

Epoxy and Urethane Adhesives

1971

Dr. M.W. Ranney

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Thirty-Six Dollars

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INTRODUCTION

The first epoxy adhesive compound was apparently developed by P. Schlock in 1934, (U.S. Patent 2,136,928; assigned to I.G. Farbenindustrie). In 1938, P. Castan (Swiss Patents 211,116 and 236,954) developed a number of epoxy resins from epichlorohydrin and bisphenol A which when cured with phthalic anhydride provided excellent adhesion to glass, porcelain and metal. In the late 1940's, Ciba Co. in Switzerland began marketing Araldite, an epoxy based adhesive.

In the United States, Shell Development Co. first offered commercial epoxy adhesives in the late 1940's. Shell scientists found that the addition of aluminum oxide, (U.S. Patent 2,528,944), aluminum powder (U.S. Patent 2,528,933) and a number of other ingredients (U.S. Patents 2,528,932 and 2,602,785) provided improved adhesion to metals. During the 1950's, increasing demand was placed on the epoxy adhesives, particularly for bonding air frame structures where high temperature resistance was required.

The growth of epoxides for adhesive applications has been rapid over the past few years. In 1966, about 15.1 million pounds of epoxide adhesives were used worldwide and they have enjoyed an annual growth rate of some 10 to 15%.

Urethane adhesives and intermediates are being used in increasing quantities in adhesive formulations. Isocyanate monomers such as toluene diisocyanate and 4,4'-diphenylmethane diisocyanate are applied in solution form to textile fibers, metals and elastomers as primers for adhesion. 4,4',4''-triphenylmethane triisocyanate provides good rubber to rayon or nylon adhesion and has been commonly used for such fabric to rubber bonding, particularly in Europe.

Polymethylene polyphenyl isocyanates are used in adhesives for bonding glass, metal, elastomers and wood to a variety of substrates. Polyurethanes, in combination with polyesters, polyamides, and elastomers, or modified with resorcinol-formaldehyde resins have been developed to meet many high performance adhesion requirements.

This book describes the process literature for epoxies, isocyanates and urethanes as it relates to these high performance adhesive intermediates in many end use formulations.

METAL TO METAL BONDING

EPOXY

Crystalline 2,2-Bis(2,3-Epoxypropoxyphenyl)Propane

H.L. Parry; U.S. Patent 3,159,595; December 1, 1964; assigned to Shell Oil Company describes adhesive compositions containing free-flowing crystals of 2,2-bis(2,3-epoxypropoxyphenyl)propane and solid curing agents.

A typical composition prepared according to the process is a free-flowing powder which melts between 100° and 120°F. The melt does not resolidify when cooled to room temperature. The powder has a shelf life of at least 6 months when stored between 32° and 40°F. when the curing agent is of the heat activated type. When stored at ambient temperature there is a slow interreaction between the polyepoxide and curing agent, resulting in a gradual increase of the viscosity of the composition when melted.

The powder composites are particularly suitable for use as adhesives. They can be used to cause adhesion between a wide variety of different materials. The powder composite, when it is to be used as an adhesive, may be applied, for example, in the following two ways:

- (1) As an even layer of powder, which may be followed by heating to sinter the mixture sufficiently to hold it in place. The physical method of applying the adhesive powder to a material to be bonded provides no special problems. The material may be applied manually, or conventional powder handling equipment may be employed. It is only necessary to avoid heating the powder at any point above a temperature of about 100°F. to avoid causing it to liquefy.
- (2) By melting the composite in a separate container by mild heating and applying a thin even layer of the resulting paste.

The parts are then assembled and held together with clamps or by other means. The composites generally require curing temperatures of about 200°F. or higher. Typical conditions are from 1/2 to 3 hours at 250°F., from 1/4 to 1 hour at 300°F. and from 2 to 30 minutes at up to 500°F. The process is illustrated by the following examples.

Example 1: A composite was prepared having the components shown on the following page.

Metal to Metal Bonding

<u>Component</u>	<u>Parts</u>
Crystalline 2,2-bis(2,3-epoxypropoxyphenyl)propane	100
Trimellitic anhydride	55
Dicyandiamide	0.5
Asbestos floats	40

In preparing the composite, the weighed dry ingredients were placed into a vessel and a sufficient amount of isooctane added to give a suspension which had the appearance of a stiff, grainy paste. This paste was then passed through a three roll paint mill several times, care being taken to avoid buildup of frictional heat to a level at which all of the solvent would have been removed by vaporization. The paste was then spread out to dry at room temperature and the resulting dry free-flowing powder placed in a container and stored in a cool place. Equally good mixing was obtained by use of a two roll plastic mill in place of the paint mill.

Example 2: A portion of the powdered composite prepared according to Example 1 is heated to about 120°F. The powder melts, resulting in a moderately thick paste of uniform composition. This paste is sufficiently thixotropic so that it can be applied to a vertical surface without running, even during cure at elevated temperature. The paste is relatively viscous at room temperature. It is still a useful adhesive after storage for 2 to 3 days at 80°F. or storage of about 1 day at 120°F.

Portions of the paste are heated to a temperature in the range between 110° and 130°F. and used to bond together two sheets of etched aluminum, utilizing a variety of curing temperatures and times. The sample sheets of aluminum are bonded by spreading adhesive over about a 3/4 inch width along an edge of each sheet and then placing the two sheets together with a 1/2 inch overlap, clamping them together and placing the assembly in a pre-heated oven provided with forced air circulation for the desired length of time. The sheets are sawed into strips in which the area of overlap is normally about 1/2 x 1 inch. The strips are then tested in tension at the desired test temperature at a loading rate of 1,400 psi per minute. The following table represents typical results of this test.

<u>Cure Cycle</u>	<u>Tensile Shear Strength, psi</u>	<u>Test Temperature, °F.</u>
2 hours at 200°F.	1,850	75
4 hours at 200°F.	2,200	75
1 hour at 250°F.	2,450	75
3 hours at 250°F.	2,600	75
1 hour at 300°F.	2,800	75
2 minutes at 400°F.	2,750	75
8 minutes at 400°F.	2,540	75
4 minutes at 500°F.	2,100	75
1/2 hour at 250°F.	3,600	200
2 hours at 250°F.	3,700	200
1/4 hour at 300°F.	3,700	200
1 hour at 300°F.	2,900	200

(continued)

Metal to Metal Bonding

<u>Cure Cycle</u>	<u>Tensile Shear Strength, psi</u>	<u>Test Temperature, °F.</u>
1/4 hour at 350°F.	4,000	200
1 hour at 300°F.	4,200	300
1/4 hour at 400°F.	3,100	400

Example 3: The procedure of Example 2 is repeated with solvent wiped steel substituted for the aluminum sheet. The tensile shear strengths obtained are approximately 10% lower than the values found with aluminum in Example 2.

Epoxy Esters of Polycarboxylic Aromatic Acids

A process described by S.R. Sandler, F.R. Berg and G. Kitazawa; U.S. Patent 3,442,752; May 6, 1969; assigned to The Borden Company involves surfaces adhesively bonded with an adhesive containing completely esterified epoxy esters of polycarboxylic aromatic acids and amine curing agents. The adhesive is cured at preferably elevated temperatures. The resulting adhesive bond between the adhered aluminum surfaces is as high as 3,390 psi when tested at temperatures of 250°F., 1,700 psi at 400°F., 2,700 to 5,037 psi at -320°F. and 2,920 psi at -453°F.

As to materials, the polycarboxylic aromatic acid is preferably a mononuclear aromatic acid having between 2 to 4 carboxylic substituent groups on the aromatic moiety. Examples of these acids include the 1,2-, 1,3- and 1,4-isomers of phthalic acid; trimesic, hemimellitic and trimellitic acid; and prehnitic, mellophanic and pyromellitic acid.

The epoxy component is an epoxidized alcohol which, when reacted with the acid or related halide, results in the ester component of the adhesive. Particularly preferred are the mono-epoxy substituted alkanols containing between 3 to 8 carbon atoms and having the epoxy group in the terminal position. Within this group, 2,3-epoxypropanol is preferred.

The adhesive is prepared by combining the ester and curing agent in the proportion of between 0.1 to 1.0 amino or amido groups of the curing agent for each epoxy group in the ester molecule. For example, a triepoxy ester requires between 0.3 to 3.0 amino or amido groups, or in terms of a specific curing agent like methylenedianiline, 0.15 to 1.5 mols for each mol of triepoxy ester.

The adhesive was tested for tensile shear strength when used to adhesively bond metal-metal surfaces. The metal was preetched in acid-oxidizing solutions, i.e., stainless steel, for example, in nitric acid and sulfuric hydrochloric-hydrofluoric acid; aluminum, in sulfuric acid-potassium dichromate solution. The cleaned metal surface was coated with the adhesive, contacted with another surface of cleaned metal, and cured at elevated temperatures, as for example above 75°C., for several hours until cured.

Optionally, both surfaces could be coated with adhesive. After curing, the samples were equilibrated in a constant temperature-humidity room; generally at room temperature and about 50% relative humidity for several days. Tensile shear strengths were determined using a Tinus Olsen Electromatic Universal Testing Machine. A cryostat was used for liquid nitrogen and helium testing. The tests at elevated temperatures were conducted in constant

Metal to Metal Bonding

temperature forced air oven. The following examples illustrate the process.

Example 1: Preparation of Triepoxy Ester of Trimesic Acid — (a) Triacid Chloride: To 1 mol of trimesic acid and 4 ml. of pyridine in a reflux kettle was added 5.6 mols of thionyl chloride. The reaction mixture was heated to reflux temperature and maintained at reflux for about 20 hours. Excess thionyl chloride was removed by distillation and the product was recovered by fractional distillation (2.5 to 4.0 mm. Hg, 150° to 159°C.).

(b) Triepoxy Ester: To a precooled (about 0°C.) mixture of 1.5 mols of glycidol is added simultaneously and separately under agitation, 1.5 mols of triethylamine and a benzene solution of 0.5 mol of trimesoyl chloride. The temperature was kept below 5°C. After the addition, the temperature was allowed to rise to room temperature. The solids were filtered out and the filtrate concentrated by evaporation of the solvent to give the product. The product was recrystallized from 1:1 petroleum ether and benzene to give white crystals, MP 58° to 63°C.

Example 2: The procedure of Example 1(a) is repeated except that the trimesic acid is replaced separately and in turn by the polycarboxylic aromatic acids disclosed herein. The proportion of thionyl chloride is about 1 to 4 mols for each mol of carboxy radical in the polycarboxylic acid. In a modification of this example, the procedure of Example 1(b) is repeated except that the glycidol is replaced separately and in turn by the epoxidized alcohols disclosed herein. The proportion of the alcohol is about 1 mol for each mol of acid chloride radical in the acid chloride.

Example 3: Preparation of the Adhesive — The liquefied esters of Examples 1 and 2 are mixed with liquefied methylenedianiline in proportion of 2-NH₂ groups of curing agent per 4 epoxy groups of ester.

Example 4: In a modification of Example 3, methylenedianiline is replaced separately and in turn by the curing agent disclosed herein in the range of proportions of between 0.25 to 1.0 amino or amido groups for each epoxy group in the molecule.

Example 5: The adhesives prepared as in Examples 3 and 4 are coated onto cleaned aluminum and stainless steel surfaces to give an adhesive layer of about 1 to 5 mils. The adhesive surface is covered by the same or other metal and cured at about 100°C. for 2 hours. The adhered metals are then equilibrated at about 23°C. and 50% relative humidity for about 7 days. Tensile strength tests were then run on samples so prepared. The following table shows the results obtained by the adhesives of this process in the extreme temperature ranges of -453° to -320°F. (cryogenic range) and 250° to 400°F. (elevated range). Bisphenol A is included by way of comparison with other epoxy products.

Tensile Shear Strength, psi, on Aluminum-Aluminum Surfaces

	<u>-453°F.</u>	<u>-320°F.</u>	<u>73°F.</u>	<u>250°F.</u>	<u>400°F.</u>
Tris(2,3-epoxypropyl)trimesoate, MdiA ¹ (3/0.6) ²	2,920	2,700	2,700	2,410	1,700

(continued)

Metal to Metal Bonding

	<u>-453°F.</u>	<u>-320°F.</u>	<u>73°F.</u>	<u>250°F.</u>	<u>400°F.</u>
Di(2,3-epoxypropyl)phthalate, MdiA (2.5/0.9)	-	5,037	4,057	1,200	-
Bisphenol A diglycidyl ether, MdiA (5/1.4)	-	2,130	1,690	1,240	556
Tetraglycidyl pyromellitate, MdiA (2.4/1)	-	1,800	2,200	2,960	1,098
Diglycidyl isophthalate, MdiA (2.8/1.0)	-	4,200	3,780	2,660	385
Di(2,3-epoxypropyl)terephthalate, MdiA (2.1/0.5)	2,270	3,350	2,740	2,220	428
Di(2,3-epoxypropyl)terephthalate, CPDA, ³ BDA ⁴ (1.7/1.0/0.03 ml.)	-	1,746	3,150	3,390	1,535
Di(2,3-epoxypropyl)isophthalate, CPDA, BDA (2.8/2.1/0.06 ml.)	-	1,650	1,560	1,730	1,210

¹MdiA is methylenedianiline.

²Molar ratio of epoxy to curing agent.

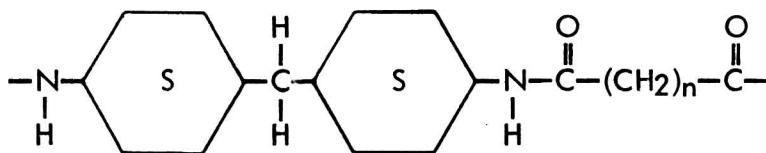
³Cyclopentane tetracarboxylic acid dianhydride.

⁴Benzyldimethylamine.

Poly[4-(4-Cyclohexylmethyl)Cyclohexyl Sebacamide]

B.S. Gorton; U.S. Patent 3,462,337; August 19, 1969; assigned to E.I. du Pont de Nemours and Company describes a polyamide-polyepoxide adhesive composition which provides good bond strengths between metal substrates and which retains adequate bond strengths at elevated temperatures, and furthermore, will retain adequate bond strengths under hot-wet conditions.

The process comprises, in general, a method of uniting surfaces of metallic elements by applying to at least one of the surfaces a composition comprising about 75 to 95 parts by weight of a polyamide having the recurring group of the formula:



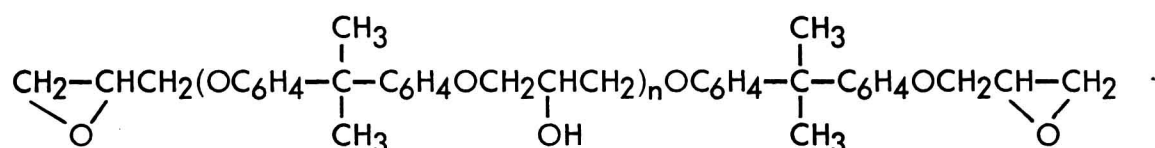
where n is an integer of from 6 to 10 inclusive, and 5 to 25 parts by weight of a polyepoxide having at least 2 epoxy groups per molecule and preferably having a viscosity of 50 to 200,000 cp. at 25°C., holding the surfaces contiguous to one another, heating the surfaces and compositions to a temperature in the range of from 400° to 600°F. for from 5 to 60 minutes and cooling.

The polyamides may be prepared by the condensation polymerization of bis(4-aminocyclohexyl)methane with sebacic acid. The polyamides may be prepared in accordance with the

Metal to Metal Bonding

general procedure described in U.S. Patent 2,715,620. It is essential that the polyamide used have a molecular weight within the range of 1,000 to 35,000. The bond strength obtained by the use of a polyamide having a molecular weight outside this range is too low to be of practical value. Furthermore, compositions derived from a polyamide having a molecular weight of less than about 1,000, do not possess adequate bond strength retention under hot-wet conditions.

In addition, polyamides having molecular weights of more than 35,000 do not readily mix with the polyepoxides of this process and also compositions prepared from such polyamides require excessive time to form a bond between substrates. Therefore, in order to obtain practical bond strengths and the desired bond strength retention under elevated temperatures and hot-wet conditions it is necessary that the polyamide have a molecular weight range of 1,000 to 35,000. Highest bond strengths are obtained by use of a polyamide having a molecular weight of about 5,000 to 15,000. The preferred polyepoxides are those obtained by the reaction of bisphenol A and epichlorohydrin which have the empirical formula:



where n has an average value of from 0 to 10. Generally, n will not be greater than 2 or 3, and it is preferably 0 to 1. It is generally preferred that the polyepoxide be a syrup, that is, have a viscosity of from 50 to 200,000 cp. at 25°C. In fact, for many uses it is essential that the polyepoxide be a syrup.

The following examples are given to illustrate the process. In each of these examples, to provide correlative data, strips of 7075-T6 Aluminum (Lyman, Ed., Metals Handbook, vol. 1, "Properties and Selection of Metals," American Society for Metals Novelty, Ohio, 8th ed., 1961, p. 948) were used as the metal substrates. These aluminum strips were 0.064 inch thick and measured 1 x 3 inches. These strips were degreased by suspending them in trichloroethylene vapor. Following the degreasing, these strips were etched in a chromium acid bath at 70°C. for 30 minutes, washed in cool water and then dried.

Standard lap joints were prepared by applying the various compositions shown onto the surface of one strip and then positioning another strip on top to form a 0.5 inch overlap (ASTM D1002-53T). These lap joints were then pressed together with 15 to 50 psi pressure at 450°F. for a specified time. The bond strengths of the various adhesive compositions were evaluated by determining the lap shear strengths of the prepared lap joints, in accordance with ASTM D1002-53T, whereby the strips were pulled apart at a rate of 0.2 in./min. at a jaw separation of 4 1/2 inches.

Example 1: A 1 g. sample of finely powdered (through 100 mesh) poly[4-(4-cyclohexylmethyl)-cyclohexyl sebacamide] having a molecular weight of about 10,000 was blended with 0.05 g. of a commercially available polyepoxide by grinding in a mortar for several minutes. The polyepoxide was the reaction product of bisphenol A and epichlorohydrin having a manufacturer's specified viscosity of 5,000 to 15,000 cp. at 25°C., an average molecular weight

Metal to Metal Bonding

of 350 to 400, and a specified epoxide equivalence of 175 to 210. Lap joints were prepared as described above, with the specified time being 15 minutes using this resultant powder, and tested. The average lap shear strength at room temperature was 5,640 psi. The average lap shear strength at 100°C. was extrapolated to be greater than 3,200 psi and at 150°C. was extrapolated to be greater than 2,200 psi.

Example 2: 50 parts by weight of a polyamide such as the reaction product of triethylene-diamine and the dimeric acid of linoleic acid having an amine equivalence of 210 to 230 which is the ml. of KOH equivalent to the base content of 1 g. of the polyamide as determined by titration with HCl, is blended with 50 parts of the polyepoxide such as used in Example 1. The average lap shear strength at room temperature is 3,200 psi, at 82°C. is 1,500 psi and at 120°C. is 600 psi. These properties are inferior to those of the composition of this process.

Example 3: A 1 g. sample of finely powdered (through 100 mesh) poly[4-(4-cyclohexylmethyl)-cyclohexyl sebacamide] having a molecular weight of approximately 10,000 was blended with 0.10 g. of the polyepoxide used in Example 1. Lap joints were made as in Example 1 with the specified time being 60 minutes. The average lap shear strength at room temperature was 5,600 psi. The average lap shear strength at 100°C. was estimated to be greater than 3,200 psi and at 150°C. was estimated to be greater than 2,200 psi.

Although the inherent viscosity of the poly[4-(4-cyclohexylmethyl)cyclohexyl sebacamide] as used in the example was 0.6, as measured in m-cresol (c. = 0.5), it should be obvious that a polyamide having any molecular weight which flows well as a blend and gives good blend strength may be advantageously utilized. Similarly, although it is provided to utilize sebacic acid as the condensation polymer, other dicarboxylic aliphatic acids such as azelaic acid may be employed.

Linear Polyamides, Epoxy Resin

J.H. Groves; U.S. Patent 2,962,468; November 29, 1960 and U.S. Patent 2,970,077; January 31, 1961; both assigned to American Can Company describes a high strength, quick setting adhesive comprising the reaction product of a linear polyamide and an epoxy resin.

When this composition of linear polyamide and epoxy resin is heated in contact with the surfaces to be joined, to a temperature above the melting point of the polyamide, and held at this temperature for a brief interval of time and cooled, upon setting and hardening of the cement or adhesive there results between the surfaces a high strength bond comparable to or greater than that of metallic solder.

Among the polyamides which are useful in the process are polypentamethylene sebacamide, polyhexamethylene adipamide, polyhexamethylene sebacamide, polydecamethylene adipamide, polydecamethylene sebacamide, poly-m-phenylene sebacamide and 6-amino-caproic acid polymers.

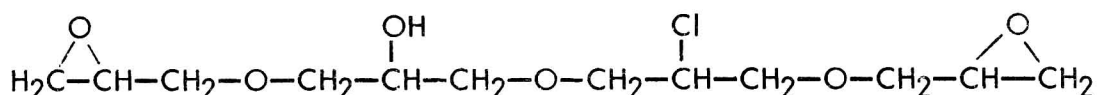
The epoxy resin adhesion promoters for the polyamides belong to a class of complex, polymeric epoxy-hydroxy ethers resulting from the catalyzed reaction of a polyhydric alcohol,

Metal to Metal Bonding

e.g., glycols, glycerine, trimethylol propane, polyhydric phenols, polyphenols, with an excess of an epoxide, e.g., epihalohydrins, alkylene oxides, as described in U.S. Patents 2,456,408 and 2,592,560, issued to S.O. Greenlee. The principal product of this reaction is a resinous epoxy glyceryl polyether comprising epoxy glyceryl radicals, hydroxyl or chloride substituted glyceryl radicals, and the divalent residue of the polyhydric alcohol all united in a chain through ether oxygen atoms. From this class of polymeric epoxy-hydroxy ethers only those that are liquid or at least flowable at room temperature, i.e., about 65°F., have an epoxide equivalent, i.e., number of grams of resin containing 1 g. equivalent of epoxide, of from 140 to 375 and have an average molecular weight of from 290 to 750 are operable.

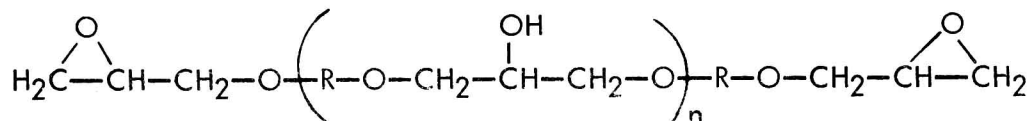
The polymeric epoxy-hydroxy ethers preferred in the process may be represented by the following structural formulas:

Polyether A —



which is the reaction product of glycerine and an epoxide such as epichlorohydrin and has an epoxide equivalent of from 140 to 165; and

Polyether B —



where n is zero or a positive number (whole or fractional) less than 2 and R is the hydrocarbon radical of p,p'-dihydroxy-diphenyl-dimethyl methane (bisphenol-A). Polyether B is the reaction product of bisphenol-A and an epoxide such as epichlorohydrin and has an epoxide equivalent of from 175 to 375 and an average molecular weight of from 380 to 750. The following examples illustrate the process.

Example 1: A preformed film of plasticized 11-amino-undecanoic acid condensation polymer described in U.S. Patent 2,071,253, about 3 to 6 mils, i.e., 0.003 to 0.006 inch, thick was immersed in about a 10% solution of the Polyether A in butanol-toluene and removed immediately. After removal from the solution, the excess solution was allowed to drain off and any residual solvent was evaporated by drying the coated tape at a moderately elevated temperature to produce an easily handled film.

A layer of the coated film of appropriate size was placed over each of two sheets of black iron, i.e., plain, sheet steel, heated to about 500°F. and held at this temperature for about 10 seconds after the film melted. The two sheets were then pressed together, cement sides facing each other, and held for an additional 15 seconds at the 500°F. temperature while maintaining a cement thickness of 2 or 3 mils between the metal sheets. The laminated sheets were then rapidly chilled to set the cement.

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The polyamide of this example contains, as plasticizers, benzomonobutylamide and a mixture of o- and p-toluene ethyl sulfonamides.

Example 2: The method set forth in Example 1 was followed except that a 30% solution of a Polyether B having an epoxide equivalent of 185 to 200 was substituted for 10% solution of the Polyether A and the holding time for the assembled sheets was 30 seconds.

Example 3: The plasticized 11-amino-undecanoic acid polymer of Example 1 was immersed in a 20% solution of a Polyether B having an epoxide equivalent of 190 to 210 in butanol-toluene and immediately removed. The film was then allowed to drain and dried for subsequent use.

To each of 2 black iron sheets, a layer of the treated film was applied. Each sheet with its resin layer was heated to 470°F. and held at this temperature for 15 seconds to permit the resin layer to melt and wet the metal surface. The 2 sheets were then pressed together with the resin adhesive disposed in between and the assembly was held in this position for another 60 seconds and at a temperature of 425°F. maintaining a glue line thickness of 2 to 3 mils. Thereafter the assembly was chilled to set the cement.

Example 4: The steps of Example 1 were repeated substituting an interpolyamide formed by the interpolymerization of (by weight) 40% hexamethylenediammonium adipate, 15% hexamethylenediammonium salts of oleic acid oxidation acids and 45% 6-amino-caproic acid as described in U.S. Patent 2,285,009, for the 11-amino-undecanoic acid polymer and a 30% solution of the Polyether A for the 10% solution. Also, the holding time after joining the molten adhesive carrying surfaces was 60 seconds.

Example 5: Example 4 was repeated using a polyamide formed by polymerizing chemically equivalent amounts of pentamethylene diamine and ethyl sebacate as described in U.S. Patent 2,130,523, in place of the interpolyamide of Example 4 and a holding time for the assembled sheets of 30 seconds.

The same procedure set forth in Example 1, except for some variation in the time-temperature cycle, was successfully employed to bond metals having surfaces of nickel, zinc, tin, brass, aluminum, copper, various organic coatings, e.g., phenolic, oleoresinous, and inorganic coatings, e.g., metal chromate. With the chromate and phenolic coatings, a Polyether B having an epoxide equivalent of from 225 to 290 was used in place of the Polyether A and with the nickel surface a Polyether B having an epoxide equivalent of from 300 to 375 was employed.

The amount of epoxy resin promoter needed to combine with the polyamide is relatively small compared to the amount of polyamide. Weight ratios in the range of from 0.025 to 0.30 part of promoter per part of polyamides are operable. If the polyamide is in the form of a solid article, film, rod, etc., an amount of promoter is used equal to about from 2.0 to 12.0 mg. of promoter per square inch of polyamide.

The following table compares the peel strength, i.e., the force required to separate 2 sheets bonded together by pulling an edge of one sheet in one direction and the opposed edge of

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the other sheet in an opposite direction over Canco roll guides at a speed of one inch per minute, of various materials bonded with an epoxy resin treated polyamide to the peel strength of the same material bonded by the same method but in which the linear polyamide is free from any epoxy resin adhesion promoter. By comparison, the peel strength of a 30% tin-70% lead solder bond is 55 lbs./0.75 in.

Surfaces Bonded	Promoter	Polyamide Described in Example	Peel Strength in lbs. per 0.75 in.	
			Untreated	Treated
Black iron	Polyether A	1	18	101
Tin plate	Polyether A	1	12	87
Zinc plate	Polyether A	1	18	68
Aluminum	Polyether A	1	9	61
Copper	Polyether A	1	4	43
Brass	Polyether A	1	9	42
Nickel plate	Polyether B epoxide equivalent of from 300 to 375	1	15	77
Chromatized steel	Polyether B epoxide equivalent from 225 to 290	1	12	49
Phenolic on metal	Polyether B epoxide equivalent from 225 to 290	1	16	79
Oleoresin on metal	Polyether A	1	10	56
Black iron	Polyether A	4	30	91
Black iron	Polyether A	5	15	97
Glass*	Polyether A	1	1,451 psi	3,315 psi
Wood*	Polyether A	1	800 psi	2,117 psi

*Laps tested in shear instead of peel.

Polyamide Resin with Phenolic Flux

E.F. Lopez; U.S. Patent 3,371,008; February 27, 1968 describes a metal adhesive which utilizes a polyamide which is insoluble in the epoxy resin in combination with a third constituent which acts as a flux and renders the epoxy resin and polyamide compatible. The flux comprises at least one di- or trihydroxy phenol and preferably a eutectic mixture of 2 or more polyhydroxy phenols. The following examples illustrate the process.

Example 1: An adhesive was formulated by mixing the following: (1) 80 parts by weight of epoxy resin comprising 20 parts by weight of the very viscous liquid triglycidyl ether of 1,1,3-trishydroxy phenol propane, produced as described in U.S. Patent 2,801,989 and commercially available from Union Carbide as ERRZ 0901 plus 60 parts by weight of a liquid epoxy novolac based on polyfunctional phenols of the novolac type, commercially available from the Dow Chemical Company as X2638.1 and having a generalized, idealized formula as shown on the following page.