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ENGINEERING DESIGN HANDBOOK



DIELECTRIC EMBEDDING OF ELECTRICAL
OR
ELECTRONIC COMPONENTS

APRIL 1979

DEPARTMENT OF THE ARMY
HEADQUARTERS US ARMY MATERIEL DEVELOPMENT AND READINESS COMMAND
5001 Eisenhower Avenue, Alexandria, VA 22333

DARCOM PAMPHLET
No. 706-315

6 April 1979

ENGINEERING DESIGN HANDBOOK
DIELECTRIC EMBEDDING OF ELECTRICAL OR ELECTRONIC
COMPONENTS

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PREFACE

The Engineering Design Handbook Series of the US Army Materiel Development and Readiness Command is a coordinated group of handbooks containing basic information and fundamental data useful in the design and development of Army materiel and systems. The handbooks are prepared for the special use of the design engineers and scientific personnel in the Government and industry engaged in the design, development, and upgrading of Army equipment, materiel, components, and techniques.

This handbook is concerned with the use of epoxies, polyurethanes, and silicones as insulating embedding agents for electrical and electronic components. These three families of resins are the materials which currently find the widest use in high performance component protection. Another material, the polyxylylenes, which are vacuum deposited on substrates as very thin dielectrics, is also discussed. The processes of embedding which are discussed include encapsulation, potting, casting, conformal coating, surface coating, impregnation, and transfer molding. It is the purpose of this handbook to acquaint Army personnel with the most important characteristics of the mentioned types of embedding agents and the typical processes of applying these insulating polymers to the circuit components. Both modified and somewhat improved products are introduced continually by various suppliers; once the basic type is selected by the user, the industrial literature provides the best up-to-date guide for the final selection of the embedding material. Confirmation with industry and Government experts for up-to-date information is strongly recommended since the technology is far from static and new-product development is very active.

The handbook was prepared by Mr. Arthur Readdy, Plastics Technical Evaluation Center (PLASTEC), the Defense Department's specialized information center on plastics located at the US Army Armament Research and Development Command, Dover, NJ.

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CHAPTER 1

INTRODUCTION

The purpose of using synthetic polymers for the embedding of electrical/electronic components — together with the advantages/disadvantages of embedding — is discussed. Primary processes for embedding are presented.

1-1 PURPOSE OF DIELECTRIC EMBEDDING

1-1.1 GENERAL

To isolate circuit components from generally degrading environmental and operational effects (of oxygen, moisture, heat and cold, electrical flashover, current leakage, and mechanical shock and vibration), the components have been coated, buried or encased in dielectric materials. The earliest substances used for such purpose were materials such as waxes and asphaltic materials. These now may be used to a limited extent; however, synthetic polymers are currently most widely used for embedding^{1,2,3}.

The materials most employed are the epoxy resins, which account for three-fourths or more of the applications. Other currently used agents finding substantial use are the polyurethanes and the silicones. Fairly new types finding special uses are the vapor-deposited polyxylylenes. There has been a decrease in the use of materials such as thermosetting hydrocarbons, thermosetting acrylics, polyesters, and polysulfide resins especially in high performance applications which are required for military items⁴.

1-1.2 ADVANTAGES AND DISADVANTAGES OF EMBEDDING

Embedding does not provide hermetic sealing; however, it increases the reliability of any given assembly by sealing it against moisture, dirt, fungi, and other contaminants. Also, components are fixed in position; mechanical strength of the embedded assembly is greatly enhanced against

vibration and shock. Embedding allows the use of unitized construction in miniaturization and provides for use of modular units. Generally, embedding allows economies to the fabricator and user of the end item^{5,6}.

There are some limitations in the use of embedded electrical and electronic assemblies. Many are hard to repair. Although flexible and rubberlike polymers can be repaired, any repair can present difficulties. Additionally, the weight of an assembly is increased by embedding since in most cases the amount of additional mechanical structure for protection without embedding can be designed to be relatively light. Embedding resins have higher dielectric constants and loss tangents than air; this is a limitation where very low electrical loss is a desirable factor.⁷ Offset by this shortcoming is the fact that voltage breakdown between two potential points is improved. The potential values as well as shortcomings of embedding are shown in Table 1-1.

1-2 METHODS OF EMBEDDING

The primary embedding processes include casting, potting, impregnating, encapsulating, and transfer molding. Coating is, in a sense, a form of embedding and includes conformal coating and other surface coatings.

1-2.1 CASTING

Casting refers to the complete burial of a circuit in surrounding material. (The term also is used when the dielectric is made of granules, powders, foams, or ceramics.) The embedment

TABLE 1-1
ADVANTAGES AND DISADVANTAGES OF
EMBEDDING ELECTRONIC/ELECTRICAL COMPONENTS

1. Advantages:

a. Use Reliability

- (1) Sealing (not fully hermetic) against fungi, water vapor, and gross moisture, dirt, gases; assemblies are fixed in resin of known mechanical and dielectric characteristics.
- (2) Packaging strength (shockproofing, antivibration response) increased.

b. Improved Design:

- (1) Air spaces are eliminated.
- (2) Components are held in compact three-dimensional form.
- (3) Wider application of module construction, miniaturization, and plug-in units is permitted.
- (4) Selection of resins allows upgrading of electrical performance (e.g., low-loss response of high frequencies, increased thermal resistance, and/or heat dissipation).
- (5) Colored resins may be used for identification of circuit components.
- (6) Electrical noise in high-gain amplifier devices is reduced.

c. Economy

- (1) Most or all mounting hardware which may add up to 25-30% weight to an assembly is eliminated.
- (2) Need for auxiliary protection for the components is reduced or removed since the resin matrix now serves this purpose.
- (3) Less skilled personnel can remove and replace embedded units.
- (4) Circuit assembly is more rapid since use of point-to-point wiring can be made (e.g., in place of circuit boards).

2. Disadvantages:

a. Difficult Repairs:

- (1) Embedded assemblies are not easily accessible for making minor repairs.
- (2) Solvent soaking procedures are difficult.
- (3) Hole-drilling (with transparent matrices) is expensive and time-consuming.
- (4) Embedded circuit must be treated as an expendable unit (though costly, embedding can be shown to increase reliability and prevent tampering).

b. Lowered Heat Dissipation:

- (1) Thermal dissipation in resins is lower than in air — temperature derating may be required.
- (2) Heat-sink and other sophisticated design variants may be required to control heat buildup.

c. Thermal Limits:

- (1) Most resin stability is limited above 200°C (certain silicones can surpass this temperature).
- (2) Certain high-temperature rated components are required in various systems and require special packaging (but in many uses moderate temperature limits are satisfactory).
- (3) With low temperatures, sharp and irregular parts of components can possibly cause resin cracking. Filled or flexible resins improve low temperature performance but at the general sacrifice of electrical properties (however, silicone elastomeric resins can be used with sharp-edge assemblies).

d. Weight Increase:

- (1) Certain applications can add excess weight to an assembly.
- (2) Design techniques may be required in certain instances (e.g., air-borne or space components) to reduce weight; (e.g., use of conformal coating rather than potting or casting).
- (3) Certain foamed resins and low density (hollow bead) compounds can be used to reduce weight.

e. Adverse Dielectric Properties:

- (1) Components can increase circuit capacitance by having dielectric constants close to that of the embedding resin.
- (2) With high frequency output, electrical losses can be increased; however, design methods can be used to compensate for known dielectric properties, uniform for given conditions, in the circuit.

f. Variable Stresses in Cured Matrix:

- (1) Shrinkage occurs during resin curing.
 - (2) Difference in coefficients of thermal expansion (resin/metal/glasses/other materials) is a source of problems — i.e., breakage, crushing, other component damage but effects are lessened with use of flexibilized resin, or elastomer coatings, e.g., silicones.
-

process generally is performed by housing the assembly or component in a mold or case (which allows for complete surrounding of the part by polymer). The mold contains the dielectric polymer during its change from liquid to solid state. The mold is removed subsequently; the final item takes the shape of the mold; and a smooth uniform surface results.

1-2.2 POTTING

Potting is similar to the casting method, except that the electronic component is placed in a can, shell, or similar container. The use of such a container is the difference between casting and potting. The container will not be removed from the finished part; thus, no release agent is used in the method.

If the container is metal, a sheet of insulating material may be placed between the electronic component and the can. This prevents shorting out of the electrical circuit if some of the conductors were to touch the inside surface of the metal can. The use of an insulation sheet is most important where the operating voltage is very high.

In potting, a clear plastic shell may be used and any internal defects which exist can be seen. However, an opaque shell or container may also serve to hide any minor surface blemishes which are operationally unimportant but not desirable as far as appearance is concerned. Many of the surface defects are meaningless in that they do not affect the function of the component.

Where adhesion to the can is defective (e.g., certain plastics such as polyesters with high shrinkage) a high strength package does not result; the can may separate from the rest of the item. The plastic shell must be selected carefully so that it bonds well with the potting resin. At times, the inside surface of the plastic can must be roughened or abraded to insure proper bonding with the resin. Another problem with a potted unit is that spillage, overflow, and dropping of the resin onto the outside surface of the plastic container may occur. Cleanup is messy. If

the resin cures on the surface of the can, the end-item looks shoddy. Solvent cleaning generally cannot be used because the solvents may dissolve or soften the shell and potting resin; scraping is generally not satisfactory because objectionable scratches and defects may be left on the surface of the part.

1-2.3 IMPREGNATION

Impregnation is the process by which all external air spaces in a component (e.g., coil or stator) are filled with a resin. This generally is performed by immersing the component in the liquid resin and applying a vacuum, pressure, or both modes to better enable filling of spaces.

In impregnation, the component or assembly is surrounded completely by the liquid resin which is forced into all of the existing spaces of the item. This resin is then cured or hardened. Impregnation may be used alone or in combination with other embedding processes such as encapsulating, casting, or potting. Impregnation results in resin penetration of the assembly, whereas encapsulation yields only a coating with minimal penetration into the component. Resin penetration is highly desirable for certain electrical parts, e.g., electronic transformers.

The assembly or component is submerged in the catalyzed resin; either internal vacuum or external pressure (or a combination) is applied. The time of this cycle is varied depending on the extent of impregnation desired, lack of air bubbles required, resin viscosity, etc. Impregnation may also be performed by centrifugal casting; the part is placed in a mold, the mold is filled with resin, and the entire set-up is spun at high speed to force the resins into the interstices of the assembly.

In certain applications, e.g., transformer applications, both encapsulation and impregnation are desired. The dip-coating can be applied first. A hole is left in this coating so that low viscosity resin can be forced into this hole after the "dipped shell" has hardened. Thus, a container for the impregnant is provided; drainoff of

the latter material prior to hardening is prevented.

1-2.4 ENCAPSULATION

Encapsulation defines any process that completely encloses a circuit or component (except for leads) in a monolithic dielectric. Its definition has been expanded (by some sources) to include a relatively thick coating applied to an assembly; this can involve dipping of the part in a high-viscosity or thixotropic material to obtain a conformal coating on the surface with a thickness of 10 to 50 mils or more. Problems which can be experienced include variable surface wetting, nonuniform resin runoff, and variations in coating thickness and surface uniformity.

1-2.5 TRANSFER MOLDING

Transfer molding is the process of forming parts in a closed mold from a thermosetting plastic conveyed under pressure (100 to 500 psi), in a hot plastic state, from a transfer cylinder'. It is a combination of injection and compression molding designed to produce thermosetting components. Encapsulation of electronic components and complete electronic modules by transfer molding is replacing liquid potting techniques. Coils, resistors, capacitors, semiconductor, and glass diodes can be encapsulated with epoxy molding powders under low pressure (50 to 200 psi) and relatively low temperatures (250° to 300°F). The following are advantages/disadvantages of transfer molding compared with potting :

<u>Advantage</u>	<u>Disadvantage</u>
1. High speed output of large volume	1. High initial cost of equipment and molds
2. Short cure cycle	2. Limitation of sensitive components or assemblies to pressure and/or temperature.
3. Lower cost	
4. Cleaner operation	

Transfer molding approximates compression molding since the thermoset plastic is cured under heat and pressure; the difference from compression molding is that the plastic is heated to a liquid or semiliquid state before molding and is hydraulically forced into the closed mold via sprues and runners. Intricate parts, with deep holes and inserts, can be processed. A dry compressed molding compound could damage metal inserts and pins for holes; the semiliquid materials used in transfer molding flow around delicate parts without damaging them. In transfer molding, a definite amount of material is heated at each cycle to fill the mold cavity; in injection molding, the plastic is kept in the heated cylinder with a part of it used at each plunger stroke.

Transfer molding may be compared with compression molding:

<u>Advantage</u>	<u>Disadvantage</u>
1. Intricate sections (thin walls) can be used	1. More waste materials (in runners, sprues)
2. Shorter loading time	2. Degassing of parts is required (to eliminate voids)
3. Closer sections and tolerances	3. More expensive equipment and molds.
4. More pieces molded in one plunge	
5. Less wear on molds (from decreased pressures)	

For purposes of electronic encapsulation, epoxies and silicones (to a lesser extent for special purposes) find wide use. Although other plastic materials can be transfer molded, higher working pressures or other restrictions obviate their use with delicate components. These relatively unsatisfactory resins include phenolics, alkyds, diallyl phthalates, and ureas.

The development of plastic compounds which can be processed at low pressures makes possible the embedment of electronic packages by transfer molding; such resins are made to have very fast cure times (of the order of seconds to several minutes). Low pressure allows embedding of the delicate electronic assemblies with no damage to the components nor distortion of the assembly in the mold cavity during the transfer process. The most widely used materials (for up to 100" to 150°C service) generally are the epoxies; these are excellent because they can be made in the B-stage or partly cured state. In this condition, the compound is a solid, dry material which quickly becomes fluid or plastic under heat and low pressure.

Typical transfer-molding compounds contain powdered fillers; materials with fibers as fillers do not usually flow well. Despite a fairly high level of fragility, some work has been done with compounds filled with hollow microspheres. Transfer-molding resins are designed to flow at low pressures, but some force will be imposed upon the circuitry which must be strong enough to resist damage. In embedding a module, care must be taken to ensure a uniform, complete filling of the cavity with low resin turbulence.

Advantages of transfer molding as compared to casting include increased production rates and cleanliness of the work area. In most cases, transfer molding when used to embed modules gives a higher quality embedment than casting.

Multiple die cavities are used to produce large numbers of embedded items per cycle. The molds are of two- or three-piece steel which may be plated, e.g., with chromium, for wear resistance. Some molds can be evacuated prior to entry of the resin; most are just vented. For embedment of electronic modules and components, molds are light and small and thus readily put into or removed from the molding machine by one operator; these molds are generally equipped with insulated handles to prevent personal injury from burns. In electronic embedment operations there is a problem of mold inventory. This

has been overcome to an extent by special mold designs which have removable metal inserts to adjust the size and shape of the cavity to one of several sizes.

1-2.6 COATINGS (CONFORMAL AND SURFACE TYPES)

Conformal coating is a term used to include any dielectric application (of more or less constant thickness) that follows the contour of the circuit assembly. It can be applied by dipping, spraying, or even brushing. The agent is high in viscosity or thixotropic; coating thickness can range from 10 to 100 mil. Though the coating may impart some mechanical strength, its main function is electrical insulation and protection against contaminants from the surrounding atmosphere.

Surface coating is a term applied to a coating that is brushed, sprayed, or vapor-deposited onto a circuit.

1-3 CONSIDERATIONS FOR CHOICE OF PROCESSES, MOLDS, ETC.

A summary of the advantages, limitations, embedding agent requirements, and typical applications is shown in Table 1-2. The five primary embedding techniques are considered. These are casting, potting, impregnation, encapsulation, and transfer molding. Table 1-3 gives some remarks concerning the choice of either a casting or potting procedure as related to item or process characteristics such as skin thickness, surface appearance, repairability, item handling, assembly, manufacturing cycle efficiency, tool preparation, and maintenance.

Table 1-4 gives information on the selection of molds when the casting procedure is used. The advantages and disadvantages of mold material and its fabrication are noted. Table 1-5 gives information on the shell or housing container when the potting process is used^a.

TABLE 1-2. BASIC CONSIDERATIONS FOR THE VARIOUS EMBEDDING PROCESSES

METHOD	ADVANTAGES	LIMITATIONS	MATERIAL REQUIREMENTS	APPLICATIONS
<i>Casting</i> consists of pouring a catalyzed or hardenable liquid into a mold. The hardened cast part takes the shape of the mold, and the mold is removed for reuse.	Requires a minimum of equipment and facilities; is ideal for short runs.	For large volume runs, molds, mold handling, and maintenance can be expensive; assemblies must be positioned so they do not touch the mold during casting; patching of surface defects can be difficult.	Viscosity must be controlled so that the embedding material completely flows around all parts in the assembly at the processing temperature and pressure.	Most mechanical or electro-mechanical assemblies within certain size limitations can be cast.
<i>Potting</i> is similar to casting except that the catalyzed or hardenable liquid is poured into a shell or housing which remains as an integral part of the unit.	Excellent for large volume runs; tooling is minimal. Presence of a shell or housing assures no exposed components, as can occur in casting.	Some materials do not adhere to shell or housing; electrical short-circuiting to the housing can occur if the housing is metal.	Same material requirements as for casting except that materials which will bond to the shells or housings are required.	Most mechanical or electro-mechanical assemblies, subject to certain size limitations and housing complexity limitations.
<i>Impregnation</i> consists of completely immersing a part in a liquid so that the interstices are thoroughly soaked and wetted; usually accomplished by vacuum and/or pressure.	The most positive method for obtaining total embedding in deep or dense assembly sections such as transformer coils.	Requires vacuum or pressure equipment which can be costly. In curing, the impregnating material tends to run out of the assembly creating internal voids unless an encapsulating coating has first been applied to the outside of the assembly.	Low viscosity materials are required for the most efficient and most thorough impregnation.	Dense assemblies which must be thoroughly soaked; electric coils are primary examples.
<i>Encapsulation</i> consists of coating (usually by dipping) a part with a curable or hardenable coating; coatings are relatively thick compared with varnish coatings.	Requires a minimum of equipment and facilities.	Obtaining a uniform, drip-free coating is difficult; specialized equipment for applying encapsulating coatings by spray techniques overcomes this problem, however.	Must be both high viscosity and thixotropic; i.e., material must not run off the part during the cure.	Parts requiring a thick outer coating, such as transformers
<i>Transfer molding</i> is the process of transferring a catalyzed or hardenable material, under pressure, from a pot or container into the mold which contains the part to be embedded.	Economical for large volume operations.	Initial facility and mold costs are high. Requires care so that parts of assemblies are not exposed. Some pressure is required, and processing temperatures are often higher than for other embedding operations.	Should be moldable at the lowest possible pressure and temperature, and should cure in the shortest possible time for lowest processing cost.	For embedding small electronic assemblies in large volume operations.

**TABLE 1-3. CONSIDERATIONS IN SELECTION OF CASTING OR
POTTING PROCESSES**

<u>CHARACTERISTIC</u>	<u>CASTING</u>	<u>POTTING</u>
Skin Thickness	Difficult to control; components can become exposed in high component density packages.	Controlled minimum wall or skin thickness, due to thickness of shell or housing.
Surface Appearance	Cavities and surface blemishes often require reworking.	Established by surface appearance of shell or housing, though problems can arise if resin spillage not controlled.
Repairability	Resin exposed for easy access.	Shell or housing must be removed and replaced.
Handling	Handling and transfer of unhoused assembly can reduce yield.	Most handling of unembedded unit can be in housing.
Assembly	If molds are not well maintained, or if unit fits tightly into mold, handling can cause breakage of components.	Assembly is simplified since new shells or housings are always used, and wall thickness is controlled.
Manufacturing Cycle Efficiency	Production rate usually limited by quantity of molds.	Output not limited by tools.
Tool Preparation and Maintenance	Relatively expensive	Costs are minimal.

TABLE 1-4. CONSIDERATIONS FOR SELECTION OF MOLDS FOR CASTING PROCESS

<u>MOLD MATERIAL AND FABRICATION</u>	<u>ADVANTAGES</u>	<u>DISADVANTAGES</u>
Machined Steel	Good dimensional control; can be made for complex shapes and insert patterns. Good heat transfer; surfaces can be polished.	Assembly sometimes difficult. Can corrode. Usually requires mold release.
Machined Aluminum	Same as machined steel except more easily machined.	Same as machined steel, except for corrosion. Easily damaged, because of softness of metal.
Cast Aluminum	None over machined aluminum, except lower mold costs for high volume operations.	Same as machined aluminum. Surface finish and tolerances usually not as good as for machined aluminum. Complex molds not as accurate as for machined metal.
Sprayed Metal*	None over machined metal. Good surface possible.	Use usually limited to simple forms. Not always easy to control mold quality. Number of quality parts per mold limited. Requires mold release.
Dip Molded* (slush casting)	Same as sprayed-metal molds.	Same as sprayed-metal molds.
Cast Epoxy	Good dimensional control; surface can be polished. Can be made for inserts and multiple part molds. Long life and low maintenance.	Dimensional control not quite as good as in machined metal molds. Requires mold release and cleaning. Low thermal conductivity compared with that of metals.
Cast Plastisols	Parts easily removed from molds. Molds are easy to make.	Short useful life. Poor dimensional control.
Cast RTV Silicone Rubber	Same as for plastisols. Better life than plastisols.	Poor dimensional control, though better than plastisols.
Machined TFE Fluorocarbon	No mold release required. Convenient to make for short runs and simple shapes. Withstands high-temperature cures.	Poor dimensional control.
Machined polyethylene and polypropylene	Same as listed for TFE fluorocarbon except temperature capability and lower cost.	Poor dimensional control.
Molded polyethylene and polypropylene	Same as listed for TFE fluorocarbon except temperature capability and lower cost.	Poor dimensional control.

*Although sprayed metal molds and dip-molded molds are similar, differences in methods of making these two types may give one an advantage over the other in specific instances.

**TABLE 1-5. CONSIDERATIONS FOR SELECTION OF SHELL OR HOUSING
FOR POTTING PROCESS**

HOUSING OR CONTAINER	ADVANTAGES	DISADVANTAGES
Steel	Many standard sizes available. Easily plated for solderability. Good thermal conductivity. Easily cleaned by vapor degreasing. Good adhesive bond formed with most resins. Easily painted. Flame-resistant.	Can corrode in salt spray and humidity. Fitting of lids sometimes a problem. Cutoff of resin-filled can is sometimes difficult. Possibility of electric short-circuiting.
Aluminum	Same as for steel except plating ease. Lightweight and corrosion resistant.	Same as for steel except aluminum is more corrosion-resistant. Not easily soldered.
Molded thermosets (epoxy, alkyd, phenolic, diallyl phthalate, etc.)	Many standard sizes available. Good insulator. Corrosion-resistant. Color or identification can be molded in. Terminals can sometimes be molded in. Cutoff of resin-filled shell easier than for metal cans. Same type of material can be used for shell and filling resin, resulting in good compatibility.	Does not always adhere to resin, especially if silicone mold releases used to make shell. Sealing of leakage joints can be difficult. Physically weaker than steel, especially in thin sections. Molding flash can cause fitting problems. Cleaning of resin spillage can break shells.
Molded thermoplastics (nylon, polyethylene, polystyrene etc.)	Same as listed for thermosets except last two items. Often less prone to cracking than thermosetting shells although this depends on resiliency of material.	Same as first three items listed in thermosets. Adhesion can be poor, owing to excellent release characteristics of most thermoplastics. Shell can distort from heat. Cutoff can be a problem due to melting or softening of thermoplastics under mechanically generated heat.

REFERENCES

1. C. Volk, J. Lefforge, and R. Stetson, *Electrical Encapsulation*, Van Reinhold Publishing Co., New York, NY, 1962.
2. C.A. Harper, *Electronic Packaging with Resins, A Practical Guide for Materials and Manufacturing Techniques*, McGraw-Hill Book Co., New York, NY, 1961.
3. C.A. Harper, *Plastics for Electronics*, Kiver Publications, New York, NY, 1964.
4. C.H. Burley, J. L. Easterday, and D.A. Kaiser, *Industrial Survey of Electronic Packaging*. (N67-19037; RSIC-614, AD 647 137) Battelle Memorial Institute, Columbus, OH, 1966.
5. C.A. Harper, "Embedding Resin Effects on Components and Circuits," *Electronic Packaging and Production* **5**, 71-8 (May 1965).
6. J.J. Licari, *Plastic Coatings for Electronics*, McGraw-Hill Book Co., New York, NY, 1970.
7. J.J. Licari and G.V. Browning, "Plastics for Packaging: Handle with Care", *Electronics* (17 April 1967).
8. E.W. Vaill, "Transfer Molding", *Modern Plastics Encyclopedia* **44**, McGraw-Hill Book Co. (1966).
9. C.A. Harper, "Embedding Processes and Materials", *Machine Design*, **38**, 150-173 (9 June 1966).

CHAPTER 2

GENERAL INFORMATION ON EMBEDDING RESINS, AND PROCEDURES FOR USE

General information on the most widely used classes of polymers—epoxy resins, urethanes, anti silicones—and polyxylylenes are presented together with their advantages/disadvantages. General procedures for potting, encapsulation, and casting are discussed. Applications of the various polymers to specific components of electrical/electronic equipment are outlined.

2-1 AGENTS USED FOR PRIMARY EMBEDMENT OF ELECTRONIC CIRCUITS

The upper-operating temperature limit of semiconductors and other active electronic components is about 85° C; thus, the service capabilities of commonly used organic resins are adequate for use at this temperature.

For most practical reliable cost-performance purposes, the greater portion of embedding of electronic modules is done with one of three classes of polymers—epoxy resins, urethanes, or silicones. (The epoxies are used most frequently.) Where performance requirements of the electronic system can be somewhat lowered, other resins which can be used (but which have been rapidly falling out of favor) include the polyesters, thermosetting hydrocarbon resins, thermosetting acrylic resins, and polysulfide polymers¹.

Another family of polymers, the polyxylylenes, are finding special use as thin hole-free dielectric coatings which are vapor-deposited on the substrate assembly². These are called Parylenes, a Union Carbide development. These find use as coatings for circuit boards, hybrid circuits, and ferrites, among other components. The thinness of the deposition gives protection without change in dimensions, shape, or magnetic properties. The Parylenes are discussed further in Chapter 6.

2-1.1 ADVANTAGES AND DISADVANTAGES OF EPOXY, URETHANE, AND SILICONE EMBEDDING AGENTS

Those epoxies, urethanes, and silicones used for module embedding have certain characteristics which are important for successful application. These polymers (with the exception of polyurethane foams) are addition-curing rather than condensation-curing—i.e., while curing they do not give off water or an electrolyte (e.g., acid) that might harm the electronic components^{3,4}. In addition, these polymers do not contain volatile solvents; they are “100% solids”. Solvent containing materials shrink greatly during curing. The solvents also can cause swelling or dissolve organic materials in the module system. The epoxies, urethanes, or silicones can be prepared as either uniform solids, or open or closed cell foams. Since they are thermosetting, or infusible when cured, they may soften slightly with the application of heat; however, they degrade by charring before they will melt.

Table 2-1 shows the pros and cons pertinent to the use of the three kinds of polymers in casting, encapsulation, and potting processes.

2-1.2 POTTING AND ENCAPSULATION WITH TWO-PART RESINS

This procedure can be used with most two-part resin systems such as epoxies, urethanes, and silicones.

TABLE 2-1. COMPARATIVE ADVANTAGES/DISADVANTAGES OF CASTING, ENCAPSULATION, AND POTTING AGENTS

MATERIAL	ADVANTAGES	DISADVANTAGES
Epoxy	Wide range of agents available	Toxicity (dermatitis)
	Low shrinkage	<i>Per se</i> , poor physicals/mechanicals (i.e., brittleness; low temperature reduction in impact strength)
	Excellent adhesion	
	Good resistance to environments, chemicals	
Silicones	Low exotherm	High cost
	Wide temperature use (−100° to +500°F)	Poor adhesion to many substrates
	Flexibility	Poor mechanical properties
Urethanes	Abrasion resistance	Toxicity (cyanate—systemic poison)
	Toughness; high impact strength	Limited temperature range (200°F max)
	Flexibility	Some resins sensitive to heat/moisture (i.e., reversion)

Molds are cleaned after each use before reapplying mold release agent. The tool for cleaning a mold is softer than the mold surface. Molds are solvent washed with each cycle to prevent unwanted buildup of release agents. The most efficient release agents are approximately 2% solvent solutions of fluorocarbons or silicones; these are spread or sprayed on the warm mold with the carrier solvent evaporating to leave a thin release film. The use of clean, fresh release agent solution is recommended.

To prevent improper bonding or inhibition of resin cure, the electronic component must be clean. Where possible, this is done by vapor degreasing (with a chlorinated solvent such as trichloroethylene or perchloroethylene). Components liable to injury by these solvents may be treated with toluene, xylene, or aliphatic or alcoholic-type solvents. The component is rinsed with clean solvent and air-dried⁵.

The cleaned parts are positioned in the mold cavity and kept from contact with the mold release agent. The mold must be assembled correctly; all retaining screws must be tight; and mold faces must be aligned. As assembled, the mold and part are heated (to the tolerance of the electronic component). These procedures drive off moisture and residual cleaning solvent which insure maximum retention of electrical properties and full resin cure. At increased temperatures, the embedment resins are more fluid and flow into the mold easily. This tends to eliminate voids and fosters better impregnation. Processing under such conditions is easier; the mold and part are at a somewhat higher temperature than the introduced resin.

The resin and activator are used as follows. All ingredients (less hardener) are added to a clean nonreactive container. This is hand-mixed with kneading for 2-3 min, followed with a 2-min mix

with a power stirrer. The hardener is added and followed by a power mix for 2-3 min. Degas, at once, at 2 mm of Hg maximum (for at least 3 min). Improper weighing or mixing of the resin components will probably degrade the physical, chemical, and electrical properties of the product; and failure in function may occur rapidly.

2-1.3 TYPICAL CASTING PROCEDURE FOR EPOXIES, URETHANES, AND SILICONES

Resin typically is introduced into the heated mold (with its contents) by pouring from the mixing container. In certain production systems, air-pressure power guns are used. The filled mold is placed in a heated vacuum chamber; pressure is reduced and held for about 5 min; and pressure is returned to atmospheric gradually. The part is removed from the vacuum chamber and placed in an oven set at the proper initial cure temperature. Without proper oven processing, the following problems may appear^{6,7}:

- 1. With too high an initial temperature—occurrence of high stresses and cracking
- 2. With too short a precure time—occurrence of deformation, reduced physical, mechanical and chemical properties
- 3. With too short a postcure time—occurrence of dimensional stability defects and degraded chemical or electrical properties.

Where the viscosity of the resin exceeds 50,000 centipoise (cP), potting under vacuum is required. Mixing, degassing, and pouring are done under reduced pressure. For practical purposes, all of the air and interfering gases are removed by this method.

For resins with a viscosity of about 10,000 to 40,000 cP, complete handling under vacuum is not required. A degasser fixture can be used with a power mixer; the stirred resin is prepared under vacuum. The material is poured into the mold under normal pressure; the mold must be open-faced to allow release of air at the top part of the mold.

For resins with viscosities lower than 10,000 cP, a standard medium-vacuum chamber can be used to degas the resin prior to pouring. Open-faced molds are not entirely necessary. With the mold at a slightly higher temperature than the resin, removal of gases is faster.

The basic difference in design of molds for embedment is that the pressure requirements are much less than that required for plastic molding (i.e., perhaps a few 1000 psi). The embedment process requires a pressure range of 1 atmosphere to perhaps less than 500 psi. Thin metal or flexible rubbery plastic molds can be used.

The pros and cons of several widely used mold materials are given in Table 2-2.

2-2 USE OF AGENTS IN COATING PROCESSES

The epoxies, polyurethanes, and silicones can be used in coating form to provide protection and insulation for electronic components*. These materials find use with circuit boards, transformers, motors, connectors, modules, resistors, diodes, etc. Circuit boards and items such as welded electronic modules are coated as the last step in fabrication. Without such protection, these products would fail from moisture effects—i.e., decrease in electrical insulation, electric shorting, and corrosion. A conformal coating imparts rigidity of leads, solder joints, and components to prevent breakage or separations. Use of conformal coatings allows the use of narrow conductive paths and closer spacing of components.

Resin choice depends upon operating conditions, storage requirements, cost considerations, and repairability needs. Generally, these are guidelines:

<u>For</u>	<u>Resin(s) Suggested</u>
High temperature application	Epoxies, silicones
Resolder capability	Polyurethanes

*the polyxylenes will be discussed in Chapter 6.

TABLE 2-2. CHARACTERISTICS OF MOLD MATERIALS

<u>MATERIALS</u>	<u>ADVANTAGES</u>	<u>DISADVANTAGES</u>
Steel	Retains dimensions. Lasts a long time. Takes abuse.	High machining cost. Can corrode. Mold release needed.
Aluminum or Brass	Fast heat dissipation. Less costly to machine.	Damaged readily. Mold release needed.
Cast Plastic (silicones, vinyl plastisols, teflon)	Low cost. Mold release not needed.	Poor dimensional control. Limited use life—subject to deterioration.
Injected Plastic (polyethylene, polypropylene)	Mold release not needed. Low cost after first cost for injection molding equipments.	Limited temperature use to 200°F or less. Lack of dimensional control.

<u>For</u>	<u>Resin(s) Suggested</u>	
Repair capability	Polyurethanes, silicones	result from shrinkage and differential thermal expansion. Especially with very costly printed circuit board assemblies that must function with long-term reliability, defective components or soldering must be replaced or repaired. In such instances, ease of removal of the dielectric resin is required. Polyurethanes and silicones are comparatively simple to remove and have found wide use in conformal coatings. The elastomeric silicones are readily removed by cutting but they are soft and show poor adhesion. Polyurethanes present more difficulty; they are removed by treating with solvents, chemical strippers, or by use of a hot soldering iron. Replacement of the cut-out or burn-out generally is performed by using the original unreacted resin for filling.
Application ease	Epoxies	
Adhesive strength	Epoxies, polyurethanes	
Moisture resistance	Epoxies, polyurethanes.	
Coating thickness can be from 0.5 to 20 mils. Some conformal coatings may be as thick as 50 or more mils. A typical use thickness might be in the order of 1 to 5 mils. Very thick coatings (e.g., with rigid coatings) can lead to cracking of components (i.e., glass diodes and resistors). Stresses		

REFERENCES

1. A. E. Molzon, *Encapsulation of Electronic Parts in Plastic—A Review*, (AD 648 420) Plastics Technical Evaluation Center, Picatinny Arsenal, Dover, NJ, 1967.
2. Parylene, *Union Carbide Product Data Bulletin*, F-43427A, Union Carbide Corporation, New York, NY, July 1974.
3. C. V. Lundberg, "Correlation of Shrinkage Pressures Developed in Epoxy, Polyurethane, and Silicone Casting Resins With Inductance Measurements on Embedded Electronic Components", paper presented at the 152nd National Meeting, Am. Chem. Soc. (New York), 11-16 September 1966, Industrial and Engineering Chemistry, Product Research and Development **6**, 92-100 (June 1967).
4. R. E. Keith, *Potting Electronic Modules*, NASA

REFERENCES (cont'd)

- SP-5077, Battelle Memorial Institute, Columbus, OH, 1965.
5. H. F. Heuring, "Cleaning Electronic Components and Subassemblies", *Electronic Packaging and Production* (June 1967).
 6. F. F. Stucki, W. D. Fuller, and R. D. Carpenter, "Internal Stress Measurement of Encapsulated Electronic Modules", *Electronic Packaging and Production* 7, 39-46 (February 1967)
 7. M. H. Smith, "Measurement of Embedment Stresses in Electronic Modules" (NAS7-101) National Electronic Packaging and Production Conference, New York, NY, 21-23, June 1966, *Proceedings of the Technical Program, Industrial and Scientific Conference Management, Inc.*, pp. 427-438, Chicago, IL, 1966.

CHAPTER 3

EPOXY EMBEDDING RESINS

The chemical, physical, and electrical Properties of the basic types of epoxies are given together with the alteration of these properties by curing agent and the addition of fillers.

3-1 GENERAL CHARACTERISTICS OF EPOXIES

Epoxies are the most important resins for electronic embedding. Reasons for this include ease of handling, broad use range in the majority of extreme environments, low shrinkage on cure, and good bonding to many materials. A very large overwhelming number of epoxies and their variants exist; variants in processing and end-product properties are marketed; and cured epoxies are extant in rigid and flexible forms. Flame retardant properties are now available.^{1,2}

Epoxy resins have an important function in the encapsulation of relatively complex, fragile components (such as synchro-motors or synchro-transformers). Such assemblies require a compound to seal, bond, and locate the coils, printed circuit board, and magnetic core components. A rigid (generally highly filled) epoxy retains the positioning and dimensional stability of the assembly. Protection from environmental effects, contaminants, etc., is established.

A potentially great source of unreliability in motors is the stator windings. Tape winding and/or varnish impregnation of the coil wires have been a common practice; this method is being replaced by the use of rigid epoxy encapsulants. The results are that such stators are cleaner, show more dimensional stability, and have enhanced insulation properties and more mechanical or environmental protection.

Common basic types of epoxies include the bisphenolics, the epoxy novolacs, and the cycloaliphatic diepoxides. Principal curing agents include the amine types, acid anhydrides, piperidine, and boron trifluoride ethylamine.

Flexibilizers have been developed to reduce the inherent cured hardness and uncured liquid viscosity of epoxy systems. Viscosity lowering allows easier working with the resins; hardness decrease makes the cured epoxy more resistant to thermal and impact shock, allows dampening, etc. Agents which may be used include polyamides, polysulfides, polycarboxylic acids, and polyurethanes. Viscosity diluents may be either reactive or unreactive. Additionally, fillers can be used as modifiers.

Epoxies are stable up to 300°F (reasonably long term); some anhydride- and aromatic amine-cured types can be used to 400°F (limited time). Beyond this, decomposition (with significant changes in electrical properties) occurs. The stability of epoxies is higher than that of polyurethanes (275°F) and lower than that of silicones (500° to 600°F).

3-1.1 ELECTRICAL PROPERTIES OF EPOXIES

The electrical properties of epoxies are good; they have been found suitable under conditions requiring high performance (e.g., to 300°F with relative humidities of 95 to 100%). Volume resistivities are temperature dependent and are of the order of 10^{12} to 10^{15} ohm•cm (25") (see Table 3-1). The low value of 10^8 ohm•cm still allows the epoxy to be suitable for many applications.

Dielectric constants and dissipation factors are low for epoxies. These range respectively from 3 to 6 and 0.003 to 0.03 (25°C at 60 to 10^3 Hz). With higher frequencies, dielectric constants drop somewhat (e.g., from 3.0 at 10^3 Hz to 2.7 at 10^6 Hz).

**TABLE 3-1. VOLUME RESISTIVITY VERSUS TEMPERATURE
FOR AN AMINE*-CURED BISPHENOL-A EPOXY**

Temperature, °C	Volume Resistivity, ohm•cm
23	2.05×10^{14}
66	1.97×10^{13}
93	9.3×10^{10}
121	2.43×10^9
149	3.68×10^8

*Diethanolamine used as hardener

Dielectric strength values are high. Ranges are 300 to 450 V/mil for 125-mil thick samples; values as high as 1500 V may be found with 1-mil thick specimens. Arc resistances of unfilled resins may range from 80 to 100 s. With the incorporation of fillers, arc resistances of 125 to 225 s can be attained (e.g., as a function of the filler and hardener). Fillers which have found to give higher values include silica, mica, zirconium silicate, and hydrated alumina. The use of 45 to 60% (by weight) of hydrous magnesium silicate is shown to improve antitracking in epoxies. Surface roughening or partial exposure of filler particles at the resin surface yields improvements in arc resistance³.

3-1.2 RESIN VISCOSITY; EXOTHERM DURING CURE

Two properties of importance are resin viscosity and the exotherm shown during cure. Basic resin viscosity, which may be too thick for embedding, is decreased by heating (Fig. 3-1); the reaction-heat of an epoxy system is partly a function of the curing agent, the cure temperature, and the bulk mass of the resin. Mass should be kept small when using certain epoxy systems which give heat on curing.

Viscosity must be low enough to allow adequate penetration and filling-in of the assembly to be embedded; temperature from reaction-to-cure should generally be kept below 150°F.

3-2 BASIC TYPES OF EPOXIES

The most common basic epoxy resin, derived from the reaction of bisphenol A with epichlorohydrin, is called the diglycidyl ether of

bisphenol A (DGEBA or *epi-bis* types). Some American trademarks for this agent include DER-332 (Dow), Epon 828 (Shell), and BK 2774 (Union Carbide "Bakelite"). The general structure of the epoxy oligomer is shown in Fig. 3-2. Such *epi-bis* epoxies are liquid at room temperature; others show increases in viscosity; and some are solids which melt at approximately 150°C. The higher the melting point of the epoxy, the less curing generally is needed. Cured properties of these resins are similar; however, toughness does increase as the melting point of the unreacted epoxy is increased. Most of these *epi-bis* resins are light yellow; transparent and colorless epoxies are available for use in optical devices.

Table 3-2 gives information on bisphenol A type epoxies from various companies.

The *cycloaliphatic epoxies* contain a saturated ring in their structure. They do not contain chlorine which may be present in some *epi-bis* epoxies (such chlorine, on hydrolysis, can degrade electrical devices). Cycloaliphatics have excellent arc-track resistance, good electrical properties under harsh environments, good weathering resistance, high heat-deflection temperatures, and good retention of color with exposure or aging. Some of the cycloaliphatics show low viscosity^{4,5,6}.

The anhydrides are typically used as curing agents for the cycloaliphatics; however, some are reactive with amines. Table 3-3 shows how blending of cycloaliphatics (flexible with a rigid resin) gives a range of properties.

Novolac epoxies are made from the reaction of phenolic or cresol novolacs with epichlorohydrin.

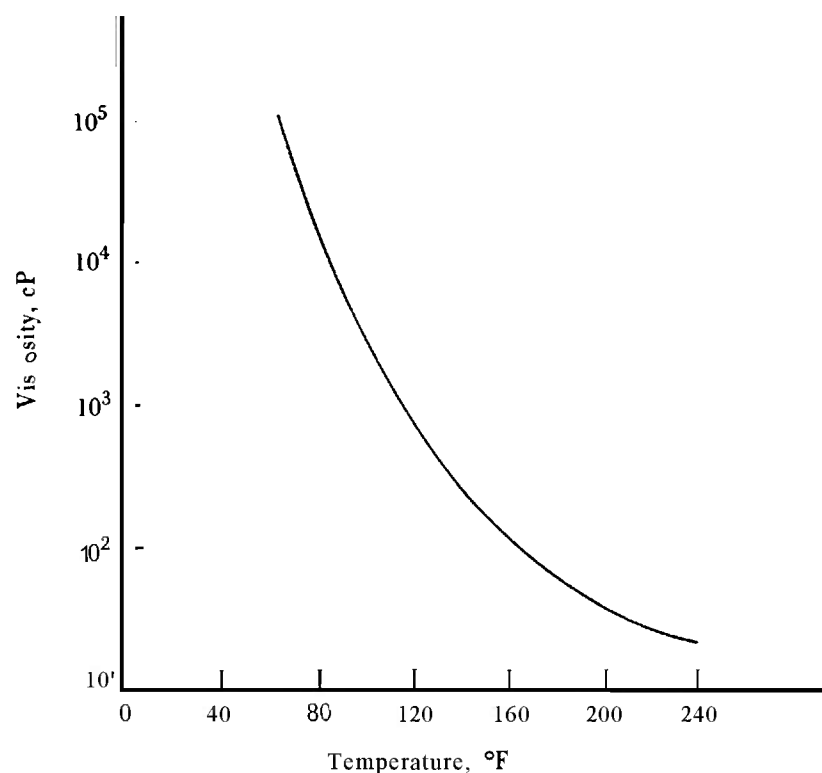


Figure 3-1. Viscosity-Temperature Curve for a Standard Bisphenol Epoxy Resin

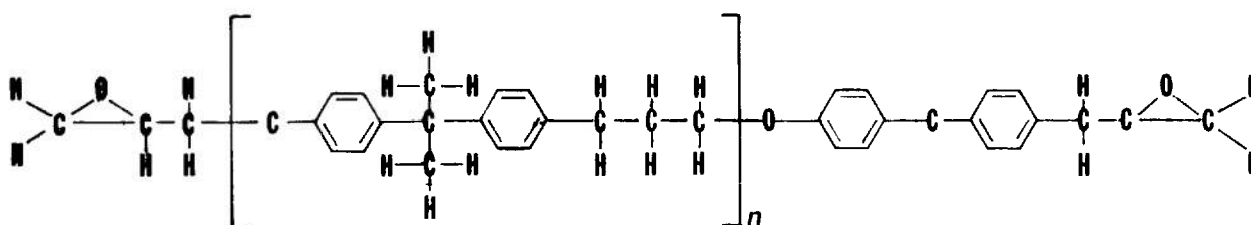


Figure 3-2. General Structure of the Epoxy Oligomer

TABLE 3-2. EQUIVALENT BISPHENOL-A TYPE EPOXIES

Ave. Molecular Weight	Viscosity at 25°C, cP	Epoxy Equiv.	Shell Epon	Dow DER	Ciba-Geigy Araldite	General Mills Gen Epoxy	Union Carbide Bakelite ERL
340-350	4000-5500 (liq.)	173-179	—	332	—	175	—
	6500-10000	178-193	826	X2633.11	6005	177	—
350-400	10000-16000	185-200	828	331	6010	190	ERL-2774
340-400	500-700	179-194	815	334	506	M180	ERL-2795
	5000-15000	175-210	820	—	6005	—	—
	>90000	225-290	834	—	6010	—	—

TABLE 3-3. CAST-RESIN DATA ON BLENDS OF CYCLOALIPHATIC EPOXY RESINS

Resin ERL-4221, * parts	100	75	50	25	0
Resin ERR-4090, * parts	0	25	50	75	100
Hardener, hexahydrophthalic (HHPA), phr†	100	83	65	50	34
Catalyst (BDMA), phr†	1	1	1	1	1
Cure, h/°C	2/120	2/120	2/120	2/120	2/120
Postcure, h/°C	4/160	4/160	4/160	4/160	4/160
Pot Life, h/°C	> 8/25	> 8/25	> 8/25	> 8/25	> 8/25
HDT (ASTM D 648), °C	190	155	100	30	-25
Flexural Strength (D 790), lb/in ²	14,000	17,000	13,500	5,000	Too Soft
Compressive Strength (D 695), lb/in ²	20,000	23,000	20,900	Too soft	Too soft
Compressive Yield (D 695), lb/in ²	18,800	17,000	12,300	Too soft	Too soft
Tensile Strength (D 638), lb/in ²	8,000-10,000	10,500	8,000	4,000	500
Tensile Elongation (D 638), %	2	6	27	70	115
Dielectric Constant (D 150), 60 Hz:					
25°C	2.8	2.7	2.9	3.7	5.6
50°C	3.0	3.1	3.4	4.5	6.0
100°C	2.7	2.8	3.2	4.9	Too high
150°C	2.4	2.6	3.3	4.6	Too high
Dissipation Factor, dimensionless:					
25°C	0.008	0.009	0.010	0.020	0.090
100°C	0.007	0.008	0.030	0.30	Too high
150°C	0.003	0.010	0.080	0.80	
Volume Resistivity (D 257), ohm-cm	1×10^{13}	1×10^{12}	1×10^{11}	1×10^8	1×10^6
Arc resistance (D 495), s	> 150‡	> 150	> 150	> 150	> 150

*Union Carbide Corp.

†Parts per 100 resin.

‡Systems started to burn at 120 s. All tests stopped at 150 s.

These resins show high-viscosity or are semisolids. They can be blended with other epoxies to improve handling characteristics. The novolac epoxies cure faster than epi-bis epoxies and show higher exotherms. The cured resins have higher heat deflection temperatures than the epi-bis resins. This is shown in Table 3-4.

Table 3-5 compares the uncured properties of an epoxy novolac and epi-bis epoxy.

Table 3-6 compares the electrical properties of a cured novolac epoxy versus an epi-bis resin.

Table 3-7 compares the chemical resistances of the novolac versus the epi-bis epoxies.

Table 3-8 shows additional epoxy novolac and other types of epoxy resins.

3-3 CURING AGENTS FOR EPOXY RESINS

On adding proper curing agents, epoxy resins are polymerized to hardened cross-linked three-

dimensional solids. This occurs by an addition or catalytic reaction⁷. In the addition reaction, the curing agent (called a hardener) combines with the epoxy polymer molecule and acts as a cross-linking agent for binding epoxy molecules; this type of reaction is called heteropolymerization. With catalytic reactions, the self-polymerization of the epoxy is enhanced; this is called homopolymerization.

Many types of hardeners and catalysts are commercially available; additionally, many variants of epoxy resins can be found¹. The hardener delineates the cure schedule—time and temperature for maximum thermoset properties—and whether the system can be cured at room temperature or requires the use of elevated temperature.

3-3.1 AMINE CURING AGENTS

Amines find use as curing agents for epoxies. These include aliphatic, aromatic, amine adduct,

TABLE 3-4. HEAT-DISTORTION TEMPERATURES* OF BLENDS OF NOVOLAC EPOXY AND EPI-BIS RESINS

Hardener	D.E.N. 438†	75/25	50/50	25/75	D.E.R. 332‡
TETA	§	§	133	126	127
MPDA	202	192	180	—	165
MDA	205	193	190	186	168
5% BF ₃ MEA	235	—	—	204	160
HET	225	213	205	203	196

*Heat-distortion temperature, °C (stoichiometric amount of curing agent—except BF₃MEA—cured 15 h at 180°C).

†Novolac resin, Dow Chemical Co.

‡Epi-bis resin, Dow Chemical Co.

§The mixture reacts too quickly to permit proper mixing by hand.

TETA = triethylenetetramine

MPDA = m-phenylene diamine

MDA = methylenedianiline

BF₃MEA = boron trifluoride monoethanolamine

HET = chlorendic anhydride

TABLE 3-5. COMPARISON OF UNCURED RESIN PROPERTIES FOR AN EPOXY NOVOLAC AND A BISPHENOL-A EPOXY

Property	D.E.N. 438 (novolac)	D.E.R. 331 (bisphenol)*
Color, (Gardner-Holdt, 1953)	5	5
Epoxide Equivalent Weight (Dow Method AS-EPK-A)	175-182	187-193
Viscosity (77°F, 25°C, Dow Method AS-EPR-B), cP	Semisolid	11,000-16,000
Viscosity (125°F, 52°C, Brookfield Model LVT, no. 4 spindle at 6 rpm), cP	30,000-90,000	—
Viscosity of elevated temperatures (conversion from Gardner-Holdt tubes), cP:		
50°C	45,000	—
60°C	11,000	—
75°C	2,600	—
90°C	900	—
Molecular Weight	600	375
Epoxy Functionality	3.3	1.90†

*D.E.R. is the trademark of The Dow Chemical Co. for epoxy resins.

†Based on experimental method giving a lower molecular weight than the true value.

alicyclic, tertiary, and latent curing amines. The characteristics of such hardeners are shown in Table 3-9.

Amines are used very widely for curing epoxy resins; rapid cures at room temperature in 1 or 2 h are possible. With slight increase in temperature (100° to 120°F), cures on the order of approximately 5 min are possible.

Polyamines are used in concentrations of 4 to 20 parts per hundred (phr) resin. The resultant

cured epoxies show excellent chemical and solvent resistance, electrical properties, and both thermal and vacuum stability. When the epoxy system is postcured at somewhat elevated temperatures, such mentioned characteristics are improved.

The primary, secondary, or tertiary amines can cause skin irritations, have an offensive odor, and are corrosive in air. For such reasons they are offered as modified materials under

TABLE 3-6. COMPARISON OF ELECTRICAL PROPERTIES FOR A CURED EPOXY NOVOLAC AND A BISPHENOL-A EPOXY*

Property	D.E.N. 438		D.E.R. 331	
	Original Sample	After 24 h in H ₂ O	Original Sample	After 24 h in H ₂ O
Dielectric constant †, dimensionless:				
60 Hz	3.78	3.82	4.12	4.19
103 Hz	3.74	3.80	4.07	4.15
10 ⁶ Hz	3.39	3.44	3.55	3.61
Dissipation factor ‡, dimensionless:				
60 Hz	0.0027	0.0021	0.0035	0.0043
103 Hz	0.012	0.012	0.015	0.016
10 ⁶ Hz	0.024	0.025	0.032	0.032
Volume resistivity §, ohm-cm	0.380 × 10 ¹⁶	0.183 × 10 ¹⁵	0.181 × 10 ¹⁶	0.231 × 10 ¹⁵

*D.E.N. is novolac; D.E.R. is bisphenol. D.E.R. 331 cured with MDA for 16 h at 25°C † 4.5 h at 166°C; D.E.N. 438 cured for 1 h at 93°C † 16 h at 177°C.

†ASTM D 150-54T before and after 24-h water soak.

‡ASTM D 669-42T before and after 24-h water soak.

§ASTM D 257-57T (1 min electrification at 500 V direct current, results in ohm-centimeters).

TABLE 3-7. COMPARISON OF CHEMICAL RESISTANCE FOR A CURED EPOXY NOVOLAC AND A BISPHENOL-A EPOXY*

Chemical	Weight Gain, † %	
	D.E.N. 438	D.E.R. 331
Acetone	1.9	12.4
Ethyl alcohol	1.0	1.5
Ethylene dichloride	2.6	6.5
Distilled water	1.6	1.5
Glacial acetic acid	0.3	1.0
30% sulfuric acid	1.9	2.1
3% sulfuric acid	1.6	1.2
10% sodium hydroxide	1.4	1.2
1% sodium hydroxide	1.6	1.3
10% ammonium hydroxide	1.1	1.3

*One-year immersion at 25°C; cured with methylene dianiline; gelled 15 h at 25°C, postcured 4.5 h at 166°C; D.E.N. 438 cured additional 3.5 h at 204°C.

†Sample size 0.5 × 0.5 × 1 in.

TABLE 3-8. OTHER EPOXY TYPES AND PROPERTIES

Trade Name	Chemical Type	Epoxy Equiv.	Specific Gravity	Viscosity at 20°-25°C, cP
Dow DEN 438	Epoxy Novolac	175-182	...	Semisolid
Ciba Araldite DP-419	Epoxy Novolac	182	...	4500
Ciba Araldite DP-412	Epoxy Novolac	208	...	11000
Union Carbide ERL-2255	Peracetic acid-bisphenol blend	160	1.16	2000
Union Carbide ERL-2256	Peracetic acid-bisphenol blend	140	1.16	700
Dow X-2673.6	Aliphatic diglycidyl ether	195	1.15	50
Dow X-2673.2	Aliphatic diglycidyl ether	330	1.06	60
Ciba Araldite DP-437	Aliphatic diglycidyl ether	385	1.13	3500
Union Carbide UNOX Epoxide 206	Vinylcyclohexene dioxide	74-76	1.1	8
Union Carbide ERL-4221	3,4 epoxyl cyclohexymethyl 3,4 epoxyl cyclohexane carboxylate	126-140	1.16-1.17	350-450

numerous tradenames. They may be supplied as eutectics, adducts with low molecular weight epoxies, or complexes with boron trifluoride. Such variants show reduced vapor pressures; action as a skin irritant also may be reduced. Another advantage of the modified amines is that the pot life of a formulation can be controlled and extended.

Information on specific types of amine curing agents, their designation, and typical sources or suppliers is shown in Table 3-10.

Other amine curing agents that can find use as epoxy hardeners include tetraethylene pentamine (TEPA); iminobispropyl amine; xylylene diamine; menthane diamine; benzyl dimethylamine; dicyandiamide; iminobispropyl amine; α -methylbenzylamine; 2(dimethylaminomethyl)-phenol; and 2,4,6-tris (dimethylaminomethyl)-phenol. Table 3-11 shows properties of castings hardened with typical aliphatic polyamines, polyamides, and derivatives.

3-3.2 CATALYTIC AGENTS

Certain Lewis acid and base compounds initiate epoxy curing to give high molecular weight polyethers.

Typical Lewis base catalysts—which can donate an electron pair in reactions—are triethylamine; uenzyldimethylamine; cy-methylbenzylamine; z-(dimethylaminomethyl)-

phenol*; and 2,4,6-tris (dimethylaminomethyl)-phenol**. Lewis acid catalysts—which can accept an electron pair in reactions—are boron trifluoride, boron trichloride, aluminum chloride, zinc chloride, ferric chloride, and stannic chloride.

Tertiary amines generally need moderately elevated temperatures to cure low molecular weight glycidyl ether resins; room temperature cures are feasible with high molecular weight epoxies having large quantities of hydroxyl groups.

Tertiary amine catalysts are used in amounts of 5 to 15 phr; Lewis acids or acid-amine complexes are used at 2 to 4 phr. Both the amine bases or acids can be difficult in handling; they are highly reactive and show very short pot lives. They may be corrosive or irritating gases; and liquids can be noxious, toxic, or skin irritants.

Boron trifluoride (BF_3) is very highly reactive in the catalytic cure of epoxies; it is impractical to handle for controlled reactions. Such a reactive agent is supplied as latent catalysts or modified to reduce vapor pressures, toxicity, and to extend pot lives. Such complexes include:

1. Boron trifluoride—monoethylamine complex (BF_3 -400)

*. ** Respectively DMP-10 and DMP-30; supplied by Rohm & Haas Co.

TABLE 3-9. CHARACTERISTICS OF AMINE CURING AGENTS FOR EPOXY RESINS

1. Aliphatic Amines:
 - a. Used to cure epoxy resins at room temperature
 - b. High exothermic reaction of the curing agent with the epoxy
 - c. Cure rapidly with rapid mold cycles
 - d. Toxic, e.g., dermatitis
 - e. Short 15-30 min pot life
 - f. Moderately low heat distortion, 150° to 200°F
 - g. Good wettability and adhesion
 - h. Careful mixing/weighing required
 - i. Some noxious odor
 - j. Liquid in form.
2. Aromatic Amines:
 - a. Used to cure at elevated temperature
 - b. Some solid forms
 - c. 4-6 h pot life
 - d. Heat distortion 250° to 320°F
 - e. Electrical properties better than with aliphatic hardeners
 - f. Brittle, may crack.
3. Amine Adducts— from reaction of aliphatic amine with nonstoichiometric fraction of butyl or phenyl glycidyl ether:
 - a. Similar to aliphatic amines in characteristics
 - b. Adducts give convenient increase in ratio of hardener/epoxy
 - c. Cure time lengthened.
4. Alicyclic Amines:
 - a. Used for heat cures with epoxies
 - b. Long pot life—8 h
 - c. Used with fillers/modifiers for potting, etc.
 - d. Toxic
 - e. Skin irritant
5. Tertiary Amines:
 - a. No available hydrogen atom
 - b. Fast reactivity with heat
 - c. Short pot life
 - d. Used to catalyze anhydride curing agents
 - e. Toxic
 - f. Skin irritant
6. Latent Curing Agents (allow 1 part epoxy system; long shelf life, e.g., 0.5 to 1 yr; cured with heat in several hours; electrical properties may be lowered)

2. Boron trifluoride— aniline complex
3. Boron trifluoride— monoethanolamine complex
4. Boron trifluoride— trimethylamine complex.

A Lewis base catalyst such as DMP-30, a tertiary amine (see Fig. 3-3) can be used as the ethyl hexoate salt; pot life is extended from 30 min to 3 to 6 h. The complexes break up gradually at room or higher temperature and liberate the active catalyst form.

3-3.3 ACID ANHYDRIDE HARDENERS

Dicarboxylic acids, such as the anhydrides, open up an epoxy ring and become part of the cross-linked structure as an ester linkage'. Compared with amine-cured systems, the anhydride-cured resins show better thermal resistance, higher distortion temperatures—300°F, about 75 deg to 100 deg F higher than amine-cured resins—and improved electrical properties. Low dielectric constants (2.8 to 3.0) can be attained. Anhydrides are used from 30 to 140 phr. Accelerators or catalysts are usually needed. With 0.1 to 5 phr tertiary amine as catalyst, epoxy compositions can be formulated which are stable to 12 h (RT), have a low viscosity, and can be cured at 250°F. Where the epoxy contains more hydroxy than epoxy groups, i.e., solid bisphenol A types, the higher hydroxy content can initiate the reaction without use of a tertiary amine catalyst. These systems have a comparatively low peak exotherm. Dermal initiation is minimized. Liquid forms of anhydride containing epoxies are extant which have a pot life of about 2 mo at 25°C. Chlorinated (or brominated) anhydrides are used for flame-retardant compounds. A commonly used agent is chlorendic anhydride; it is highly reactive and does not need the use of an accelerator.

Table 3-12 gives information on the types, designations, and sources of commonly-used anhydride curing agents.

3-4 FLEXIBILIZATION AND MODIFICATION OF EPOXIES

Modified polyamides are common flexibilizers for epoxy resins. Epoxy-curing polyamides are condensation products of dimer or trimer vegetable oils or of polyunsaturated fatty acids with

TABLE 3-10. AMINE CURING AGENTS COMMONLY USED WITH EPOXIES

<u>TYPE</u>	<u>DESIGNATION</u>	<u>TYPICAL SOURCE:</u>
<u>Aliphatic Amines:</u>		
diethylenetriamine	DTA or DETA	Dow, Jefferson, Union Carbide
triethylenetetramine	TETA	Jefferson, Union Carbide, Shell
hexamethylenediamine	HMDA	Du Pont, Celanese
silicone amine	DC-XR-6-2 114	Dow-Corning
<u>Aromatic Amines:</u>		
m-phenylene diamine	MPDA	Du Pont, Allied
diamino diphenylsulfone	DDS	Polychemical Labs, RSA Corp.
methylenedianiline	MDA	Allied, Dow
<u>Amine Adducts:</u>		
diethylaminopropylamine	DEAPA	Shell, Union Carbide
olefin oxide-polyamines	—	Shell, Union Carbide, Ciba
glycidyl ether-polyamines	—	Shell, Union Carbide, Ciba
<u>Alicyclic Amines:</u>		
piperidine	—	Bacon, Du Pont, Riley Tar
N-aminoethyl piperazine	AEP	Jefferson, Union Carbide
<u>Tertiary Amines:</u>		
triethylamine	TEA	Pennsalt, Union Carbide
<u>Latent Catalysts/Curing Agents:</u>		
boron trifluoride monoethylamine complex	BF ₃ -400	Union Carbide, Ciba, Harshaw
boron trifluoride monoethanolamine complex	—	Harshaw
dicyandiamide	"dicy"	American Cyanamid

polyamines. The amino groups (primary and secondary) are epoxyreactive (not the amide groups). General Mills Versamid—i.e., 115, 125, etc.—are quite often used; these are viscous slightly colored fluids.

These Versamids and related modified polyamides act as flexibilizers; polyamide content greater than the equivalent reactive quantity adds flexibility to the epoxy resin (Table 3-13). Epoxy-polyamides can be rigid, semirigid, or flexible. The resins are very good for potting and casting. They bond to most metals, thermoplastics, and thermoset resins. Properties include high impact strength, good chemical and solvent resistance, low shrinkage and exotherm, low- to no-toxicity, and good handling properties. Pot life is 2 to 4 h; curing is at 25°C or higher. A typical semirigid potting agent might

be 1 part polyamide with 1 part standard bisphenol-A epoxy plus about 10-25% filler to decrease shrinkage and reduce excess flow.

Organics that modify epoxies are reactive diluents, polysulfide elastomers (Thiokols), polyurethanes and certain plasticizers, polyglycols, polyesters, trimeric acids, etc.¹⁰. Properties of these organics follow:

1. Reactive diluents react and become an inherent part of the cured epoxy. Some of these include phenyl glycidyl ether, allyl glycidyl ether, and styrene oxide. These lower viscosity and exotherm; pot life and flexibility are increased. Disadvantages include dermatitis, and physical and electrical characteristics of the thermoset resin can be lowered—to partly prevent this only 10 to 15 phr resin are typically used.

TABLE 3-11
PROPERTIES OF CURED CASTINGS ACHIEVED WITH TYPICAL ALIPHATIC POLYAMINES,
POLYAMIDES, AND DERIVATIVES^a

Property	Diethylene- triamine	Menthane- diamine	N-Aminoethyl Piperazine	Polyamide ^c	Glycidyl Ether Poly- amine Adduct
Concentration of Curing Agent ^b	12	22	20	100	25
Gel Time ^d , min	30	480	20-30	180	20-30
Curing Cycle	Gel at 25°C + 2 h at 100°C	2 h at 100°C + 3 h at 200°C	Gel at 25°C + 2 h at 150°C	Gel at 25°C + 3 h at 120°C	10 days at 23°C
Heat-Distortion Temp., °C	122	151	110	58	102
Compressive Strength:					
Ultimate, psi	16,700	19,500	13,800	7,200	
Yield Stress, psi	9,800	10,500	8,700		15,000
Modulus, psi	520,000	390,000	280,000	205,000	590,000
Deformation at Yield, %		3.9	3.5		
Deformation at Ultimate, %		8.0	10.5	13.0	
Tensile Strength:					
Ultimate, psi	10,900	9,000	9,600	5,500	7,500
Yield Stress, psi	5,300	6,000	5,000	2,200	10,500
Modulus, psi	410,000	440,000	400,000	245,000	510,000
Elongation at Yield, %	1.5	1.5	1.4	3.8	1.7
Elongation at Ultimate, %	6.3	2.9	8.8	9.0	2.4
Notched Izod Impact Test, ft•lb/in. width	0.59	0.70	0.85	1.2	0.6
Arc Resistance, ASTM D-495, s	85	102	78	80	92
Dielectric Strength, ASTM D-149-55J, S/S at 23°C, V/mil	465	460	400	+ 70	450
Dielectric Constant at 23°C, dimensionless :					
60 Hz	4.1	5.3	3.0	3.2	4.3
103Hz	3.85	5.15	2.95	3.1	4.1
Dissipation Factor at 23°C, dimensionless					
60 Hz	0.015	0.005	0.018	0.035	0.0115
103Hz	0.020	0.018	0.025	0.033	0.0260
Chemical Resistance, % weight gain:					
After 3 h in boiling acetone	0.63	1.70	Disintegrates	Disintegrates	1.50
After 24 h in boiling H ₂ O	0.51	1.5	2.8	3.6	2.0

^aBasis: diglycidyl ether of bisphenol A, epoxy equivalent 180-195.

^bAmine value 215 (mg KOH equivalent to basic nitrogen of a 1-g sample).

^cConcentration in parts per hundred, phr = $\frac{\text{equiv. wt of amine}}{\text{epoxide equiv. of epoxide}} \times 100$.

^dGel time at 23°C in 1-qt mass.

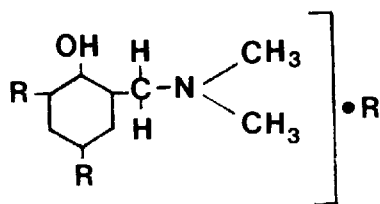


Figure 3-3. General Form of Lewis Based Catalyst DMP-30

TABLE 3-12. ANHYDRIDE CURING AGENTS USED WITH EPOXIES

TYPE	DESIGNATION	TYPICAL SOURCE
Aliphatic		
dodecenylsuccinic polysebacic	DDSA* PSA	Allied, Monsanto, Shell Wallace and Tiernan, Inc
Aromatic:		
phthalic	PA	Many suppliers
trimellitic	TMA	Amoco
nadic methyl*	NMA	Allied
tetrahydrophthalic	THP	Allied, Petrotex
pyromellitic		Aceto, Du Pont, Guardian Chem
Alicyclic:		
hexahydrophthalic*		Allied, Petrotex
chlorendic (1,4,5,6,7,7-hexachlorobicyclo [2.2.1]-5-heptene-2,3 dicarboxylic	CA (see below, HET)	Velsicol, Hooker
Nadic	HET anhydride NA	Hooker Allied
1,2,3,4-cyclopentane tetracarboxylic acid	CPDA	UOP Chemical

*Very commonly used generally because of handling ease.

TABLE 2-13. PROPERTIES OF EPOXY-POLYAMIDE SYSTEMS

Epoxy-Polyamide Weight Ratio	80:20	70:30	60:40	50:50	40:60
Heat-Distortion Temperature, °F	220	215	136	100	65
Hardness, Shore D	98	95	90	80	60
Specific Resistivity, ohm-cm	10 ¹⁵	10 ¹⁵	10 ¹⁴	10 ¹²	10 ¹⁰
Moisture Absorption, %	0.15	—	0.20	—	0.50

2. Polysulfides are basically low in toxicity. High flexibility is attained with their use. A disadvantage is that they deteriorate somewhat over 200°F.

3. Fixed plasticizers are compatible with epoxies; though nonreactive, they produce good flexibility. These agents reduce viscosity and aid low temperature impact resistance. Bleeding out of the hardened resin is common.

4. Polyurethanes are used to increase crack resistance, toughness, and flexibility of epoxies". Table 3-14 shows the effects of epoxy-polyurethane weight ratios.

3-5 EFFECTS OF FILLERS IN EPOXIES

In epoxy systems fillers have these primary effects:

1. Reduce cost
2. Lower thermal expansion effects
3. Increase heat conduction
4. Increase viscosity

5. Slow reaction rates (greater pot life, less peak exotherm).

The more important fillers used include silica, calcium carbonate, talc, aluminum oxide, iron oxide, feldspar silicates, quartz, asbestos, ground ceramics, and glass powders. Particle size is critical; particles too large settle out rapidly, and powders too fine may cause an undesirable viscosity increase. The filler is introduced into the fluid epoxy slowly to prevent trapping of air and to insure proper dispersion. In many cases final mechanical mixing of the compound is done under nominal vacuum conditions.

Other effects that may be attributed to the use of fillers are reduction in weight loss of the cured epoxy under use-conditions and improvement in fire retardance (i.e., burning rates can be decreased through the incorporation of antimony oxide or phosphates)¹².

Table 3-15 gives data on the effects of calcium carbonate or mica filler on a general type epoxy. Reductions in compressive and tensile strengths

TABLE 3-14. PROPERTIES OF EPOXY-POLYURETHANE SYSTEMS

Epoxy-Polyurethane Weight Ratio	25:75	50:50	75:25	100:0
Ultimate Tensile Strength, psi	2050	6000	10,000	10,000
Ultimate Elongation, %	350	10	10	10
Hardness, Shore D	15	80	85	90
Heat-Distortion Temperature, °F	—	100	176	260

TABLE 3-15. EFFECTS OF FILLERS ON EPOXY RESIN PROPERTIES

Property	Unfilled	Calcium Carbonate	Mica
Coefficient of Linear Expansion, $10^{-6}/^{\circ}\text{C}$	7.2	57	43
Thermal Conductivity, $\text{W}/\text{in}^2\cdot^{\circ}\text{C}\cdot\text{in.}^{-1}$	0.008	0.014	0.012
Water Absorption, mg/g	24	20	22
Specific Gravity	1.16	1.6	1.7
Compressive Strength, psi	15,900	7540	5700
Tensile Strength, psi	9700	6000	5650
Dielectric Strength, V/mil	320	370	420

are significant but are not particularly deleterious to use in embedment processes.

Table 3-16 shows the nominal rise (at room temperature) of viscosity of a bis-phenol A epoxy with varying contents of lithium aluminum silicate (feldspar-type) filler.

Table 3-17 shows the range of properties for unfilled and silica-filled epoxy resins¹³.

3-6 EPOXY TRANSFER MOLDING COMPOUNDS

An epoxy powder compound can be made as:¹⁴

1. Resin/filler/other additives (except the hardener) are mixed.
2. Fluid hardener is added.
3. Compound/hardener are blended and poured into trays
4. Mix is cooled to 25°C.

This mix is aged at room temperature to a predetermined reaction point which can be measured by a flow test. Then the material is granulated for use; the formulation can be further treated by compacting into tablets or preforms. This procedure removes the need for weighing powder for each cycle and increases production rates in high volume work.

Compounds made in this manner are called B-stage epoxies; they show good stability at low temperatures. Shelf life is limited from weeks to a year, depending on the formula. Another type of compound is called an A-stage epoxy. This is a dry blend of epoxy granules, hardener granules,

and filler. The hardener part is made so that no reaction with the epoxy occurs except at higher temperature. A-stage formulas usually have a longer shelf life at room temperatures; refrigerated storage is not required. A- and B-stages are hygroscopic and must be protected against humidity since water absorption changes flow properties and increases cure time¹⁵.

Epoxy compounds are marketed with a broad range of properties—from soft mineral-filled to high impact hard glass-filled compounds. Variants exist in molding properties, hardening time, and colors; cure time can range from 20-30 s to 3-5 min; and molding temperatures are 250° to 300° F (some are as low as 200°F). All the desired properties of a long-time cured epoxy item also are exhibited by a cured transfer-molded epoxy part. Table 3-18 gives information on four typical compounds.

These properties are desirable in an epoxy molding compound¹⁶:

1. Sharp gel points; low molding pressure (for limited leakage out of molds and less chance of damage or displacement of embedded components).
2. Extended shelf life (with B-stage resins the reaction can continue at room temperature; A-stage resins can be stable up to several years at 25°C).
3. Complete cure in the transfer mold (for minimum warpage and breaking of parts on ejection from the mold).
4. Built-in or inherent mold release character (proper mold design is required for ease of removing end item).

3-7 EPOXY FOAMS

Epoxy foams employ an additive blowing agent. This agent decomposes on heating to release a gas that expands the resin to the foamed form. Close control of the processing is required since the epoxy reaction and gas liberation must be synchronized. These foams can have a wide range of desirable properties—there are numerous choices of activators, blowing agents, and

TABLE 3-16. NOMINAL EFFECT OF LITHIUM ALUMINUM SILICATE ON EPOXY SYSTEM VISCOSITY

Filler, %	Viscosity, RT, cP
0	700
10	800
20	1,000
30	2,000
40	4,000
50	7,000
60	10,000
70	50,000
80	"solid" in form

**TABLE 3-17. PROPERTY RANGE OF CURED EPOXY RESINS
(UNFILLED AND SILICA-FILLED)**

Property	Unfilled Resin	Silica-Filled Resin
Mold Shrinkage, in./in.	0.001 - 0.004	0.0005 - 0.002
Specific Gravity	1.11 - 1.23	1.6 - 2.0
Specific Volume, in ³ /lb	24.9 - 22.5	13.9 - 17.3
Tensile Strength, psi	4000 - 13,000	5000 - 8000
Modulus of Elasticity in Tension, 10 ⁶ psi	4.5	
Compressive Strength, psi	15,000 - 18,000	17,000 - 28,000
Flexural Strength, psi	14,000 - 21,000	8000 - 14,000
Impact Strength, Izod*, ft•lb/in. notch	0.2 - 0.6	0.3 - 0.45
Hardness, Rockwell	M80 - M100	M85 - M120
Thermal Conductivity, 10 ⁴ cal/s•cm ² •°C•cm ⁻¹	4 - 5	10 - 20
Specific Heat, cal/°C•g		0.20 - 0.27
Thermal Expansion, 10 ⁻⁶ /°C	4.5 - 6.5	2.0 - 4.0
Resistance to Heat (continuous), °F	250 - 600	250 - 600
Heat-Distortion Temperature (at 50% RH and 23°C), °F	115 - 550	160 - 550
Volume Resistivity, ohm•cm	10 ¹² - 10 ¹⁷	10 ¹³ - 10 ¹⁸
Dielectric Strength, 1/8-in. thickness, V/mil:		
Short-time	400 - 500	400 - 500
Step-by-step	380	
Dielectric Constant, dimensionless:		
60 Hz	3.5 - 5.0	3.2 - 4.5
10 ³ Hz	3.5 - 4.5	3.2 - 4.0
10 ⁶ Hz	3.3 - 4.0	3.0 - 3.8
Dissipation (power) Factor, dimensionless:		
60 Hz	0.002 - 0.010	0.008 - 0.03
10 ³ Hz	0.002 - 0.02	0.008 - 0.03
10 ⁶ Hz	0.030 - 0.050	0.02 - 0.04
Arc Resistance, s	45 - 120	150 - 300
Water Absorption (24 h, 1/8-in. thickness), %	0.08 - 0.13	0.04 - 0.10
Burning Rate	Slow	Self-extinguishing
Effect of Sunlight	None	None
Effect of Weak Acids	None	None
Effect of Strong Acids	Attacked by some	Attacked by some
Effect of Weak Alkalies	None	None
Effect of Strong Alkalies	Slight	Slight
Effect of Organic Solvents	Generally resistant	Generally resistant
Machining Qualities	Good	Poor
Clarity	Translucent	Opaque

*Izod test, 0.5 X 0.5 in. notched bar.

modifiers. Ease of handling is good. One component dry powder or two component liquid systems are available. Shrinkage upon hardening is low; dimensional stability is good. As expected, adhesion to most surfaces is very good. Chemical/solvent resistance and electrical properties are very good.

As a finished product, the foam is rigid—either in closed-cell or open-cell structures. The unreacted systems are available as either a pack-in-place or foam-in-place material. The pack-in-place materials are pushed into a cavity to be filled. A closed-cell mass is formed on curing;

there is little waste of material. The pack-in-place compound finds use as an encapsulant. Other applications for such materials are in making microwave lenses, radome cores, antennas, and various light-weight structures. The foam-in-place epoxies (resin/blowing agent/surfactant/etc.) are poured into the bottom of the cavity and foamed (25°C or higher). Open- or closed-cell forms are available. Such epoxy foams find use where light-weight, high performance encapsulation of electronic assemblies is required.

TABLE 3-18. TYPICAL DATA ON EPOXY TRANSFER-MOLDING COMPOUNDS

Test	Method	Furane 403-S-3 (Furane Plastics, Inc.)	Furane 8339	Hysol XM G5F E582 (Hysol Div., The Dexter Co.)	Hysol XM G5 E437
Dielectric Strength, V/mil	MIL-1-16923 ^a	417.7	329.1	302.5	304.7
Dielectric Constant at 1 kHz, dimensionless	FTMS-406 ^b	6.73	5.43	5.18	5.12
Dissipation Factor at 1 kHz, dimensionless	FTMS-406	0.022	0.010	0.004	0.003
Volume Resistivity, ohm-cm	MIL-1-16923	4.3×10^{13}	7.19×10^{13}	7.9×10^{13}	8.63×10^{13}
Surface Resistivity, ohm	ASTM D257	1.52×10^{13}	1.52×10^{13}	1.37×10^{13}	1.32×10^{13}
Arc Resistance, s	ASTM D495	182.8	132.3	71.9	99.9
Thermal Conductivity, Btu/h-ft ² -°F-ft ⁻¹	Comparative 50°C	0.229	0.196	0.144	0.210
	Comparative 100°C	0.236	0.214	0.167	0.221
Fungous Resistance	MIL-E-5272	No signs of fungous growth			
Specific Gravity	FTMS-406	1.67	1.60	2.06	1.79
Water Absorption, %	ASTM D570	0.073	0.086	0.083	0.100
Thermal Shock Resistance	MIL-1-16923	No failures			
	Type B cycle				
Coefficient of Linear Thermal Expansion, in./in.-°C	ASTM D696	4.51×10^{-5}	4.60×10^{-5}	5.95×10^{-5}	5.37×10^{-5}
Compressive Strength, psi	ASTM D695	15,500	21,940	20,563	19,570
Flexural Strength, psi	ASTM D790	9,759	11,780	10,000	10,450
Tensile Strength, psi	ASTM D638	5,331	6,036	5,006	4,696
Volume Shrinkage, %		2.040	2.959	3.046	2.353
Hardness, Shore D	FTMS-406	90	90	90	90
Flow, in.	EMMI 1-66 ^c	34	37	56	28

^aInsulating Compound, Electrical, Embedding^bFederal Test Method Standard^cEpoxy Materials Manufacturing Institute

REFERENCES

1. H. Lee and K. Neville, *Epoxy Resins*, McGraw Hill Co., New York, NY, 1967
2. J. Delmonte, "Epoxy Molding Compounds: Materials, Molding and Applications", *Insulation* **13**, 59-63 (February 1967).
3. R. F. Gould (ed.), *Epoxy Resins*, American Chemical Society Monograph Series, 1970
4. E. N. Dorman, "Cycloaliphatic Epoxy Resins: Premium Properties for Electrical Insulation", Sec. 21-2, *Proceedings, Society of Plastics Engineers*, 21st Annual Technical Conference, Boston, MA, March 1965.
5. C. T. Patrick, Jr., and C. W. McCary, Jr., "Cycloaliphatic Epoxy Resins in Electrical Insulation", Sec. 5-3, *Proceedings, Society of Plastics Engineers*, 22nd Annual Technical Conference, Montreal, Canada, 7-10 March 1966.
6. A. S. Burhans and A. C. Soldatos, "Cycloaliphatic Epoxy Resins With Improved Strength and Impact Coupled With High Heat Distortion Temperature", *Society of the Plastics Industry*, 25th Annual Technical Conference, Washington, DC, February 1970.
7. G. Salensky, "Epoxy Resin Systems for Electrical/ Electronic Encapsulation", *Insulation/Circuits*, 19-25 (May 1972).
8. J. C. Illman, "Cure of Epoxy Resins With Aromatic Amines—High Heat Distortion Studies", Sec. 4-1, *Proceedings, Society of Plastics Engineers*, 22nd Annual Technical Conference, Montreal, Canada, 7-10 March 1966.
9. S. H. Christie, W. E. Derrich, J. R. Hallstrom and J. C. Powell, "Anhydride Blends as Curing Agents for Epoxy Resin",

REFERENCES (cont'd)

- Sec. 5-1, *Proceedings, Society of Plastics Engineers*, 22nd Annual Technical Conference, Montreal, Canada, 7-10 March 1966.
10. A. S. Burhans, J. J. Madden, W. P. Mulvanen, R. F. Sellers, and S. G. Smith, "Designing Epoxy Resins With Improved Toughness", Sec. 26-1, *Proceedings, Society of Plastics Engineers*, 21st Annual Technical Conference, Boston, MA, March 1965.
11. J. J. Bielawski, "Development of a Flexible Epoxy for Encapsulation of Electronic Components", *Proceedings, Society of Plastics Engineers*, 28th Annual Technical Conference, Plastics 1970 "Yesterday's Imagination—Tomorrow's Realization", **16**, 515-8, New York, NY (4-7 May 1970).
12. F. T. Parr, "Qualifying an Epoxy Resin System for Embedding Electronic Devices for Aerospace Applications", *American Chemical Society*, 150th Meeting **28**, 226-35, Atlantic City, NJ (8-13 September 1968).
13. R. J. Tetreault and A. H. Sharbaugh, "On the Electrical Properties of a Filled and Flexibilized Epoxy Formulation", Sec. 5-4, *Proceedings, Society of Plastics Engineers*, 22nd Annual Technical Conference, Montreal, Canada, 7-10 March 1966.
14. R. Drake and A. Siebert, "Elastomer-Modified Epoxy Resins for Structural Applications", *20th National SAMPE Symposium and Exhibition*, San Diego, CA, 29-30 April and 1 May, 1975.
15. R. F. Zecker, "Designing Electrical Components for Transfer Molding", *Plastic Design and Processing* (December 1968).
16. K. N. Mathes, "Selection of an Insulation System in Product Design", *Insulation* (October 1967).

CHAPTER 4

POLYURETHANE EMBEDDING AGENTS

The chemical, physical, and electrical Properties of the polyurethanes are given. The chemistry of the polyurethanes and the products of the reactants are discussed. Brief comments on the toxicity of polyurethane reversion are presented. Types of polyurethanes by ASTD designation are given together with suppliers and trade names. Casting systems are also discussed.

4-1 GENERAL CHARACTERISTICS OF POLYURETHANES

Polyurethanes are very versatile elastomers; they have a unique combination of properties and are amenable to various processing methods. They show properties such as abrasion resistance, oil and solvent resistance, tensile and tear strength, and range of hardness or modulus not readily available with other elastomers.

Most of the polyurethane elastomers commercially available are based on low molecular weight polyester or polyether polymers that are terminated with hydroxyl groups. The other starting materials or intermediates consist of di- or polyfunctional isocyanates and (in generally most formulations) low molecular weight polyfunctional alcohols or amines.

The liquid starting polymer is generally in the range of 500 to 3000 molecular weight. Variations in the characteristics of this starting polymer and the concentration, type, and arrangement of the isocyanate and other small molecules used for chain extension provide a broad range of different polyurethane elastomers.

Polyurethanes show very good tensile strengths and elongations. Table 4-1 shows additional important characteristics.

Polyurethanes can be made to have very high toughness — tear strength and cracking resistance are high compared to most other flexible materials. These resins find use at low temperatures and show good electrical properties. With polyurethanes, stresses on electrical components

under thermal or nominal mechanical stressing are low. Adhesion is better than that of silicones but falls short of the bonding strengths of epoxies.

Polyurethanes react with moisture; under processing all parts and materials must be dry. Reversion may occur with some types of resins under exposure to high heat and humidity. Such reversion had been a problem in the failure of potted aircraft connectors. Publications on this problem are continually available⁸.

TABLE 4-1. SALIENT PROPERTIES OF POLYURETHANES

Heat Resistance — service to 150° to 200°F

Cold Temperature — service to about -60°F

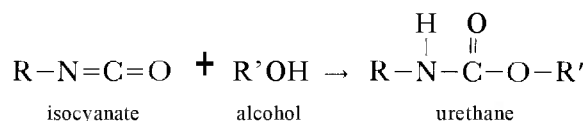
Abrasion Resistance — elastomers have excellent resistance to abrasion (typically three times that of conventional rubbers)

Hardness/Resilience — high hardness plus resilience is primarily responsible for toughness (10 to 80 Durometer A is general hardness range; 70 Durometer A can show 250% plus elongation)

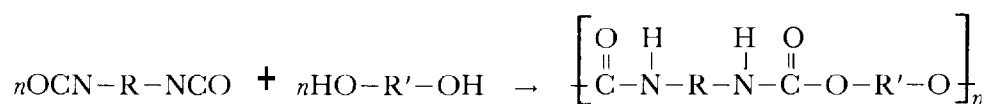
Chemical Resistance — fair resistance to many reagents (aliphatics, alcohols, conventional fuels/oils); may be attacked by hot water, highly polar solvents, concentrated acids/bases); oxygen/ozone/corona resistance very good.

4-2 BASIC CHEMISTRY OF POLYURETHANES

The term polyurethane refers to the product that results from the reaction of an isocyanate and an alcohol:

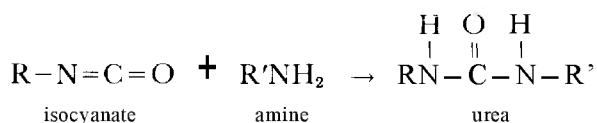


By this reaction, difunctional or polyfunctional isocyanates and hydroxyl-terminated low molecular weight polymers will give high molecular weight polymers if the molar ratios are properly controlled:



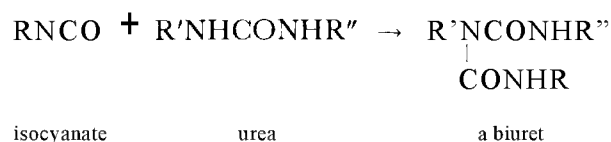
This chemical reaction shows how the urethane reaction is used to couple the segments designated R and R'. R and R' segments of many different types are used in commercial polyurethane elastomers.

Another coupling reaction that is widely used along with the isocyanate-hydroxyl reaction is that between an isocyanate and an amine to give a urea



These reactions are far from simple; there are always competing reactions possible. Close attention must be given to reaction rates, order of addition of ingredients, and catalysis of certain reactions in preference to others. The isocyanate is capable of reacting with the active hydrogen on a urethane or a urea group to give branching or cross-linking:





Control of the stoichiometry of the polymeric polyol, isocyanate, and low molecular weight polyol or amine, the temperature, the order of addition, and sometimes the use of catalysts can produce compositions with properties typical of a cross-linking high-molecular weight elastomer.

Some of the structures typical of the liquid polymers used in polyurethane elastomers are shown in Table 4-2.

The isocyanates used in polyurethane elastomers also vary considerably in structure. Some of the common isocyanate structures are shown in Table 4-3. Other isocyanates used in special cases such as for nondiscoloring polyurethane elastomers are hexamethylene diisocyanate (HDI) and hydrogenated MDI.

The low molecular weight diol, triol, or diamine, one of the three principal starting materials, provides an additional means of regulating properties. These are usually called chain extenders. Cross-linking can be introduced with an

extender that is a triol, for example, or the hardness can be increased by raising the level of isocyanate and the extender which increases the amount of rigid polar entities consisting of the urethane and urea groups in the polymer. The

TABLE 4-2
HYDROXYL TERMINATED POLYMERS

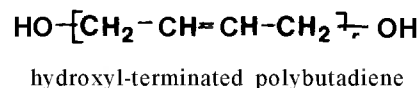
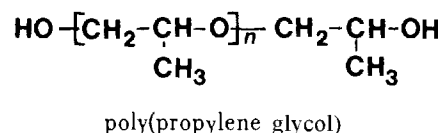
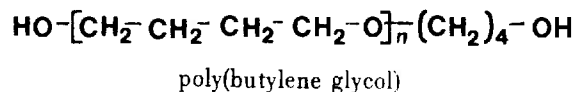
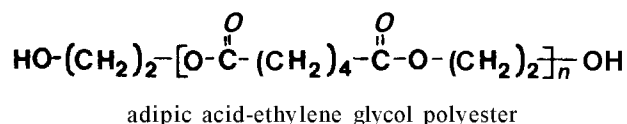
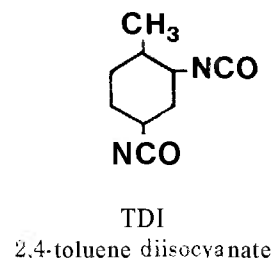
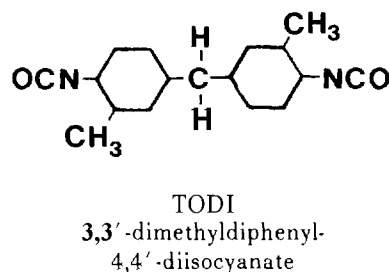
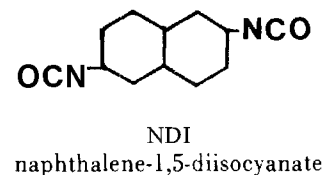
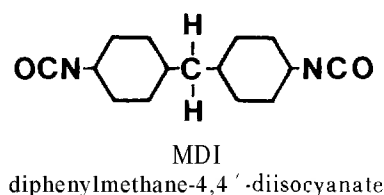


TABLE 4-3. ISOCYANATES USED IN POLYURETHANE ELASTOMERS



chain extending agents commonly used in polyurethane elastomers are shown in Table 4-4 along with the abbreviations frequently used⁹

In addition to the given reactions, other materials—such as the aromatic diol N,N'-bis (2-hydroxypropyl)-aniline, and even water—can be used to couple the isocyanate terminated chains to give useful products.

The reaction of isocyanates with water or with an organic acid is generally undesirable for elastomer formation unless a cellular product is desired. Both of these reactions give CO₂ as a gaseous by-product but also serve to couple one polymer chain to another:¹⁰

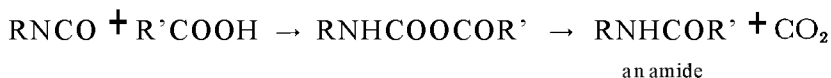
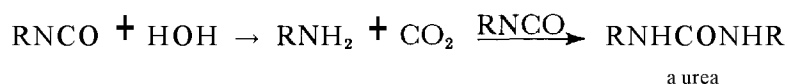
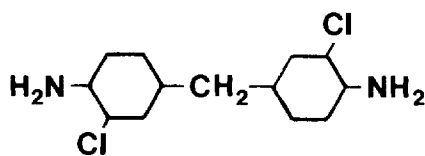
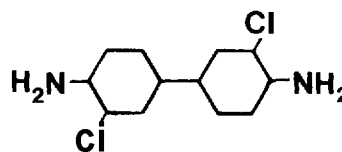


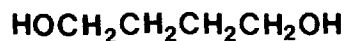
TABLE 4-4. CHAIN EXTENDING AGENTS



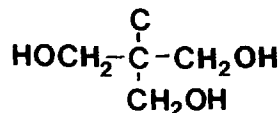
MOCA*
4,4'-methylene bis
(orthochloroaniline)



DCB
dichlorobenzidine



1,4-butanediol



TMP
trimethylolpropane

*Found to be carcinogenic; banned by OSHA. Work is in progress to find suitable replacements for this agent. As of

1977, no definitive replacement material has been generally accepted by all sectors involved in the technology.

4-3 TYPES OF POLYURETHANES BY ASTM DESIGNATIONS

By ASTM designation, polyurethanes are divided into five types. Three of these are one-component systems and two are two-component systems. These are:

Type 1. One-component prereacted. These are urethane-oil or uralkyd types in which polyisocyanates are reacted with a polyhydric alcohol ester of a vegetable fatty acid. These cure by oxidation and ambient or slightly higher temperatures (5 min to 1 h). These are not widely used for electrical applications (such as the blocked polymers or two-component systems) because overall performance characteristics are not high.

Type 2. One-component moisture-cured. These have free reactive isocyanate groups which cross-link with ambient moisture. (They cure more slowly than Type 1, in 1 to 12 h.) The use of these types (even as thin moisture-reactive coatings) in electronics is limited because cure-time is a function of relative humidity and resin thickness.

Type 3. One-component heat-cured. These are nonreactive through blocking by phenolics; at elevated temperatures the blocking agent is released and the isocyanate is available for reaction. These find use particularly for wire coatings; the temperature needed to break the phenol adduct is approximately 320°F. Such temperature limits the use of Type 3 polymethanes; they cannot be used with temperature-sensitive electronic components. They are suitable for wire/coil insulation and other high-temperature resistant substrates prior to attachment of the more sensitive electronic components. Adducts with somewhat lower block-release temperatures are known (e.g., the malonic ester adduct, activated at 266°F).

Type 4. Two-component catalyst-cured. These are prepolymers or adducts having free reactive isocyanate groups in one component and a catalyst in the second component. The rate of

hardening is proportional to the catalyst concentration; catalysts can be polyol monomers, tertiary amines, or polyamines. Pot life after mixing is generally short. Other catalysts or accelerators used include triethylamine, dimethylethanolamine, N,N'-diethylcyclohexylamine, N-methylmorpholine, N-methyldiethanolamine, tributyltin acetate, dibutyltin diacetate, triethylenediamine, and cobalt naphthenate.

Type 5. With these materials, one component is a prepolymer or adduct having free isocyanate groups; the other part has reactive hydrogen atoms such as hydroxyl-terminated polyesters or polyols, e.g., castor oil. These find wide use for protective insulating embedments. The first component is generally a tolylene diisocyanate or a polyisocyanate prepolymer, i.e., an adduct. The second component is a hydroxyl-containing material such as hydroxyl-terminated polyesters, polyethers, polyols, castor oil, and some epoxies (with hydroxyl groups along the chain). The polyethers are synthesized from propylene oxide and are called polypropylene glycols.

4-4 SOME TRADE NAMES AND SUPPLIERS OF POLYURETHANE EMBEDMENTS

Table 4-5 lists typical trade names and suppliers of Types 4 and 5 polyurethanes which find use in embedments.

Table 4-6 lists some basic and modified isocyanates.

Hydroxyl-terminated polyesters, polyethers, and other polyols commonly used to produce polyurethanes are shown in Table 4-7.

4-5 END PRODUCTS OF REACTANTS

As a function of the initial reactants and synthesis conditions, the end products are elastomers, foams, or coatings.

The elastomers are made from diisocyanates and a linear polyester or polyether oligomer with a low molecular-weight curing agent, e.g., glycol or diamine. In casting an isocyanate prepolymer is used after mixing with the curing agent, and

**TABLE 4-5. SOME TRADENAMES/SUPPLIERS OF POLYURETHANE EMBEDMENTS
(TYPES 4 AND 5)**

Type 4 (two-component catalyst-cured)		
Chemglaze series with catalyst 9966		Hughson
Metex Conformal Coating with catalyst XH-18		MacDermid
Spengel DV-1078, DV-1088, DV-1079 with catalyst C87-100, P93		Spencer Kellogg
HumiSeal IA27 with Drier No. 27		Columbia Technical
Type 5 (two-component prepolymer polyol)		
Conathane 1155		Conap
Spengel P23-60CX, P49-60CX, DV-1531, DV-1699		Spencer Kellogg
HumiSeal 2A56, 2A60, 2A61		Columbia Technical
Eccocoat RTU, IC-2		Emerson & Cuming
Uralane 5712, 241		Furane
Seotchcast 221	Minnesota Mining and Manufacturing	
PT 750-1	Product Techniques	
PR-1566, 1538	Products Research	
Solithane systems	Thiokol	
Multrathane systems	Mobay	
PC 26, XPC-A656	Hysol	

TABLE 4-6. TYPICAL ISOCYANATES USED IN POLYURETHANE FORMULATIONS

Trade Name	Supplier	Chemical Type	Appearance	% NCO
Mondur TDS	Mobay	2, 4-TDI	Colorless to light yellow liquid	
Mondur TD80	Mobay	An 80/20 mixture of 2,4-and 2,6-TDI isomers	Water-clear liquid	48
Naceonate 4040	National Aniline	An 80/20 mixture of 2,4-and 2,6-TDI isomers	Water-clear liquid	48
Hylene TR	Du Pont	An 80/20 mixture of 2,4-and 2,6-TDI isomers	Water-clear liquid	48
PAPI	Carwin	Polymethylene polyphenyl isocyanate	Dark amber liquid	31
Mondur S	Mobay	A phenol-blocked TDI adduct	Light-colored solid	11.5-13.5
Mondur SH	Mobay	A phenol-blocked polyisocyanate adduct	Colored solid	10.5-13.5
E-268	Mobay	Light-stable adduct	Colored liquid	11.0-11.6
E-244	Mobay	Light-stable monomer	White liquid/solid	31.4-32
E-262	Mobay	Light-stable monomer	Off-white liquid	45.3
P93-100	Spencer Kellogg	Type 4 prepolymer, no solvent	Clear liquid, Gardner color 2	7.7
XP-1152	Spencer Kellogg	Type 5 polyurethane prepolymer, no solvent	Clear liquid, Gardner color 4	29.5
XP-1662	Spencer Kellogg	Type 5 polyurethane prepolymer, no solvent	Clear liquid, Gardner color 2	10.1
ZP-1663	Spencer Kellogg	Type 5 polyurethane prepolymer, no solvent	Clear liquid, Gardner color 2	14.9
Vorite 63	Baker Castor Oil	Ricinoleate polyester diisocyanate prepolymer	Clear liquid	

poured into the mold. Mold time is 20 to 30 min; post-heat curing may be required.

Flexible foams are made typically from polyethers or polyesters, diisocyanates, and water plus catalysts. Carbon dioxide, released from a

water-isocyanate reaction, functions as the blowing agent to yield open-celled forms. Rigid foams are similarly made except that a fluorocarbon replaces water. Monofluorochloromethane and difluorochloromethane are useful blowing agents.

TABLE 4-7. TYPICAL POLYOLS USED IN POLYURETHANE FORMULATIONS

Trade Name	Chemical Type	Ave Equiv. Weight	Hydroxyl No.	Coating Applications
Mobay Multron R-2	Polyester	140	390-420	Surface coatings with Mondur S and CB; solderable wire enamels when formulated with Mondur S
Mobay Multron R-4	Highly branched polyester	200	270-290	Hard, abrasion-resistant surface coatings with Mondurs CB and S
Mobay Multron R-10	Polyester	265	205-221	Surface coatings
Mobay Multron R-12	Moderately branched polyester	335	158-175	Surface coatings
Mobay Multron R-16	Polyester	1,275	41-47	Flexible film coatings when combined with other polyesters
Mobay Multron R-18	Polyester	935	57-63	Flexible coatings
Mobay Multron R-22	Oil-modified alkyd resin	375	140-160	Surface coatings, mostly for exterior exposure
Mobay Multirathane R-26	Hydroxyl-terminated polyester	...	57-63	Elastomers and elastomeric coatings
Mobay Multron R-38	Polyester	415	120-150	Heat-stable nonsolderable wire enamels when treated with Mondur SH
Mobay Multron R-68	Polyester	1,155	45-52	Flexible coatings
Mobay Multron R-74	Polyester	1,120	47-53	Flexible coatings
Baker Castor Oil AA	Refined castor oil	342-345	163	Electrical-grade coatings
Spencer Kellogg OX-50	Blown castor oil	430	131	Electrical-grade coatings
Baker Castor Oil Polycin 54	Blown castor oil	380	135-140	Designed primarily for use as the curing polyol in coatings of the polyisocyanate type
Spencer Kellogg D-I Castor Oil	Specially processed raw castor oil	340	164	Used with Type 5 polyisocyanate adducts to produce coatings with moisture resistance, high film build, and low-temperature flexibility
Spencer Kellogg Castor 1066	A chemically modified castor oil	200	275-280	Same as D-I Castor Oil
Spencer Kellogg XP-1631	A chemically modified castor oil	170	328	Same as D-I Castor Oil

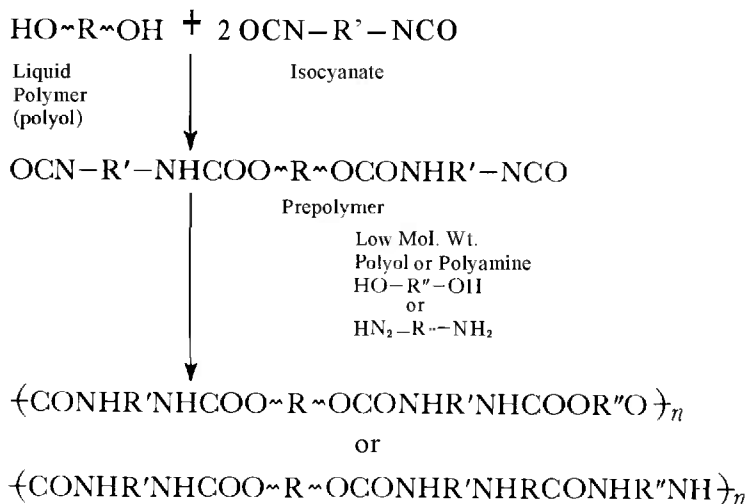
The exotherm boils out the "Freon" as gas and a cell-foam structure results.

4-6 POLYURETHANE CASTING SYSTEMS

Urethane polymers that are converted into end items directly from a liquid or semiliquid state are called casting systems. Commercial systems

in this class are available from all the base polymers such as polyester, polyether, and also hydrocarbons such as polybutadiene. Polyurethane casting systems generally consist of the three starting materials described earlier—namely, a liquid polymer with hydroxyl end groups, a polyfunctional isocyanate, and a low molecular weight polyol or polyamine". In low hardness

compositions, however, the formulation may involve only a polymeric polyol and a polyfunctional isocyanate. A general scheme of the steps involved in the preparation of a polyurethane casting system is shown:



The production of castings from polyurethane casting systems involves processing steps quite different from those used in conventional production of elastomers. The casting procedure follows one of the two techniques known as the prepolymer route or one-shot technique. The prepolymer route involves the following principal steps:

1. Preparation of Prepolymer. The polyol and diisocyanate are heated in an inert atmosphere to form a liquid polymer terminated in isocyanate groups as just shown. The reaction can be followed by the exotherm and/or by the $-\text{NCO}$ number. If one of the commercial prepolymers is used as a starting material, this step will be eliminated.

2. Prepolymer Degassing. The prepolymer is heated to casting temperature or slightly higher and subjected to a vacuum to remove dissolved gases. Continuous degassing devices are available. This step is necessary if bubble-free castings are to be produced.

3. Addition of Curing Agents. A low molecular weight polyol or polyamine is added at this stage

with thorough mixing. The mixing may be accomplished in a batch process or by a continuous mixing device. The temperature of the prepolymer and the curing agent is first adjusted to provide low viscosity and a satisfactory reaction rate.

4. Casting, Curing, Postcure. The completed mix is poured or injected into a heated mold in a manner designed to prevent the entrapment of air bubbles. The object is cured in the mold for a period that may range from a few minutes to an hour or more. Temperatures of 200° to 300°F usually are used. Longer time at lower temperatures is used with delicate electrical/electronic equipment. Common procedures for postcure consist of placing the formed part in an oven for a period of one to twenty-four hours at elevated temperatures or, in some systems, storing for one week at room temperature¹².

4-7 POLYURETHANE FOAM SYSTEMS

Plastic foams can be used as low-density potting materials for electrical or electronic equipment; these foams find primary use in aircraft and missile equipment. Modules for a missile may use such an encapsulant to give vibration and shock damping, decrease weight, and add thermal insulation. The foams which find use in embedding are the polyurethanes, the epoxies, and the silicones. Use of such foams in electronic embedment results in reduced weight and cost.

Polyurethane foams are used to protect electronic components and assemblies; a lightweight package results. Though many resins can be foamed with some choice of blowing agent, the polyurethanes are used because of their relatively low cost and ease of processing. For most non-stringent conditions, such foams give adequate protection for electronic components.

Urethane foams are made by reacting hydroxyl-terminated polyols—castor oil, glycols, polyesters, etc.—with a diisocyanate (and water); catalysts and surface-active agents are

also used. (A popular reagent is toluene diisocyanate.) Two steps occur in producing the foam. The diisocyanate reacts with the polyol hydroxyl group to lengthen the polyol chain; the latter is terminated by the NCO group.

In the fabrication of polyurethane foams, either the *one-shot* or *prepolymer* method is used.

In the *one-shot* method, all compound components are mixed together immediately; the foam is produced by reaction of the materials. There are certain disadvantages to this technique: reaction is fast and can produce handling and processing problems; components may not be properly dispersed; the diisocyanate is highly toxic (e.g., irritation of eyes and respiratory system) and consequently good ventilation is needed; and the reaction is highly exothermic—this may cause charring, particularly in the center of the foam. Advantages of the method are: a shorter cure cycle is obtained; a prepolymer does not have to be made; and the mixture for foaming has good flow characteristics.

In the *prepolymer* method, the polyol and isocyanate are reacted to give a fluid low molecular weight resin. Subsequently, the catalyst, water, and emulsifier are added to cause foaming. The prepolymer can be tailor-made for desired viscosity and percent of free isocyanate. The ratio of the catalyst/water/emulsifier to prepolymer is typically about 5 to 100.

Polyols used in foams include polyesters (with excess hydroxyl groups), dimer-acid polymers, polyether glycols, and hydroxyl-bearing oils. (Many other types find use.) Catalysts — i.e., tertiary amines, or methyl or ethyl morpholines — are used to produce foams; these catalysts control curing rates. The reaction is fast (order of 60 s or less); a balance is made between the working life and cure time. Surfactants, e.g. emulsifiers and wetting-agent, are used to give finer and uniform cell structures. In addition or as replacement of at least part of the water for the blowing-agent function, other agents which have found use for foaming (and are generally suitable for electrical end-use) include fluorinated

hydrocarbons, (e.g., Freons), and decomposable agents such as nitroso, azo, hydrazide, azide, and borohydride compounds.

The exotherm step generates gas and yields the expanded structure, and the isocyanate reacts with water to form carbamic acid. This latter acid breaks down to give a primary amine and carbon dioxide gas (which acts as the blowing agent). Cross-linking can occur through the urethane linkages (to give what are called allophanates.). Such linking determines the characteristics of the foam — i.e., whether it is flexible, semirigid, or rigid.

4-8 VARIOUS EMBEDMENT MATERIAL — TYPICAL PROPERTIES OF AVAILABLE PRODUCTS

Tables 4-8 through 4-16 give properties of typical polyurethane products used in embedding, encapsulation, coating, etc.

4-9 COMMENTS ON POLYURETHANE REVERSION AND TOXICITY PROBLEMS

In the late 1960's, instances of polyurethane agents changing to a liquid form, known as reversion, were discovered on military electronic and electrical end items. Such reversion has been the result of hydrolytic attack during service. Since this time, a number of Department of Defense installations and laboratories have continued studies to evaluate and investigate this problem¹⁷⁻¹⁸

The investigations were centered on the general aspects of reversion; later studies were concerned with effects in specific uses in particular end items. Up to this time, investigations continue, particularly since newer types of urethanes are being developed and introduced to bypass certain problems of toxicity in using old standard reagents such as MOCA.

It had been found, earlier in the studies, that a number of common encapsulating compounds were subject to hydrolytic attack and reverted or

depolymerized in humid environments. Testing the materials for Shore A hardness periodically as they were aged at 95% RH at temperatures ranging from 50° to 97°C revealed that increasing the temperature accelerated the rate of degradation^{16,17}.

By using a Shore A hardness of less than one as the failure criterion in these tests on polymeric compounds, and plotting the failure times at different temperatures at 95% RH against the temperature in degrees Celsius on a semilogarithmic reciprocal temperature graph, it can be found that the plots are straight lines according to the Arrhenius model. Therefore, the failure times at lower temperatures — such as those found in normal service — could be extrapolated with reasonable confidence. Such a method is now described as a Standard Recommended Practice for *Determining Hydrolytic Stability of Plastic Encapsulants for Electronic Devices*, ASTM F 74-73.

It must be mentioned that under certain hot, humid conditions certain epoxy resins can undergo a reversion. It appears that the incidence of costly failure with epoxies will not approach the early catastrophic problems with the polyurethanes. Fairly recent work has been sponsored on detecting and defining water-induced reversion of epoxy and polyurethane embedding agents. Initial work has shown that chemiluminescence, infrared, and nuclear magnetic resonance methods can be used to delineate changes in epoxy and urethane systems which soften when subject to moisture and/or temperature. Measurements from these procedures give data which correlate with changes in the polymers as determined by weight gain/loss and hardness tests¹⁹

By spectroscopic data, chemical changes induced by moisture can be distinguished from chemical changes caused by temperature. Any of these changes can be differentiated from changes induced by a combination of moisture and temperature. The ability to relate the cause and type of chemical change within the context of hardness measurements indicates that specific chemical changes appear to be directly related to

**TABLE 4-8. PROPERTIES OF URETHANE CASTING/ENCAPSULATING ELASTOMERS
(SOURCE: HEXCEL CORP., REZOLIN DIVISION)"**

Property	Test Method	URALITE 3130 Value	URALITE 3127 Value	URALITE 3121S Value
Shore Hardness A/D	ASTM D 2240-68	80-85/25-30	no value/75	85-90/45-50
Viscosity, cP:	ASTM D2393-71			
Part A		3400	—	—
Part B		120	—	—
Mixed		2000	1050	2000
Tensile Strength, psi	ASTM D 412-68	2750	4500	5000
Elongation, %	ASTM D 412-68	250	80	300
Tear Strength, pli ^b	ASTM D 624-Die C	250	44s	400
Dielectric Strength, step at 25°C (77°F), V/mil	ASTM D 149-64	240	—	—
Dielectric Constant at 25°C (77°F), dimensionless:	ASTM D 150-54T			
103 Hz		7.2	—	—
10 ⁶ Hz		5.6	—	—
Volume Resistivity at 25°C (77°F) 1000 V, ohm•cm	ASTM D 257-70	1 x 10 ¹³	—	—
Surface Resistivity at 25°C (77°F) 1000 V, ohm	ASTM D 257-70	2 x 10 ³	—	—
Insulation Resistance at 25°C (77°F) after 28 days at 35°C (95°F) 95% RH, ohm	W.E. ATS 612	1 x 10 ¹¹	—	—
Pot Life at 25°C (77°F), min	ASTM D 2471-71	14	50	15
Shrinkage, in./in.	ASTM D 2566-69	0.0016	0.0015	0.003
Density ^c	ASTMD 792-66			
Cured Compound (sp. grav.)		1.079	1.162	1.107
Part A (sp. grav.)		1.028	—	—
Part B (sp. grav.)		1.096	—	—
Demolding Time, h:				
at 25°C (77°F)		4	24	5
at 70°C (175°F)		1	2	—
Complete Cure:				
at 25°C (77°F), day		2.4	4-7	2
at 79°C (175°F), h		2.3	—	—
Color		black	yellow, translucent	amber
Ratio, by weight:				
Part A		100	100	100
Part B		30	68	40
Ratio, by volume:				
Part A		100	—	—
Part B		28	—	—

^aOne or more of these three resins show low moisture sensitivity, excellent hydrolytic stability (reversion resistance), no TDI, no 4,4'-methyl-bis-(2 chloroaniline i.e., MOCA), very good electrical properties, low shrinkage, and low viscosity.

^bpli = pounds per linear inch

^cSpecific gravity of 1.000 = 1g/cm³ = 0.036 lb/in.³ (approx) = 8.3454 lb/gal = 62.247 lb/ft³.

the softening or reversion process. Further work is required to ascertain more completely the chemical changes directly related to the reversion, and which of the measurement techniques best characterizes the polymer softening and degradation.

MOCA, a chlorinated diamine, had been a highly accepted chain extending curing agent.

Also, this Du Pont material tended to be a required component in high performance polyurethane systems. The Department of Labor, through the Occupational Safety and Health Administration (OSHA), in 1974 issued a Standard on Carcinogens which, as presently interpreted, severely restricts the use of certain agents suspected of being an active carcinogenic.

**TABLE 4-9. PROPERTIES OF PERMANENT POLYURETHANE
ENCAPSULATING COMPOUND**

Example: *HEXCEL 185N* (used for encapsulating telecommunication cable, splicing, and to form moisture and gas pressure blocks in aerial and buried, plastic insulated cable.)

Property	Value	Test Method
Gel Time at 77°F, 1 lb, min	10	Rezolin Lab
Viscosity, mixture at 77°F, cP	2000	Brookfield
Maximum Exotherm at 77°F, °F	148	W. E. AT-8612
Moisture Absorption, 7 days immersion, 75°F, distilled water, %	1.1	W. E. AT-8612
Hardness at 77°F, Shore A	85	ASTM D 1706-61
Specific Gravity	1.07	ASTM D 792-66
NCO Content, %	6.8	Analytical
Apparent Free TDI, %	0	ASTM D 2615-70
Fungous Resistance	Does not support growth	MIL-E-5272C
Stress Cracking of Polyethylene	None	ASTM D 1693
Dielectric Strength, step at 77°F, V/mil	240	ASTM D 149-64
Dielectric Constant, at 77°F, dimensionless		ASTM D 150-54T
103 Hz	7.4	
10 ⁶ Hz	5.8	
Volume Resistivity, 1 kV at 75°F, ohm•cm	1×10^{13}	ASTM D 257-70
Surface Resistivity, 1 kV at 75°F, ohm	2×10^{13}	ASTM D 257-70
Insulation Resistance, ohm	2×10^{10}	W. E. AT-8612

This agent shows positive moisture/electrical/mechanical protection, fast curing, low exotherm, good hydrolytic stability (reversion resistance), good resistance to dry heat aging, low water absorption, fungous resistance, noncorrosivity, low moisture sensitivity, nonexpanding, reduced risk of latent compound shrinkage, excellent insulation, no free TDI content, transparency, flexibility, and toughness.

**TABLE 4-10. PROPERTIES OF RE-ENTERABLE POLYURETHANE
ENCAPSULATING COMPOUND**

Example: *HEXCEL 190 RE* (used for encapsulating telecommunication cable, etc.)

Property	Value	Test Method
Color	Clear, colorless	Visual
Viscosity, mixture at 75°F, cP	1600	Brookfield
Gel Time, 180 g, min		
at 75°F	25	W.E. AT-8612
at 110°F	9	
Peak Exotherm, 180 g, °F		
at 75°F	132	W.E. AT-8612
at 110°F	171	
Hardness at 75°F, Shore A	50	ASTM D 1706-61
Water Absorption at 75°F, %	0.59	ASTM D 543
Specific Gravity	1.06	ASTM D 792-66
Fungous Resistance	Does not support growth	ASTM G 21
Stress Cracking of Polyethylene	None	ASTM D 1693
Shrinkage, in./in.	0.002	ASTM D 2566-69
Volume Resistivity, 1 kV at 75°F, ohm•cm	6×10^{13}	ASTM D 257-72
Insulation Resistance, ohm	2.2×10^{12}	ASTM D 257-72
Mix Ratio, by weight	1 to 1	

This agent shows easy re-enterability, exclusion of moisture, crystal clear transparency, one-to-one mixing ratio (by weight), no attack on common cable and closure materials, no TDI content, no MOCA, nonexpansion, fungous resistance, noncorrosivity, low exotherm, and excellent insulation.

**TABLE 4-11. PROPERTIES OF PERMANENT POLYURETHANE ENCAPSULATING
AND GAS-BLOCKING COMPOUND**

Example: *HEXCEL 7200* (used for gas blocks in electrical and communication cable, encapsulation of splices and electrical/electronic components.)

<u>Property</u>	<u>Value</u>	<u>Test Method</u>
Color	Light Yellow, transparent	Visual
Hardness, Shore D	75	ASTM D 2240-68
Compressive Strength, psi	10,000	ASTM D 695-69
Tensile strength, psi	4,350	ASTM D 412-68
Elongation, %	50	ASTM D 412-68
Water Absorption, %	0.043	ASTM D 570-63
Shrinkage, in./in.	0.0015	ASTM D 2566-69
Dielectric Strength, V/mil	390	ASTM D 149-64
Dielectric Constant 10 ⁶ Hz, dimensionless	4.1	ASTM D 150-70
Dissipation Factor, dimensionless	0.017	ASTM D 150-70
Volume Resistivity, ohm-cm	3×10^{15}	ASTM D 257-66
Insulation Resistance, ohm	5×10^{15}	ASTM D 257-66
Mixed Viscosity, cP	1,700	ASTM D 2393-71
Pot Life at 77°F (25°C), min	50	ASTM D 2471-71
Peak Exotherm, °F	175	5 lb mass in 3 in. dia mold in 100°F environment
Ratios.		
By weight: Part A/Part B	100/86	
By volume: Part A/Part B	1/1	

This agent shows very good moisture/electrical/mechanical protection, excellent elongation and high strength for 75 Shore D elastomer, low viscosity, low water absorption, fungous resistance, noncorrosivity, long pot life, room temperature cure, excellent dielectric properties, no free TDI, no MOCA, and simple 1 to 1 by volume ratio mixing.

**TABLE 4-12. PROPERTIES OF POLYURETHANE CASTING COMPOUND
(MOCA-FREE; DEVELOPMENT PRODUCT) DUROMETER HARDNESS 90 A SCALE**

Example: *URALANE X-87665-A/B*, Furane Plastics Inc., Subs. of M & T Chemicals, Inc

<u>Tests</u>	<u>Results</u>	<u>Test Methods</u>
Viscosity, cP:		
Part A, 77°F	8000 ± 500	ASTM D-2393
Part B, 77°F	2000 ± 200	
Mixed, after 5 min, 90°F	15,000-18,000	
Density, g/cm ³ :		
Part A	1.07 ± 0.02	ASTM D-792
Part B	1.2 ± 0.02	
Durometer Hardness, A scale:		
at RT	90 (50D)	ASTM D-2240
at 200°F	50	
Tensile Strength, psi	7200	ASTM D-412
Elongation, %	490	ASTM D-412
Tear Strength, pli	570	ASTM D-624, Die B

Compound available in amber or black; pourable and curable at room temperature; high clarity when vacuum treated prior to casting; mix ratio 100 parts, by weight, A to 26 parts, by weight, B or B-40 (black); pot life 100 g — gel time 15 min at 77°F; cured at RT in 3 days; cured at 150°F in 2 to 3 h.

TABLE 4-13. PROPERTIES OF POLYURETHANE CASTING COMPOUND (MOCA-FREE; DEVELOPMENT PRODUCT) DUROMETER HARDNESS 77 A SCALEExample: *URALANE X-87645-A/B*, Furane Plastics Inc., Subs. of M & T Chemicals, Inc.

<u>Tests</u>	<u>Results</u>	<u>Test Methods</u>
Viscosity, cP:		
Part A, 77°F	8000 ± 500	ASTM D-2393
Part B, 77°F	2000 ± 200	
Mixed, after 5 min, 90°F	12,000-15,000	
Density, g/cm ³ :		
Part A	1.07 ± 0.02	ASTM D-792
Part B	1.2 ± 0.02	
Durometer Hardness, A Scale:		
at R T	77	ASTM D-2240
at 200°F	68	
Tensile Strength, psi	5290	ASTM D-412
Elongation, %	490	ASTM D-412
Tear Strength, pli	440	ASTM D-624
Taber Abrasion, weight loss, mg	94	Die B H22/ 1000/ 1000
Electrical Properties:		
Dielectric Constant/Dissipation Factor, dimensionless		
at 60 Hz	6.3/0.085	ASTM D-150
at 1 kHz	5.4/0.067	
at 10 kHz	5.0/0.047	
at 1 MHz	4.5/0.043	
at 10 MHz	4.2/0.044	
Volume Resistivity at R T, ohm•cm	2.0 X 10 ¹³	ASTM D-257

Compound available in amber or black; pourable and curable at room temperature; high clarity when vacuum treated prior to casting; mix ratio 100 parts, by weight, A to 22 parts, by weight, B or B-40 (black); pot life 100 g — gel time 25 to 30 min at 77°F; cured at R T in 3 days; cured at 150°F in 2 to 3 h.

TABLE 4-14. PROPERTIES OF FLEXIBLE POLYURETHANE CASTING COMPOUND (MOCA-FREE; DEVELOPMENT PRODUCT) DUROMETER HARDNESS 41 A SCALEExample: *URALANE X-87644-A/B*, Furane Plastics Inc., Subs. of M & T Chemicals, Inc.

<u>Tests</u>	<u>Results</u>	<u>Test Methods</u>
Viscosity, at 77°F, cP:		
Part A	4500 ± 500	ASTM D-2393
Part B	2000 ± 200	
Density, g/cm ³ :		
Part A	1.07 ± 0.05	ASTM D-792
Part B	1.2 ± 0.02	
Durometer Hardness, A Scale:		ASTM D-2240
at R T	41	
at 200°F	32	
Tensile Strength, psi	530	ASTM D-412
Elongation, %	330	ASTM D-412
Tear Strength, pli	70	ASTM D-624, Die B
Taber Abrasion, weight loss, mg	535	H22/ 1000/ 1000

Compound available in amber or black; can be cured at 70° to 80°F; mix ratio 100 parts, by weight, A to 70 parts, by weight B or B-40 (black); pot life 100 g — gel time 90 to 110 min at 77°F; cured at R T in 6 to 7 days; cured at 200°F in 2 h.

**TABLE 4-15. PROPERTIES OF REVERSION RESISTANT, LOW DUROMETER
POLYURETHANE ENCAPSULATING AND MOLDING COMPOUND — DUROMETER
HARDNESS 55-65 A SCALE**

Example: *URALANE 5753-A/B*, Furane Plastics Inc., Subs. of M & T Chemicals, Inc.

(A) Typical Handling Characteristics

Viscosity, at 23°C, cP	Part A	100	(clear liquid)	Typical Cure	6 h at 65°C + 24 h at 23°C
	Part B	20,000	(cream or black)	Schedule to Reach	or
				Minimum Shore A	16 h at 23°C to 85°C
				Hardness of 55	or
Mix Ratio	To 100 parts by weight of URALANE 5753-B, add 20 parts by weight of URALANE 5753-A				1 h at 95°C + 2 h at 150°C
					or
					48 h at Room Temp. (23°C)
Work Life, 23°C	Initial	20,000			For best properties, allow additional
(75°F) Viscosity, cP	30 min	50,000			2-3 days cure at Room Temp. (23°C)
	40 min	100,000			before testing.
	50 min	175,000			
				Typical Demold Time	00 min at 150°C
					75 min at 120°C
					90 min at 95°C

(cont'd on next page)

TABLE 4-15 (cont'd)

(B) Typical Properties (Specimens cured 16 h at 85°C plus 3 days at RT)					
Property	Results	Test Method	Property	Results	Test Method
Reversion Resistance		MIL-M-24041	Dissipation Factor, dimensionless:		
Insulation Resistance, 1000 megohms min	pass 1.4x10 megohms	(165°F/95% RH for 120 days)	1 kHz	0.021 0.024	ASTM D-150
Hardness (Shore A), max 20% loss	No loss		40 kHz at R T	0.025 0.030	
			100kHz at R T	0.019 0.024	
			1 MHz	0.025 —	
Shrinkage, max, %	3.0	MSFC-SPEC-202-A	Dissipation Factor after Humidity Aging (168°F/95%RH)		
Hardness, Durometer A	55 to 65	ASTM D-2240	After 3 days,		
Tensile Strength, psi	600	ASTM D-412	1 MHz at R T	0.020	ASTM D-150
Elongation, min, %	350	ASTM D-412	After 8 days,		
Tear Strength, (average), pli	130	ASTM D-624, Die B	1 MHz at R T	0.020	
Compressive Set (as cured), 70	30	FTMS 601, Method 3311	After 35 days,		
Peel Strength, to Steel with Primer A, lb/in.	30	MIL-M-24041, Amend. 1	1 MHz at R T	0.018	
Lap Shear, Al/Al, psi	600	ASTM D-1002	Volume Resistivity, ohm•cm		
Moisture Absorption, %	3.0	ASTM D-570	23°C	5.0 X 10 ¹⁶	ASTM D-257
Fungous Resistance	Non-nutrient	MIL-E-5272	125°C	1.5 X 10 ¹⁶	
Dielectric Strength, (1/8 in. thickness, V/mil)	350	ASTM D-149	After 13 cycles mois- ture conditioning per per MIL-STD-202D, Method 106, Tested at 23°C/92%RH	3.8 X 10 ¹⁵	
Dielectric Constant, dimensionless:	R T 200°F	ASTM D-150	Insulation Resistance, at 23°C, ohm	1.0 X 10 ¹⁶	ASTM D-257
1 kHz	3.2 3.6		Flame Resistance	No ignition	55 A dc, through embedded wire (#16) for 2.5 min 23°C
10 kHz	3.0 3.5				
100 kHz	3.0 3.0				
1 MHz	3.0 —				

Compound available in semitransparent or black; non-MOCA curable — exempt from OSHA Emergency Standard Title #29; low durometer suitable for flexible end items; no significant change in physical properties on exposure to high temperature/humidity, i.e., 95°C/98% RH; low dielectric constant, minimum stress on sensitive components; fast gel and cure for high production use. Possible end uses include cable/connector potting, wire wound device encapsulation, electronic module potting, and pressure sensitive component encapsulation.

TABLE 4-16. PROPERTIES OF POLYURETHANE CIRCUIT BOARD COATING

Example: *URALANE 5750 A/B*, Furane Plastics Inc., Subs. of M & T Chemicals, Inc.

(A) Typical Handling and Physical Characteristics				
<u>Property</u>	<u>Values</u>	<u>Property</u>	<u>Value</u>	<u>Test Method</u>
Viscosity, 25°C, cP:		Density, cured, g/cm ³	1.00 ± 0.003	ASTM D-792
Part A	35-100			
Part B	1500-2500	Durometer A Hardness	42-53	ASTM D-2240
Mixed	1000-2000			
Solids, %	84.5 ± 1.0	Tensile Strength, psi	700-1000	ASTM D-412
Mix Ratio, Part A to Part B	18/100	Tensile Strength, after 30 days at 100°C/98% RH, psi	900-1100	
Work Life, 25°C, cP:		Tensile elongation, %	250-360	ASTM D-412
after 1 h	2000-5000			
after 2-2.5 h	9000-30,000	Reversion Resistance, Durometer A Hardness:		
usable work life	—	after 50-h pressure cooker, 10-15 psi	40	
Time Required Before Applying Second Coat, min		after 30 days at 100°C 98% of RH	42	
65°C	75			
85°C	45			
95°C	30			
Cure (time at temperature), h:				
65°C	9			
85°C	8			
95°C	6			

(cont'd on next page)

TABLE 4-16. (cont'd)

(B) Typical Properties of Circuit Board Coating		
Property	Results	Test Method
Insulation Resistance, ohm		
Initial at 25°C	1.0×10^{15}	MIL-I-46058C*
at 65°C	1.0×10^{13}	
After 10 cycles	1.0×10^{10}	MIL-STD-202, Method 106
Volume Resistivity, at 25°C ohm•cm	1.0×10^{15}	ASTM D-257
Dielectric Constant/Dissipation Factor, dimensionless		
1 kHz, at 25°C	3.2/0.021	ASTM D-150
1 kHz, at 100°C	3.6/0.024	
Dielectric Strength, V/mil (5 mil specimen)	1500	ASTM D-149
Change in "Q" of circuit board after application of coating, 70	Less than 10 of all frequencies	MIL-I-46058C
Change in "Q" of circuit board after water immersion, 70	Less than 10 of all frequencies	MIL-I-46058C
Reversion Resistance		
Volume Resistivity, ohm•cm after 30 days 100°C/98% RH	1.0×10^{13}	MIL-I-46058C (ASTM D-257)
MIL-I-46058 Reversion Test	Passes	

*Insulation Compound, Electrical, Printed Circuit Assemblies

Coating available in transparent form; non-MOCA curable — exempt from OSHA Emergency Standard Title #29; shows excellent long-term stability under high humidity exposure; resilient throughout temperature range of -65° to +100°C; has good repairability; and has low modulus for minimum component stress.

MOCA, 4,4' methylene bis (2 chloroaniline) is one of these. MOCA had been specified as a curative in all the compounds qualified to MIL-M-24041, *Polyurethane Molding and Potting Compound, Chemically Cured*. Thus, it is easy to visualize that the problem of reversion resistance must be further checked as promising "nontoxic" substitutes for MOCA become available.

As a result of a suit, reported in early January 1975 — initiated in the US Court of Appeals for the Third Circuit, the Synthetic Organic Chemical Manufacturers Association, *et al.*, versus

Brennan (No. 74-1129) — the permanent standard for 4,4' methylene bis (2-chloroaniline) was remanded to the Secretary of Labor because of a procedural error in publishing the proposed standard. OSHA has started proceedings for publishing a new standard according to the procedures set forth in the Occupational Safety and Health Act; accordingly, some of the restrictions may be reinterpreted. Even so, there will still be a highly probable need for a substitute material not subject to handling, processing, or use restriction²³

REFERENCES

1. K. Cressy and R. McKinney, "New Materials for Urethane Encapsulation", National Electronic Packaging and Production Conference, (NEPCON), Long Beach, CA, 31 January - 2 February 1967, and New York, NY, 13-15 June 1967, *Proceedings of the Technical Program, Conference Sponsored by the Electronic Production and Packaging Magazine*, Chicago, IL, 363-6. 1967.
2. G. Magnus, R. A. Dunleavy, and F. E. Critchfield, "Stability of Urethane Elastomers in Water, Dry Air and Moist Air Environments", Meeting Division of Rubber Chemistry, *American Chemical Society*, San Francisco, CA, 3-6 May 1966.
3. F. H. Gahimer and F. W. Nieske, "Navy Investigates Reversion Phenomena of Two Elastomers", *Insulation*, 39-44 (August 1968).
4. F. H. Gahimer and F. W. Nieske, "Hydrolytic Stability of Urethane and Polyacrylate Elastomers in Humid Environments", *Journal of Elastoplastics* **1**, 266-80 (October 1969).
5. F. A. Leute, "Urethanes Made Stable at Elevated Temperature and Humidity", *Insulation*, 86-90 (August 1969).
6. P. A. House, "Hydrolytic Stability of Electrical Potting Compounds", Proceedings of National SAMPE Technical Conference — Aerospace Adhesives and Elastomers **2**, 609-42 (October 1970).
7. R. M. Houghton and D. A. Williamson, "Polyurethanes for Use in Adverse Environments", *Proceedings, Society of Plastics Engineers, 29th Annual Technical Conference*, Washington, DC, 31-3, 10-13 May 1971.
8. P. A. House, "Hydrolytic Stability of Electrical Potting Compounds", Proceedings, National SAMPE Technical Conference **2**, 609-42, Aerospace Adhesives and Elastomers, Dallas, TX (6-8 October 1970).
9. C. L. Gable, "Thermoplastic Polyurethanes", *Plastic Design and Processing*, 16-22 (May 1968).
10. T. C. Patton, "Fundamentals and Advances in Urethane Coating Technology", *Journal Paint Technology* **39** (September 1967).
11. S. L. Lieberman, *Production Development of Organic Non-flammable Spacecraft Potting, Encapsulating and Conformal Coating Compounds*, NASA-CR-134234, NASA-CR-134235, NASA-CR-134236, NASA-CR-134237, January 1974.
12. A. Rios, "Preparation of Urethane Elastomers for Encapsulation and Casting of Electrical Parts", *Journal of Elastoplastics* **2**, 247-56 (October 1970).
13. L. B. Jensen and H. P. Marshall, "Response of Some Polyurethanes to Humid Environment", *Proceedings: Compatibility of Propellants, Explosives and Pyrotechnics With Plastics and Additives*, Paper No. 111-E, Picatinny Arsenal,

REFERENCES (cont'd)

- Dover, NJ, 3-4 December 1974.
14. F. H. Gahimer and F. W. Nieske, "Testing the Hydrolytic Stability of Encapsulants", *Insulation/Circuits*, 15-23 (August 1972).
 15. F. H. Gahimer, "Hydrolytic Stability of Electrical Insulation Materials", *37th Society of Plastics Engineers Annual Technical Conference*, Montreal, Canada, 7-10 May 1973.
 16. F. O'Shaughnessy and G. K. Hoeschele, "Hydrolytic Stability of a New Urethane Elastomer", *Rubber Chemistry and Technology* **44**, 52-61 (March 1971).
 17. C. S. Schollenberger and F. D. Steward, "Thermoplastic Polyurethane Hydrolysis Stability", *Journal of Elastoplastics* **3**, 28-56 (January 1971).
 18. R. J. Jakobsen, P. A. Clarke, R. A. Markle, and G. D. Mendenhall, *Detection and Characterization of Water-Induced Reversion of Epoxy and Urethane Potting Compounds*, Battelle Columbus Laboratories for Naval Air Systems Command, Columbus, OH, August 1976.
 19. E. J. Eisenback, R. W. Burdick, and V. J. Gajewski, *Apocure 601 — Novel Curing Agent for Urethane Systems*, M & T Chemicals Inc., paper at the Polyurethane Manufacturers Association, November 1976.
 20. D. J. Caruthers et al., *Hydrolytic Stability of Adiprene L-100 and Alternate Materials*, Report BDX-6 13-1489, Bendix Corp., Kansas City, MO, August 1976.
 21. C. Nadler and R. Wieczorek, *Evaluation of the Electrical Properties of MOCA-free Polyurethane Potting and Molding Compounds*, Report NADC-75011-30, Naval Air Development Center, PA, April 1975.
 22. K. E. Creed, Jr., *Evaluation of Non-MOCA Polyurethane Elastomer Encapsulant*, GEPP-128 General Electric Co., St. Petersburg, FL, May 1974.
 23. E. H. Gahimer, "Evaluating the New Urethanes", *Bicentennial of Materials Progress, Proceedings of the 21st National Symposium and Exhibition*, SAMPE, CA, 286-97, April 1976.

CHAPTER 5

SILICONE EMBEDDING AGENTS

The chemical, physical, and electrical properties of silicones — room temperature vulcanates, one- and two-component flexible compounds, and rigid transfer molding compounds — together with the alteration of these Properties by curing agents/processes and the addition of fillers are given. Specific applications of the silicones to electrical/electronic components are presented. The basic chemistry of the silicones and some effects of structure are discussed.

5-1 GENERAL CHARACTERISTICS OF SILICONES

Silicones are marketed in forms as molding compounds, resins, elastomers, coatings, and greases. Processing applicable to electronic embeddings includes transfer molding, coating, impregnating, casting, foaming, and possibly laminating¹⁻³

Silicones are available as:

1. Room-temperature vulcanizates (RTV's)
2. One- and two-component flexible compounds
3. Rigid transfer-molding compounds.

Silicon elastomers have a sales volume of about 20 million pounds; these materials show a combination of properties that are unique. These properties are dependent upon the unusual molecular structure of the polymer, which consists of long chains of alternating silicon and oxygen atoms encased by organic groups. These chains have an organic-inorganic nature and, compared to organic rubber polymer chains, they have a large molar volume and very low intermolecular attractive forces. The molecules are unusually flexible and mobile, and can coil and uncoil very freely over a relatively wide temperature range. The most outstanding property is a very broad service temperature range that exceeds that of any other commercially available elastomer. Silicones can be compounded to perform for long periods at -150° to $+600^{\circ}$ F under static conditions⁴ and at -100° to $+500^{\circ}$ F under dynamic conditions^{4, 6}.

5-1.1 MECHANICAL AND ELECTRICAL PROPERTIES

The characteristics which make silicones highly suitable for high performance electronic or electrical use are their stability over a wide temperature range and the retention of very good electrical properties under extremes of environmental conditions. Resiliency is retained as low as -150° F (-100° C); mechanical and electrical properties are not degraded at continuous temperatures of 500° F (260° C) and short-term temperatures up to 600° F (315° C). Silicones are classified as Class H insulation (safely used to 356° F (180° C) for a long time, i.e., 5 to 10 yr service). Prior to the use of silicones, electrical item temperature use was limited to 266° F (130° C) (Class B, maximum operating temperature). The

TABLE 5-1. SALIENT PROPERTIES OF SILICONES

Heat Resistance — stable to approximately 600° F (highest with glass, mica, asbestos, fillers, etc.); little or no flammability; long time service is from about 400° to 500° F.

Cold Temperature — service to approximately -100° F.

Electrical Properties — very high dielectrics (also after cyclic exposure to humidity/elevated temperatures); low power factor in very wide frequency range; molded surfaces have little tendency to track (carbon-type conduction from heat or arcing defect).

Chemical/Water Resistance — water repellent; weather resistant; little or no degradation with weak acids or weak alkalies; slight to severe reaction with strong acids or strong alkalies; insoluble in most organic solvents but swelled by some agents.

use life of silicone insulated equipment at the 266°F (130°C) range is relatively unlimited (beyond 40 yr) — see Fig. 5-1.

Young's modulus of an extreme low temperature silicone rubber shows very little change down to -100°F, (-73°C) and eventually reaches 10,000 psi at -150°F (-100°C). The tensile strength, measured at room temperature, is less than that of most organic rubbers; however, it is superior when measured at 400°F (204°C). Also, at 400°F, the silicone rubber has an estimated useful life of the order of 10 yr, while most organics will fail within a few days. Silicone rubber will maintain its elastometric properties almost indefinitely at moderately elevated temperatures. Life of elastic properties has been estimated at 5 to 10 yr at 300°F (149°C), and 10 to 20 yr at 250°F (121°C). As an example, silicone rubber performs unusually well when used as a gasket or O-ring in sealing applications. Over the

entire temperature range of -120° to +500°F, (-84°C to +260°C) no available elastomer can match its low compression set⁷.

Fig. 5-1 shows insulation class versus life expectancy.

The electrical characteristics of silicones are much better than those of other conventional polymer types (including epoxies). Dielectric constants (at 25°C and 100 Hz) for most commercial materials lie in the short range of 2.8 to 3.8. Very little changes in dielectric constant or dissipation factor are caused by higher frequencies, temperatures, or humidities'. Value can even decrease with a temperature rise. The k-value for Dow Corning's Sylgard 183 drops from 3.3 (75°F) to 2.6 (392°F).

Table 5-2 shows data on typical Dow-Corning KTV silicones.

Table 5-3 gives information on typical General Electric RTV silicones.

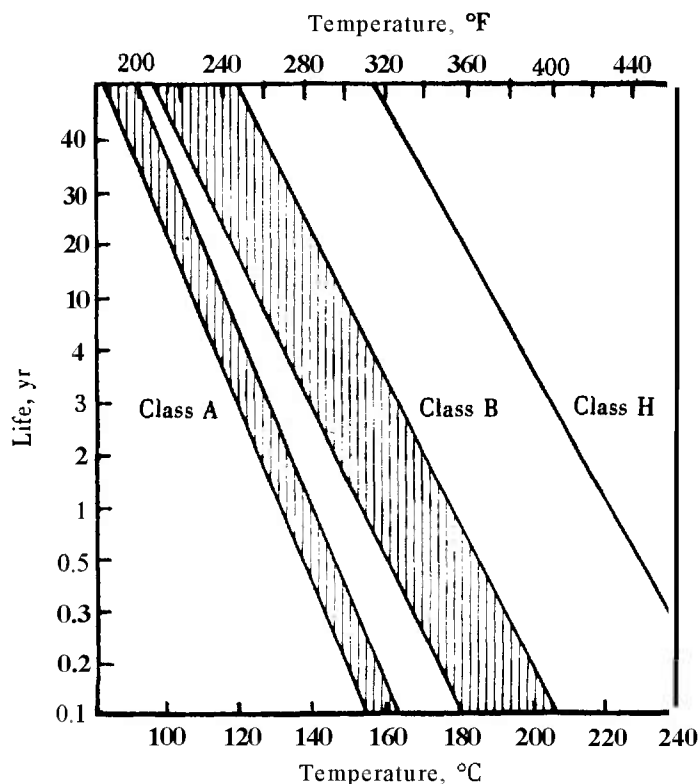


Figure 5-1. Comparable Life (yr) vs Temperature for Various Classes of Insulation

TABLE 5-2. DATA ON SOME DOW-CORNING RTV SILICONES

Property \ Silicone	DC-3110	DC-3116	DC-3120	DC-3140
Viscosity at 25°C, cP	12,500	50,000	30,000	66,000
Specific gravity at 25°C	1.1	1.13	1.47	1.09
Pot Life, h	3	3	3	0.5-1
Cure Schedule	24 hat 25°C	24 hat 25°C	24 hat 25°C	24 hat 25°C
Radiation Resistance (Cobalt-60 Source), rad	10 ⁸	10 ⁸	10 ⁸	—
Water Absorption in 7 Days at 25°C, %	0.4	0.4	0.2	0.05
Thermal Conductivity cal/s•cm ² •°C•cm ⁻¹	5 × 10 ⁻⁴	5.2 × 10 ⁻⁴	7.7 × 10 ⁻⁴	2.91 × 10 ⁻⁴
Weight Loss in 96 h at 200°C, %	6	6.3	5.7	—
Arc Resistance, s	90	90	125	50
Dielectric Constant, dimensionless				
10 ² Hz	3.0	3.0	3.8	2.9
10 ⁶ Hz	2.9	2.9	3.7	2.9
10 ⁸ Hz	2.89	2.89	3.50	—
Dissipation Factor, dimensionless				
10 ² Hz	0.012	0.015	0.030	0.003
10 ⁶ Hz	0.003	0.005	0.003	0.003
10 ⁸ Hz	0.006	0.006	0.004	—
Dielectric Strength (62-mil thickness), V/mil	600	600	550	500

5-1.2 SILICONE RESISTANCE TO THERMAL AGING AND OTHER HARSH EXPOSURES

Silicones can be aged at 300°C for 1000 h with no significant change in dielectric constant. Dielectric breakdown voltages are high, 500 to 2000 V/mil (a function of the compound and film thickness). Volume resistivities of at least 10¹² ohm•cm are retained^{9,10}— see Fig. 5-2.

Many types of wire and cable and other electrical equipment are insulated with silicone rubber because its excellent electrical properties are maintained at elevated temperatures. Even when

the insulation is exposed to a direct flame, it burns to a nonconducting ash; this ash continues to function as insulation in a suitably designed cable. The ozone and corona resistance of silicone rubber is outstanding, approaching that of mica. These properties are important in many electrical applications, and in exposure to outdoor weathering.

Many samples of elastometric silicones have been exposed to outdoor weathering for 15 yr with no significant loss of physical properties. This demonstrates unique resistance to temperature extremes, sunlight, water, and ozone and other

**TABLE 5-3. DATA ON SOME
GENERAL ELECTRIC RTV SILICONES**

P—Silicone	RTV-11	KTV-60
Viscosity at 25°C, cP	12,000	55,000
Specific Gravity at 25°C	1.18	1.45
Pot Life, h	1-4*	1-2
Cure Schedule	72 h at 25°C	72 h at 25°C
Water Absorption in 7 Days at 25°C, %	0.038	0.04
Thermal Conductivity, cal/s·cm ² ·°C·cm ⁻¹	6.9 × 10 ⁻⁴	7.5 × 10 ⁻⁴
Weight Loss in 96 h at 200°C, %	3.47	2.5
Arc Resistance, s	no arcing	no arcing
Dielectric Constant, dimensionless		
60 Hz	3.6	4.0
10 ⁶ Hz	3.4	3.7
Dissipation Factor, dimensionless		
60 Hz	0.019	0.020
10 ⁶ Hz	0.005	0.003

*Pot life is a function of hardener type and percent.

gases. The rubber will not support fungous growth if properly cured, and it has good resistance to the low concentrations of acids, bases, and salts normally found in surface water. It has been estimated that a silicone elastomer will last in excess of 30 yr under weathering conditions that would cause the best organic rubbers to fail within a few years. Silicone rubber is odorless, tasteless, and nontoxic. When properly fabricated, it does not stain, corrode, or in any way deteriorate materials with which it comes in contact".

5-1.3 APPLICATIONS

Because of its exceptional mechanical and electrical performance under extreme temperature conditions, silicone rubber is widely

used in hundreds of commercial and military applications¹². In many uses, its inertness, non-toxicity, ease of processing, and resistance to ozone and weathering are also of critical importance. The following typical applications, listed by industry, show the versatility of this unique specialty elastomer:

1. Aerospace :

- Hot air ducts (for de-icing, cabin heating, etc.)
- Dust shields and limit switch boots
- O-rings, seals, and gaskets for lubricating and hydraulic systems
- Airframe and spacecraft body sealants
- Aircraft and missile wire insulation.

2. Automotive Industry :

- Spark plug boots
- Ignition cable jacket
- Sealants
- Hose.

3. Appliances :

- Oven door and washer-dryer gaskets
- Seals, gaskets, and insulation in steam irons, frying pans, coffee makers, etc.

4. Electrical Industry:

- Capacitor bushings
- Rubber coated glass sleeving
- Rubber tubing
- Electrical potting, impregnation, and encapsulation
- Unsupported and cloth supported electrical insulating tapes
- Apparatus lead wire
- Appliance and fixture wire
- Electronic hook-up wire
- Nuclear power cable.

5. Miscellaneous :

- Construction sealants for expansion joints and glazing applications
- Weather coatings (wall, roof, and deck)
- Rubber rolls
- Sponge
- Flexible mold fabrication
- Prosthetic devices.

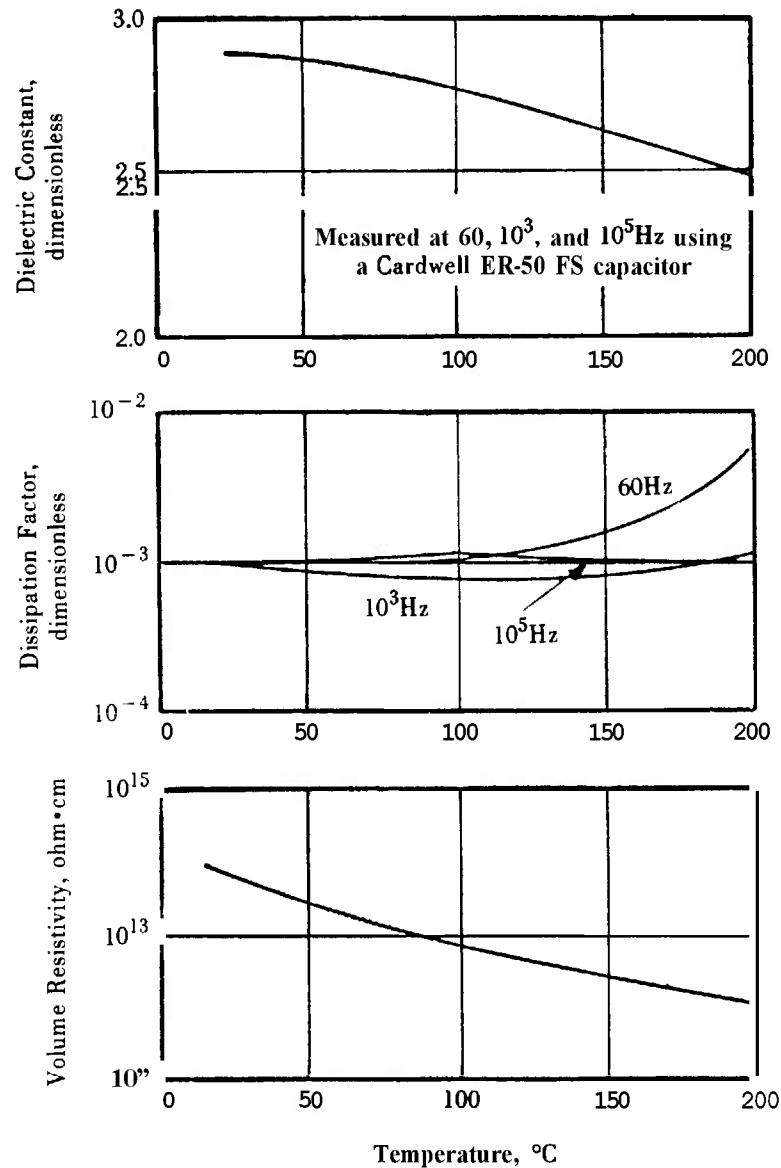
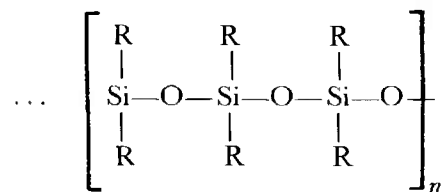


Figure 5-2. Properties of Dow-Corning Sylgard® 182 Resin vs Temperature

5-2 BASIC CHEMISTRY OF SILICONES; SOME EFFECTS OF STRUCTURE

Silicones are organopolysiloxanes; the primary chain is composed of alternating silicon and oxygen atoms (similar to the inorganic quartz or mica), i.e.,



The R groups can be methyl, vinyl, or phenyl. The length of the . . .Si-O . . . chain (and molecular weight) may be from a few to several thousand atoms.

The synthesis of polydimethylsiloxane usually involves the direct process for manufacture of the intermediate dimethyldichlorosilane from methyl chloride and elemental silicon¹⁸, i.e.,

1. $\text{SiO}_2 + 2\text{C} \rightarrow \text{Si} + 2\text{CO}$
2. $\text{CH}_3\text{OH} + \text{HCl} \rightarrow \text{CH}_3\text{Cl} + \text{H}_2\text{O}$
3. Direct Process

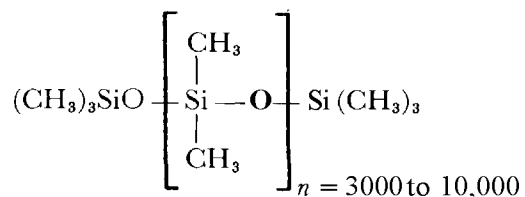
$$2\text{CH}_3\text{Cl} + \text{Si} \xrightarrow[\text{catalyst}]{\text{heat}} (\text{CH}_3)_2\text{SiCl}_2$$

Though it is possible to direct this reaction to produce large amounts of the dimethyldichlorosilane, a mixture of silanes is actually formed. The desired product must be distilled from the reaction mixture.

4. $(\text{CH}_3)_2\text{SiCl}_2 + 2\text{H}_2\text{O} \rightarrow (\text{CH}_3)_2\text{Si}(\text{OH})_2 + 2\text{HCl}$

The dimethylsilanediol is not stable, and it continues to condense, with the evolution of water, to form a mixture of linear and cyclic polydimethylsiloxanes of relatively low molecular weight. The cyclic siloxanes are separated, and then polymerized to high molecular weight by heat in the presence of acidic or basic catalysts.

The resulting polymer, used in the commercially available silicone elastomers, is a very high viscosity fluid or gum which is composed mainly of linear polydimethylsiloxane chains. The commercial gums usually contain between 3000 and 10,000 dimethyl siloxy units in the average chain, i.e.,



These polymers have essentially the most probable molecular weight distribution, although this can vary with the purity of the monomers.

If less than one half of one percent of the methyl groups are replaced by vinyl groups ($-\text{CH}=\text{CH}_2$), the resulting polymer makes more efficient use of peroxide vulcanization agents, requires less peroxide for cure, and forms a vulcanizate that is more resistant to the rearrangements that cause reversion and high compression set. As a consequence, nearly all commercial gums and compounds now contain the vinyl modified polymers.

Dimethyl silicone rubber tends to become stiff below -60°F . However, the low temperature flexibility may be improved by substitution of phenyl ($-\text{C}_6\text{H}_5$) or ethyl ($-\text{CH}_2\text{CH}_3$) groups for some of the methyl groups attached to the silicon atoms in the polymer chain. Replacement of only 5 to 10% of the methyl groups by phenyl groups will lower the crystallization temperature and extend the useful service temperature range to below -130°F .

The dimethyl elastomers swell more in aliphatic and aromatic hydrocarbons than they do in acetone and diesters. This performance can be reversed by the replacement of one methyl group on each silicon atom by a more polar group. Available polymers of this type contain the trifluoropropyl group ($-\text{CH}_2\text{CH}_2\text{CF}_3$) (Ref. 14). These polymers have a brittle point of -80° to -90°F .

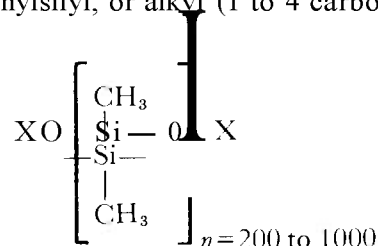
5-3 ROOM TEMPERATURE VULCANIZED (RTV) SILICONE ELASTOMERS/COMPOUNDS

Patent references to the RTV liquid silicone agents appeared in the mid 1960's. Since that time, the applications and technology have developed to where RTV materials represent a substantial part of the total silicone polymer market. These products are fairly complex to make though the basic techniques are defined". A great deal of the compounding and packaging processes are proprietary to the basic suppliers. RTV compounds are sold as ready-to-use products.

The liquid rubber compounds are based on low molecular weight silicone polymers with reactive end groups. As with the high molecular

weight heat cured silicones, some of the methyl groups can be replaced by phenyl groups for better low temperature flexibility. Substitution of the methyl with trifluoropropyl groups gives improved resistance to jet fuels.

The reactivity of the end group depends upon the cure system; X is generally hydrogen, dimethylvinylsilyl, or alkyl (1 to 4 carbon atoms).



Resin molecular weight depends upon the filler and plasticizers employed. The viscosity of the finished compound is a function of the polymer molecular weight, and the type and amounts of fillers and other added components. Typically, compounding agents include the usual reinforcing and extending fillers, color pigments, and heat aging additives. Thickeners, plasticizers, and other additives enhancing or modifying the RTV systems are used. The patent literature on room temperature vulcanization of silicone is quite broad in scope. Such vulcanization can be attained by the addition of low molecular weight polyfunctional silicone or silicate curing agents which are reactive with the polymer end groups at room temperature. A vulcanizing catalyst is also usually needed^{16,17}.

The unique curing system for the RTV rubbers can be one of three general classifications. These are condensation-cure/moisture independent) condensation-cure/moisture dependent, and addition cure. Each curing system is discussed in the paragraphs that follow.

Liquid metal soaps are conventional catalysts used in the curing of RTV silicones. Some of these are:

1. Dibutyltin dilaurate—
M&T Chemical's Thermolite-12
2. Stannous octoate—
Nuodex's Silicure T-773 or Nuocure-28

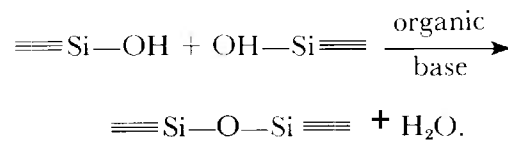
3. Lead octoate—

Nuodex's Silicure L-24

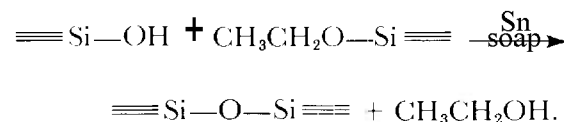
Catalyst concentrations used are of the order of 0.1 to 1.0%

5-3.1 RTV CONDENSATION-CURE/ MOISTURE INDEPENDENT

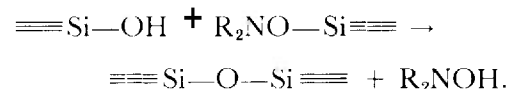
With such systems, the reactive end group is usually silanol, ($\equiv \text{Si}-\text{OH}$). The curing agent requires a functionality equal to or greater than 3. This crosslinker can be a silanol-containing silicone. In this case, an organic base can be used as a condensation catalyst. The reaction is schematically as follows:



An alkoxy type crosslinker, e.g., ethyl o-silicate, requires a tin-soap catalyst.



A catalyst is not absolutely required when polyfunctional aminoxy silicon compounds are used as crosslinkers:



RTV materials with these or related curing systems will cure in deep sections. Curing occurs independently of atmospheric moisture. These RTV products are known as "two-part RTV's". The curing agent with or without catalyst must be added prior to use.

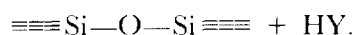
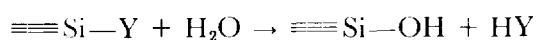
Applications include encapsulants, coatings, adhesives, medical or therapeutic gels, and molds for plastic parts. Typical physical property ranges of "two-part" or ("two-package") materials are given in Table 5-4.

TABLE 5-4. PROPERTY RANGES OF TWO-PART ROOM TEMPERATURE VULCANIZING (CONDENSATION-CURE/MOISTURE INDEPENDENT) SILICONES

Property	Value
Hardness, Shore A	15-70
Tensile Strength, psi	200-900
Elongation, %	100-800
Tear Strength, (Die B), pli	15-125

5-3.2 RTV CONDENSATION-CURE/MOISTURE DEPENDENT

With certain of these RTV compounds, a polyfunctional silicon-containing curing agent may be added to the compound; the compound contains a silanol terminated polymer. Others are made by compounding a polymer that is end-stopped with the curing agent. In most cases, a condensation catalyst is also added. Condensation cure occurs when the compound is exposed to moisture. Vulcanization takes place first at the surface and progresses inwardly with the diffusion of moisture into the rubber. With a polymer end-stopped with a curing agent, the reaction is:



(Y is one of the reactive groups on the curing agent which terminates the polymer chain.)

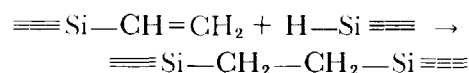
A wide variety of polyfunctional silicon containing curing agents can be used in designing curing systems of this type. Useful reactive functional groups include acryloxy, alkoxy, amino, ketoximo, aldoximo, and amide. These generally require the use of a condensation catalyst.

Moisture dependent RTV compounds are known as one-package RTV's. The curing agent

and catalyst are incorporated in the base compound at the time of manufacture. Main applications are in the areas where deep section cure is not needed. These products are excellent adhesive sealants; they can be used for form films from solvent dispersion. Excellent physical properties are obtainable with their use, as indicated in Table 5-5.

5-3.3 ADDITION CURE

Such a system involves the metal ion-catalyzed addition of a polyfunctional silicon hydride cross-linker to a dimethyl-vinylsiloxyl terminated polymer:



Cure occurs without evolution of volatile by-products and without depending upon air or atmospheric moisture. The products are suitable for deep section cures in a confined space. They show excellent resistance to compression set and to reversion (even when subject to high pressure steam). The properties shown in Table 5-6 are typical.

Addition cure products generally are sold as two-package RTV's, but a one-package system is possible with the use of an inhibitor. Here, the inhibitor can be volatilized or deactivated by heat in order to allow curing to occur. Applications include flexible molds, dip coating and potting, or encapsulation of electrical and electronic components.

**TABLE 5-5
PROPERTY RANGES OF ONE-PART RTV
(CONDENSATION-CURE/MOISTURE)
DEPENDENT SILICONES**

Property	Value
Hardness, Shore A	15-50
Tensile Strength, psi	200-900
Elongation, %	150-900
Tear Strength, (Die B), pli	25-150

TABLE 5-6
PROPERTY RANGES OF TWO-PART RTV
(ADDITION CURE/MOISTURE
INDEPENDENT) SILICONES

Property	Value
Hardness, Shore A	30-60
Tensile Strength, psi	600-800
Elongation, %	100-400
Tear Strength, (Die B), pli	50-120

The cure rate and physical properties of the various RTV compounds can be modified over a fairly wide range by proper choice of polymer type and molecular weight, filler, curing agent, and different concentration of catalysts.

5-4 HEAT VULCANIZED SILICONE ELASTOMERIC COMPOUNDS

5-4.1 GENERAL

Silicone elastomer compounds are generally cured with heat^{17,18} and the use of one or several of the organic peroxides shown in Table 5-7. Other peroxides are used, but the first four are the most important. In the cure of a dimethyl polymer with a diaroyl peroxide, the following seems to be a well-delineated cure mechanism:

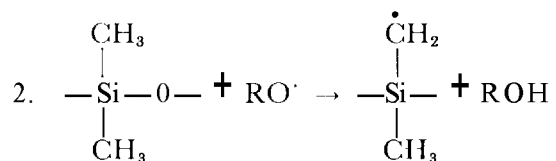
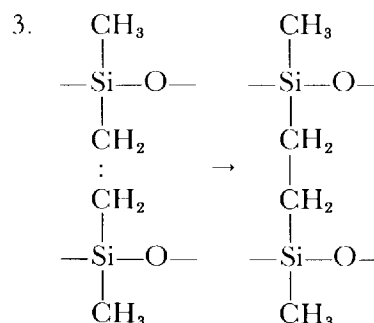


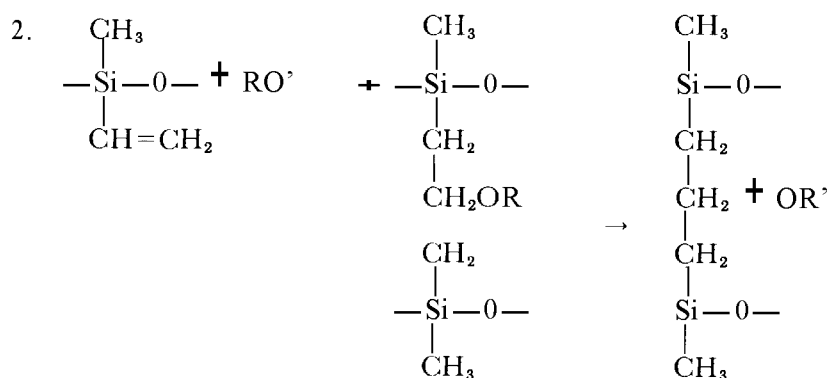
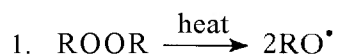
TABLE 5-7. ORGANIC PEROXIDES
USED FOR
SILICONE RUBBER VULCANIZATION

Peroxide	Temperature for Half Life of 1 min, 0°F
Bis (2,4)-dichlorobenzoyl peroxide	234
Di-benzoyl peroxide	271
Dicumyl peroxide	340
2,5-dimethyl-2,5 bis (t-butyl peroxy) hexane	354
Di-tertiary butyl peroxide	379



These reactions can produce no greater than one mole of chemical crosslinks per mole of peroxide. The hydrogen removal reaction is about 50% efficient; the ethylene bridging is about 40% efficient. The actual crosslink yield in an unfilled resin is 0.1 to 0.3 moles of crosslinking per mole of diaroyl peroxide. This is a crosslink density C_c of 0.6 to 1×10^{-5} mole per gram of polymer. It is not considered feasible to increase the crosslinking further by raising the concentration of peroxide in the resin system.

With methyl vinyl siloxy type copolymers, the cure mechanism is not well defined. A possible mechanism is shown:



3. Additional cure steps followed by termination.

This predicts more than 1 mole of crosslinks per mole of peroxide, and not more than 1 mole of crosslinks per mole of vinyl groups.

With unfilled methyl vinyl siloxy containing copolymers, actual crosslink yields have also been measured. Data on a polymer with Vi/Si = 0.0026 are shown in Table 5-8. Efficiencies are high, and these results are consistent with the "trimethylene bridge" cure mechanism.

The following are considered to be "vinyl specific)" in that good cures are obtained only with vinyl containing polymer:

1. 2,5 dimethyl-2,5-bis(t-butyl peroxy) hexane
2. dicumyl peroxide
3. di-t-butyl peroxide.

TABLE 5-8. CROSSLINKING EFFICIENCY
Polydimethylmethylvinylsiloxane (Vi/Si = 0.0026)

Peroxide	% Peroxide (Optimum Level), %	Moles Chemical Crosslinks per Gram Polymer $\times 10^{-5}$	Moles Chemical Crosslinks per Mole Peroxide	Moles Chemical Crosslinks per Mole Vinyl
2,5-dimethyl-2,5-bis(t-butyl peroxy) hexane	0.315	3.2	3.2	0.9
Dicumyl peroxide	0.315	3.3	3.0	0.9
Di-t-butyl peroxide	0.21	3.3	2.4	0.9

5-4.2 PEROXIDE CURING AGENTS FOR SILICONES — ADDITIONAL DETAILS

The two peroxides, benzoyl and bis(2,4-dichlorobenzoyl), cure both vinyl and nonvinyl containing silicones. This is shown in Fig. 5-3. Di-tertiary butyl peroxide is truly vinyl specific since the chemical crosslink density is constant in the 0-2 to 6% peroxide range. However, crosslink density depends upon peroxide concentration with use of bis(2,4-dichlorobenzoyl) peroxide^{18,19}.

Fig. 5-4 gives additional information on the effect of vinyl on cured vulcanizate properties. By use of 1.95×10^{-5} mole of bis(2,4-dichlorobenzoyl) peroxide per gram of polymer, the crosslink per gram of polymer is 0.6×10^{-5} mole. Doubling the peroxide concentration increases crosslinking to 0.74×10^{-5} mole; a density of 2×10^{-5} mole is obtained by adding 0.2 mole % of methyl vinyl siloxy units to the polymer. Thus, with a vinyl containing resin, it is possible to attain a higher level of primary valence crosslinking than with a nonvinyl containing silicone gum.

Also, this can be done with lower concentrations of peroxide. Since there are more bonds to be broken, a "tight" network should show less tendency to revert than a lightly formed one — particularly if the concentration of acidic peroxide decomposition products, which can degrade the polymer, has been significantly reduced. Compounds containing the methyl vinyl copolymers do show improved vulcanization characteristics, less tendency to revert in cure or post bake, and lower compression set at elevated temperatures.

Vulcanization rates can be studied with the Monsanto Rheometer. This apparatus provides a measure of dynamic shear modulus while the elastomer is cured in a mold under pressure and heat. Torque is measured on a conical disk rotor that is embedded in the rubber, and is being sinusoidally oscillated through a small arc. Torque is a linear function of crosslink density as determined by swelling measurements; the proportionally constant varies with the stock. The torque readings can be considered as relative crosslink densities. From a rheograph, it is possible to get an idea of how the compound will flow

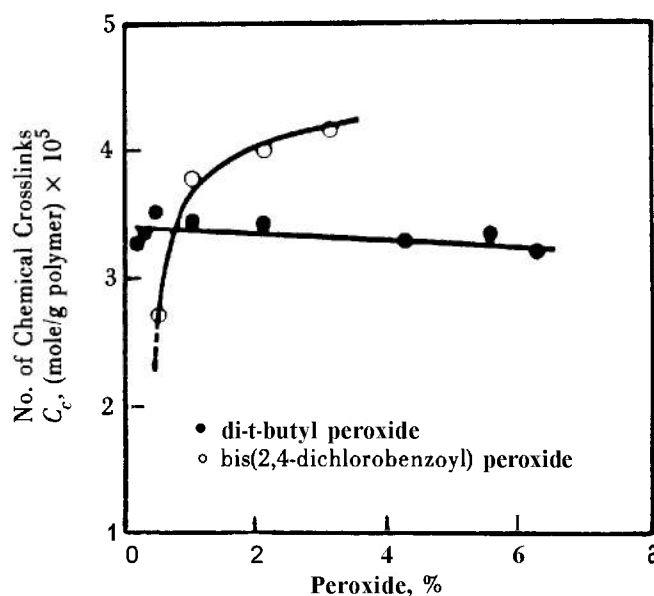


Figure 5-3. Variation of Chemical Crosslink Density With Peroxide Concentration (○, bis(2,4-dichlorobenzoyl) peroxide. ●, di-t-butyl peroxide.)

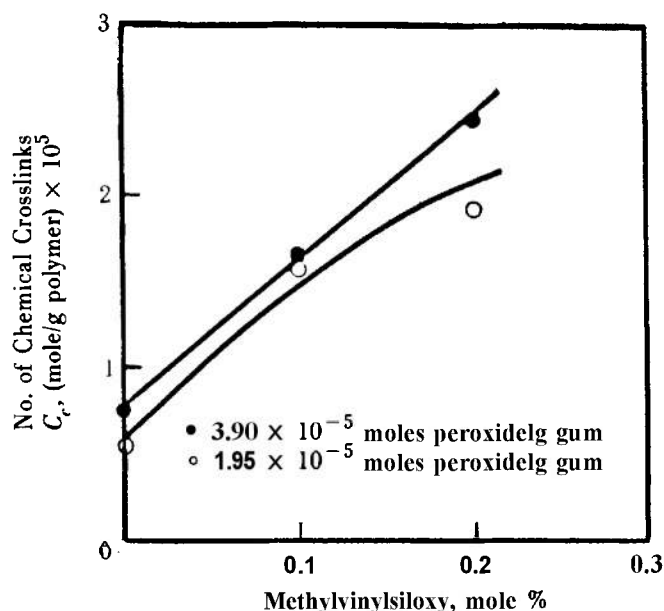


Figure 5-4. Variation of Chemical Crosslink Density With Vinyl Level and Concentration of Bis(2,4-dichlorobenzoyl) Peroxide (○, 1.95×10^{-5} moles peroxide/g gum. ●, 3.90×10^{-5} moles peroxide/g gum.)

in the mold before cure starts (minimum viscosity and scorch time), cure rate (and consequently time to various degrees of cure), and a measure of the final crosslink density. If a series of these curves is run at different temperatures with the various peroxides, the data may be used to estimate hot mold residence times required to effect a given degree of cure at a given temperature with a given peroxide. Figs. 5-5, 5-6, and 5-7 can be used to make close estimates for vulcanization of high tear strength methyl vinyl compounds.

With bis(2,4-dichlorobenzoyl) peroxide at 0.65 phr, and at a temperature of 230°F, the induction period is 2 min. The hot mold residence time is 4 min for 90% cure, and 8 min for full cure. A technically sound cure (in terms of durometer, tensile strength, and elongation) is obtained by introduction of 90% of the crosslinks; however, a full cure is required to obtain the lowest compression set.

In order to obtain full cure in 8 min, the mold temperature should be 230°F for bis(2,4-

dichlorobenzoyl) peroxide; 270°F for benzoyl peroxide; 255°F for dicumyl peroxide; and 365°F for 2,5-dimethyl-2,5-bis(t-butyl peroxy) hexane.

Because of the relatively high volatility of its decomposition products, benzoic acid and benzene, external pressure is needed to prevent porosity when compounds are cured with benzoyl peroxide. However, external pressure is not required with very thin sections, e.g., in tower coating of fabrics from solvent dispersions of silicone rubber. For fabric coating, benzoyl peroxide generally is preferred because it has long shelf life in the dip tanks; also, it is not volatilized from the silicone during the solvent removal operation prior to cure.

Low compression set rubber can be made with either the dichlorobenzoyl or benzoyl peroxide. For this, the polymer must contain vinyl groups; the acidic decomposition products are removed in a post cure bake cycle. The aroyl peroxides are not suitable for curing silicones containing carbon black; however, the "vinyl specific" peroxides can

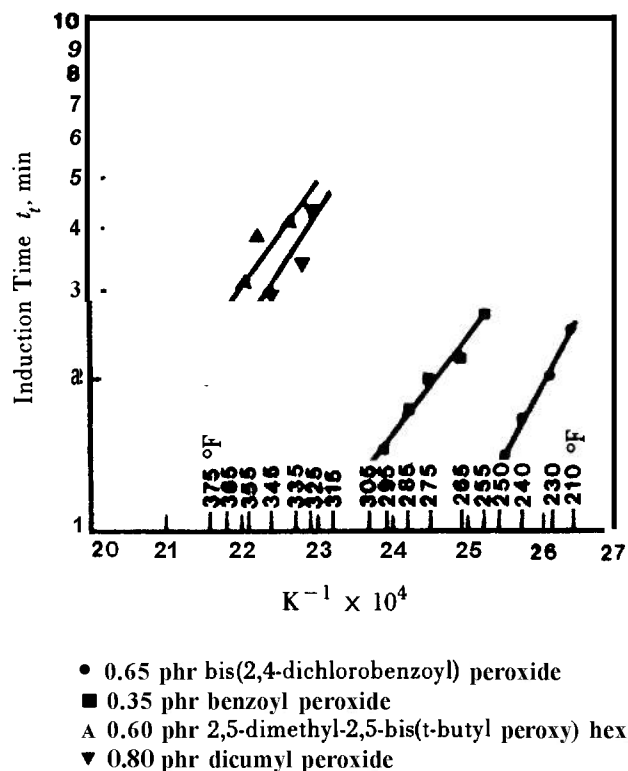


Figure 5-5. Induction Times for Cure With Various Peroxides

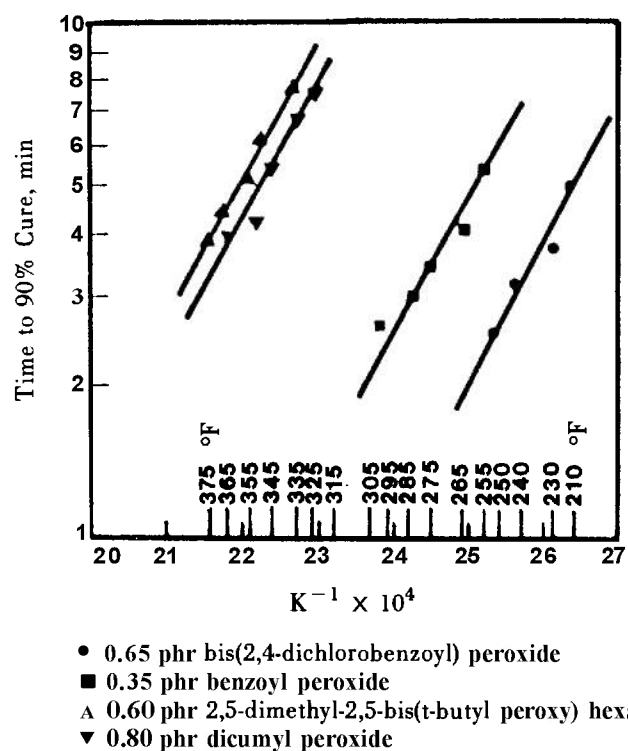


Figure 5-6. Time to 90% Cure With Various Peroxides

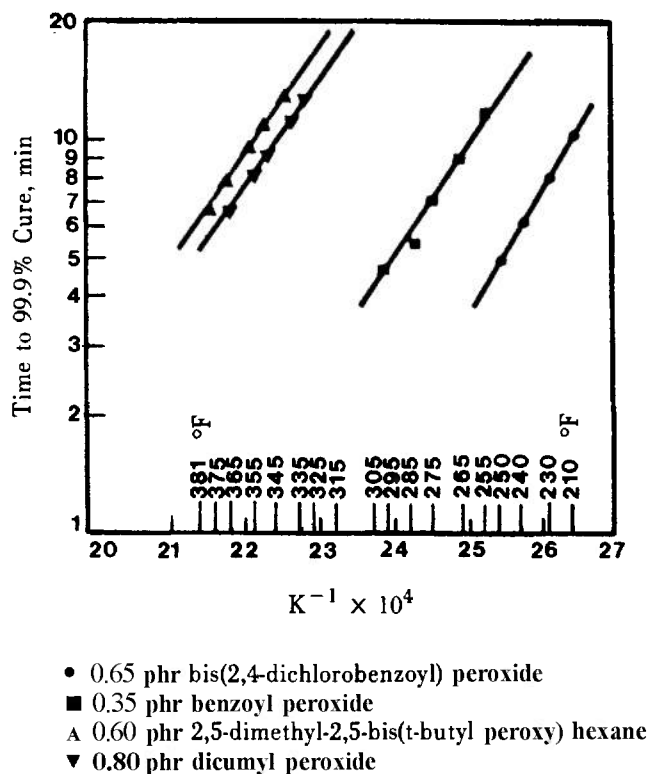


Figure 5-7. Time to Full Cure With Various Peroxides

be used to vulcanize stocks filled with carbon black. When using dicumyl peroxide, such compounds can be vulcanized by use of hot air.

The three "vinyl specific" peroxides are suitable for thick section molding. Dicumyl peroxide shows a slight tendency to be inhibited by air and for this reason is less preferred as a curing agent. Also, dicumyl peroxide has decomposition products which are slightly less volatile (acetophenone and α , α -dimethylbenzyl alcohol) than the decomposition products of the other two agents. External pressure during cure is less important but is still needed. Longer oven post bakes are required for thick sections than in the case of the other two peroxides. As with the diaryl peroxides, optimum properties necessitate close control of the dicumyl peroxide concentration.

Since the decomposition products are not acidic, the "vinyl specific" peroxides require less post bake after vulcanization. In addition, closely programmed post bakes are not required. Lower

compression set is obtained with these agents than with the general purpose curing agents. When vulcanizing with di-t-butyl peroxide, external pressure is always required since the peroxide as well as its decomposition products (acetone and methane) is highly volatile. The extent of cure is determined primarily by the vinyl content of the polymer and not by the peroxide concentration. Air inhibition is not observed. Pre-vulcanization or scorch never occurs. The harmless decomposition products can be removed by short, high-temperature oven post bakes. This peroxide produces a rubber with the best overall balance of properties. The main problem exists with its extreme volatility. A stock must be molded with external pressure shortly after the di-t-butyl peroxide has been added.

Though the final elastomer is not generally as good in balance of properties, the agent, 2,5-dimethyl-2,5-bis(t-butyl peroxy) hexane is very similar to d-t-butyl peroxide in performance. This

agent has the advantage of lower vapor pressure at room temperature. It can be added to a silicone compound 1 or 2 mo before vulcanization. But, external pressure is still needed during cure to the relatively high volatility of its decomposition products²⁰.

In actual use, none of the six commonly favored peroxides is considered a universal curing agent. The three aryl peroxides, shown in Table 5-9, are general purpose in that they can cure both nonvinyl and vinyl containing silicones. No one of them is suitable in all types of fabrication procedures. The three dialkyl type peroxides, Table 5-10, are "vinyl specific". They give good cures only with vinyl containing polymers²⁰.

Bis(2,4-dichlorobenzoyl) peroxide requires a cure temperature of about 220° to 250°F. The decomposition products (2,4-dichlorobenzoic acid and 2,4-dichlorobenzene) volatilize slowly at the stated cure temperatures. Thus, compounds containing this peroxide may be cured without external pressure; however, air removal and forming have to be performed (by extrusion or calendaring) prior to heating. One of the primary uses of this peroxide is in extruded compounds which can be subjected to hot air vulcanization in a few seconds at 600° to 800°F. This peroxide can be used for molding but it has some undesirable characteristics. It starts to crosslink at a fairly rapid rate as low as 200°F; thin sections may easily gel before flow and air removal are completed. With thick sections, curing must be precisely programmed through a post vulcanization oven bake cycle in order to remove acidic decomposition products without degrading the interior of the part. This peroxide can be used for steam cures in autoclaves or in continuous steam vulcanizers.

When compared to bis(2,4-dichlorobenzoyl) peroxide, benzoyl peroxide is a more suitable agent especially with continuous steam vulcanization. Benzoyl peroxide has a higher cure temperature (240° to 270°F). There is less tendency for this compound to scorch in the dies

when extruding at high speed into a steam vulcanizer that is operating at 100 to 200 psi steam pressure.

5-5 COMPOUNDING INGREDIENTS

A typical silicone elastomer formulation contains a silicone polymer, reinforcing and extending fillers, process aids or softeners to plasticize and retard crepe aging, special additives (e.g., heat aging additives and blowing agents for sponge), color pigments, and one or more peroxide curing agents. This schedule can be applicable to both RTV and heat cure of materials"

5-5.1 BASIC RESINS; FILLERS

Pure silicone rubber polymers, differing from one another in polymer type and molecular weight, are available from the basic suppliers. These gums are listed and described in Table 5-11.

Though pure silicone resin can be used, it is generally easier and more economical to compound from silicone rubber reinforced gum. These are mixtures of pure silicone gum, process aids, and highly reinforcing silica. Such silica is highly processed. Such mixtures may contain additives for special characteristics, e.g., improved heat aging or bonding properties. Table 5-12 lists some typical silicone reinforced gums.

Table 5-13 lists some reinforcing fillers for silicone rubber. Fume process silicas show reinforcement to a greater extent than any other filler. These high purity silicas retain excellent dielectric and insulating properties in the cured elastomer. Silica-filled silicones show excellent retention of electrical properties, particularly under wet conditions.

Silica aerogels give moderately high reinforcement. Rubber containing silica aerogels has relatively high water absorption due to the small amounts of water, alcohol, sodium sulfate, and free acid on the filler surface. These silica aerogel compounds are generally inferior to fume silica

TABLE 5-9. PEROXIDE CURING AGENTS FOR SILICONE RUBBER: GENERAL PURPOSE

Peroxide	Commercial Designation	Form	Assay, %	Cure Temperature, °F	Decomposition Products	Uses
Bis(2,4-dichlorobenzoyl) peroxide	CADOX TS-50"	Paste	50	220-250	"Nonvolatile" Acidic	Hot Air Vulcanization
	LUPERCO CST ^b	Paste	50			Continuous Steam Vulcanization Autoclave Thick Section Molding Low Compression Set
Benzoyl Peroxide	CADOX BSG-50"	Paste	50	240-270	Volatile Acidic	Continuous Steam Vulcanization
	LUPERCO AST ^b	Paste	50			Autoclave
	CADOX 99" (200 mesh)	Powder	99			Tower Coating Low Compression Set Thin Section Molding
Tertiary Butyl Perbenzoate	t-Butyl Perbenzoate ^b	Liquid	95	290-310	Volatile Acidic	Usually with other peroxides; sponge; generally for high temperature activation

^aMcKesson & Robbins distributor. CADOX is a trademark of Chemetron Corp.

^bLucidol Division, Penwalt Corp. LUPERCO is a trademark of Lucidol Division, Penwalt Corp.

TABLE 5-10. PEROXIDE CURING AGENTS FOR SILICONE RUBBER: VINYL SPECIFIC

<u>Peroxide</u>	<u>Commercial Designation</u>	<u>Form</u>	<u>Assay, %</u>	<u>Cure Temperature, °F</u>	<u>Decomposition Products</u>	<u>Uses</u>
Dicumyl Peroxide	DICUP R ^a DICUP 40C ^a	Solid Powder	95 40	300-320	Fairly Volatile	Thick Section Molding Low Compression Set (Carbon Black filled)*
2,5-Dimethyl- 2,5-Bis(t-butyl peroxy) Hexane	VAROX ^b	Powder	50	330-350	Volatile	Thick Section Molding Low Compression Set (Carbon Black filled)*
	LUPERSOL 101 ^c	Liquid	95			
	LUPERCO 101XL ^c	Powder	50			
Di-tertiary Butyl Peroxide	Di-t-butyl Peroxide ^{c,d} cw-2015 ^e	Liquid Powder	97 20	340-360	Volatile	Thick Section Molding Low Compression Set (Carbon Black filled)*

^aHercules, Inc. DICUP is a trademark of Hercules, Inc.

^bR. T. Vanderbilt Co. VAROX is a trademark of R. T. Vanderbilt Co.

^cLucidol Division, Pennwalt Corp. LUPERSOL is a trademark of Lucidol Division, Pennwalt Corp.

^dShell Chemical Corp.

^eHarwick Standard Chemicals

*The agents can be used to cure carbon-filled silicone components.

TABLE 5-11. SILICONE GUMS*

ASTM D-1418 Designation	Description	Specific Gravity	Shrinkage"	Commercial Designation		
				GE ^b	D-C ^c	UC ^d
MQ	General Purpose	0.98	High	SE-76	Silastic 400	W-95
MQ	General Purpose	0.98	Low	SE-30	—	—
VMQ	General Purpose	0.98	High	—	—	W-96
	Low Compression Set					
VMQ	General Purpose	0.98	Low	SE-33	Silastic 430	W-98
	Low Compression Set					
PVMQ	Extreme Low Temperature	0.98	High	—	Silastic 440	—
PVMQ	Extreme Low Temperature	0.98	Low	SE-54	—	—
FVMQ	Solvent Resistant	1.30	—	—	Silastic LS-420	—

"High shrinkage $\approx$ 5-6%; low shrinkage $\approx$ 3%.

^bGeneral Electric Company, Silicone Products Department, Wterford, NY 12118.

^cDow-Corning Corporation, Midland, Michigan 48640. Silastic is a registered trademark of Dow Corning Corp.

^dUnion Carbide Corporation, Chemicals and Plastics Division, 270 Park Ave., New York, NY 10017.

*1973 time frame.

TABLE 5-12. SILICONE REINFORCED GUMS*

ASTM D 1418 Designation	Description	Specific Gravity	Commercial Designation		
			GE	D-C	UC
VMQ	General Purpose	1.10	SE-404	Silastic 432	KW-1300
VMQ	General Purpose (makes stiffer and drier compounds than SE-404)	1.10	SE-406	—	—
VMQ	General Purpose (low compression set, long freshened life, 600°F capability)	1.08	SE-421	Silastic 433	KW-1320
VMQ	General Purpose (accepts high loadings of extending filler)	1.09	SE-463	Silastic 437	—
VMQ	General Purpose (requires no post bake)	1.09	SE-465	Silastic 740	—
PVMQ	Extreme Low Temperature, High Strength	1.12-1.20	SE-505	Silastic 446	—
PVMQ	Extreme Low Temperature, High Strength (improved physicals and processing)	1.13	SE-517	—	—
FVMQ	Solvent Resistant	1.38	—	Silastic LS-422	—

*1973 time frame

compounds in wet electrical properties, compression set, and reversion resistance.

Carbon black gives moderate reinforcement. However, the blacks inhibit cure with the aroyl peroxide vulcanizing agents. This limits their use mainly to the production of electrically conductive or semiconductive rubber. The high structure blacks, such as acetylene black, are suitable for this purpose.

There are certain types of fillers which find use as semireinforcing or extending agents. These fillers find use in order to obtain an optimum balance of physical properties, cost, and processibility. These fillers include calcined diatomaceous silicas, iron oxide, ground silica, zirconium silicate, titanium dioxide, calcined kaolin, precipitated calcium carbonate, and zinc oxide. Table 5-14 gives further information on such types. Tradenames, supplier, particle size, surface area, specific gravity, and reinforcement produced in pure silicone gum (tensile strength range and elongation range) are detailed.

Ground silica and calcined kaolin do not give much reinforcement. They are thus used as additives in relatively large quantities in order to reduce cost per weight or volume. These two fillers

find use in both mechanical and electrical grade rubber. Reinforcement attained with calcined diatomaceous silica is greater, though generally modest, than that obtained with other extenders. As an extender, calcined kaolin is not as useful as ground silica. But diatomaceous silica is used in electrical stocks, low compression set stocks, and in general mechanical stocks to reduce tack and modify handling properties. Calcium carbonate and zirconium silicate are special purpose extenders. They are used primarily in pastes which are coated on fabrics from solvent dispersion. Zinc oxide is used as a colorant and plasticizer. It imparts tack and adhesive properties to a compound.

Processing aids are used with highly reinforcing silica fillers. These aids have a softening or plasticizing effect; they retard crepe-aging, structuring or pseudocure of the raw silicone compound. These effects tend to occur due to the high reactivity of the reinforcing filler with the silicone resin.

Table 5-15 lists some available silicone rubber compounds (designation as of 1973). General Electric Co., Dow-Corning Corp., and Union Carbide Corp. are primary suppliers of such

TABLE 5-13. REINFORCING FILLERS ON SILICONE RUBBER

Filler	Type	Particle Size, Mean Diameter, millimicrons	Surface Area, m ² /g	Specific Gravity	Supplier	Reinforcement Produced in Pure Silicone Gum	
						Tensile Strength Range, psi	Elongation Range, %
CAB-O-SIL HS-5	Fumed Silica	10	300-350	2.20	Cabot Corporation 125 High Street Boston, MA	600-1800	200-800
CAB-O-SIL MS-7	Fumed Silica	15	175-200	2.20	Cabot Corporation 125 High Street Boston, MA	600-1200	200-600
SANTOCEL CS and FRC	Silica Aerogel	30	110-150	2.20	Monsanto Chemical Co. Inorganic Chemical Div. St. Louis, MO	600-900	200-350
SHAWINIGAN Black	Acetylene Black	45	75-85	1.85	Shawinigan Products Corp. New York, NY	600-900	200-350

NOTE: The following are trade marks of the companies shown: CAB-O-SIL—Cabot Corporation.
SANTOCEL — Monsanto Chemical Co.

TABLE 5-14. SEMIREINFORCING OR EXTENDING FILLERS FOR SILICONE RUBBER

Filler	Type	Particle Size Mean Diameter, μ	Surface Area, m^2/g	Specific Gravity	Supplier	Reinforcement Produced in Pure Silicone Gum	
						Tensile Strength Range, psi	Elongation Range %
BLANC ROUGE	Iron Oxide Red	1-5	<5	2.65	Illinois Mineral Co.	100-400	200-300
CELITE SUPER FLOSS	Flux Calcined Diatomaceous Silica	1-5	<5	2.30	Johns-Manville	400-800	75-200
CELITE 350	Calcined Diatomaceous Silica	1-5	<5	2.15	Johns-Manville	400-800	75-200
Dicalite PS	Calcined Diatomaceous Silica	1-5	<5	2.25	Dicalite Division Great Lakes Carbon Corp.	400-800	75-200
Dicalite White	Flux Calcined Diatomaceous Silica	1-5	<5	2.33	Dicalite Division Great Lakes Carbon Corp.	400-800	75-200
Iron Oxide KO-3097	Iron Oxide	1	—	4.80	Chas. Pfizer & Co., Inc.	200-500	100-300
Iron Oxide KY-2196	Iron Oxide	<1	—	4.95	Chas. Pfizer & Co., Inc.	200-500	100-300
Isco 1240 Silica	Ground Silica	5-10	—	2.65	Innis Speiden & Co., Inc.	100-400	200-300
MIN-U-SIL 5 μ	Ground Silica	5	<5	2.65	Pennsylvania Pulverizing Co.	100-400	200-300
10 μ		10	<5	2.65			
15 μ		15	<5	2.65			
NEO NOVACITE	Ground Silica	1-10	—	2.65	Malvern Minerals Co.	100-400	200-300
SUPEKPAX	Zirconium Silicate	—	—	4.50	Titanium Alloy Mfg. Div. National Lead Co.	400-600	100-300
THERMOMIST	—	10-20	<5	2.60	Indian Mountain Minerals	100-400	200-300
TITANOX RA	Titanium Dioxide	0.3	—	4.2	Titanium Pigment Corp.	200-500	300-400
Whitetex Clay	Calcined Kaolin	1-5	<5	2.55	Southern Clays Inc.	400-800	75-200
WITCARBR	Precipitated Calcium Carbonate	0.03-0.05	32	2.65	Witco Chemical Co.	400-600	100-300
ALBACAR	Precipitated Calcium	1-4	8	2.71	Chas. Pfizer & Co., Inc.	400-000	100-300
Zinc Oxide xx-78	Zinc Oxide	0.3	3.0	5.6	New Jersey Zinc Co.	200-500	100-300

NOTE: The following are trademarks of the companies shown

CELITE	Johns-Manville
MIN-U-SIL	Pennsylvania Pulverizing Co
NEO NOVACITE	Malvern Minerals Co
SUPERPAX	National Lead Co

THERMOMIST	Indian Mountain Minerals
TITANOX	Titanium Pigment Corp
WITCARB	Witco Chemical Co
ALBACAR	Chas. Pfizer & Co., Inc

compounds. Depending upon the temperature tolerance of the electrical or electronic component to be embedded, certain of these (or variants) find use as high performance dielectrics and insulations.

5-5.2 DYES AND PIGMENTS FOR SILICONES

Most organic dyes and some inorganic pigments have deleterious effects on the heat aging

**TABLE 5-15. COMMERCIALY AVAILABLE SILICONE
RUBBER COMPOUNDS***

ASTM D-1418 Designation	Description	Durometer	Commercial Designation**		
			GE	D-C	UC
VMQ	General Purpose, Low Compression Set	40	SE-4401	Silastic 241	K-1034
		40	SE-4404		K-1044R
VMQ	General Purpose, Low Compression Set, No Post Bake Required	50	SE-4511	Silastic 745	K-1365
		60	SE-4611	Silastic 746	K-1366
		70	SE-4711	Silastic 747	K-1367
		80	SE-4811	Silastic 748	K-1368
VMQ	General Purpose, High Tear, Resilient	50	SE-456	Silastic 55	
VMQ	Low Compression Set	60	SE-3613	Silastic 2096	
		70	SE-3713	Silastic 2097	K-1037
		80	SE-3813	Silastic 2098	
VMQ	Low Compression Set	75	SE-3701		
	High Temperature	70	SE-3715		
PVMQ	Extreme Low Temperature	25	SE-5211	Silastic 6508	
		25	SE-525		
		50	SE-551	Silastic 6526	
PVMQ	Extreme Low Temperature Low Compression Set	40	SE-5401		
		50	SE-540/SE-5601	Silastic 651	
		60	SE-5601		
		70	SE-5701	Silastic 675	
PVMQ	Extreme Low Temperature, High Strength	50	SE-555	Silastic 916	
		50	SE-557	Silastic 955	
		60	SE-565	Silastic 960	
FVMQ	Solvent Resistant	60		Silastic LS-53	
		60		Silastic LS-63	
MQ	Cloth Coating		SE-100	Silastic 132	K-1014
	Electrical		SE-1170	Silastic 9119	
MQ	Cloth Coating Mechanical		SE-701	Silastic 6535	
PVMQ	Flame Retardant	50	SE-5549	Silastic 2351	
VMQ	Wire and Cable		SE-9008	Silastic 1601	
			SE-9011	Silastic 1602	
			SE-9016	Silastic 2083	
			SE-9028	Silastic 2287	
			SE-9035		
			SE-9044		
			SE-9058		
PVMQ	Wire and Cable		SE-9025		
			SE-9090	Silastic 1603	

*1973 time frame

**Stocks from different manufacturers are not necessarily equivalent.

of silicones. The inorganic pigments, listed in Table 5-16 are suitable for use. About 0.5 to 2 parts per 100 parts of compound are used for tinting purposes. Color pigments are typically available as a concentrated masterbatch in order to get good dispersion and good color matches. Red iron oxide is used as a color pigment and as a heat aging additive. Two to four parts per hun-

dred parts of gum give improved heat stability to 600°F.

5-6 SILICONE FOAMS; BLOWING AGENTS

Silicone foaming compounds are available as powdered or liquid forms. The powdered form hardens to a rigid foam; the liquid forms give

TABLE 5-16. COLOR PIGMENTS FOR SILICONE RUBBER

Color	Dye/Pigment
Reds	Red (RY-2196)" Red (RO-3097)" Red (F-5893)' Maroon (F-5891)" Dark Red (F-5892)'
Greens	Chromium Oxide Green (X-1134) ^b Chromium Oxide Green (G-6099)" Yellow Green (F-5688)' Blue Green (F-5687)' Turquoise (F-5686) ^g
Blues	Cobalt Aluminum Blue (E-6279) ^g Medium Blue (I-5274)* Dark Blue (F-6279)" Violet Blue (F-5273)'
Oranges	Mapico Tan #20 ^c Orange Red (F-5894) ^g Orange (F-5895)' Light Orange (F-5896)'
Whites	Titanium Dioxide (TITANOXRA) ^d Titanium Dioxide (TITANOXALO) ^d
Yellows	Cadmolith Yellow ^{b,e} Cadmium Yellow (F-5897) ^g Lemon Yellow (F-5512) ^g
Bufs	Dark Buff (F-6115) ^g Buff (F-2967)'
Black	P-33 Carbon Black Black Iron Oxide (Drakenfeld 10395)"
Browns	Light Yellow Brown (F-6109) ^g Medium Brown (E-6111)* Red Brown (F-6112) ^g

"Chas. Pfizer & Co., Inc.
^bHercules, Inc., Imperial Color Division.
^cCities Service Corp., Columbian Division.
^dTitanium Pigments Corp.
^eChemical & Pigment Div. of Glidden Co.
^fR. T. Vanderbilt Co., Inc.
^gFerro Corp.
^hStandard Bronze Works, Inc., Drakenfeld Div.

rigid, semirigid, or flexible foams²¹. Both contain blowing agents as formulated or generally mixed prior to use.

Characteristics of two well-known blowing agents used for silicone rubbers are given in Table 5-17. With decomposition, UNICEL ND releases nitrogen and formaldehyde; the residue is hexamine and inert filler. Nitrogen and a resi-

due of dimethyl terephthalate are formed by decomposition of NITROSAN. The two agents can be used in combination to control cell structure. Both should be added in masterbatch form, although UNICEL ND disperses more readily than NITROSAN.

The *Powder forms* are foamed by an incorporated blowing agent which decomposes into nitrogen. The premix (polysiloxane resin, blowing agent, fillers) is heated to about 325°F. The resin liquifies; the blowing agent breaks down (releasing nitrogen gas); and its amine by-products catalyze the hardening of the siloxane through condensation of hydroxyl groups. Foams made by this method have the following properties:

1. Resistant to thermal shock
2. 10 to 20 lb/ft³ in density
3. Resistant to cracking or breakdown (room temperature to 600°F thermal cycling)
4. Nonburning
5. Relatively good in compressive strength (100 to 325 psi).

(Molds suitable for use may be made of metals, wood, glass, or certain nonadhering plastics.)

The *liquid-based resins* are foamed at room temperature; the heat of reaction liberates hydrogen which acts as the blowing agent. The liquid system is made by mixing two components in the presence of a catalyst; this must be used at once. With rigid and semirigid foams, reaction is complete in 15-20 min; optimal properties are developed in about 24 h. The density is about 4 lb/ft³. These can be used to about 600°F. They show high fire resistance, low water absorption, and good electrical properties. With materials for flexible foams, mixing is done very quickly, e.g., 1 min, and the silicone is quickly poured for embedment. The end item can be removed from the mold in about 5 min (with about three-fourths of the final strength developed); full strength develops in about 24 h.

Foams based on powder find use as insulation for instruments. The elastomeric types are used as antivibration agents, damping mediums, and

TABLE 5-17. BLOWING AGENTS FOR SILICONE RUBBER SPONGE

Commercial Designation	Composition	Decomposition Temperature, °F	Some Characteristics
UNICEL ND	42% N, N'-dinitroso-pentamethylene tetramine 58% inert filler	300-500	Can use t-butyl perbenzoate and (or) benzoyl peroxide. Blow at >300°F Large cell sponge
NITROSAN	70% N, N'-dimethyl-N, N'-dinitroso-terephthalamide 30% Mineral Oil	220	Can use bis (2,4-dichlorobenzoyl) peroxide and t-butyl perbenzoate. Blow at >240°F Fine cell sponge

NOTE: UNICEL and NITROSAN are trademarks of E. I. Du Pont de Nemours Co.

cushioning around delicate electronic components for protection during subsequent encapsulation (e.g., with a rigid epoxy). The silicone elastomers also can be used as primary embedments.

5-7 SOME CURRENTLY AVAILABLE SILICONE COMPOUNDS; MISCELLANEOUS STATEMENTS

Tables 5-18 through 5-29 give information on some marketed silicones available from Dow-Corning (D-C) and General Electric Co. Uses are given. A description of table contents follows:

1. Table 5-18 covers some D-C *one-part* RTV's.

2. Table 5-19 gives properties of D-C *one-part* RTV's.

3. Table 5-20 lists some GE *one-part* RTV's.

4. Table 5-21 gives properties of some GE *one-part* RTV's.

5. Table 5-22 covers some D-C *two-part* RTV's.

6. Table 5-23 covers uses/properties of some GE *two-part* RTV's.

7. Table 5-24 covers some D-C *two-part* heat cure and/or RTV Sylgard® silicone materials.

8. Table 5-25 lists properties of some D-C *two-part* heat cure and/or RTV Sylgard® silicone materials.

9. Table 5-26 covers some D-C semiconductor molding compounds.

10. Table 5-27 gives properties of some D-C semiconductor junction coating resins.

11. Table 5-28 lists some D-C conformal and printed-circuit board coatings.

12. Table 5-29 covers some D-C impregnating varnishes and resins.

Some general references (Refs. 22-26) are given. Primary sources of information are company technical bulletins, data sheets, etc. (Refs. 27-37).

Room temperature cured RTV silicones are excellent for embedding electronic assemblies and modules. Protection against contamination plus structural support is provided. Additionally, they can be repaired and replaced. When required, the cured silicones may be cut away from the faulty component; the latter is then removed and replaced with a replacement unit. A catalyzed unhardened silicone is then used to reseal the cut-out portion.

Silicones have certain limitations. Some tend to migrate to other sections of an assembly. Since they show good release properties, this migration may interfere with the adhesion of encapsulants (or other agents) to specific portions of an electronic item. This undesirable effect can be avoided by using silicones in the latter part of a process or else carefully isolating the silicone use from the overall manufacturing procedure^{38, 39}.

**TABLE 5-18. SOME CURRENT (1977) DOW-CORNING
ONE-PART RTV MATERIALS**

PRODUCT/FEATURES	USE/AREA
Silastic® 738 RTV Adhesive/Sealant: Noncorrosive cure, good tear strength, excellent dielectric properties, meets FDA and UL requirements, lower cost than previous noncorrosive silicones. Meets MIL-A-46146*, Type I. Service temperature range -85°F to 392°F (-65°C to 200°C). Nonslumping; white; general purpose.	Bonding, sealing, embedding corrosion-sensitive electrical/electronic components
Dow Corning® 3145 RTV Adhesive/Sealant, clear: Noncorrosive cure, high strength, excellent dielectric properties, withstands long-term exposure at -85°F to 392°F (-65°C to 200°C). Nonslumping; high tear strength.	Same as Silastic® 738 RTV. For high temperature applications where high strength is also important; bonding wires and terminals, mounting resistors, convectors, and other components.
Dow Corning® 3145 RTV Adhesive/Sealant, Grey: Same as Dow Corning 3145 RTV clear except temperature range is -85°F to 482°F (-65°C to 250°C). Color: gray. Meets MIL-A-46146, Type I.	Same as Silastic® 3145 RTV; somewhat broader temperature range.
Silastic® 732 RTV Adhesive/Sealant: Recognized by UL. Meets FDA regulations for transitory and incidental food contact. Meets USDA and NSF standards. Meets MIL-A-46106A**, Type I. Nonslumping; general purpose food grade; color: aluminum, black, clear, white.	General purpose bonding, sealing, caulking, embedding of noncorrosion sensitive electrical/electronic equipment.
Silastic® 733 RTV Fluorosilicone Sealant: Fuel-resistant fluorosilicone. Retains flexibility from -70°F to 392°F (-57°C to 200°C). Also resists dilute solutions of strong acids and bases. Nonslumping; fuel resistant fluorosilicone. Color: aluminum.	Same as Silastic® 732 RTV; used where there is immersion or exposure to fumes and splash conditions from solvents and fuels.
Silastic® 734 RTV Adhesive/Sealant: UL recognized, nonshrink, stays flexible from -85°F to 392°F (-65°C to 200°C). Meets MIL-A-46106A, Type II. Free-flowing and self-leveling; general purpose. Color: white, clear.	General purpose potting, coating, sealing, with pourable self-leveling sealant that fills minute crevices and voids; for noncorrosion sensitive electrical/electronic equipment.

* Adhesive-sealants, Silicone, RTV, Noncorrosive

** Adhesive-sealants, Silicone, RTV, General Purpose

Silicones have excellent thermal stability and very good electrical characteristics—e.g., low values of dielectric constant and dissipation factor which are quite constant with temperature and flexibility. Flexibility of some types is held to -100°F ; silicone viscosities prior to cure tend to be stable in comparison with urethanes and e-

poxies. Low exotherms are shown during cure. Primary drawbacks are the high cost of the basic resin; general poor bonding to metals, glasses, and many plastics; and lack of compatibility with certain cure-inhibiting materials (e.g., Teflons, amines, and sulfur-containing elastomers).

**TABLE 5-19. NOMINAL PROPERTIES OF SOME CURRENT DOW-CORNING
ONE-PART RTV MATERIALS**

Property	728	3145	732	734
Specific Gravity at 25°C	1.04	1.12	1.07	1.05
Useful Temperature Range, °C	-65 to 260	-65 to 250	-65 to 260	-65 to 260
Dielectric Strength, V/mil	500	600	550	600
Volume Resistivity, ohm-cm	3.6×10^{15}	5×10^{17}	1×10^{14}	10×10^{14}
Dielectric Constant at 25°C, dimensionless				
100Hz	2.88	2.81	2.8	2.7
100kHz	2.88	2.78	2.8	2.7
Dissipation Factor at 25°C, dimensionless				
100Hz	—	0.0015	0.015	0.006
100kHz	—	0.0028	0.015	0.002
Hardness, Shore A	25	33	25	35
Tensile Strength, psi	275	700	250	300
Tear Strength, pli	—	125	28	20
Peel Strength, ppi	16	65	20	—
Shelf Life, mo	6	6	6	6.

**TABLE 5-20. SOME CURRENT (1976) GENERAL ELECTRIC
ONE-PART RTV MATERIALS**

PRODUCT/FEATURES	USE/AREA
RTV 102, (white), 103 (black), 108 (translucent), 109 (aluminum) — paste-like, standard grade	For use on horizontal, vertical, or overhead surfaces for applications such as bonding, sealing, electrical insulation, and formed-in-place gaskets.
RTV 112 (white), 118 (translucent) — pourable self-leveling standard grade	Uses requiring flow into small surface crevices or hard-to-reach places for bonding, sealing, electrical insulation, encapsulating, protective coatings, and thin section potting.
RTV 154 (grey), 156 (red) — high strength	Uses requiring high mechanical bond strength; for bonding, sealing; aerospace, auto, and industrial assembly; high stress applications; RTV 156 for high strength, high temperature resistances.
RTV 106 (red), paste like 116 (red) flowable — high temperature use	Use requiring high temperature resistance in encapsulating and sealing of heating elements in appliances; aerospace gaskets and seals; critical bonding, sealing, potting, insulating, encapsulating, and coating applications where parts are designed for very high temperature service.
RTV 162 (white) — noncorrosive to sensitive parts; odorless	Electrical/electronic/aerospace applications where neutral cure by-products are required to lessen chance of corrosion to copper and other reactive metals. Typical uses include coatings for integrated circuits, semiconductors, copper connections, electronic part assemblies, and appliances.

**TABLE 5-21. NOMINAL PROPERTIES OF SOME CURRENT GENERAL ELECTRIC
ONE-PART RTV MATERIALS**

	RTV 102, 103 108, 109	112, 118	154, 156	106, 116	162
TYPICAL UNCURED PROPERTIES:					
Color	white, black, clear, aluminum	white, clear	grey, red	red	white
Consistency	paste-like	pourable, self-leveling	paste-like	paste; flowable	flowable
Viscosity, P	very high	300; 350	very high	high; 350	—
Shelf Life, mo	12	12	12	12	12
TYPICAL CURED PROPERTIES:					
Specific Gravity	1.07	1.06; 1.07	1.10; 1.11	1.07; 1.09	1.08
Hardness, Shore A Durometer	30	30; 22	32	33; 26	33
Tensile Strength, psi	350	300; 450	850	350; 445	400
Elongation, %	400	300; 430	800	400; 350	500
Tear Resistance, die B, pli	45	25; 33	130	50; 51	70
Brittle Point, °F	below -75°F	below -75°F	—	below -75°F	—
Linear Shrinkage, %	1.0	1.0; 0.6	—	0.5; 0.3	—
TYPICAL THERMAL PROPERTIES:					
Thermal Conductivity at 200°F, Btu/h•ft ² •°F•ft ⁻¹	0.12	0.12	—	0.12	—
Coefficient of Thermal Expansion at 350°F, in./in.•°F	<15 x 10 ⁻⁵	<15 x 10 ⁻⁵	—	<15 x 10 ⁻⁵	—
Continuous Heat Service, °F	400	400	,400; 500	500	400
TYPICAL ELECTRICAL PROPERTIES:					
Dielectric Strength, 0.075 in. thick, V/mil	500	500	—	500	—
Dielectric Constant at 60 Hz, dimensionless	2.8	2.8; 2.7	—	2.8; 2.7	—
Dissipation Factor at 60 Hz, dimensionless	0.0026	0.0004	—	0.0026	—
Volume Resistivity, ohm•cm	3 x 10 ¹⁵	2 x 10 ¹⁵	—	3 x 10 ¹⁵ ; 2 x 10 ¹⁵	—

TABLE 5-23. SOME CURRENT DOW-CORNING *TWO-PART* RTV MATERIALS

PRODUCT/FEATURES	USE/AREA
<i>Dow-Corning@ 3110R T V Silicone Rubber</i> Viscosity: 125 P. Cures to Shore A hardness: 45. Remains flexible: from -65° to 200°C (-85° to 392°F). Color: White (can be tinted); general purpose; variable cure at room temperature from 12 min to 12 h.	General potting/encapsulation of electrical/electronic products and equipment, components, circuit boards, modules, relays, power supplies, amplifiers, transformers, ferrite cores, connectors, motor end turns, terminal boards and boxes, precoating assemblies before embedment in rigid compounds
<i>Dow-Corning@ 3112R T V Silicone Rubber:</i> Viscosity: 300 P. Cures to Shore A hardness: 60. Remains flexible from: -65° to 250°C (-85 to 482°F). Good wet arc-track resistance. Color: white (can be tinted), medium viscosity, high durometer; variable cure at room temperature from 12 min to 12 h.	Same as 3110RTV.
<i>Dow-Corning@3120RTV Silicone Rubber:</i> Viscosity: 300 P. Cures to Shore A hardness: 65. Remains flexible from: -65° to 300°C (-85 to 572°F). Color: red; general purpose, medium viscosity, high durometer; variable cure at room temperature from 12 min to 7.5 h.	Same as 3110RTV.
<i>Dow-Corning@ 93-500 RTV Space-Grade Encapsulant:</i> Very low outgassing, reversion resistant, high cost. Color: clear; for high vacuum environments; curable at room temperature or to 150°C if required.	Same as 3110RTV

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TABLE 5-23. USES AND NOMINAL PROPERTIES OF SOME CURRENT (1976) GENERAL ELECTRIC TWO-PART RTV MATERIALS

	Methyl-Phenyl RTV Compounds				Dimethyl RTV Compounds														
	-511	-560	-577	-580	-602	-615	-616	-630	-631	-632	-634	-11	-21	-30	-41	-60	-77	-88	-90
MAJOR USES:																			
Sealing and Bonding	X	X	X	X					X	X	X			X		X	X	X	X
Potting, Encapsulating	X	X			X	X	X				X	X	X	X	X	X			
Flexible Mold Material								X	X	X		X	X	X	X	X			
Aerospace (high temperature)	X	X	X	X		X	X							X		X		X	X
TYPICAL UNCURED PROPERTIES:																			
Color	White	Red	White	Red	Clear	Clear	Black	Blue	Bl-grn	Bl-grn	Green	White	Pink	Red	White	Red	White	Red	Red
Consistency	Easily Pourable	Pourable	Spreadable Thixotropic Paste	Spreadable Thixotropic Paste	Easily Pourable			Pourable	Pourable	Pourable	Easily Pourable	Easily Pourable	Pourable	Pourable	Pourable	Pourable	Spreadable Thixotropic Paste	Stiff Paste	
Vicosity, P	200	400	6000	8000	12	40	90	1800	1350	480	80	120	250	250	400	500	6000	6000	12,000
Shelf Life, mo	6	6	6	6	6	6	6	6	6	6	6	6	6	6	6	6	6	6	6
TYPICAL CURED PROPERTIES:																			
Specific Gravity	1.18	1.42	1.35	1.49	0.99	1.02	1.22	1.28	1.18	1.24	1.18	1.18	1.31	1.45	1.31	1.47	1.33	1.48	1.50
Hardness, Shore A Durometer	45	60	50	65	15	35	45	70	68	55	35	45	50	60	50	60	50	65	60
								850	1000	700	400	350	550	750	500	800	500	750	750
Elongation, %	180	160	180	110	200	150	125	300	190	180	220	180	180			130	220	110	150
Tear Resistance, die B, lb/in.	25	45	25	40	10	25	25	90	95	50	20	15	30			40	25	40	75
Brittle Point, °F	Below -175	Below -175	Below -175	Below -175	Below -75	Below -75	Below -75	Below -75				Below -75	Below -75			Below -75	Below -75		Below -75
Linear Shrinkage, %	0.2-0.6	0.2-0.6	0.2-0.6	0.2-0.6	<0.2	<0.2	<0.2	<0.2				0.2-0.6	0.2-0.6			0.2-0.6	0.2-0.6	0.2-0.6	0.2-0.6
TYPICAL THERMAL PROPERTIES:																			
Thermal Conductivity at 200°F, Btu/h•ft²•F°•ft⁻¹	0.15	0.18	0.18	0.18	0.10	0.11	0.16	0.18				0.17	0.18			0.18	0.18	0.18	0.18
Coefficient of Thermal Expansion at 0°-350°F, in./in.°F	12x10⁻⁵	11.4x10⁻⁵	11.4x10⁻⁵	11.4x10⁻⁵	16.2x10⁻⁵	15.3x10⁻⁵	15x10⁻⁵	11.4x10⁻⁵	2.6x10⁻⁵	11.4x10⁻⁵	11.4x10⁻⁵	14.1x10⁻⁵	11.4x10⁻⁵	11.4x10⁻⁵	11.4x10⁻⁵	11.4x10⁻⁵	11.4x10⁻⁵	11.4x10⁻⁵	11.4x10⁻⁵
Continuous Heat Source, °F	400	500	400	500	400	400	400	400	400	400	400	400	400	500	400	520	400	500	520
TYPICAL ELECTRICAL PROPERTIES:																			
Dielectric Strength, 0.075 in. thick, V/m	550	550	485	470	500	500	500	500	500	500	500	500	500	475	500	500	475	450	500
Dielectric Constant at 60 Hz, dimensionless	4.1	4.4	4.1	4.1	3.0	3.0	3.0	3.2	3.1	3.1	3.1	3.6	3.4	4.0	3.8	3.7	4.0	4.0	4.0
Dissipation Factor at 60 Hz, dimensionless	0.005	0.006	0.006	0.006	0.001	0.001	0.001	0.019	0.023	0.012	0.023	0.019	0.01	0.025	0.02	0.020	0.018	0.023	0.020
Volume Resistivity, ohm•cm	1x10¹⁵	1x10¹⁵	1x10¹⁵	1x10¹⁵	1x10¹⁴	1x10¹⁵	1x10¹⁵	6x10¹¹	4x10¹¹	1x10¹⁵	4x10¹¹	6x10¹⁴	8.8x10¹⁴	2.9x10¹⁵	1.5x10¹⁴	1.3x10¹⁴	1x10¹⁵	1x10¹⁴	1.3x10¹¹

**TABLE 5-24. SOME CURRENT (1977) DOW-CORNING TWO-PART HEAT CURE
AND/OR TRV SYLGARD® MATERIALS**

PRODUCT/FEATURES	USE/AREA
<i>Sylgard® 170 A & B Silicone Elastomer:</i> Catalyzed viscosity: 30 P. Cures to Shore A hardness: 55. Retains physical and electrical properties from: -60° to 200°C (-76° to 392°F). Color-black; low cost-best flamer retardancy; room temperature or heat cure (25" to 160°C).	General potting/encapsulating of modules, relays, power supplies, amplifiers, transformers, ferrite cores, connectors, encapsulation of components and circuit boards; adhesive for solar cells, for handling beam-lead integrated circuits during processing; formed in-place seals.
<i>Sylgard® 182 Encapsulating Resin:</i> Catalyzed viscosity: 39 P. Cures to Shore A hardness: 40. Retains physical and electrical properties from: -65" to 200°C (-85" to 392°F). Color-clear; general purpose; heat cure only (65" to 150°C).	Same as Sylgard® 170 A and B.
<i>Sylgard® 184 Silicone Elastomer:</i> Catalyzed viscosity: 39 P. Cures to Shore A hardness: 35. Retains physical and electrical properties from: -65°C to 200°C (-85" to 392°F). Color-clear; general purpose; room temperature or heat cure (25" to 150°C).	Same as Sylgard® 170 A and B.
<i>Sylgard® 186 Silicone Elastomer:</i> Catalyzed viscosity: 450 P. Cures to Shore A hardness: 32. Retains physical and electrical properties from: -65" to 250°C (-85" to 482°F). Color-clear; outstanding tear strength; room temperature or heat cure (25" to 110°C).	Same as Sylgard® 170 A and B.

**TABLE 5-25. NOMINAL PROPERTIES OF SOME CURRENT
DOW-CORNING *TWO-PART* HEAT CURE AND/OR RTV SYLGARD®
MATERIALS**

	<u>Flame Retardant</u> 170 A & B	<u>Primarily Heat Cure</u> 182	<u>Primarily RTV</u> 184	<u>High Tear Strength</u> 186
Color	black	clear	clear	translucent
Serviceable Temperature Range, °C	–60 to 200	–65 to 200	–65 to 200	–65 to 250
Pot Life at 25 °C*, h	1	8	2	2
Recommended Cure	8 h/25°C 3 min/150°C	4 h/65°C	24 h/25°C	24 h/25°C
Dielectric Strength, V/mil	450	550	550	575
Volume Resistivity, ohm•cm	1.0×10^{16}	2×10^{14}	1×10^{14}	2×10^{15}
Dielectric Constant, dimensionless				
at 100Hz	3.15	2.70	2.75	3.01
at 100kHz	3.10	2.70	2.75	3.00
Dissipation Factor, dimensionless				
at 100Hz	0.008	0.001	0.001	0.0009
at 100kHz	0.002	0.001	0.001	0.001
Viscosity at 25°C, (mixed), P	30	30	30	800
Hardness, Shore A	55	40	35	32
Tear Strength, Die B, pli	—	15	15	90
Shelf Life, mo	6	12	6	6

*Pot life is the time required for viscosity of catalyzed resin to double.

TABLE 5-26. SOME CURRENT (1977) DOW-CORNING SEMICONDUCTOR MOLDING COMPOUNDS

PRODUCT/FEATURES	USE/AREA
<i>Dow-Corning@ 302 Molding Compound:</i> Glass filled structural plastic with exceptional flexural strength (16,000 psi) and impact strength for continuous duty up to 410°C (770°F) Red. Molded by compression method.	Structural parts such as standoff insulators, switches, terminal strips, coil forms and bobbins, heat barriers, connectors and connector inserts, fuses and fuse holder, arc suppressors, covers and cases for electrical/electronic equipment.
<i>Dow-Corning@308 Molding Compound:</i> Specially formulated for fast (economical) molding, mold cycles as short as 30 s, maintains excellent dielectric properties over operating temperature range of -65° to 175°C (-85° to 347°F) Dark gray. Molded by transfer method.	Encapsulation of small-signal transistors, IC's, capacitors, thyristors, varistors, modules.
<i>Dow Corning@306 Molding Compound:</i> Versatile, resilient, formulated for outstanding thermal shock resistance, also used in high temperature electronic and electrical connectors; operating temperature range -65° to 300°C (85° to 572°F). Dark gray. Molded by injection of transfer method.	Encapsulation of power transistors, IC's, SCR's (semiconductor-controlled rectifiers).
<i>Dow-Corning® 480 Molding Compound:</i> Specially formulated for very low coefficient of thermal expansion, laboratory and field tests prove the elimination (or substantial reduction) of thermal intermittent opens caused by thermal cycle and thermal shock; outstanding resistance to salt spray, operating temperature range -65° to 200°C (-85° to 392°F). Gray. Molded by injection of transfer method.	Same as Dow-Corning@306 molding compound.
<i>Dow-Corning@307 Molding Compound:</i> Specially formulated to provide maximum thermal shock resistance, withstands repeated cycling from -65° to 350°C (-85° to 662°F); low dielectric loss under extremes of moisture; temperature, and high frequencies. Dark gray. Molded by injection or transfer method.	Encapsulation of wire wound power resistors and high power semiconductor devices.

TABLE 5-27. NOMINAL PROPERTIES OF SOME DOW-CORNING SEMICONDUCTOR JUNCTION COATING RESINS*

	DOW-CORNING SEMICONDUCTOR JUNCTION COATINGS							
	RIGID			FLEXIBLE				
				TWO-COMPONENT			ONE-COMPONENT	
	643	648	649	R-6103	R-6104	R-6100	R-6101	R-6102
Viscosity, Base Resin, at 77°F (25°C), cP	125	110	125	5500	—	—	—	—
Dielectric Constant, dimensionless:								
at 10 ² Hz	3.30	3.22	3.29	2.70	2.75	3.01	3.01	3.011
at 10 ⁶ Hz	3.12	3.15	3.15	2.70	2.73	3.00	3.00	3.00
Dissipation Factor, dimensionless:								
at 10 ² Hz	0.014	0.008	0.013	0.001	0.001	0.001	0.001	0.001
at 10 ⁶ Hz	0.010	0.004	0.008	0.001	0.001	0.001	0.001	0.001
Volume Resistivity, ohm•cm X 10 ¹⁶	30	26	21	2.0	3.0	2.0	2.0	2.0

* These are silicones and modified silicone materials for use as protective and passivating coatings for semiconductor junctions. They are designed to be ion-free; their use minimizes drifting of semiconductor-device characteristics.

TABLE 5-28. SOME CURRENT (1977) DOW-CORNING CONFORMAL AND PRINTED-CIRCUIT BOARD COATINGS

PRODUCT/FEATURE	USE/AREA
<i>Dow-Corning® 3140 RTV Coating:</i> Clear, self-leveling, medium viscosity, ready-to-use-silicone rubber, cures without releasing acetic acid or other corrosive by-products; provides moisture and abrasion protection, good durability; easy to repair, remains rubbery from -65° to 200°C (-85° to 392°F). (A white version of this is Dow-Corning 3141 RTV coating.) One part RTV silicone compound.	Conformal coating on printed circuit assemblies and electronic components; encapsulating small circuits or connectors; for corrosion-sensitive electrical/electronic equipment.
<i>Dow-Corning® R-4-3117 Conformal Coating:</i> Room temperature-curing silicone resin, supplied as a 75% solids dispersion in solvent for easy coating. Cures without evolving corrosive by-products to form a tough, smooth surface, much harder than rubbery silicone coatings. Superior durability, heat stability, and moisture resistance. One part silicone coating.	Same as Dow-Corning® 3140 RTV coating.
<i>Dow-Corning® 1890 Protective Sealer:</i> Easy to apply (by brushing or spraying), gray thick liquid dispersion of RTV silicone rubber, dries tack free within 20 min, cures to rubbery solid, provides moisture and abrasion protection; adheres to most surfaces; remains flexible from -73° to 204°C (-100° to 400°F); retains good electrical properties. Solvent dispersion of one-part RTV silicone (rubbery film).	General purpose coating for electrical power applications, motor stator windings, bus bars, bus dust sealing and water-proofing, splices and connections, distribution transformer tops, wooden pole tops, and insulator pins; protective coating for related hardware.

TABLE 5-29. SOME CURRENT (1977) DOW-CORNING IMPREGNATING VARNISHES AND RESINS

PRODUCT/FEATURES	USE/AREA
<i>Dow-Corning@R-4-3 157 Solventless Resin:</i> Completely solvent free; cures without evolving any volatile material; withstands continuous service at 220°C (428°F). Excellent radiation resistance; good wetting and penetrating qualities; good thermal conductivity; good strength at elevated temperatures. Designed for use in form-wound equipment. Solventless resin.	Impregnating and insulating form-wound motor stator coils and generator coils; used on rotating and nonrotating elements and equipment.
<i>Dow-Corning@GP-77NP Varnish:</i> Medium viscosity 50% solids solvent solution of silicone-organic copolymer. Offers good bond strength, no baking between dips, flexible cure schedule, good thermal stability up to 200°C (392°F). Solvent system.	Dipping, flooding, or impregnating stators, dry-type transformers, armatures, or wound rotors; conductor bond and adhesive for silicone-rubber insulated form-wound coils; impregnant for bonding glass armor type to insulated coils; used on rotating and nonrotating elements.
<i>Dow-Corning@997 Varnish:</i> (heat cure) Easy-to-use 50% solution of silicone resin in xylene. For 180°, 200°, and 220°C (356°, 392°, and 428°F) systems. Has viscosity of 110 cP, but may be thinned. Flexible heat-cure schedule allows optimum development of properties, excellent retention of bond strength, long service life (reliable even at 220°C (428°F) hottest spot temperature), excellent moisture resistance and electrical properties. Solvent system.	Impregnating and insulating motor stator coils; generator coils, solenoids, transformer windings, inverters; used on rotating and nonrotating elements of rotating equipment.
<i>Dow-Corning@991 Varnish</i> (air-dry/heat-cure) A 50% solution of silicone resin in xylene. As supplied, has viscosity suitable for dipping (150 cP), but may be thinned with xylene, toluene, chlorinated solvents, ketones, or acetates. Air dries in 1 to 5 h at room temperature; can be heat accelerated.	Improving surface resistivity of printed circuits, electronic units or equipment exposed to high humidity; reducing moisture absorption and surface contamination of equipment during storage; used on rotating and nonrotating elements of rotating equipment.

REFERENCES

1. E. Sailer and A. Kennedy, "The Use of Silicones in a Low Cost High Reliability Micro-circuit Package", *Proceedings National Electronic Packaging Conference (NEPCON)*, New York, NY, 21-23 June 1966.
2. F. J. Lockhart, "The Role of Silicone Packaging Materials in the Semiconductor Industry", National Electronic Packaging and Production Conference (NEPCON), Long Beach, CA, 31 January-2 February 1967, and New York, NY, 13-15 June 1967, *Proceedings of the Technical Program*, Conference sponsored by the Electronic Production and Packaging Magazine, pp. 355-62, Chicago, IL.
3. J. A. Black, D. J. Lyman, and D. B. Parkinson, *Development of Material Specifications and Qualifications of Polymeric Materials for the JPL Spacecraft Materials Guidebook. 11: RTV Silicone Adhesives and Potting Compounds*, NASA CR-64208, 1965.
4. W. Nill, *Chemistry and Technology of Silicones*, Academic Press, New York, NY, 1968.
5. E. G. Rochow, *An Introduction to the Chemistry & Silicones*, Academic Press, New York, NY 1968.
6. M. M. Prisco, Chapter "Silicone Elastomers", *The Vanderbilt Rubber Handbook*, R. T. Vanderbilt Co., Inc., New York, NY, 1968, pp. 174-188.
7. S. Fordham, ed., "Silicones", *Industrial Manufacture and Application*, Philosophical Library, Inc., New York, NY, 1960, pp. 107 et seq.

REFERENCES (cont'd)

8. W. Brenner, D. Lum, and M. W. Riley, "High Temperature Resins", Reinhold, New York, NY, 1962.
9. D. F. Christensen, ("Environmental Evaluation Data for Silicone Encapsulants", *Electrical Manufacturing* **66**, 117-20 (July 1960).
10. B. J. Culbertson, "Weathering of One-Component Silicone Building Sealants", *Conference on Elastoplastic Technology*, Society of the Plastics Industry, Wayne State University, Detroit, MI, 1964.
11. R. N. Meals and F. M. Lewis, "Silicones", *Plastics Application Series*, Reinhold, New York, NY, 1961.
12. R. R. McGregor, *Silicones and Their Uses*, McGraw-Hill, New York, NY, 1954.
13. W. J. Bobear, Chapter 15, "Silicone Rubber", M. Morton, ed., *Rubber-Technology — 2nd Edition*, Van Nostrand Reinhold Co., New York, NY, 1973.
4. Dow-Corning Corp., technical bulletin/data sheets, no dates; "Silastic LS Facts", data sheets, no dates; "Technical Data Sheets on LS-53, LS-63U, LS-422, LS 2249U"; (Fluorosilicone Rubbers), no dates.
15. Various Patents:
US Patents Nos. 3,205,283; 3,035,016; 3,133,891; 3,334,067; 3,294,739; 3,032,528; 3,291,277.
French Patent No. 1,432,799
Belgian Patent No. 659,254
16. C. Eaborn, *Organosilicon Compounds*, Academic Press, New York, NY, 1960.
17. V. Bazant, V. Chvalovsky, and J. Rathonsky, *Organosilicon Compounds*, Academic Press, New York, NY, 1965.
18. A. J. Barry and N. S. Beck, Chapter 5, "Silicone Polymers" in F. G. A. Stone and W. A. G. Graham, eds., *Inorganic Polymers*, Academic Press, New York, NY, 1962.
19. G. Alliger and I. J. Sjothun, eds., *Vulcanization of Elastomers*, Reinhold, New York, NY, 1964.
20. P. F. Bruins, ed., *Silicone Technology — Applied Polymer Science Symposium No. 14*, Wiley-Interscience, New York, NY, 1970.
21. C. J. Benning, Vol. 1, Chapter 11, "Principles of Foam Formation: Synthetic Rubber and Silicone Foams", *Plastic Foams: the Physics and Chemistry of Product Performance and Process Technology*, Wiley-Interscience, New York, NY, 1969.
22. G. J. Kookootsedes and F. J. Lockhart, "Silicone Molding Compounds for Semiconductor Devices", *153rd Meeting American Chemical Society*, Miami, FL, 9-14 April 1967.
23. C. Nadler, *Investigation of Various High Temperature (250° - 450°F) Electrical Sealants for Aircraft Electrical Connectors and Electric Systems; Development of Improved Silicone Sealant Compounds*, AML Report No. NAMC-AML-1697, Naval Air Development Center, PA, 1 July 1963.
24. F. J. Modic, "New Fast Curing Silicone Polymers for Electrical and Electronic Uses", *Proceedings of the Sixth Electrical Insulation Conference*, pp. 131-34. Conference sponsored by IEEE, NEMA, and Navy Bureau of Ships, New York, NY, 13-16 September 1965.
25. G. J. Kookootsedes and F. J. Lockhart, "Silicone Molding Compounds for Semiconductor Devices", *Modern Plastics* (January 1968).
26. No author, "Process Gives Low Volatility Materials Aimed at Use in Space", *Chemical and Engineering News*, p. 24 (8 April 1968).
27. *Technical Data Book S-35 RTV Silicone Rubber*, General Electric Co., Bulletin 1268 R-769, 1976.
28. *Technical Data Book S-35A Two-Component RTV Silicone Rubber*, Bulletin (no number designation), General Electric Co., 1976.
29. *Silicone Elastomers — Applications/Product Selection Guide*, Data Sheet 61-212A-76, Dow-Corning Corp., 1976.
30. *A Guide to Dow-Corning Products*, Bulletins 01-238 4/1973 and 01-320-77, Dow-Corning Corp., 1977.
31. *Information About Electrical/Electronic Materials*

REFERENCES (cont'd)

- *Dow-Corning Semiconductor Junction Coatings*, Data Sheet 23-021 A-76, Dow-Corning Corp., 1976.
- 32. *Fluid Resistance of Silastic® Silicone Rubber*, Bulletin 17-052A 3/79, Dow-Corning Corp., 1976.
- 33. *Information About Silastic® Silicone Rubber — Selection Guide to Silastic® Silicone Bases*, Data Sheet 11-19A-76, Dow-Corning Corp., 1976.
- 34. *Silicone Semiconductor Molding Compounds and Selection Guide*, Bulletin 32-161 4/73, 1973; and *Information About Semiconductor Molding Compounds — Dow-Corning 480 Compound*, Bulletin 23-179A 6/75, Dow-Corning Corp., 1975.
- 35. *Silicones for Electrical Design*, Bulletin 01-235 11/72, Dow-Corning Corp., 1972.
- 36. *A Guide to Dow-Corning Electrical and Electronic Materials*, Bulletin 01-276B-76, Dow-Corning Corp., 1976.
- 37. *Government Buyer's Guide to Silicones*, Bulletin 01-239B 1/77, Dow-Corning Corp., 1977.
- 38. C. Nadler, *Corrosion Properties of RTV-60 Silicone Compound*, Report No. NAMC-AML 1218, Naval Air Development Center, PA, 22 June 1961.
- 39. R. L. Patrick, ed., *Treatise on Adhesion and Adhesives*, Vol. 2. *Materials*, pp. 119-21, Marcel Dekker, New York, NY, 1969.
- 40. S. B. Twiss, *Symposium on Structural Adhesive Bonding*, sponsored by Picatinny Arsenal, Preprint 2, pp. 820-87, Stevens Institute of Technology, Hoboken, NJ, September 1968.
- 41. M. Dale Beers, Chapter 39, "Silicone Adhesive Sealants", I. Skeist, ed., *Handbook of Adhesives — 2nd Edition*, Van Nostrand Reinhold Co., New York, NY, 1977.

CHAPTER 6

VAPOR-DEPOSITED POLY-p-XYLYLENE DIELECTRICS

The chemical, physical, and electrical properties of Parylenes together with their advantages are given. General applications are presented.

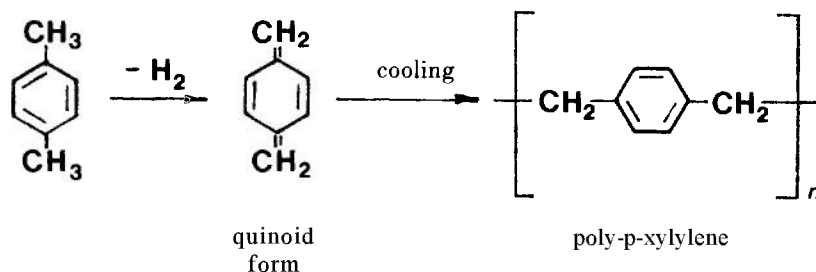
6-1 ADVANTAGES OF THE PARYLENES

The excellent properties of Parylene coatings are said to be due to the vapor deposition process and the immediate polymerization on the surface substrate. The technique allows close control of coating thickness and uniformity; at a thickness of 0.1 mil, the deposition is both tough and free of pinholes. Barrier properties exceed those attained with epoxy, silicone, or urethane conformal coatings. Resistance to most solvents and aggressive chemicals is very good. Mechanical properties are retained over the temperature of -200°C to $+275^{\circ}\text{C}$. The resins are suitable for long-time use in air up to 150°C ; in the absence of oxygen, temperatures as high as 220°C are allowable. The one-step deposition method is quick; no catalysts, high surface temperatures, radiation, or other special processings (which might degrade certain electronic components) are required.

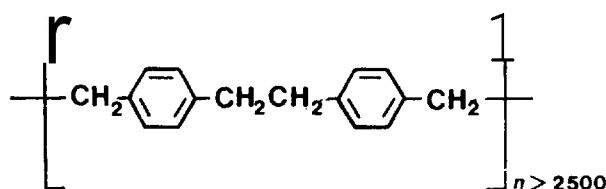
Unlike dip, spray or conformal coating, vapor coating with substrate condensation does not cause run-off or sagging. The vapor deposition is not line-of-sight but coats evenly over points, edges, and internal areas. Coating occurs without bridging; holes are kept distinct and evenly insulated. Masking tape is used to prevent undesired coating on certain assembly areas. Coating thickness can be controlled by establishing the weight of the dimer which will be vaporized.

6-2 GENERAL CHARACTERISTICS OF DEPOSITED XYLYLENE DIELECTRICS

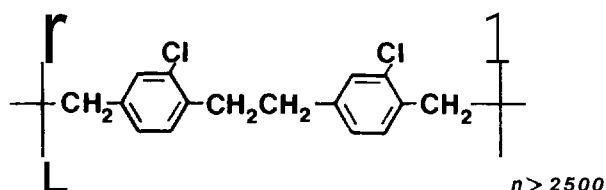
Poly-p-xylylenes can be deposited on electronic assemblies as films or coating. The reaction of polymerization is via the pyrolytic dehydrogenation of p-xylene gas (700°C to 1100°C , 1 to 5 mm mercury pressure):



Work in the early 1950's gave a cross-linked polymer which could not be processed. Work by Union Carbide eventually led to linear non-crosslinked forms; these were introduced in 1965 and called Parylenes. In this process, the polymer is prepared by converting p-xylene to di-p-xylylene (a solid dimer); this is pyrolyzed at 650°C at 0.1 to 0.5 torr (about 0.1 to 0.5 mm of mercury pressure). The dimers break down to unsaturated or diradical monomers which polymerized on contacting any surface (25° to 150°C substrate temperature).^{1,2,3} Two major Parylenes are designated N and C. The C is a chlorinated variant of N. These are shown:



Parylene N

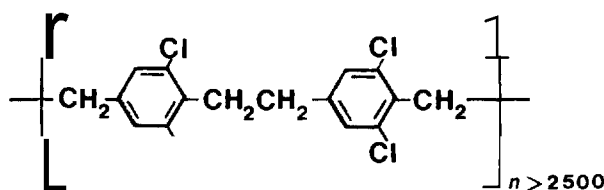


Parylene C

Parylene N, the basic polymer, exhibits very good electrical properties which vary very little with temperature change; deposited in very thin coatings, the heat is easily dispersed. Differences in thermal expansions are less than with other conformal coatings.

Parylene C finds the widest use because of its excellent barrier properties. Permeability to moisture and gases—e.g. nitrogen, oxygen, carbon dioxide, hydrogen sulfide, sulfur dioxide, and chlorine—is low.

Another variant, introduced somewhat later, is Parylene D. This contains two chlorine atoms on each benzene ring. Its distinguishing property is said to be suitability in air somewhat beyond 150°C (Ref.4).



Parylene D

(The Union Carbide process is covered by various patents, i.e., US Patents 3,288,728 and 3,342,754; licenses for its use are available.)

For end-product use, Parylene is deposited in thicknesses from 0.25 to 1.5 mils in a single operation. This gives physical and barrier characteristics which are equal to or better than 2 to 6 mil thicknesses of epoxies, silicones, or urethanes. (The latter three resins may require a multiple coat operation to eliminate

Fig. 6-1 shows important parts of the process.

6-3 THE DEPOSITION PROCEDURE

Deposition chambers now in use range in volume from 500 to 28,000 in³. Large parts, i.e., 5 ft long and 1.5 ft high, can be coated in the latter chamber. Scale-up of chamber size is possible; in large chambers, coating of many small parts of different geometries can be performed. Time and labor savings can be attained by this method.

6-4 ELECTRICAL PROPERTIES

The dielectric strength and volume/surface resistivities of Parylenes are very good. The dielectric constants and dissipation factors are very low (lower than for most epoxies, silicones, or polyurethanes but higher than values for fluorocarbon resins). Such properties along with the low deposition temperatures make the Parylenes very useful as conformal coatings for high-frequency components and as basic insulation for conductors and metal substrates. The best electrical properties are shown by the non-halogenated N type. Type C, the chlorinated analog, has the higher dielectric constant and dissipation factor. But Type C is better than Type N for dc breakdown voltage for depositions under 5 microns. Table 6-1 gives comparative electrical properties.

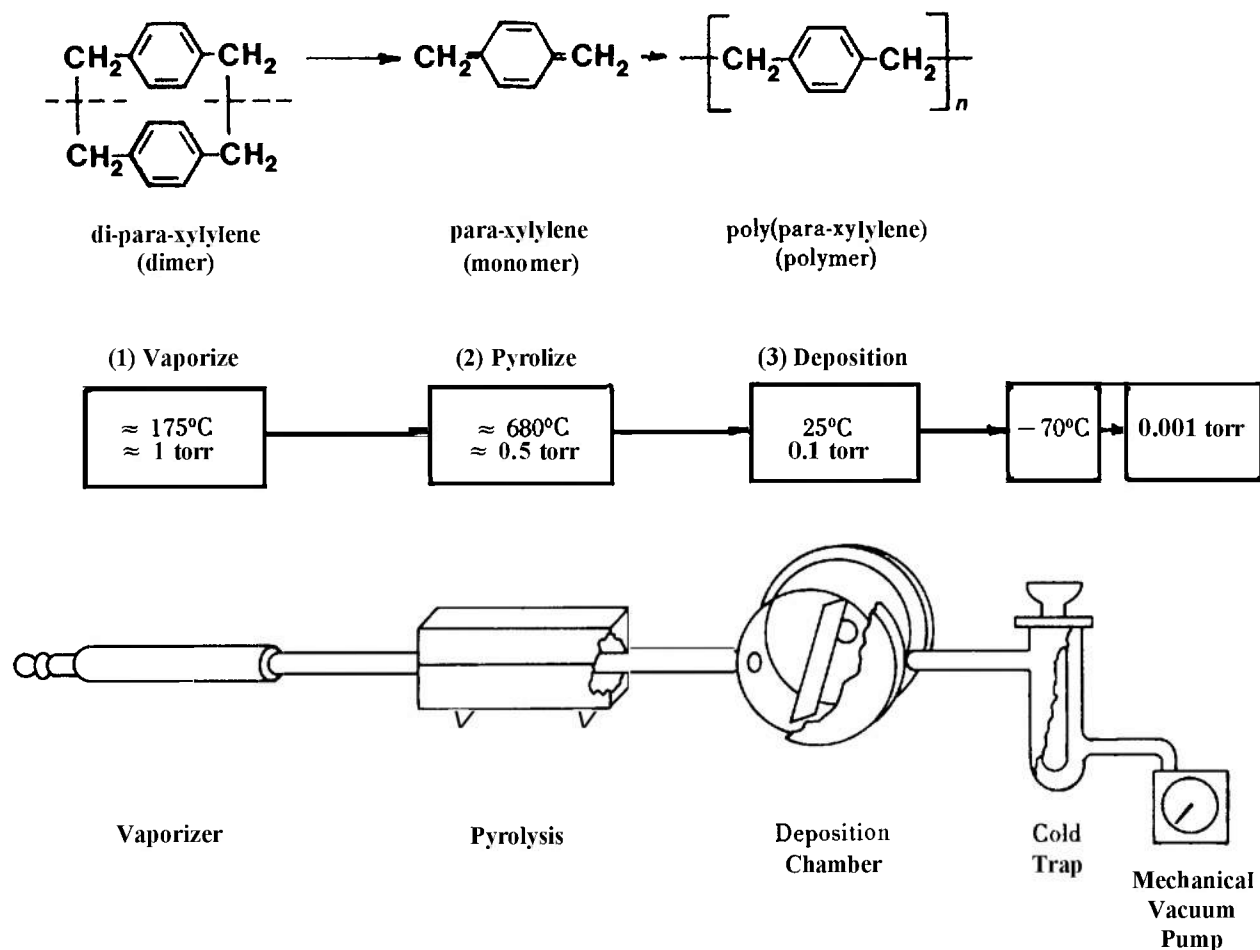


Figure 6-1. Diagram of the Parylene Process

TABLE 6-1. TYPICAL ELECTRICAL PROPERTIES
(PARYLENES VS OTHER DIELECTRIC POLYMERS)

Property	Parylene N	Parylene C	Parylene D	Epoxy	Silicone	Urethane
Dielectric Strength, Short Time, V/mil at 1 mil	7000	5600	5500	2300	2000	3500
Volume Resistivity, 23°C, 50% RH, ohm-cm	1×10^{17}	6×10^{16}	2×10^{16}	1×10^{14}	1×10^{15}	2×10^{15}
Surface Resistivity, 23°C, 50%RH, ohm	10^{13}	10^{14}	5×10^{16}	5×10^{13}	3×10^{13}	6×10^{14}
Dielectric Constant, dimensionless						
60 Hz	2.65	3.15	2.84	4.2	2.6	3.5
103 Hz	2.65	3.10	2.82	3.9	2.6	3.4
10^6 Hz	2.65	2.95	2.80	3.4	2.6	3.2
Dissipation Factor, dimensionless						
60 Hz	0.0002	0.020	0.004	0.03	0.0005	0.01
10^3 Hz	0.0002	0.019	0.003	0.03	0.0004	0.01
10^6 Hz	0.0006	0.013	0.002	0.04	0.0008	0.01

6-5 PHYSICAL/MECHANICAL, THERMAL, AND GAS BARRIER PROPERTIES

Tables 6-2, 6-3 and 6-4 give physical/mechanical, thermal, and gas permeability data on the Parylenes (compared with typical values for epoxy, silicone and urethane class plastics).

6-6 EFFECTS OF IMMERSION IN CHEMICALS

Dimensional response to various immersions is described in the paragraphs that follow.

6-6.1 IMMERSION IN ORGANIC SOLVENTS AT ROOM TEMPERATURE

Films of Parylenes N, C, and D were immersed in test liquids for 90 min at room temperature.

Table 6-5 shows swelling caused by such exposure. Slight, but measurable swelling was detected in each case, the maximum being 3% caused by o-dichlorobenzene on Parylene C. (This, incidently, is a solvent for Parylene C removal at its boiling point of 180°C.) After drying under vacuum, the films returned to their original dimensions.

6-6.2 IMMERSION IN ORGANIC SOLVENTS AT ELEVATED TEMPERATURE

Parylene strips were immersed in organic solvents at elevated temperatures. These temperatures were either the boiling point of the solvents or 75°C (whichever was lower). Immersion time was 120 min; longer times did not cause added dimension changes. Results are given in Table 6-6.

TABLE 6-2. TYPICAL PHYSICAL/MECHANICAL PROPERTIES (PARYLENES VS OTHER INSULATING POLYMERS)

Property	Parylene N	Parylene C	Parylene D	Epoxy	Silicone	Urethane
Tensile Strength, psi	6500	10,000	11,000	4,000-13,000	800-1000	175-10,000
Yield Strength, psi	6100	8000	9000	—	—	—
Elongation to Break, %	30	200	10	3-6	100	100-1000
Yield Elongation, %	2.5	2.9	5	—	—	—
Specific Gravity	1.11	1.289	1.418	1.11-1.40	1.05-1.23	1.10-2.5
Coefficient of Friction, dimensionless						
Static	0.25	0.29	0.33	—	—	—
Dynamic	0.25	0.29	0.31	—	—	—
Water Absorption, 24 h, %	0.06	0.01	—	0.08-0.15	0.12 (7 days)	0.02-1.5
Index of Refraction, n_D 23°C, dimensionless	1.661	1.639	1.669	1.55-1.61	1.43	1.50-1.60

TABLE 6-3. TYPICAL THERMAL PROPERTIES (PARYLENES)

Property	Parylene N	Parylene C	Parylene D	Epoxy	Silicone	Urethane
Melting or Heat Distortion Temperature, °C	405	280	> 350	up to 220	up to 300	170
Linear Coefficient of Expansion, $10^{-5}/^{\circ}\text{C}$	3.5	6.9	—	4.5-6.5	25-30	10-20
Thermal Conductivity, $(10^{-4} \text{ cal/s}\cdot\text{cm}^2\cdot^{\circ}\text{C}\cdot\text{cm}^{-1})$	— 3	—	—	4-5	3.5-7.5	5

TABLE 6-4. TYPICAL BARRIER PROPERTIES (PARYLENES)

Polymer	Gas Permeability at 23°C cm ³ •mil/100in ² •24h•atm						Moisture Vapor Transmission at 37°C and 90% RH, g•mil/100in ² •24h
	N ₂	O ₂	CO ₂	H ₂ S	SO ₂	Cl ₂	
Parylene N	7.7	39.2	214	795	1890	74	1.6
Parylene C	1.0	7.2	7.7	13	11	0.35	0.5
Parylene D	4.5	32	13	1.45	4.75	0.55	0.25
Epoxy	16	66	9	—	—	—	7
Silicone	15	22	45	—	—	—	290
Urethane	3	3	8	—	—	—	12

TABLE 6-5
SWELLING OF PARYLENES CAUSED BY ORGANIC
SOLVENTS AT ROOM TEMPERATURE

Solvents		Swelling, %		
		Parylene		
Class	Test Member	N	C	D
Alcohol	Isopropyl	0.3	0.1	0.1
Aliphatic Hydrocarbon	Iso-Octane	0.2	0.4	0.3
Amines	Pyridine	0.2	0.5	0.5
Aromatic Hydrocarbon	Xylene (mixed)	1.4	2.3	1.1
Chlorinated Aliphatic	Trichloroethylene (TCE)	0.5	0.8	0.8
Chlorinated Aromatic	Chlorobenzene	1.1	1.5	1.5
Chlorinated Aromatic	0-Dichlorobenzene	0.2	3.0	1.8
Freon	Trichlorotrifluoroethane	0.2	0.2	0.2
Ketone	Acetone	0.3	0.9	0.4
Ketone	2,4-Pentanedione	0.6	1.2	1.4

A maximum swelling of 3.3% was observed with mixed xylene on Parylene C. When test strips were dried overnight in vacuum, thickness returned to original values. At temperatures under 75°C, organic solvents have a slight swelling effect on Parylenes; this effect is entirely reversible. The swelling effect is most pronounced with aromatic liquids, particularly chlorinated aromatics. Alcohols, aliphatic hydrocarbons, and Freons have the least effect.

6-6.3 IMMERSION IN INORGANIC REAGENTS AT ROOM TEMPERATURE

Parylene films were immersed in inorganic reagents at room temperature. After 90 min of such treatment, thickness was measured by infrared spectorscopy. Except for oxidizing agents, equilibrium thickness was reached before the 90-min time period. Results are shown in Table 6-7.

TABLE 6-6.
SWELLING OF PARYLENES CAUSED BY ORGANIC SOLVENTS
AT ELEVATED TEMPERATURES

Solvents		Test Temp, °C	Swelling, %		
Class	Member		N	Parylene C	D
Alcohol	Isopropyl	75	0.3	0.2	0.1
Aliphatic Hydrocarbon	Iso-Octane	75	0.3	0.5	0.3
Amines	Pyridine	75	0.4	0.7	0.7
Aromatic Hydrocarbon	Xylene (mixed)	75	2.1	3.3	1.9
Chlorinated Aliphatic	Trichloroethylene (TCE)	74	0.7	0.9	0.9
Chlorinated Aromatic	Chlorobenzene	75	1.7	2.0	2.1
Chlorinated Aromatic	0-Dichlorobenzene	75	0.3	1.4	0.8
Freon	Trichlorotrifluoroethane	37	0.2	0.3	0.2
Ketone	Acetone	56	0.4	0.9	0.4
Ketone	2,4-Pentanedione	75	0.7	1.8	1.6

TABLE 6-7.
SWELLING OF PARYLENES CAUSED BY INORGANIC REAGENTS
AT ROOM TEMPERATURE

			Swelling		
Class	Test Member	Concentration, %	Parylene		
			N	C	D
Non-Oxidizing Acid	Hydrochloric	10	0.0	0.0	0.1
Non-Oxidizing Acid	Hydrochloric	37	0.2	0.0	0.5
Non-Oxidizing Acid	Sulfuric	10	0.1	0.3	0.2
Non-Oxidizing Acid	Sulfuric	95-98	0.2	0.4	0.8
Oxidizing Acid	Nitric	10	0.1	0.1	0.2
Oxidizing Acid	Nitric	71	0.2	0.2	0.5
Oxidizing Acid	Chromic	10	0.1	0.1	0.1
Oxidizing Acid	Chromic	74	0.3	0.0	0.2
Base	Sodium Hydroxide	10	0.1	0.0	0.1
Base	Ammonium Hydroxide	10	0.3	0.2	0.1
Inert	Deionized Water	100	0.0	0.0	0.0

Slight swelling was found in most cases; no attempt was made to measure reversibility.

6-6.4 IMMERSION IN INORGANIC REAGENTS AT 75°C

Film specimens were also tested at 75°C in the inorganics but for 120 min. Results are given

in Table 6-8. Under conditions of increased temperature there was a definite increase in swelling effect with reagent concentration. Dilute solutions cause little swelling (maximum 1.2% by chromic acid on Parylene N); concentrated oxidizing acids caused severe degradation of Parylenes N and C; sulfuric acid caused significant swelling of all three Parylenes. Bases cause

TABLE 6-8.
SWELLING CAUSED BY INORGANIC REAGENTS AT 75°C

Reagent			Swelling		
Class	Test Member	Concentration, %	N	Parylene C	D
Non-Oxidizing Acid	Hydrochloric	10	0.0	0.0	0.0
Non-Oxidizing Acid	Hydrochloric	37	2.3	4.1	0.7
Non-Oxidizing Acid	Sulfuric	10	0.2	0.2	0.6
Non-Oxidizing Acid	Sulfuric	95-98	5.3	5.1	7.8
Oxidizing Acid	Nitric	10	0.2	0.1	0.1
Oxidizing Acid	Nitric	71	*	1.8**	4.9
Oxidizing Acid	Chromic	10	1.2	0.0	0.1
Oxidizing Acid	Chromic	74	8.2	7.8	4.0
Base	Sodium Hydroxide	10	0.0	0.5	0.4
Base	Ammonium Hydroxide	10	0.4	0.4	0.9
Inert	Deionized Water	100	0.0	0.0	0.0

*Became brittle and fell apart

**Turned light brown.

minor but measurable swelling. No examinations were made for reversibility; the effects of concentrated nitric acid are, of course, permanent; some sulfonation by the hot sulfuric acid can be expected.

6-7 APPLICATIONS; BRIEF SUMMATION; MISCELLANEOUS

Parylenes find use as coatings for circuit boards, hybrid circuits, and ferrites. A large number of ferrites can be tumble-coated in one operation. For example, in the toroid form, the deposited coating does not interfere with desired close tolerances. The thin coat gives protection without changing dimensions, shape, or magnetic properties. Abrasion resistance during subsequent winding or stringing processes is excellent; inner diameter coverage of the toroid is uniform.

With circuit boards having complex and high-density positioning of electronic components, the Parylene process has the unique ability to penetrate around and under close-spaced

components; this cannot be done with spray-type coatings. Microscopic examination shows that Parylene uniformly coats spaces of dimensions 2 mils or less (between components, wires, etc. and the supporting board). This helps prevent inclusions of contaminants which might cause corrosion or deterioration of electrical properties. The high initial electrical insulating properties show little or no deterioration after humidity and temperature cycling'.

Another use for the Parylenes is as an insulation and barrier coating deposited over the inorganic passivation layers of semiconductors or thin film-devices. Coatings as thin as 3 to 7 microns may be used on transistors, diodes, resistors, capacitors, and other components.

Overall, these agents combine stability of aromatic phenylene groups with the flexibility of aliphatic linkages. Polymerization to linear resins occurs below 50°C (after the vapor deposition process). The thermal stabilities are good, but not exceptional. In an inert atmosphere, the agent provides long-term service to about 220°C and short term to 350°C. Service use below about 80°C are more realistic in air.

At cryogenic conditions, the materials show very good flexibility even at -201°C . Electrical insulation properties are good even near absolute zero. Electrical properties are good at elevated temperatures even after mechanical properties begin to degrade.

The Parylenes are not suitable for outdoor exposure or natural weathering. Ultraviolet radiation is a primary culprit but other parameters or factors are probably quite active in the break-

down of the polymer integrity.

The agents are insoluble in all organic solvents below 150°C . Resistance to permeation is shown to all solvents, except aromatic hydrocarbons. The films show excellent barrier characteristics against gases and moisture.

Additionally, poly-p-xylylenes have been made into tough, uniform moldings at 400°C , 2000 psi.

REFERENCES

1. W. F. Gorham, "A New General Synthetic Method for the Preparation of Linear Poly-p-xylylene", *Journal Polymer Science* **4**, 3027-39 (1966).
2. W. F. Gorham, "Para-xylylene Copolymers", US Patent 3288728, 29 November 1966.
3. W. F. Gorham, "Para-xylylene Polymers", US Patent 3342754, 19 September 1967.
4. *Parylene*, Union Carbide Product Data Bulletin F-43427A, no date.
5. W. E. Loeb, F. R. Tittman, and J. H. Bowen, "Apparatus for Vapor Deposition", US Patent 3246627, 19 April 1966.
6. W. E. Loeb and C. E. White, "Parylene for Conformal Insulation", *Proceedings National Electronic Packaging Convention*, Long Beach, CA, 30 January 1968.
7. *Parylene for Electronics*, Union Carbide Corp., Bound Brook, NJ, 1968.
8. S. M. Lee, J. J. Licari, and I. Litant, "Reliability of Parylene Films", *Proceedings of the Metallurgical Society Technology Conference, Defects Electronic Material Devices*, Boston, MA, March 1970.

CHAPTER 7

USE OF FILLERS

The effects of various fillers on the chemical, physical, and electrical Properties of various resins are given.

7-1 GENERAL MODIFICATIONS THROUGH USE OF FILLERS

Fillers play important roles in the application of resins for packaging electronic units. They allow resin users to overcome many of the limitations of the basic resins. Through the proper use of fillers, major changes can be made in important resin properties such as thermal conductivity, coefficient of thermal expansion, shrinkage, thermal shock resistance, density, exotherm, viscosity, and cost^{1,2}. Such changes are applicable to epoxies (studied most to date), polyurethanes, and silicones.

Table 7-1 shows costs and application effects of the more commonly used fillers. Owing to the large number of materials and suppliers available, this listing is not comprehensive. It does, however, give basic information on the more commonly used fillers. In general, the fillers mentioned in Table 7-1 are used in particle sizes of 200-mesh or finer—except sand, hollow spheres, and reinforcing fillers which depend on particle configuration for their effect.

7-1.1 FILLER CONTENT AND PROPERTY CHANGES

Different fillers affect a given resin property in varying degrees; the effect is often similar regardless of the filler employed. The effect a filler has on a given property seems to be closely associated with the amount of filler used. Figs. 7-1 through 7-5 demonstrate this fact, i.e.,

1. Fig. 7-1 shows the effects of filler content on exotherms.

2. Fig. 7-2 shows the effects of filler content on shrinkage.

3. Fig. 7-3 shows the effects of filler content on the coefficient of thermal expansion.

4. Fig. 7-4 shows the effects of filler content on arc resistance.

5. Fig. 7-5 shows the effects of filler content on viscosity.

The data shown are averaged for several fillers. For more specific data, Table 7-2 shows the effects of mica, glass, and calcium carbonate on physical and electrical properties of epoxy resins.

7-1.2 EFFECTS ON THERMAL PROPERTIES

A problem with most resin systems is their tendency to crack because of the difference in thermal expansion between embedded parts and the embedment material. This difference is shown in Fig. 7-6 which compares the thermal expansion of various other materials with that of filled and unfilled epoxy resins. By using Fig. 7-6, in comparison with Fig. 7-3, it can be seen that by adding sufficient filler, the thermal expansion of epoxy resins (and this should also be approximately true of other embedding resins) can be brought down to the same range of thermal expansion found for metals. Again, although the trend is the same for most fillers, specific fillers vary to some degree in their effect. The effect of various fillers on the coefficient of thermal expansion is shown in Fig. 7-7.

Besides the beneficial effects of reducing the thermal expansion of a given resin, fillers also have the effects of increasing the thermal conductivity and reducing the weight loss (during heat aging)⁴.

Weight loss is reduced by the temperature stability of fillers. The greater the amount of filler in a resin, the lower will be the weight loss of that

TABLE 7-1 COST AND EFFECTS OF COMMONLY USED FILLERS^a

Filler	Approximate Price, cents/lb ^c	Effects ^b												
		Increase							Decrease					
		Thermal Conductivity	Thermal Shock Resistance	Impact Resistance	Compressive Strength	Arc Resistance	Machinability	Electrical Conductivity	Cost	Cracking	Exotherm	Coefficient of Expansion	Density	Shrinkage
sand silica talc clay calcium carbonate calcium sulfate (anhydrous)	1	×			×				+		×	×	×	×
	1-2	×			×				+		×	×	×	×
	1-4								×		×	×	×	×
	1-3		×				+	+	×		×	×	×	×
	0.5-5								×		×	×	×	×
Reinforcing Fillers	2-4	×			×	+			■		×	×	×	×
	3-9								×					
	2-5		×	+	×				×	×				
	2-3	×	×	+					×	×				
	45		×	+					×	×				
Specialty Fillers			×	×	×	×		×	×				+	
	quartz	2-5	×		×									
	aluminum	5-15	×	×		×				×	+		×	×
	hydrated alumina	3-6		×			+			×	+		×	×
	lithium aluminum silicate													
	beryl		×										×	×
	silica aerogel	30-80				×				×	+		×	×
	barium sulfate	5-45												
	graphite	6-30												
	powder metals		×	×	×	×	×	+		×	×	×	×	×
low-density spheres	75-150								×	×	×	×	×	+

^a Failure sizes of fillers listed are 200-mesh or finer except for sand, hollow spheres, and reinforcing fillers that depend on particle configuration for the desired effect.

^b x, effective; +, most significant effect.

^c As of 1978, multiply these prices by 1.5 to 2.

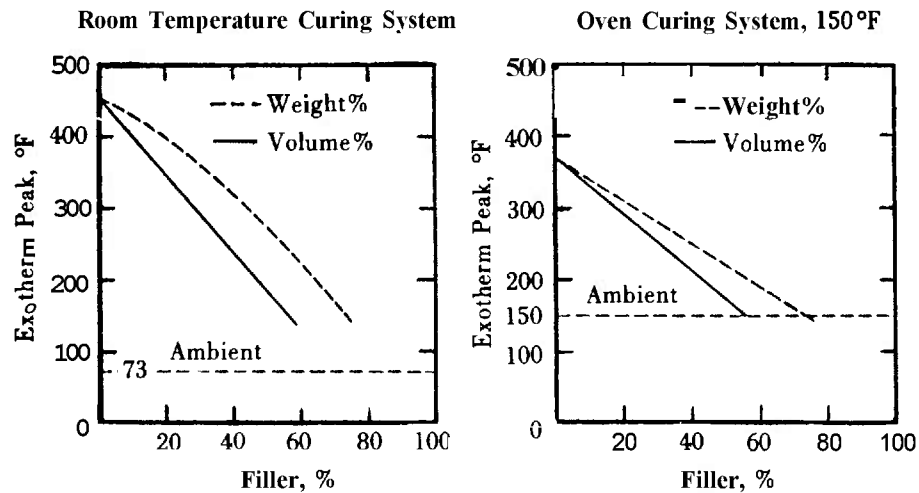


Figure 7-1. Effect of Filler Concentration on Exotherm of 100-cm³ Sample of an Epoxy Resin

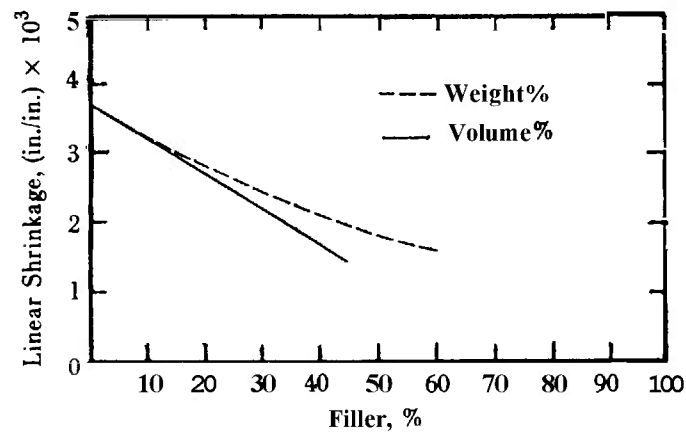


Figure 7-2. Effect of Filler Concentration on Shrinkage of an Epoxy Resin

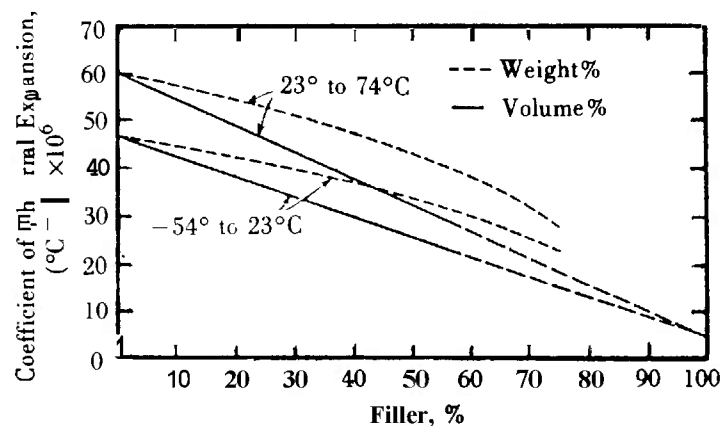


Figure 7-3. Effect of Filler Concentration on Coefficient of Thermal Expansion of an Epoxy Resin

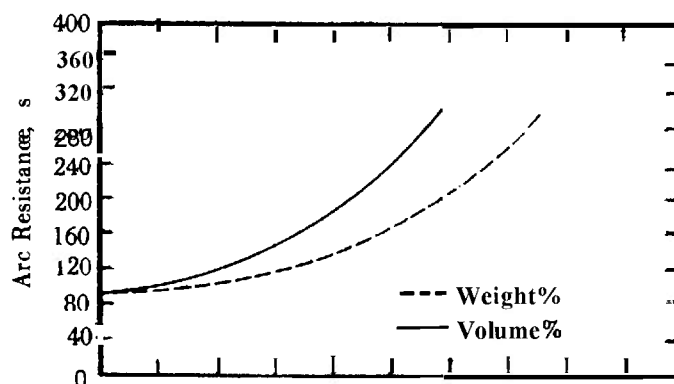


Figure 7-4. Effect of Filler Concentration on Arc Resistance of an Epoxy Resin

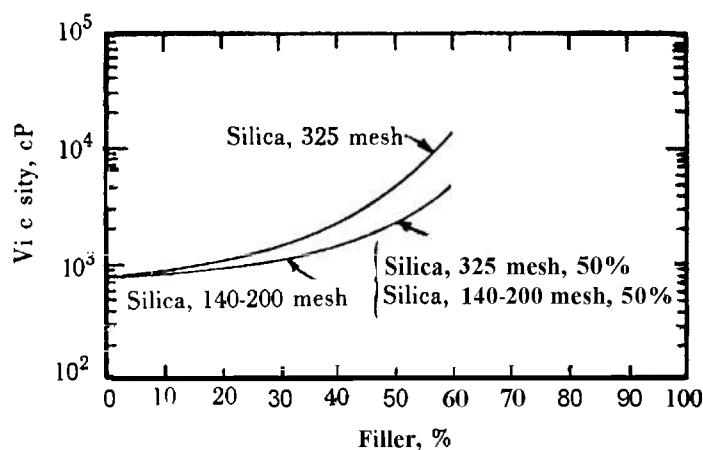


Figure 7-5. Effect of Fillers on Viscosity of an Epoxy Resin

system during heat aging. Although the resin portion of the system will degrade upon heat aging, the performance of the total system is generally always improved by the use of fillers. This is the result, not only of reduced weight loss, but also of shrinkage reduction and thermal-conductivity increases caused by incorporation of filler into the system.

Another effect of fillers on the properties of a resin system is reduction in the exotherm of the system during the curing cycle (see Fig. 7-1). This effect, with reduced shrinkage and decreased thermal expansion, gives many resin

systems minimal resin cracking. This is important in cases where the exothermic reaction tends to cause cracking of the resin during polymerization. The addition of filler will often remedy this problem and change a normally unsuitable system into a very usable system with respect to cracking⁵.

Another characteristic that can be modified by the thermal effect of fillers is pot life. The thermal conductivity of the filler will transfer some of the heat from the unit being cured, thus increasing the pot life. The extension of pot life is related to the control of the exothermic heat of the system.

TABLE 7-2 EFFECTS OF FILLERS ON EPOXY RESIN PROPERTIES

Property	Unfilled	Calcium carbonate	Mica	Glass
Coefficient of Linear Expansion at 60°-80°C, °C ⁻¹	72 X 10 ⁻⁶	57 X 10 ⁻⁶	43 X 10 ⁻⁶	—
Thermal Conductivity, W/in ² •°C•in ⁻¹ .	0.008	0.014	0.012	0.012
Water Absorption, mg	24	20	22	24
Specific Gravity	12	15.8	14.1	15.2
Compressive Strength, psi	15,900	7540	5700	—
Tensile Strength, psi	9700	6000	5650	—
Dielectric Strength, V/mil	320	370	420	370
Dissipation Factor, dimensionless				
10 ⁶ Hz	0.029	0.026	0.035	0.026
10 X 10 ⁶ Hz	0.029	0.026	0.034	0.026
20 X 10 ⁶ Hz	0.028	0.026	0.032	0.026
50 X 10 ⁶ Hz	0.026	0.025	0.030	0.025
100 X 10 ⁶ Hz	0.020	0.023	0.026	0.023
Dielectric Constant, dimensionless				
10 ⁶ Hz	3.9	4.45	4.05	4.05
10 X 10 ⁶ Hz	3.75	4.2	3.9	3.9
20 X 10 ⁶ Hz	3.7	4.2	3.85	3.85
50 X 10 ⁶ Hz	3.65	4.15	3.75	3.8
100 X 10 ⁶ Hz	3.6	4.03	3.7	3.75
Remarks		best general charac- teristics	best for high dielectric strengths	

Another thermal property that can be improved by the use of fillers is fire resistance or burning rate. The burning rate is reduced considerably, and burning is even eliminated in many cases through the addition of a filler such as antimony oxide. Also, certain phosphates can be used to reduce the flammability of embedding resins.

7-1.3 EFFECTS ON MECHANICAL PROPERTIES

With respect to their effects on mechanical properties of a resin system, fillers are often classed as reinforcing and nonreinforcing, or fibrous and nonfibrous. Nonreinforcing or nonfibrous fillers are also sometimes referred to as bulk fillers.

Hardness and machineability depend on the specific filler; hardness is increased and machineability made worse by the use of fillers.

Difficult machining problems result from the use of abrasive fillers such as silica and sand.

Impact strength and tensile strength can be increased by the use of reinforcing fillers but normally are decreased by the use of bulk fillers. Milled or chopped glass fibers are especially good reinforcing fillers.

7-1.4 EFFECTS ON ELECTRICAL PROPERTIES

Although certain electrical characteristics of a resin system can be improved for specific uses by the incorporation of selective fillers and filler concentrations, this effect of fillers on a resin system is not as pronounced as the effect of fillers on the mechanical and thermal properties of the system. For instance, dielectric strength is not normally improved by filler addition. Dielectric strength may even be decreased if the filler has absorbed any moisture or contaminant. Dissipation factor and dielectric constant can be controlled,

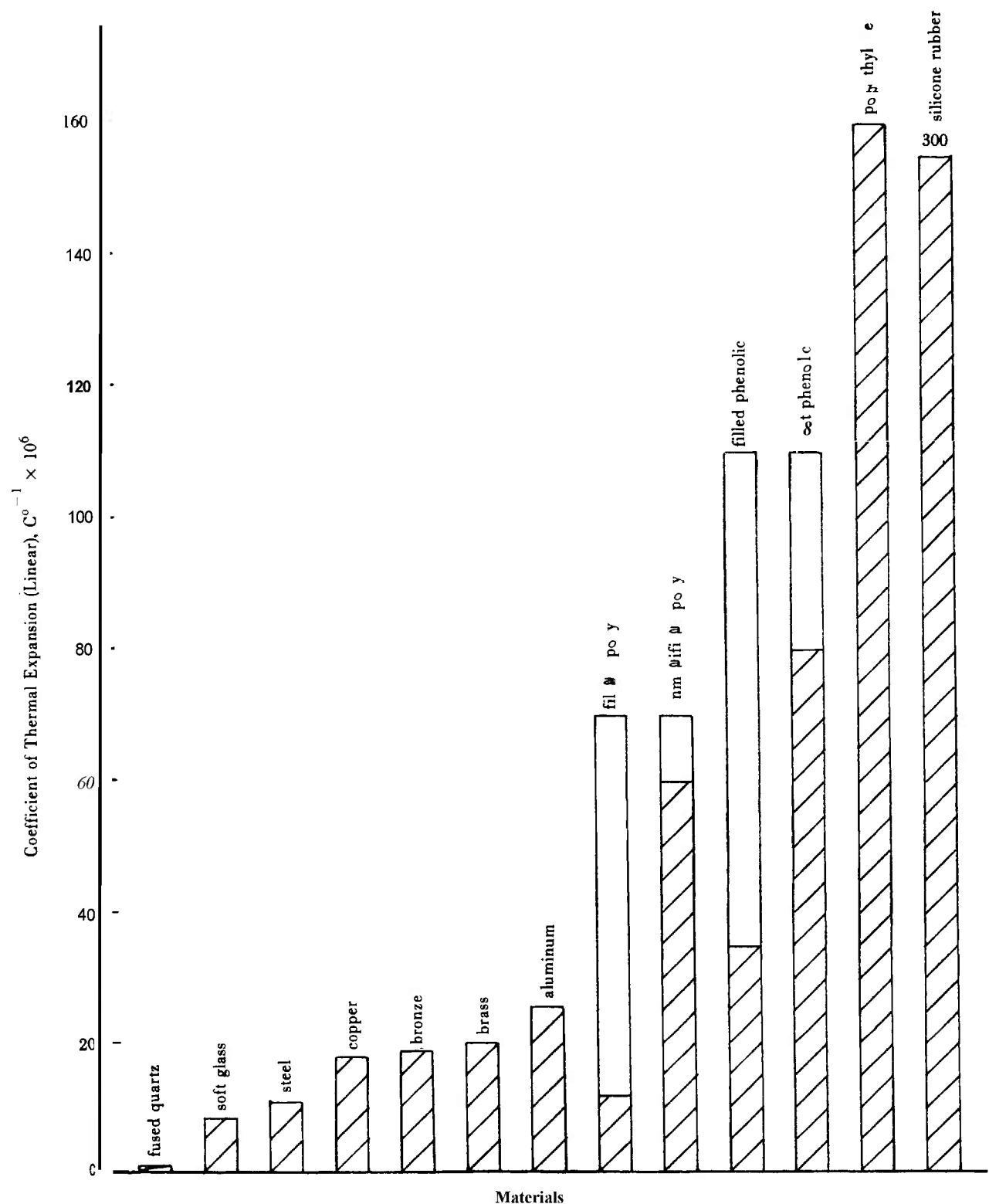


Figure 7-6. Coefficients of Thermal Expansion of Embedding Resins Compared With Those of Other Types of Materials
(Sectioned bars represent variations within the given type of material.)

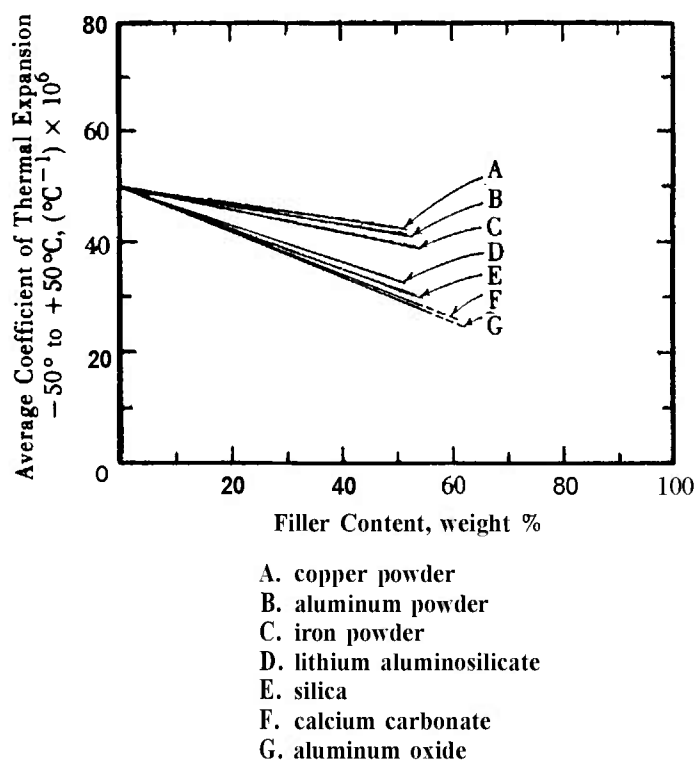


Figure 7-7. Effect of Various Fillers on Coefficients of Thermal Expansion of an Epoxy Resin With 15 phr m-phenylenediamine Curing Agent

however, by the use of low-density fillers and other 'selective fillers such as barium titanate'.

7-2 USE OF MILLED GLASS FIBER

Milled fibers normally come in screen sizes of 1/32, 1/16, 1/8, and 1/4 in. They are made by hammer milling glass-fiber strands and screening them through screens of the proper-sized openings. The effect of milled fibers on the impact strength of epoxy resins is shown in Fig. 7-8.

Where it is difficult to control the seepage of resin from fine parting lines in a mold, the use of 5% milled glass fibers, particularly the 1/32-in. fibers, provides an effective control against such seepage if the glass fibers are incorporated along with the other fillers.

Of pertinence in the selection of a glass filler is the type of material used as a binder on the glass. This will have an effect on the insulating properties of the fiber-filled compound. Binders or siz-

ings are applied to glass fibers to improve the adhesion of the fibers to the resin and the end-strength properties. The binders or sizings can be a starch treatment, a silane treatment, a chromic chloride treatment, or others. There are many pros and cons in choosing which sizing is better for which use; in general, a starch sizing will tend to allow moisture penetration along the fibers and thus reduce the insulation resistance of a glass-filled compound, particularly if the compound is subjected to high humidity. This is not so true with either of the other two finishes. The effects of a chromic chloride sizing are shown in Fig. 7-9.

7-3 USE OF LOW-DENSITY FILLERS

One of the methods for achieving a low-density casting or potting resin is the incorporation of low-density fillers into the resin. It is generally not possible to achieve the low resin density

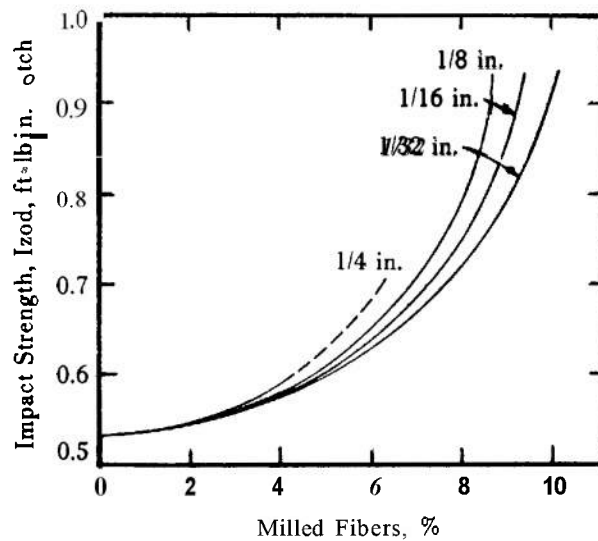


Figure 7-8. Effect of Milled Glass Fibers on Impact Strength of an Epoxy Resin
 — Fractions indicate fiber length.
 (Epoxy castings were made 1/2 in. thick using Epon 828 and Curing Agent Z (Shell Chemical Corp.) and cured 1 h at 240°F)

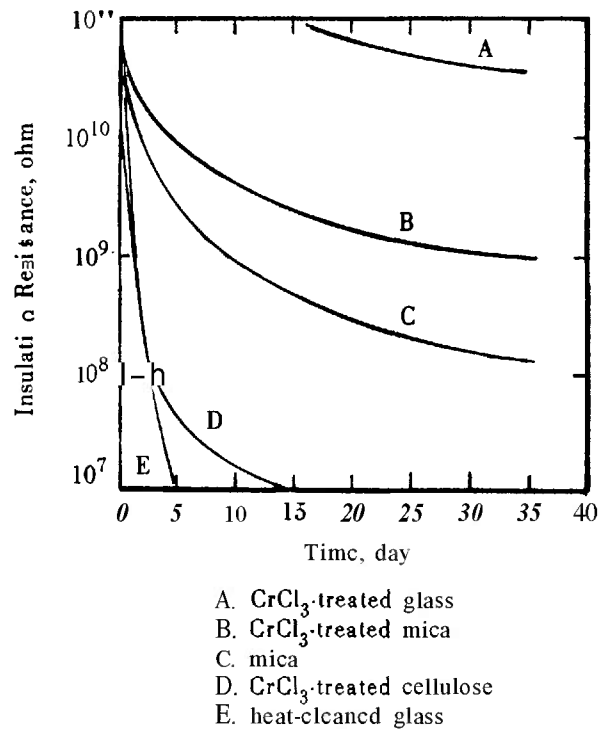


Figure 7-9. Effect of Chromic Chloride Treatment of Fillers
 — Insulation resistance of epoxy castings at 140°F and 95% RH
 (chromic chloride sizing, Volan, marketed by Du Pont)

(Value of resistance of insulation given is that of an insulator measured between two electrodes and represents resistance of the weakest mode of insulation for a given set of conditions.)

available in foams but it is possible to obtain a sizeable density reduction with minimum sacrifice of other resin properties. Often, this can result in a resin which is preferable to foams. Table 7-3 shows some of the properties obtainable with low-density fillers and compares these properties with the properties of unfilled and silica-filled epoxy resins.

7-4 COST

An advantage of fillers is that, in most cases, fillers cost much less than the base resins. The

end cost of the compound will then depend upon both the filler concentration and the cost of the base resin used⁷.

Where economy is a consideration, it is desirable to use the largest practical filler concentration. The actual economy should be calculated for any system of interest, however, since the weight-percentage loading can be misleading in some cases. Higher loading will really produce a higher density rather than a larger volume of compound. In most cases it is the cost per volume that is really important because in electronic packaging a certain volume must be filled⁸.

TABLE 7-3 PROPERTIES OF EPOXY RESIN COMPOUNDS WITH VARIOUS LOW-DENSITY FILLERS

Resin Formulation	Shrinkage, Linear, %	Hardness After Cure, Shore D	Compound Specific Gravity at 21°C	Tensile Strength at 25°C, psi	Thermal Conductivity Btu/h·ft ² ·°F·in. ⁻¹	Thermal Expansion, Linear, at 25°-100°C, in./in.·°C	Brookfield Viscosity at 25°C, cP	Stress Index, 10° to -65°C, psi	Stress Index, 10° to +85°C, psi	Dielectric Constant at 25°C, d'less	Power Factor at 25°C, d'less	Volume Resistivity, ohm·cm	Dielectric Strength at 25°C, V/mil
100 parts Epon 828, 10.5 parts Shell curing agent D ^a	0.12	80-85	1.17	8000	2.68	8.7×10^{-5}	13,500-19,500			1 kHz: 3.8 1 MHz: 3.7	1 kHz: 0.0035 1 MHz: 0.015	25°C: 8.7×10^{14} 10°C: 5×10^{11} 150°C: 1×10^9	400-500
100 parts Epon 828, 100 parts 325-mesh silica, 10.5 parts Shell curing agent D ^a	0.08	80-85	1.59	5500	6.38	8.6×10^{-5}	43,000-48,000	20.0	28.0	1 kHz: 3.4 1 MHz: 3.4	1 kHz: 0.003 1 MHz: 0.012	25°C: 1.3×10^{14} 65°C: 6.2×10^{12}	> 330
100 parts Epon 828, 15 parts BJOA-0840 Microballoons ^b , 10.5 parts Shell Curing agent D	0.14	80-84	0.86	3300	1.91	8.2×10^{-5}	34,000-38,500	6.7	9.1	kHz: 3.2 MHz: 2.7	1 kHz: 0.003 1 MHz: 0.014	25°C: 1.0×10^{14} 65°C: 5.3×10^{13}	> 300
100 parts Epon 828, 34 parts Kanamite ^c , 10.5 parts Shell curing agent D	0.06	75-80	1.01	2000	2.47	6.7×10^{-5}	34,000-39,000	8.5	13.3				
100 parts Epon 828, 4 parts Colfoam ^d , 10.5 parts Shell curing agent D	0.17	80-85	1.01	4050	4.15	8.6×10^{-5}	45,000-48,000	10.4	10.5				
100 parts Epon 828, 14 parts CPR-2077 glass Microballoons ^e , 10.5 parts Shell curing agent D	0.25	80-85	0.95	4200	4.56	8.2×10^{-5}	44,000-47,000						

^aHigh density formulation included for comparison.^bUnion Carbide, hollow, phenolic.^cFerro Corp., unicellular clay material, aluminum silicate type^dColton Chemical Co., urea-formaldehyde spheres^eStandard Oil of Ohio, hollow glass spheres.

REFERENCES

1. R. B. Seymour, "Fillers for Molding Compounds," *Modern Plastics Encyclopedia*, McGraw-Hill Book Co., New York, NY, pp. 194-200, 1975-76.
2. J. Z. Keating, S. A. Grove, J. Rea, and T. Cook, "Fillers", *Modern Plastics Encyclopedia*, McGraw-Hill Book Co., New York, NY, 1977-78, pp 183, 187, 189, 192.
3. W. J. Frissell, "Fillers", Vol. 6, *Encyclopedia of Polymer Science and Technology*, John Wiley-Interscience, New York, NY, 1967, pp 740-63.
4. A. M. Merrill, ed., "Materials and Compounding Ingredients for Rubber and Plastics,,," *Rubber World*, 424-77, New York, NY (1965).
5. R. C. Hosford, "A Guide to Fillers and Reinforcement for Thermosets", *Plastics Technology*, 11, 34-41 (1965).
6. R. B. Seymour, "Functional Fillers Extend Resin Without Degrading Physical Properties", *Plastics Design and Processing*, 15-7 (July 1976).
7. E. Gilbride and S. B. Levenson, "Limestone Fillers in Epoxy Systems", *Modern Plastics* 42, 147 (1975).
8. R. Eller, "How to Figure the Economics of Filled vs Unfilled Resins", *Plastics World*, 70-2 (15 July 1974).

CHAPTER 8

EMBEDMENTS AND ELECTRICAL PROPERTIES

The role that embedding plays in making miniature and microelectronic assemblies possible is discussed. Electrical properties—surface and volume resistivities, dielectric strength, dielectric constant, dissipation factor, loss factor, power factor, and arc resistance—as a function of resin ratios and cure conditions are given

8-1 GENERAL ELECTRICAL CONSIDERATIONS

Fragile microelectronic parts assemblies need embedment for protection against abrasion, handling, shock, and vibration. Embedments play a vital part in the successful operation of electronic assemblies. Without the use of high performance resins, many of the highly dense and intricate windings, coils, and components in small or miniature assemblies would not be possible.

One of the most important functions of organic embedments is to provide electrical insulation and dielectric isolation for active and passive electronic components. Effectiveness in this respect is expressed in terms of insulation resistance, volume resistivity, surface resistivity, and dielectric strength. Other functions include the storage of electric current. These are expressed in terms of dielectric constant, capacitance, and dissipation factor. A knowledge of exact electrical values and how these parameters vary with changes in composition, purity, structure, or environment is important in selecting the most reliable resins for electronic equipment!

8-2 RESISTANCE AND RESISTIVITY

Insulation resistance is expressed in ohms as the ratio of applied voltage to the total current between two electrodes in contact with a specific material. This resistance is directly proportional to the length and inversely proportional to the area of the specimen according to the equation

$$R = \frac{\rho \ell}{A} \quad (8-1)$$

where

R = insulation resistance, ohm

ℓ = length, cm

A = area, cm²

ρ = a proportionality constant called the *specific resistance* or *resistivity*, ohm•cm.

Different materials can be compared in terms of their resistivity values because these values reduce resistance measurements to a common denominator. The frequently used volume resistivity, for example, is the ohmic resistance of a cube of bulk dielectric material 1 cm (or 1 in.) per side and is expressed in ohm•centimeters (or ohm•inches) (Ref. 2). Surface resistivity is the resistance between two electrodes on the surface of an insulating material, expressed in ohms per square centimeter.

All materials may be roughly classified according to their ability to conduct or impede the flow of electricity. They range from metals, which are extremely good conductors, to plastics, which are very good insulators. Materials intermediate between these two types are referred to as semiconductors, but this does not necessarily mean that they have properties suitable for semiconductor devices. A select few inorganic materials, such as doped germanium or silicon, are the basis for the fabrication of semiconductor electronic devices, but organic semiconducting types have not as yet been found useful for making such devices.

8-2.1 VOLUME RESISTIVITY OF MATERIALS

Materials are generally classed into one of three groups according to their volume resistivities:

1. Good conductors 10^{-6} - 10^0 ohm•cm
2. Semiconductors 10^2 - 10^9 ohm•cm
3. Good insulators (poor conductors)
 $> 10^9$ ohm•cm.

Most organic plastics *per se* are good electrical insulators and find use in electrical/electronic applications. The resistivity of plastics is usually greater than 10^{12} ohm•cm, and the current which “leaks-through” generally is negligible for most equipment applications. However, in some electronic products, even this small current flow can be prohibitive. A knowledge of the electrical tolerances that a device must meet is important before an embedment can be chosen. Volume resistivities of some materials are compared in Fig. 8-1. There is a difference of 24 orders of magnitude between the most conductive (i.e., silver or copper metal) and the least conductive (i.e., polytetrafluoroethylene).

8-2.2 PARAMETERS AFFECTING RESISTIVITY — RESIN COMPOSITION

Though resistivity is generally a constant property of a resin, many variables can cause variations in this characteristic. Changes in composition can have significant effects. The effect of blending a flexibilizing resin, e.g., polyamide, into an epoxy is shown in Fig. 8-2. The electrical properties of the epoxy, i.e., 10^{14} to 10^{16} ohm•cm, decrease rapidly after the amount of polyamide exceeds 40%. Reduction of resistivity is attributed to an unreacted quantity of polyamide.

Minor amounts of impurities have effects on resistivities. The variation of resistance with impurities is undesirable, especially as it affects the performance of organic insulating coatings. Ionic impurities in plastics, coupled with the presence of moisture, are known to lower resistivity values by as much as 6 to 11 orders of magnitude.

Resistivity also depends on the degree of cure or advancement in the state of polymerization of the coating resin. As the cure advances, electrical resistivity increases. (A small decrease may be noted when the material first reaches its peak

exothermic temperature.) Two competing phenomena are occurring: (1) a decrease in resistance as the temperature rises to reaction exotherm, and (2) an increase in resistance as the resin polymerizes and becomes fully cured. This is shown for an amine-cured epoxy system in Figs. 8-3 and 8-4. These curves can also be useful in determining when resin polymerization is essentially completed³

8-2.3 DELETERIOUS EFFECTS ON SURFACE RESISTIVITY

Moisture and contaminants affect surface resistivity more than volume resistivity. It can take up to a number of weeks for volume resistivity to change under humid or “dirty” environments; surface changes occur almost at once. Fingerprint contamination under humid conditions may change surface resistivity by a factor of 10^{10} (Ref. 4).

Fig. 8-5 shows the effect of humidity on the surface resistivity of epoxies cured with different hardeners. Electrical stability as a function of relative humidity is highly dependent on the hardener used. Aromatic amine-cured epoxies were found to be stable at higher relative-humidity levels than anhydride- or aliphatic amine-cured types. In the anhydride-cured sample, resistivity leveled off to about 5×10^{12} —a value that is still considered adequate for most electrical applications. Resistivities recover after removal from the humid environment; the aromatic amine-cured epoxies displayed the fastest rate of recovery as shown in Fig. 8-6 (Ref. 5).

8-2.4 TEMPERATURE EFFECTS ON RESISTIVITY

Resistivity varies with temperature. Plastics show negative temperature coefficients of resistivities. A dielectric resin which is a good insulator at 25°C may not be suitable at elevated temperatures. Fig. 8-7 shows curves for some polymers.

The temperature dependence of resistivity is given by the equation

$$\rho = \rho_0 \exp[\Delta E / (2KT)] \quad (8-2)$$

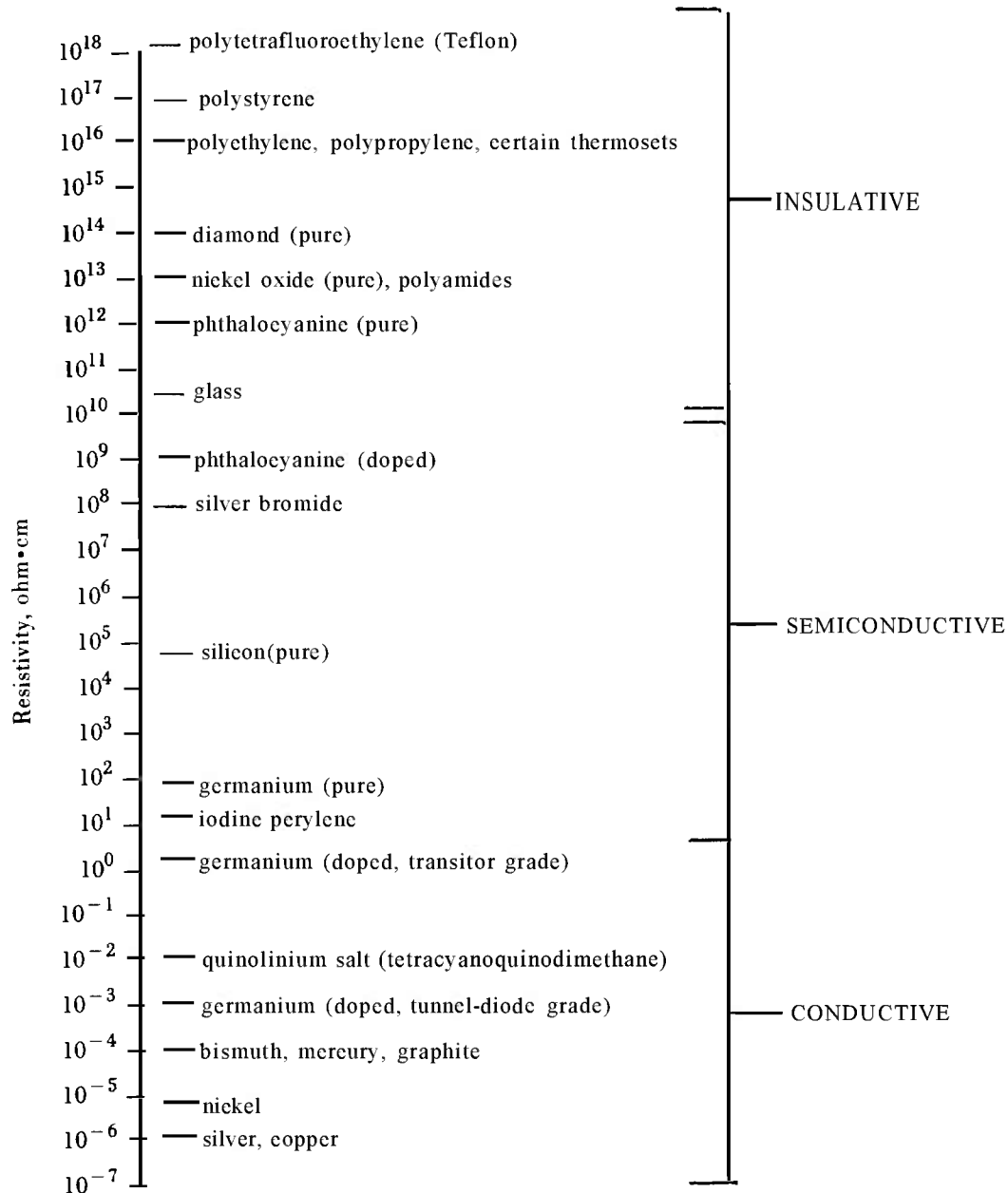


Figure 8-1. Comparative Electrical Resistivities of Some Materials

where

ρ = resistivity at temperature T

ρ_0 = limiting low temperature resistivity

K = Boltzmann constant, erg/K

AE = energy, erg

T = absolute temperature, K.

8-3 DIELECTRIC CONSTANT

Dielectric constants of materials arise from their electronic polarizability. Materials with polar groups—i.e., those having permanent dipole moments, such as C O or COOH—will have

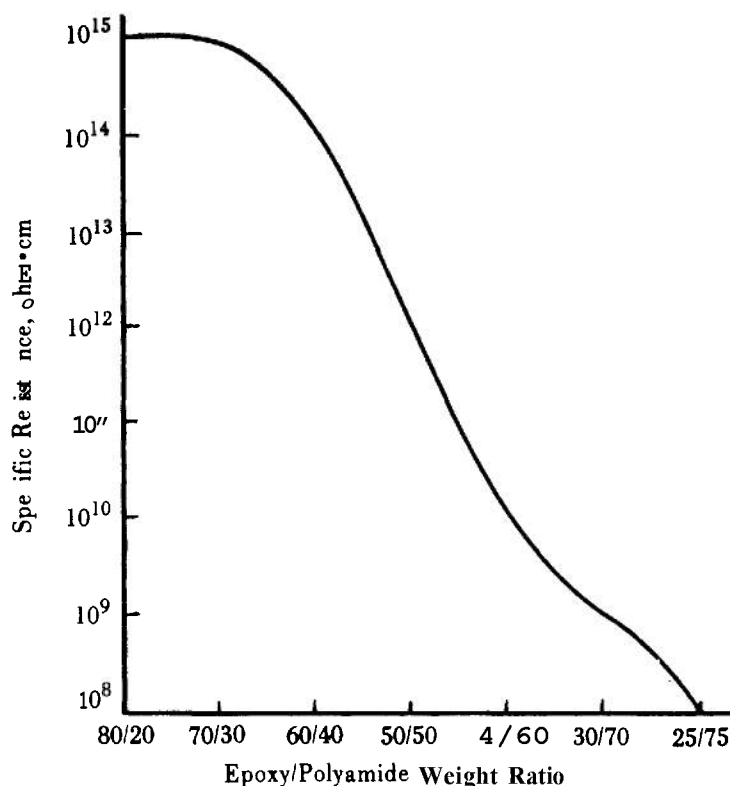


Figure 8-2. Variation of Resistivity With Change in Epoxy/Polyamide Ratios

large dielectric constants because of the orientation of the dipoles in an applied field. Polar polymers tend to absorb more water from the atmosphere, which again will impair their electrical properties.

Dielectric constants for the embedments discussed in this handbook range from 2.8 to about 4.6. This is shown in Table 8-1 (Ref. 6).

Resins which have low dielectric constants (and low dissipation values) which are retained low over a wide temperature/humidity range are preferred as insulation. Those with high dielectric constants and low dissipation factors find use in capacitors since they enable the storage of large amounts of electrical energy.

Dielectric constants of 4.5 maximum (1,000 Hz and 77°F) are generally satisfactory for insulating electrical or electronic assemblies (minimum requirements for MIL-1-16923). But for microelectronic and miniaturized circuits operating at high frequencies, capacitance effects must

be low; this requires the use of resins with very low dielectric constants at operating efficiencies.

The dielectric constant of a resin type can increase or decrease; this is a function of its composition. Adding glass or ceramic fillers (that have high dielectric constants) increases the value for the resin. Blending of resins with different constants gives an intermediate value of the dielectric constant for the blend. A nominal calculation of the dielectric constant of a system made of two materials with different k values, e.g. resin and filler, can be made by means of Eq. 8-3.

$$\log k_x = v_1 \log k_1 + v_2 \log k_2, \text{ dimensionless} \quad (8-3)$$

where

k_x = dielectric constant of composite, dimensionless

v_1 = volume fraction of the first component, dimensionless

k_1 = dielectric constant of the first component, dimensionless

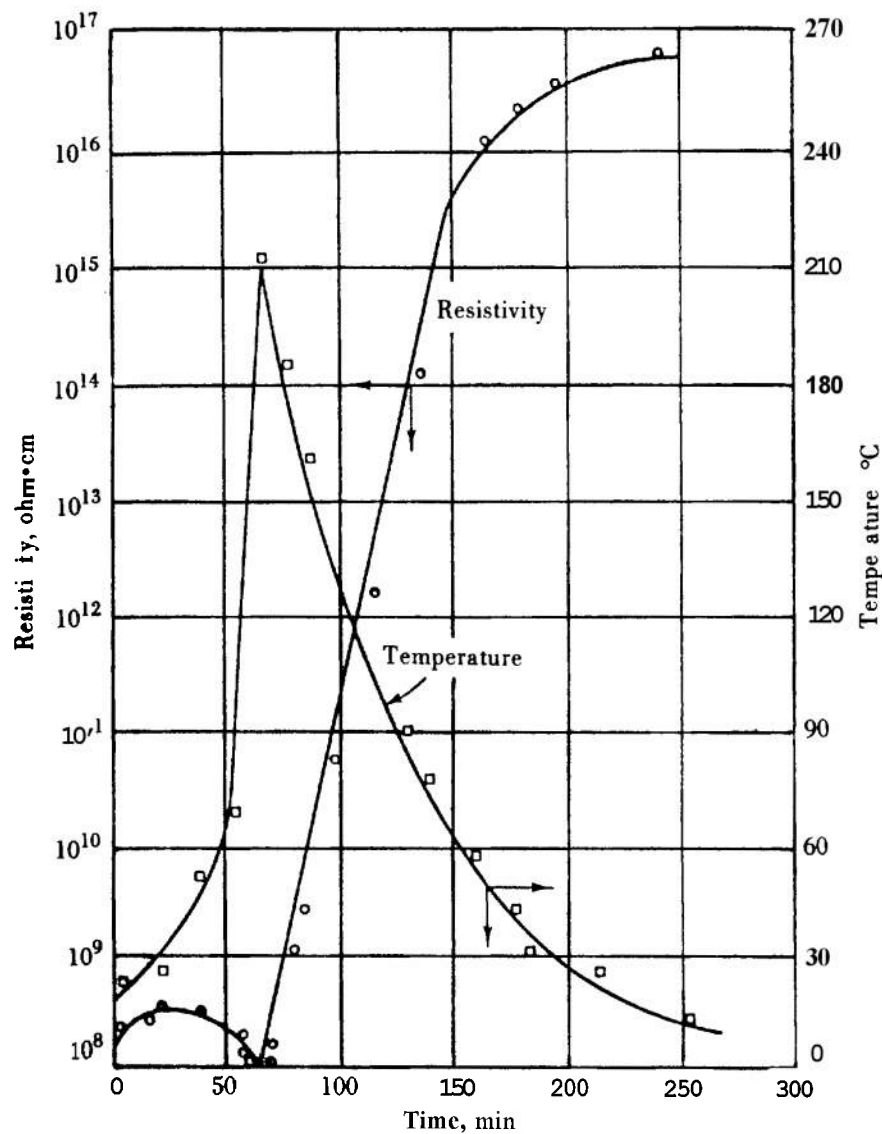


Figure 8-3. Electrical Resistivity as a Function of Cure Conditions

v_2 = volume fraction of the second component, dimensionless

k_2 = dielectric constant of the second component, dimensionless.

8-4 DIELECTRIC STRENGTH

Dielectric strength is the ability of a polymer to withstand voltage without breakdown (or passage of electricity). Dielectric strength is the minimum voltage (as volts per mil thickness of insulation) at or below which breakdown does

not occur. Accurate data are needed when designing reliability in electrical parts with high component density. For either high or low voltage use, polymers find use because of their high dielectric strengths; these can be generally higher than inorganic or ceramic insulators.

The values of the dielectric strengths should be obtained carefully under specified conditions to permit reproducible results and a reliable comparison between materials or samples. A large number of test conditions are known to affect

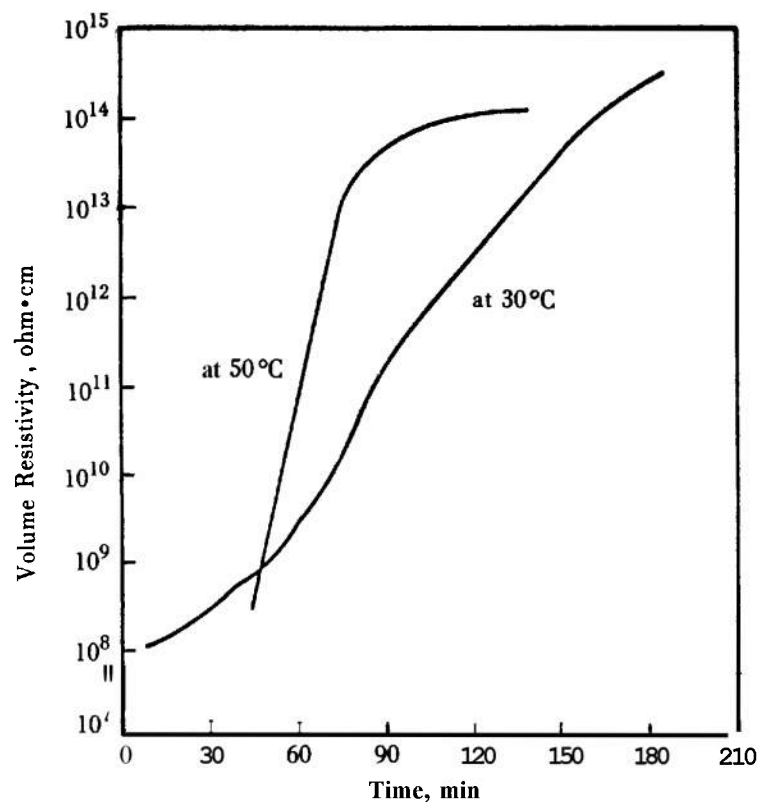
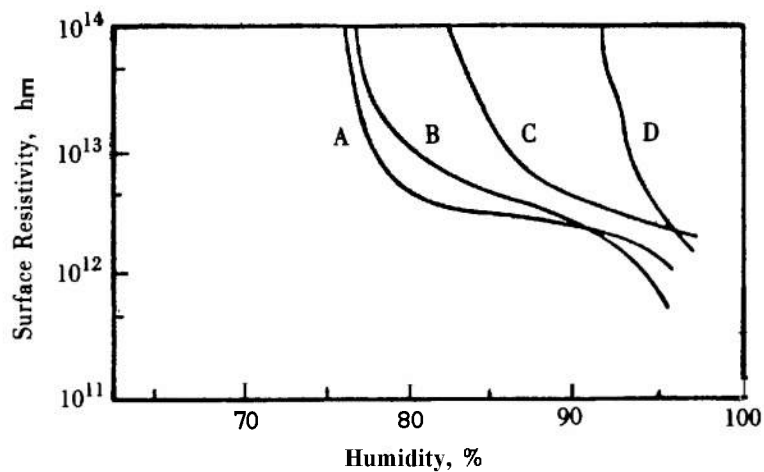
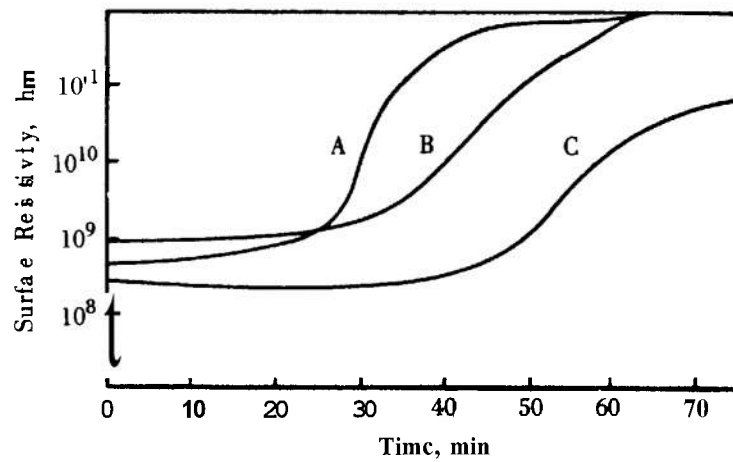


Figure 8-4. Isothermal Polymerization of an Amine-Cured Epoxy as a Function of Volume Resistivity



- A. epoxy resin cured with methyl nadic anhydride
- B. epoxy resin cured with diethylenetriamine
- C. epoxy resin cured with aromatic amine
- D. Novolac-epoxy resin cured with aromatic amine

Figure 8-5. Effect of Humidity on Surface Resistivity of Cured Epoxy Resins at 35°C



- A. epoxy cured with aromatic amine
- B. epoxy cured with methyl nadic anhydride
- C. epoxy cured with diethylenetriamine

Figure 8-6. Recovery of Surface Resistivity for Cured Epoxy Resins at 25°C and 80%RH

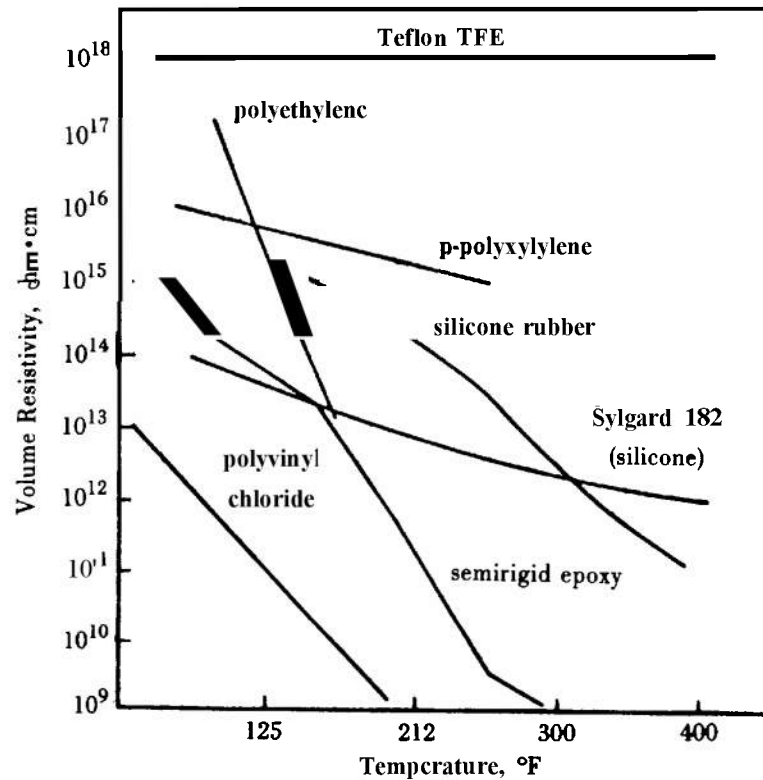


Figure 8-7. Electrical Resistivity—Temperature Curves of Several Polymer Types

**TABLE 8-1. DIELECTRIC CONSTANTS
OF SPECIFIC TYPES OF RESINS**

Material	60-100Hz	10 ⁸ Hz	10 ⁹ Hz
<i>Epoxy, anhydride-castor oil adduct</i>	3.4	3.1	2.9 (10 ⁷ Hz)
Cured with diethylene-triamine	4.1	4.2	4.1
Cured with dodecylsuccinic anhydride	2.8	—	—
Cured with metaphenylene diamine	4.6	3.8	3.25 (10 ¹⁰ Hz)
Cured with methyl nadic anhydride	3.3	—	—
<i>Epoxy polyamide:</i>			
40% Versamid 125, 60% epoxy	3.4	3.1	—
50% Versamid 125, 50% epoxy	3.2	3.0	—
<i>Polyurethane:</i>			
1 component	4.1	3.8	—
2 component	6.8 (10 ⁸ Hz)	4.4	—
2 component (castor-oil cured)	—	3.0-3.2	—
<i>Silicone:</i>			
Gel	3.0	—	—
RTV types	3.3-4.2	3.1-4.0	—
Sylgard elastomer	2.9	2.9	—
<i>Polyxylylene:</i>			
Parylene G	3.1	2.9	—
Parylene D	2.9	2.8	—
Parylene N	2.7	2.7	—

dielectric-strength values. It is important to standardize the electrode configuration and the thickness of the specimen. Although all values are ultimately reduced to volts per mil thickness, the thickness of the sample has a marked effect on the values obtained (see Fig. 8-8). Thin specimens result in higher values than thicker ones; in most cases the 17-mil thickness specified in the ASTM procedure is too thick. The same test procedure, however, may be followed with samples of 2 to 5 mils. Variables which affect readings are the manner in which the voltage is applied (continuously or stepwise), the rate or voltage increase, the frequency of the applied power, and the purity of the sample.

Table 8-2 gives typical dielectric strength values for epoxies, polyurethanes, polyxylylenes, and silicones.

8-5 DISSIPATION, POWER, AND LOSS FACTORS

The *dissipation factor* D is the ratio of the current I_r of the component to the current I_c of the capacitive component, and is equal to the tangent of the dielectric loss angle δ , i.e.,

$$D = \frac{I_r}{I_c} = \tan \delta. \quad (8-4)$$

The *power factor* PF is the ratio of power (watts) dissipated to the product of the effective volts X amperes power output; it is a measure of the dielectric loss in the insulation (which acts as a capacitor). Power factor is related to the dissipation factor:

$$D = \frac{PF}{\sqrt{1 - (PF)^2}}. \quad (8-5)$$

Since power factors for resins are low, dissipation factors are about equal to power factors. These terms are thus used interchangeably. (Specifications such as MIL-1-16923 specify D values no greater than 0.02 at 1000 Hz and 77°F.)

The *loss factor* is the product of the power factor and dielectric constant k . This is a measure of energy absorption, i.e.,

$$\text{loss factor} \approx \text{watts loss} \approx k \tan \delta \approx kD. \quad (8-6)$$

Low values are desired for these power and loss factors particularly with high-speed, high frequency circuits operating in the 10- to 10,000-MHz spectrum. With low values, there is a minimal conversion of electrical energy to heat energy; power loss for the system is reduced. These dissipating factors are generally functions of frequency, temperature, humidity, and purity—i.e. lack of contaminants—in the dielectric polymer.

Dissipation factors for some embedments are shown in Table 8-3.

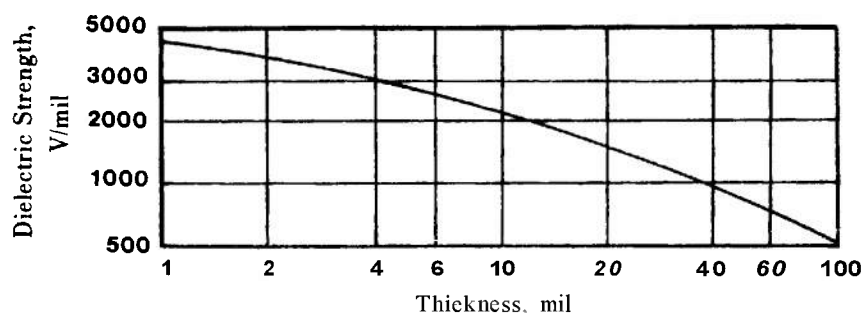


Figure 8-8. Effect of Thickness on Dielectric Strength of Teflon TFE

TABLE 8-2. DIELECTRIC STRENGTHS OF SPECIFIC TYPES OF RESINS

Material	Dielectric Strength, V/mil
Epoxy	1300 (10 mil thickness)
Epoxy (cured with anhydride-castor oil adduct)	650-730 (125 mil thickness)
Epoxy (modified)	1200-2000 (2 mil thickness)
Polyurethane (1 component)	3800 (1 mil thickness)
Polyurethane (1 component)	2500 (2 mil thickness)
Polyurethane (2 component—castor-oil cured)	530-1010 (125 mil thickness)
Polyurethane (2 component—100% solids)	275 (125 mil thickness) 750 (25 mil thickness)
Polyxylenes*:	
Parylene C	3700 (short time) 1200 (step-by-step)
Parylene D	5500 (short time) 4500 (step-by-step)
Parylene N	6500 (short time) 6000 (step-by-step)
Silicone gel	800 (125 mil thickness)
RTV silicone	550-650 (125 mil thickness)
Sylgard 182 elastomer	500 (125 mil thickness)

*Thin vapor-deposited specimens

TABLE 8-3. DISSIPATION FACTORS AT 25°C OF SPECIFIC TYPES OF RESIN

Material	60-100 Hz	10 ⁶ Hz	> 10 ⁶ Hz
Epoxy, anhydride-castor oil adduct	0.0084	0.0165	0.0240
Epoxy polyamide:			
40% Versamid 125, 60% epoxy	0.0085	0.0213	—
50% Versamid 125, 50% epoxy	0.009	0.0170	—
Polyurethane:			
1 component	0.038	0.070	—
2 component (castor-oil cured)	—	0.016-0.036	—
Silicone:			
Gel	0.0005	—	—
RTV types	0.011-0.02	0.003-0.006	—
Sylgard elastomer	0.001	0.001	—
Polyxylylene:			
Parylene C	0.02	0.0128	—
Parylene D	0.004	0.002	—
Parylene N	0.0002	0.0006	—

8-6 ARC RESISTANCE

Arc resistance, measured in seconds, is the time that an arc can cross the surface of an insulation before electrical breakdown occurs. A high voltage, low amperage arc is used to approach use-condition—i.e., ac circuits at high voltages; currents in milliamperes. A frequently used test method is ASTM D 495. The specimens are

placed between electrodes and an arc is generated at scheduled intervals and specific current densities.

There are three ways in which failure from arcing can occur:

1. By tracking (formation of a thin wirelike line between the electrodes)

2. By surface carbonization due to heating—i.e., the formation of carbon forms a path having

less resistance to electrical flow than the original insulation

3. By ignition of the surface (without formation of a visible coherent conductive path).

Table 8-4 shows the arc resistance of some typical embedment polymers. The resistances show wide variability; this can be a function of molecular structure. Constituents such as the curing agent and the kind and amount of filler can affect arc resistance.

Fillers have a significant effect; arc resistance generally is improved. Typical fillers such as mica, alumina, and gypsum may double or triple the arc resistance of an initially unfilled epoxy system.⁷ For epoxies, aromatic amines and anhydride curing agents give epoxies with higher arc resistance than systems cured with aliphatic amines.

Not all polymerics show precise arc resistance properties. When this property is reasonably fixed, it can be due to the basic stability of the polymer, purity, and surface cleanliness. Arc resistance can be enhanced by keeping the surface dry and free from contaminants. By touching the surface, arc resistance can be reduced; the contaminants in this case are moisture, salts, and grease from the fingers.

TABLE 8-4. ARC RESISTANCE OF SOME POLYMERS

Material	Arc Resistance, s
Epoxy (control) A	64
A + 100%alumina	78
A + 100%gypsum	102
A + 75% mica	79
A + 100% silica	124
Epoxy polyamide: 50%epoxy, 50% Versamide 115	76
Epoxy polyamide: 60% epoxy, 40% Versamide 125	82
Polyurethane — one component	40
Polyurethane — two component, castor-oil cured	88-140
Silicones	120-200
RTV Silicones	90-130

8-7 OTHER EFFECTS ON ELECTRICAL PROPERTIES

8-7.1 CAPACITANCE EFFECTS AT HIGH FREQUENCIES

With very high frequency radar circuits, capacitance effects due to plastic substrates can be critical to proper functioning of the electronic item. High capacitance can give delays in switching times and changes in component values. Computer operations can be limited by the coupling capacitance between circuit paths and integrated circuits on multilayer boards. The computing speed between integrated circuits is reduced by this capacitance, and the power required to operate them is increased. Since most systems will employ many metal-oxide semiconductor devices, these problems will be compounded; the coupling capacitance has a greater effect on computer speed.

Reductions in unwanted capacitance can be had through proper selection of embedment and design of the circuit geometry. With further use of microminiaturization and very thin conductor lines, close spacings, and thin insulation, the insulating plastics must show high performance. Such polymers must have very small dielectric constants and also retain other desirable properties—i.e., ease of fabrication, retention of strength, heat resistance, etc. With high-frequency linear circuits—such as those used in radar assemblies—the dielectric constant of insulators again becomes important, especially since it may vary with changes in frequency. Graphs of the k -behavior of some commonly used polymers as a function of frequency are given in Fig. 8-9.

Capacitance C is directly proportional to the dielectric constant of the insulator separating the conductors, directly proportional to the area of the conductors, and inversely proportional to the distance between conductors, i.e.,

$$C = \frac{kA}{d} \quad (8-7)$$

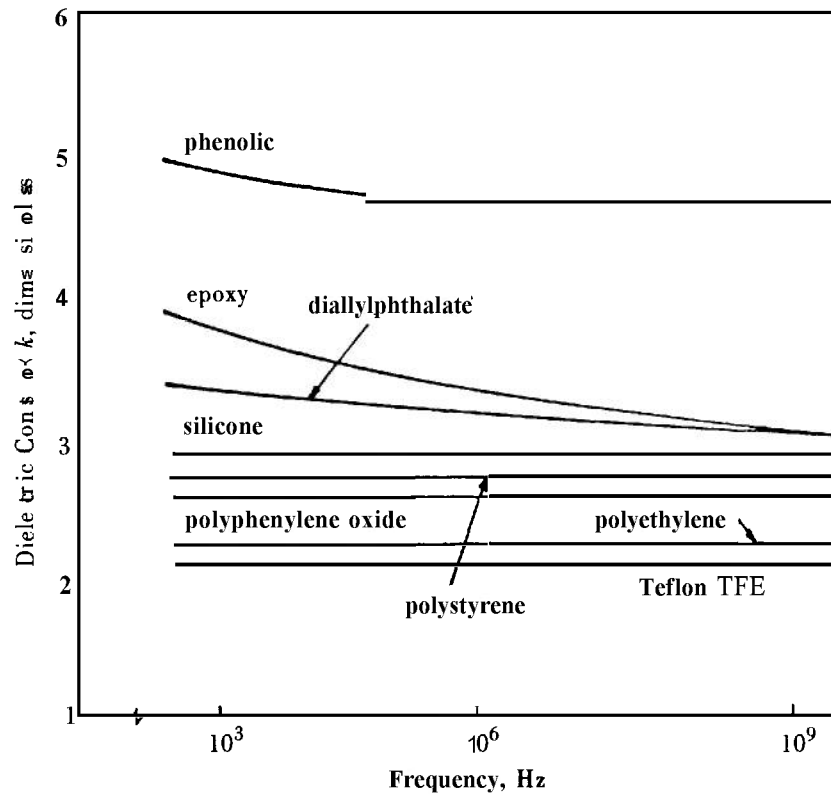


Figure 8-9. Variation of Dielectric Constant With Frequency

where

- k = dielectric constant
- A = area of the plates or conductors
- d = distance between the plates or conductors.

Hence low capacitance may be achieved by keeping A low, k low, and d high.

When the space between parallel plates of a capacitor is filled with an insulating resin, capacitance will be increased by a factor called k , the dielectric constant. This is specific for a particular material.

$$C_m = kC_v \text{ or } K = \frac{C_m}{C_v} \quad (8-8)$$

where

- k = dielectric constant (or permittivity)
- C_m = capacitance of the dielectric resin
- C_v = capacitance of vacuum.

The dielectric material affects the force with which opposite electrical charges attract. Hence,

k is also defined as the relative effect of the dielectric of the force of attraction,

$$F = \frac{QQ_1}{kd^2} \text{ or } k = \frac{QQ_1}{Fd^2} \quad (8-9)$$

where

- F = force of attraction between the two unlike charges
- Q = charge on one plate
- Q_1 = charge on the second plate
- k = dielectric constant
- d = distance between plates.

The higher the dielectric constant of the material between the plates, the less will be the force of attraction between the plates. The dielectric constant of a vacuum is 1; and since the dielectric constant of air is just slightly above 1, for all practical purposes it is also taken as 1, which simplifies the measurement. (Details of sample preparation, measuring methods, and equipment for measuring dielectric constants are given in ASTM D 150-59T).

8-7.2 TEMPERATURE EFFECTS ON DIELECTRIC CONSTANT AND DISSIPATION FACTOR

With frequency constant, the dielectric constant and dissipation factor for an insulating plastic generally increase with higher temperature use. This can be due to lack of absolute uniformity or minor volatile contents which dissipate heat. No simple linearity with temperature may be shown. Figs. 8-10 and 8-11 show the dielectric constant and dissipation factor versus temperature for an epoxy cured with an

anhydride-castor oil adduct. Change with temperature can be further complicated by a form of post-curing at the higher temperatures.

8-7.3 DEGREE OF POLYMER CURE

An indication of the cure of a polymer can be the rate of change of the dielectric constant or dissipation factor with temperature increase? Properties of a fully cured plastic change gradually with a rise in temperature; a polymer still undergoing cure shows more significant changes. Table 8-5 shows the effect of degree of cure on

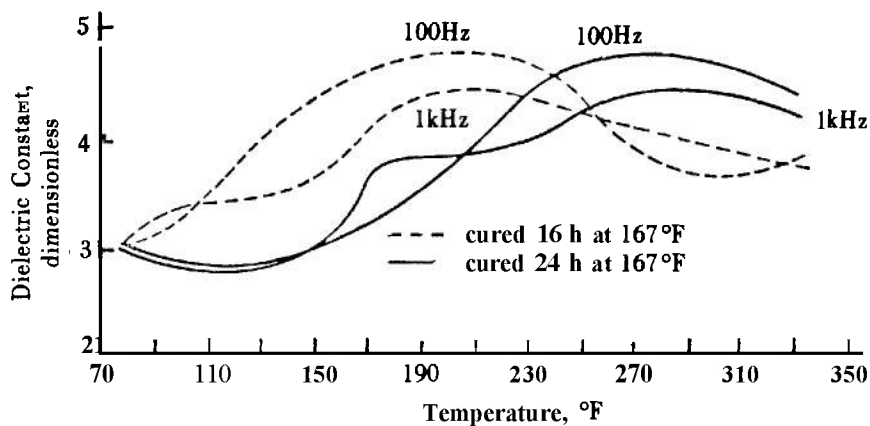


Figure 8-10. Variation of Dielectric Constant With Temperature, Degree of Cure, and Frequency for an Epoxy Cured With Anhydride-Castor Oil Adduct

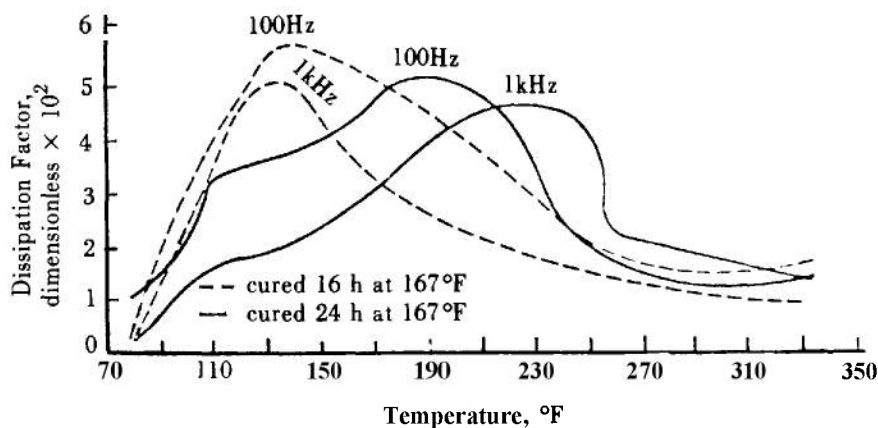


Figure 8-11. Variation of Dissipation Factor With Temperature, Degree of Cure, and Frequency for an Epoxy Cured With Anhydride-Castor Oil Adduct

TABLE 8-5. EFFECT* OF CURE ON ELECTRICAL PROPERTIES OF EPOXY (EPON 828) CURED WITH ANHYDRIDE-CASTOR OIL ADDUCT

Sample	After cure of 16 h at 165" '5°F	After Postcure of 5 h at 165" '5°F	After Additional Postcure of 16h at 250" '5°F
Dielectric Constant			
At 100Hz			
1	4.31	3.77	3.08
2	4.30	3.73	3.04
3	4.32	—	3.07
At 1kHz			
1	3.91	3.52	3.07
2	3.87	3.49	3.02
3	3.93	—	3.07
At 10kHz			
1	3.63	3.39	3.05
2	3.57	3.35	3.00
3	3.65	—	3.04
At 100kHz			
1	3.45	3.28	3.03
2	3.40	3.24	2.96
3	3.49	—	3.01
Dissipation Factor			
At 100kHz			
1	0.0844	0.0664	0.0039
2	0.0912	0.0690	0.0040
3	0.0841	—	0.0036
At 1 kHz			
1	0.0626	0.0385	0.0037
2	0.0668	0.0396	0.0038
3	0.0586	—	0.0035
At 10kHz			
1	0.0433	0.0257	0.0051
2	0.0452	0.0266	0.0053
3	0.0398	—	0.0048
At 100kHz			
1	0.0371	0.0254	0.0091
2	0.0380	0.0259	0.0094
3	0.0343	—	0.0083

*Measured at 73°F

electrical properties (epoxy-anhydride/castor oil adduct system). At all frequencies, the dielectric constant and dissipation factor decreased as the cure was advanced.

Figs. 8-12 and 8-13 give the concept of an approach to determining optimum cure time and temperature for an epoxy system based upon reaching low plateau values of dielectric constant and dissipation factor. Values soon after mixing a two-component system or pushing the reaction of a one-component form are high; the dielectric constant and dissipation factor are substantially lowered with polymerization and curing. At an optimum time, the values level off and reach a minimum. The curves show a completion of cure in 3.5 h (250°F) or 12 h (150°F). It has also been shown that the degree of hardening or cross-linking of an epoxy system can be followed by dielectric determination over a frequency range of about 50 to 10¹⁰ Hz.

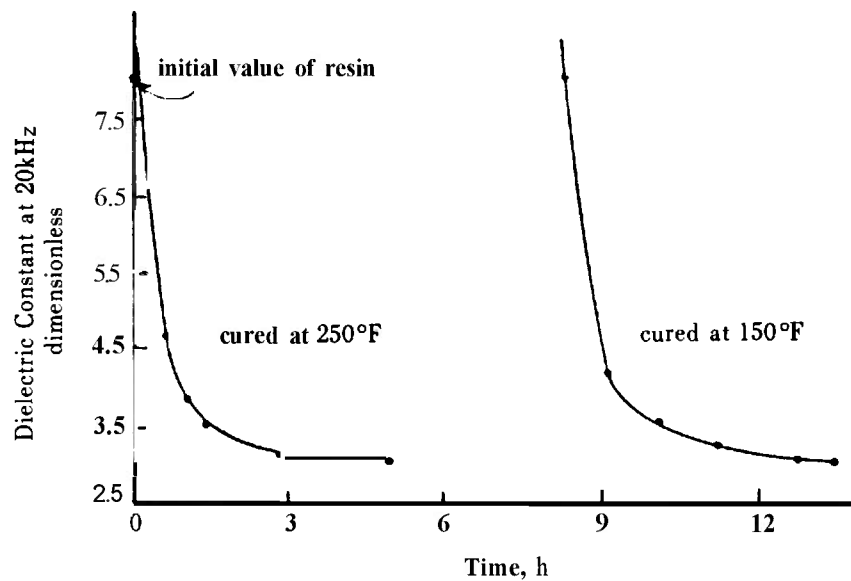


Figure 8-12. Establishment of Epoxy Cure Schedule from Dielectric-Constant Data

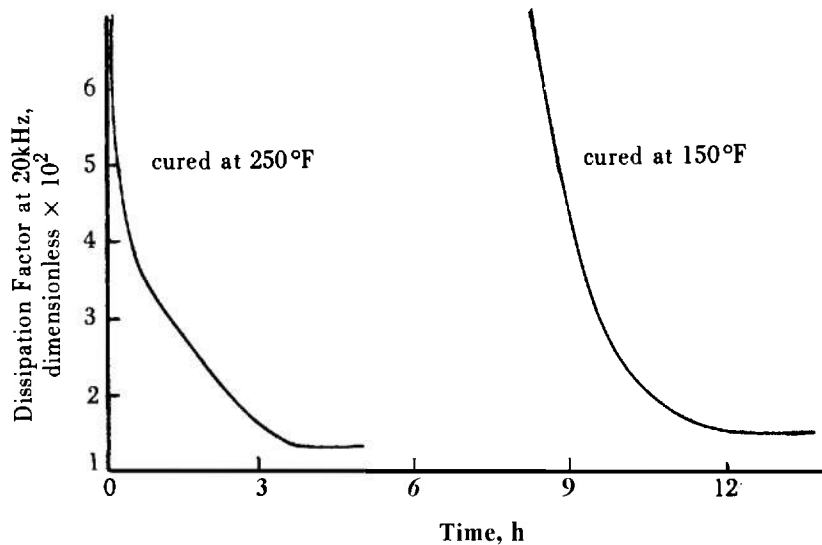


Figure 8-13. Establishment of Epoxy Cure Schedule from Dissipation-Factor Data

REFERENCES

1. C. A. Harper, "Electrical Insulating Materials", *Machine Design*, **39**, pp 134-62 (28 September 1967).
2. K. N. Mathes, "Electrical Properties of Insulating Materials", *Proceedings of the Seventh Electrical Insulation Conference*, Chicago, IL, 15-19 October 1967.
3. J. W. Klapheke, W. H. Veazie, J. C. Holt, and J. L. Easterday, *Electronic Packaging: A Bibliography*, (RSIC-534, AD-634004), Battelle Memorial Institute, Columbus, OH, 1966.
4. W. M. Robinson and H. R. Lee, "Pitfalls and Progress in Plastic Encapsulation of Semiconductors", *Insulation* (December 1967).

REFERENCES (cont'd)

5. C. F. Chadwick, "The Effect of Moisture on Molded Composition Resistors; Plastics in Electronics", *Society of Plastics Engineers Regional Technical Conference*, pp. 77-80, Syracuse, NY, 18 April 1963.
6. Cree W. Stout, J. E. Sergeant, and S. V. Caruso, *Electrical Properties of Adhesives Used in Hybrid Microelectronic Applications*, Electronic Components Convention, San Francisco, CA, April 1976.
7. I. J. Steinhardt, P. Vadopalas, and H. Plutchok, "Performance of Fillers at Microwave Frequencies", *Proceedings of the Sixth Electrical Insulation Conference*, pp. 3-6, Conference Sponsored by IEEE, NEMA, and Navy Bureau of Ships, New York, NY, 13-16 September 1965.
8. J. T. Milek, *Effects of Fillers on the Electrical Properties of Plastics and Elastomer Materials*, ERIC IR-58, Hughes Aircraft Co., Culver City, CA, 1967.
9. M. Olyphant, Jr., "Effects of Cure and Aging on Dielectric Properties", *Proceedings of the Sixth Electrical Insulation Conference*, pp. 12-9, Conference Sponsored by IEEE, NEMA, and Navy Bureau of Ships, New York, NY, 13-16 September 1965.

CHAPTER 9

FACTORS OF RESIN PURITY AND COMPONENT CLEANING

The importance of resin and solvent purity on the dielectric properties of embedments is presented. Tests to determine resin purities are listed. The importance of the proper cleaning of components prior to embedment and the use of clean rooms is emphasized. Proper cleaning methods and techniques are discussed.

9-1 RESIN PURITY

Purity is an important factor for plastic insulations used in any electronic assembly. It is especially critical for materials that are to be applied directly to active microelectric devices. Some devices appear to be less sensitive to surface contaminants than others and are therefore better suited for plastic encapsulation. Digital integrated circuits are less surface active than linear circuits. Metal-oxide semiconductors are more sensitive than pnp* bipolar transistors; the latter are more sensitive than npn** bipolar transistors. If the active devices are well passivated, purity of the plastic is not as critical! The success of many plastic-packaged devices presently available has been due primarily to improvements in the reliability of inorganic passivation layers such as glass and silicon nitride. Silicon nitride has been shown to be one of the best barriers against sodium ions. It is impervious to ion migration even at temperatures above 200°C.

9-1.1 GENERAL TYPES OF IMPURITIES IN RESINS

Plastics can contain many types of impurities; the most important ones are ions, both cation

and anions? They can impair the insulating properties of a plastic, change the electrical characteristics of a component, and under certain conditions cause corrosion of metal portions of a device. Other impurities consist of unreacted organic compounds such as amines (in epoxy resin), outgassing products, and additives such as plasticizers and flame retardants.

9-1.2 IONIC IMPURITIES

Insulation materials containing ionic impurities in contact with active or passive device surfaces can affect the electrical parameters of the devices. Sodium, potassium, and lithium ions cause inversion layers, high leakage currents, and decreases in breakdown voltages of diodes and transistors. These effects and a decrease in electrical insulating properties of plastics are further increased by mobility of the charged carriers, brought about by moisture, electrical stress, or elevated temperature.

Ionic impurities also result in electrochemical processes inducing corrosion and sometimes the disappearance of metal films. With an applied potential, the usual faradaic electrolysis can take place. Electrical opens in wire-wound resistors and deterioration or disappearance of conductors and resistors in hybrid thin-film circuits can occur by this mechanism. In wire-wound or thin metal-film resistors, voltage gradients, together with ionic conductivity, cause dissolution of metal from anodic areas, decreasing the cross-sectional areas of the resistive metal and increasing resistance values. Under more severe conditions, the etching of metal continues until the

*pnp bipolar transistors— These have an n-type base between a p-type emitter and a p-type collector.

**nnp bipolar transistors— These have a p-type base between an n-type emitter and an n-type collector; the emitter should then be negative with respect to the base, and the collector should be positive with respect to the base.

Both pnp and npn semiconductive transistors are double junction, i.e., bipolar, transistors. An n-type semiconductor has a large number of electrons present in the conduction band due to donor impurities. A p-type semiconductor has a large number of holes in the valence band due to acceptor impurities.

metal is completely removed and an electrical open occurs.

Most plastic dielectrics, as supplied by manufacturers, contain ionic impurities. Ions are either initially present or can be formed from inorganic compounds in the presence of moisture or water vapor.

Reactants used in the synthesis of the resin, catalyst, or hardener may give rise to ions. Unless steps are taken to purify during or after the synthesis of the resin, these impurities will be carried over into the final cured resin. More than 12 steps are required to synthesize epoxies. Sodium hydroxide is widely used in the preparation of epoxies. Thus, sodium and chloride ions may arise from the sodium chloride by-product. The presence of varying amounts of chloride ions has been shown in epoxies, as well as in silicones. Amounts ranging from 25 to 500 ppm and 5 to 100 ppm have been found in commercial-grade epoxies and silicones, respectively.

Ionic impurities may also come from additives such as fillers, thixotropic agents, and flame retardants used in the formulation. Glass fillers can be a major source of sodium ion contamination. A third source of ion contamination is the metal or glass kettles, mixers, or other equipment used in processing. Epoxy resins mixed in metal containers will acquire trace amounts of the metal.

9-1.3 OTHER IMPURITIES

Reactive outgassing products can evolve from plastics under ambient conditions, and even more so on thermal aging. Work with epoxies and silicones has shown the outgassing of numerous chemical species, some of which are active, i.e., either deleterious to device performance or corrosive to metal surfaces³ Specimens were sealed in an inert environment in glass ampules and aged at 300°F for 5 days. The gases evolved were then analyzed by means of both gas-chromatographic and infrared-spectrographic techniques. Of the outgassing products detected, those considered active were the aldehydes, vinyl acetate, the amines, carbon dioxide, and moisture.

9-2

9-2 OPTIMUM RESIN-TO-HARDENER WEIGHT RATIOS

A stoichiometric mixture of a two-component coating (resin and hardener) consists of the two components mixed in amounts proportional to their respective molecular weights according to a balanced equation. If the mixture is not stoichiometric, either some of the resin or some of the hardener can be left unreacted. The optimum ratios may not coincide with actual stoichiometric ratios, and compositions which are slightly high in resin content may be used. Too high or too low a resin content can render the plastic susceptible to moisture penetration and can lessen its electrical insulating properties. The *unreacted constituents may contain active polar or ionic groups* which can further affect the electrical parameters of the device. A plot of the electrical resistivities of water extracts for various resin-to-hardener ratios can give some indication of optimum ratios⁴

9-3 TESTS FOR RESIN PURITY

A quantitative test for the total amount of ionized and ionizable constituents of a polymer consists of measuring the electrical conductivity of extracts of the plastics in either water or organic solvents. One test consists of digesting 1 g of powdered sample in 100 cm³ of deionized water at 160°F for 7 days. The mixture is cooled to room temperature and the electrical resistivity of the water extract is measured by means of a conductivity bridge. Plastics used in semiconductor packaging vary widely in this property. There is some correlation between purity as defined by the water-extract resistivity and performance of the device. Those silicones having the highest water resistivities (lowest ionic impurities) provided the lowest number of failures on components after 1,000 h of testing (see Tables 9-1 and 9-2).

A test which is sensitive to organic ionic impurities is similar to that previously described. A 1-g sample of resin is extracted with 10 cm³ of

TABLE 9-1. WATER-EXTRACT RESISTIVITY DATA (SILICONES AND EPOXIES)

Material	Sample Size	Resistivity Range, ohm-cm	Some High-Value Materials Within Range	
			Material	Resistivity ohm-cm
Silicone junction coating	15	33,000-425,000	Dow-Corning R-90-703	415,000
			Dow-Corning R-60-093	425,000
			Dow-Corning K-62-044	400,000
			Dow-Corning DC-51	360,000
			General Electric SK-78	510,000
			Union Carbide K-620	450,000
Silicone transfer-molding compound	5	30,000-280,000	Dow-Corning DC-304	280,000
Epoxy transfer-molding compound	6	4900-50,000	Dow-Corning DC-305	240,000
Epoxy casting compound	6	32,500-250,000	Epon 825 with nadicmethyl anhydride and benzyldimethyl-amine	210,000
			Dow DER-332 with nadicmethyl anhydride and benzyldimethyl-amine	190,000
			Ciba Araldite 6010 with nadicmethyl anhydride and benzyldimethyl-amine	250,000

(Control: deionized water 600,000-700,000 ohm-cm)

TABLE 9-2. TYPICAL FAILURE DATA FOR SILICONE-COATED METAL-OXIDE SEMICONDUCTOR DEVICES (Static Tested at 125°C/150 mW)

Sample	Water Extract Resistivity, ohm-cm	Sample Size	Total Failures*	
			After 1000 h	After 2000 h
Silicone B	80,000	7	3	—
Silicone E	180,000	13	2	—
Silicone F	170,000	7	3	—
Silicone G	300,000	11	1	—
Dow-Corning DC-51	360,000	10	0	0
Dow-Corning XK-62-044	660,000	10	0	0

*Failure indicators: threshold voltage, breakdown voltage, leakage current.

purified trichloroethylene. The electrical conductance of this extract is measured.

The test is sensitive to about 1 ppm ionic content. Other tests for assessing metal-ion impurities in plastics include emission-spectrographic analysis, atomic-absorption analysis, and flame-photometric analysis. The latter two tests are particularly sensitive for sodium and potassium in concentrations as low as parts per billion.

The elevated temperature reverse-bias test is very sensitive and provides an indirect method of establishing the presence of ions. Under these test conditions semiconductor devices containing mobile ions form inversion layers and exhibit high reverse-leakage currents. The inversion layer is formed if ionic contaminants on the surface or in the oxide layer are mobilized at elevated temperatures and aligned by the application

of an electrical field. Stress conditions generally used are 150°C and about 20 V reverse bias.

The chloride-ion content of a plastic may be determined quantitatively by the potentiometric-titration procedure. The plastic sample is powdered and extracted with water, and the extract is titrated with a standard solution of silver nitrate.

9-4 CLEANING OF COMPONENTS/ASSEMBLIES PRIOR TO EMBEDDING

The cleaning of a component or circuit assembly before embedding or dielectric coating is a very important procedure. Proper cleaning is required for both the immediate and long-term operation of the dielectric and the electrical/electronic end items.⁶ Surface contamination with salts, electrolytes, oils, or particulate contaminants may result in undesirable effects such as corrosion, electrical failure, and poor bonding of the resin to substrate surfaces. In order to choose an effective cleaning method, the nature of the contaminants must be known, the probable damage to the end-item performance from such "dirt" must be established, and the advantages/disadvantages of a cleaning technique must be defined. The availability of tests to define adequate removal is desirable. Table 9-3 gives information on possible contaminants and their sources.⁶

With thin-film circuits contaminated by fingerprints, nichrome resistors were observed to disappear when tested with applied voltage in a humid environment; an electrolytic cell was created in which one of the resistors ionized and went into solution. This was not observed when the resistor surface had been kept completely clean and dry. In another case, fingerprints left beneath the coating on a circuit board caused visible blistering of the coating over them after exposure to humidity. Poor surface cleaning can result in peeling, lifting, or blistering of the coating

TABLE 9-3. TYPICAL CONTAMINANTS AND THEIR SOURCES

Contaminant	Possible Source
Fibers (nylon, cellulose, etc.)	Clothing, paper towels, tissues, and other paper products
Silicates	Rocks, sand, soil, fly ash
Oxides and scale	Oxidation products from some metals
Oils and greases	Oils from machining, fingerprints, body greases, hair sprays, tonics, lotions, and ointments
Silicones	Hair sprays, shaving cream, aftershave lotions, hand lotions, soap
Metals	Slivers and powder from grinding, machining, and fabricating of metal parts; particles from metal storage cans and other metal containers
Ionic residues	Perspiration, fingerprints (sodium chloride); residues from cleaning solutions containing ionic detergents; certain fluxes such as the glutamic acid-hydrochloride types; residues from previous chemical steps such as etching or plating
Nonionic residues	Rosin fluxes, nonionic detergents, organic processing materials
Solvent residues	Cleaning solvents and solutions

either immediately after drying or after a period of high-humidity exposure.

Contamination has been a serious problem in the manufacture and operation of electronic equipment? With recent advancements in high-density microelectronic assemblies, the total size of a component may be smaller than a speck of dirt. Here, the effects of particulate contaminants become very critical. There are hundreds of different types of contaminants; those most often found on electronic hardware were shown in Table 9-3. Many of these particles are not visible to the naked eye but are disclosed only by separation and magnification.

The incomplete removal or the entrapment of these contaminants under an embedment or

coating can result in electrical short circuits, corrosion, and deterioration of the coating. Increased penetration of moisture and other contaminants is possible. The severity of these effects depends on the nature and amounts of contaminants and on the amount of moisture and applied voltage.

9-4.1 CONTAMINANTS IN CLEANING SOLVENTS

Even traces of metal particles on electronic devices or circuits can lead to failure. A single metal particle bridging two closely spaced conductors can give a short circuit with immediate failure; on the other hand, corrosion from the metal inclusion can lead to electrolyte formation which eventually leads to breakdown of the circuit. The use of a commercial type of cleaning solvent that has been stored in a metal container may introduce metal particles or rust onto the surface of a circuit. Other contaminants such as fibers, grease, or minerals have been found. Depending upon the circuit application, these contaminants can degrade the function of the system!

A solvent can be analyzed for contaminants. A known volume of solvent is passed through a paper or similar filter and the particles retained on the filter are counted for various size ranges. Typical results are shown in Table 9-4. To identify the particles, the specimens are examined

with a microscope and compared with known standards⁸

9-4.2 USE OF CLEAN ROOMS

To eliminate the deposition of contaminants on end items, it may be necessary to use ultra-clean environments—e.g., class 100 clean rooms—for the production and fabrication of delicate, sensitive electronic devices. In conjunction with the clean-room area, it may be necessary to use laminar-flow work stations, ovens, spray booths, and other methods of end-item isolation. Ultrapure highly filtered solvents and high-purity chemicals must be used in processing. An effective standardized cleaning procedure must be determined to insure the absence of contaminants before, during, and after the dielectric embedding or coating?

9-5 INFORMATION ON CLEANING SOLVENTS

Cleaning solvents or solutions can be classified into three types; this is shown in Table 9-5. The hydrophobics are those which remove water-insolubles such as grease, oils, and nonpolar organic materials. The hydrophilics can remove water-soluble contaminants such as ionic salts. Since both water-insolubles and water-solubles generally are present as contaminants on electronic assemblies, a definitive practice is to use

TABLE 9-4. PARTICULATE CONTAMINANTS IN CLEANING SOLVENTS

Solvent *	No. of particles per size range per 100cm ³ †		
	5-65 microns	Over 65 microns	Fibers
Du Pont Freon 'IF	180	10	1
	540	21	3
	‡		
Acetone		192	71
Ethyl alcohol	980	9	0
Methyl chloroform	1750	10	0
Trichloroethylene	400	20	0

*All solvents are as received.

†These values may vary considerably for the same solvent, depending on processing and storage conditions.

‡Too contaminated to count.

TABLE 9-5. TYPES OF SOLUTIONS AND SOLVENTS FOR SUBSTRATE CLEANING

<u>Chemical Type</u>	<u>Examples</u>
Hydrophobic:	
Organic solvents	Napthas, xylene, toluene
Fluorocarbons	Freon TF, Freon TMC
Chlorinated hydrocarbons	1,1,1-Trichloroethane, perchloroethylene, trichloroethylene
Hydrophilic:	
Organic solvents	Acetone, methyl ethyl ketone (MEK), methanol, ethanol, isopropanol
Ionic	Alkaline, acid, and detergent water solutions
Nonionic	Detergent-water solutions
Water	Tap, deionized, or distilled
Hydrophobic-hydrophilic	Alcohol naphtha (50:50 mixture), Dupont TWD-602 (a Freon-water emulsion containing a surfactant), Freon TA (an azeotrope of Freon TF and acetone), Freon T-E35 (a blend of Freon TF and ethyl alcohol)

both types of solvents in a two-step process. Another procedure is to combine the two types of solvents as a hydrophobic-hydrophilic mixture and use a one- or two-step process in cleaning.

Solvents for cleaning electronic assemblies prior to coating may contain amounts of particle and nonvolatile contaminants which can lead to deterioration of circuit performance. The amounts of contaminants can be determined by standard methods; residues may be extremely small (parts per million range) but even such quantities may be critical to the proper performance of the system. Adequate rinsing with clean ethanol, chlorinated hydrocarbon, and distilled water may remove these residues. But when ionic or nonionic detergent cleaners have been used earlier, repeated rinsing with distilled water or fresh solvent is required. Rinsing with agitation is a recommended procedure.

The presence of ionic or ionizable impurities in solvents may be determined by evaporating to dryness a given volume of solvent, extracting the

residues with distilled water, and measuring the electrical resistivity of the water extract. The lower the resistivity value, the greater the concentration of the ionic impurities which were extracted. Other tests include measurements of the nonvolatile residues and particle analysis.

Many Government specifications are available for the procurement of solvents and chemicals; however, few provide sufficient control over very low levels of particulate contamination. Many firms therefore have found it necessary to use tighter requirements. For space applications, some firms are specifying that deionized water and other solvents must contain no particles above 20 microns in size. The purest grades of commercial solvents seldom meet this requirement; even those that do initially, quickly become contaminated through storage conditions and handling. It has been necessary to apply rather elaborate filtering techniques just before the solvents are employed and to use laminar-flow stations for all processing and assembly operations.

The requirement that solvents contain no particles greater than 20 microns can be met by filtering the solvents through a series of three consecutive membrane filters of 10-, 2-, and 0.5-micron pore sizes, respectively. It is a safe practice in all microelectronic fabrication processes to use solvents and cleaning solutions that have been filtered through membrane filters immediately before use. Such filters are available in various pore-diameter sizes, ranging from 0.1 micron up. Major suppliers in the United States are the Millipore Corporation and Gelman Industries.

9-6 GENERAL METHODS OF CLEANING

There are three primary means of removing contaminants from electronic substrate surfaces prior to embedment, namely:

1. Solution cleaning—e.g., sodium chloride is dissolved by water; fingerprint residues are removed by alcohol.

2. Chemical reaction cleaning—e.g., metal oxides and scale are treated by acid and/or alkaline treatments to give soluble products which subsequently can be rinsed away.

3. Mechanical dislodging of particles by liquid or gas spray—e.g., metal or fiber particles removed by jets or ultrasonic energy.

There are about six methods of cleaning. For particular cleaning problems a number of modifications or combinations of the primary methods can have practical use, namely:

1. Solvent or solution spray
2. Solvent or solution dip
3. Solvent or solution brushing
4. Vapor degreasing
5. Ultrasonic cleaning
6. Pulsating spray.

The first three techniques are obvious methods and are not described. The latter three techniques, however, are described.

9-6.1 VAPOR DEGREASING

Vapor degreasing is a widely used efficient process for cleaning electronic parts. The assembly is suspended in a specially designed chamber which allows the vapors of a heated solvent to condense on the surface and flush it clean. The part is thus washed repeatedly with fresh solvent, as opposed to hand scrubbing or other manual cleaning methods. There are variations of the vapor-degreasing method. The basic method uses vapor alone and is efficient when only small amounts of oil and grease contaminants are present. A variation is to combine vapor degreasing with a liquid-spray technique. The part to be cleaned is suspended in the solvent vapors until condensation ceases and is then sprayed with clean solvent for about 30 s and returned to the vapor. Another variation entails immersion in warm water, followed by vapor degreasing. Detailed instructions for vapor degreasing are given by equipment manufacturers.

Trichloroethylene and perchloroethylene are two widely used solvents for removing greases

and hydrophobic contamination by vapor degreasing. Both agents are relatively nontoxic and stable; trichloroethylene is stabilized against hydrolytic breakdown; perchloroethylene needs little or no stabilization. The compatibility of these chlorinated solvents with the substrates must be confirmed before using the agents in a production process. It has been shown that with some circuit board laminates, cleaning with halogenated hydrocarbons can lead to removal of the resin, delamination of the board, discoloration, and electrical degradation.

9-6.2 ULTRASONIC CLEANING

The use of an ultrasonically energized bath is a very effective method for cleaning immersed parts. A high amount of energy is imparted to the solvent, and contaminants are readily removed from even the most difficult to reach areas. Vibrations are in the range of 20 to 40 kHz; this causes cavitation, and a rapid buildup and collapse of very small bubbles in the liquid cleaning agent. Energy is thus transferred to the part to be cleaned; "scrubbing" action is strong and extensive. Ultrasonic cleaning is very rapid; cleaning time is perhaps a few minutes per part.

Many and various solvents and cleaning solutions are available for the liquid bath in ultrasonic cleaning. The choice of agent is constrained by its corrosive effects on the tank, toxicity or flammability, and its vibration-damping characteristics. Certain liquids show excess damping properties. Concentrated detergent solutions and acetone show such effects. Freons show less energy absorption. For the highest efficiency, solvents should be at about room temperature. Cooling is required since ultrasonic energy heats the solvent after continuous operation for a number of hours. Water/detergent and alkaline solutions give best results in the temperature range of 100° to 140°F.

Ultrasonic cleaning, though, giving very good results, has certain disadvantages. The bath becomes contaminated in a short time; the solvent

must be filtered, purified, or replaced on a definite time schedule. Fragile items such as glass diodes and other glass-sealed semiconductor devices can fail mechanically or electrically by cracking or lead separation from the ultrasonic vibrations. Incipient failures may not be found early; there is always some possibility that the cleaning stresses can reduce the long-term reliability and use-life of the component. Because of this, ultrasonic cleaning finds most use in the cleaning of bare substrates or circuits before the placement of sensitive devices.

9-6.3 PULSATING SPRAY

In the pulsating spray method, the solvent or solution is pulsed 20,000 to 30,000 times per second when it is sprayed. The spray reaches the part at a pressure about 500 psi. The primary advantages of this method over ultrasonic cleaning are the elimination of cavitation erosion of metal

surfaces and the lack of recontamination from immersion in liquids which gradually become dirty. A typical spray unit is the Heinicke Corporation parts washer—such equipment can be used for very efficient cleaning of printed circuit boards, wire harnesses, and other electrical or electronic parts. A typical automatic cleaning cycle consists of a high pressure wash with a pulsating jet of cleaning solution, a tap-water rinse, and a final rinse with distilled or filtered deionized water. This is one of the best methods for removing contamination particles 5 microns or larger in size. Most cleaning needs are satisfied by the use of water solutions with subsequent hot tap and then distilled water rinses. Such equipment also can be designed to use organic solvents. Each operation is timed to a predetermined cycle; the total cleaning time is about 5 min. The number of components that can be cleaned in one operation is determined by their size and placement in the washing chamber.

REFERENCES

1. S. V. Caruso, *Design Guidelines for Use of Adhesives and Organic Coating in Hybrid Microelectronics*, NASA Technical Memorandum TM X-64908, December 1976.
2. E. H. Snow, A. S. Grove, B. E. Deal, and C. T. Sah, "Low Transport Phenomena in Insulating Films", *Journal Applied Physics* **36**, 1664 (1965).
3. W. F. Garland, "Effect of Decomposition Products from Electrical Insulation on Metal and Metal Finishes", *Proceedings of the Sixth Electrical Insulation Conference*, pp. 56-60, Conference Sponsored by IEEE, NEMA, and Navy Bureau of Ships, New York, NY, 13-16 September 1965.
4. S. M. Lee, J. J. Licari, and A. G. Valles, "Properties of Plastic Materials and How They Relate to Device Failure Mechanisms", M. E. Goldberg and J. Vaccaro, eds., *Physics of Failure in Electronics*, **4**, RADC Series on Reliability, Defense Documentation Center, Alexandria, VA, 1966.
5. F. N. LeDoux, *Handling, Cleaning, Decontamination and Encapsulation of Mosfets Circuitry*, NASA TM X-55338, 1965.
6. J. Agnew, "Cleaning Guide for Hybrid Circuit Manufacturing", *Insulation/Circuits*, 39-42 (August 1974).
7. H. F. Heuring, "Cleaning Electronic Components and Subassemblies", *Electronic Packaging and Production*, June 1967.
8. C. J. Tautscher, "Cleanliness Standards Required for Preventing Blister Formation on Printed Circuit Cards", *Insulation/Circuits*, 31-2 (July 1973).
9. W. C. McCrone, R. G. Drafty, and J. J. Delley, *The Particle Atlas*, Ann Arbor Science Publishers, Ann Arbor, MI, 1967.
10. Federal Standard No. 209, *Clean Room and Work Station Requirements*.

CHAPTER 10

PROTECTION AGAINST MOISTURE, CORROSION, AND BIOLOGICAL DEGRADATION

Various failure modes of dielectrics—moisture pickup, corrosion, and biological degradation—are presented. Advice is given on the proper selection and application of embedments which will minimize failures, and thus permit long-term storage and/or operation.

10-1 MINIMIZATION OF FAILURES BY MEANS OF EMBEDMENTS

A very important purpose of polymer embedments for electronic assemblies and circuits is to prevent moisture and gas penetration; the latter vapors lead to corrosion or breakdown of insulation. All current organic polymers absorb water to some degree and show permeability to moisture vapor and other gases. Embedments are not true hermetic seals; this absolute resistance to permeation is only characteristic of completely sealed, e.g., welded, metal packaging. It is, however, possible to select plastics which will minimize vapor or water penetration significantly to allow assemblies or components to pass long-term storage and remain operational.

10-2 'FAILURE DUE TO MOISTURE

Failures from moisture pickup can be of two types. Moisture mobilizes ionic contaminants in the plastic (or on the surface of the device) and results in the deterioration of electrical insulation or the formation of inversion layers in semiconductor devices. Moisture, again in the presence of impurity ions, permits electrolytic corrosion to take place. Therefore both active and passive devices such as transistors, diodes, and resistors are hermetically sealed in metal packages, and entire electronic assemblies must be sealed in dry inert-gas atmospheres when extreme requirements for reliability are stressed. Hermetic sealing is expensive; it is not practicable for most commercial applications; however,

to date, it is definitely required for certain military equipment. Organic coatings or plastic encapsulants may provide adequate protection in consumer type products.

All polymers are permeable to moisture; resistance to water varies in degrees. Water resistance can be stated as a function of three factors:

1. Percent absorption of water by the resin at constant temperature for a period of time
2. Rate of water-vapor transmission
3. Operability of embedded electronic circuit after humidity cycling tests.

Resins containing hydrophilic polar groups such as hydroxyl or amide or those containing low molecular weight water-soluble additives generally will have high water-absorption values. Semirigid polymers tend to absorb more water than highly cross-linked systems. In time, the percentage of water absorption becomes constant at constant temperature for each material, but equilibrium may be achieved only after 1 or more weeks of immersion. Most reported data are for a 24-h immersion period and do not give the true equilibrium values, which are often higher. Twenty-four-hour data are meaningful for practical applications only where the test conditions are equal to or more severe than those to which the part will be subjected in actual operation.

The value for percent water absorption should be related to the possible damaging effect to the embedment resin or the system which is protected by the insulation. Examples of adverse effects

include corrosion, insulation breakdown, hydrolysis of the polymer, dimensional change, delamination, or loss of adhesion.

Water pickup is an important factor in the degradation of electrical properties; however, other factors are contributory. Electrolyte impurities and the polarity of the polymer play a role. With some polymer systems, electrical properties are degraded with only a small amount of water absorption. Other polymers, on the other hand, may retain their properties with a relatively high pickup of water. As a rule, surface and volume resistivity decrease and dissipation factors increase with increase in the amount of absorbed water. Table 10-1 shows water pickup data for a number of epoxy systems.

10-2.1 RESIN FACTORS AFFECTING MOISTURE PERMEABILITY

Moisture may seep, especially through thin resin sections, by several mechanisms. One is the passage through microcracks, channels, or pinholes due to imperfections in the embedment. Another moisture-penetration mechanism is one due to the molecular structure of polymers which allows permeation of water-vapor molecules through the space between polymer molecules?

Such permeability or moisture-vapor transmission rate (*MVTR*), measured in grams per

hour per square centimeter per centimeter, is a more significant value than water absorption in defining water resistance. Under controlled conditions of humidity and temperature, *MVTR* is expressed by

$$MVTR = \frac{Ql}{at} \quad (10-1)$$

where

Q = water vapor permeating the resin, g

l = dielectric thickness, cm

a = film area, cm²

t = time, h.

Eq. 10-1 can be converted to grams in 24 h per 100 in² per mil by multiplying $24 \times 645.2/0.00254$ or 6.1×10^6

Polymers vary in permeability because of differences in molecular structure. A highly cross-linked compact structure should be less permeable than a loose, only partly cross-linked plastic network. The geometry and size of a vapor molecule also determine its permeability. Permeation rate is inversely proportional to the size of the permeating gas. In addition to the size considerations, the chemical natures of the gas (or vapor) and the plastic are important factors. Hydrophobic polar groups in a polymer chain can provide cohesive strength and can give a dielectric which is highly resistant to moisture.

TABLE 10-1. WATER-ABSORPTION VALUES FOR EPOXIES AFTER 2-h AT 77°F

Resin and Curing Agent	Curing Schedule	Water Absorption, %
Epi-Rez* 508		
85 phr Allied Nadic methyl anhydride	2 h at 200°F + 2 h at 400°F	0.19
87 phr FMC LA-1 (liquid anhydride eutectic)	2 h at 200°F + 2 h at 400°F	0.12
24.5 phr Epi-Cure 841 (liquid aromatic amine eutectic)	2 h at 200°F + 2 h at 400°F	0.20
15.5 phr metaphenylenediamine	2 h at 200°F + 2 h at 400°F	0.20
3 phr boron trifluoride-monoethylamine complex	4 h at 300°F	0.17
Epi-Rez 510		
12 phr TETA (triethylene tetramine)	16 h at 77°F + 2 h at 212°F	0.17
20 phr <i>N</i> -aminoethylpiperazine	16 h at 77°F + 2 h at 212°F	0.24
10 phr Epi-Cure 86	1 h at 212°F	0.19
3 phr BF ₃ -MEA	4 h at 300°F	0.19
14.2 phr m-phenylenediamine	2 h at 200°F + 2 h at 400°F	0.19

*Celanese trademark

Permeation is also a function of the nature and amount of filler used in the composition. Filled systems have lower permeabilities because of the longer path the water molecules must travel to penetrate the thickness of the plastic. The nature of the filler, its shape (e.g., spherical or flake), and the packing density all affect moisture permeability. Permeation values drop with an increase in the filler concentration up to a critical volume ratio. This critical ratio differs for various fillers and ranges from about 40 to 70%. Several other factors that affect permeability are shown in Table 10-2.

Table 10-3 gives moisture vapor transmission rates of some resins.

TABLE 10-2. FACTORS AFFECTING MOISTURE PERMEABILITY

Factor	Usual Effect on Permeability
Solvent entrapment	Increase
Plasticizers	Increase
Structure of film:	
Polar, hydrophobic	Decrease
Polar, hydrophilic	Increase
Nonpolar	Decrease
Degree of cross-linking	Decrease
Crystallinity	Decrease

TABLE 10-3. MOISTURE VAPOR TRANSMISSION RATES OF SOME RESINS

Polymer	$MITR$, g/mil·100 in ² ·24 h
Epoxy:	
cured with anhydride	2.4
cured with aromatic amine	1.8
Polyurethane:	
isocyanate/castor oil	4.3
isocyanate/polyester	8.7
Polyxylylene:	
Parylene C	1
Parylene N	14
Silicone:	
gel type	112.5
methyl phenyl	38.3
RTV's	120.8

10-2.2 CIRCUIT BOARD FAILURE DUE TO MOISTURE

As an example, several types of failure can result from the absorption and permeation of moisture in circuit boards. A basic one is the marked decrease in the electrical insulating properties of circuit-board laminates when they are exposed to warm humid environments. Decreases of as much as nine decades in insulation resistance values have been reported for uncoated laminates. With a suitable protective coating, however, the decrease is only one to three decades under the same conditions. Coatings afford similar protection to epoxy-glass laminates under the more severe stresses of combined temperature, humidity, and voltage.

The sharp and rapid decrease in the insulation resistance of some coatings has been found to occur primarily during the first humidity cycle, with some recovery in subsequent cycles. Dielectric coatings absorb water during the first humidity cycle; acceleration by an applied voltage causes hydrolysis of some of the coating constituents. This then results in a breakdown of the coating in the region of the "hot" conductors and causes the insulation resistance to drop off rapidly. Not all coatings undergo this initial sharp drop in resistance because of difference in their moisture-absorption and permeability characteristics.

Hydrolysis is not the only mechanism for electrolytic reactions. Coatings may contain ions or ionizable impurities that can migrate under an imposed potential. Hence, a coating between two conductors may function as an electrolyte, causing a local cell to form in which one of the conductors becomes oxidized and corroded.

In addition to minimizing the breakdown of electrical properties in laminates, coatings can also minimize or prevent discoloration caused by moisture and processing conditions. Some laminates, including epoxy glass, will whiten, or "measle", when they undergo many processing steps and are then subjected to a warm humid

environment. Coated, etched, copper-clad laminates which had not undergone processing were found to pass humidity cycling with no whitening. The use of a coating with good humidity-resistance properties minimizes or eliminates this defect⁵

The curing schedule for a coating has a significant effect on its moisture-barrier properties. An extended cure at elevated temperature enhances the performance of the coating. This improvement is probably due to elimination of residual solvents and further cross-linking of the polymer.

10-3 FAILURE DUE TO CORROSION

Resins applied to circuits which contain metal components or parts protect these metal parts from corrosive effects of the surrounding environment.⁶ Typical types of corrosive environments are listed in Table 10-4.

Some of the methods in which metals or alloys, used in electronic assemblies, fail are given in Table 10-5. Such corrosion occurs by chemical or electrochemical means but in nearly all cases moisture is required. Thus, the moisture resistance and barrier properties of the embedment are a major factor in corrosion prevention.

TABLE 10-4. ENVIRONMENTS AND THEIR CORROSIVE CONSTITUENTS

Environment	Corrosive Constituents
Normal Air Ambient	Moisture, oxygen, sulfur dioxide, carbon dioxide
Water	Calcium salts and other metal salts, ions
Salt water or salt spray	Sodium and chloride ions, marine organisms
Chemicals and solvents	Numerous acids, bases, oxidizing or reducing agents, solvents, strippers, etc., which may come into contact with the part during processing or operating
Soil	Moisture, fungus, other microorganisms

10-4 FAILURE DUE TO MICROORGANISMS

Microorganisms cause much loss yearly through material deterioration. Such degradation causes corrosion of metals and bimetallic combinations, and the deterioration of mechanical or electrical properties of resins or substrates. The resistance of insulation to attack by microorganisms is important for electronic hardware that must be stored or operated in humid, tropical, or semitropical environments. Contact of materials with moist soil is an ideal condition for microbial growth; 1 cm³ of soil contains as many as 50,000 fungi, 500 million bacteria, and 250 million actinomycetes (plant or animal biotics, a class of molds midway between fungi and bacteria).

Most microorganisms can thrive in an environment of only 50%RH and temperatures ranging from 70° to 100°F, and some may even adapt and grow well under less favorable conditions. Most plastics are resistant to microorganisms by virtue of their inherent nonnutrient characteristics or because of the fungicides or bactericides used as additives in the formulation. In fact, because of their fungous-resistant properties, certain organic coatings are often used as barriers to protect otherwise nutrient substrates.^{7,8}

Generally, the epoxies, silicones, and polyurethanes are inherently fungous resistant. Some formulations may not be as resistant as others because of the presence of plasticizers or other nutrient additives, and some may deteriorate with age or exposure to humidity, producing nutrient substances or hydrolysis products. If a nutrient is co-reacted with the base resin and becomes an integral part of the polymer structure, the plastic is not likely to be a source of microbial food. One example is the use of castor oil in curing isocyanate resins. The resulting polyurethane resins are generally fungous inert. When vegetable oil is physically admixed in the formulation and does not become chemically bound with the polymer structure, it is probable that the formulation will support microorganisms to some degree. A

**TABLE 10-5. CORROSION MODES FOR METALS AND ALLOYS COMMONLY USED
IN ELECTRONIC ASSEMBLIES**

<u>Metal or Alloy</u>	<u>Type of Corrosion</u>
Copper	Thermal air exposure results in black oxidation product; forms green copper carbonate (verdigris) which inhibits further corrosion except as accelerated by galvanic coupling; exposure to salt environment produces high electrical resistance due to formation of copper salts; tarnishes in sulfur containing ambients.
Copper-nickel alloys & copper-beryllium alloys	Tarnishes in sulfur containing ambients and in moist air.
Aluminum, pure or 5052, 6061, 1100, or 3003	Forms white oxide, which is usually superficial and entails no structural damage.
Aluminum high-strength alloys 2024, 2014	Susceptible to tunneling, exfoliation, and stress corrosion.
Aluminum high-strength alloys 7075, 7079	Susceptible to stress corrosion.
Aluminum alloys, general	Galvanic corrosion from dissimilar-metal couples.
Magnesium AZ31B	Rapid local dissolving at breaks in metallic coatings or at points of coupling with nobler metals; oxidizes slowly in moist air.
Magnesium-lithium alloy	Interaction of moisture with the lithium portion of the alloy, resulting in rapid evolution of hydrogen and formation of white lithium hydroxide; organic protective coatings used are permeable to moisture, and blister and lift due to hydrogen generation; also reacts with carbon dioxide from the ambient environment to give white lithium carbonate.
Magnesium-thorium alloy	Very susceptible to moist ambient.
Beryllium	Stable in air; forms a metal-oxide protective layer on heating in air; will react rapidly with methyl alcohol; attacked by alkalis with evolution of hydrogen.
Nickel	Little corrosion problem except for galvanic couples; very stable in air and water owing to presence of nickel oxide layer
Silver	Black silver sulfide "tarnish" on exposure to ambient owing to interaction with SO ₂ and H ₂ S contaminants in air
Gold	Extremely inert, no corrosion products

knowledge of the composition and chemistry of a formulation is helpful in predicting its fungous-resistant properties.

Plasticizers are probably the greatest cause for fungous and bacterial growth. On the basis of available information, the plasticizers which are good nutrients are diesters of saturated aliphatic dibasic acids containing 12 or more carbon atoms. Some common nutrient plasticizers are di-n-hexyladipate, di-2-ethyl-hexylazelaate, epoxidized soybean oil, triethylene glycol, derivatives of soybean or tall oil fatty acids, methyl acetylricinoleate, dioctylsebacate, and tetrahydrofurfuryloleate. The maleates are somewhat fungous resistant, as are the alkyl derivatives of phosphoric

and phthalic acids. Polyhydric alcohols can be readily assimilated by fungi and bacteria if the hydroxyl groups are on the adjacent or terminal carbon atoms.⁹ Ether linkages in a polymer structure, as in epoxies, tend to reduce fungous growth. Much of the success of epoxy resins has been due to their fungous-resistant properties.

As mentioned, the epoxies, the polyurethanes, and silicones show good resistance to microorganisms. The parylenes also show good resistance. Where conditions for attack may be overwhelming, the formulator has access to a number of agents which can aid in preventing biodegradation". Table 10-6 lists biocides which have found use in various resin systems.

**TABLE 10-6. BIOCIDES COMMONLY
USED IN POLYMERS**

Salicylanilide
Brominated salicylanilides
Organotin compounds
Bis(8-quinolinolato) copper or zinc
Phenylmercuric oleate, salicylate, stearate, or phthalate
Di(phenylmercuric) dodecenylsuccinate
N-(trichloromethylthio) phthalimide
Phenylmercuric-0-benzoic sulfimide
Zinc dimethyldithiocarbamate
2-Mercaptobenzothiazole
Zinc pentachlorophenoxide
Pentachlorophenol
Quaternary ammonium carboxylates
Bis(tri-n-butyltin) oxide
Sodium or zinc pyridinethioine N-oxide
p-Toluenesulfonamide

REFERENCES

1. S. Sacharow, "The Permeability of Flexible Plastic Films", *Plastic Design and Processing* (September 1965).
2. D. L. Killam, "Effects of Humidity on the Dielectric Properties of Some Polymers", *Electrical Insulation Conference*, National Academy of Science Publication 1238, Washington, DC., 1965.
3. C. H. Burley, J. L. Easterday, and D. A. Kaiser, *Industrial Survey of Electronic Packaging*, N67-19037, RSIC-614, (AD-647 137), Battelle Memorial Institute, Columbus, OH, 1966.
4. E. McKenna, "Mechanical and Environmental Tests: Encapsulated Transistors", Harry Diamond Laboratories Report TR-1346, Washington, DC, March 1967.
5. J. W. Klapheke, W. H. Veazie, J. C. Holt, and J. L. Easterday, *Electronic Packaging: A Bibliography*, RSIC-534, (AD-634 004) Battelle Memorial Institute, Columbus, OH, 1966.
6. R. E. Freeman, "Reliability Improvement Through Stabilized Environments", National Electronic Packaging and Production Conference, Long Beach, CA, 31 January - 2 February 1967, and New York, NY, 13-15 June 1967, *Proceedings of the Technical Program*, pp. 565-82, Conference Sponsored by the Electronic Production and Packaging Magazine, Chicago, IL, 1967.
7. A. L. Baseman, "Antimicrobial Agents for Plastics" *Plastics Technology* (September 1966).
8. Anon., *Use of Sporicides and Heat to Sterilize Resins*, US Army Chemical Corps, Protection Branch, Report of Test No. 4-64, 16 September 1963.
9. S. Berk, H. Ebert, and L. Teitell, "Utilization of Plasticizers and Related Organic Compounds by Fungi", *Industrial Engineering Chemistry*, **49** (1957).
10. J. P. Scullin, M. D. Dudarevitch, and A. I. Lowell, "Biocides" *Encyclopedia of Polymer Science and Technology*, Vol. 2, Interscience Publishers, New York, NY, 1965.

CHAPTER 11

COATINGS FOR CIRCUIT BOARDS AND SIMILAR SUBSTRATES

The protection afforded circuit boards by epoxies, polyurethanes, and silicones is presented. Coating thickness as it relates to the reliability of the component is discussed. The importance of reworkable coatings for complex/expensive components is discussed.

11-1 TYPES OF COATINGS

The most commonly used coatings for circuit-board insulation and protection are the polyurethanes, epoxies, and silicones. The choice among them depends largely on the operating and storage requirements of the circuit boards. For high-temperature applications, for example, only silicones should be used. For reworkability, polyurethanes are outstanding; and epoxies are preferable for adhesion and resistance to moisture. The most widely used circuit-board coatings are covered by military specification MIL-I-46058* which defines the following four types:

- | | |
|-------------|--------------|
| 1. Type ER | Epoxy |
| 2. Type PUR | Polyurethane |
| 3. Type SR | Silicone |
| 4. Type PO | Polystyrene. |

Types ER and PUR are general-purpose coatings. Type SR is used for applications requiring resistance to high temperatures, Type PO is used when low dielectric loss is a requirement, particularly under conditions of very high exposure.

Many excellent circuit-board formulations are on the market. Several of these and their main characteristics are listed in Table 11-1.

11-2 IMPROVEMENT IN RELIABILITY

Printed-circuit boards are coated as the last step, after the components have been assembled and joined. Application of a coating improves the reliability of the entire assembly. This is important for circuit boards used in military elec-

tronics, where the expense of a completely assembled board may be in the \$3000 to \$5000 range and the storage or operational life expectancies may be 10 yr or more. Unprotected electronic assemblies exposed to severe environments will fail because of moisture penetration, large decreases in insulation properties, electrical shorting, or corrosion. On an uncoated circuit board there can develop excessive corrosion on components, solder, and conductor lines after short-time exposure at 95% RH. A similar board coated with 1.5 mils of polyurethane may show no signs of corrosion and pass all required electrical tests after 6 mo in a 95% humidity chamber. For protection against both humidity and salt spray, a coating or some type of encapsulant protection is mandatory^{2,3}.

For maximum reliability of circuit boards and other electronic assemblies, defense contracts specify that hardware shall meet the stringent environmental tests called out in such specifications as MIL-E-5272^a) MIL-E-16400^b, and MIL-STD-202^c. In addition to humidity and temperature tests, these specifications define salt-spray, abrasion, impact, fungous, and other tests. Table 11-2 lists tests defined in MIL-STD-202. Many of these are applicable to coatings alone, other embedments, or in conjunction with electronic components.

The use of conformal coatings for printed circuits allows the designer greater freedom in

*Insulating Compound, Electrical (for Coating Printed Circuit Assemblies)

^aElectronic Interior Communication and Navigational Equipment, Naval Ship and Shore, General Specifications for

^bEnvironmental Testing, Aeronautical and Associated Equipment, General Specifications for

^cTest Methods for Electronics and Electrical Component Parts

TABLE 11-1. TYPICAL COATINGS DESIGNED FOR CIRCUIT-BOARD PROTECTION

Trade Name	Chemical Type	Characteristics
Conap CE-1	Epoxy	A two-component 100%solids dip coating; water absorption in 24 h 0.32%; cures at 122" to 140°F.
Conap CE-1153A	Moisture-curing polyurethane	One component; cures at room temperature.
Conap 1155	Polyurethane	A two-component coating conforming to MIL-1-46058, Type PUR.
Conap Conathane DP-2226	Polyurethane	A two-component coating; cures at room temperature.
Furane Uralane 241	Polyurethane	A two-component 50%solids clear coating; easily repaired by soldering through; cures at room temperature.
Furane Uralane 8267	Polyurethane	A one-component 50%solids clear coating; cures at room temperature; available in aerosol spray can.
Hysol PC12-007, PC12-007M	Epoxy	A 100%solids epoxy coating suitable for operation up to 125°C; meets requirements of NASA specification; widely used for commercial printed circuits; the M version conforms to MIL-I-46058B, Type ER.
Hysol PC 17 STD	Epoxy	Solvent based; may be air dried or heat cured; may be used as an epoxy varnish or as a primer to improve the adhesion of subsequent encapsulants; maximum continuous operating temperature is 125°C.
Hysol PC16 STD, PC16-M	Epoxy	A 100%solids coating similar to PC12-007, except modified to increase film thickness, shelf stability, and appearance; may be applied with vapor-spray equipment; the M version conforms to MIL-1-46058, Type ER.
Hysol PC15 STD	Polyurethane	A two-component coating that is flexible at room temperature and at low temperatures; easily repaired by soldering through; contains fluorescent dye for inspection.
Hysol PC18 STD	Polyurethane	A one-component solvent based coating; may be air dried or cured at low temperature; may be repaired by soldering through.
Hysol PC22 STD	Polyurethane	Designed especially for space applications; meets the requirements of NASA; may be melted with a hot solder iron. Two-component coating.
Hysol PC26 STD, PC26-M	Ether-ester-type Polyurethane	A 100%solids two component low-stress coating suitable for application to stress-sensitive devices; suitable for continuous operation up to 125°C; the M version is qualified to MIL-I-46058B, Type PUR.
Dow-corning DC-630	Silicone	50% solution in xylene; air dries to a waxy film in 2 h; can be removed with xylene.
Dow-Corning DC-991	Silicone varnish	50% solution in xylene; air dries in 1 to 5 h; improved properties are obtained by curing 4 h at 212°F or higher.
GE SS-4175	Silicone	30%solids in xylene; cures quickly at 125" to 150°C to a clear, tough, rubberlike film.
Furane Uralane 5712	Polyurethane	A two-component coating which meets NASA and military specifications.
HumiSeal 1A27A	Polyurethane	One component; cures at room temperature to a flexible moisture-resistant film; operational temperature of 250°F.
Products Research PR-1538	Polyurethane	A 100%solids two-component coating which meets NASA specifications; suitable over a temperature range of -70" to 300°F.
Union Carbide Parylene	Polyxylylene	A one-component vapor-deposited coating (see Chapter 6 for properties).

TABLE 11-2. MIL-STD-202 TEST METHODS (FOR ELECTRONICS AND ELECTRICAL COMPONENT PARTS)

Test	Method
Environment (100 Class):	
Salt spray (corrosion)	101C
Temperature cycling	102A
Humidity (steady state)	103B
Immersion	104A
Barometric pressure	105C
Moisture resistance	106B
Thermal shock	107B
Life (at elevated ambient temperature)	108A
Explosion	109A
Sand and Dust	110
Flammability (external flame)	111
Seal	112A
Physical Characteristics (200 Class):	
Vibration	201A
Shock (specimens weighing not more than 4 lb)	202B
Shock (specified pulse)	213
Random drop	203A
Vibration, high frequency	204A
Vibration, random	214
Shock, medium impact	205C
Life (rotational)	206
Shock, high impact	207A
Solderability	208B
Resistance to solvents	215
Electrical characteristics (300 Class):	
Dielectric withstanding voltage	301
Insulation resistance	302
dc resistance	303
Resistance-temperature characteristic	304
Capacitance	305
Q-factor	306
Contact resistance	307
Current-noise test for fixed resistors	308
Voltage coefficient of resistance	309
Contact-chatter monitoring	310

achieving narrower conductor lines and closer spacings (see Table 11-3). Without such coatings, impurities, moisture, and other contaminants can bridge the conductors; thus causing decreases in the insulation resistance or arcing between conductors. The dielectric-breakdown voltage across a clean, dry surface is very high; however, it is extremely difficult to maintain a surface in this condition.

Coatings also serve other functions which contribute to the overall reliability of the assembly.

One of these is the rigidity imparted to thin leads, solder joints, and components, which prevents their breaking or lifting during normal handling or vibration testing.

11-3 CONDUCTOR SPACING ON PRINTED-CIRCUIT BOARDS

By using coating dielectrics, the allowable spacings between conductors can be substantially reduced (See Table 11-3).

11-4 COATING THICKNESS AND COVERAGE

The thicker the coating, the better its humidity-barrier properties, because the amount of moisture permeating a coating is inversely related to thickness. This holds true fairly well for the 100% solids coatings. However, it is not always true in the case of solvent-based coatings because the probability that solvent volatiles will be entrapped in the cured coating is greater with thicker coatings. In a thinner coating, these volatiles are more easily released. A thick coating with entrapped solvent molecules produces a more porous structure in which water can be more readily absorbed and transmitted, causing blistering, corrosion, and large decreases in insulation resistance values. However, solvent-based coatings may be formulated that contain various additives permitting rapid release of solvents on curing. Cure cycles can be optimized to achieve the same results. Thus, with optimum application techniques, both 100% solids and solvent-based coatings will afford better protection against humidity if their thickness is increased.

Most circuit-board manufacturers use coatings 0.5 to 3 mils thick. Thicker coatings cause components such as glass diodes or glass-sealed resistors to crack. Cracking is attributed to stresses from shrinkage of the coating when the solvent evaporates off, shrinkage from polymerization during curing, or large differences in the coefficients of expansion between the glass and

**TABLE 11-3. MINIMUM ALLOWABLE SPACING BETWEEN CONDUCTORS ON
PRINTED-CIRCUIT BOARDS PER MIL-STD-275B***

Uncoated Boards, Sea Level to 10,000ft		Uncoated Boards, Over 10,000ft		Coated Boards, All Altitudes	
Peak Voltage, V	Min Spacing, in.	Peak Voltage, V	Min Spacing, in.	Peak Voltage, V	Min Spacing, in.
0-150	0.025	0-50	0.025	0-30	0.010
151-300	0.050	51-100	0.060	31-50	0.015
301-500	0.100	101-170	0.125	51-150	0.020
Over 500	0.0002	171-250	0.250	151-300	0.030
	(in./V)	251-500	0.500	301-500	0.060
		Over 500	0.001	Over 500	0.00012
			(in./V)		(in./V)

*Printed Wiring for Electronic Equipment.

the plastic coating. Cracking may occur soon after curing, or later during testing or rework operations, when additional stresses are imposed. For stress-sensitive components, it is therefore important to avoid very thick coatings and, if filletting is used, to avoid bridging between component ~ ~ ~ !

Most circuit-board manufacturers use protective coatings containing small amounts of fluorescent pigments to allow visual or ultraviolet-light inspection and to assure that all areas have been coated thoroughly. Two examples of fluorescent indicators used in polyurethane formulations are rhodamine B which is pink to red in both the visual and ultraviolet regions of the spectrum, and 2,6-distyrylpyridine which is colorless in the visual region and intensely blue in the ultraviolet region. Fluorescent or visual indicating pigments may be incorporated in the formulation in small concentrations of 0.5 to 2% to give the desired results. Bare spots, pinholes, and other discontinuities can easily be detected. Fluorescent indicators are also used to determine whether particles of coatings are migrating and contaminating other portions of a system. Particle migration is especially critical to the functioning of parts in the immediate vicinity of the circuit board—such as gyros, accelerometers, bearings, and rotating memory disks.

11-5 COATINGS FOR THIN- AND THICK-FILM CIRCUITS

Coatings, either alone or in conjunction with encapsulants, can be employed as a method of packaging both thin- and thick-film circuits. Economies can be achieved over the normal packaging methods involving hermetically sealed metal cans. However, because of the close electrical tolerances to which thin- or thick-film elements such as resistors must be held, and because of the sensitivity of these elements to changes in ambient conditions, hermetically sealed packages containing an inert gas are still mandatory for many applications. When organic coatings are planned, they first should be checked for compatibility with the resistors, capacitors, conductors, and other circuit elements. This may be established by:

1. Assessing changes in electrical values after coating
2. Determining electrical values after environmental testing such as thermal cycling and humidity exposure
3. Determining the degree of adhesion of the coating to the various substrates and surfaces comprising the circuit'
4. Checking for corrosion to metal surfaces by long-term or accelerated aging.

Most of the criteria described as applicable to the selection of conformal coatings for etched printed-circuit boards also apply to thick-film circuit protection. Hence moisture resistance, stability of electrical insulating properties, adhesion, solder-through properties, and transparency are desirable attributes. Many coatings used for epoxy circuit boards, however, cannot be used for ceramic circuits because of differences in adhesion to the substrate. Organic coatings generally have poorer adhesion to ceramic than to epoxy substrates. Primers may be needed to achieve both adhesion and other desirable properties.

Polymer coatings or encapsulants used over thick-film circuits should also be chosen carefully for purity and stability. Outgassing or contaminants of a reducing nature, such as hydrogen gas, evolving from the polymer will lower resistance values for certain metal-metal oxide depositions⁶.

11-6 REWORKABILITY OF COATED ASSEMBLIES

Many electronic modules are designed as throwaway items, and hence no coating or, at most, a relatively inexpensive varnish or polyester is employed. For more complex and expensive equipment special coatings are needed for long-term reliability. Because of the probability that one or more defective components or solder joints will have to be repaired, it is required that the module be reworkable! In addition to meeting the numerous engineering and manufacturing requirements, the coating must be easily removable so that defective components may be replaced. The removal technique must be one which does little or no damage to adjacent components, surfaces, and markings. Combining these desirable features in one material can be a difficult problem. Where ambient or service temperatures are less than 275°F, polyurethanes are popular because, being thermoplastic, they can be melted in localized areas

with a hot soldering iron. Epoxy polyamides and epoxy amines also can be softened and removed with a hot soldering iron. But, if heat is applied for too long a period of time, decomposition and carbonization of the epoxy polymer result. Such dark-colored residues not only give a poor appearance, but also may affect subsequent solderability. Epoxies cured with amines or with other catalysts behave similarly; many of them will char immediately without going through a softening stage. Silicone-elastomeric coatings are soft enough to be removed easily with a sharp knife. Because they are thermosetting, they will not soften or melt with heat, but will eventually decompose.

Silicones and other thermosetting plastics may swell on prolonged contact with chlorinated or fluorinated solvents such as methylene chloride or trichloroethylene, but they do not truly dissolve. In general, there are four problems encountered in removal with solvents:

1. Solvents do not dissolve the plastic. The plastic can absorb large amounts of solvent and swell; and the softened material may then be removed by mechanical means.
2. The solvent cannot be localized; usually the entire assembly must be immersed, which then presents the risk of damaging other areas.
3. Swelling of the plastic can generate high stresses which may then induce other types of failure.
4. The process is slow, requiring immersion for 1 or 2 days.

There have been some attempts to localize the solvent by preparing a thixotropic form of it with an additive such as Cab-O-Sil. Thixotropic compositions containing over 90% solvent will not flow under normal conditions and assume the consistency of solids. This method is also extremely slow, however, and presents the additional problem of solvent evaporation and the need for its frequent replenishment. Table 11-4 gives information on removal of epoxies and a urethane.

TABLE 11-4. REMOVABILITY CHARACTERISTICS OF CIRCUIT-BOARD COATINGS*

Coating	Composition			Cure Schedule h/°F	Removability With Hot Soldering Iron (600°F Tip, 20-s Dwell)
	Part A	Part B	Parts by Weight		
Epoxy polyamide	Epon 828 Ketone	Versamid 115, Shell Curing Agent Z	50:50	3/150	Softens and becomes cheesy
Epoxy amine	Epon 1001	Diethylene triamine	60:15	3/150	Softens and becomes cheesy
Epoxy polyamide	Epon 1001	Versamid 115, Shell Curing Agent Z	100:30	3/150	Softens and becomes cheesy
Epoxy amine	Epon 828 Ketone	Versamid 115, Shell Curing Agent Z	—	2/175 + 2/300	Softens and becomes cheesy
Polyurethane	Mobay Mondur CB-60	Castor Oil	—	3/150	Liquefies

*All were formulated with suitable solvents for spray or dip applications.

REFERENCES

1. C. F. Coombs, ed., *Printed Circuits Handbook*, McGraw-Hill, New York, NY, 1967.
2. J. T. Milek, *A Survey of Conformal Coatings for Printed Circuit Boards*, EPIC IR-46, Hughes Aircraft Company, Culver City, CA, 1967.
3. D. L. Holland, "Liquid Covercoats for Flexible Printed Circuits", *Insulation/Circuits*, 28-32 (May 1972).
4. J. Waryold, "A Conformal Coating Primer, Circuits Manufacturing", November 1976, pp. 24-32.
5. J. Waryold, "How to Select a Conformal Coating for Printed Circuit Boards", *Insulation/Circuits*, 29-31 (July 1977).
6. J. P. Carey, "Encapsulation of Thick-Film Substrates", National Electronic Packaging and Production Conference, Long Beach, CA, 31 January - 2 February 1967, and New York, NY, 13-15 June 1967, *Proceedings of the Technical Program*, pp. 549-57, Conference Sponsored by the Electronic Production and Packaging Magazine, Chicago, IL, 1967.
7. C. J. Tautscher, "Causes and Prevention of Blisters in Conformal Printed Circuit Coatings", *Insulation/Circuits*, 32-33 (June 1972).
8. A. J. Beccasio and L. S. Keefer, "Effects of Conformal Coatings on Printed Circuit Assemblies", *Proceedings, National Electronic Packaging and Production Conference (NEPCON)*, pp. 347-63, Long Beach, CA, 8-10 June 1965.

CHAPTER 12

STRESS; RESIN TYPE CHOICE; CORRECTION OF DEFECTIVE EMBEDMENTS

The fact that embedments can intensify or relieve stress is presented — the proper selection of material and method of application is important. Checkpoints are given as a guide for designing embedments.

12-1 CONDITIONS AFFECTING EMBEDDED POLYMERIC DEVICES; STRESS

The general parameters of dielectrics, which act as closely related factors, that may affect device reliability include:

1. Permeability
2. Purity
3. Induced corrosivity
4. Induced mechanical stress
5. Adhesion.

Interrelationships can exist with two or more of these five general parameters. Poor resin adhesion can increase water permeability, water plus impurities can lead to corrosion, corrosion (aside from destroying discrete conductive paths) can induce mechanical stress of further loss of adhesion, etc.¹

Soft or flexible resins, as thin coatings, can be first applied to electronic components to minimize or eliminate stresses from subsequent use of transfer-molding or casting compounds. The initial coating also acts to protect the device from vibration or shock.

The stress-relief agents selected must be flexible and possess a low modulus of elasticity. Silicones, both the heat cured (i.e., two part Silastic) and the room temperature vulcanizing types, meet these requirements and have found many applications in component packaging. For example, transistor components can be coated with 10 to 20 mils of silicone and then encapsulated with an m-phenylenediamine-cured epoxy. Other semiconductor methods can employ small amounts of silicone barrier coatings and then

transfer-mold the semiconductor with silicone or epoxy.

The value of flexible dip coatings in relieving stresses has been gaining wide acceptance. Total stresses of 5000 psi at -40°C were measured for components embedded in a silica-filled epoxy resin; the stresses were greatly reduced when the components were precoated with room-temperature vulcanizing elastomeric silicone. At -40°C , a 1-mil silicone coating reduced the total pressure to 3500 psi, and an 8-mil coating reduced the pressure to less than 400 psi.

12-1.1 MECHANICAL PROTECTION TO ABSORB STRESS

Rigid compounds that are transfer molded or cast over a coated or uncoated device give added mechanical protection to the end item. The value of plastics in damping vibration within components can be readily shown. Plastic-packaged devices generally withstand vibration and impact better than their metal-packaged counterparts. The resin grips and secures all connections, wires, posts, and other projections. Loads to components are frequently applied through the wire leads. Plastics absorb these stresses and lessen their transfer to the component^{2,3}.

The excellent shock and vibration protection provided by epoxy encapsulation has been demonstrated in tests of many protected transistors. Epoxy-encased transistors that were subjected to 100,000 g acceleration forces for 1 min and to vertical-recovery gun shock have shown no significant changes in electrical characteristics.

12-1.2 STRESS MINIMIZATION THROUGH DESIGN

Although dielectric resins can protect components from mechanical stress, such plastics with improper use may also be responsible for adding to a stress problem. High stresses can be imparted to electronic components by shrinkage of the plastic during its cure. Mismatches in coefficients of expansion between the plastic and the various metallic and ceramic surfaces to which it adheres can also cause problems. Cure shrinkages and expansion coefficients vary widely among plastics; these depend on the type of polymer used and the volume percentage and type of filler employed. The percentage of shrinkage depends on the temperature of cure, the geometry of the part, and the amount of plastic used?

Problems of failure in an integrated circuit may at times be attributed to both the cure and cooling shrinkage of an insulating coating. The coating layer can be too thick; this can be further complicated if the resin is unfilled and contains a solvent which evaporates in time.

Unfilled plastics generally have much higher cure-shrinkage values and higher coefficients of expansion than filled plastics. A thinner application of a coating and a stepwise increase of the curing temperature can minimize stresses and avoid lead wire or component breakage.

Plastic systems with more than one coating or type of plastic can present problems if the inner coating has a higher coefficient of expansion than the outer one. An increase in temperature will cause the inner coating to exert pressure against the confining outer shell. This can happen with the use of an inner unfilled silicone coating and an outer epoxy shell in some resistor and semiconductor devices. Stress problems can be eliminated either by using a thinner inner silicone coating or by providing space between the inner coating and the outer shell into which the silicone can expand.

Transfer-molding or casting operations can induce other kinds of stresses. Some arise from the

molding operation and others are a function of the plastic material itself. The combined pressure and heat during molding can result in momentary stress gradients of sufficient magnitude to cause stress failure in some materials. During the cure process, an exothermic reaction can raise the temperature within the plastic mass higher than the applied curing temperature; the cure shrinkage that occurs immediately with cooling results in considerable compressive stress on the component.

Removal of the part from the mold can impart stresses. This depends on the mold design, the efficiency of the mold-release agent used, the type of molding material, and the care exercised by the operator. The hot strength of a molding compound determines the ease in removing the components from the mold. Hot materials, soft at molding temperatures (about 300° to 400°F), allow stresses to be transferred to the component. Epoxies, not fully cured, are generally soft and pliable when hot; greater care must be taken in handling them^{4,5}.

Cooling of the molded parts can yield further stresses, owing to differences in coefficients of expansion of the various materials used in the construction and encapsulation of the device. These internal stresses can change as the materials stress-relieve themselves upon standing at room temperature. There is a certain amount of creep which occurs with time. Internal stress often can be relieved if the molded part is postcured or postbaked. Postbaking is usually performed as a practical way to complete the cure of the plastic or to stabilize the electrical characteristics of the device⁶.

12-2 RESIN SELECTION AND DESIGN

The following are statements regarding major checkpoints which should be considered in designing an embedded assembly^{2,8,9,10}.

1. Give attention to sensitive and critical components; they may require protection by coating with a flexible agent, e.g., silicone.

2. Minimize stress points; these are areas of possible cracking. Typical crack locations are around or near the fillets of protruding terminals, on thin flat areas where the bond to the substrate is poor or faulty, at transitions between thick and thin resin sections, and at sharp or acute variations in the shape of the components.

3. Minimize overall stresses by precoating the assembly or embedding it in low-stress materials.

4. Check properties of the resin system at operating temperatures. Many resins change properties drastically—both mechanically and electrically—as a function of temperature.

5. Keep in mind the possible need for repairability or maintainability. Most resin systems are not easy to remove or repair because of hardness, inertness to solvents, and other factors.

6. Calculate tooling and housing costs versus volume; review the advantage and disadvantages of various housings, shells, and molds.

7. Consider reaction conditions during cure as they affect components (e.g., high exothermic temperatures and stresses from rapid cure) and as they affect handling (e.g., resin gets too thin during heat curing), and viscosity as it determines optimum flow.

8. Consider the compatibility of the resin and the components which are to be embedded.

Table 12-1 gives an overview of the purpose of an embedment procedure or effect and also ties in with the resin materials previously mentioned^{11, 12, 13} serving the purposes.

12-3 DIAGNOSIS/CORRECTION OF DEFECTIVE EMBEDMENT

Table 12-2 summarizes checkpoints regarding defects, probable causes, and corrective actions¹⁴⁻¹⁷.

**TABLE 12-1. DESIGN OBJECTIVES
MATCHED TO MATERIALS**

Objective	Choice of Materials
Adhesion of resin to assembly	Epoxies, urethanes. Cleanliness of parts and use of primers can improve adhesion.
Low dielectric constant and/or loss	Silicones. These retain good electrical properties and high temperatures and frequencies.
Thermal Stability	Silicones, novolak epoxies, anhydrid-cured epoxies, aromatic-amine-cured epoxies. Thermal stability with regard to weight loss and retention of mechanical properties can be increased with fibrous fillers.
cost	Epoxies or polyurethanes as solids or foams. Use of high level of fillers.
Room temperature cure	Silicones (RTV), urethanes, and epoxies. Formulated for low temperature reactions.
Low-temperature flexibility	Silicones and certain low-hardness polyurethanes.
Rigidity	Epoxies. Some trade-offs must be made between hardness, toughness, brittleness, and crack resistance.
Flexibility	RTV silicones and polyurethanes. Additionally flexible epoxies can be made from rigid resins through the addition of flexibilizers or modification of the base materials. Epoxies are available in flexible formulations.
Clarity	Epoxies and silicones. Clear silicones are soft and flexible; other resins, e.g., epoxies, are amber or light colored so that internal parts can be seen.
Repairability	Silicone gels and highly flexibilized epoxies or urethanes. Rigid resins can only be repaired by initial softening or dissolving in solvents.
Low weight	Low density foams, hollow bead-filled resins, urethanes (rigid or flexible) commonly used. Bead-filled systems have higher density but physical properties are better.
High thermal conductivity	High levels of large particle fillers are used—e.g., coarse sand, aluminum oxide, magnesium oxide or beryllium oxide are used with epoxies, urethanes, or silicones.

**TABLE 12-2. DIAGNOSING AND CORRECTING DEFECTIVE EMBEDMENTS
(PRIMARILY MOLDED STRUCTURES)**

<u>Appearance</u>	<u>Probable Cause</u>	<u>Corrective Action</u>
1. Resin uncured	Cure too hot; too large a resin mass (with highly exothermic systems).	Resin oven temperature in 10 deg C stages; pour casting in stages; allow first stage to gel before pouring second, etc.
2. Resin appears burned (especially in center)	Cure too hot; mass of high exotherm resin too large.	Reduce cure temperature, reduce mass of resin, or use external cooling with room temperature systems.
3. Resin releases from components at edges, corners or terminals	Surface contaminated with oil, grease, mold-release agent, or skin oil.	Degrease component before casting; handle with gloves.
	Nonbondable surfaces. Oxidized metal surfaces (resin bonds to oxide which releases from metal).	Replace or prime surfaces. Abrade or chemically clean surfaces just prior to casting or use primers.
4. Casting warps or distorts from desired mold shape	Cure temperature too hot	Reduce cure temperature; keep mold temperature uniform.
	Insufficient resin.	Allow larger sprue volume or recap casting.
	Poor design.	Keep resin wall thickness uniform; add ribs.
	Excessive shrinkage.	Use more filler; in extreme cases pack mold with porous filler and then impregnate with resin.
5. Resin remains liquid or soft and sticky	Cure temperature too low.	Increase oven temperature.
	Cure time too short.	Extend cure time.
	Mix ratio incorrect.	Check mixing process; adjust equipment
	Insufficient mixing.	Mix thoroughly. Color, if the resin is pigmented, should be uniform.
	Separate parts not mixed.	Stir separate system constituents before blending.
	Contamination.	Keep molds, parts, and resin clean.
6. Casting opens; liquid oozes out of fissure or around terminals and lugs	Moisture.	Dry component thoroughly; (paper or fiber parts are prime offenders).
	Incompatible insulation.	See Item No. 7
7. Casting appears normal at room temperature but becomes liquid or tacky at high temperatures (cross-linking not complete)	Mix ratio incorrect.	Check and adjust mixing process.
	Excess use of mold release.	Use agents sparingly.
	Moisture.	Dry component thoroughly before casting.
	Contamination.	Check resin area for oils, dirt, greases, or waxes.
	Incompatible insulation.	Check components for thermoplastics (plasticized or not) that liquefy at operating temperatures of part or at cure temperature of embedding agent.
8. Surface rough or spotted	Rough mold surface.	Clean or polish mold.
	Excess mold release.	Use release agent sparingly or use "thin" type agents.

(cont'd on next page)

TABLE 12-2 (cont'd)

9. Exterior of casting has soft or sticky areas, possibly with voids	Excess mold release.	Use release agents sparingly; dilute with solvent.
	Dirty mold.	Clean after use.
10. Bubbles or holes in surface.	Rough mold surface.	Polish surface.
	Leaky molds (air enters during vacuum cycle).	Seal molds, polish joints, replace gaskets, release vacuum slowly.
	Poor mold design; horizontal "shelf" areas trap air.	Redesign molds, taper "shelves" for air exit.
11. Bubbles, voids, or dry areas in casting; low corona-starting voltage	Insufficient resin.	Provide a "bead" of resin over component to allow for escaping air.
	Insufficient vacuum.	Evacuate resin and part prior to casting, and pour under vacuum. Allow lower vacuum or extend time; try pressure after vacuum.
	Resin cured before air escaped	Use slower curing system or lower temperature.
	Resin too thick.	Heat component, mold, and resin to reduce viscosity or use thinner resin.
	Poor component design.	Modify component layer
12. All or part of mold difficult to remove	Undercuts in mold.	Remove undercuts and repolish mold.
	Insufficient mold release.	Reapply release agent.
	Mold not broken in.	Reapply release agent before each casting; use mold several times.
	Rough mold surface.	Polish surface.
	Permanent-type release agent worn or abraded.	Reapply or regrind Teflon-type coatings.
13. Fissures develop during cure, cooling, or subsequent thermal shock.	Resin not cured.	Increase cure time.
	Sticking.	Resin damaged during mold removal; recast.
	Wrong resin.	Flexible or filled resins should be considered
	Oven too hot.	Check oven temperature.
	Gel temperature too high.	Use lowest possible temperature to minimize stresses.
	Poor component or mold design.	Design so that resin thickness is uniform around component (at least 1/16 in.); fill sharp internal corners with heavily filled resin before casting; reinforce crack areas with glass cloth or glass-reinforced tape.

REFERENCES

1. E. P. Campbell, "The Effects of Encapsulation on Electronic Components", *Electronic Engineering* **32**, 366-71 (June 1960).
2. F. L. Howland and C. H. Zeidt, Chapter 7, "Device Encapsulation and Evaluation", D. Baker, D. C. Koehler, W. O. Fleckenstein, C. E. Rodin, R. Sabin et al. (Bell Telephone Laboratories, others), *Physical Design of Electronic Systems—Vol. III Integrated Device and Connection Technology*, Prentice-Hall, Englewood Cliffs, NJ, 1971.
3. R. L. Beadles, "Integrated Silicon Device Technology", Vol. XIV, *Interconnection and Encapsulation* (AD-654 630) Technical Rept. for January 1966 to March 1967, Research Triangle Institute, Durham, NC, 1967.
4. T. Hamburger and S. Gourse, *Microelectronic Packaging Concepts* (AD-619 444). Prepared by Westinghouse Electric Corporation for Rome Air Development Center, NY, 1 January 1964 to 31 December 1964.
5. C. V. Lundberg, "Correlation of Shrinkage Pressures Developed in Epoxy, Polyurethane, and Silicone Casting Resins With Inductance Measurements on Embedded Electronic Components". Paper presented at the 152nd National Meeting, Am. Chem. Soc., New York, NY, 11-16 September 1966, *Industrial and Engineering Chemistry, Product Research and Development*, Vol. 6, pp. 92-100, June 1967.
6. H. Dorfman, "Weld Stress Evaluation—Electronic Modules", *Proceedings of the SAE Sponsored Electronic Packaging Conference*, pp. 49-53, Los Angeles, CA, 20-21 October 1965.
8. D. V. Steele, *Internal Stresses Developed in an Epoxy Resin Potting Compound During Long Term Storage*, (AD-411 514) Chemistry Research Division, Naval Ordnance Laboratory, White Oak, MD, 1962.
9. M. H. Smith, "Measurement of Embedment Stresses in Electronic Modules", (NAS7-101) National Electronic Packaging and Production Conference, New York, NY, 21-23 June 1966, *Proceedings of the Technical Program*, pp. 427-38, Industrial and Scientific Conference Management, Inc., Chicago, IL, 1966.
10. F. F. Stucki, W. D. Fuller, and R. D. Carpenter, "Internal Stress Measurement of Encapsulated Electronic Modules", *Electronic Packaging and Production* **7**, 39-46 (February 1967).
11. C. A. Harper, "Embedding Resin Effects on Components and Circuits", *Electronic Packaging and Production* **5**, 71-8 (May 1965).
12. R. A. Fischbein and J. V. Dichiaro, *Determination of the Shrinkage of Adhesives During Cure*, AEC Research and Development Report, Monsanto Research Corporation, 20 January 1967.
13. R. Fountain, "Analyses for Mechanical and Electrical Properties of Epoxy Resins Used as Potting Compounds", *Polymer Engineering and Science* **14** (June 1974).
14. P. N. Everett, *Lead Attachment and Encapsulation Techniques for Thin Film Microcircuits* (AD-611 752) Mitre Corporation, Bedford, MA, 1965.
15. L. I. Johnson and R. J. Ryan, "Encapsulated Component Stress Testing", *Proceedings of the Sixth Electrical Insulation Conference*, pp. 11-5, New York, NY, 13-16 September 1965, Conference Sponsored by IEEE, NEMA, and Navy Bureau of Ships, 1965.
16. G. Gillemot, "A New, Reenterable Polyurethane Compound for Primary Use in Telephone Cable Splices", *Proceedings: 22nd International Wire and Cable Symposium*, Atlantic City, NJ, 4-6 December 1973.
17. G. R. Dallimore, F. S. Stucki, and D. Kasper, "Measurement of Internal Stresses in Electronic Encapsulating Resins with a Small Solid State Transducer", *Society of Plastics Engineers-Journal* **20**, 544-6 (1964).

CHAPTER 13

EPILOGUE — APPENDIXES; CHANGES IN THE TECHNOLOGY; UP-TO-DATE ADVICE ON EMBEDDING

Examples of product literature are given. Military specifications, and specifications and standards related to dielectrics are documented.

Appendix A gives the reader some examples of the types of product literature, available from companies, regarding embedment materials. Appendix B gives Military Specifications concerning potting/encapsulation materials. Appendix C lists specifications and standards covering test procedures (electrical/electronic requirements). Appendix D notes specific test methods (ASTM, others).

The formulations and technology of epoxy, polyurethane, and silicone embedding agents undergo revisions and improvements. Added to this normal pace of changes is the impetus given by Federal Government guidelines regarding reduction in toxicity and hazards of certain chemicals and their industrial/consumer uses.* The

Occupational Safety and Health Administration (OSHA) develops and promulgates occupational safety and health standards. The Environmental Protection Agency (EPA.) closely monitors pollution problems under various laws including the Toxic Substances Control Act. In close cooperation with industry, these federal and other groups have been establishing requirements for proper use or elimination/modification of various chemicals and processes that present hazards.

This handbook gives basic information on the use of embedding agents for electrical or electronic components. When unusual questions arise regarding the application of such agents, it is suggested that the user or potential user request up-to-date guides from the manufacturer. Problems can also be referred to the Plastics Technical Evaluation Center (PLASTEC), (201)-328-4222 or Autovon 880-4222.

*Up to this time, early 1978, no obvious problems of toxicity or hazards have arisen with respect to the poly-p-xylylene materials or process.

APPENDIX A

SOME TYPICALLY AVAILABLE COMPANY PRODUCT LITERATURE

Bacon Industries Inc.— Series 1000 Encapsulating and Potting Compounds:

- Data Sheet 1001—Regular and Lightweight Epoxy Compounds
- Data Sheet 1001—Thermally Conductive Compounds
- Data Sheet 1043—Non-magnetic Potting Compounds
- Data Sheet 1380—Instrument Potting Compounds
- Data Sheet 1386—Microcircuit Grade Potting Compound
- Data Sheet 1511—Thermally Conductive Silicone Potting Compounds
- Data Sheet 1513—High Loss Silicone Compound.

Castall, Inc. — Tech. Bull., Castall Dielectric and Thermal Compounds for . . . Casting, Potting, Bonding, Coating .

Ciba-Geigy Corp. — Instructions and Data Bulletin for Electrical Casting Systems: Araldite CY183 with Hardeners H T 907 and HY 920

Dow-Corning Corp.:

- Bull. 61-225, 6/1974 Silicone Materials for Gasketing, Bonding, Sealing, Potting, Encapsulating, Mold Making, and Tooling
- Bull. 01-237, 11/1972 Silicones for Power System Maintenance
- Bull. 01-235, 11/1972 Silicones for Electrical Design
- Bull. 01-236, 11/1972 Silicones for Electronic Design
- Bull. 23-179(a) (and others) 6/1975 Information About Semiconductor Molding Compounds
- Bull. 23-161 4/1973 Silicone Semiconductor Molding Compounds and Selection Guide
- Bull. 01-238 4/1973 A Guide to Dow-Corning Products
- Bull. 61-212 11/1972 Encapsulants and Sealants
- Bull. 17-198 (and others) 11/1974 Information About Silastic Silicone Rubbers
- Bull. 61-283 (and others) 9/1974 Information About Electrical/Electronic Materials
- Bull. 01-207 10/1970 Selection Guide to Electrical/Electronic Materials from Dow-Corning Distributors
- Bull. 01-23B 1/1977 Government Buyers Guide to Silicones
- Bull. 23-208 9/1975 Elastoplastic Silicones: Clear, Easy-to-use Conformal Coatings.

Emerson & Cuming Inc. — Tech. Bull. on:

- Stycast Casting Resins (epoxies, others; rigid and flexible)
- Eccocoat Surface Coatings
- Eccomold Molding Powders
- Eccosil RTV Silicones (and other silicones)
- Eccofoam Plastic and Ceramic Foams
- Eccotherm Thermally Conductive Dielectrics
- Eccoclear Crystal Clear Casting Resins.

Epic Resins Division — RTE Corp: Various technical data sheets.

Fenwal Inc. — Tech. Bull./Data Sheets—Resin Packs—Formulations and Systems.

Formulated Resins Inc. — Various technical data sheets.

Furane Plastics Inc.:

Data Sheet Uralane X-87645-A/B and B-40 Urethane Casting Compound
Data Sheet Uralane X-87644-A/B and B-40 Flexible Urethane Casting Compound
Data Sheet Uralane X-87665-A/B and B-40 Urethane Casting Compound
Tech. Bull. Uralane 5753-A/B (Semi-transparent) and Uralane 5753-A/B-40 (Black)—Reversion Resistant, Low Parameter Encapsulating and Molding Compound
Tech. Bull. Uralane 5750-A/B (Urethane Circuit Board Coating) and Uralane 5753-A/C (Staking Compound).

General Electric Co. (Silicones Products Dept.):

Tech. Data Books S-1D—Silicone Rubber for Design Engineers
Tech. Bull. CDS-1342—Silicones RTV700 Series Super Tough Silicone Liquid Rubber
Tech. Bull. 5-36—Silicone Rubber RTV Compounds (for MIL-S-23586A)
Tech. Data Book S-35A—RTV Room Temperature Vulcanizing Silicone Rubber
Tech. Bull. S-35-2—Room Temperature Curing RTV-619 Silicone Gel
Tech. Data Book S-1E Silicone Rubber Technical Information for Designers and Specifiers of Rubber Parts.

B. F. Goodrich Chemical Co.:

Tech. Bull.—In-Situ Reinforced Hycar Reactive Liquid Polymers
Tech. Bull.—Hycar Reactive Liquid Polymers
Tech. Bull.—Hycar Reactive Liquid Polymers-Product Description
Tech. Bull.—Hycar Vinyl-Terminated Liquid Polymers
Tech. Bull.—Hycar Reactive Liquid Polymers (CTB, CTBN)
Tech. Bull.—Hycar ATBN-Amine Terminated Butadiene/Acrylonitrile Liquid Polymers

Hexcel Corp., Rezolin Div.:

Data Sheet 185N Urethane, Compound for Permanent Encapsulation of Telecommunications Cable.
Data Sheet 7200 Urethane Encapsulant, Compound for Permanent Encapsulation and Gas Blocking of Electrical and Communications Cable
Data Sheet 190RE Urethane Compound for Encapsulating Telecommunications Cable Where Re-entry is Desired
Data Sheet Uralite 3130 Urethane Casting Elastomer 25-30 Shore D
Data Sheet Uralite 3127 Urethane Casting Elastomer 75 Shore D
Data Sheet Uralite 3121S Urethane Casting Elastomer 50 Shore D.

Humiseal Div., Columbia Technical Corp. — Humiseal Protective Coatings—Formulated Specifically for Electronic Applications.

Isochem Resins Co. — Catalog — All Purpose Resin Selections (Epoxies, urethanes, silicones, etc.).

The Polymer Corporation:

Tech. Bull. Corvel Coating Powders

Tech. Bull. Corvel Epoxy Coating Powders.

SWS Silicones Corp. — Tech. Bull. SILGAN (Reinforced silicone elastomer).

Thiokol Chemical Division — Tech. Bull Solithane Resin (Solithane 113 Urethane Prepolymer).

Transene Co. Inc. — Encapsulants for Electronic Packaging (Epoxy, Silicones, Junction Coatings, etc.).

Union Carbide Corp:

Technology Letters

New Business Dept. Paralene (various bulletins on Parylene coatings) 1972 and later dates

Tech. Bull. Parylene Conformal Coatings.

APPENDIX B

MILITARY SPECIFICATIONS OF PERTINENCE

Number	Title	Date
MIL-S-8660	<i>Silicone Compound</i>	1967
MIL-V-13497A	<i>Varnish, Impregnating, Electrical Insulating (For Fire Control Instruments)</i>	1962
MIL-T-13867B	<i>Treatment, Moisture and Fungus Resistant ~~for~~ Fire Control Electrical and Electronic Instruments and Equipment</i>	1971
MIL-I-16923G	<i>Insulating Compound, Electrical, Embedding</i>	1975
MIL-R-21931A	<i>Resin, Epoxy</i>	1977
MIL-I-22266C	<i>Insulating Compound, Electrical (For Field Splicing Applications)</i>	1973
MIL-C-22627	<i>Coating, Conformal, Resin</i>	1964
MIL-C-22750C	<i>Coating, Epoxy, Polyamide</i>	1972
MIL-S-23586	<i>Sealing Compound, Electrical, Silicone Rubber, Accelerator Required</i>	1973
MIL-M-24041A	<i>Molding and Potting Compound, Chemically Cured, Polyurethane (Polyether Based)</i>	1972
MIL-I-24092B	<i>Insulating Varnish, Electrical, Impregnating, Solvent Containing</i>	1976
MIL-I-46058C	<i>Insulating Compound, Electrical (For Coating Printed Circuit Assemblies,)</i>	1976
MIL-P-46067B	<i>Plastic Embedding Compound, Epoxy Resin System</i>	1977
MIL-R-46092	<i>Rubber, Silicone, Encapsulating Compound</i>	1975
MIL-A-46106A	<i>Adhesive Sealants, Silicone, RTV, General Purpose</i>	1974
MIL-P-46121	<i>Plastic Sheet and Coating Material, Para-xylylene Polymers</i>	1971
MIL-A-46146	<i>Adhesive Sealants, Silicone, RTV, Non-corrosive (For Use with Sensitive Equipment)</i>	1974
MIL-P-46838	<i>Potting Compound, Silicone Rubber, Room Temperature Vulcanizing</i>	1977
MIL-P-46847A	<i>Plastic Material, Foamed Polyurethane For Encapsulating Electronic Components</i>	1969
MIL-I-46865	<i>Insulating Compound, Electrical, Epoxy, Colloidal Silica Filled ~~for~~ Potting and Encapsulation</i>	1973
MIL-I-46879	<i>Insulating Compound, Electrical, Epoxy Base Resin</i>	1973
MIL-C-46881	<i>Coating, Transparent, Epoxy Resin</i>	1973
MIL-V-47006	<i>Varnish, Insulating, Electrical, Unmodified Epoxy Base</i>	1974
MIL-F-47095A	<i>Foam, Polyurethane, For Embedding Electronic Components and Boards</i>	1974
MIL-C-47097	<i>Coating, Two Part, Epoxy Resin Base, Clear</i>	1974
MIL-P-47099	<i>Polyurethane Foam, Rigid, For Packaging and Encapsulation of Electronic Components and Boards</i>	1974
MIL-(2-47102	<i>Coating, Polyurethane, For Electronic Components, Metals and Plastics</i>	1974
MIL-P-47104	<i>Potting Compound, Epoxy Resin, Thermosetting</i>	1974

APPENDIX B (cont'd)

Number	Title	Date
MIL-C-47131	<i>Compound, Molding and Potting, Polyurethane</i>	1974
MIL-C-47153	<i>Compound, Insulating, Potting and Encapsulating, Epoxy Resin</i>	1974
MIL-C-47163	<i>Compound, Rubber, Silicone, High Dielectric Properties, Room Temperature Vulcanizing</i>	1975
MIL-C-47175	<i>Compound, Polyurethane, For Conformal Coating of Electronic Circuitry</i>	1974
MIL-P-47199	<i>Potting Compound, Low Viscosity, Silicone Rubber</i>	1976
MIL-C-47200	<i>Compound, Coating, Polyurethane, Electrical Insulating, Room Temperature Cure</i>	1974
MIL-V-47242	<i>Varnish, Insulating, Electrical</i>	1974
MIL-C-47255	<i>Coating, Protective, For Printed Wiring Boards</i>	1974
MIL-C-47256	<i>Coating, For Printed Wiring Boards, Application of</i>	1974
MIL-C-47272	<i>Compound, Epoxy, Electrical Insulating</i>	1974
MIL-P-47298	<i>Polyurethane Molding Compound, Chemically Cured (Polyether Based)</i>	1975
MIL-M-81999	<i>Molding Compound, Reversion Resistant, Non-Carcinogen Curing Polyurethane, Aircraft structure</i>	1975
MIL-C-82644	<i>Compounds, Epoxy, Encapsulating</i>	1975
MIL-P-83455	<i>Potting Compound, Two Component, RTV, Fluorosilicone</i>	1974

APPENDIX C
SPECIFICATIONS/STANDARDS
TEST PROCEDURES; ELECTRICAL/ELECTRONIC REQUIREMENTS

<u>Number</u>	<u>Title</u>
MIL-STD-202	<i>Test Methods for Electronic and Electrical Component Parts</i>
FED. STD. No. 406	<i>Plastics, Methods of Testing</i>
MIL-1-16923	<i>Insulating Compound, Electrical Embedding</i>
MIL-STD-810	<i>Environmental Test Methods for Aerospace and Ground Equipment</i>
MIL-E-5272	<i>Environmental Testing, Aeronautical and Associated Equipment</i>
MIL-E-5400	<i>Electronic Equipment, Aircraft, General Specification for</i>
MIL-STD-454	<i>Standard General Requirements for Electronic Equipment</i>
MIL-STD-202	<i>Test Methods for Electronic and Electrical Component Parts</i>
MIL-T-945	<i>Test Equipment, for Use with Electronic Equipment, General Specification</i>
MIL-STD-750	<i>Test Methods for Semiconductor Devices</i>
MIL-STD-883	<i>Test Methods and Procedures for Microelectronics</i>
MIL-STD-446	<i>Environmental Requirements for Electronic Parts, Tubes, and Solid State Devices</i>
MIL-S-19500	<i>Semiconductor Devices, General Specification for</i>

APPENDIX D

SPECIFIC TEST METHODS, ASTM, OTHERS

Type of Test	ASTM	Others	
		Fed-Std-406	MIL-STD-202
Arc Resistance	D 495	(4011)	(303)
Capacitance	D 150	(4021)	(305)
Corona	D 1868		
Corrosion	D 130, D 849		
Corrosivity Index		(7071)	
Dielectric Constant	D 150, D 229 D 669	(4021)	(301)
Dissipation Factor	D 150	(4021)	
Electrical Insulation Resistance	D 257, D 229	(4041)	(302)
Epoxy Equivalent	D 1652		
Expansion Coefficient (Thermal)	D 696, D229, D 1674	(2031)	
Fungous Resistance	D 1924		
Gas Transmission Rate	D 1434		
Gel Time	D 1955		
Hardness	D 676, D 1674, D 314, D 1474		
Moisture Absorption	D 570		
Moisture Resistance			(106)
Moisture Vapor Permeability	D 1653		(7032)
Reversion (Hydrolytic Stability)	F 74-73		
Specific Gravity	D 792, D 115, D 1475	(5011)	
Thermal Stability	D 794, D 2307		(108)
Volume Resistivity		(4042')	

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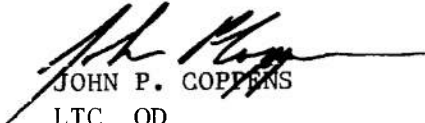
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