# NATIONAL BUREAU OF STANDARDS REPORT

6134

# Structural Epoxy Adhesives

by

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and
Frank W. Reinhart

NBS

U. S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS

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## TABLE OF CONTENTS

# FOREWORD

The information in this report istaken from the literature references listed in Section 8 Bibliography.

# Structural Epoxy Adhesives

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## 1. Introduction

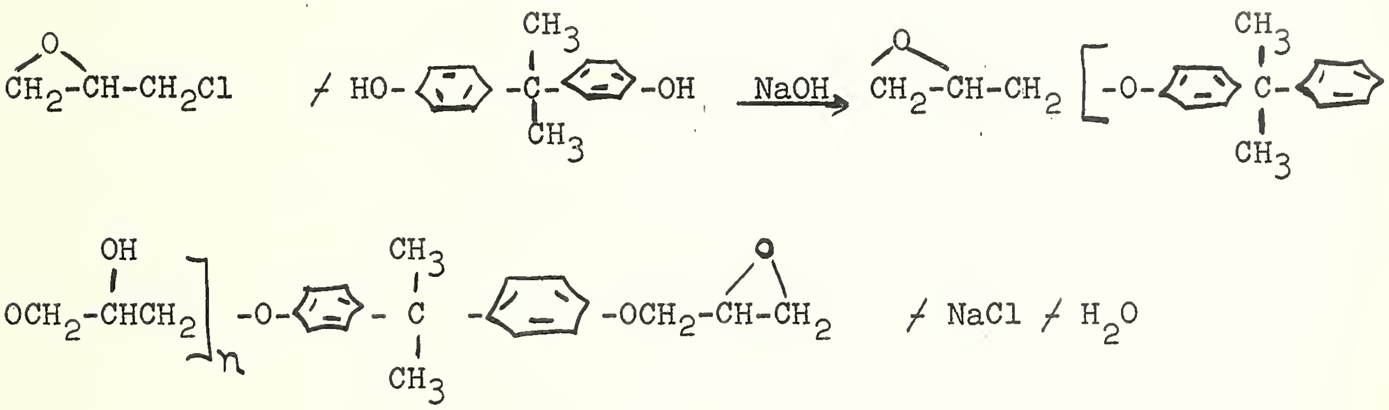
Although the epoxy resins were discovered as early as 1863, it was only during World War II that manufacturing and processing techniques for this interesting type of resins were developed. The manufacture and consumption of epoxy resins increased from none prior to 1950 to about 90 million pounds in 1956. This includes molding, laminating, potting, casting, coating, and adhesive compounds. The resins possess outstanding adhesive properties which can be improved selectively by the addition of suitable fillers, diluents, and/or resinous modifiers thus providing a class of adhesives of great versatility. Depending on the formulation the adhesives may be either rigid or flexible, and for certain applications, short-time temperatures of about 300°C may be tolerated. Most of the research on epoxy adhesives has been in the development of those for metals, reinforced plastics, glass, and combinations of these.

This report is primarily concerned with room-temperature setting structural epoxy adhesives for bonding wood and metal. The literature reviewed is discussed under the headings of chemistry, manufacturers, applications, bonding procedures, test methods, and properties.

## 2. Chemistry

Epoxy adhesives are based on resins made by the reaction of epoxides or oxiranes with other materials such as amines, alcohols, phenols, carboxylic acids, acid anhydrides, and unsaturated compounds. The chemistry to produce the final adhesive material involves two steps. The first step, usually

carried out in a chemical manufacturing plant or laboratory, involves the production of a thermoplastic resin or high molecular weight liquid that contains epoxide terminal groups. An example of this step is the reaction of epichlorohydrin with a polyhydric material such as bisphenol-A. In this typical basic reaction, epichlorohydrin reacts with bisphenol-A at temperatures of 60°-120°C in the presence of aqueous sodium hydroxide in the following manner:



By varying the operating conditions and the proportions of epichlorohydrin and bisphenol-A the n in the above formula can be changed to produce resins with molecular weights from 400 to 8000. When bisphenol derived from cashew nut shell oil is used in place of the bisphenol-A, epoxies are obtained that are more flexible. Other modifiers may produce similar or totally different results.

The second step results in the bond formation and is carried out in the final bonding processes. This step is often called curing of the adhesive. The liquid resin and the curing agent are mixed in the proper proportions immediately before applying to the surfaces to be bonded. In this step the thermoplastic or liquid resin is converted into a crosslinked or thermoset polymer. This hardening or "curing" procedure may involve a variety of chemical reactions in which the epoxy groups take part. Simple heating does not cure epoxy resins; they do not contain heat-reactive groups which will permit efficient conversions into infusible resins as do the phenolics and other formaldehyde-based resins. Modifying resins, coupling agents, or catalysts

are required for cure. Secondary and tertiary amines are used to cure epoxy materials at room temperature. The terminal epoxy groups on each molecule of the thermoplastic or liquid resin furnish the necessary crosslinking sites.

The curing of the resin is exothermic and is accelerated by heat. Because of this heat effect, many catalysts are too reactive for general use. For example Lewis acids such as borontrifluoride and stannic chloride give gelled products during mixing with liquid epoxy resina and hence are unsuitable.

In practice the resins are normally blended with a specific hardener or curing agent so that the desired physical and working properties are obtained. Therefore, since the unmodified epoxy resin made with bisphenol-A is hard and brittle when cured by catalysts, it is often modified with a polysulfide, polyamide, or other flexible coupling resins to impart higher peel and impact strength. These chemical modifiers also affect other chemical and physical properties and compromises must be made in order that important properties are not adversely affected. But with proper modification the epoxy resins can almost be called the universal adhesive.

A filler is often incorporated into the epoxy resin during its formulation as an adhesive. Usually these fillers are chemically inert materials that are incorporated to increase the impact strength, increase or decrease the electrical resistance, improve the heat resistance and water vapor transmission rate, or change some other property. Some common fillers are mica, asbestos, silica, talc, aluminum oxide, and titanium oxide.

Detailed information on the chemistry, curing reactions, relations between structure and properties, and formulation of epoxy resinous products are given by Lee and Neville (1)[a] Bruin (a), Kirk and Othmer (3), and Stivala (4).

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[a] Numerals in parentheses apply to cited references starting in Chapter 8.

## 3. Manufacturers

A large variety of epoxy adhesives are commercially available, and manufacturers and suppliers are constantly developing new formulations with different properties. Tables 1 and 2 contain the names of manufacturers, suppliers, and trade names of epoxy resin adhesives and polyamide-epoxy resin adhesives, respectively. Both tables are taken from the Adhesive Chart, published in the 1957 Modern Plastics Encyclopedia (5). These lists may not be entirely complete. Some of the manufacturers are also formulators and will assist the prospective user with detailed information; others sell the raw materials to formulators who will perform the same assistance. References 6 through 13 contain information and data on room-temperature setting epoxy adhesives published by some manufacturers and suppliers.

## 4. Applications

Dietz (14) reports on the use of epoxy resin adhesives in the "House of the Future", developed under a project sponsored by the Monsanto Chemical Company by the Massachusetts Institute of Technology. The house is now located in Anaheim, California. It consists of a core with projecting reinforced plastic wings which are attached to the central supporting core by overlapping joints in which the strength is largely supplied by epoxy adhesives put initially under pressure by bolts. No mention is made of the kind of epoxy adhesives used. Dietz states that there has been no indication of adhesive failure after the wear and stress produced by over a million visitors in a year.

General information on epoxy resins and their applications as adhesives are described by Preiswerk and associates (15), two German Publications (16, 17), Preiswerk (18), Modern Plastics (19), Carey and Nock (20), and Carey (21). The Interscience Encyclopedia (3) in addition to their chemistry gives a survey of applications in laminates, encapsulation, adhesives, etc. The relative merits of epoxide,

polyester, and phenolic resins are discussed by Vaughan (22). Lee and Neville (1) in their book on epoxy resins give a comprehensive review of the present status of applications and technology. In 1956, symposia on epoxies were conducted by the Diamond Ordnance Fuze Laboratories (23) and the Journal for Industrial and Engineering Chemistry (24). Adhesives as such were not discussed but the excellent adhesive properties of the epoxies account to a large extent for their applications as coatings, laminating resins, sealers, castings, potting, etc. Elam and Hopper (25) report on structural epoxy-resin laminates. Moss (26) reports on applications in the engineering industries of hot-setting and room-temperature setting epoxies for joining metal-to-metal and dissimilar materials, such as glass-to-metal. Zolin and Green (27) report on epoxy resins as engineering materials for the chemical industry. Narracott (28) discusses applications of some epoxy resins in the plastics industry. Rudoff and Rzeszotarski (29) report on applications of epoxy resins for electrical applications. The bonding of cementitious materials with epoxy resins is described by Goeke (30). High-temperature setting epoxy resins were tested at low temperature for evaluation as cryogenic structural adhesives by the National Bureau of Standards (31). Modern Plastics (32) describes an epoxy adhesive for bonding quick curing concrete to the base which it contacts. Farr (33) joined pipes with epoxy adhesives. Another article reports on the reduction of rejected grinding wheels due to the application of epoxy resins (34). Epoxy resins used as sealants for high vacuum systems are reported by Stivala and Denniger (35).

Since the greatest interest in epoxy adhesives has been in the aircraft industry the literature in this field is quite voluminous. DeBruyne (36), Epstein (37), Bandaruk(38), Black and Blomquist (39, 40) to name only a few, have investigated presently available adhesives, the possibility of developing new epoxies with higher heat-resistance, bonding techniques, etc. The Forest Products Laboratory, Wright Air Development Center, and the manufacturers have been extremely active in this field. A general survey of data on the reliability of metal bonding adhesive processes was made by Eickner (41). Most of the investigations in this field have

been on high-temperature curing epoxy adhesives.

No published data have been located on the application of epoxy adhesives for wood–to-wood and wood-to-metal. The lack of activity in the field of wood adhesives is attributed to the fact that other adhesives are available in greater abundance and at much lower prices. While epoxy adhesives can be used to bond other materials to wood or to itself, this type product has not been generally used in the wood working industry. The economics of melamine, urea, or polyvinyl acetate adhesives are more favorable.

Stark and Glickman (42) investigated the use of epoxy resins in bonding polystyrene foam to Douglas fir, but the resulting shear strengths data of 29 to 31 psi at 70°F and 24 to 25 psi after 16 hours at 120°F are not indicative of the properties of the adhesive because the failure occurred in the foam material at very low stresses. Marmion (43) reports that epoxy adhesives are mostly used in the aircraft industry for metal-to-metal bonding but that they will join almost any combination of polar materials.

## 5. <u>Bonding Procedures</u>

The choice of any particular epoxy composition for an adhesive application depends on the desired strength properties, the temperature to which the bond will be subjected, the configuration of the bonded parts, the adherends, etc. Factors influencing the bonding techniques in general are discussed by Delmonte (44), by Koehn (45) and by Thielsch (46). Tompkins (47) discusses the selection of the proper epoxy compound.

The following bonding qualities are characteristic of epoxy adhesives:

1. One hundred percent solids, no volatile solvent present.
2. Low pressure curing, only contact pressure is required.
3. Low-temperature and high-temperature curing.
4. Versatility, high bond strength with many different materials.
5. Thermosetting, good heat and solvent resistance.
6. Low-shrinkage.

The latter quality is one of the shortcomings of the presently used wood adhesives, according to Marra (48).

One major limitation of the epoxy adhesives is the relatively limited pot life of the liquid resin after it is mixed with the curing agent or hardener. Been (49) states that the use of a room-temperature curing epoxy adhesive usually imposes the following important limitations:

1. A two-part system, consisting of resin plus hardener (there are no one-component room-temperature curing epoxy adhesives).

2. Limited pot life of the mixed material.

3. Long curing time to achieve optimum bond characteristics.

4. Limited high-temperature service.

A relatively limited pot life is inherent in most of these systems. If the curing agent used gives a fast cure, it will start the curing action just as soon as it is mixed with the resin. This, in turn, means short working life of the mixed material. If a longer pot life in the mixed adhesive is essential for the production cycle, a slower-acting hardener must be used. This retards the curing action and development of strength in the bond.

The following rules should be observed to obtain the longest pot life:

1) Start with a cool mixture and work in a cool room.
2) Mix no more than necessary at one time. In other words, mix small batches.
3) Mix the materials in a shallow, oversize metal container and work from this container.

The curing of an epoxy resin is a chemical reaction that liberates heat. Unless this heat can escape from the resin to the surroundings, it increases the temperature of

the resin and the curing reaction goes faster. As the curing reaction goes faster, the rate at which heat is evolved increases, the mixture gets even hotter, and so on. The problem is to hold down the rate of curing in the mixing pot. This can be achieved by starting out at a low temperature, by keeping the total amount of heat generated to a minimum, and by making it easy for this heat of reaction to escape. Thus the work should be done with a small total volume, this volume should be spread over a large area of contact with the surroundings, the surroundings should be kept cool, and the transfer of heat should be speeded by using metal containers.

The curves in fig. 1 show the viscosity of the mixed resin versus time for three different batches. Curve A represents the behavior of a 330-gram batch of Bondmaster M648 mixed at 77°F. In 1 hour it reaches a viscosity of 75,000 centipoises. Curve B, representing a 1000-gram batch of the same resin mixed at the same temperature, rises more steeply and after 60 minutes has a viscosity of over 400,000 centipoises. Curve C, representing a 330-gram batch mixed at 100° F rises even more steeply than the others. A viscosity of 30,000 centipoises is about maximum for easy application by brush. While these graphs are typical of a great many epoxy adhesives, it should be kept in mind that many factors affect pot life. Examples of these are the composition of the resin, the type of curing agent, and the ratio of mixing. Many large users of epoxy adhesives find it more economical to mix several small batches per shift than to risk premature "setting-up" of the adhesive that might be encountered in one large batch.

One different approach to the pot life problem would be to develop a method for continuously metering, mixing, and dispensing the adhesive as needed. Equipment to do this especially for materials having short pot lives is being developed.

Since the pot life of the epoxy adhesives is limited, the curing agent or hardner should not be added to the resin solution or liquid resin until immediately before use.

Most of the epoxy adhesive systems are the two-container type and may be applied either as liquids by spraying, brushing, dipping, or rolling. However, other systems may be used, as listed below.

1. Latent curing agents give bonds of good adhesive strength and permit the formulation of extremely convenient one-container 100 percent solids systems, where the high curing temperatures can be accommodated.

2. One-container adhesive solutions may be formulated with high molecular weight epoxy resins. The retained solvents in the adhesive layer will blister the adhesive layer unless handled properly. The reduction in bond strengths may be as high as 15 percent, when compared with the strengths obtained with a similar hot-melt system.

3. Both supported and unsupported tapes may be employed. The tapes virtually eliminate handling difficulties and provide highly reproducible results in production situations. Tape formulations, however, have limited shelf lives at room temperature and may require storage under refrigeration.

4. One-container adhesive powders are available and are useful for a limited amount of adhesive work, such as bonding larger areas and in special production situations.

5. Solid heat-flowing adhesives are useful for a number of structural applications.

6. Solid two-part adhesive systems may be formulated for special applications. These formulations involve the preparation of high molecular weight resin curing agent soluble in acetone. This is applied in solution to one bonding surface. A coating of a high molecular weight homolog of diglycidyl ether of bisphenol—A is applied to the second bonding surface. The prepared system is indefinitely stable at room temperature, but if the two layers are joined under heat and pressure, good bonds may be obtained (1).

The development of an aluminum-epoxy adhesive for room-temperature curing is reported by Modern Plastics (50). This adhesive comes in two tubes. Other epoxy pastes are described by Gould (51) and Delmonte (52).

Another important factor in the bonding process is the proper surface preparation of the adherends. Epoxy adhesives will give excellent bonds to steel, aluminum, brass, copper, and most other metals; to most thermosetting plastics (phenolics, polyesters, epoxies) and most thermoplastics (vinyl, chlorides, cellulose acetate butyrates, styrenes, etc.), though here formulation may become increasingly critical; and to glass, wood, concrete, paper, cloth, etc. For many applications, thorough degreasing with solvents, wire brushing, or sandblasting, will provide a satisfactory surface. However, when higher adhesive strengths are required, attention should be given to chemical means of surface preparation. Careful preparation has resulted in up to a fourfold increase in bond strengths. The following treatments may be recommended. Where appropriate, they are followed by a neutralizing rinse and drying. In some cases, however, it may be necessary to apply a primer coat to the adherends if inservice moisture and vibration are severe.

Steel. Sandblast with clean grease-free sand or wire brush, and degrease with a 10 per cent solution of sodium metasilicate for 10 minutes at 60°C.

Stainless Steel. Dip for 10 minutes at 65°C in the following cleaning solution, parts by weight:

| | |
|---|---|
| Concentrated hydrochloric acid | 50 parts |
| 30% hydrogen peroxide | 2 parts |
| Formalin solution | 10 parts |
| Water | 45 parts |

Copper Alloys. Etch for 1 to 2 minutes at room temperature in the following solution, parts by volume:

| | |
|---|---|
| 42% ferric chloride | 15 parts |
| Concentrated nitric acid | 30 parts |
| Water | 197 parts |

Titanium Alloys. Dip for 20 minutes at 50°C in the following solution, parts by volume:

| | |
|---|---|
| Concentrated nitric acid | 9 parts |
| 50% hydrofluoric acid | 1 part |
| Water | 30 parts |

This treatment will provide increased bond strength, but it does not appear to be optimum.

Glass and Aluminum. Dip for 10 minutes at 70°C in the following solution, parts by weight:

| | |
|---|---|
| Sodium dichromate . . . . . . | 66 parts |
| 96% sulfuric acid . . . . . . | 666 parts |
| Water . . . . . . . . . . . . . | 1,000 parts |

Rubber. Immerce for 10 (±5) minutes at room temperature in concentrated sulfuric acid, or apply a sulfuric acid paste made by adding barytes to sulfuric acid. Bonding strengths can frequently be improved by flexing the rubber to produce tiny surface cracks.

Plastics. Sanding, buffing, or flame treatment is recommended in some cases.

Wood. Freshly planed surfaces are recommended.

Porous Surfaces. Porous surfaces, such as concrete, do not require special treatment, but sufficient adhesive should be used to allow for absorption (1).

For most other adhesives, the thickness of the adhesive layer is a critical factor for the bond strength. However, the epoxy resins appear to be somewhat unique in that the thickness of the adhesive layer may be varied from 1 to 12 mils, although narrower limits may be required for more complex joints, without seriously affecting the joint strength. For supported tapes, thicknesses up to 30 mils may be used, depending on the nature of the bond. The production tooling will to a very considerable degree dictate the thickness for a specific application (1). The difference in behavior between epoxy and other adhesives may be attributed in part to difference in the degree of shrinkage on curing.

The open assembly time, the period during which freshly coated surfaces are permitted to remain open to the air before assembly, depends on the curing agent, which is usually a somewhat volatile amine. It is therefore recommended that this time be held to 20 minutes or less. With longer open assembly times, sufficient curing agent is lost to give lower bond strengths after curing (28).

Although one of the chief advantages of epoxy adhesives is that no solvent is required, there are occasions when the use of solvents may be helpful, for example in applying the adhesive over a large area. In such case a fast-evaporating, active solvent is desired to minimize the amount of solvent used and shorten the open-assembly time. Methylal, methylene chloride, and the low-boiling aromatic solvents have been found satisfactory for this use. Although ketones and esters make excellent solvents for epoxy resins, they tend to remain in the adhesive film. Esters may also react with amine curing agents and thus inhibit cure to some extent (10).

The curing pressure for unsupported epoxy adhesives is usually contact pressure. Contact pressure is that required to just achieve good contact of the adhesive layer to the adherend surfaces being bonded. The usual range for supported tapes is from less than 5 to 50 psi, although in special cases pressures up to 100 psi may be needed. In all cases pressure should be sufficient to assure complete wetting of the adherend surfaces and even distribution of the adhesive over the bonding surface but not high enough to give starved areas. The selected pressure must be maintained throughout the initial phase of the cure (1). The smoothness and flatness of the adherend surfaces is a factor influencing the magnitude of the pressure.

Curing of room-temperature setting epoxy adhesives begins as soon as the resin and catalyst are mixed and in many cases the bond will be strong enough to withstand handling and stocking within 6 to 24 hours. This rapid gain in strength in the early hours of a week-long cure is called "handling time" and often goes unmentioned in the manufacturers' data sheet. Optimum strength requires a curing time from 120 to 144 hours. (28, 49). The cure can of course be accelerated by raising the temperature. The strength properties of room-temperature curing epoxy adhesives can be increased considerably by postcuring at temperatures not exceeding 120°C. When larger volumes of fillers are employed, such as 100 parts per hundred or more, a room-temperature cure of about 6 days or more is required to obtain maximum shear strengths, with heat and chemical resistance increasing even more slowly. (1).

Been (49) investigated the relation of the curing time required to develop 85 percent maximum strength versus curing temperature, and the strength as a function of temperature for some epoxy-based adhesives. The results are shown in figures 2 and 3, respectively. The curve in figure 2 slopes very steeply at the lower temperatures and gradually becomes less steep at the higher temperatures. If the cure were carried to exactly the same degree of completion at all temperatures, it would be expected from the theory of chemical reaction rates that the curve would be nearly straight like the dashed line. However, some of the amine **hardener** is lost by vaporization at the higher temperatures, and the rate is affected. Another factor is the partial permanent loss of strength of some resins due to degradation at the higher temperatures. To offset this loss of strength, the resin must be more highly cured at the higher temperatures to reach the same strength. For these reasons, the actual curing time is considerably longer than would be expected from extrapolation of the low-temperature rates. But in spite of degradation and loss of **hardener**, the curing time can be sharply reduced by raising the temperature.

The majority of the manufacturers' data sheets provide information on the effect of curing temperature of room-temperature setting epoxy adhesives on their physical properties.

The retention of high strength in the cured bonds at elevated temperatures requires the use of special heat-resistant adhesives. The curves in figure 3 show the strengths of three epoxy adhesives at elevated temperatures. The ones having higher resistance at elevated temperatures are more expensive than the others (49).

The hardening or curing agent is generally an organic amine. Hence, precautions similar to those for other strong alkalies or amines should be observed in handling it. Ventilation should be adequate to prevent inhalation of the vapors, and contact with the skin should be avoided to prevent dermatitis and burns.

Precautions should also be taken in handling the liquid epoxy resins, especially to avoid skin contact which may give rise to dermatitis in some sensitive individuals.

In general, operators should observe strict personal hygiene in the handling of both the resin and the curing agent. The resin is generally less toxic and less dangerous than the hardening agent.

During curing, the hardening agent is almost entirely consumed in the reaction with the epoxy resin and ceases to be a health hazard (4). The epoxy resin also loses its harmful properties at this time. Dermatosis with respect to epoxy resins is discussed by Dorman (53).

Because the epoxies are extremely resistant to solvents, they are difficult to remove from surfaces once they are cured. Excess uncured adhesive or adhesive that is dropped during application should be cleaned off immediately with solvent. Thoroughly cured and filled systems must be soaked for long periods in special solvents before they can be removed. A proprietary solvent that works well with aliphatic amine cured systems is DeSolv 292 (Ram Chemical). From a practical standpoint, it is often less expensive to scrap small components than to remove the epoxy resins particularly on aromatic-diamine cured systems. The resin on larger components can be removed by sandblasting or burning off at temperatures above 400°C (1).

## 6. Specifications and Test Methods

No Federal or ASTM materials specifications or standards have been issued for epoxy adhesives. Military specification MIL-A-8623 (54) covers structural heat-curing epoxy resin adhesives for metal-to-metal adherends; MIL-A-14042 (Ord) (55) covers room-temperature curing adhesives.

General testing methods for adhesives have been issued by the American Society for Testing Materials. They are constantly being revised and new ones are being developed. The latest issue "ASTM Standards on Adhesives (With Related Information)", (56), published December 1957, contains specifications, physical tests, and definitions.

A.S.T.M. adhesive standards are under the jurisdiction of Committee D-14. Federal Test Method Standard No. 175 (57) contains the Federal standard methods for testing adhesives. MIL-A-5090B (58) contains the requirements that can at present only be met by high-temperature curing epoxy adhesives. Military Qualified Products List (QPL) for MIL-A-928A (59) does not specify epoxy resins for structural metal-to-wood adhesives.

Test method for adhesives suffer from many limitations due to the multitude of variables encountered in the problem, such as the variety of chemical types involved (resin, filler, catalyst, etc.), the difference in the thermal expansion of adhesive and adherend, the bonding process itself, effect of temperature and humidity, geometry of the bond, and a host of others. All the standard test methods for strength properties of adhesive bonds adopted by Committee D-14 on adhesivescarry a long preamble defining many of the variables involved and specifying that bonding conditions shall be as described by the manufacturer who shall furnish numerical values and other specific information for all the variables named in the preamble.

All destructive test methods for adhesives give strength values that usually show a high degree of variation in replica test specimens. As a result, a rather large number of specimens must be prepared and tested, and the data have to be treated statistically before reliable comparisons can be made. All these limitations make it evident that no one single test method is sufficient to characterize the strength properties of an adhesive. Tensile shear strength tests at various temperature and exposure conditions (ASTM D 1002-53T and Federal Standard Method 1033.1-T), peel strength (ASTM D 903-49 and Federal Standard Methods 1041.1 and 1042-T), impact strength (ASTM D 950-54 and Federal Standard Method 1051), and fatigue strength (Federal Standard Method 1061) are some of the most commonly specified test methods for the strength properties of adhesives. The epoxy adhesives being primarily used as structural adhesives for metals are generally tested to meet the requirements of MIL-A-5090B, Adhesive: airframe structural, metal-to-metal. Most of the manufacturers' data for epoxy adhesives are based on this military specification. It contains a bend test where a 1-inch wide specimen is loaded

at the center of the bonded area as a simple beam with a 1 1/2-inch span. The loading block and end supports contact the full width of the specimen and are rounded at the line of contact with the specimen to a specified radius. The load required to produce failure in the bond is reported.

Dietz (14) points out that for the application of adhesives in building the pressing problem in the evaluation of new materials is to find a completely reliable method of accelerated testing which accurately predicts the long-time behavior of materials in building because here the time scale is long compared to airplanes or automobiles, for instance. This is not an easy task. The complexities of weather with the many subtle interactions of ultraviolet, visible, and infrared radiation with the components of the atmosphere, changing temperatures and moisture in vapor, liquid, and frozen form make laboratory reproduction, especially in accelerated form, a most difficult problem. Add to this the extreme variability of the weather itself even in a given locality and the wide departure in a given location on a given building from the mean weather for the locality, and the problem becomes a formidable one. This problem has been considered by Reinhart (60).

Merriman (61) states that in any bonded structure complete inspection of the finished assembly is difficult. Therefore, to produce bonded structures with any degree of reliability, it is very important to follow correct procedures and to maintain rigorous control through every step of the process. This includes control during fabrication and final inspection of the finished assembly. A process control chart for adhesive bonding of sandwich construction is shown in figure 4. Although the use of this assembly requires complete reliability, the process control chart for the assembly indicates items that should be considered. Less rigorous applications than this aircraft use will require less control.

In 1956 Eickner (41) made a statistical analysis of data obtained during a survey of fabricators of epoxy bonded metal constructions. The data were obtained from individual adhesive-bonded lap joints which had been tested for the purpose of production control, laboratory control, adhesive acceptance tests, and storage tests. The number of specimens tested ranged from 15,000 for production control to 44 for adhesive acceptance tests. The coefficients of variation for the joints bonded with epoxy adhesives varied from 7 to 29 percent. The individual means varied from 1700 psi to 3900 psi for the tensile-

lap-shear strength of joints made with individual adhesives.

Another approach to better production control is the development of non-destructive tests. An early evaluation of adhesion by ultrasonic vibrations was made by Moses and Witt (62). Dietz (14) reports that especially in sandwich constructions actual voids in a bond are not particularly difficult to detect. Tapping, the ultrasonic reflectoscope, or vibrating a horizontal panel with a layer of powder on the surface, where unbonded areas are revealed from the pattern developed, will be sufficient to locate actual voids. The difficulty is to locate weakly bonded areas. Dietz, Closman, Kavanagh, and Rossen (63) found on a laboratory scale with laboratory specimens that the dynamic modulus of elasticity of adhesive bonds, as determined at ultrasonic frequencies, is roughly related to strength. In general, the higher the modulus of elasticity, the stronger the bond. This method is applicable to adhesive-adherend systems in which the modulus of elasticity of the adhesive is markedly different from that of the adherend.

Arnold (64) developed the so-called STUB-Meter (STanford Ultrasonic Bond-meter). This instrument is based on the use of sonic methods in the evaluation of structural adhesive bonds. Although it has been used in some production control the requirements for highly trained observers and standard panels limit its usage also to laboratory controls.

The University of Louisville Institute of Industrial Research (65) developed methods for the non-destructive testing of wood laminates for the Office of Naval Research. The investigation included an ultrasonic, a sonic, and a "brittle lacquer" method, none of which are very promising.

## 7. Properties

The information on general properties of epoxy adhesives in the Adhesives Chart in the 1957 Modern Plastics Encyclopedia (5) may be summarized as follows:

Bond formation of epoxy resins takes place through chemical reaction either at room temperature (70° - 80°F), moderate temperatures (150° - 200°F), or at elevated temperatures (275° - 310°F). Epoxy adhesives have excellent resistance to water, solvents, heat, cold, and fungus. They form excellent bonds with wood, metals, glass, leather, paper, textiles, and ceramics, and good bonds with rubber. No solvents are needed.

Another group of epoxy adhesives listed in this chart are the phenolic-epoxy resins. They are cured only at elevated temperatures, require no solvents, and have excellent resistance to water, solvents, heat, cold, and fungus. They form excellent bonds with wood, metals, rubber, glass, leather, textiles, and ceramics, and good bonds with paper.

The third group listed in the chart are the polyamide-epoxy adhesives. They form bonds by curing at room or elevated temperatures or by solvent release. The solvents may be alcohols or ketones. These adhesives have excellent resistance to water, solvents, cold, fungus, and good resistance to heat. They form excellent bonds with wood, metals, glass, leather, paper, textiles, and ceramics, and good bonds with rubber.

The average bond strength of some epoxy adhesive-adherend systems is given in table 3 (66). The effect of fillers on the tensile-shear strength of epoxy adhesive formulations is given in table 4 (1). The effect of the amount of filler on the tensile-shear strength is shown in table 5 (1, 67). Lee and Neville (1) state in this connection that the specific loading volume is somewhat dependent on the viscosity of the resin used and also will be a function of cure time, since higher volumes of filler lengthen the cure time required for optimum bonding values. Engineering data for some proprietary room-temperature curing epoxy adhesives for aluminum, brass, and steel are given in table 6(6).

Eickner (68) made extensive tensile-shear tests with aluminum joints bonded with 3 heat-cured epoxy (Epon ) adhesives. The original shear strengths, the shear strengths after various laboratory exposure conditions, and after exposure to several climatic conditions are listed in table 7. Exposures in Wisconsin, Alaska, and New Mexico although much less severe than those in Florida and the Canal Zone caused appreciable deterioration of the stressed Epon VIII specimens. The stressed and unstressed Epon VI and Epon VIII specimens generally showed appreciable deterioration after 1 year of exposure, averaging less than 30 to 40 percent of their original strengths. Not all the exposure tests with the Epon 422J adhesive tape are complete.

Stivala's investigation (4) was directed toward improving the impact characteristics of room-temperature curing epoxy resins while simultaneously retaining or not appreciably altering the valuable properties of the rigid system. It was found that an epoxy resin (Cardolite 7019) based on a bisphenol derived from cashew nut oil is superior in impact strength, shear strength, and tensile

strength to epoxy resins based on bisphenol A-epichlorohydrin. Comparative strengths of some commercial epoxy resins at 73.5°F are shown in table 8. The effects of plasticizer on the shear, impact, and tensile strengths of Epon 828 and Cardolite 7019 are shown in table 9.

The development of experimental resorcinol epoxide resins as high strength, room-temperature curing, structural adhesives for metals is reported by St. Clair and Moult (69, 70). They confirmed the findings reported previously that the strength of an epoxy bond whether tested at room temperature or at 180°F is directly proportional to the temperature and pH of the rinse water which is used after aluminum has been degreased and etched. They ascribe this to the oxide film formed after these cleaning operations. Figure 5 shows that the bond strength is proportional to the rinse water temperature up to 160°F. When the resorcinol epoxides were cured with liquid aliphatic polyamines, the adhesives were brittle and the pot life short. Solid polyamines ground with Thiokol plasticizer gave longer pot lives but the adhesive was still too brittle. Optimum bond strengths were obtained with an adhesive having a resin/resorcinol glycidyl ether ratio in mol/mol of 50/50 as shown in figure 6. This experimental room-temperature curing epoxy-resorcinol resin met all the requirements for a heat-curing metal structural adhesive of the type specified in MIL-A-5090B (58), except for pot life which was only 1.7 hours instead of the specified 4 hours. Average tensile shear strength and bond strength for three specimens of 2024 T3 clad aluminum bonded with this adhesive are as follows:

| Tensile shear strength, psi | | | Bend strength |
|---|---|---|---|
| Room temperature | 180°F | -65°F | lb |
| 2865 | 2005 | 2550 | 160 |

Naps (71) reports on new experimental elevated temperature-resistant epoxide adhesives developed for the Air Force. The shear strength properties of five of these adhesives are given in figures 7 and 8. The aluminum bonded assemblies were cured at 330°F.

Merriman and Goplen (72) conducted a very thorough investigation of structural adhesive properties over a wide temperature range. The adherends were 0.064-inch thick, type 301, 1/2-hard, 2D finish stainless steel and 0.064-inch thick 2024-T3 alclad aluminum. Epon VIII epoxide (Shell Chemical Corp.) and 422 J epoxide-phenolic (Shell Development Co.) were among the adhesives tested for tensile shear, creep rupture, impact, cleavage, tensile, bend, peel, and fatigue tests. The peel tests were conducted at room temperature in a climbing drum apparatus similarly to Federal Test Method 1042T. As expected, the epoxy resins had poor peel strength: Epon VIII 7.0 in.-lb; Shell 422J 4.2 in.-lb. It should be noted that the peel strength obtained is a function of the surface preparation method equally as much as it is a function of the adhesive being tested. Therefore, comparisons of peel strength of various adhesives may be made only when a highly controlled surface preparation method is used for all test specimens. Note also that peel strength represents the load required to continue failure. The peel strength of an adhesive may be roughly defined as its resistance to further failure. This implies that some failure has already occurred. Thus the load required to initiate failure in an adhesive will not necessarily be in ratio to its peel resistance (72). The peel resistance of unmodified adhesives can be improved by changing the formulation, as is also the case with impact resistance.

Compression data for epoxy adhesives are not available although this test is often performed with wood-to-wood adhesives.

One manufacturer (13) quotes a compressive strength of 14,000 psi. without reference to the test method used. This same manufacturer gives the value for the refractive index as 1.562 which is in good agreement with data obtained for this property in tests made at the National Bureau of Standards. This property is of importance for bonding glass and/or quartz where optical clarity is required.

The sales literature for the epoxy adhesives quotes specific gravities in the range of 0.90 to 1.2, depending on the composition and formulation.

The chemical resistance of the epoxy resin adhesives is reported as very good in the literature, but it is dependent on the curing agent. The chemical resistance for an epoxy resin adhesive cured with amine-resin adduct tested at room temperature as reported by Lee and Neville (1) is presented in Table 10.

Military Specification MIL-A-5090B (58) requires a minimum of 2,500 psi tensile shear strength after exposure to various liquids. St. Clair and Moult (69, 70) state that their formula 761 meets these requirements. No data were given to substantiate this claim.

Table 11 gives tensile shear strength data for four Thiokol-epoxy resin adhesives after immersion in solvents for 30 days (11).

Fillers may affect the moisture resistance, the moisture-vapor transmission, and the solvent resistance either adversely or advantageously. The effectsof several fillers on these properties are presented in figures 9, 10, 11 (66).

The electrical properties of epoxies used as adhesives proper are not reported in the literature. Data for electrical properties of straight epoxy and modified epoxy resins are found in the symposium on Casting Resins (23). The data in table 12 (73) show the electrical properties of various epoxy resins. The typical electrical properties of resin cured with diethylene triamine are given in table13 (74). The volume resistivity versus temperature is given in figure 12 (74). Linden (75) also reports on the effect of temperature on the electrical properties of encapsulating materials.

Borders (76) investigated the effect of nuclear irradiation on structural adhesives. The deteriorating effect on the tensile shear strength of three epoxy adhesives is shown in figure 13 and the effect on bend strength in figure 14. The tests were made at room temperature in accordance with methods 4.3.2.1 and 4.3.2.9 of MIL-A-5090B, respectively, on standard 1-inch 2024T3 aluminum alloy lap joints. The tests showed considerable deterioration except in the case of the high-temperature curing epoxy-phenolic tape 422J.

Mixer (77) reports that attempts have been made to improve the irradiation resistance of commercially compounded adhesives with protective agents. Epon VIII was chosen because of its ease of handling and the ease with which the additive can be incorporated into the adhesive. Without additive tensile shear specimens from Epon VIII lost 40% of their original strength. Additions of N-vinylcarbazole at concentrations of one and nine percent showed a deleterious effect on the adhesive. One percent

of 2,5-diphenyloxazole showed no change in the properties of the adhesive. Nine percent of 2,5-diphenyloxazole, however, showed a marked improvement in the radiation resistance of the adhesive which lost only 11% of its initial strength at 800 megarep.

Lee and Neville (1) report that the low temperature strength of epoxy resins at -50°C can be improved by flexibilizers. They appear to offer no immediate promise for improving performance at temperatures much above 100°C because of the loss of strength of such modified resins at these temperatures.

Phenolic resins, in higher loading volumes, have been used with limited success in epoxy adhesives for operations in the 250°C range. Considerable effort is being directed toward extending the upper operating temperature limits to even higher values. Three approaches are being followed to achieve adhesives for higher-temperature operations: development of more satisfactory resinous modifiers, development of better curing agents, and synthesis of epoxy resins with improved temperature resistance. For intermediate-range work, "bodying" resins with phenolics and anhydrides has been suggested, but little work has been accomplished.

Even below 250°C, the upper temperature limit is critical for many compounds. With systems suitable for operation in the 150 to 200°C range, there is usually a moderate increase in bond strength as temperature rises; but thereafter, the bond strength decreases with further temperature increase to a drop-off point beyond which loss of properties is rapid. A single batch of adhesive for a single application will give loss in strengths that vary over a 5 to 10°C range.

Because the high, compared to metals, coefficient of thermal expansion of the unmodified epoxy resins tends to disrupt the adhesive bond with changes in temperature, reductions in this value have the effect of extending the upper operating temperature limit.

Fillers are most effective in reducing the value, as shown in figure 15. Ideally, the coefficient of thermal expansion should be lowered to match that of the material being bonded, or, in the case of like-on-unlike bonds, to a value between the two materials. In practice, however, it is often not possible to employ a sufficiently large loading volume. High loading volumes increase viscosity to the point where thin, regular glue lines cannot easily be obtained

and in other ways tend to degrade, rather than improve, the bond. For some applications and some fillers, loading volumes up to 200 parts per hundred may be employed, but optimum shear-strength values are usually obtained with lesser amounts. Suggested loading volumes for some good adhesive fillers are mica, 14 parts per hundred; short-fiber asbestos, 25 parts per hundred; aluminum oxide, 50 parts per hundred; talc, 80 parts per hundred; and zinc dust, 100 parts per hundred. These, of course, are not optimum for all applications or in all formulations.

Turner and associates (78, 79) considered the filler problem in heterogeneous materials from a more basic viewpoint. When temperature limits permit, it is useful to compensate for differentials in the coefficient of thermal expansion by the use of flexibilizers to absorb the internal stresses during thermal cycling. For short periods at higher temperatures, supported tapes will somewhat improve performance by more uniform distribution of stresses.

Table 14 summarizes expansion coefficients for some commonly used building materials. For purposes of comparison the dimensional changes of a 10-foot length of material accompanying a 100°F temperature change are also shown. Dietz (14) states that such changes in dimensions of materials with changes in temperature, moisture, and other factors are of crucial importance in the application of adhesives. Although the changes may be relatively small in comparison to the structure as a whole, they are extremely large compared to the dimensions of the adhesive.

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## Table 1

## List of Manufacturers, Suppliers, and Trade Names of Epoxy Resin Adhesives

| Firm name and address | Trade name |
|---|---|
| Adhesive Engineering, San Carlos, Calif. | Metalfil |
| Adhesive Products Corp., 1660 Boone Ave., New York 60, New York | Adgrip |
| Alkydol Labs. 3242 S. 50th Ave., Cicero 50, Illinois | Alk-O-Flex |
| Am. Latex Products Corp., Hawthorne, Calif | Staybond |
| Angier Adhesives, Div. of Interchemical Corp., 120 Potter St., Cambridge 42, Mass. | -- |
| Armstrong Cork Co., Lancaster, Penna. | |
| Armstrong Products Co., P.O. Box 1, Warsaw, Ind. | |
| Atlas Mineral Products Co., Metztown, Pa. | Alfane, Amphesive, Nepoxide |
| Atlas Synthetics Corp., Long Island City 1, New York | |
| Bakelite Corp., Div. of Union Carbide Corp., 30 E. 42nd Street., New York 17, N. Y. | Bakelite |
| Carl H. Biggs Co., Inc., 2255 Barry Ave., Los Angeles 64, Calif. | Bonding Agent |
| Bloomingdale Rubber Co., Aberdeen, Md. | BRC |
| Bond Adhesives Co., Box 406 Main P.O., Jersey City 4, N. J. | Bond |
| The Borden Co., Chem. Div., 350 Madison Ave., New York 17, New York | Epiphen |
| Brit. Resin Products, Ltd. Devonshire House, Picadilly, London, England | Cellobond |
| Carboline Co., 331 Thornton Ave, St. Louis 19, Mo. | Carboline |
| Chemical Coatings and Eng. Co., 2633 Westchester Pike, Edgemont, Pa. | Corrocote |
| Chemical Development Corp., Endicott St., Danvers, Mass. | C. D. Cement |
| Ciba Co., Inc., Plastics Div., Kimberton, Pa. | Araldite |
| Cordo Chem. Co., 34 Smith St., Norwalk, Conn. | Cordo-Bond |
| Cycleweld Cement Prod. Div., Chrysler Corp., 5437 W. Jefferson, Trenton, Michigan | Cycleweld |
| Emerson and Cuming, Inc., 869 Washington St., Canton, Mass. | Ecco |
| Epoxylite Corp., 10829 E. Central Ave., El Monte, Calif. | Epoxylite |
| Ferrington Texol Corp., 2000 Main St., Walpole, Mass | |

Table 1 (continued)

| Firm name and address | Trade name |
|---|---|
| Paisley Products, Inc., Div. Morningstar Nicol, Inc., 630 W. 51st Street, New York 19, New York | Paisley |
| Poly Resins, 11661 Wicks St., Sun Valley, Calif. | -- |
| Polymer Chemical Co., 5920 Carthage Ave., Cincinnati 12, Ohio | Polypreg |
| Polymer Industries, Inc. Springdale, Conn. | |
| Reichhold Chemicals, Inc., 525 N. Broadway, White Plains, New York | Polyox, Polytool |
| Ren Plastics, Inc., 5422 S. Cedar St., Lansing 17, Mich. | Ren |
| Rubber and Asbestos Corp., 234 Belleville Ave., Bloomfield, New Jersey | Bondmaster, Brushmaster, Plymaster |
| Shell Chemical Corp., 380 Madison Ave., New York 17, New York | Epon |
| Slomons Labs., Inc., 31-27 Thomson Ave., Long Island 1, New York | --- |
| Thiokol Chem. Corp. 780 N. Clinton St., Trenton 7, New Jersey | Thiokol |
| United States Stoneware Co., Tallmadge Ave., Box 350, Akron 9, Ohio | Tygofil, Tygoweld |
| Willross Products Co., 20 4th Ave., Hawthorne, New Jersey | |

## Table 2

### List of Manufacturers, Suppliers, and Trade Names of Modified-Epoxy Resin Adhesives

| Firm name and address | Trade name |
|---|---|
| Polyamide Modified | |
| Adhesives Engineering, San Carlos, Calif. | Metalfil, Aerobond |
| Adhesives Products Corp., 1660 Boone Ave., New York 60, New York | Adlok |
| Angier Adhesives, Div. of Interchemical Corp., 120 Potter St., Cambridge 42, Mass. | --- |
| Bond Adhesives Co., Box 406 Main P.O., Jersey City 4, N. J. | Bond |
| The Borden Co., Chem. Div., 350 Madison Ave., New York 17, New York | Arcco, Placco, Reslac |
| Chem. Coatings and Eng. Co., 2633 Westchester Pike, Edgemont, Penna. | Corrocote |
| Dennis Chemical Co., 2701 Papin Street, St. Louis 3, Mo. | --- |
| General Mills, Inc., Chem. Div., So. Kensington Rd., Kankakee, Ill. | |
| Gordon-Lacey Chem. Prod. Co., Inc., 57-02 48th St., Maspeth 78, N. Y. | --- |
| Houghton Labs., Inc., 322 Houghton Ave., Olean, N. Y. | Hysol |
| Hughes Glue Co., 3500 Aubin Street., Detroit, Michigan | --- |
| Lawrence Adhesives and Chem. Co., Inc., 19 S. Canal St., Lawrence, Mass. | Epolac |
| Midland Adhesives and Chem. Corp., 2600 Goodrich, Ferndale 20, Mich. | Midland |
| Miracle Adhesives Corp., 250 Petit Ave., Bellmore, L. I., N. Y. | Miracle |
| Narmco Resins and Coatings Co., 600 Victoria St., Costa Mesa, Calif. | Narmco |
| National Adhesives Div., National Starch Products, Inc., 270 Madison Ave., New York 16, N. Y. | Duro-lok |
| Nureco, Inc., 1100 Pontiac Ave., Cranston 10, R. I. | Nureco |
| Ohio Adhesives Corp., Maple Ave., Ext. New Philadelphia, Ohio | Ohio |
| Rubber and Asbestos Corp., 234 Belleville Ave., Bloomfield, N. J. | Bondmaster |
| Willross Products Co., 20 4th Ave., Hawthorne, New Jersey | --- |

Table 2 (continued)

### Phenolic Modified

| | |
|---|---|
| Adhesives Engineering, San Carlos, Calif. | Aerobond |
| Bloomingdale Rubber Co., Aberdeen, Md. | BRC |
| Lebec Chemical Corp., Paramount, Calif. | Lebec |
| Narmco Resins and Coatings Co., 600 Victoria St., Costa Mesa, Calif. | Metlbond |
| Plastics Engineering Co., 1607 Geele Ave., Sheboygen, Wis. | Plenco |
| United States Stoneware Co., Tallmage Ave., Box 350, Akron 9, Ohio | Tygoweld |

### Polysulfide Modified

| | |
|---|---|
| Adhesive Engineering, San Carlos, Calif. | Aerobond |

## Table 3. Strengths of Typical Epoxy Adhesive-Adherend Systems

| Formulation | Parts | Average tensile-lap-shear strength<br>Steel<br>psi | <br>Brass<br>psi | <br>Aluminum<br>psi |
|---|---|---|---|---|
| Epoxy resin[a]<br>Hardener 1[b] | 100<br>25 | 720 | 1400 | 1570 |
| Epoxy resin<br>Hardener 1<br>Filler[d] | 100<br>25<br>35 | 1500 | 1950 | --- |
| Epoxy resin<br>Hardener 2[c] | 100<br>5 | 1750 | 2650 | 4500 |
| Epoxy resin<br>Hardener 2<br>Filler | 100<br>5<br>90 | 2050 | 3025 | 4750 |
| Epoxy resin<br>Resin modifier[e]<br>Hardener 2<br>Filler | 100<br>5<br>5<br>90 | 2400 | 4500 | 5400 |

a. Epoxy resin BRR 18795 (Bakelite Co.)
b. Hardener 1 BRR 18793 ( do. )
c. Hardener 2 (pyrrolidine)
d. Filler Titanium oxide
e. Resin modifier polyvinyl acetal

Table 4

## Effect of Various Fillers on Tensile-Shear Strength of Aluminum Assemblies Bonded with Epoxy Adhesives [a]

| Filler | Tensile-shear strength room temp | Tensile-shear strength 105°C |
|---|---|---|
| | psi | psi |
| Ignited $Al_2O_3$ | 1650 | 1150 |
| Short-fiber asbestos[b] | 2180 | 3910 |
| Carbon black | 2000 | 1170 |
| Silica OBI | 1530 | 600 |
| Zinc dust | 4080 | 3865 |

a. Room temperature curing adhesive of the following composition: Mixed polymer/epoxy resin: 100 parts; allyl glycidyl ether: 10 parts; filler: 100 parts; triethylamine 12.5 parts.

b. 24 parts.

Table 5.

## Effect of Filler Loading Volumes on Tensile-Shear Strength of Epoxy Adhesive

| Filler | Amount, parts/100 | Tensile-shear strength for aluminum assemblies 23° C | 60°C |
|---|---|---|---|
| | | psi | psi |
| None | — | 1,030 | 1,205 |
| Aluminum | 40 | 2,525 | 3,725 |
| | 60 | 2,525 | 3,580 |
| | 80 | 2,390 | 2,620 |
| Aluminum oxide | 30 | 2,505 | 2,805 |
| | 50 | 3,615 | 3,600 |
| | 70 | 2,555 | 2,665 |
| Mica | 6 | 2,210 | 1,810 |
| | 14 | 2,360 | 2,815 |
| | 26 | 1,055 | 1,210 |
| Silica | 40 | 600 | 610 |
| | 90 | 1,460 | 1,225 |
| Talc | 30 | 1,870 | 2,360 |
| | 60 | 2,650 | 2,655 |
| | 80 | 2,520 | 2,400 |

Table 6

## Strengths of Some Room-Temperature Curing Epoxy Adhesives[a] for Various Metals

| Properties | EC-1294 with EC-1295 accelerator | EC-1294 with EC-1468 accelerator | EC-1474 with EC-1475 accelerator | EC-1472 with EC-1473 accelerator |
|---|---|---|---|---|
| Working life | 15 min | 2 hr | 2 hr | 1 hr |
| Tensile-shear strength, psi To aluminum[b] | | | | |
| After 7 days' curing at room temperature | | | | |
| tested at room temp. | 2,700 | 1,600 | 2,000 | 3,400 |
| tested at -65°F | 810 | 1,100 | 530 | 2,000 |
| tested at 180°F | 180 | 890 | 430 | 660 |
| After 7 days in tap water | 4,200 | 2,200 | 2,000 | 3,100 |
| After 30 days do. | 3,000 | 3,300 | 2,900 | 2,700 |
| After 7 days at 120°F + 100 % relative humidity | 3,200 | 3,300 | 4,700 | 2,200 |
| After 30 days do. | 2,900 | 3,000 | 4,000 | 1,400 |
| After 0.5-hr curing at 200°F | | | | |
| tested at room temperature | 4,500 | 3,500 | 2,100 | 1,800 |
| tested at -65°F | 2,800 | 2,700 | 690 | 3,800 |
| tested at 180°F | 960 | 1,500 | 750 | 190 |
| After 7 days in tap water | 4,400 | 4,100 | 2,400 | 1,300 |
| After 30 days do. | 4,400 | 4,000 | 3,400 | 1,100 |
| After 7 days at 120°F at 100% relative humidity | 3,300 | 3,700 | 4,300 | 740 |
| After 30 days do. | 2,500 | 3,100 | 3,600 | 410 |

Table 6 (continued)

| Properties | EC-1294 with EC-1295 accelerator | EC-1294 with EC-1468 accelerator | EC-1474 with EC-1475 accelerator | EC-1472 with EC-1473 accelerator |
|---|---|---|---|---|
| After 7 days curing at room temperature | | | | |
| To brass | 290 | 1,000 | 980 | 1,500 |
| To steel | 540 | 800 | 790 | 1,200 |
| Bend strength, lb[c] | | | | |
| To aluminum[b] | | | | |
| After 7 days curing at room temperature | 280 | 100 | 130 | 260 |
| After 0.5 hr curing at 200°F | 270 | 160 | 150 | 200 |

a Proprietary adhesives.

b 1/2-inch overlap specimens of 24ST3 alclad aluminum.

c Probably tested in accordance with method 4.3.2.9 in MIL-A-5090B (58).

## Table 7

Results of Tensile-Shear Tests on 1/2-inch Lap Joints of 0.064-in. Clad Aluminum bonded with High-Temperature-Setting Epoxy Adhesives After Various Exposures$^{a}$

| Exposure | Epon VI |  |  | Epon VIII |  |  | Epon 422J$^{b}$ |  |  |
|---|---|---|---|---|---|---|---|---|---|
|  | Shear strength, average | Percent of original strength | Cohesive failure | Shear strength | Percent of original strength | Cohesive failure | Shear strength | Percent of original strength | Cohesive failure |
|  | psi | percent | percent | psi | percent | percent | psi | percent | percent |
| Original | 4,000 | --- | 99 | 3,400 | --- | 96 | 3,000 | --- | 97 |
| 120°F, 97% relative humidity |  |  |  |  |  |  |  |  |  |
| 3 months | 3,300 | 80 | 98 | 2,200 | 61 | 38 | 2,400 | 88 | 81 |
| 6 months | 1,700 | 41 | 51$^{c}$ | 1,800 | 53 | 20 | 2,500 | 93 | 86 |
| 36 months | 50 | 1 | 0$^{c}$ |  |  |  |  |  |  |
| Cyclic$^{d}$ |  |  |  |  |  |  |  |  |  |
| 2 cycles (10 weeks) | 3,400 | 89 | 95 | 2,400 | 71 | 72 | 2,700 | 91 | 97 |
| 5 cycles (25 weeks) | 2,300 | 57 | 66$^{c}$ | 1,800 | 54 | 45 | 2,500 | 88 | 77 |
| 7 cycles (35 weeks) | 1,400 | 36 | 45$^{c}$ | 1,600 | 48 | 29 | 2,500 | 84 | 92 |
| 10 cycles (50 weeks) | 2,500 | 64 | 60$^{c}$ | 1,900 | 54 | 64 | 2,300 | 81 | 79 |
| Salt-water boil |  |  |  |  |  |  |  |  |  |
| 1 hour | 3,900 | 98 | 99 | 3,200 | 92 | 99 | 2,700 | 94 | 100 |
| 3 hours | 3,900 | 97 | 98 | 2,800 | 87 | 95 | 2,600 | 91 | 97 |
| 6 hours | 3,600 | 93 | 98 | 3,200 | 89 | 100 | 2,800 | 90 | 100 |
| Salt-water spray |  |  |  |  |  |  |  |  |  |
| 30 days | 2,700 | 68 | 77$^{c}$ | 0 | 0 | 0$^{c}$ | 2,800 | 92 | 100 |
| Madison, Wis, outdoors |  |  |  |  |  |  |  |  |  |
| 3 months stressed | 3,600 | 90 | 98 | 0 | 0 | 10 | 2,900 | 100 | 97 |
| do, unstressed | 3,500 | 93 | 99 | 3,000 | 87 | 95 | 2,800 | 95 | 95 |
| 12 months, stressed | 3,500 | 83 | 100 | 1,400 | 42 | 38 | 2,900 | 96 | 100 |
| do, unstressed | 3,800 | 96 | 100 | 2,500 | 67 | 79 | 2,900 | 99 | 95 |
| 36 months, stressed | 1,300 | 32 | 46$^{c}$ | --- | --- |  | --- | --- |  |
| do, unstressed | 3,200 | 79 | 99 | --- | --- |  | --- | --- |  |
| Panama Zone, outdoors |  |  |  |  |  |  |  |  |  |
| 3 months, stressed | 3,600 | 91 | 96 | 0 | 0 | 10 | 2,600 | 97 | 92 |
| do, unstressed | 3,100 | 79 | 92 | 500 | 14 | 13 | 2,900 | 100 | 98 |

Table 7 (continued)

| Exposure | Epon VI<br>Shear strength, average psi | Epon VI<br>Percent of original strength percent | Epon VI<br>Cohesive failure percent | Epon VIII<br>Shear strength psi | Epon VIII<br>Percent of original strength percent | Epon VIII<br>Cohesive failure percent | Epon 422J[b]<br>Shear strength psi | Epon 422J[b]<br>Percent of original strength percent | Epon 422J[b]<br>Cohesive failure percent |
|---|---|---|---|---|---|---|---|---|---|
| 12 months, stressed | 520 | 13 | 16[c] | 0 | 0 | 10 | 2,600 | 87 | 95 |
| do, unstressed | 3,200 | 78 | 86 | 0 | 0 | 10 | 2,700 | 90 | 84 |
| 36 months, stressed | 0 | 0 | 0[c] | --- | --- | | --- | | |
| do, unstressed | 1,600 | 40 | 55 | --- | --- | | --- | | |
| Fairbanks, Alaska, outdoors | | | | | | | | | |
| 3 months, stressed | 3,800 | 91 | 100 | 1,200 | 37 | 33 | 2,900 | 98 | 100 |
| do, unstressed | 3,600 | 94 | 100 | 2,800 | 80 | 74 | 2,900 | 100 | 100 |
| 12 months, stressed | 3,500 | 90 | 93 | 1,500 | 43 | 54 | 2,600 | 93 | 95 |
| do, unstressed | 3,500 | 86 | 99 | 3,000 | 83 | 92 | 2,700 | 93 | 93 |
| 36 months, stressed | 3,200 | 81 | 99 | --- | --- | --- | --- | --- | --- |
| do, unstressed | 3,500 | 89 | 99 | --- | --- | --- | --- | --- | --- |
| New Mexico, outdoors | | | | | | | | | |
| 3 months, unstressed | 4,000 | 100 | 100 | 3,200 | 89 | 87 | 3,000 | 100 | 100 |
| 12 months, unstressed | 3,600 | 92 | 100 | 3,200 | 91 | 99 | 900 | 98 | 90 |
| 36 months, unstressed | 3,400 | 86 | 100 | --- | --- | --- | --- | --- | --- |
| Florida, outdoors | | | | | | | | | |
| 3 months, unstressed | 3,300 | 87 | 100 | 2,500 | 72 | 89 | 2,700 | 94 | 99 |
| 12 months, unstressed | 3,000 | 76 | 88[c] | 0[c] | 0 | 10[c] | 2,800 | 94 | 98 |
| 36 months, unstressed | 600 | 15 | 22[c] | --- | --- | --- | --- | --- | --- |

a) The values for percent of original strength were computed using the average original control test values obtained on the end specimens from the same panels exposed and tested at the particular exposure condition.

b) A high-temperature setting formulation of the phenol epoxy type, supported on a woven glass-fiber fabric.

c) Some evidence of corrosion of metal was noted at bond line.

d) The following cycle was used: 120°F, 97% relative humidity, 158°F, 20% relative humidity; 0°F.

## Table 8

## Comparative Strengths of Commercial Epoxy Resins at 73.5°F

| Resin | Tensile,[a] psi | Tensile-Shear | | Impact[a] ft-lb/in.$^2$ |
|---|---|---|---|---|
| | | Al-to-Al psi | Steel-to-Steel psi | |
| Cycleweld C-14 | 2713 | 1314 | 1872 | 11.7 |
| Araldite CN 502 | 3095 | 940 | 1706 | 11.3 |
| Araldite CN 503 | 3890 | 728 | 1298 | 4.0 |
| Epon 828 | 3640 | 960 | 1743 | 7.7 |
| Cardolite 7019 | 3760 | 1058 | 2524 | 6.2 |

a. Steel-to-steel.

Table 9

Properties of Epon 828 and Cardolite 7019 Adhesives, Both Plasticized with Cardolite 6885a

| | | Percent of Cardolite 6885 Added Center | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Epon 828 | Temperature °F | 0 | 5 | 10 | 15 | 30 | 25 | 30 | 40 | 50 |
| Shear$^b$, psi | -65 | 433 | 920 | 859 | 1027 | 1025 | | | | |
| | 73.5 | 408 | 597 | 587 | 601 | 734 | | | | |
| | 160 | 260 | 397 | 393 | 385 | 597 | | | | |
| Impact$^c$, ft-lb/in.$^2$ | -65 | 3.3 | 9.5 | 10.8 | 9.1 | 14.9 | 10.5 | 5.0 | 5.8 | 7.1 |
| | 73.5 | 3.3 | 4.1 | 12.8 | 12.8 | 18.6 | 4.5 | 3.3 | 2.7 | 4.9 |
| | 160 | 8.8 | 8.1 | 7.5 | 4.9 | 5.1 | --- | 4.9 | 1.7 | 1.1 |
| Tensile$^d$, psi | -65 | 4242 | | 5716 | 6876 | 6255 | | | | |
| | 73.5 | 3128 | | 3079 | 3164 | 2553 | | | | |
| | 160 | 1467 | | 749 | 581 | 540 | | | | |
| Cordolite 7019 | | | | | | | | | | |
| Shear$^b$, psi | -65 | 523 | 1006 | 914 | 940 | 931 | | | | |
| | 73.5 | 845 | 496 | 485 | 568 | 471 | | | | |
| | 160 | 186 | 170 | 157 | 107 | 103 | | | | |
| Impact$^c$, ft-lb/in.$^2$ | -65 | 5.1 | 7.2 | 7.4 | 7.7 | 6.2 | --- | 6.1 | 3.2 | 1.5 |
| | 73.5 | 10.7 | 8.8 | 8.8 | 11.4 | 11.8 | 4.2 | 5.9 | 3.6 | 1.3 |
| | 160 | 3.6 | 4.5 | 1.8 | 3.1 | 2.4 | | | | |

a Adhesive cured with 7 parts triethylene tetramine per 100 parts of resin mixture at room temperature for two weeks. All surfaces vapor-degreased. Bond thickness between 0.002 to 0.004 inch in all cases. Steel-to-steel.
b One square inch lap joint (1" x 1") and adherend thickness of 1/8 of an inch.
c Impact area of 0.766 square inch (7/8" x 7/8").
d One square inch bonding surface.

## Table 10.

### Chemical Resistance of an Epoxy Resin Cured with Amine-Resin Adduct

| System tested in | gain in weight, 7 days' immersion<br>% |
|---|---|
| 10% caustic | Negligible |
| Ethyl alcohol | do. |
| Kerosene | do. |
| Toluol | do. |
| Ethyl acetate | do. |
| 30% sulfuric acid | 0.88 |
| Ethyl ether | 0.55 |
| Chloroform | 1.81 |
| Acetic acid | 2.88 |
| Acetone | 0.83 |
| Trichlorethylene | 0.13 |

Table 11
Tensile Shear Strengths after Optimum Cure at 250°F and Solvent Immersion at 80°F. for 30 Days

| Solvent | Formulation<br>T-120-1<br>psi | <br>T-120-2<br>psi | <br>T-120-3<br>psi | <br>T-120-6<br>psi |
|---|---|---|---|---|
| Tap water | 3200 | 800 | 1200 | 2700 |
| Sea water | 2900 | 1100 | 700 | 2800 |
| Type III fuel | 3300 | 3400 | 3200 | 3600 |
| JP-4 fuel | 3400 | 3200 | 2800 | 3400 |
| Engine oil | 3500 | 3200 | 3100 | 3100 |
| Isopropyl alcohol | 3700 | 3200 | 2800 | 3500 |
| Ethylene glycol | 3400 | 3700 | 3600 | 2900 |
| 10% soln. $Al_2(SO_4)_3$ | 3200 | 2000 | 1800 | 2800 |
| 10% soln. $Na_2CO_3$ | 3500 | 2800 | 1400 | 3600 |
| Methyl ethyl ketone | 2700 | 400 | disintegrated | 2600 |
| Dibutyl phthalate | 3200 | 3400 | 3500 | 4100 |

Table 12

Electrical Properties of Various Epoxy Potting Resins

| Potting resin Component | Formulation Parts by wt | Dielectric constant at $10^5$ cycles per sec | Dissipation factor at $10^5$ cycles per sec | Volume resistivity ohm-cm |
|---|---|---|---|---|
| Epoxy<br>Polysulfide<br>DEAPA[a] | 60<br>40<br>6 | 4.69 | .0476 | $5x10^{12}$ |
| Epoxy<br>Polysulfide<br>DET[b] | 50<br>50<br>5 | 6.181 | .0560 | $3x10^{11}$ |
| Epoxy<br>DET[b] | 100<br>10 | 3.65 | .0089 | $10^{16}$ |

a. DEAPA = Diethylaminopropylamine
b. DET = Diethylene triamine

## Table 13

### Typical Electrical Properties of Epoxy Resin Cured with Diethylene Triamine

| Property | Frequency, cycles/sec | | | | | |
|---|---|---|---|---|---|---|
| | $10^2$ | $10^3$ | $10^4$ | $10^5$ | $10^6$ | $10^7$ |
| Power factor: | | | | | | |
| -40°C | 0.0220 | 0.0200 | 0.0195 | 0.0175 | 0.0165 | 0.0170 |
| -20°C | 0.0300 | 0.0500 | 0.0500 | 0.0700 | 0.0900 | 0.1000 |
| 20°C | 0.0090 | 0.0400 | 0.0480 | 0.0800 | 0.1000 | 0.1300 |
| 60°C | 0.0045 | 0.0100 | 0.0600 | 0.0750 | 0.1100 | 0.1500 |
| 100°C | 0.0175 | 0.0165 | 0.0300 | 0.0600 | 0.1200 | 0.2000 |
| Dielectric constant: | | | | | | |
| -40°C | 3.4 | 3.35 | 3.3 | 3.3 | 3.2 | 3.1 |
| -20°C | 3.8 | 3.8 | 3.75 | 3.7 | 3.6 | 3.4 |
| 20°C | 4.1 | 4.2 | 4.2 | 4.1 | 4.2 | 4.1 |
| 60°C | 4.3 | 4.4 | 4.6 | 4.6 | 4.5 | 4.4 |
| 100°C | 4.5 | 4.6 | 4.7 | 4.8 | 4.9 | 5.0 |
| Volume resistivity: | | | | | | |
| 25°C | | $2 \times 10^{16}$ ohm-cm | | | | |
| 50°C | | $6 \times 10^{14}$ ohm-cm | | | | |
| 75°C | | $5 \times 10^{13}$ ohm-cm | | | | |
| 100°C | | $5 \times 10^{12}$ ohm-cm | | | | |
| 125°C | | $5 \times 10^{11}$ ohm-cm | | | | |

Table 14

Expansion and Contraction of Some Building Materials

| Material | Thermal Coefficient of Expansion $10^{-6}$ in./in./°F | Dimensional Change in 10 ft for 100°F. Temp. Change inches |
|---|---|---|
| Aluminum Alloys, Wrght. | 11.1-13.5 | 0.133-0.162 |
| Copper Alloys | 9.0-11.8 | 0.108-0.142 |
| Glass | 4.4-5.1 | 0.053-0.061 |
| Plastics | 5-210 | 0.069-2.51 |
| Steel, carbon 0.20C | 6.7 | 0.081 |
| " stainless 18-8 | 0.6 | 0.105 |
| Brick | 5-7 | 0.060-0.084 |
| Concrete | 4-6.5 | 0.048-0.078 |
| Wood, parallel to grain | 1.1-5.3 | 0.013-0.063 |
| " perp. to grain | 14.6034.1 | 0.175-0.410 |

| | Moisture, Expansion and Contraction | Dimensional Change in 10 ft. |
|---|---|---|
| Brick | 5-150x$10^6$ in./in. | 0.0006-0.0126 |
| Concrete (1year at 50% relative humidity) | 250-1160x$10^6$ in./in. | 0.018-0.139 |
| Wood, parallel to grain | 0.1-0.2 percent | 0.120-0.240 |
| " perp. to grain | 2-14 percent | 2.40-16.8 |

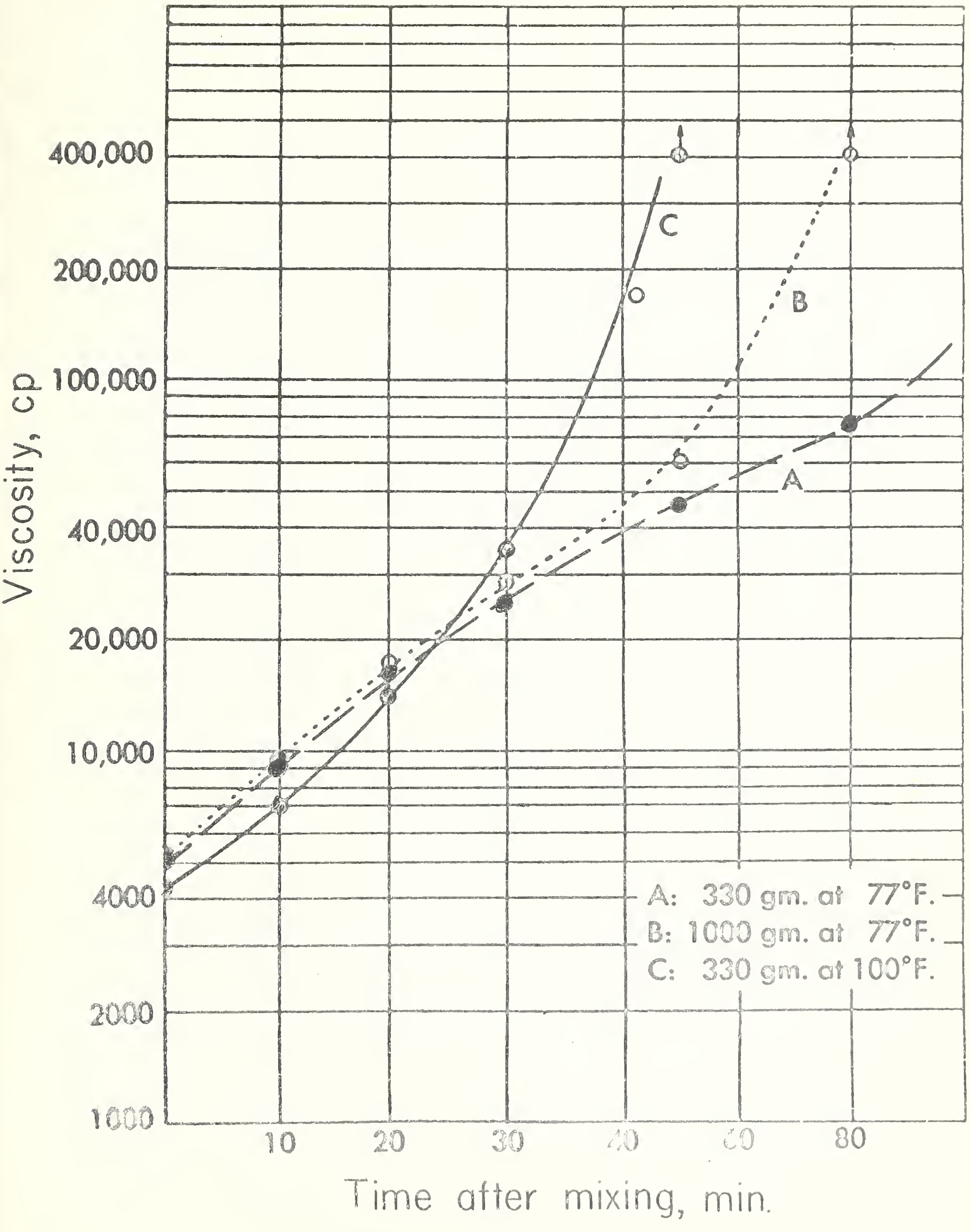

Fig. 1 Pot life of mixed epoxy resin

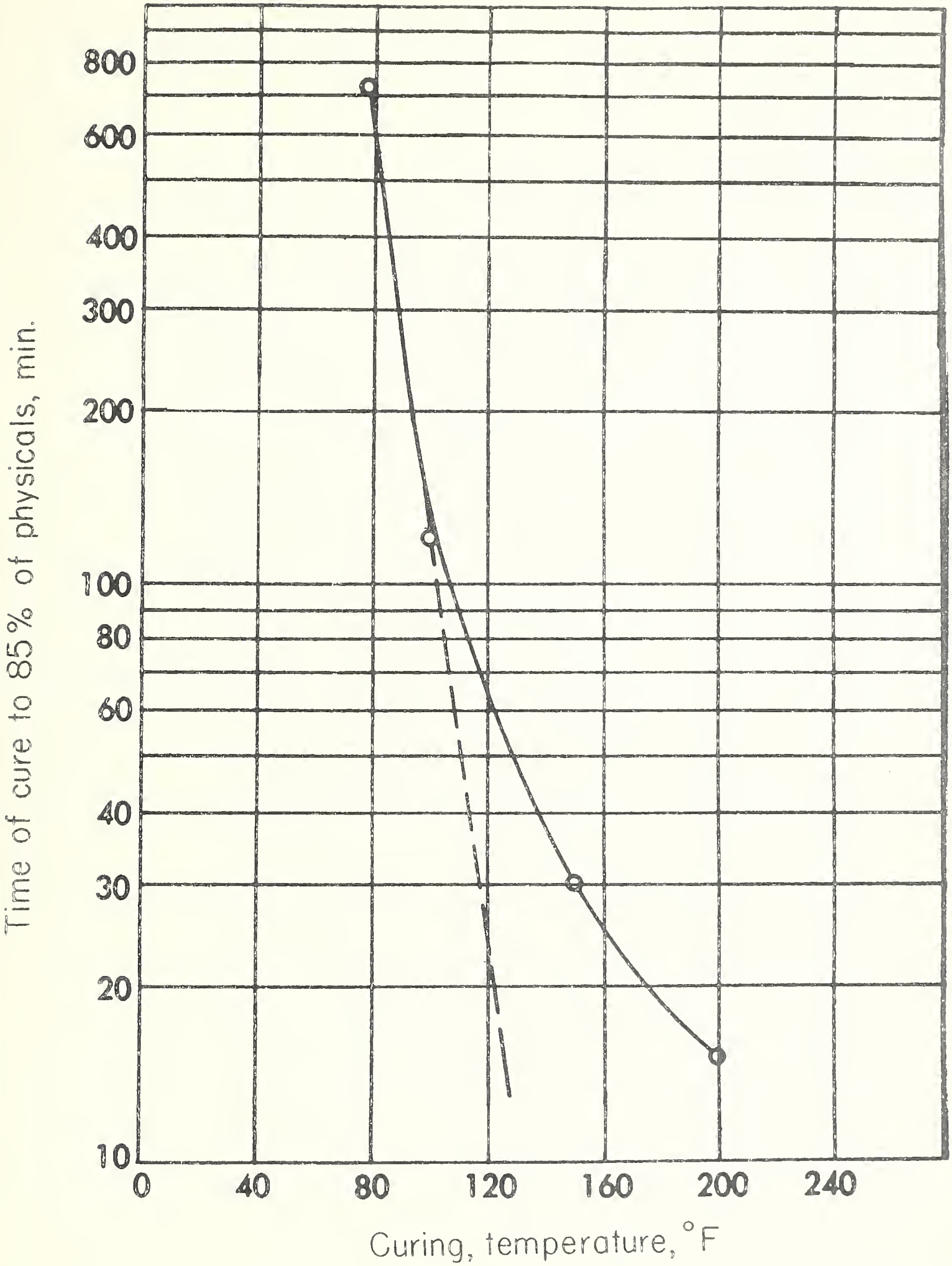

Fig. 2 Curing time versus temperature for epoxy adhesive

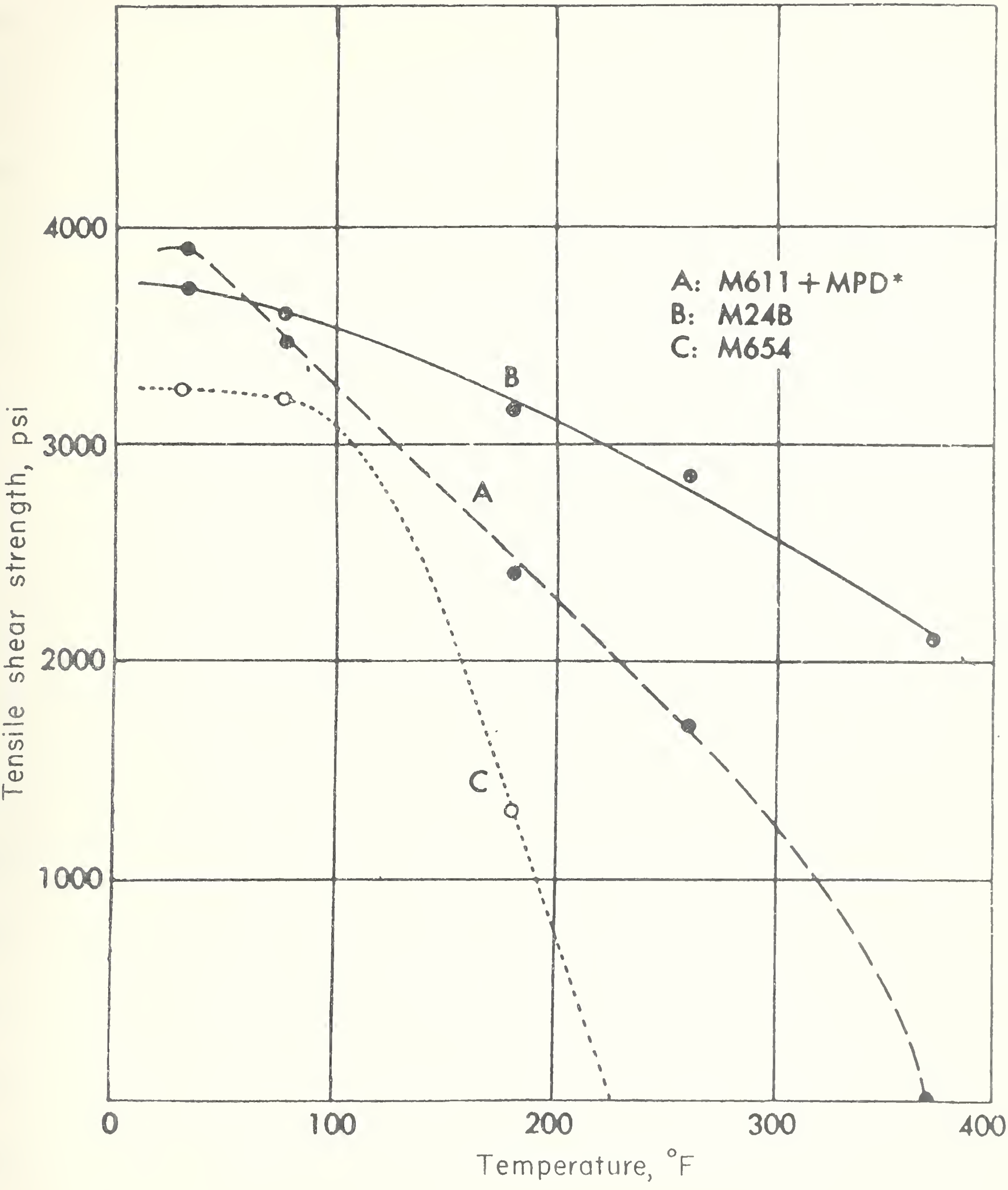

Fig. 3 Strength versus temperature for epoxy adhesives

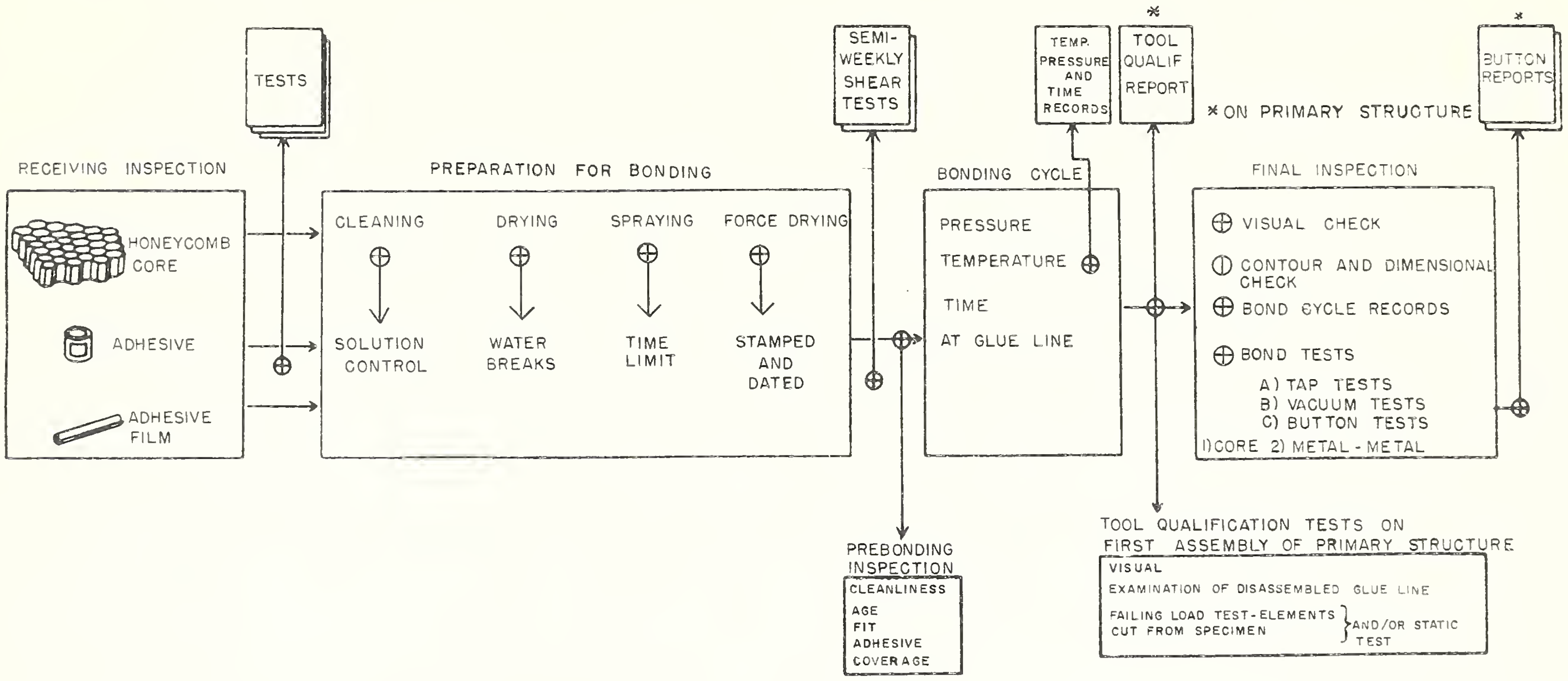

Fig. 4 Process control for adhesive bonding

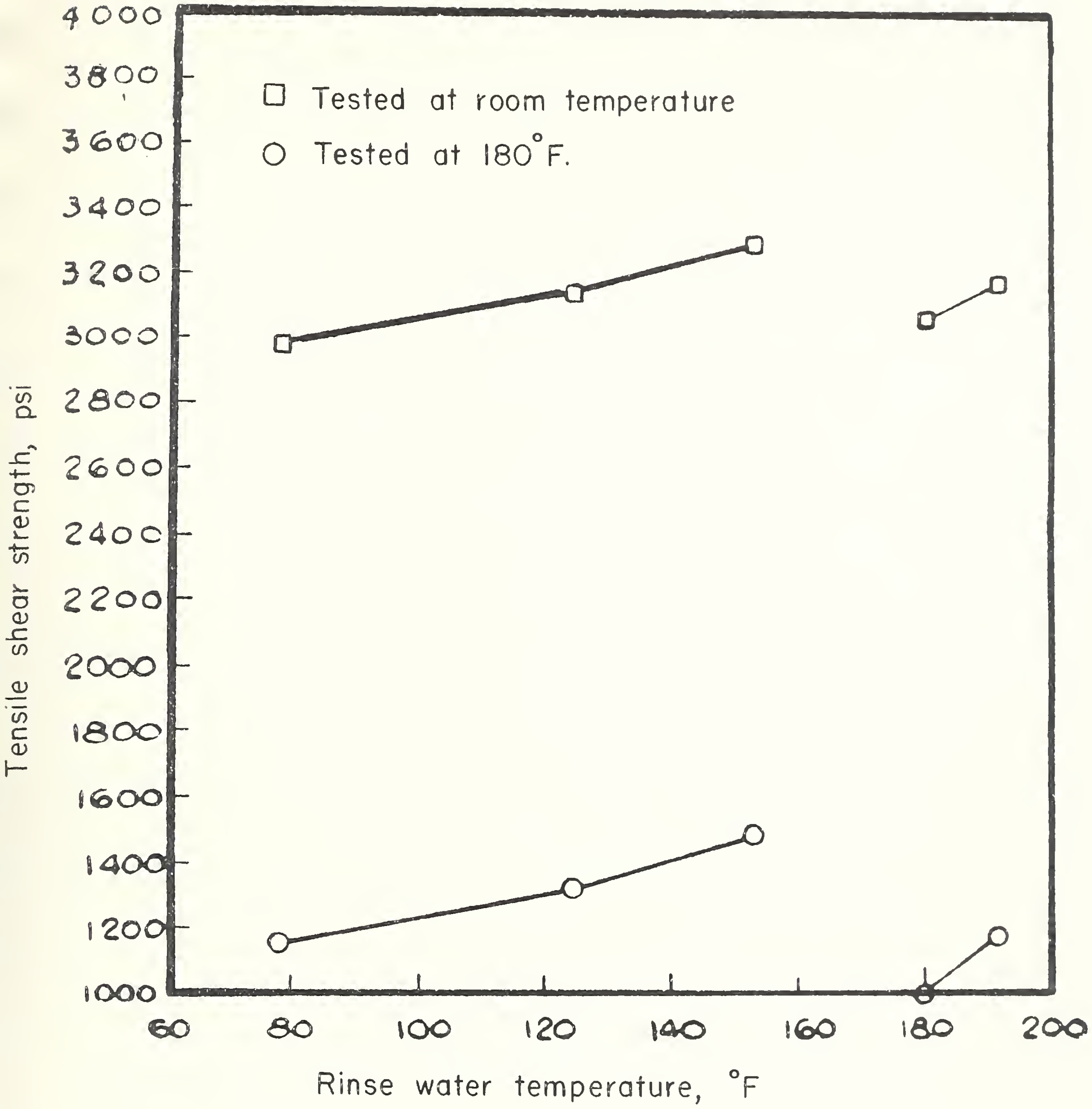

**Figure** 5. Influence of surface condition of aluminum on bond strength using resorcinol epoxy adhesive

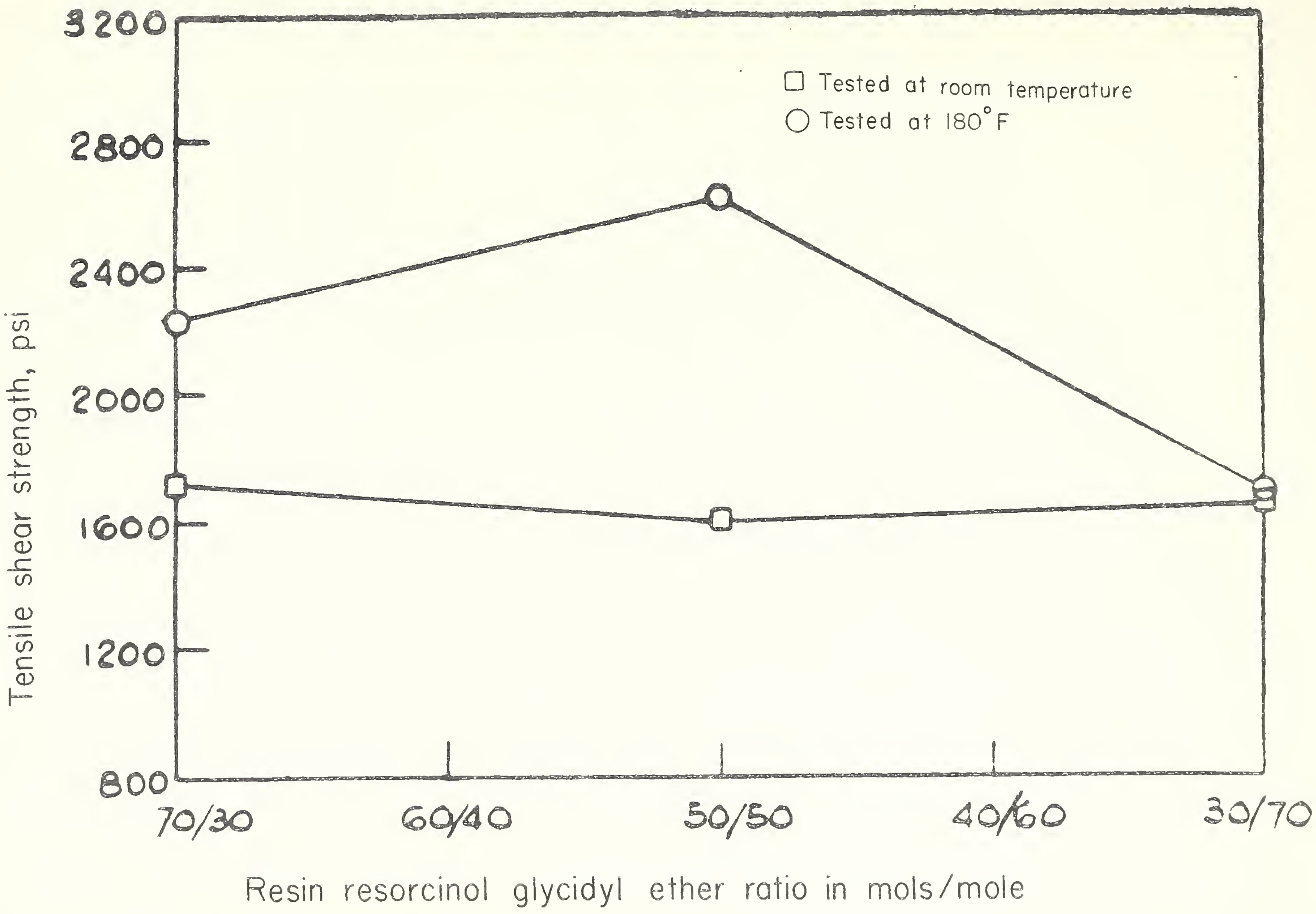

Fig. 6 Effect of resin-resorcinol ratio on bond strength

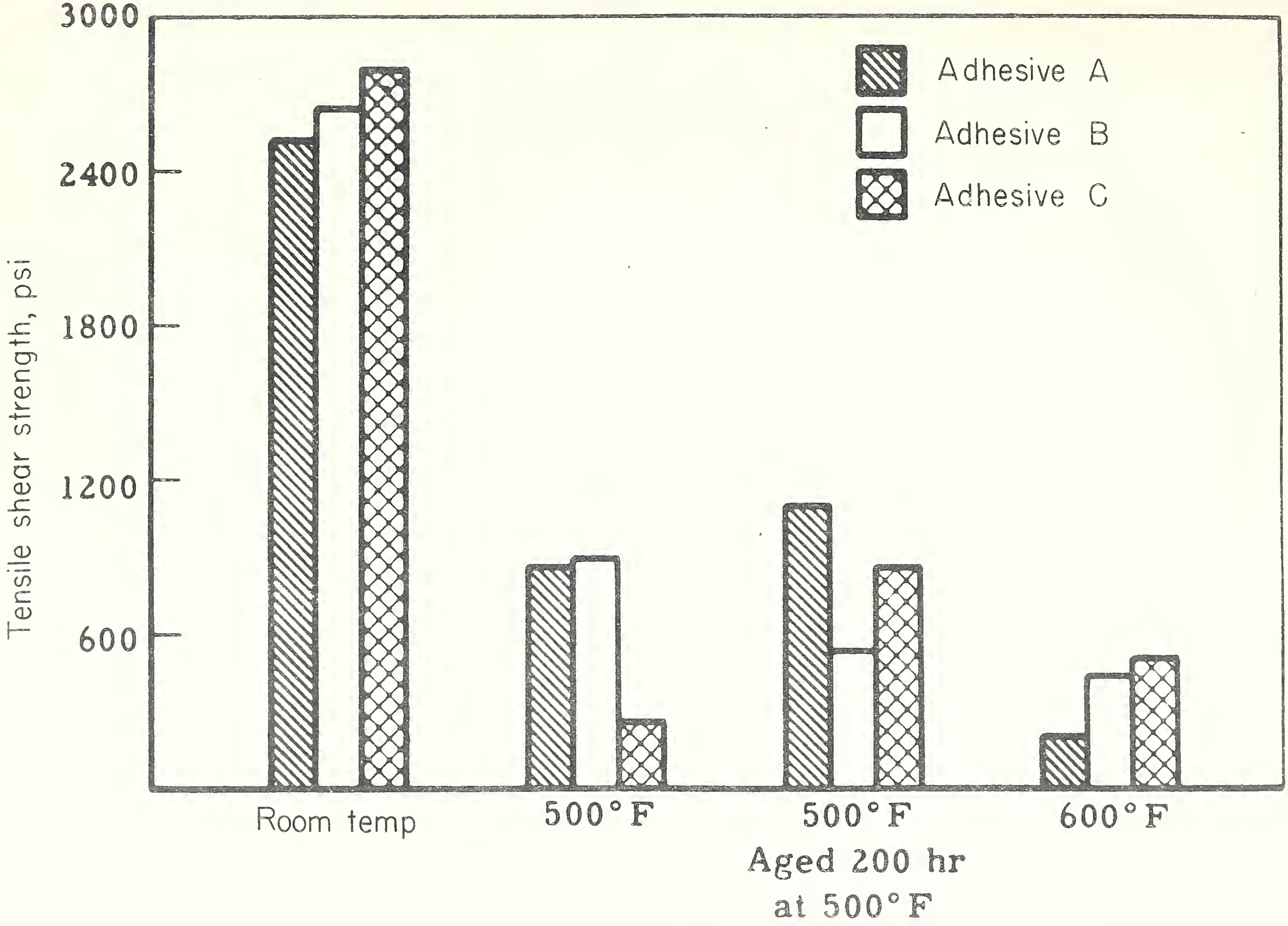

Fig.7 Comparison of three epoxy adhesives containing polyvinyl formal resin

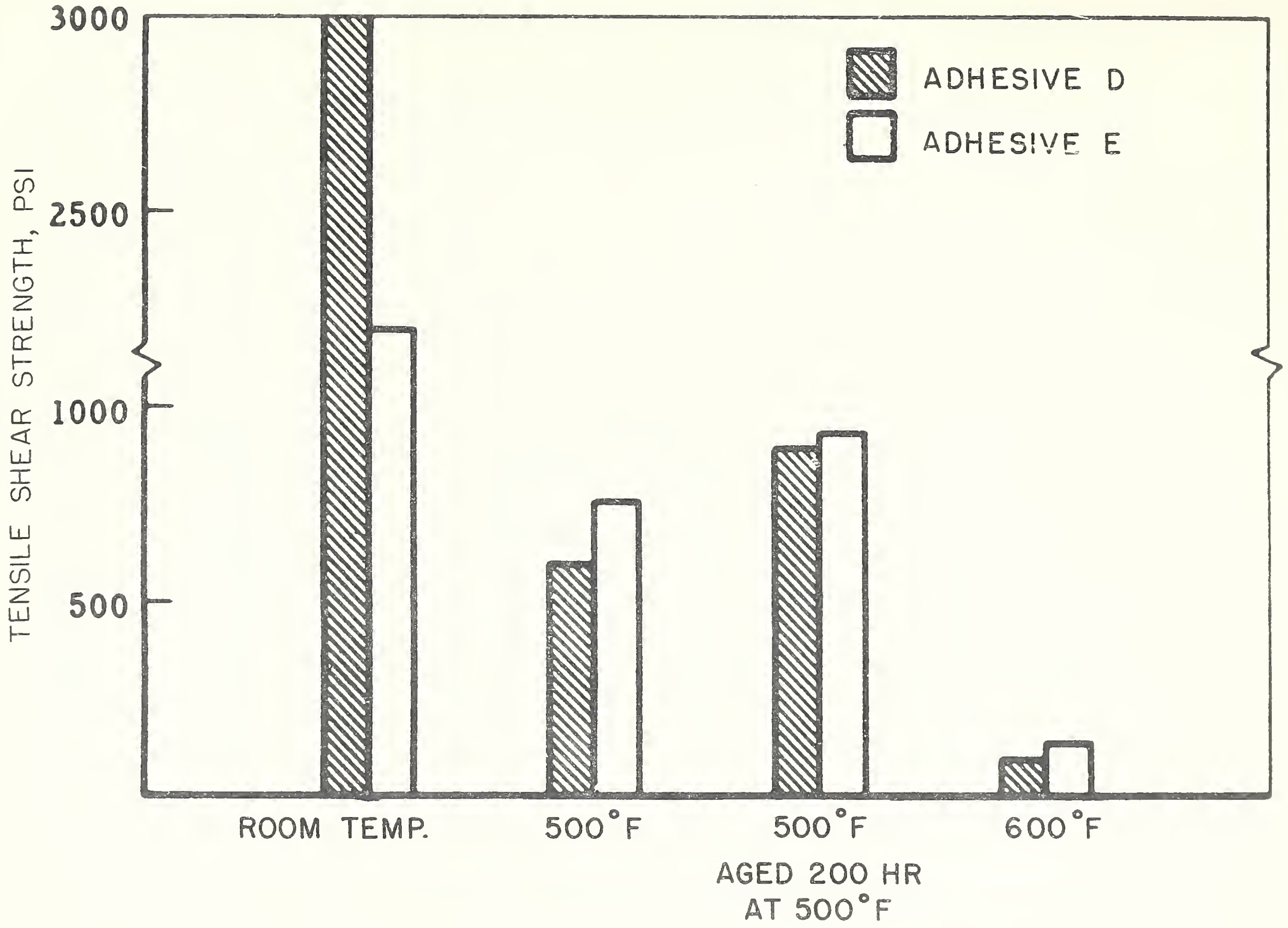

FIGURE 8. COMPARISON OF TWO EPOXY ADHESIVES

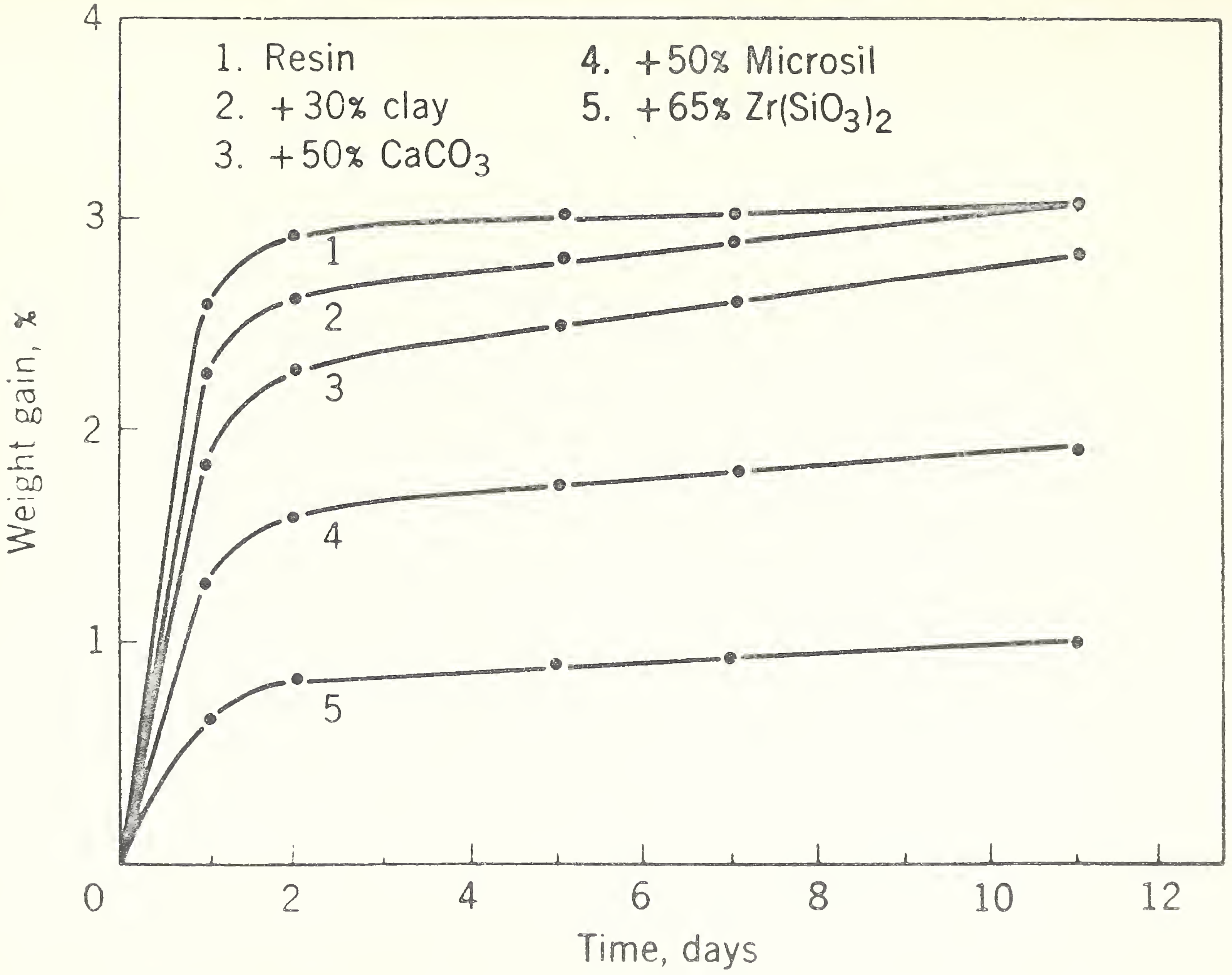

FIG.9 Water adsorption at 40°C. for filled epoxy adhesives

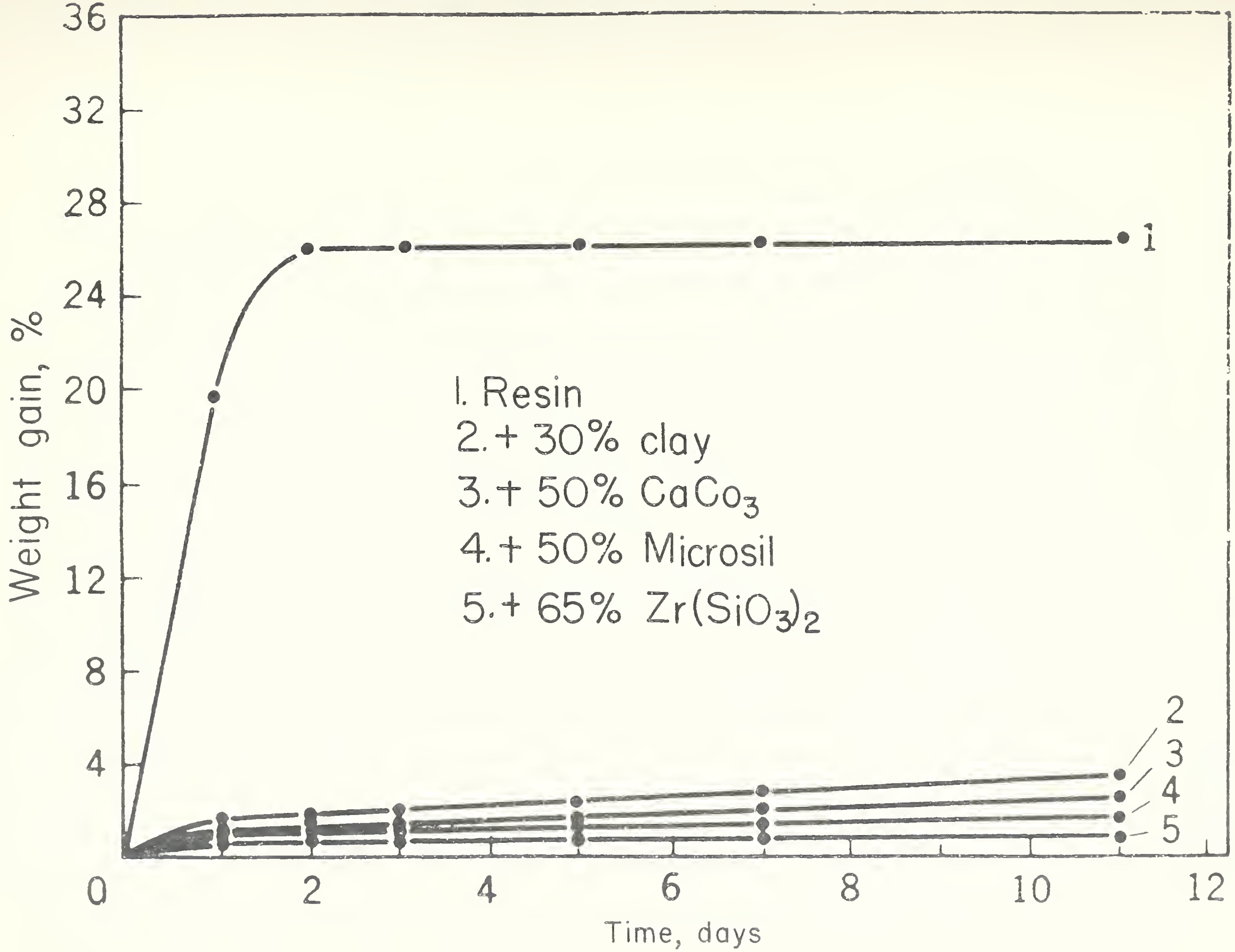

FIG 10 Benzene adsorption at 40°C for filled epoxy adhesives

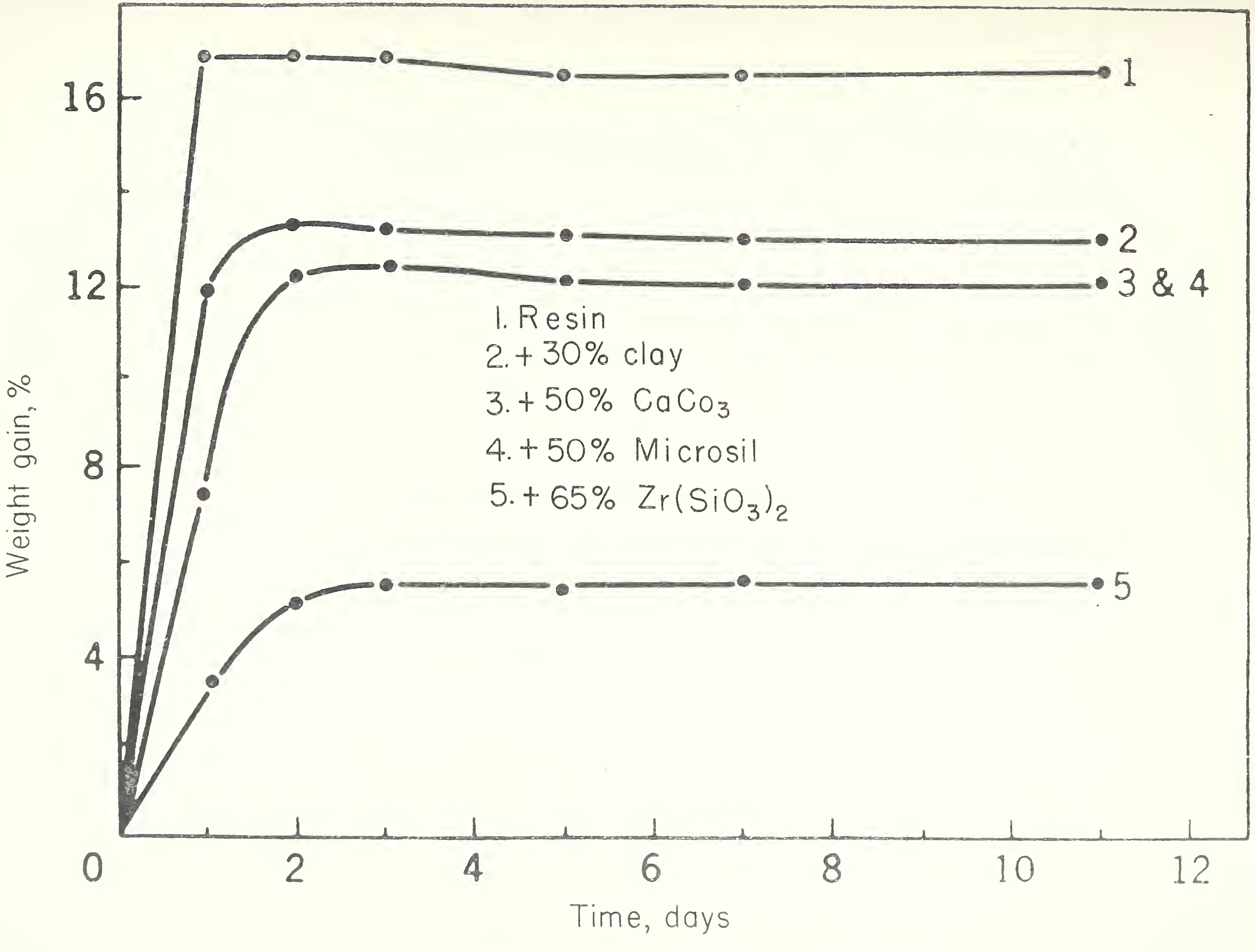

Fig.11 Ethyl alcohol adsorption at 40°C for filled epoxy adhesives

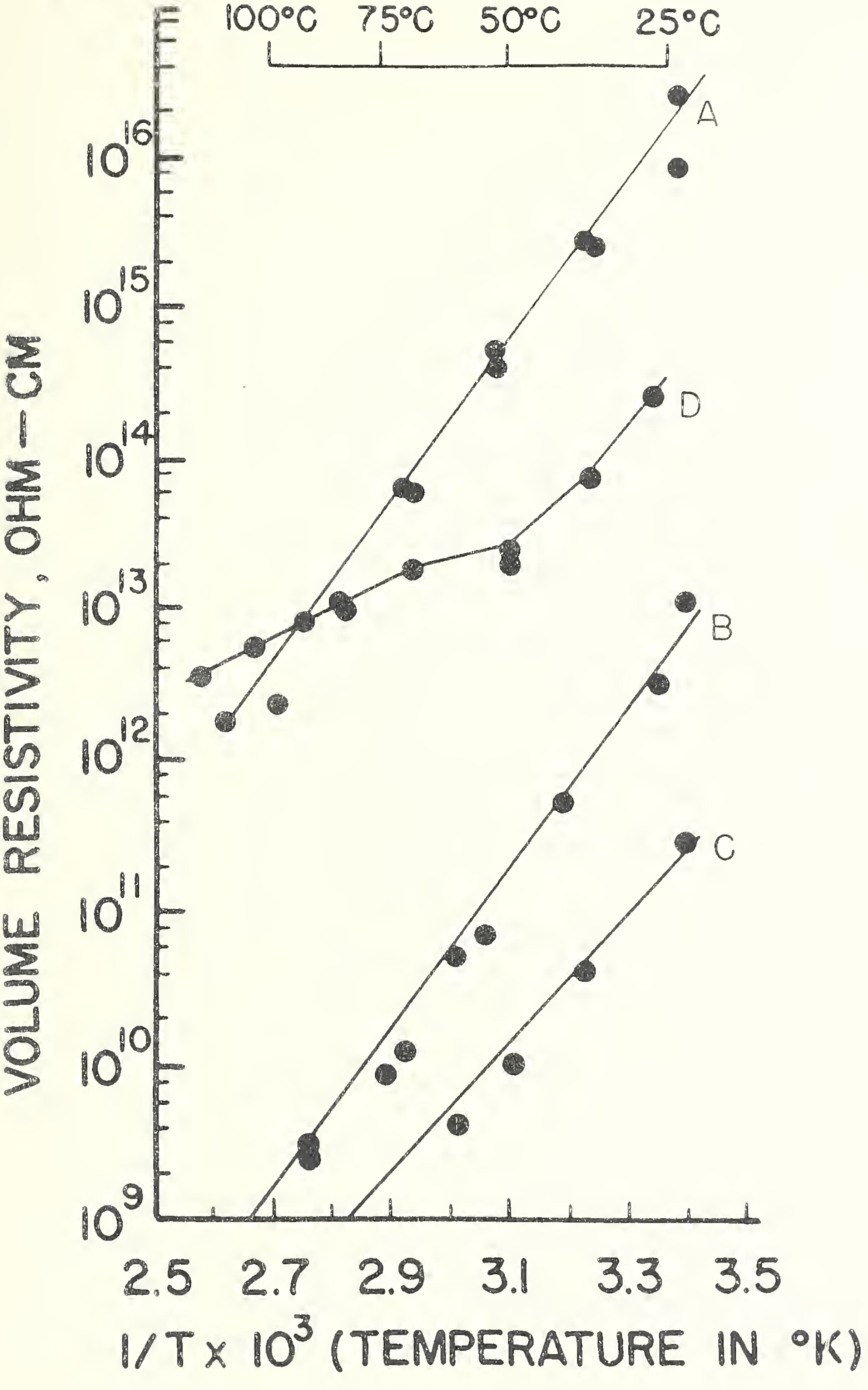

Fig.12 Volume resistivity as a function of temperature for epoxy and modified epoxy resins: Resin A, epoxy cured with diethylene triamine; Resin B, 100 parts epoxy-60 parts polysulfide rubber; Resin C, 100 parts epoxy-100 parts polysulfide rubber; Resin D, epoxidized polybutadiene

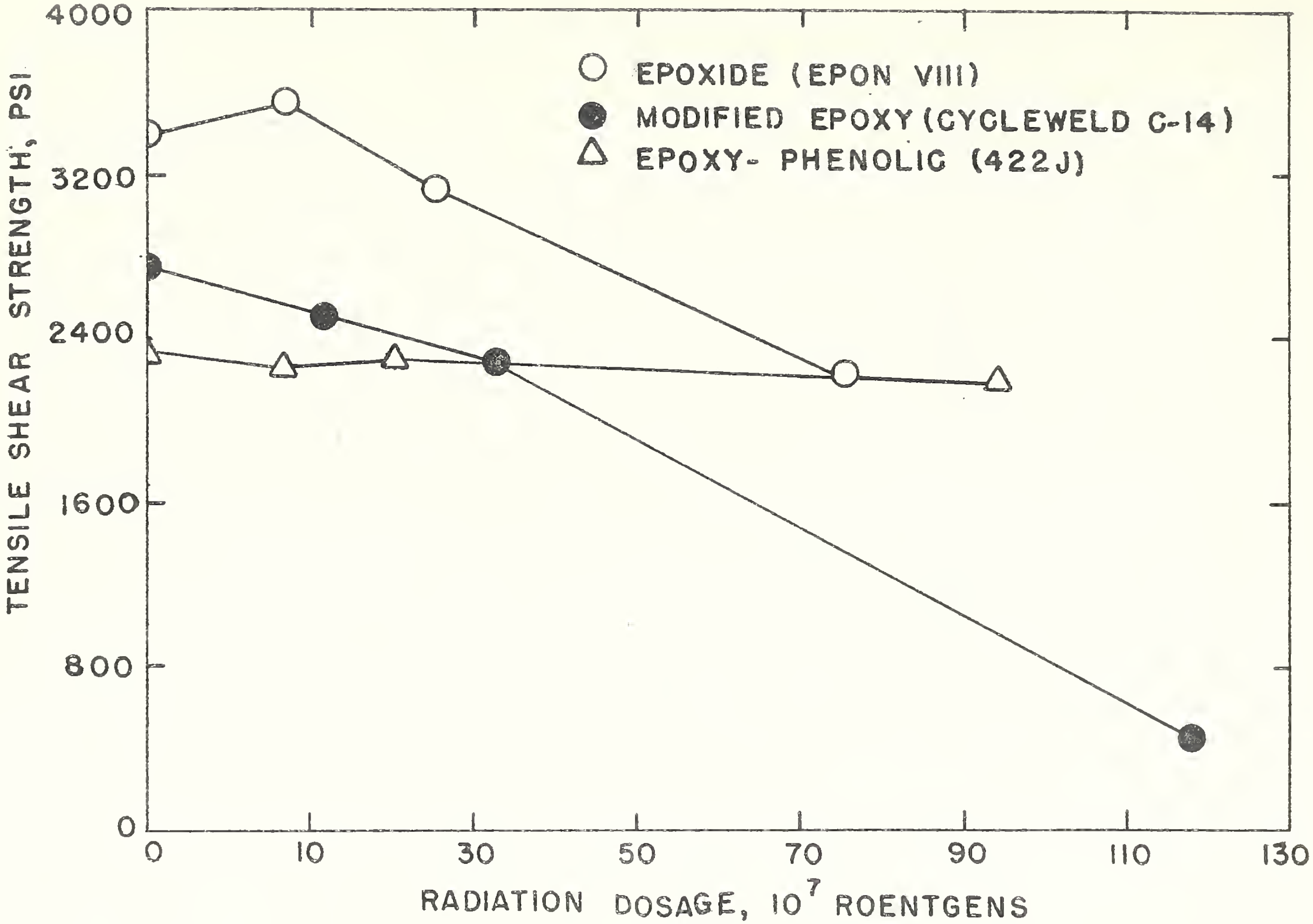

FIGURE 13.- EFFECT OF NUCLEAR RADIATION ON TENSILE SHEAR STRENGTH OF EPOXY ADHESIVES AT ROOM TEMPERATURE

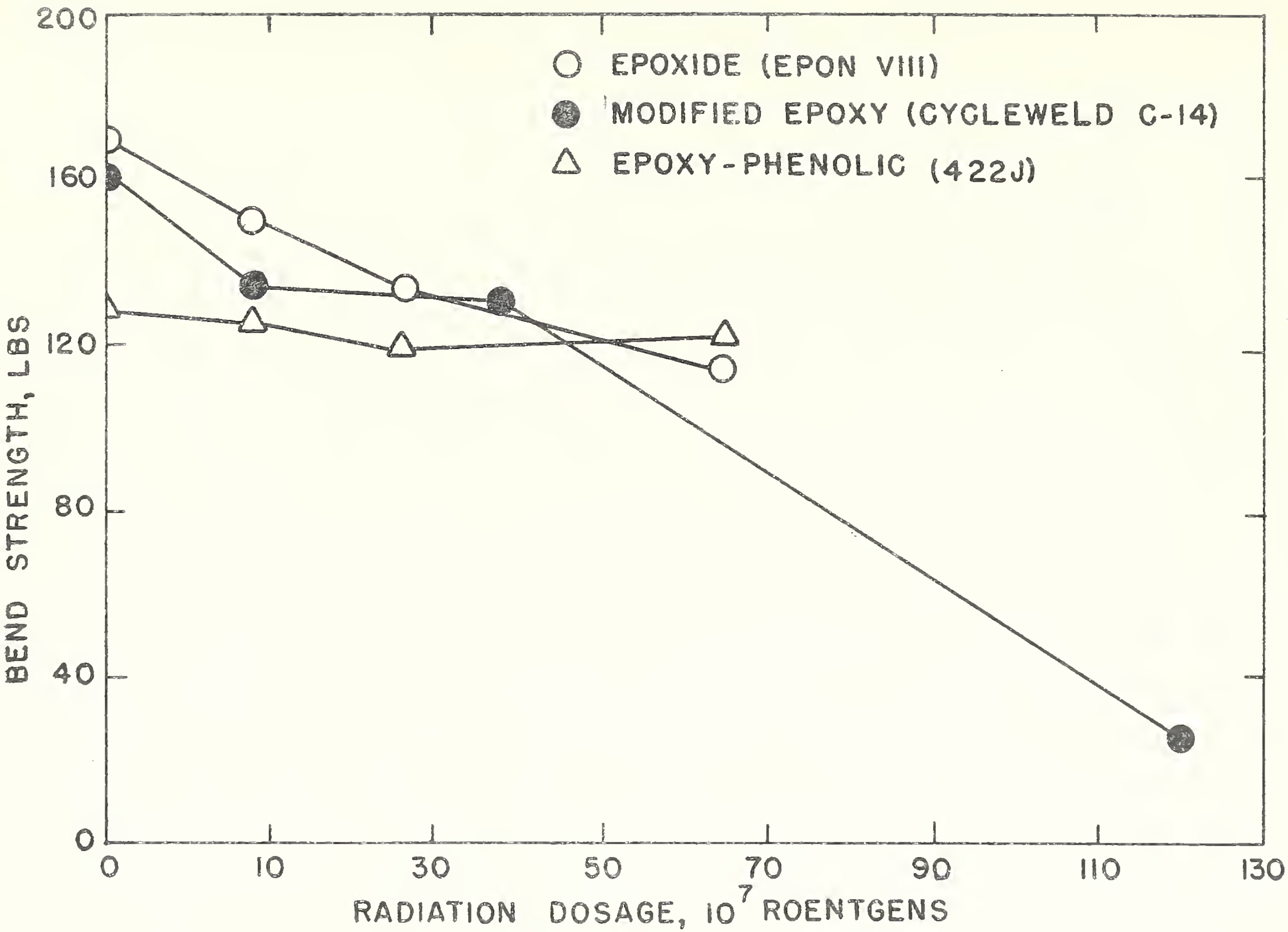

FIGURE 14.- EFFECT OF NUCLEAR RADIATION ON BEND STRENGTH OF EPOXY ADHESIVES AT ROOM TEMPERATURE

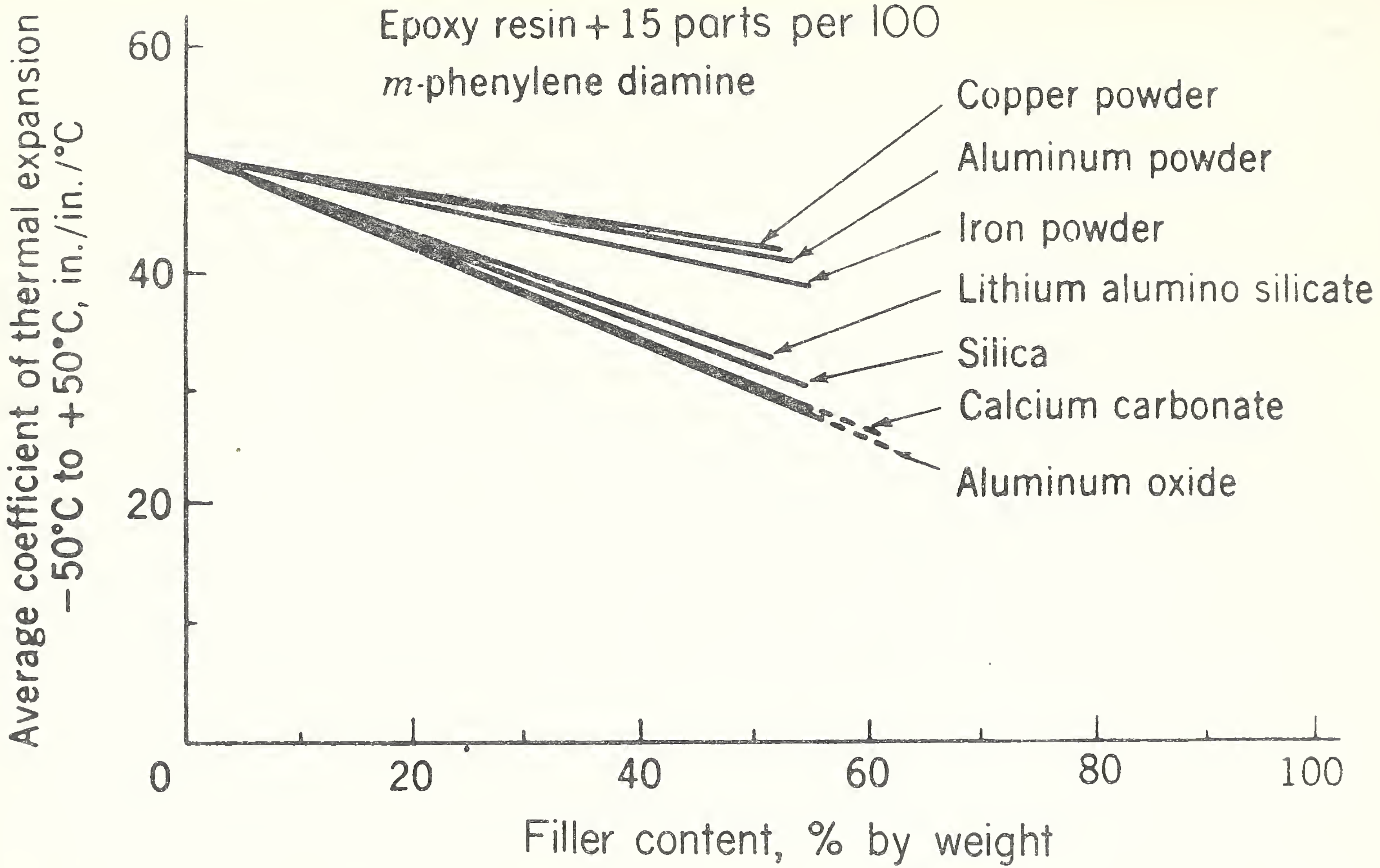

FIG. 15 Effect of various fillers on coefficient of thermal expansion of epoxy adhesives

U. S. DEPARTMENT OF COMMERCE
Sinclair Weeks, *Secretary*

NATIONAL BUREAU OF STANDARDS
A. V. Astin, *Director*

# THE NATIONAL BUREAU OF STANDARDS

The scope of activities of the National Bureau of Standards at its headquarters in Washington, D. C., and its major laboratories in Boulder, Colo., is suggested in the following listing of the divisions and sections engaged in technical work. In general, each section carries out specialized research, development, and engineering in the field indicated by its title. A brief description of the activities, and of the resultant publications, appears on the inside front cover.

## WASHINGTON, D. C.

**Electricity and Electronics.** Resistance and Reactance. Electron Devices. Electrical Instruments. Magnetic Measurements. Dielectrics. Engineering Electronics. Electronic Instrumentation. Electrochemistry.

**Optics and Metrology.** Photometry and Colorimetry. Optical Instruments. Photographic Technology. Length. Engineering Metrology.

**Heat.** Temperature Physics. Thermodynamics. Cryogenic Physics. Rheology. Engine Fuels. Free Radicals Research.

**Atomic and Radiation Physics.** Spectroscopy. Radiometry. Mass Spectrometry. Solid State Physics. Electron Physics. Atomic Physics. Neutron Physics. Nuclear Physics. Radioactivity. X-rays. Betatron. Nucleonic Instrumentation. Radiological Equipment.

**Chemistry.** Organic Coatings. Surface Chemistry. Organic Chemistry. Analytical Chemistry. Inorganic Chemistry. Electrodeposition. Molecular Structure and Properties of Gases. Physical Chemistry. Thermochemistry. Spectrochemistry. Pure Substances.

**Mechanics.** Sound. Mechanical Instruments. Fluid Mechanics. Engineering Mechanics. Mass and Scale. Capacity, Density, and Fluid Meters. Combustion Controls.

**Organic and Fibrous Materials.** Rubber. Textiles. Paper. Leather. Testing and Specifications. Polymer Structure. Plastics. Dental Research.

**Metallurgy.** Thermal Metallurgy. Chemical Metallurgy. Mechanical Metallurgy. Corrosion. Metal Physics.

**Mineral Products.** Engineering Ceramics. Glass. Refractories. Enameled Metals. Concreting Materials. Constitution and Microstructure.

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**Data Processing Systems.** SEAC Engineering Group. Components and Techniques. Digital Circuitry. Digital Systems. Analog Systems. Application Engineering.

- Office of Basic Instrumentation.
- Office of Weights and Measures.

## BOULDER, COLORADO

**Cryogenic Engineering.** Cryogenic Equipment. Cryogenic Processes. Properties of Materials. Gas Liquefaction.

**Radio Propagation Physics.** Upper Atmosphere Research. Ionospheric Research. Regular Propagation Services. Sun-Earth Relationships. VHF Research.

**Radio Propagation Engineering.** Data Reduction Instrumentation. Modulation Systems. Navigation Systems. Radio Noise. Tropospheric Measurements. Tropospheric Analysis. Radio Systems Application Engineering. Radio Meteorology.

**Radio Standards.** High Frequency Electrical Standards. Radio Broadcast Service. High Frequency Impedance Standards. Calibration Center. Microwave Physics. Microwave Circuit Standards.


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