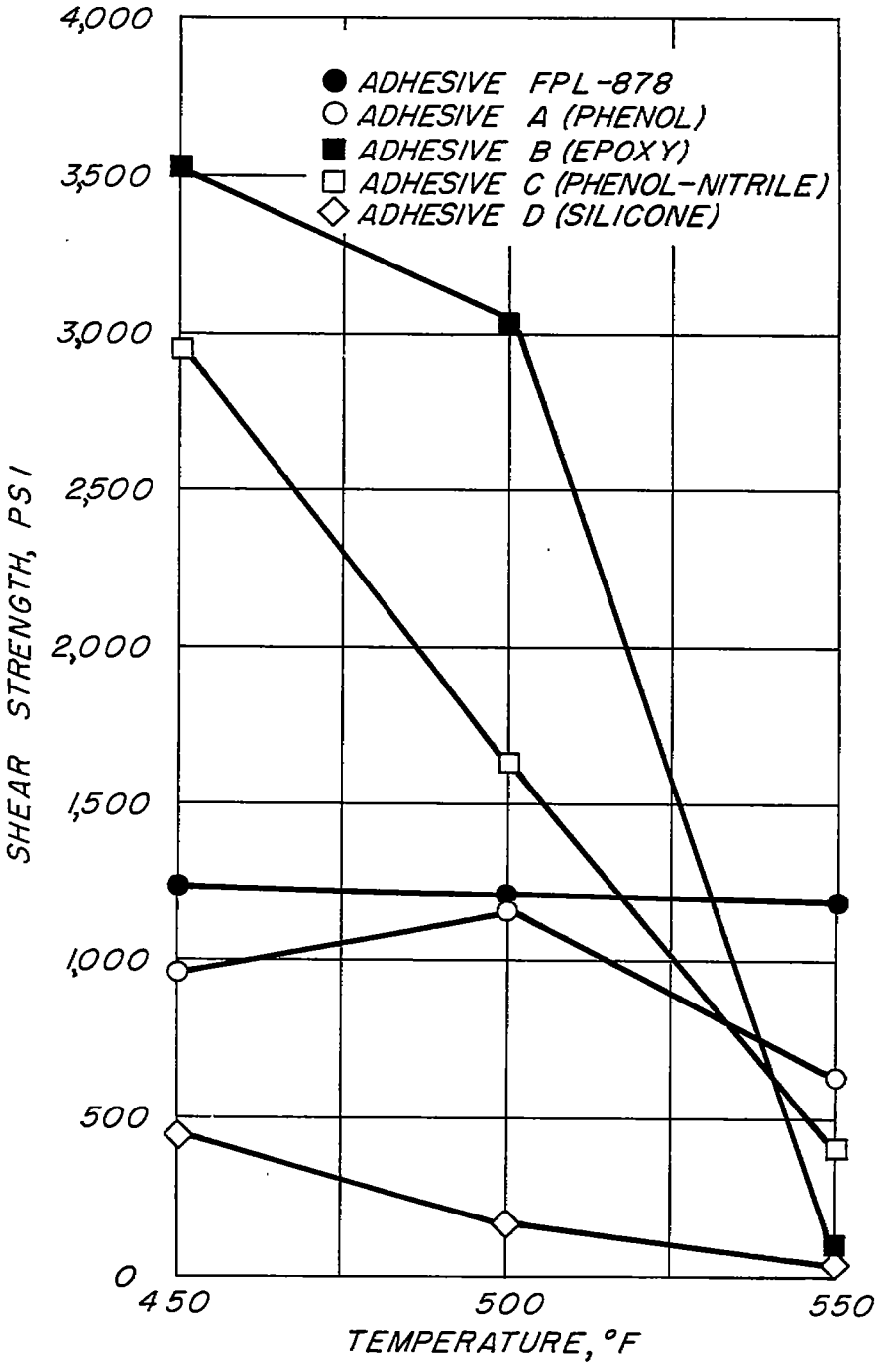

Figure 1.- Shear strength plotted against aging temperature for adhesive bonds between aluminum-alloy plates. Specimens were tested at 80° F after aging for 50 hours.

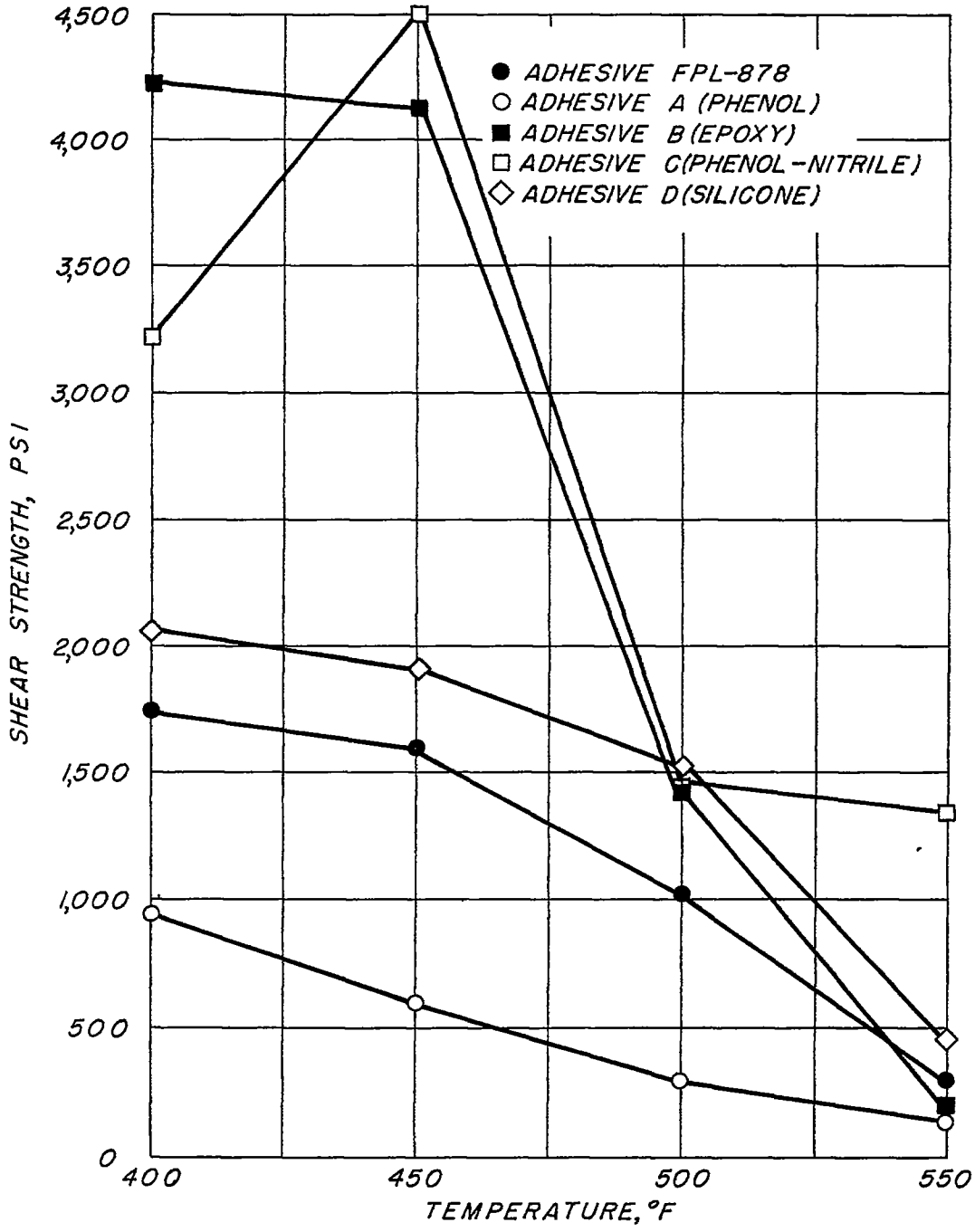

Figure 2.- Shear strength plotted against aging temperature for adhesive bonds between stainless-steel plates. Specimens were tested at 80° F after aging for 50 hours.

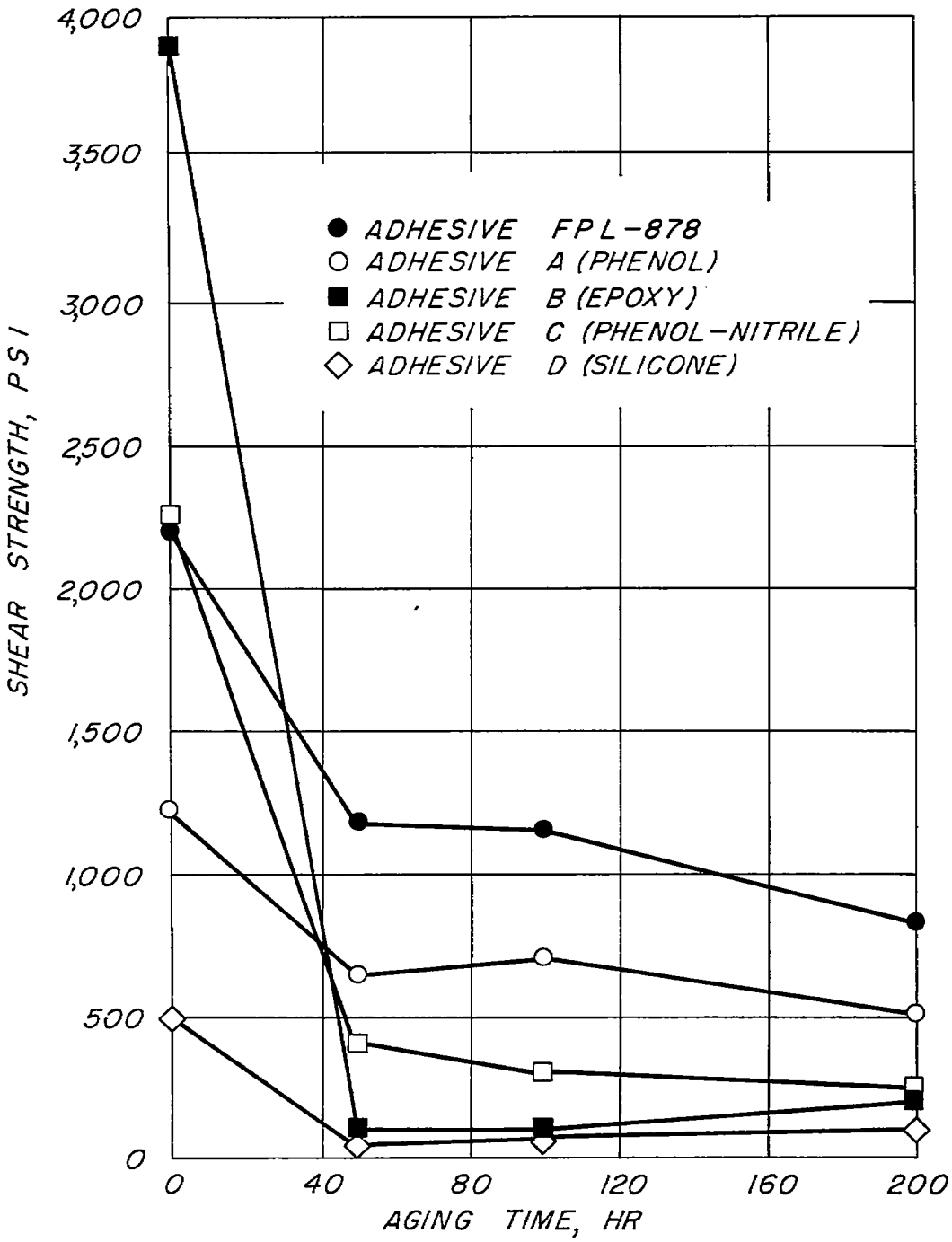

Figure 3.- Shear strength plotted against aging time for adhesive bonds between aluminum-alloy plates. Specimens were tested at 80° F after aging at 550° F.

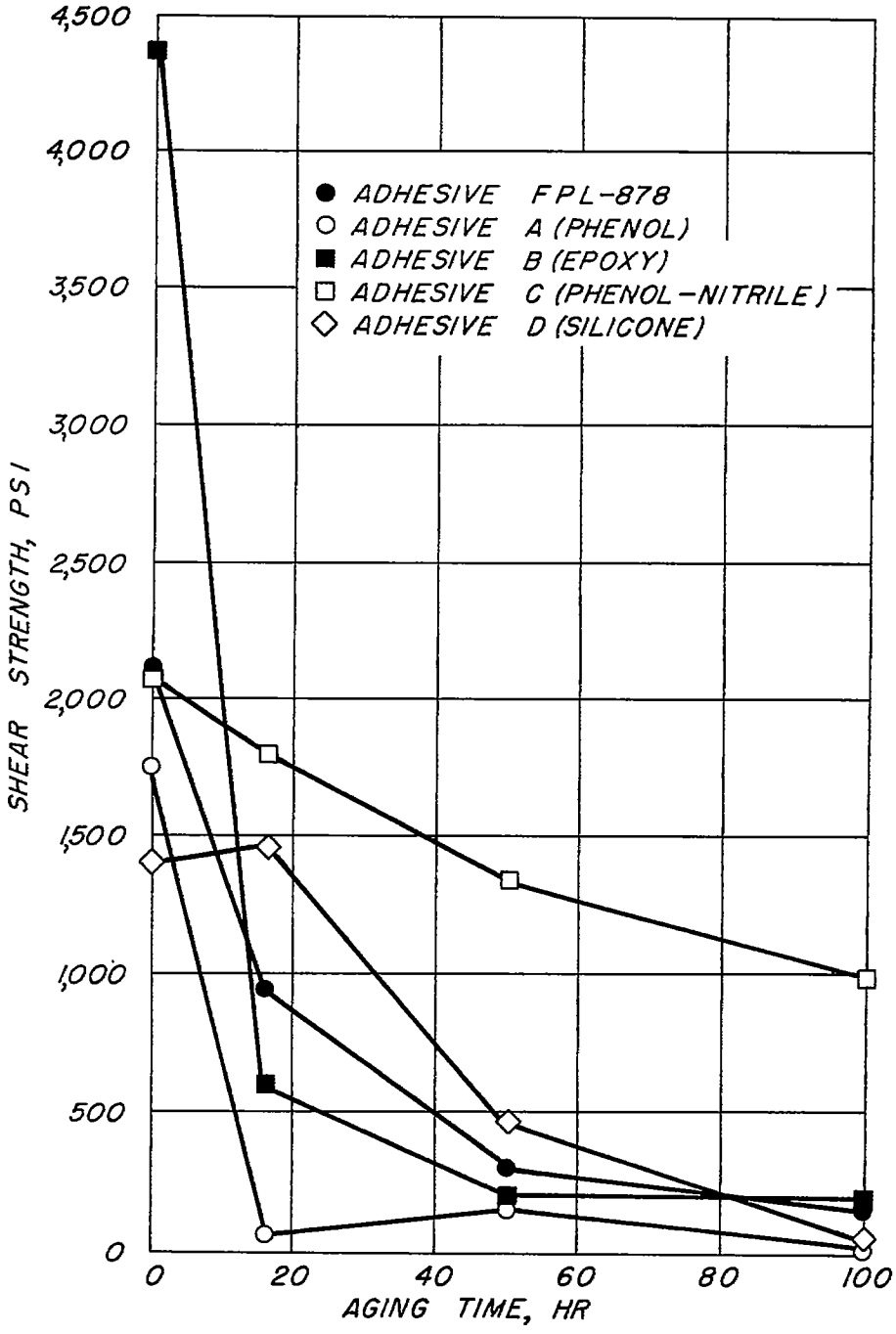

Figure 4.- Shear strength plotted against aging time for adhesive bonds between stainless-steel plates. Specimens were tested at 80° F after aging at 550° F.

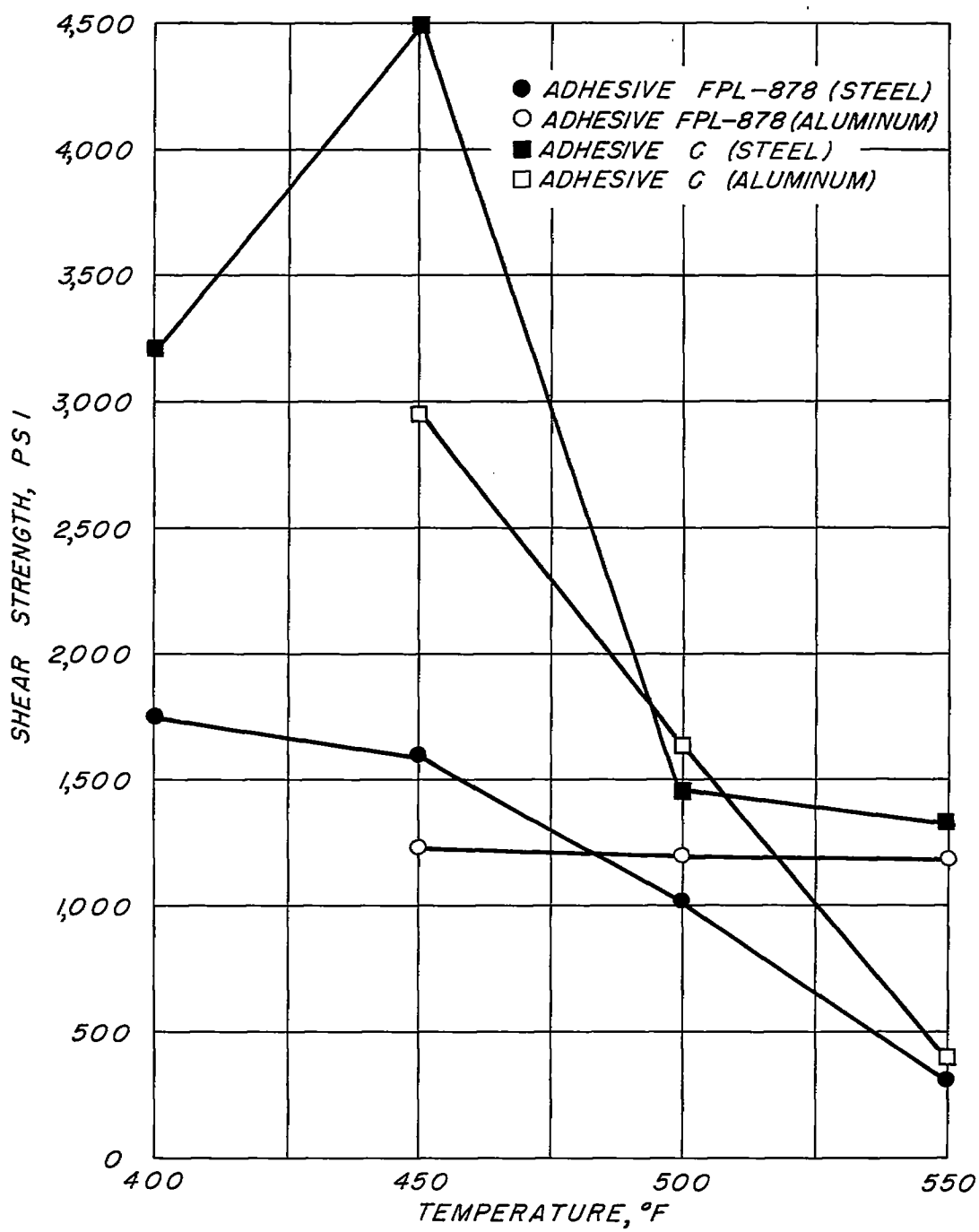

Figure 5.- Shear strength plotted against aging temperature for FPL-878 and phenol-nitrile adhesive bonds between aluminum-alloy and stainless-steel plates. Specimens were tested at 80° F after aging for 50 hours.

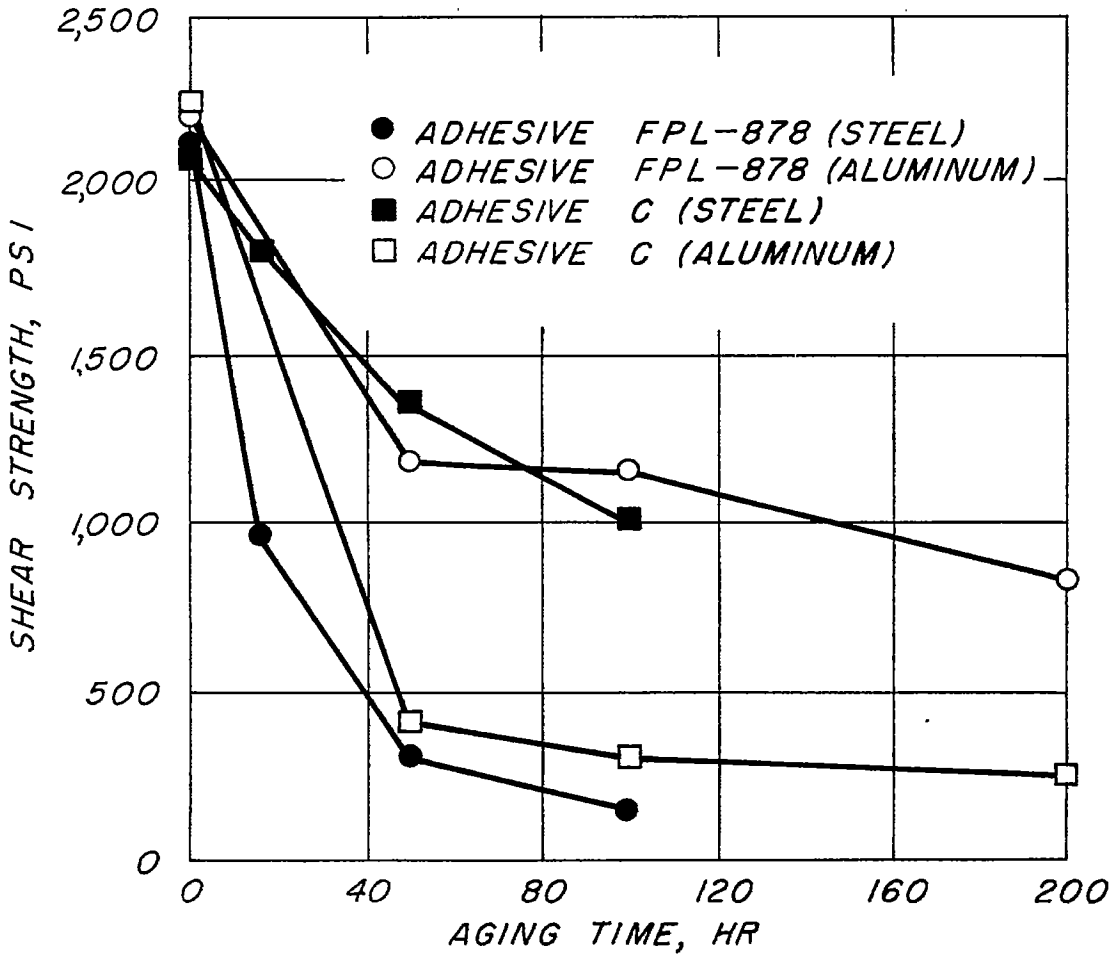

Figure 6.- Shear strength plotted against aging time for FPL-878 and phenol-nitrile adhesive bonds between aluminum-alloy and stainless-steel plates. Specimens were tested at 80° F after aging at 550° F.