

Plastic Mortars, Sealants, and Caulking Compounds

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FOREWORD

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PREFACE

The annual production of plastic mortars, sealants, and caulking compositions is greater than the entire production of plastics prior to World War II. This volume is growing at an annual rate greater than that of high solvent coatings and adhesives. Polymer concrete (PC), which is characterized by its resistance to frost damage, excellent surface finish, and superior strength, has been widely accepted outside the USA and is now being considered as a construction material in America.

One of the drawbacks to the use of PC is the need to premix measured amounts of resin and filler. This objection has been overcome by the use of over 250 continuous casting machines in some 40 countries outside the USA. The first continuous casting machine used in the U.S. was in 1978.

Japan's Nippon Telephone and Telegraph Co. has installed forty thousand precast PC manholes since 1971. The Electric Power Research Institute (EPRI) has already selected a PC called Polysil for making centrifugally cast power poles.

While polyester is the most economical choice for the resin in PC, epoxy resins, PMMA, and PV are also being used. Of course, larger amounts of these and other resins will be used as construction engineers recognize the advantages of PC technology.

Latex emulsions have improved the qualities of nonplastic concrete. The slow growth of this advance in construction may be attributable to the lack of dialogue between the civil and plastic engineer. However, there are already enough case histories available to convince the civil engineer of the advantages of this improved hydraulic cement.

Modern construction techniques require the use of superior sealants and caulking compositions. Fortunately, the producers of these materials have provided a strong technical service backup for the civil engineer. Hence, these products are now accepted as standard materials of construction.

While PC, latex emulsion concrete, and caulking compositions represent only a small percentage of the entire plastics business, they are one of the most important to the construction industry. The American construction industry has been dependent on plastic sealants and caulking compositions but has been slow to accept plastic concrete. Fortunately, the latter has been successfully used for many years in other countries and it is now being accepted in the U.S.

Hopefully, the information in this book will help hasten the adoption of plastic cements and assure the construction engineer of the merits of the widely used sealants and caulking compositions.

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Plastic Mortars

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There is no sharp dividing line between plastic mortars and sealants, but the former are usually in situ-polymerized, highly-filled, rigid composites while the latter are usually in situ-polymerized, flexible polymers. Since plastic mortars do not require expensive molds, the phenolic and urea plastic mortars were the pioneer plastics. The interest in these readily fabricated, labor-intensive, plastics decreased as automated molding processes were developed. However, because of their excellent properties and the need to conserve energy, there is an renewed interest in these materials.

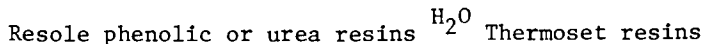
One of the first commercial resinous mortars called Asplit was prepared by mixing a silica or carbon aggregate containing a solid organic acid, such as benzene sulfonyl chloride, with a liquid phenolic resole resin.¹ These mortars, of course, were the pioneer high solids composites. Many related coatings were dependent on solvent additives but because of Environmental Protective Agency (EPA) Regulations, the solvent content of these coatings are being reduced and they now approach the solvent content of plastic mortars. According to Luberoff, "everyone is vaguely aware, that sooner or later, less volatile will become no volatiles."² Of course, in essence, this means a return to the original plastic mortars.

Other resins, such as resorcinol and cashew nut resins, other acidic catalysts, such as p-toluene sulfonic acid and other aggregates, such as asbestos, glass flakes, and slag microfibers (PMF) have been substituted for the original ingredients but basically the formulations for the relatively widely used phenolic resin mortars have not changed radically during more than a half century of satisfactory use.

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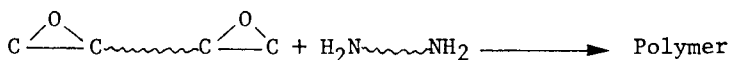
When urea-formaldehyde resins were first introduced, it was relatively easy to substitute aqueous solutions of these resins for the phenolic resole resins and to obtain a colorless urea plastic mortar by use of acid curing agents. While the phenolic resins mortars were used originally as acid resistant cements, the in situ-polymerized urea resin compositions were used primarily as adhesives and as rigid plastic foams.³ Kaolinite-filled-oxalic acid-cured urea resins are also used for sealing underground rocks⁴ and for the fabrication of irrigation pipe. The general equations for these in situ reactions are shown below:



The two principal objections to use of phenolic resin mortars, i.e., short shelf life and lack of resistance to alkalis were overcome by substituting furfuryl alcohol-based furan resins for phenolic resins. The liquid phase of the original furan mortar called Alkor was a furfuryl alcohol solution of polybutyl methacrylate⁵ which polymerized in situ by the use of p-toluene sulfonic acid which was dispersed in the carbon filler. Information on applications and chemical resistance of these dark colored resinous mortars are available,⁶ and more information on furan resinous cements is supplied in Chapter 2.

Objections to the high exotherms in the curing of furan resinous cements was overcome by substituting epoxy resins for the liquid furan prepolymer. The epoxy resins which were developed in 1934⁷, were introduced originally as resinous cements and grouting materials under the trade names of Alfane and Furnane in the early 1950's.⁸

In contrast to the phenolic, urea and furan resinous cements, the liquid epoxy resin in the epoxy cements is cured by a reaction with a polyfunctional amine, such as polyethyleneamine or an active polyamide (Versamid) which is dispersed in the carbon or silica filler as shown in the following equation.⁹



These composites may be flexibilized by the addition of polyethylene sulfide (Thiokol) or a carboxyl terminated butadiene polymer. Coal tar may also be added as an extender, polyvinyl-p-vinylphenol may be used as the curing component and hard aggregates may be added to improve wear resistance.¹⁰

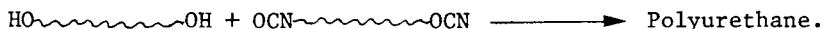
Epoxy resin cements have been used to seal leaking metal gas pipes¹¹ and for many civil engineering applications, such as steel wire-reinforced epoxy resin cements¹² and the reconstruction of the Abu-Simbul Temple in Egypt.¹³ Epoxy resin cements whose physical properties are similar to those of concrete¹⁴ are discussed more completely in Chapters 3, 4 and 5.

Polyurethanes were developed as alternatives to nylon by

Otto Bayer in 1937.¹⁵ These polymers, which are produced by the reaction of a polyhydroxy compound and an organic diisocyanate are available as fibers, elastomers, moldings, foams, adhesives, and cements.

One of the pioneer polyurethane products was a wood flour-filled composite prepared from a hydroxyl terminated polyester and tolylene diisocyanate (TDI) or its dimer (MDI).¹⁶ These composites were also used in solid fuel propellants¹⁷ and sealants.¹⁸

However, until recently, the principal application of polyurethanes has been as *in situ*-polymerized rigid and flexible foams used for insulation and cushioning, respectively.^{19,20} Unlike the phenolic, urea and furan mortars, in which the high polymer formation is the result of the chain extension and crosslinking of a prepolymer, the final polyurethane product is the result of a reaction between hydroxyl and isocyanate groups as shown by the following equation:



Almost 15 thousand tons of polyurethanes were used as binders for sand in foundries in 1978 but the principal non-foam *in situ*-polymerization of urethanes was used for reactive injection molding (RIM) and reinforced RIM (RRIM) of relatively large automotive parts.²¹ Comparable techniques without the use of a molding press were used for the production of mortars and for maxillofacial prosthodontics, i.e., the replacement of facial features.

Oxazolidene/aliphatic diisocyanates can be used as one pot resin systems which cure in the presence of water at ordinary temperatures and pressure.²² Flexible bubble-free coatings of polyurethanes have been produced by the use of vacuum centrifugal coating techniques.²³ New amine catalysts may be used to reduce curing time of polymerization for the production of cast urethanes.²⁴ Additional information on polyurethanes sealants is supplied Chapter 4.

Unlike the polyurethanes and other previously discussed mortars, polyester cements are produced by a free radical chain copolymerization of a liquid unsaturated polyester and styrene. While most polyester composites are reinforced by fiber glass, polyester mortars are usually filled with silica, clay or alumina trihydrate (ATH).

Polyester cements were originally developed as grouting materials for brickwork in chlorine dioxide bleaching systems under the trade name of *Vitroplast*.²⁵ These products which are also used for the production of cultured marble and large pipes are discussed in detail in Chapters 6 and 7.

Since any polymeric system that will harden at ordinary temperatures *in situ* may be used as a resinous mortar, many other polymers have been employed for this simple end use. Hot melt

systems which are also used as sealants are not included in this report.^{26,27,28}

It is important to point out that since these composites usually cure at room temperature and do not release solvents that they conserve energy and do not contribute to pollution. Possibly more important is the utilization of silane and titanate coupling agents which, when properly selected and used in optimum quantities, result in a reduction in the viscosity of the mortar which permits the use of larger quantities of filler and assure the attainment of adequate interfacial bonds between the filler and resin.

These resin cement systems require only moderate capital investment, yet can yield dramatic results. For example, the many thousands of cracks in the Los Angeles City Hall produced by the 1971 earthquake were repaired by the use of 20 thousand gallons of an aluminum and ceramic filled epoxy resin mortar.²⁹ Likewise, wood whose cracks have been sealed by polyurethane mortars is suitable for continuous lathe cutting for veneer manufacture.

It is important to point out that in spite of the ease of use, these resinous mortars, like many other chemical compositions, are toxic and adequate precautions must be taken to protect the health of the applicators. For example, the skin should be protected from the setting agents used in phenolic, urea, furan, and epoxy cements and adequate ventilation should be provided during the application of polyurethane and polyester cements to prevent the inhalation of volatile isocyanates and styrene respectively. However, once they are cured, these resinous cements are not hazardous. Actually, they are important energy conserving materials of construction.

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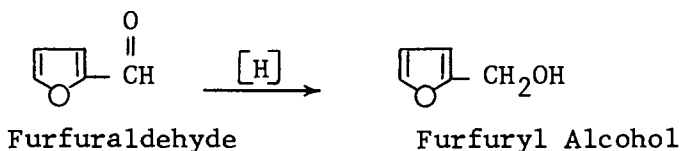
Furan Resinous Cements

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Furan resins when cured with acidic catalysts give black, somewhat brittle, highly cross-linked composites which are unsuited for use as caulks and sealants but are used extensively in grouts, mortars, and cements. When extended with reinforcing fillers such as silica, carbon flour, or fiberglass, these resins are resistant to highly corrosive acidic or basic aqueous media and to powerful organic solvents such as ketones, aromatics, and chlorinated solvents. They are especially useful where resistance to mixed media such as aqueous acids and organic solvents is needed as in chemical plant process and waste streams. Furan resins are attacked, however, by strong oxidizing media such as nitric acid, peroxides, halogens, or hypochlorites. Furan resins tend to form a tenacious char on combustion, hence these resins give low flame spread and low smoke generation values in small-scale tests such as the NBS Smoke Chamber and in large-scale tests such as the UL E-84 Tunnel and Enclosed Room Burn.

The starting material for furan resins is furfuryl alcohol which is prepared by the hydrogenation of furfuraldehyde.

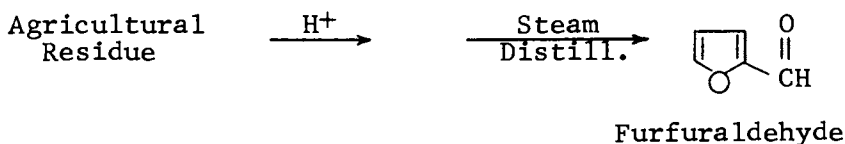


Furfuraldehyde is prepared from agricultural residues such as corncobs, rice hulls, oat hulls or sugarcane bagasse by digestion with acid followed by steam distillation. Agricultural residues are rich in C₅

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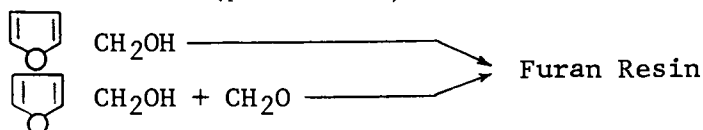
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sugars, hence are preferred raw materials.



Furan Resin Chemistry

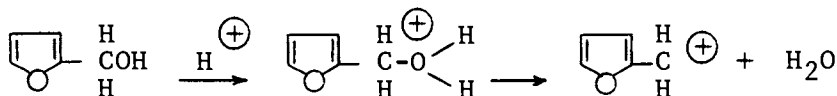
Furan resins are prepared by the homopolymerization of furfuryl alcohol or by the copolymerization of furfuryl alcohol with formaldehyde under mildly acidic conditions (pH 2.0-2.5).



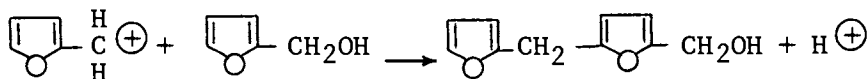
Note: Under strongly acidic conditions, furfuryl alcohol can polymerize with explosive violence.

Resins prepared in this fashion contain low levels of hydroxyl ($\sim 6\%$), hence are relatively nonreactive requiring a cross-linker such as furfuryl alcohol or furfuraldehyde to effect cure especially under room temperature conditions.

The commonly accepted mechanism for the polymerization of furfuryl alcohol is initial protonation of the furfuryl alcohol followed by splitting off a molecule of water to give a carbonium ion.



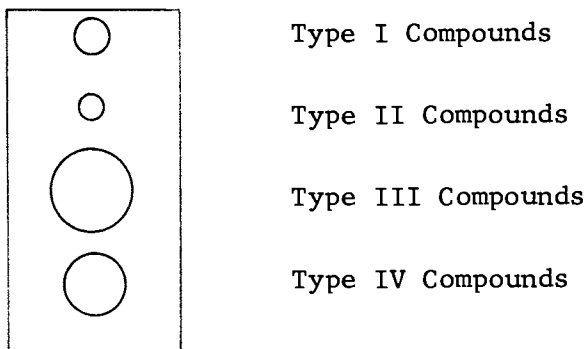
The carbonium ion then attacks the 5 position on a second furfuryl alcohol molecule to give a higher homolog of furfuryl alcohol and regeneration of the proton.



This process is repeated to give increasingly higher homologs until the reaction is terminated by neutralization of the acid catalyst when the desired viscosity is reached.

That this reaction scheme is too simplistic to

explain the polymerization of furfuryl alcohol is readily seen if one prepares a TLC (Thin Layer Chromatographic) plate of a conventional furan resin.

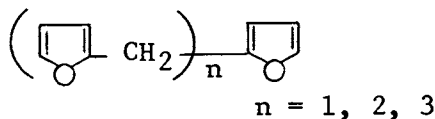


By using a Kontes Model K-4 95000 Densitometer, the quantity of the various types of compounds can be determined as follows:

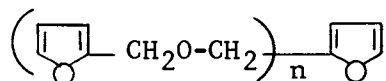
Type I	~ 10%
Type II	~ 5%
Type III	~ 45%
Type IV	~ 40%

By using larger samples, sufficient quantities of the various types of compounds can be separated by Column Chromatography and each type of compound can be further separated by Gel Permeation Chromatography or Size Exclusion Chromatography so that individual compounds can be identified by NMR (Nuclear Magnetic Resonance), IR (Infrared), and other analytical techniques. In this manner the compounds were identified as follows:

Type I Homologs of Difurylmethane

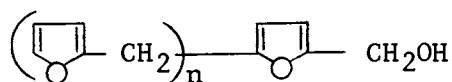


Type II Homologs of Difurfuryl Ether



$$n = 1, 2, 3$$

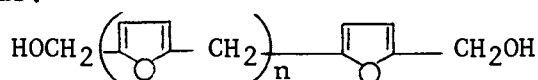
Type III Homologs of Furfuryl Alcohol



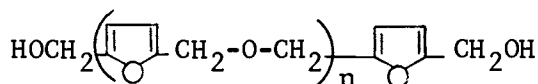
$$n = 0, 1, 2, 3$$

Type IV Polyfunctional Resin

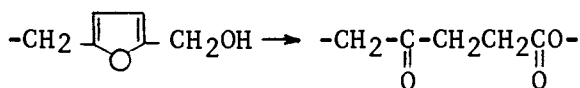
This material did not migrate from the origin because of high polarity. Based on NMR, IR, and other data, it is believed to consist primarily of polymer terminated on both ends by hydroxyl groups such as:



or

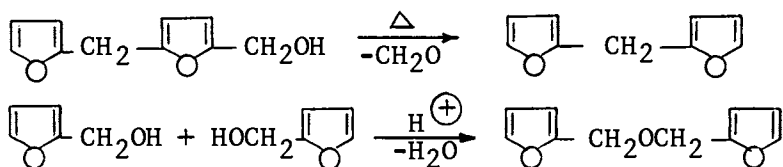


The polymer contains some carbonyl groups suggesting opening the furan ring to make derivatives of levulinic acid:

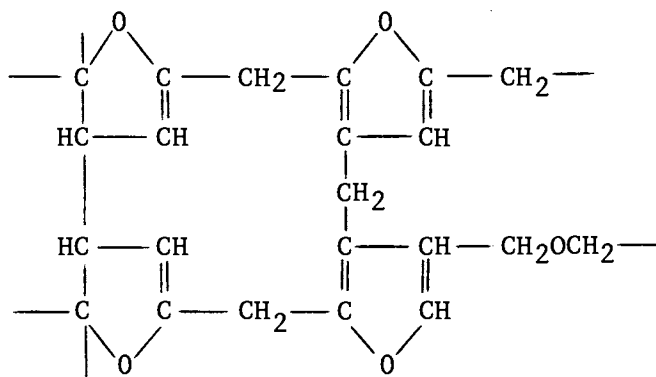


These results confirm the work of Wewerka, Loughran, and Walters (1) who separated and identified compounds of Types I, II, and III from acid-polymerized furan

resins. They speculated that compounds of Types I and II result from the following mechanisms:



These mechanisms explain the reactions which appear to occur during the cooks to make the prepolymer resins but do not explain the subsequent cross-linking during cure to give the highly-intractable, solvent-resistant resins which result during final cure. It has been postulated by Schmitt (2) that ring-ring interaction occurs through double bond polymerization as well as methylene bridging between the 2 and 3 positions on the furan rings to give polymers of the following structure:



Conventional furan resins, whether homopolymers of furfuryl alcohol or copolymers of furfuryl alcohol with formaldehyde, give basically the same type of TLC analysis.

Recently a proprietary procedure has been developed for making a highly-reactive, self-polymerizable, furan resin, FaRez B-260, which contains about 16% hydroxyl groups. This resin, which is prepared by polymerizing bis(hydroxymethyl)furan, gives a significantly different TLC result in that no Type I or Type II homologs are detected; and only 10 to 15% of the Type III polyfurfuryl alcohol homologs are formed. The majority of the resin (85-90%) consists of highly reactive, polyfunctional, Type IV homologs. Because of its high hydroxyl content, this resin shows promise

as a polyol for urethane foam, especially for urethane-modified isocyanurate foam. It is also expected that FaRez B-260 will find application in mortars, grouts, and adhesives.

Cementitious Applications of Furan Resins

A. Binder for Foundry Sand. The major industrial use of furan resins is as a binder for foundry sand. Low levels of resin binder (0.8 to 2%) are used to bond the sand as cores and molds for molten metal. By use of continuous mixers and appropriate levels of strong, acidic catalysts, set and strip times as low as 45 seconds at ambient temperature are attainable (see Figures 1 and 2). The furan resins work ideally in this application since they have sufficient thermal stability to retain the shape of the mold until the metal sets, then subsequently carbonize to allow shake-out of the sand after the metal hardens.

An interesting new development in the foundry binder area is the "Insta-Draw Process" (3) based on technology licensed from S.A.P.I.C. (4) where almost instantaneous cure is effected by gassing a core with sulfur dioxide. A peroxide, blended with the furan resin and sand in a continuous mixer, oxidizes the sulfur dioxide to a strong acid which catalyzes the polymerization of the furan resin. An adaptation of this concept to give rapid molding of cores is possible with equipment such as an automatic core blower shown in Figure 3. A precatalyzed resin mix (shelf life about 36 hours) is rammed into a split cavity mold, the mold is indexed with a gassing unit, the mold is gassed with sulfur dioxide for 1 to 2 seconds and then purged with air for 5-10 seconds. The lower half of the mold drops to the ramming position so the parts can be removed. The upper half of the mold then indexes, and the cycle is repeated. In this manner, two cores can be produced in the two-cavity mold on a cycle as low as 12 seconds.

B. Corrosion-Resistant Binder for Fiberglass Composites. A second application of furan resins is as a premium, corrosion-resistant binder for fiberglass for fabrication of FRP structures for the chemical process industry. Structures can be easily fabricated using "hand lay-up" techniques used to fabricate polyester composites (see Figure 4). In this fashion, pipes, ducts, tanks, scrubbers, etc., are produced for use with process media which quickly



Figure 1. Continuous foundry mixer

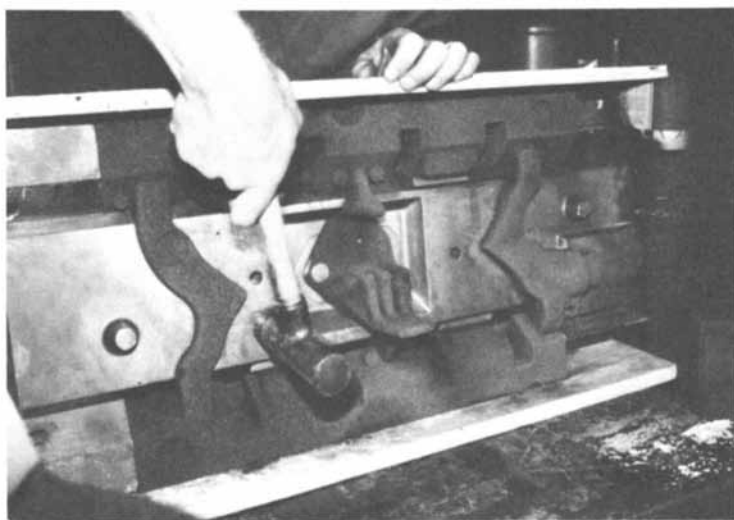


Figure 2. Stripping a foundry core

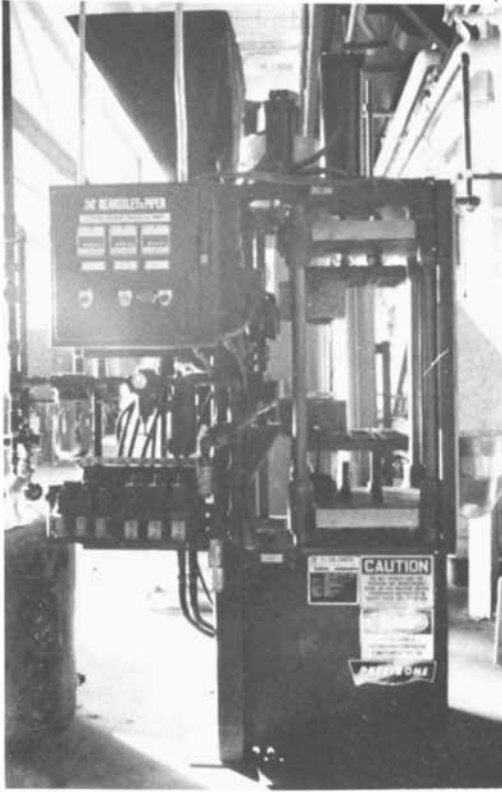


Figure 3. Automatic core blower

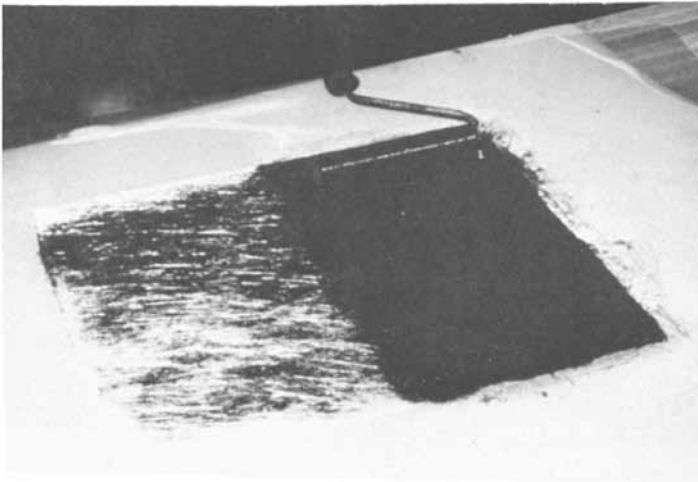


Figure 4. HLU laminate fabrication

destroy conventional metal and polyester FRP structures. Furans are especially useful for handling mixed media consisting of aromatic or chlorinated solvents and strong acids such as HCl. A typical scrubber is shown in Figure 5. The lower units are 12 feet in diameter and 60 feet high. The upper stacks are 7 feet in diameter and 50 feet high.

C. High Carbon Yielding Binder and Impregnant.

A third application for furan resins is as a high carbon yielding binder or impregnant for carbon composites such as electrodes. Furfuryl alcohol alone or solutions of lower cost resinous materials, such as pitch or phenolic novolaks in furfuryl alcohol, containing zinc chloride are stable at ambient conditions for months but rapidly cure at temperatures above 100°C. When properly post-cured and carbonized at high temperatures in a nonoxidizing atmosphere such as nitrogen, carbon yields from 45-55% can be achieved. With multiple impregnation and carbonization, porosity of carbon composites can be reduced to essentially zero.

D. Mortars, Cements, and Grouts.

Although the above three applications of furan resins would appear to fit the definition in Webster's Dictionary for cement as being "a substance to make objects adhere to each other," one usually thinks of "cement" as being a material for holding bricks and masonry together. Such usage was one of the original applications for furan resins and continues to be a major use for these resins. The first chemical-setting, furan resin-based, corrosion-proof cement was introduced in 1941 by Atlas Minerals & Chemicals, Inc. under the trade name ALKOR. A number of companies currently market furan mortars and grouts besides Atlas Minerals & Chemicals, namely, M. A. Knight Company, Electrochemical, Stebbins, Pennwalt, and Ameron.

Furan resins have been used extensively for formulating mortars, grouts, and "setting beds" for brick linings for structures exposed to highly corrosive media, especially concentrated acids, and for setting tile for floors exposed to harsh, alkaline, cleaning solutions or highly corrosive chemical media. Mortars and grouts for these applications are usually formulated as a two-package system which is mixed just prior to use. Silica fillers are satisfactory for many applications; however, carbon flour is used where resistance to hydrogen fluoride, fluoride salts, or hot, concentrated, alkaline cleaning solutions is

needed. An acid-curing catalyst is predispersed on the selected filler by the manufacturer prior to packaging and storage. Just prior to use, the filler is stirred into the liquid to give a mix of the desired consistency for the particular application. For mortar applications, the usual mix ratio is about two parts of filler to one part of resin to give a "butter" consistency. For grouting applications, the mix ratio is more nearly one to one such as 6 parts of filler to 5 parts of resin. Typical properties for silica and carbon filled mortars are given in Table I.

Table I

<u>Physical Property</u> (5)	<u>ASTM Test</u>	<u>Silica</u>	<u>Carbon</u>
Density (lbs/ft ³)	D 792	108	100
Tensile Strength (psi, 75°F, 7 days)	C 307	1000	1200
Compressive Strength (psi, 75°F, 7 days)	C 579	7000	9200
Modulus of Rupture (psi @ 75°F)	C 580	1700	3800
Bond Strength, psi	C 321	150	200
Water Absorption	C 413	0.2	0.2
Linear Shrinkage (%, 30 days @ RT)	C 531	0.24	0.24
Coefficient of Expansion (in/in/°F X10 ⁻⁵)	C 531	3.4	2.1

Corrosion-resistant floors and linings can be installed using either "tiletsetter's" or "brick-layer's" methods. By definition, a "tile" is anything up to 1-3/16" thick, and a "brick" is anything thicker than 1-3/16". Each of these procedures will be described in detail.

1. Tiletsetter's Method. Furan-bonded floors are usually applied by the "Tiletsetter's Method" using 6" x 6" x 1/2" or 3/4" quarry tile with smooth, non-skid, or abrasive surface or 8" x 3-7/8" x 1-3/16" or 1-3/8" "pavers" depending on the use for which the floor is intended. For illustrative purposes only,

Atlas Minerals & Chemicals' recommended procedure (6) for installation of floors using their FURNANE system will be described. This installation procedure consists of the following steps:

a. A concrete floor base is normally used. The concrete surface must be clean, dry, have a smooth surface, be free of ridges and depressions, and have a pitch of about 1/4 inch per foot to all drains and gutters.

b. Paraffin wax is applied to the top surface of the tile to facilitate clean-up after the installation is complete and the resin allowed to thoroughly cure. Paraffin wax may be applied either by the manufacturer or at the work site by the contractor. Care must be exercised to insure that no wax gets on the bottom or side surfaces of the tile.

c. RED FURNANE is spread uniformly over the concrete surface to form a "setting" bed (see Figure 6) with a minimum thickness of 1/8". RED FURNANE is a modified epoxy resin which adheres tenaciously to the concrete and tile surfaces. The mix is made by stirring 5 ounces of hardener into 3 pounds of the liquid resin followed by 9 pounds of RED FURNANE powder which is an inert silica compounded with a red pigment. The cement will remain workable for about 60 minutes at 75°F and will attain its initial set within 7 hours at 75°F.

d. The waxed tiles are set in the freshly applied, unset RED FURNANE bedding compound with the wax surface up. A 1/4" vertical joint is maintained between the individual tiles (see Figure 7).

e. After the RED FURNANE bedding compound has set, 6 parts by weight of BLACK FURNANE powder is stirred into 5 parts by weight of BLACK FURNANE liquid resin. The powder is a carbon flour to which a strong, inorganic, acid-setting agent has been applied. The liquid resin is a furan, corrosion-resistant resin. The mixed grout is fairly low in viscosity and is poured on the surface of the tile. The grout is worked into the vertical joints between the tiles with a KR Groutmaster (8) or a steel trowel (see Figure 8). When using a steel trowel, it is recommended that a final pass be made with a rubber squeegee to insure full flush joints with minimum grouting residue remaining on the surface of the tile.

f. After allowing the grouted tile to set undisturbed for at least 24 hours at 80°F, the furan mortar should be cured sufficiently to allow steam-

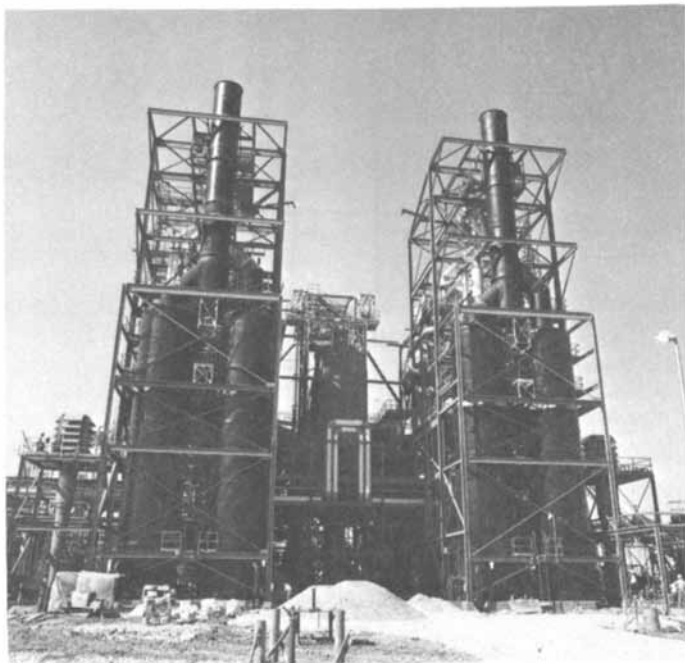


Figure 5. Bayport scrubber



Figure 6. Spreading setting bed

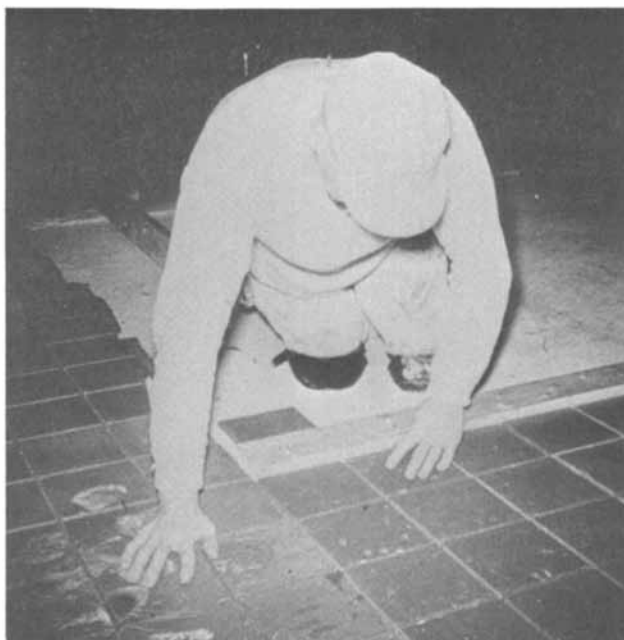


Figure 7. Setting tile in setting bed



Figure 8. Grouting tile

cleaning using about 60 pounds per square inch at the nozzle (see Figure 9). Steam-cleaning should remove wax, resin, and dirt from the tile to give an attractive floor (see Figure 10) with outstanding chemical resistance to highly alkaline cleaning agents as well as most industrial chemical contaminants. Floors of this type are used in kitchens and dining halls of prisons, hospitals, and airports; are used in food processing plants and slaughterhouses; and are widely used in chemical process plants.

2. Bricklayer's Method. Acid-resistant brick linings are used where immersion in highly corrosive chemicals is involved or where severe thermal shock conditions exist. Furan resins have been used for years for such applications. As with the furan grouts previously discussed, a number of companies manufacture and market furan mortar systems for acid-resistant brick linings. Most, if not all, of these companies also install the complete lining system.

Depending on end-use conditions, three types of brick are used for installation of acid-resistant brick linings, namely:

a. Red Shale Brick. Red shale brick has the highest level of chemical resistance. Being fired to a higher temperature, these brick are less resilient, hence are more subject to damage by physical impact or thermal shock. Standard brick size is 8" long by 3-3/4" wide.

b. Fire Clay Brick. Fire clay brick is somewhat less chemically resistant, but having been fired to a lower temperature, these brick are more resilient, hence less subject to damage by physical impact or thermal shock. Standard brick size is 9" long by 4-1/2" wide.

c. Carbon Brick. Carbon brick is used where resistance to hydrofluoric acid; fluoride salts; or hot, strong alkalis is needed. These brick are also used where extreme thermal shock conditions are encountered. Carbon brick is more porous than the other acid-resistant bricks, hence requires a greater concern over the chemical resistance of the membrane between the brick and the structure.

Brick linings, like other masonry structures, have low flexural and tensile strength but high compressive strength. Brick linings, especially on vertical walls, must, therefore, be designed so that the bricks and mortar are always under a compressive load-



Figure 9. Steam-cleaning tile



Figure 10. Completed floor

ing even under extreme conditions of temperature cycling. This is relatively easy to do for circular tanks, but requires special proprietary techniques for square or rectangular tanks. Even when the best known techniques are used, minute cracks can occur allowing seepage of the media through the brick lining. Hence, an effective, chemically resistant membrane must be used between the brick lining, which is essentially self-supporting, and the outside supporting structure which is usually made of concrete or steel. In most instances, a principal function of the brick lining is to protect the membrane and supporting structure from the high temperature of the media.

For illustrative purposes only, instructions for installing an acid-resistant lining with PERMANITE resin from Maurice A. Knight Company will be presented (9). Other companies mentioned previously have comparable products. The steps involved are as follows:

a. Because furan resin cements are cured with acidic catalysts, PERMANITE cement cannot be applied directly to concrete until free alkali on the surface is neutralized. The surface of Portland cement can be effectively neutralized with 10% muriatic acid (HCl) or 20% sulfuric acid. Special treating solutions such as Knight Concrete Prep can give improved results. After the concrete has been allowed to dry, preferred practice is to apply a primer such as PERMANITE 1642 Primer to enhance bonding of the PERMANITE mortar which may be troweled directly over the primer after it has been allowed to dry. The mortar also may be applied over concrete surfaces which have been coated with hot asphalt, quick-drying asphalt emulsions, or rubber-base paint.

b. PERMANITE cement cannot be applied directly to mild steel because the acidic catalyst will attack the steel. The steel must be lined with a suitable membrane or acid-resistant coating. When no lining is used, two coats of PERMANITE 1642 Primer may suffice.

c. When installing the bricks, it is recommended that the joints be made as thin as possible, preferably 1/8".

d. The furan PERMANITE Cement Mortar is prepared by mixing two parts of PERMANITE powder with one part of PERMANITE solution to give a paste consistency. A word of caution is in order in that the furan mortar has a relatively short pot life, and only enough mortar should be mixed at a time which can be easily used up before gelation and exotherm

occurs. In thick "piles," furan mortar will set exothermically giving off copious amounts of noxious fumes.

e. The bottom and two sides of each brick are "buttered" with the mortar (Figure 11), and the brick is carefully pushed into place so as to insure that there are no void spaces between the membrane or adjoining bricks. To form the walls, bricks are laid in a circumferential pattern around the perimeter of the tank one course at a time to allow time for the mortar to set before the next course is set. The courses of brick are laid in a "broken bond" pattern in this manner until the wall is complete.

f. Atlas Minerals & Chemicals uses a "Modified Dual Construction" procedure for tanks (10) whereby the bricks are only buttered on the bottom and one end so that a mortar-free space of 1/4" is retained between the brick and the membrane. When a complete course of brick is laid, the space between the brick and membrane is filled with a specially formulated plasticized sulfur cement.

g. The floor may be laid in a similar fashion either before or after the walls are lined depending on individual circumstances involved. In Figure 12, the floor is being installed before the walls are lined.

h. The completed lining (Figure 13) is allowed to cure thoroughly before being put into service. Cure time depends on ambient temperature and can vary from 24 hours to several days.

Summary

Furan resins have excellent resistance to most acidic or basic aqueous media as well as to strong, polar solvents such as ketones, aromatics, and chlorinated compounds. Mortars and grouts can be readily formulated with these resins for use with chemically resistant brick to install floors or linings, using either Tilesetter's or Bricklayer's procedures, which are resistant to strong nonoxidizing acids, hot alkaline cleaning solutions, and most organic solvents. Such linings also exhibit excellent resistance to elevated temperatures and to extreme thermal shock.

Acknowledgment

I wish to thank Mr. A. A. (Gus) Boova of Atlas Minerals & Chemicals, Inc., and Mr. David Cooper of Maurice A. Knight Company for providing information



Figure 11. "Buttering" brick



Figure 12. Installation of acid-resistant floor

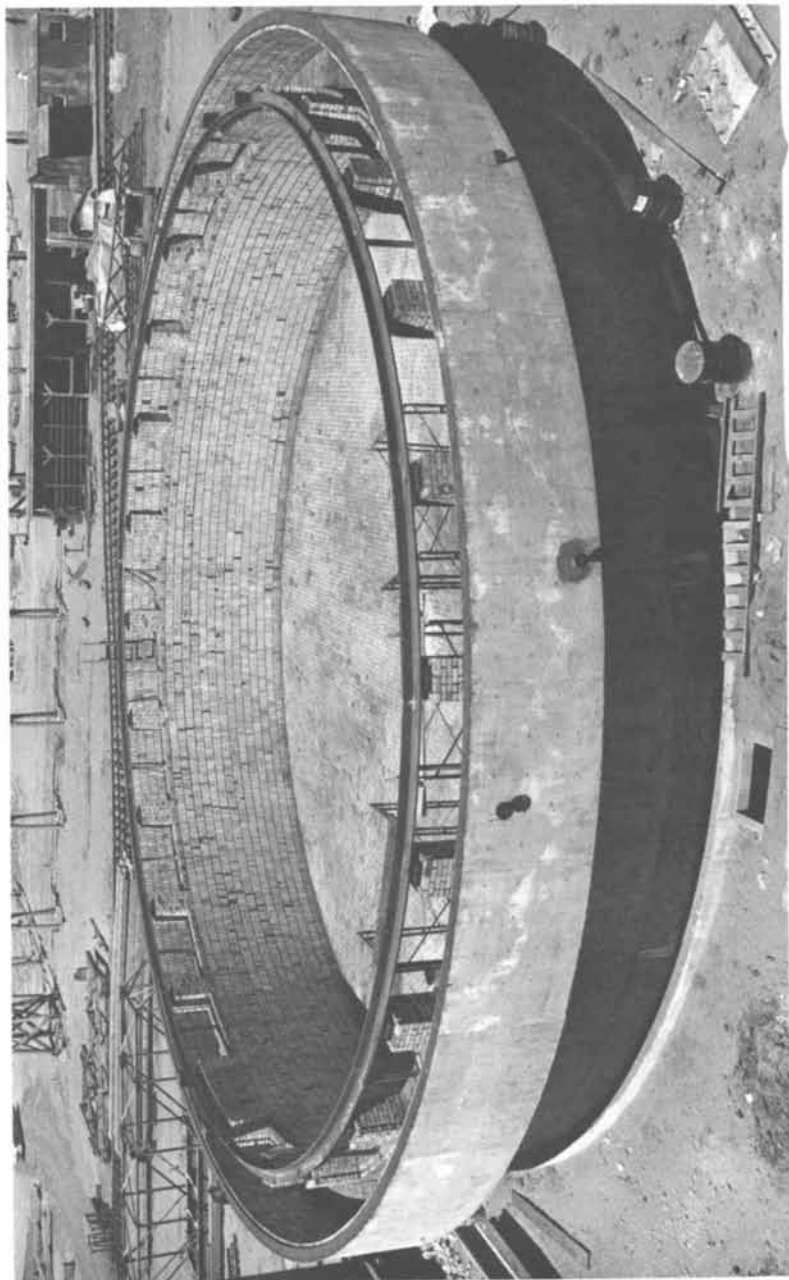


Figure 13. Completed brick lining

and pictures used in this paper.

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Epoxy Resin Cements

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Probably few materials have captured the interest of the construction industries as have epoxy resins. Although these so called miracle materials were introduced in the early 1930's, they were not used in large-scale trials until the mid 1950's. In 1977, in the U.S., 260 million pounds of unmodified epoxy resins were produced (1), thus, these materials account for about seven per cent of all the thermosets produced and less than 0.8% of all the plastics produced in the U.S. In 1978, 283 million pounds of epoxy resins were consumed. It is estimated that about fifty percent of the epoxy resins produced end-up as coatings (2). As early as 1950 the high cost of the basic materials was considered a serious handicap to the successful acceptance of epoxy resins in areas besides the coatings industry. Despite their cost, however, several properties make these resin outperform other thermosets and as a result these materials are used extensively in composites or laminates and to a lesser extent in plastic concretes, mortars, and grouts and as encapsulating and trowelling compounds.

Presently, epoxy resins sell for 81¢/lb. Compared to unsaturated polyesters at 38¢/lb., phenolics at 40¢/lb. and urea molding compounds at 56¢/lb., epoxy resins are still more expensive and perhaps will continue to be so. A brief breakdown of the reported uses for these resin in 1978 is given.

Table 1. Use of Epoxy Resins.^a

Uses	Consumption in Million lbs.	% Total
Adhesives and bonding	18.4	6.5
Flooring, paving, aggregates	17.0	6.0
Protective coatings	128.0	45.3
Laminates and windings	47.0	16.6
Tooling, coating, molding	23.4	8.3
Export	25.0	8.8
Other	24.0	8.5
	TOTAL	282.8
		100

a) Source Modern Plastics (ref. 2).

The literature on epoxy resins is vast and it is expanding

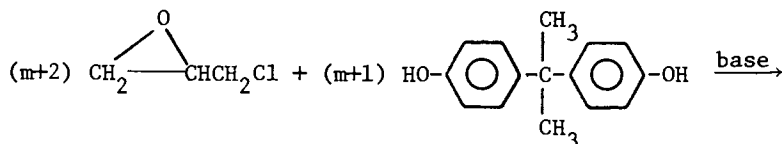
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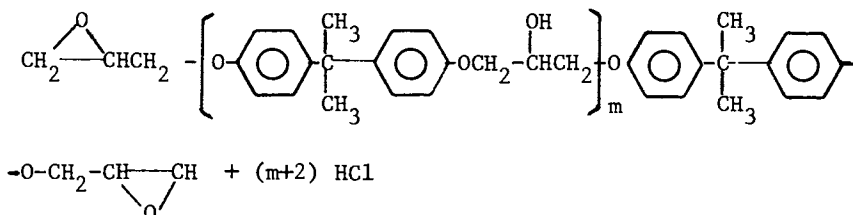
very rapidly. Several excellent books on the subject have been published (3-9) as well as many excellent reviews. In keeping with the symposium theme, an attempt is made to present primarily the status of epoxy resins in applications where these materials are used as binders or cementing agents in plastic concretes, mortars, grouts, caulking and trowelling compounds. It may be of interest to note that of the literature considered pertinent to the present subject, after 1976, 48% was in Japanese journals or patents, 23% in English (U.S.), 20% in Russian, 9% in German and 6% all other. Since a large number of foreign journals are not available in most university libraries the literature cited is of necessity selective.

Basic Chemistry of Epoxy Resins

Epoxy resins are a class of polymers that can be crosslinked to yield materials with a wide range of physical and chemical properties. Usually, linear, low-molecular weight products, known as pre-polymers or first-stage polymers are polyethers with reactive epoxide endgroups. The most commonly used prepolymer is prepared by the condensation or step-growth polymerization of epichlorohydrin and bisphenol A as shown by the following equation:



Equation 1



By careful control of reactant ratios and reaction conditions, both the molecular weights and the degree of branching can be controlled. In general, epoxy pre-polymers have molecular weights below 7000-8000 and are considered to be linear. It is readily apparent, that a wide variety of epoxy prepolymers can be produced by changing the structures of the reactive epoxide, the reactive nucleophile or both. Resins that have enjoyed commercial success are usually of four types: glycidyl ethers of bisphenol A or bisphenol F, epoxidized novalacs, and glycidyl ethers of glycerol. More recently, brominated derivatives of bisphenol A have gained acceptance due to their improved fire-resistance. The following table lists trademarks of some commercially avail-

able diglycidyl ethers of Bisphenol A (DGEBA) (ideally $m = 0$ in Equation 1), which can be considered the workhorse of the prepolymers for most controls and pre-trials as well as for many large-scale applications. Molecular weights, viscosity and epoxide equivalents (gram of sample/one equivalent of epoxide functionality) are important parameters in deciding which prepolymers to use. Over 250 commercially available epoxide prepolymers are listed by Tanaka, Okada and Tomizuka (10).

Table II. Some Commercially Available Diglycidyl Ethers of Bisphenol A with Similar Physical Properties

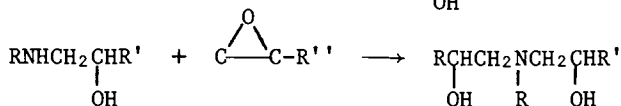
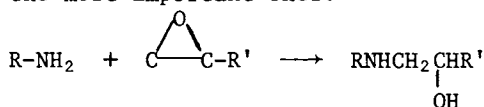
Manufacturer	Epoxy Equivalent	Viscosity Kp at 25°C	Av. Mol. Weight
Bakelite ERL-2774	185-200	10,500	350-400
Ciba Araldite 6005	190	8,000	--
Dow DER 331	187-193	11,000	350-400
Jones-Dabney			
Epi-Rez 510	180-200	9,000	350-400
Reichold 37-139	182-195	6 000	--
Shell Epon 828	175-210	10,000	350-400
Union Carbide			
ERL-2200	175-185	7,000	--

While epoxy prepolymers are utilized as additives and plasticizers, the large majority of epoxy resins are crosslinked to yield thermosets with a wide variety of properties. Over fifteen classes of organic compounds have been reported as being suitable curing or hardening agents for epoxy resins. Among the most commonly used crosslinking agents are aliphatic and aromatic polyamines and polyamides, acid anhydrides, polymercaptans and polyphenols. To produce thermosetting resins, the epoxy prepolymers are mixed with the hardening agent usually in concentrations ranging from 15-100 parts per hundred and allowed to gel either at room temperature or at elevated temperatures depending on the rate of the reaction. Once the prepolymer and the hardener are mixed the mixture must be used before it sets or hardens. The useful pot life of an epoxy resin can be made as short as thirty minutes or as long as several months by using accelerators or latent curing systems such as metal alkoxides or BF_3 -amine complexes. Table III indicates the wide-range of curing conditions that can be obtained by using different hardners.

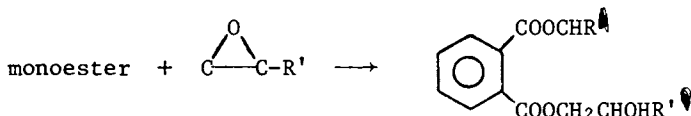
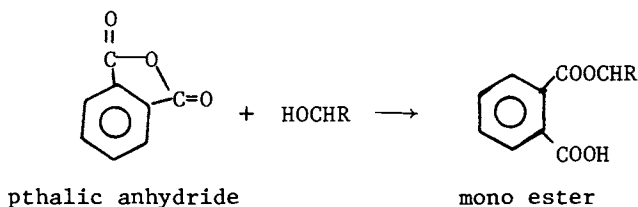
Table III. Typical Hardners Used With Epoxy Prepolymers.

Hardners	Conc PHR	Pot Life	Curing Conditions
m-phenylene diamine	14	8 hrs at 25°C	2 hr at 85°C or 1 hr at 175°C
Diethylenetriamine	12	30 min.	2 hr at 100°C
Polyamide	100	180 min	3 hr at 120°C
Phthalic anhydride	75	180 min	3 hr at 120°C
Aluminum isopropoxide	2	1 month	16 hr at 150°C and 6 hr at 200°C

The crosslinking mechanisms for the amines and anhydrides have been studied and the following reactions are believed to be the most important ones:



R can be alkyl or aromatic. R' and R'' represent different chain lengths.



T. Mika (11) has reviewed the chemistry of curing agents and how these influence the properties of the cured resins. Compounds such as phenol and boron trifluoride are effective accelerators for epoxide-amine reactions, while solvents usually slow down this same reaction due the lower concentration of reactants and/or to specific hydrogen bond interactions.

General Properties of Cured Epoxy Resins

The electrical, chemical and physical properties of epoxy resins vary widely and depend on the curing agents and other additives that may be employed. Since polyamines and anhydrides have been used widely as curing agents with DGEBA, typical properties

are listed for DGEBA - ethylene triamine ($\text{NH}_2\text{-CH}_2\text{-CH}_2\text{-}\overset{\text{H}}{\text{N}}\text{-CH}_2\text{-CH}_2\text{-NH}_2$) and DGEBA - phthalic anhydride systems.

Table IV. Electrical, Chemical and Physical Properties of Ethylenetriamine-Cured DGEBA (A) and DGEBA - Phthalic Anhydride (B) (DGEBA Epoxide Equivalent of 200)

	<u>A</u>	<u>B</u>
Power factor (20°C, 10 ⁵ cps)	.080	.002

Dielectric constant (20°, 10 ⁵ cps)	4.1	3.6
Volume resistivity (25°C, ohm-cm)	2 x 10 ⁶	78.0 x 10 ¹³
Tensile strength (psi)	8000-9000	5,000-7,000
Compressive strength (psi)	16,000	21,000-22,000
Flexural strength	17,000-18,000	15,000-16,000
Izod impact strength	0.3-0.4	0.5
Hardness, Rockwell	99-108	100
Heat distortion temperature	70°C	100
H ₂ O absorption 24-hr immersion	0.11%	.053%
Resistance to 10% NaOH	excellent	poor
ethyl alcohol	excellent	excellent
kerosene	excellent	excellent
30% sulfuric acid	excellent	excellent
85% sulfuric acid	good	good
10% HCl	good	good
20% nitric	good	good

Electrical and chemical properties of epoxy resins can be changed dramatically depending on the curing agents especially if organic acids or salts are used. In general, the following properties make epoxy resins good competitors: a wide-range of curing recipes are available, good adhesion, strength and toughness and an excellent resistance to solvents and to most acids and bases. These properties combine to make these resins excellent as coatings. The wide use of epoxy resins in laminates is a good example of the adhesive properties as well as their excellent chemical resistance. These properties also suggested that suitable materials for the maintenance, repair, protection and strengthening of concrete structures could be obtained. Epoxy mortars and concretes were used in the mid-50's in California to repair pot holes and cracks in concrete highways and bridges. Epoxy mortars have been used as patching materials for quick repairs. Since these materials can be trowelled to an eighth of an inch or less and cured rapidly by heating artificially they have displaced cheaper materials that do not perform as well.

Use of Epoxy Resins as Binders or Cements

The recent literature abounds with ideas as to how epoxy resins can be used as binding agents in new and novel applications. A brief review intended to show the development of the epoxy resins in the field of mortars and concretes is presented.

In the mid-1950's the New Jersey Turnpike authority experimented with an epoxy system consisting of a liquid prepolymer extended with coal tar and cured with diethylenetriamine to real bridge surfaces, and later spent one-million dollars in sealing bridges with a similar epoxy coating that offered excellent resistance to de-icing chemicals, greases and oils, in addition, to being an effective moisture barrier.

Epoxy resin mortars have been used in repairing or conserving massive concrete structures. It has been found that the adhesive properties of epoxy resins modified with polysulfides is

exceptional. One of the earliest use of epoxy mortars was in 1962, when three tons were used to fill more than 4000 linear feet of cracks that developed in the concrete supports of the wharf at the Los Angeles Port (12). A typical epoxy mortar recipe consists of 1 part polysulfide, 1.8 parts epoxy resin and 11.3 parts of natural sand (U.S. Std Sieves No. 4 - No. 50) (13). Usually the amine hardner is incorporated with the polysulfide component. The two components are thoroughly mixed and then the sand is added and mixed until all the particles are coated. The approximate pot life of the mortar varies from 30-45 minutes. Epoxy concrete can be made utilizing the same recipe given using larger aggregates. Trowelling components, mastics and glazing compounds have also been employed to protect steel, iron, stucco, concrete block, and wood (9,14).

Another area in which epoxy resins act as a continuous matrix is that of composites and molding compounds. Epoxy-based composites are reinforced with glass, carbon, or boron fibers to yield products whose properties differ significantly from those of the starting materials. The use of composites in translucent panels, automobile bodies, and boat hulls are well-known. Resin to fiber ratios vary from 0.2-0.6 depending on the application. Molding compounds are prepared by mixing epoxy resins with a variety of powdered fillers such as silica flour, titanium dioxide, and acetylene black.

In the different applications mentioned, epoxy resins serve as the matrix that forms strong interactions with the fillers or with the materials they are to protect. Formulations that are useful in binding inorganic fillers or polar materials are the most common. Of special interest, recently, are the epoxy-resin formulations cured with polyamides that have been shown to adhere to non-polar fillers such as rubber (13). Polyamides derived from unsaturated fatty acids and aryl or alkyl polyamines (such as Versamid, General Mills) when used to cure epoxy resins show remarkable adhesion to polyethylene. A rubber-bonding formulation composed of equal parts of a polyamide (amine value 210-230) and an epoxy resin gave shear strengths of up to 1000 psi on aluminum-rubber bonds with failure occurring mostly with the rubber material.

New Developments in Epoxy Resin Mortars, Concretes and Sealants

Since W.G. Potter (9) has presented the many ways epoxy resins have been used up to 1976 and does an outstanding job of discussing the technical and economical aspects of these materials, the reader is referred to this excellent book. The two ways in which epoxy resins are commonly employed in concrete or mortar applications involve using the resin as a binder, as Portland cement, would be used or to add the resin in low percentages to typical Portland cement mortars or concretes. In sealants, mastics, grouting or trowelling compounds, the resins are extended with aphalts, coal tar, talcs, asbestos, thermoplastic or elastomers. In all these applications, usually the excellent strength

and adhesive properties of the resins are most important. Since cost becomes an even more important factor when these resins make up more than 15 to 20% by weight of the total material, in large applications cost vs performance data may be difficult to obtain. For example, typical epoxy grouting materials have compressive and tensile strengths in the order of 14,000 and 7,000 psi, respectively. While similar Portland cement grouts for filling cracks have strengths that are much lower (compressive 5000 psi, tensile 500 psi). Thus, if hairline cracks need to be sealed, epoxy grouts may be advantageous to reinforce a structure. On the other hand, when non-supportive structures develop large cracks, it may not be economical or necessary to use epoxy resin to repair such structures.

Developments in epoxy resin technology are occurring in three broad areas: (1) formulations with improved properties, (2) curing agents for specific applications, and (3) prepolymers with new or novel structures. However, the technology of plastic cements is relatively new and most of the applications rely on formulations using the more common DGEBA-amine systems. Thus, the more important applications of epoxy resins as cements attempt to improve specific properties of an inert-filled DGEBA-amine system with different additives. Some of these formulations will be discussed to indicate the state-of-the-art of epoxy cements and areas where new developments will be forthcoming.

A recent patent (16) describes how several of the properties of plastic concretes can be improved by using the following formulation:

- 5-13 wt % poly(oxyalkenemethane) diepoxide
- 12-25 wt % polyamide hardner
- 6-14 wt % aminophenol (accelerator)
- 0.2-0.7 wt % ethylsilicate
- 0.5 4 wt % pigment
- 76-44 wt % mineral filler

The strength of polymer concretes can also be increased during the early setting stages by adding 0.12-0.32 wt % of a sec-alkyl-sulfate to typical epoxy concretes hardened with polyalkylamines (17). Undesirable mechanical properties, such as high hardness and brittleness, can be diminished in plastic concretes by the addition of internal softening agents (18). Thus, 8-10 wt % of a polysulfide rubber used in a typical epoxy resin concrete increased the crushing and tensile strengths by 16-26%. Higher concentrations of the rubber decreased these two properties. Chlorinated polyethylene has also been used to increase the mechanical strength of rapidly-cured epoxy concretes (19). Recent developments in this field seem to suggest that both epoxy or polyester resins are often times used for similar applications with no apparent difference in the performance of the materials. Ohama and co-workers (15) compared the resistance of polymer concretes to boiling water for periods of up to 12 months and found that epoxy resins were more resistant than orthophthalate based

polyesters. Short-term resistance to boiling water was similar for both resins.

Epoxy mortars with the following composition have been used in oil-wells: 1.0-2.5 wt % epoxy resin, 0.1-0.2 % curing agent, 0.001-0.002 % of sodium or potassium salts of C₁₀-C₁₇ alkyhydroxamic acids, and the balance of an inert filler (20). Mortar compositions containing water that bond well to concretes have also been described (21). Similar epoxy mortars have been employed to plug subterranean earth formations. Reports indicate an increase in oil production from 9 to 65 barrels/day while reducing water production from 720 to 520 barrels/day (22).

Sealants based on epoxy resins extended with still residues demonstrate good anticorrosive properties and can also serve as grouts for applying ceramic tile to metal or concrete (23). Compositions suitable for paving streets containing as much as 56 wt % asphalt have been prepared (24). Metal-patching compositions filled with about 10% asbestos and cured with a torch or a hot air source until an azo dye changes color to indicate completeness of cure have been reported (25). Bitumen-filled epoxy resins that can be cured in the presence of water are useful as coatings, sealants and binders in the construction industry (37). These compositions cure at room temperature and have pot lives up to twelve hours.

Typical formulations for caulking and glazing compounds use a mixture composed of 100 parts epoxy, 20 parts aluminum stearate, 70-90 parts titanium dioxide 55-75 parts calcium carbonate and cured with a mixture of 150 parts polyamine, 20 parts aluminum stearate and 225 parts calcium carbonate. Excellent steel to concrete and steel to wood seals are obtained and the formulation has a pot life of three hours. A caulking gun, knife putty or a high pressure caulking gun can be used to apply the material. A good grouting compound can be made from 100 parts epoxy, 300 parts river sand, and 70 parts flexible polyamine curing agent. This formulation is often used as a trowelling compound to provide non-skid surfaces. By substituting larger aggregates for river sand, a plastic concrete can be obtained.

Attempts have also been made to improve the physical properties of epoxy resin compositions by using curing agents with special structural features. The flexibility of cured products using poly(adipic anhydride) is improved as well as the thermal and shock resistance (26). However, the development of curing systems have centered on rapidly-hardening, storage-stable and radiation or light-induced curing compositions. Markowitz (27) reports that the reactivity of epoxy groups can be controlled over a broad range by organometallic catalysts (bis-tributyltin and aluminum acetyl acetonate) with phenolic accelerators. Diamine or polyamine-epoxy systems are rapidly cured by polymercaptans (28). The steel-to-steel bonding strength of such formulations increased by a factor of ten. Storage-stable compositions that would eliminate the in situ mixing of prepolymer and hardner also abound in

the literature. The influence of various catalysts on shelf-life and the degree of cure has been investigated for dough moulding compounds (29). Activation energies for phenylphosphonic and phenylphosphoric aromatic amine salts have been found to be around 25 K cal/mole which are similar to those of BF_3 -amine complex hardners. The pot-life of the epoxy composition increased as expected with increasing temperature for achieving the maximum reaction rate with these compounds (30). A mixture of 4,4'-diphenylmethane isocyanate and methyl cyanoacetate has been found to give curing agents for epoxy resins that have a shelf-life of 100 days at 60°C (32). Reaction rate constants for the reaction of compounds containing epoxy groups with amines containing primary, secondary or tertiary hydrogens have been reported. An approximately linear correlation between log rate constant and pK_a of the amines was encountered in both ethanol and in the absence of solvents (31). Tertiary amines that contain carboxy groups (33), a cross-linking agent prepared from an alkyl-substituted imidazole and an epoxide (34), and alkyl substituted imidazolium chloride with an ion scavenger, such as iron octylate (35), have been found to produce storage-stable compositions.

Developments in the use of epoxy resins in the areas of protective coatings, laminates and adhesives will no doubt influence the use of these materials in the field of cements, mortars and sealants. However, an attempt has been made to focus only on the technology of epoxys that pertains to the use of these materials as mortars, trowelling compounds, sealants, and cements. It appears that research on curing systems that give longer pot lives for these materials are needed and will be a major research area in the future. Economics will probably continue to inhibit a more rapid development of these materials, but additives that will allow smaller amounts of the more expensive compound to be used should be forthcoming. Recent reports that epichlorohydrin, a key component of epoxy resins, at levels as low as .09% causes lung cancer (36) may require a closer look at some of the areas of application of epoxys. These findings will require that these materials be analyzed for levels of epichlorohydrin and certainly guidelines as to the use of these compounds will be issued in the future. Whether the epoxy group is responsible for the carcinogenic nature of this monomer is unknown, but epoxy resins will undoubtedly receive their share of attention.

Epoxy resin consumption increased 12% from 1977 to 1978. This exceeded all expectations, since an annual growth rate of about 7% was expected and is predicted for 1979. The use of epoxy resins in flooring, paving and aggregates jumped 25% from 1977 to 1978. It appears that the epoxy resins will continue to be low-volume, specialty chemicals when compared to thermoplastics and the other thermosets, but they will continue to find applications in special areas.

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Epoxy Resins with Concrete

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PART A - CHEMISTRY OF EPOXY RESINS

In all the history of the coatings and plastics industries, more especially, since synthetically prepared raw materials have taken their principal position in the technology, there has not appeared a resin which has lent itself to so wide a variety of uses, to so wide a variety of applications, and which has been shown to have such a wide field of technical and economic utility, as does epoxy.

Epoxy resins are essentially condensation products of epichlorhydrin and diphenylolpropane. The latter has been known as the usual phenolic compound of "reduced phenolics." Epichlorhydrin, closely related to glycerol, is readily obtained from natural glycerol, or in the process of making the synthetic product. It is usually obtained by the latter method.

The epoxies represent a group of resins which range from low viscosity, solventless liquids, to high-melting-point solids. The name for this group of resins, "epoxy," has its origin in the Greek. "Epoxy" stems from the word "epi", meaning "on the outside of", and "oxygen". The combined words actually describe the position of the oxygen atom in the molecular structure, which is found at each end of an epoxy molecule. Epoxy resins also contain hydroxyl radicals, ether groups and phenolic groups. Each of these contributes highly desirable properties. The high polarity of the molecule and the hydroxyl radicals produce excellent adhesion. The long, chain-like structure of the polymer promotes outstanding flexibility. The epoxide groups and hy-

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droxyl radicals are the highly reactive points of the resins. The ether groups produce excellent chemical resistance. Finally, when properly reacted, the phenolic groups make the epoxy resins highly resistant to breakdown.

Epoxy resins are not usable by themselves, since they lack adequate molecular size. They must be further polymerized or chemically cross-linked to form useful compounds. There are several methods of modification which enable epoxy resins to achieve their maximum benefits. One of the earliest methods was to react an epoxy resin with an acid of a drying oil, generally called a fatty acid, to form an epoxy ester. This is comparable to an alkyd resin and the curing mechanism is by oxidation of the drying oil, since the epoxy and hydroxyl groups have been esterified with the fatty acid. These epoxy esters are sometimes called "one-component epoxy systems". They can also be blended with urea formaldehyde, melamine formaldehyde and phenol formaldehyde resins, to form baking coatings. Baking finishes may also be formulated, using high-molecular weight epoxy resins, reacted with the same formaldehyde resins.

The most widely used epoxy systems are those which are based on pure epoxy resins, hardened with a curing agent. Curing of epoxy resins containing two epoxy groups per molecule can be readily accomplished by the addition of primary polyamines, such as ethylene diamine, diethylene triamine, triethylene tetramine, tetraethylene pentamine, etc. Aliphatic polyamines produce cured resins with the greatest chemical resistance. However, these systems have inadequate durability, weather resistance and film-forming properties. They are sensitive to humidity, errors in addition rates are quite possible, and the catalysts are relatively toxic.

In addition to primary polyamines, secondary and tertiary amines are also utilized. The tertiary amines, such as methylated aliphatic aromatic amines, are most commonly utilized. They can best be described as catalysts, rather than hardeners, since they speed up a reaction and contribute to cross-linking, rather than entering into the reaction itself.

Another method of curing epoxy resins is by the use of polyamides, which are made from polyamines re-

acted with dimerized and trimerized fatty acids. These polyamides lend themselves to a wide range of combinations with epoxy resins. They contribute a greater degree of flexibility, but solvent and chemical resistance is reduced. They contribute better heat resistance and have a minimum dermatitic effect. They also minimize chalking tendencies in outdoor exposure. Even greater flexibility in epoxy resin systems is obtained by the use of polysulfide resins. Polysulfides react with epoxy resins through mercaptan groups, but very slowly. Tertiary amines are utilized to speed the reaction. All of these systems may be used with high molecular weight, solid epoxy resins which must be dissolved in solvents, as well as with liquid, low-molecular weight resins, which do not require solvents and may be utilized at 100% solids. These systems, based on liquid epoxy resins, are the ones most widely used in the construction industry.

The principal characteristics of epoxy resins, as used with concrete, in the construction industry, include:

- (a) High strength adhesion to most building materials;
- (b) Very low shrinkage during and after cure;
- (c) Outstanding dimensional stability;
- (d) Void filling qualities;
- (e) Thermosetting - resistance to softening;
- (f) Optimum chemical resistance;
- (g) Fatigue resistance;
- (h) Creep resistance;
- (i) Ability to withstand thermocycling;
- (j) Good electrical insulation.

PART B - USE OF EPOXIES IN NEW CONSTRUCTION

The basic epoxy resin most often used with concrete is a light, amber-colored liquid, about the viscosity of a heavy motor oil. Liquid epoxy resins are generally made by the same process as that used to make solid epoxy resins. The ratio of epichlorhydrin to bisphenol controls the type of resin produced. The higher the ratio of epichlorhydrin to bisphenol, the lower the viscosity of the final resin, and the lower its molecular weight.

In what ways are epoxy resin systems utilized in new construction? When it is considered that concrete and steel are very often welded, it would seem reasonable to assume that the welding would be more effective if an epoxy adhesive were used. As an example, composite beams of concrete on steel are often included in design specifications. It had been the practice to weld protruding lugs on the steel beam, which would become an integral part of the plastic concrete placed on the beam. Today, structural engineers are using specially formulated epoxy adhesives to bond concrete to steel without the use of lugs.

Floors and walls of structures are obvious areas where epoxy systems may be utilized to prevent deterioration from abrasion and chemical attack. Such systems are now to be found in original specifications. Wall surfaces may be coated with epoxy systems based on solid resins dissolved in solvents and hardened with polyamines and/or polyamides. Porous surfaces, such as concrete blocks, are first prepared with fillers to provide a smooth surface for application of coatings. These systems are described as "tile-like" coatings.

In addition to finishing wall surfaces on site with epoxy systems, the construction industry utilizes concrete blocks which are finished in plant with an epoxy facing. Architects recognize that these epoxy facings will have a tendency to chalk and yellow when used on exterior surfaces. The problem of chalking and yellowing limits the use of epoxy resin systems for decorative purposes on exteriors. The yellowing phenomenon is directly attributable to the phenolic base of the epoxy resin. The chalking develops from the combination of water, oxygen and ultraviolet light. The chalking is not a degrading chalk, but, rather, a surface phenomenon which acts as a passivating film to prevent further action on the underlying surface.

Of course, floors in a structure receive the greatest abuse. Where deterioration occurs in such areas, epoxy resin systems have been widely used for repairs. Industrial floors are now constructed with initial specifications calling for an epoxy mortar, usually, 1/4 inch in thickness, to provide a chemically and physically resistant surface. Slip-resistant aggregates may be embedded in such epoxy toppings. The same tech-

nique is utilized in providing skid-resistant overlays on highways. In such applications, 100% solid epoxy resin systems are applied at thicknesses of 10-15 mils onto which is broadcast sand, emery, pumice or quartz.

In recent years, epoxy resin systems have been utilized for special applications on the exteriors of buildings. One of these systems involves the use of an epoxy plaster, which is troweled onto the surface of an exposed wall, into which are set stone aggregates. This surfacing resembles a pre-cast concrete panel with an exposed aggregate facing. This method is utilized, not only in new construction, but in re-surfacing deteriorated areas.

Pre-cast concrete has achieved a recognized position in the construction industry. Quite often, it is necessary to provide a decorative surface to these panels. A common method is to produce an exposed aggregate finish. Many architects now specify concrete panels having a veneer of marble, granite, limestone or other decorative natural stone. These veneers are applied in sections no thicker than 3/4 inch. Epoxy adhesives are used to bond the concrete to the veneer. Of course, reinforcing anchors are used at the corners of each panel to provide additional assurance.

The advances in formulations and application techniques, as well as field experience, have developed considerable information as to the capabilities and limitations in the use of epoxy resin systems in construction. The architect and engineer must be aware of the properties of these systems and should be knowledgeable about pertinent specifications.

PART C - EPOXY RESIN ADHESIVES FOR BONDING CONCRETE

There are many reasons why epoxies make good adhesives. Among these are:

- (a) Compounds can be in liquid form and contain no volatile solid;
- (b) They adhere to most materials of construction;
- (c) There are no by-products during the curing periods;
- (d) There is limited shrinkage during and after cure;
- (e) Cured epoxies have dimensional stability;

(f) Cured epoxies have tensile strengths and compressive strengths as high, and higher than, concrete.

Table 1 compares the strength characteristics of epoxy compounds with those of structural concrete.

Table 1.-Strength Comparisons - Epoxies vs. Concrete

	<u>Flexural</u> <u>(psi)</u>	<u>Tensile</u> <u>(psi)</u>	<u>Compressive</u> <u>(psi)</u>
Structural Concrete	500-800	100-400	3000-10,000
Epoxy Compounds	1500-5000	500-5000	5000-12,000

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The factor of thermal expansion is most important when considering the use of epoxies with steel and concrete. Steel and concrete are almost perfectly matched. When concrete is bonded to other materials, stress often occurs. Epoxies can elongate under stress to accommodate differences resulting from thermal effects. The coefficient of thermal expansion of an epoxy can be equalized to that of concrete by the proper incorporation of fillers, such as sand. When the sand:epoxy ratio approaches 4:1 up to 7:1, the coefficient of thermal expansion will approach $4-6 \times 10^{-6}$ in/in/°F. Shrinkage of concrete during cure is widely recognized. Epoxies show a minimal degree of shrinkage, in the order of 0.0010 in/in.

The preparation of surfaces to receive epoxy compounds is as important as the selection of the proper system for bonding. Concrete surfaces must be freshly exposed, free of loose and unsound material and should be at proper surface temperatures at the time of epoxy application. Among the methods for preparation of concrete surfaces are sandblasting, mechanical scarification and acid etching. The same procedures may be followed for preparation of steel surfaces. Temperature conditions for epoxy application should be in the range of 60°F. to 90°F. Temperature conditions will also affect pot life of mixed compounds, as well as curing time.

There are several guide specifications for epoxy resin based materials for use with concrete, as adhe-

sives, crack sealers, patching materials and non-skid treatments. One of the very first specifications to be developed is one sponsored by the United States Army Corps of Engineers, and it includes descriptions of an epoxy resin binder, and an epoxy resin grout. The specifications are as follows:

(a) Federal Specification MMM-B-350 "Binder, Adhesive, Epoxy Resin, Flexible."

(b) Federal Specification MMM-G-650 "Grout, Adhesive, Epoxy Resin, Flexible, Filled."

Both specifications spell out the formulations required, in complete detail. They utilize an epoxy resin with an epoxide equivalent in the range of 175-210. Epoxide equivalent is the weight of resin containing 1 molecular weight of epoxy groups. The lower epoxide equivalent, the lower the viscosity of epoxy resin. The polysulfide resin called for in these specifications is a dichloroethylformal polysulfide in the 1000 molecular weight range. The accelerators are tertiary amines consisting of a blend of 2, 4, 6-tridimethylaminomethyl phenol (DMP-30), and dimethylaminoethyl phenol (DMP-10).

Typical formulations for Binder and Grout are given in Figure 1.

<u>Materials (Part A)</u>	<u>Binder</u> (lbs/100 gals.)	<u>Grout</u> (lbs/100 gals)
Liquid epoxy resin	630	450
Aerated silica	--	40
	<u>630 gals.</u>	<u>50 gals.</u>
 <u>Materials (Part B)</u>		
Polysulfide polymer	314	225
Silica flour	--	485
DMP-10	20	14.5
DMP-30	23	16.5
	<u>33 gals.</u>	<u>50 gals.</u>

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Figure 1. Binder and grout formulation

Figures 2 and 3 present typical formulations for a polyamide:epoxy bonding agent and a modified coal-tar

epoxy resin system for skid-resistant overlays.

<u>Materials (Part A)</u>	<u>Pounds/100 Gallons</u>
Liquid epoxy resin	267
Chlorinated biphenyl or Dipropylene glycol dibenzoate	106
Titanium dioxide	36
Magnesium silicate	179
Calcium carbonate	13
Asbestos fibre	4
Xylol	44
	<hr/> 649 =50 gals.

Materials (Part B)

Polyamide resin (Amine value=350-400)	267
DMP-30	12
Magnesium silicate	126
Asbestos fibre	5
Toluol	80
	<hr/> 490 =50 gals.

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Figure 2. Polyamide-epoxy bonding agent

<u>Materials (Part A)</u>	<u>Pounds/100 Gallons</u>
Liquid epoxy resin	381
Pine oil	76
Phenol (95% Technical Grade)	19
	<hr/> 476 =50 gals.

Materials (Part B)

Refined coal-tar oil	420
Diethylene Triamine	64
	<hr/> 484 =50 gals.

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Figure 3. Epoxy-coal-tar road sealer

There are other types of epoxy adhesives and bonding agents utilized for special purposes. Among these are rapid-setting adhesives for use by State Highway Commissions for bonding traffic markers. Special formulations are also utilized for producing polymer concrete.

PART D - REPAIRING OF CRACKED CONCRETE

Structures built of cast-in-place Portland cement concrete had an undesirable tendency to crack, even though proper provision is made for expansion and contraction by engineered joint design. On horizontal slabs, cracking may develop because of a number of reasons, even though expansion joints have been provided at minimal centers. On vertical placements, severe stresses and strains will inevitably result in cracking.

Heretofore, the most commonly used method of repairing cracks in concrete was by injection of a cement slurry grout. It is obvious that such a grout, based on a cementitious composition, would shrink and not fill the void completely. It is also highly likely that such a grout, after curing, would crack again at the same stress points.

Liquid epoxy resin systems of low viscosity are now being utilized successfully in filling and repairing structural cracks in concrete members. The usual epoxy resin compounds utilized for this purpose are the epoxy:polysulfide type, such as the Corps of Engineers Binder, MMM-B-350, or AASHO Specification M-200, Type A, or ASTM Specification for "Epoxy Resin Base Bonding Systems for Concrete," Type I, Grade 1 and, generally, Class A, for low temperature use. The viscosity of such compounds generally runs to about 2,000 centipoises. These compounds may be mixed in small volumes and introduced into a structural crack, bonding the two separate members with an adhesive force which is higher than the tensile strength of the concrete itself. Since the material is 100% in solids and develops no shrinkage in curing, the entire crack is filled. Should further stress be placed on the concrete member, cracking will inevitably occur at another location and never at the epoxy-repaired point.

The epoxy polysulfide formulations are comparatively fast setting, with a short pot life. In filling a crack on a horizontal slab, the crack is widened by mechanical means to form a slight trough. The mixed compound may then be introduced into the crack by means of a caulking gun, or dispensed through a narrow spout. If the crack is deep, the epoxy binder may be introduced in stages, to permit deep penetration. Succeeding pours

may be made in a time sequence to allow previously applied material to begin polymerization.

The repair of cracks in vertical structures may be performed with the same systems. In such situations, an injection procedure is followed. The crack itself is first sealed on the outside face with a fast-setting epoxy compound formulated to have thixotropic properties, so as to prevent sagging. This compound is spread over the face of the crack to prevent the liquid epoxy binder from oozing out. At designated intervals along the crack, nipples made of metallic tubing are inserted into the crack and held in place by the epoxy mastic. Once the mastic has cured, the epoxy resin binder may then be pumped in. The binder may be mixed in small batches and injected under pressure. In large operations, the binder may be fed through two separate lines, from separate containers, mixed at a single nozzle, and pumped under pressure. The binder may be injected with pressures of 1000 pounds per square inch, or more, as necessary. The binder is pumped into one nozzle until it begins to appear at the nozzle above it. This procedure is carried out to the full length of the crack. After a curing period, the nozzles are cut flush to the crack. This method of repairing vertical cracks may also be used for horizontal cracks. The method insures a complete filling of the crack in rapid time. Cores taken from such repairs invariably indicate that cracks may be completely sealed by this method, and tests run on such cores always result in fracture of the concrete at a point other than the repaired crack line.

PART E - PATCHING AND GROUTING OF CONCRETE

The various epoxy resins described as unfilled binders, are utilized to make epoxy mortars and epoxy concrete for patching and grouting Portland cement concrete, and for producing epoxy mortars for complete overlays. The aggregates to be used should be dry and salt-free. The maximum size of the aggregate to be used will depend upon the dimensions of the fill. A good rule to follow is that the maximum size aggregate should not exceed one-fourth of the smallest dimensions of the fill. For an epoxy concrete to be used where a large volume of fill is required, gravel or crushed

stone, 1/2 to 3/4 inch maximum size, uniformly graded, may be used. For most work, the aggregate for an epoxy mortar should conform to the following grading limits:

<u>Sieve Size</u>	<u>Percent Retained, Cum.</u>
No. 4 (4.76 mm)	0-5
No. 8 (2.38 mm)	0-20
No. 16 (1.19 mm)	15-50
No. 30 (595 microns)	40-75
No. 50 (297 microns)	70-90
No. 100 (149 microns)	90-100

The sand to meet this specification is a rounded grain type. It has physical properties as follows:

Moh Hardness	7 Minimum
Specific Gravity	2.60 Minimum
Percent Silica	99.5 Minimum

Higher strengths and better workability may be obtained if all material passing the No. 50 sieve is screened out. The more fines, the less aggregate may be blended in with the epoxy resin. Where it is desired to fill shallow spalled areas, a relatively fine sand of uniform grading may be used, particularly, where feather-edging is to be done.

The two components of the epoxy binder are thoroughly mixed together, after which the selective aggregate is added, with continued mixing. The ratio of aggregate to epoxy binder may range from 3:1 to 10:1, by weight, depending upon the mesh size and gradation of the aggregate.

Priming is often necessary before placement of the mortar. A small amount of the mixed epoxy binder may be used to be applied to the surface on which the epoxy mortar is to be bonded. The volume of a batch of epoxy mortar should not exceed that which can be placed within one hour. Working time of the mixture may be extended by spreading the mixture out to prevent the development of an excessive exotherm.

Areas to be patched should be chipped out so that the edges will be essentially perpendicular to the top surface of the finished patch. It is advisable to

avoid feather-edging. Working of the epoxy mortar while putting it in place, should be kept to a minimum to prevent the binder portion from being worked up to the surface of the mortar. Where deep patches have to be placed, it is advisable to install the epoxy mortar in layers. This will prevent the development of high exotherm in excessive thicknesses which could result in stress cracking of the mortar. After the epoxy mortar has set, an epoxy sealer may be applied to the surface. This sealer is particularly recommended if a high aggregate to binder ratio is used and the resultant mortar is porous. The sealer may be the same binder formulation.

PART F - EPOXIES AS FLOORING MATERIALS

Epoxy Mortars.

A sand-filled epoxy compound will have lower stresses because the coefficient of thermal expansion will have been reduced and will have been brought closer to the coefficient of thermal expansion of Portland cement concrete. Some of the requirements for an epoxy system, based on a polysulfide-modified epoxy binder, are typically as follows:

- (a) Pot life is usually between 30 minutes and 2 hours;
- (b) The binder, without sand, is generally tack-free in 8 to 12 hours. When filled, this period is shortened considerably.
- (c) Ultimate tensile strength is between 3,000 and 3,500 psi, and there is an elongation of at least 25% immediately after cure;
- (d) The modulus of elasticity in tension does not exceed 100 psi.;
- (e) The modulus of toughness generally runs at least 400 in. lb. per cubic inch;
- (f) Percent weight gain in water absorption seldom exceeds 1.0%;
- (g) Tensile strength of heat-aged specimens is between 200 and 1,500 psi. Elongation is less than 10%. This is an indication of what changes may occur in an epoxy compound upon aging.
- (h) Impact strength may run as high as 90 foot pounds;

(i) Bond strength will show at least 90% of the failure in the concrete;

(j) Elongation at low temperatures (32°F) is much lower than at normal temperatures, usually, about 5% in the initial stages;

(k) Tensile strength may go as high as 1,800 psi and compressive strengths may reach 15,000 psi in the filled systems.

Reinforcement may be utilized with epoxy compounds to lower shrinkage, lower expansion coefficient, and add strength. The following procedure is a technique for using fiberglass cloth with an epoxy mortar. It is recommended for concrete floors where there is evidence of excessive movement, as indicated by cracking. Cracking of the base slab will generally result in cracking of the topping at the same location. Concrete slabs, not on grade, subjected to heavy loads, may flex. Retopping such members requires that the epoxy mortar be integrally reinforced to further increase resistance to cracking. Provision must, of course, be made to maintain expansion and contraction joints in the base slab. These joints should be filled with an elastomeric sealant. The epoxy mortar should not bridge these joints, which should be carried through the epoxy mortar and should also be sealed with an elastomeric sealant.

A primer adhesive is first applied to a properly prepared concrete surface. A thin coat of epoxy mortar is then applied with a trowel. While this thin coat is still wet, a fiberglass membrane is rolled into the mortar. The edges of the membrane should be overlapped 2 inches. The mortar will squeeze up through the voids in the fiberglass mesh, resulting in adhesive base to which the final epoxy mortar will adhere. While this first application of mortar is still tacky, the second layer of epoxy mortar is applied over the glass cloth. This second layer may then be screeded and leveled.

Expanded metal lathe and/or wire mesh may be utilized in the same way as fiberglass membrane, particularly, when applying an epoxy mortar onto a wooden floor. It is recommended that a preliminary repair of a wood floor be made first by securing 3/4 inch Douglas fir plywood to the wooden substrate by proper nailing.

This is to insure a rigidity in the wood floor, which may not be present in the original substrate. It also insures a comparatively clean wooden substrate for treatment. The plywood should be free of protective oil. The lathe or wire mesh is nailed to the wood base, allowing a 1/16th inch clearance. The epoxy mortar is applied in the first pass so as to penetrate the lathe or mesh, and make intimate contact with the wood substrate. The plywood should be treated with a primer in the same way that concrete is first primed. The epoxy mortar is compressed to fill all the voids in the reinforcing mesh. A second application of epoxy mortar is then placed over the first, covering the mesh. This system provides maximum assurance of keeping the epoxy mortar secured to the wooden substrate by chemical and physical means. It also minimizes the possibility of cracking and/or delaminating, because of the reinforcing strengths contributed by the lathe and/or mesh.

A typical formula for an epoxy mortar is given in Figure 4:

<u>Materials (Part A)</u>	<u>Pounds</u>
Liquid epoxy resin	750
Butyl glycidyl ether (reactive diluent)	<u>176</u>
	926=100 gals.
<u>Materials (Part B)</u>	
Polyamide resin (amine value=350)	617
Tertiary amine	<u>166</u>
	783=100 gals.
<u>Materials (Part C)</u>	
Flintshot silica sand	720
Emery, 30-80 mesh	240
Titanium dioxide	40
Lampblack	<u>tint</u>
	1,000

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Figure 4. Epoxy mortar topping

The epoxy mortar topping is prepared in kits,

comprised of three components, as follows:

<u>Materials</u>	<u>1 Gallon Kit</u>	<u>5 Gallon Kit</u>
Part A-epoxy resin	2.25 lbs.	11.25 lbs.
Part B-curing agent	0.75 lbs.	3.75 lbs.
Part C-aggregate	<u>14.50 lbs.</u>	<u>72.50 lbs.</u>
	17.50 lbs.	87.50 lbs.

Epoxy Terrazzo

With the development of epoxy resin systems as toppings, it was only natural that these systems would have been adapted in terrazzo applications. The advantages of epoxy-based terrazzo include rapid cure, as compared to conventional cement terrazzo, and light-weight of 1-3 lbs. per square foot, as compared to 10-20 lbs. per square foot for Portland cement terrazzo.

There are many commercial formulations for epoxy terrazzo. Many depend on a primary polyamine hardening agent as a means of obtaining the hardest cured matrix. Although this is desirable, the use of the primary polyamine may be hazardous because of its possible dermatitic effects. Other systems involve the use of polyamide hardeners, with modified aliphatic amines or tertiary amines as catalysts. The epoxy binder is normally filled with an extender pigment and colored to provide shades which are complimentary to the colored marble chips which are used. The marble chips and the designs may be taken from the standard Terrazzo Association plates. The marble chips are blended with the epoxy binder in a mechanical mixer and applied to the divided floor area. Since expansion and contraction is greater than for a sand-filled epoxy mortar, it is advisable to use the same brass, zinc, aluminum or plastic divider strips to control any possible cracking, as well as providing for a decorative design system. These strips are placed with a 1/4 inch height. The epoxy terrazzo mix is then screeded to the proper height and additional marble chips are broadcast over the surface at the rate of 2 to 4 pounds per square yard. The surface is then rolled with a conventional terrazzo roller.

Grinding may begin 16 hours after application, but should not be delayed more than 48 hours since grinding will become more difficult as cure progresses. After the first grinding, the surface is grouted with a

binder, colored with the same pigments as in the epoxy terrazzo. This final application is also polished in the same way as conventional terrazzo.

A typical formula for an epoxy terrazzo is given in Figure 5:

<u>Materials</u>	<u>Pounds</u>
Liquid epoxy resin	100
Magnesium silicate filler	50
Coloring pigments	10
#1 Marble chips	400
Triethylene tetramine (packaged separately)	<u>10</u>
	570

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Figure 5. Epoxy terrazzo

PART G - SPECIFICATIONS AND TESTS

Various specifications which are pertinent to epoxy compounds for use with concrete have already been listed. There are many others which are specific with individual governmental agencies, private agencies, architectural and engineering groups. There are also standard ASTM procedures for testing tensile, compressive and bond strengths, as well as many other properties. Some of these tests are, of course, designed for concrete. Others have been developed primarily for the plastics industry and may be adapted for testing epoxy compounds. A number of special tests have been devised to aid in the evaluation of particular epoxy compounds. Some of the tests may be described as follows:

(a) Flexural Beam Test. This test was developed by the California Highway Department. Concrete beams, 6"x6"x30", similar to those described in ASTM C-78, are prepared as specimens. After proper curing, the beams are broken in flexure, using third point loading. The two halves of one beam are cemented together with an epoxy adhesive and allowed to cure. Another broken beam is coated with adhesive on the broken end, and fresh concrete is cast against it to reconstruct a new beam. In both cases, after the adhesive and concrete have fully cured, the beams are again subjected to

flexure, using third-point loading. If the beam breaks at points other than along the bond line, it is an indication that the adhesive bond is stronger than the concrete.

(b) Double Vertical Shear Test. This test was developed, particularly, for the U.S. Army Corps of Engineers specifications MMM-B-350a and MMM-G-650a. The test involves bonding three 2 inch mortar cubes together, with the center cube extended to 1/2 the height of the adjacent cubes. The area in contact between the cubes is coated with an epoxy adhesive to a thickness of 50 mils. After curing, a three-point loading is applied, which tests compressive shear strength.

(c) Shear Bond Test. This method was developed in the Bureau of Reclamation Engineering Laboratories. A cylinder mold, 2 inches in diameter and 4 inches long, is filled 3 inches deep with mortar, and the mortar is cured. Then one end of the mortar cylinder is thoroughly cleaned and replaced in the mold. An epoxy adhesive is then applied to the cleaned, exposed end and the remaining space in the mold is filled with fresh mortar. The result is a cylinder with a bond line cutting laterally through it one inch from the end. The test is performed by shearing the end slice from the cylinder and computing the shear bond stress at the bond line by dividing the total force applied by the cross-sectional area of the cylinder.

(d) Tensile Strength of Bonded Standard Mortar Briquettes. This test is based on the ASTM procedure for testing tensile strength of plastics. The specimen is a dumbbell-shaped mortar briquette which is broken at the narrow portion, and the two pieces are bonded together with an epoxy adhesive. After complete cure, the specimen is tested for tensile strength. Normal failure is in the cementitious briquette, rather than at the bond line.

(e) Composite Cylinder Test. Concrete strengths are normally determined by the compression test on the standard 6"x12" cylinder. When it is necessary to bond new concrete to old concrete with an epoxy adhesive, the adhesive must be able to transfer all compressive, shear and tensile stresses which the original and new concrete are expected to carry.

The specimen used for this test is a standard

6"x12" concrete cylinder with a diagonal bond line of epoxy compound joining the two portions of the cylinder at a plane of 30 degrees from the longitudinal axis. The composite cylinder is tested in compression. If the composite cylinder has a strength of 90% of that of a standard concrete cylinder, the epoxy compound is adequate for use with concrete.

The composite cylinder is made by placing a specially made dummy section into the cylinder mold so that it bisects the cylinder equally at an angle of 30 degrees from the longitudinal axis. Concrete is cast into the mold and cured. The cylinder is then removed from the mold, the sloping face is acid etched, and the cylinder is then slipped back into the mold, which is lined with waxed paper. The cylinder is tilted so that the slope is horizontal, the epoxy adhesive is applied, followed by a layer of fresh concrete, to fill up the entire mold. After complete cure, the cylinder is tested under compression. This test represents a condition closer to the actual use of the epoxy compound in structures, especially when compared with tests relying on the tensile strength of the concrete as a failure criterion. If the epoxy compound is inadequate, failure takes place on the bond line. This test may also be used for testing the adhesive strength of an epoxy compound in bonding concrete to steel, bonding hardened concrete to hardened concrete, for damp or dry surfaces, and at various temperature conditions.

(f) Creep Test. This test evaluates the creep of the epoxy resin bonding system at low temperatures and at high temperatures. The test involves measuring the penetration of a small steel ball into a flat specimen of the cured resin, and is measured as a function of time. The test utilizes a cylinder of metal or other rigid material on top of which is placed a flat specimen of cured epoxy compound, cast on a suitable substrate. Ball bearings, having diameters of 0.25 inches, may be used as the steel spheres. A metal plate is used to bear a weight, and a dial indicator is used to measure the deformation. The entire unit, including specimen, is conditioned for at least 8 hours at the specified temperature, before starting the test, without the weights. An initial reading is taken, after which weights are placed on top of the plate. A stop

watch measures the time allowed for the test, at which the dial indicator is read again. The penetration of the spheres as a function of time is a measure of the creep of the epoxy resin system.

PART H - HANDLING METHODS AND SAFETY PRECAUTIONS

Contact with epoxy resin systems may lead to allergic epidermal eczema. The irritating agent appears to be primarily the curing compound used to harden the epoxy resin, rather than the epoxy resin itself. The curing compound may involve primary polyamines, secondary polyamines, tertiary polyamines and polyamides, all of which contain amino groups. The action of the irritant on the skin usually proceeds as follows: After an interval free of symptoms, which may last a week, or longer, red patches (erythema) about the size of a coin first appear. These patches itch intensely. This first stage may heal by scaling of the patches after a short period, and the itching then disappears.

If the first stage of dermatosis does not heal, the second stage consists of the formation of a true cutaneous eruption with red pimples and the formation of blisters. The intense itching causes the patient to scratch, opening blisters, swelling the skin and causing the inflamed tissue to exude fluid.

With some users, the dermatosis never goes beyond the first stage; i.e., the skin adapts and is desensitized. It is best not to remove a mechanic from his job of using epoxy compounds at the first symptoms, so that it may be seen whether he is adapting, or desensitizing. If continuation of work leads to the second stage, it is best to remove such a mechanic from contact with epoxy resin systems completely.

There are a series of preventive measures in handling epoxy resin systems:

(a) Inspectors and foremen should be informed of all these measures which should be passed on to workmen using these systems.

(b) There should be good ventilation of the work areas.

(c) Gloves should be worn at all times. The use of solvents should be reduced to an absolute minimum since solvents can carry diluted resinous components

LATEX AND EPOXY ADHESIVES
COMPARATIVE

A. Latex

	Appearance	Solids Content	Primary Use	Application Methods	Applications	Specifications	Cleaning Surface Preparation	Finishing Procedures	Chemical Resistance of Mortar ASTM-C-267-S1T
A. Acrylic	Milky White	45.0%	Bonding fresh concrete to old concrete. Concrete admixture. Thin layer toppings.	Brush, broom spray, roller as adhesive. Trowel as topping.	Underlayments Stucco Grouting-mortar Terrazzo Home Kits Crack Fillers	MIL-B-19235	A. Remove oil, grease. Wet surface.	Steel trowel, wood float. No excessive trowelling.	Acids—Fair Alkalis—Very Good Salts—Very Good Solvents—Fair-Good
B. Polyvinyl-Acetate Non-Re-Emulsifiable	Milky White	55.0%	Bonding fresh concrete to old concrete. Concrete admixture. Thin layer toppings.	Brush, broom spray, roller as adhesive. Trowel as topping.	Underlayments Stucco Grouting-mortar Terrazzo Home Kits Crack Fillers	MIL-B-19235	B. Remove oil, grease. Wet surface.	Steel trowel, wood float. No excessive trowelling.	Acids—Fair Alkalis—Very Good Salts—Very Good Solvents—Fair-Good
C. Butadiene-Styrene	Milky White	48.0%	Bonding fresh concrete to old concrete. Concrete admixture. Thin layer toppings.	Brush, broom spray, roller as adhesive. Trowel as topping.	Underlayments Stucco Grouting-mortar Terrazzo Home Kits Crack Fillers	MIL-B-19235	C. Remove oil, grease. Wet surface.	Steel trowel, wood float. No excessive trowelling.	Acids—Fair Alkalis—Very Good Salts—Very Good Solvents—Fair-Good
D. Polyvinyl-Acetate Re-Emulsifiable	Milky White or Pink	50.0%	Bonding of plaster. Not used as an admixture.	Brush, spray roller.		MIL-B-19235	MIX — Cement: Sand = 1:3 Latex Solids on Cement = 10-20% Water: Cement Ratio = 0.45		

B. Epoxies

	Mix Ratio	Appearance	Solids Content	Working Life	Covering Rate	Uses and Applications	Specifications	Chemical Resistance
I. Epoxy — Polyamide a. Unfilled Binder b. Filled	1:1 by volume Part A and Part B	Light straw to amber	100%	a. 30-60 min. b. 30-60 min.	a. 100 sq. ft. per gal. as mortar 25 sq. ft. 1/8" thick, containing sand. b. 25-38 sq. ft. per gal.	a. Bonding hardened concrete and other materials to hardened concrete. Setting dowels. Type Ib, IIb. b. Filling cracks in concrete to crack both sides of crack into an integral member. Type Ia and IIa.	I. a. ASTM-B-350A b. ASTM-G-650A New Jersey Turnpike Section 4.9.3 Standard Specifications 1965 AASHTO Specification Designation M-200-631	Excellent to acids, alkalis, solvents, salts with
II. Epoxy — Polyamide a. Unfilled Binder b. Filled	1:1 by volume Part A and Part B	Light straw to amber	95-100%	a. 1-3 hours b. 1-3 hours	a. 100 sq. ft. per gal. as mortar 25 sq. ft. 1/8" thick, containing sand. b. 100-150 sq. ft. per gal.	c. Bonding plastic concrete to hardened concrete. Type Ib and IIb. d. Preparation of epoxy mortars by adding sand. Types Ia, IIa, III.	II. Virginia Dept. of Highways AASHTO Specification Designation M-200-631 III. AASHTO Specification Designation M-200-631	maximum. properties. Also maximum resistance
III. Epoxy — Coal Tar a. Unfilled	1:1 by volume Part A and Part B	Part A — Light straw Part B — Black Combined — Black	100%	30-60 min.	a. 30-50 sq. ft. per gal.	e. Bonding skid-resistant materials to hardened concrete. Types Ib, IIb, III. f. Membrane between asphalt and concrete. Type III.	New Jersey Turnpike Section 4.8.2. Standard Specifications 1965 N. Y. State Dept. of Public Works Item #6008	to hydro- static water pressure.

AND BONDING AGENTS
CHART

Compressive Strength: 2" Cubes ASTM-C-109-56	Tensile Strength: 1" Thick Briquettes ASTM-C-190-59	Flexural Strength: Bar ASTM-C-348-617	Tensile Strength ASTM-C-190-59	Shear Strength ASTM-C-109-56	Where To Use	Where Not To Use
3200 psi-4100 psi	580 psi-615 psi	950 psi-1400 psi	D. Polyvinyl-Acetate Emulsifiable	Neat cement — 250-300 psi 1:3 Ottawa sand mortar 350-420 psi	A. Acrylic	Indoor and outdoor exposures. On concrete, steel, wood. Guniting. Thin section topping. May be used as a plaster bond within 45-60 min. Not for extreme chemical exposure. Do not use with air-entrainers. Not for conditions of high hydrostatic pressure.
3400 psi-3600 psi	350 psi-450 psi	1000 psi-1250 psi	NOTE— These compositions do not contain latex, but are applied over the latex film previously applied as an adhesive.	1:3 Perlite plaster 150-200 psi Finish plaster 30% Gauging plaster 70% Lime plaster 120-150 psi	B. Polyvinyl-Acetate Non-Re-Emulsifiable	Indoor and outdoor exposures. On concrete, steel, wood. Guniting. Thin section topping can be used with accelerators, retarders, water reducing agents. May be used as a plaster bond within 45-60 min. Not for extreme chemical exposure. Do not use with air-entrainers. Not for conditions of high hydrostatic pressure.
3300 psi-4000 psi	450 psi-580 psi	1250 psi-1650 psi		1:3 Cowboy sand mortar 200-290 psi Acoustical plaster 100-170 psi 1:3 Brown coat 100-150 psi	C. Butadiene-Styrene	Indoor and outdoor exposures. On concrete, steel, wood. Guniting. Thin section topping. May be used as a plaster bond within 45-60 min. Do not use with accelerators. Not for extreme chemical. Not for constant water immersion. Do not use with air-entrainers.
Unmodified mortar. 3000 psi Wet cure	Unmodified mortar. 410 psi Wet cure	Unmodified mortar. 750 psi	VIBRATION TESTS — No failure DETERGENTS & ACIDS — No failure, slight stain		D. Polyvinyl-Acetate Re-Emulsifiable	Indoors — ceilings primarily. Limited use as a concrete bonding agent. Do not use as an admixture. Do not use under wet or humid conditions. Do not use at temperatures below 50°F.

Compressive Strength ASTM-C-109	Tensile Strength ASTM-D-634	Tensile Elongation ASTM-D-368	Compressive Double Shear Strength MMSM-D-858A	Where To Use	Where Not To Use
a. Binder with sand 12,000-15,000 psi b. Unfilled 8,000-10,000 psi	a. 3000-3500 psi	a. 2.5-15%	a. 900-1000 psi b. 700-1000 psi	I. a. Generally on government agency projects. b. Cost is highest. c. For maximum chemical and physical properties.	a. On surfaces treated with rubber or resin curing membranes. b. On dirty surfaces. c. On weak concrete. d. On bituminous surfaces.
a. Binder with sand 10,000-13,000 psi b. Unfilled 6,000-8,000 psi	b. 3500-4000 psi	a. 6-25%	a. 400-500 psi b. 500-650 psi	II. a. Generally proprietary compounds. b. Use where longer life is required and cost is factor. c. For maximum chemical and physical properties.	a. On surfaces treated with rubber or resin curing membranes. b. On dirty surfaces. c. On weak concrete. d. On bituminous surfaces.
Binder with sand 4000-5000 psi Unfilled 3000-4000 psi	a. 400-800 psi	a. 35-40%	a. 300-400 psi	III. a. For lower cost applications of non-skid membranes. b. On bituminous concrete. c. For resistance to grease, oil, gasoline and traffic wear.	a. Do not use for bonding new wet concrete to old. b. Do not use where black color will be undesirable.

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more readily to skin areas.

(d) Protective cutaneous ointments are helpful for the back of the hands, the forearms and the face. These ointments are applied before beginning work.

(e) Work clothes should be clean at all times, and it is recommended that a change of clothes be made each day.

(f) Hands should be washed with mild soap and water before and after work, before and after going to the lavatories, before and after lengthy interruptions at work, and each time immediately after coming into contact with liquid resin mixtures. Fingernails should be cut short and clean.

It is sometimes recommended that persons subject to allergy should not be allowed to come in contact with epoxy resin systems. This would be an improbably measure to observe. It must be kept in mind that exposure to epoxy resin systems cannot cause anything but skin dermatitis. There has been absolutely no evidence of any carcinogenic effect from contact with these systems. Where slight irritations occur, desensitization should first be attempted. If eczema occurs, standard medical treatment should be provided. Antihistamine drugs may be used only to reduce itching. In severe cases, such as in the second stage of dermatosis, cortisone ointments have been used successfully to relieve the symptoms. It should be kept in mind that if protective measures are scrupulously observed, incidents of dermatoses from epoxy resin systems can be kept to a very low minimum. There is no reason for any concern in the use of these systems in the construction industry.

Epoxy resin compounds are being recognized by architects and engineers for their varied chemical and physical properties. As technical people become more aware of the potential values of these systems, in use with concrete in the construction industries, greater uses will be made of a greater variety of formulations. However, caution should be exercised by all those who specify these compounds, that the epoxies are not a cure-all for all problems, that epoxies may be detrimental in some applications, and that proprietary compounds should be thoroughly evaluated before they are used. To epoxy or not to epoxy - is a question to be thoroughly analyzed by the specifying engineer.

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Polyester Mortars

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While commercial polyesters are relatively new, they were synthesized by Berzelius in 1849 by the condensation of glycerol and tartaric acid.¹ The first commercial polyesters called Glyptals were produced in the early part of the 20th Century by the controlled condensation of trifunctional glycerol and difunctional phthalic anhydride.^{2,3}

Vorlander described unsaturated polyesters which were produced from ethylene glycol and maleic anhydride in 1894,⁴ but commercial unsaturated polyesters were not introduced until the 1920's. The first commercial free radical-curable unsaturated polyesters were produced by Kienle and Hovey, who condensed difunctional glycols, such as ethylene glycol with phthalic anhydride and an unsaturated aliphatic acid such as oleic acid.^{5,6,7} The name alkyd, which was derived from the prefix in alcohol and the suffix in incorrectly spelled "akyd" was used to describe these important polyesters.

The degree of unsaturation in these oil-modified alkyds was controlled by the amount and type of unsaturated acid used in the formation of the polyester. These unsaturated polymers cured or "dried" through auto-oxidation by oxygen from the air which reacted with the unsaturated carbon atoms on the surface of the freshly deposited film. This crosslinking reaction, like that of the "drying" of oil-based paints, was catalyzed by heavy metal salts, such as lead or cobalt salts of organic acids. Alkyds, which are some of the most important paint resins, are produced at an annual rate in excess of 300 thousand tons.

Carothers repeated Vorlander's synthesis of ethylene glycol maleates⁸ but found that the crosslinking reaction of these solid unsaturated polyesters was too slow to be of practical use.

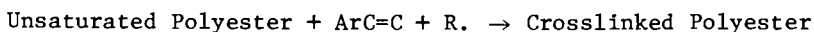
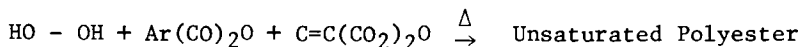
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Ellis and Rust solved this problem by dissolving the solid unsaturated polyesters in a liquid vinyl monomer, such as vinyl acetate.^{9,10} However, the less volatile and more widely available styrene monomer was used instead of vinyl acetate for most of the fiber glass-reinforced "low pressure" polyester plastics that were produced during World War II and since that time.

A typical formulation for a general purpose unsaturated polyester resin is as follows:¹¹ phthalic anhydride (2 moles), maleic anhydride (1 mole), and propylene glycol (3.15 moles). The unsaturated polyester obtained by the thermal condensation of these reactants and removal of water plus excess propylene glycol is dissolved in styrene (2.7 moles) containing 0.01% of hydroquinone inhibitor. This unsaturated polyester is then cured by the addition of a peroxy compound, such as benzoyl peroxide which produces free radicals (R.) for the crosslinking reaction.

A simulated equation for these reactions is as follows:



Several reviews on unsaturated polyester resin technology are available.^{12,13,14,15}

Network polymers were produced by *in situ* free radical-initiated polymerization of diethylene bis(allyl carbonate) during World War II and unfilled clear castings of this resin are still available under the trade name of CR-39 (16). This monomer was also copolymerized with diallyl phthalate and prepolymers of the latter called DAP to produce polyesters.^{17,18}

The heat resistance of polyesters may be improved by the addition of triallyl cyanurate as one of the monomers¹⁹ and their flame resistance may be reduced by replacing part of the phthalic anhydride by chlorendic,²⁰ tetrachlorophthalic,²¹ tetrabromophthalic anhydride²² or the Diels-Alder adduct of hexachloropentadiene and tetrahydrophthalic anhydride.²³ The fire retardant properties of polyesters have also been improved by the use of external flame retardants, such as antimony oxide and organic halogen compounds,²⁴ borates, basic magnesium carbonate and alumina trihydrate (ATH).^{25,26}

The flexibility of unsaturated polyesters may be improved by replacing some of the phthalic anhydride by aliphatic dibasic acids, such as adipic, azelaic, sebacic, diglycolic or dimer vegetable oil acids and by replacing propylene glycol by dipropylene glycol or higher homologs such as tripropylene glycol.

The resistance of unsaturated polyester resins to solvents and corrosives may be improved by the use of isophthalic or terephthalic acid in place of phthalic anhydride and by the use of highly branched diols, such as 2,2,4-trimethyl-1,3-pentanediol, 1,3-cyclohexanediol, hydrogenated bis phenol A or the reaction

product of the latter and propylene oxide in place of propylene glycol.

The characteristic brittleness of unsaturated polyester resins was overcome by reinforcement with silane-treated fiber glass. While over 750 thousand tons of these reinforced plastics are produced annually in the U.S., the emphasis in this chapter will be on room temperature-curable-filled unsaturated polyester mortars or concrete. As discussed in Chapters 1 and 7, these anaerobic polyester mortars are widely used as materials of construction.²⁷

As described in Chapter 1, the original silica-filled unsaturated polyester mortar, called Vitroplast is used as a grouting composition for joining bricks for filling cracks, as a monolithic floor or wall coating, and as a casting composition for articles, such as drain pipes and bathroom fixtures.

A typical two package polyester cement consists of an unsaturated polyester (41), cellulose acetate butyrate or polyvinyl acetate (1.8) and N,N-dimethylaniline (1) dissolved in styrene (18). This liquid (binder) is intimately mixed with a filler consisting of graded silica or solid glass spheres (15.5), talc (23), titanium dioxide (1.0) and benzoyl peroxide (1.0). The setting time of this mortar may be regulated by the amount of benzoyl peroxide initiator used in the formulation.

It is advantageous to add silane or titanate coupling agents to the filler in order to aid the mixing, increase the adhesion between the resin and filler and to reduce the viscosity of the mortar. Thixotropes, such as pyrogenic silica may be added to control the flow of the mortar on vertical surfaces.

It is essential that the concentration of volatile styrene monomer be kept within acceptable limits.²⁸ The concentration of volatiles may also be reduced by the use of higher boiling monomers, such as vinyltoluene or tert. butylstyrene. The latter^{29, 30} as well as graded aggregate fillers will reduce the shrinkage when the resin cures.³¹ (The normal shrinkage is about 17%.) The resistance of polyester concrete to hot water may be improved by the use of TMPD glycol polyesters, diallyl phthalate or cross-linking acrylic resins.³²

The water resistance of "cultural marble" produced from clay or calcium carbonate-filled polyester mortars has been improved by treating the filler with a silane, such as gamma-methacryloylpropyltriethoxysilane.³³ The translucency of "cultured marble" may be improved by the use of ATH as a filler.

The physical properties of a typical room temperature-cured polyester concrete is as follows: Barcol hardness (50), tensile strength (500 kg cm⁻²), elongation (0.45%), compressive strength (1400 kg cm⁻²) flexural strength (1050 kg cm⁻²) and heat deflection (41°C). The latter may be increased by 30° by the use of fumaric acid instead of maleic acid.

Plastic concrete produced from general purpose polyester and filled with limestone has limited resistance to acids and alkalis,

but is more resistant to aqueous salt solutions than hydraulic cements. The relationships between molecular structure and resistance to corrosives and tests for such resistance have been described.^{34,35} The chemical resistance of polyester concrete is related to the unsaturated polyesters used and the styrene content of the cured plastics. The corrosive resistance of these cements to acids, alkalis, salts, and oxidizing chemicals, such as chlorine dioxide, may be improved by using bis phenol A diacrylate (vinyl ester) as the prepolymer and by adding glass flakes to the mixture of silica filler and coupling agents.³⁶

Spode, which is a well known manufacturer of chinaware, is now producing its plates, cups, and saucers in molds cast from polyester mortar.³⁷ Polyester cements are also being used as roofing composition³⁸ and a mixture of polyester resin and Portland cement called Estercrete is being used to surface bridges.³⁹

Ultraviolet radiation-curable filled urethane dimethacrylate cements have been used as dental restorative compositions.⁴⁰ While relatively large objects may be cast in molds from polyester mortars, molds are not always essential. For example, a reproduction of the 20 m long John Paul Jones' first ship, the Providence, was fabricated by applying a polyester mortar to fiber glass-reinforced polyester planking.

The reaction in rejection molding process (RIM), which has been used for large polyurethane moldings, may also be used with filled polyesters (RRIM). Likewise, much hydraulic cement art may be adapted to polyester cement technology. Both of these cements have been reinforced with silica and asbestos. Actually, over 3 million tons of asbestos has been used annually, world wide, for the reinforcement of hydraulic cements to produce composite corrugated sheet and pipe.

Some of the asbestos filler in hydraulic cements has been replaced by fibrillated polypropylene. More than 500 thousand shell piles of this fibrillated polypropylene-filled Portland cement, called "Caricrete" are produced annually in England.^{41,42}

One may ask, why a hydrophobic fiber, like polypropylene, was used with Portland cement instead of a more compatible fiber, such as fibrillated polyvinyl alcohol? Likewise, one may also ask why the latter has not been used to upgrade polyester concrete? Presumably, the answer to the first question is, those with expertise in hydraulic cements are not well versed in organic polymer science and technology.

The answer to the second is that, in spite of large scale use of fiberglass-reinforced polyesters and "cultured marble", too few organic polymer scientists and technologists are interested in investigating polyester concrete. Fortunately, as discussed by Dr. Ohama in Chapter 7, some investigation are being undertaken and these should lead to dramatic improvements in construction through the use of polyester concrete.

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Length Change of Polyester Resin Concrete

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In the past twenty years, polyester resin concrete has been widely studied as a construction material in the world. Polyester resin concrete is extensively used in both precast and cast-in-place applications in the field of construction works. In these practical applications styrene monomer is often added into polyester resin concrete as a diluent in order to improve chiefly its workability. It is well-known that polyester resin concrete possesses large setting shrinkage of about ten times that of portland cement concrete. The shrinkage is one of serious disadvantages to be improved in its precast product and cast-in-place applications. Although a number of investigations of polyester resin concrete have been reported till now, the papers concerning its length change are hardly found out in them¹⁾.

In this paper, polyester resin concrete using two types of unsaturated polyester resins as binding materials is prepared with various contents of styrene, shrinkage-reducing agent, catalyst and accelerator, and its early aged length change to 24 hours after mixing (strictly speaking, after adding catalyst to unsaturated polyester resin) is studied. An experimental automatic apparatus for measuring the length change of polyester resin concrete is also reported.

Materials

Two types of commercially available orthophthalate-type unsaturated polyester resins (UP) were used as liquid resins, together with a 55% DMP (dimethyl phthalate) solution of methyl ethyl ketone peroxide (MEKPO) as a catalyst and a 8% mineral turpentine of cobalt octoate (CoOc) as an accelerator. UP-2 containing CoOc accelerator of 0.75phr (parts per hundred parts of resin). The properties of the unsaturated polyester resins are listed in Table I.

Two types of commercially available shrinkage-reducing agents (SR) were used. They were produced by dissolving polystyrene in

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Table I. Properties of Unsaturated Polyester Resins.

Type of Polyester Resin	Acid Value	Specific Gravity (20°C)	Viscosity (20°C, cP)	Styrene Content (%)
UP-1	22.2	1.135	819	36.3
UP-2	25.9	1.160	1940	29.8

styrene, and supplied making a set with the unsaturated polyester resins.

Styrene monomer (St) for industrial use was used as a diluent.

Commercially available calcium carbonate ("heavy" grade) was used as a filler, Hatsukari crushed andesite (size, 5-10 and 10-20mm) as coarse aggregate, and Abukumagawa river sand (size, 1.2-5 and 1.2mm or finer) as fine aggregate. Their water contents were controlled to be less than 0.1%. The properties of the filler and aggregates are shown in Table II.

Table II. Properties of Filler and Aggregates.

Type of Filler and Aggregate	Grading (mm)	Specific Gravity (20°C)	Water Content (%)	Organic Impurities
Calcium Carbonate, Heavy	<2.5 x 10 ⁻³	2.70	0.1	Nil
Hatsukari Crushed Andesite	10 - 20	2.58	0.1	Nil
	5 - 10	2.58	0.1	Nil
Abukumagawa River Sand	1.2 - 5	2.56	0.1	Nil
	<1.2	2.54	0.1	Nil

Testing Procedures

Polyester resin concrete was mixed and molded to the desired specimens according to JIS A 1181 (Method of Making Polyester Resin Concrete Specimens) at 20°C, 50% R.H. The formulations of its binder and the mix proportion are given in Tables III and IV respectively. Size of the specimens was $\phi 10 \times 20$ cm. Then the specimens were cured at 20°C, 50% R.H. for the desired curing time.

Embedded strain gages with 100mm of gage length, were installed in polyester resin concrete when the specimens were molded. The length change was measured by static strain meter connected with a timer at 20°C, 50% R.H. The measurements were conducted at intervals of 5 minutes for 60 minutes after adding the catalyst to

Table III. Formulations of Binder for Polyester Resin Concrete.

Type of Polyester Resin	Formulation No.	Formulation by Weight				
		UP	SR	St	CoOc	MEKPO
UP - 1	ST - 40	100	0	6.4	1.0	1.0
	STO-0.3-0.3			12	0.3	0.3
	STO-0.3-0.5					0.5
	STO-0.3-1.0					1.0
	STO-0.5-0.3					0.3
	STO-0.5-0.5			0.5		
	STO-0.5-1.0			1.0		
	STO-1.0-0.3			1.0	0.3	
	STO-1.0-0.5				0.5	
	STO-1.0-1.0				1.0	
	ST - 60	90	10	59	1.0	1.0
	ST - 80			220	1.0	1.0
	SR10 - 0.5	80	*20	12	0.5	0.5
	SR10 - 1.0				1.0	1.0
	SR20 - 0.5	50	50		0.5	0.5
SR20 - 1.0	1.0				1.0	
SR50 - 0.5	50	50	0.5	0.5		
SR50 - 1.0			1.0	1.0		
UP - 2	SR 0 - 0.5	100	0	12	/	
	SR 0 - 1.0			1.0	1.0	
	ST - 40			17	1.0	1.0
	ST - 60			76	1.0	1.0
	ST - 80	250	1.0	1.0		
	SR15 - 0.5	85	15	/		
	SR15 - 1.0			1.0	1.0	
	SR35 - 0.5	65	*35	12	0.5	0.5
	SR35 - 1.0				1.0	1.0
	SR50 - 0.5	50	50		0.5	0.5
SR50 - 1.0	1.0				1.0	

Note, *Most suitable content recommended by resin manufacturer for nonshrinkage.

Table IV. Mix Proportion of Polyester Resin Concrete.

Material		Weight Percent
Binder		11.25
Filler, Calcium Carbonate		11.25
Aggregate	Crushed Andesite	Size, 10-20 (mm)
		5-10 (mm)
	River Sand	Size, 1.2-5 (mm)
		<1.2 (mm)

the unsaturated polyester resin, and at intervals of 1 hour for 23 hours after that. An automatic apparatus for the length change measurements is built experimentally as represented in Figs. 1, 2, and 3. A pair of differential transformers is attached to both ends of the mold (75 x 75 x 300mm), in which the resin concrete sample is cast in order to detect its length change (shrinkage or expansion) during the hardening reaction. The measured value divided by the length (300mm) of the sample gives as four figures and is printed out with an accuracy of 10^{-6} . The capability of the apparatus is evaluated by using polyester resin concrete with Formulation No. UP-1:SRO-0.5, SRO-1.0 and UP-2:SRO-1.0 in Table III and the mix proportion in Table IV, and it is compared with the data measured by the embedded strain gages.

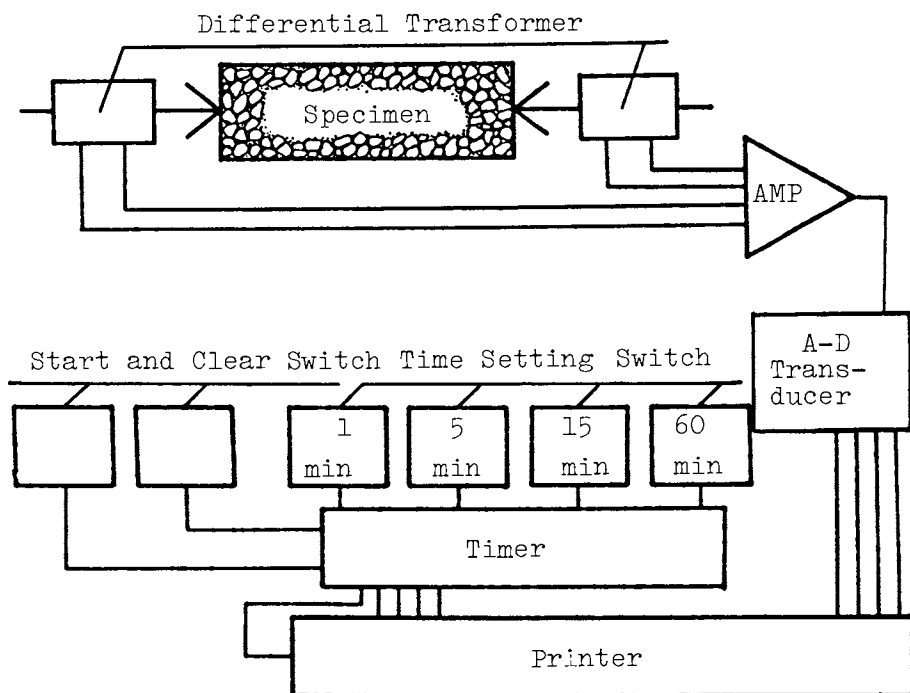


Figure 1. Block diagram for instrument system

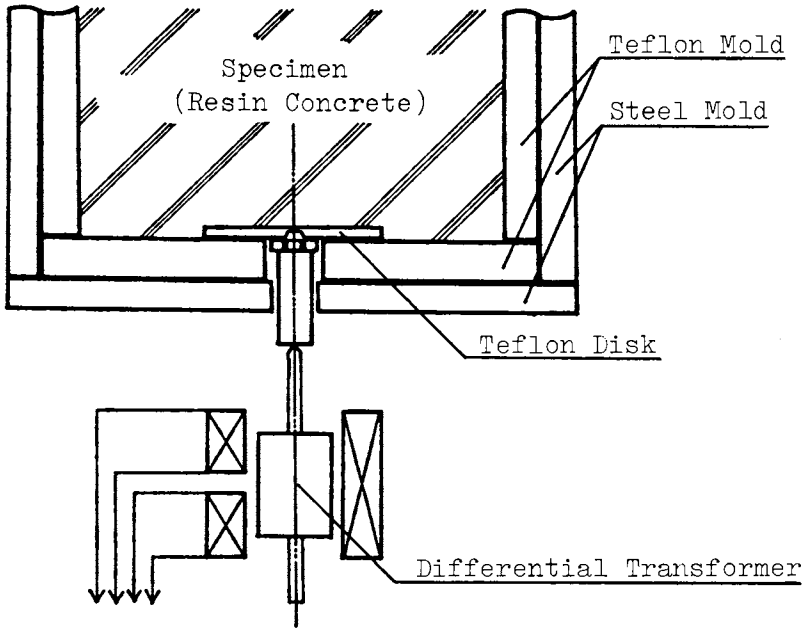


Figure 2. Details of strain detection part

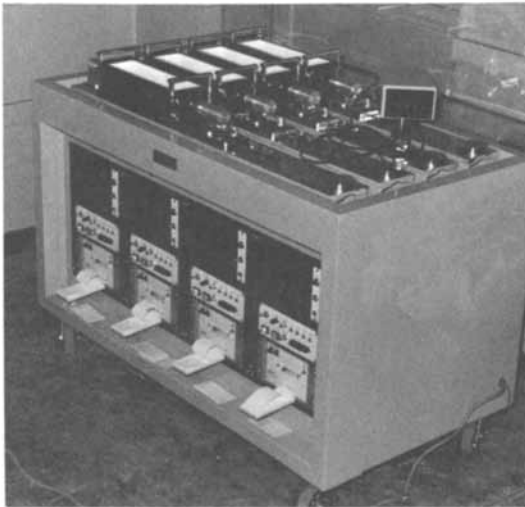


Figure 3. General view of automatic apparatus for measuring the length change, built by the authors

Test Results and Discussion

Fig. 4 shows the effects of CoOc and MEKPO contents on setting shrinkage of polyester resin concrete. The setting shrinkage increases with rising contents of CoOc and MEKPO. In particular, the shrinkage is remarkably affected by MEKPO (catalyst) content rather than CoOc (accelerator) content.

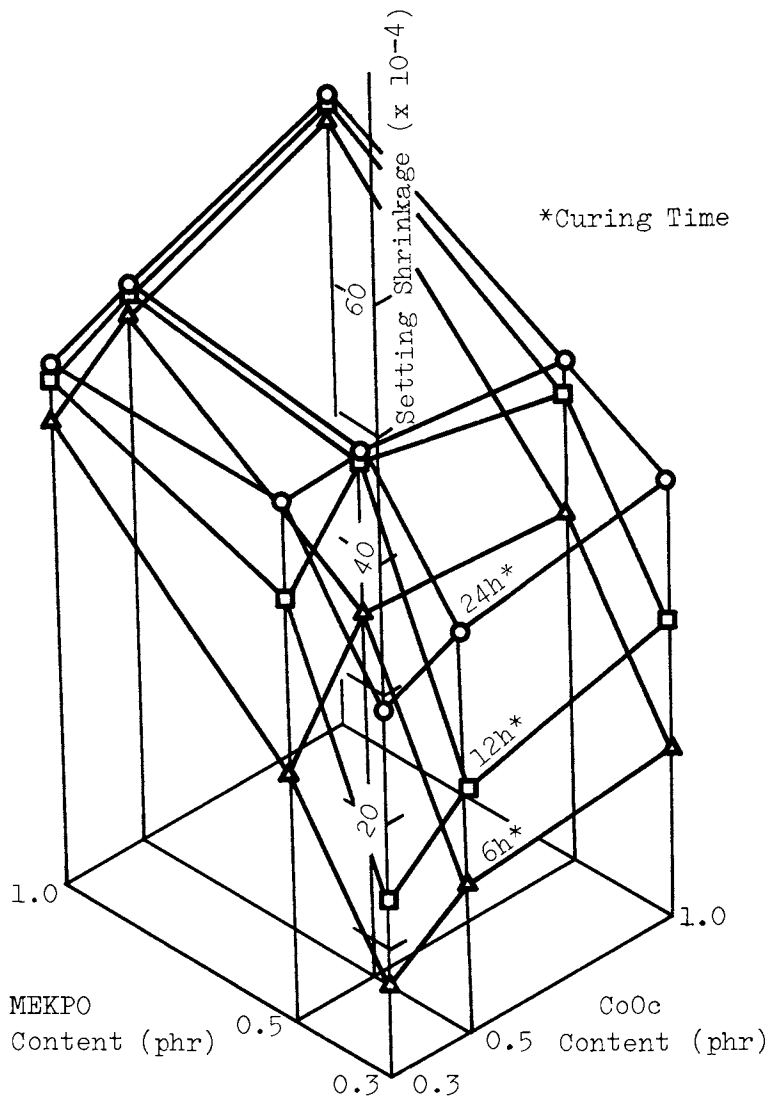
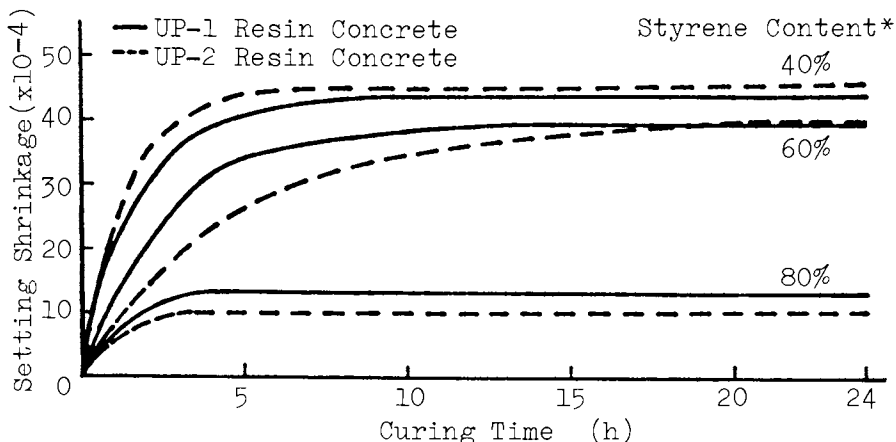


Figure 4. Effects of CoOc and MEKPO contents on setting shrinkage

Figs. 5 and 6 show the effects of curing time and styrene content on setting shrinkage of polyester resin concrete. The setting shrinkage of polyester resin concrete with various styrene contents increases with additional curing time, and tends to become nearly constant within 15 hours, in spite of type of the resin. The shrinkage decreases with an increase in the styrene content. The results do not agree with the data of polyester resin-filler composition by K. Kircher²⁾. This suggests that a large excess of styrene may act as a shrinkage-reducing agent in hardening process of the resin concrete.



Note, *Contents of styrene contained in binder.

Figure 5. Relationship between curing time and setting shrinkage of polyester resin concrete

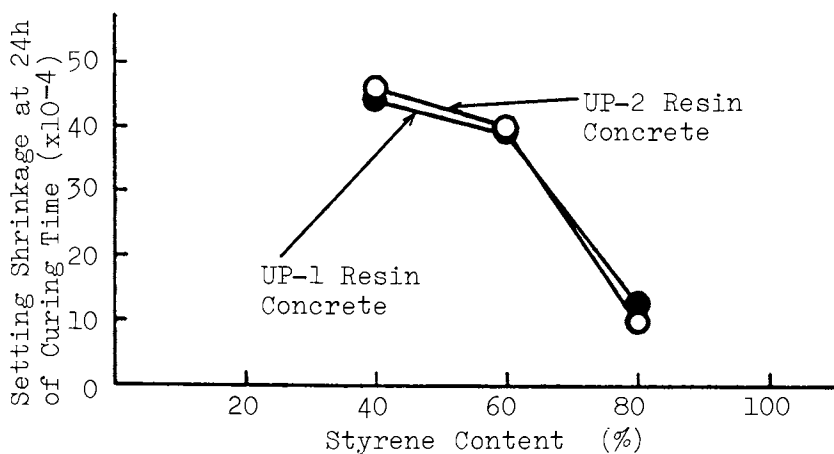


Figure 6. Styrene content vs. 24-hr setting shrinkage of polyester resin concrete

Figs. 7 and 8 exhibit the relationship between curing time and length change of polyester resin concrete using UP-1 and UP-2. The effect of the content of shrinkage-reducing agent on length change is given in Fig. 9. Generally, as the curing time elapses, the length change of polyester resin concrete converts from shrinkage into expansion with increasing content of shrinkage-reducing agent, and reaches a constant at the curing time of 24 hours.

Namely, the setting shrinkage of polyester resin concrete certainly decreases with an increase in the content of shrinkage-reducing agent. However, it is suggested from these data that the most appropriate content of shrinkage-reducing agent, recommended for nonshrinkage by the resin manufacturer, is impertinent. At higher catalyst and accelerator contents the shrinkage increases and the expansion decreases through the curing time, and the length change tends to become nearly constant at an early curing time. At 2 to 3 hours of the curing time, slight expansion of polyester resin concrete with 0.5 phr catalyst and 0.5 phr accelerator is attributed to the looseness of compaction due to the setting retardation of the concrete.

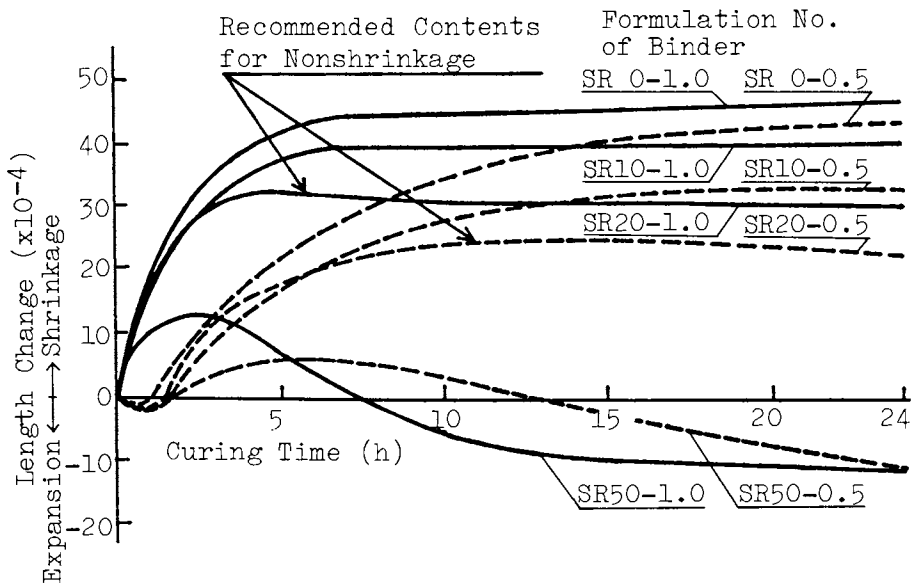


Figure 7. Relationship between curing time and length change of UP-1 resin concrete with various contents of shrinkage-reducing agents

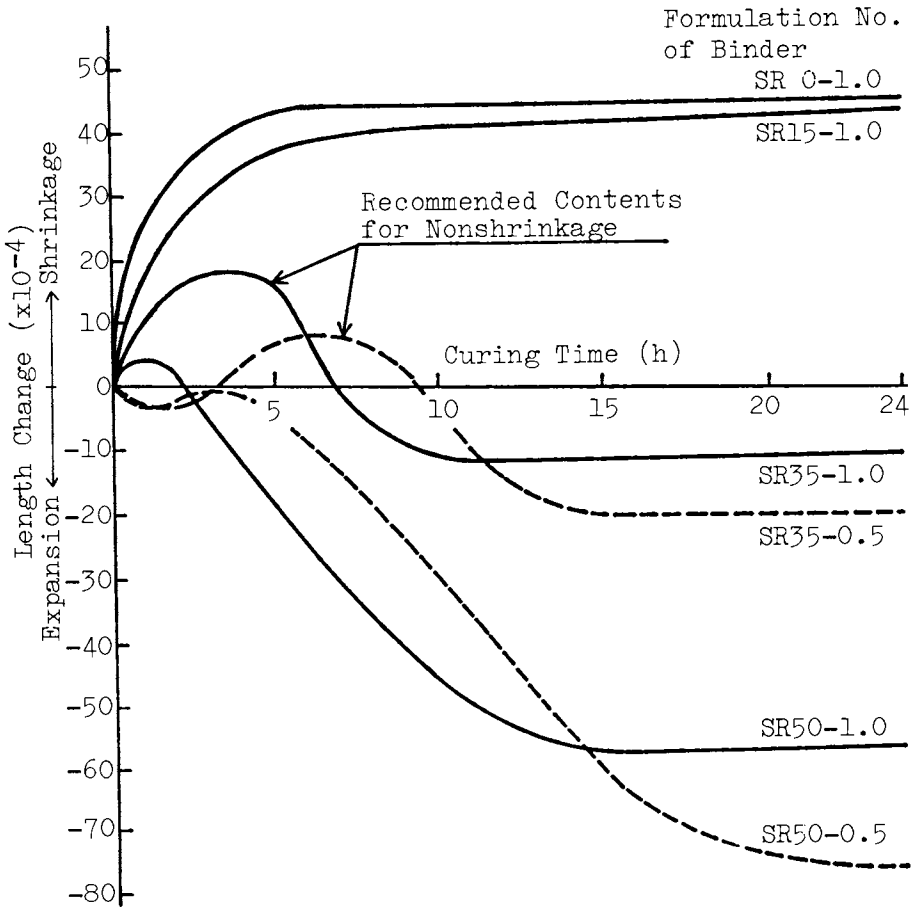


Figure 8. Relationship between curing time and length change of UP-2 resin concrete with various contents of shrinkage-reducing agents

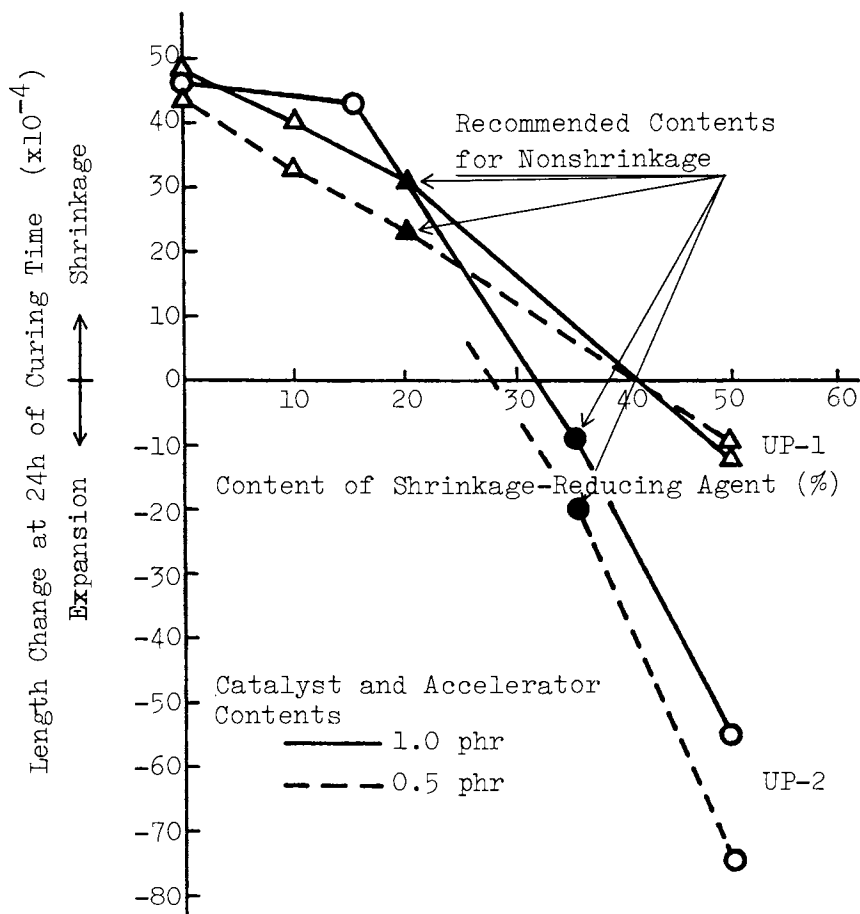


Figure 9. Content of shrinkage-reducing agent vs. 24-hr length change of polyester resin concrete

Fig. 10 shows the comparison of data on setting shrinkage of polyester resin concrete determined by the experimental automatic apparatus and embedded strain gages.

In comparing the data obtained by the apparatus developed by the authors with those from the embedded strain gages, slight differences in setting shrinkages are observed in the earlier stage of the curing time. However, the differences at 5 to 10 hours of the curing time are very small, and the differences at 24 hours are hardly recognized.

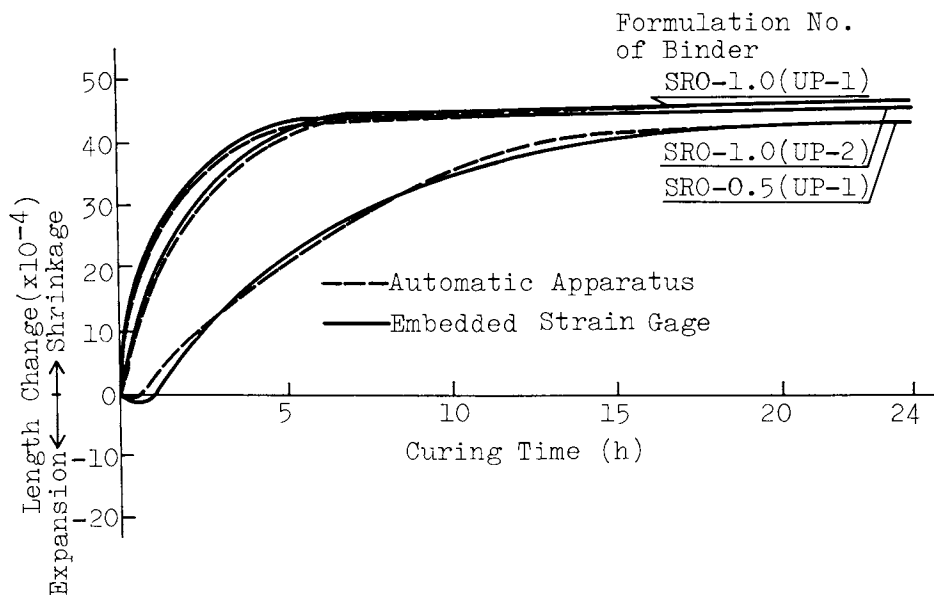


Figure 10. Comparison of data on setting shrinkage of polyester resin concrete, measured by automatic apparatus and embedded strain gages.

Conclusions

- (1) The setting shrinkage of polyester resin concrete increases with a rise in contents of catalyst and accelerator, and is markedly affected by catalyst content rather than accelerator content.
- (2) The shrinkage of polyester resin concrete decreases with increasing content of styrene contained in its binder.

(3) The setting shrinkage of polyester resin concrete certainly decreases with increasing content of shrinkage-reducing agent, and the concrete expands at high content of shrinkage-reducing agent. At higher catalyst and accelerator contents, the shrinkage increases and the expansion decreases through the curing time, and the length change tends to become nearly constant at an early curing time.

(4) It is demonstrated that the automatic length change measuring apparatus which was built for this work is most useful for evaluating the length change (especially shrinkage) of resin concrete, such as polyester resin concrete.

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Latex Emulsions with Concrete

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PART A - THEORY OF EMULSIONS

Emulsions are intimate mixtures of two immiscible liquids, one of them being dispersed in the other in the form of fine droplets. A mixture of two miscible liquids, e.g., water and alcohol, or oil and kerosene, will not produce an emulsion, but a more intimate degree of dispersion: a solution. On the other hand, it is not possible to form an emulsion with two immiscible liquids alone, since such a system would lack the important factor of stability. In shaking straight water with toluene, for instance, the two liquids will separate immediately when shaking is discontinued.

The conditions change completely when a dilute soap solution, instead of straight water, is used and it is shaken with an oil. In doing so, a milky liquid develops, which remains in this state without separating for a considerable length of time. Then, a typical emulsion is formed. Therefore, three components are necessary to produce emulsions: two immiscible liquids, and a substance which helps to promote the emulsion and to keep it stable, i.e., the emulsifying agent, or emulsifier.

To the naked eye, emulsions appear as uniform, opaque liquids or pastes of white or slightly yellowish color. The microscope reveals that emulsions are by no means uniform substances. They are non-uniform and consist of a multitude of small droplets, usually of spherical shape, and varying diameters, floating in the surrounding liquid. Emulsions with particles

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of large diameter are called coarse emulsions, and those with small particles are fine emulsions. The particles and the liquids in which they float are called the phases of an emulsion. The particles are referred to as the discontinuous phase, and the medium which is the dispersion liquid is called the continuous phase. Also, since the droplets of the discontinuous phase are enclosed from all sides, it is also called the internal phase, and the continuous phase is also called the external phase.

In the majority of all emulsions, one of the phases is water, or an aqueous solution containing salts, soluble organic material, colloids, etc. This is also called the water phase. The other phase, the particles or droplets, is called the oil phase, even if it does not consist of oil. Many substances constitute the oil phase, all having one important common property; namely, their insolubility in water. These may include hydrocarbons, resins, waxes, nitrocellulose, alkyds, rubber, vinyls and acrylics. They are referred to as "oil" since they behave in emulsions very much like oil.

The substances used in emulsions may be classified into two groups: those which enter the water phase, and those which go into the oil phase. The first group making up the aqueous portion, must be water soluble, or show a certain affinity toward water. This group has the general name of hydrophilic substances (from the Greek "hydor", water, and "philos", loving). The other group of substances which go into the oil phase have no affinity for water, are water-repellent, but show marked attraction to oil or oil-like material. They are known as hydrophobic substances (from "phobos", fearing).

Typical hydrophilic substances are water-soluble compounds, many metal salts, and substances containing a relatively large number of oxy- or hydroxyl groups. Typical hydrophobic substances are oils, fats, waxes and all compounds containing mainly carbon with few or no polar groups. This difference is important in the selection of other materials which will be blended with the emulsion, such as pigments, fillers, cement, sand, and all other ingredients which may go into the making of a concrete or mortar.

With any given pair of immiscible liquids, two types of emulsions are possible. One is that in which water is the external, and oil, the internal phase, known as oil-in-water emulsion, or water outside emulsion (O/W). The other type, with oil as external, and water as the internal phase, is known as water-in-oil emulsion, or oil outside emulsion (W/O). If an emulsion contains 50% water or other aqueous solution, and 50% oil or oil-like substance, it is possible to produce an O/W or a W/O emulsion, which will show the same percent composition but, nevertheless, be two entirely different emulsions. This all depends on the method of emulsification, the emulsifying agent, the soluble materials in the water phase, and the fineness of particles.

The characteristic properties of an emulsion are dictated by the external phase. If water is the external phase (O/W), the emulsion may be diluted with water and not with oil or organic solvents. Just the opposite is the case with a W/O emulsion, where the oil is the external phase, and it can be thinned with organic solvents. Should water be added to this type of emulsion, the viscosity will increase. This is one way of visually distinguishing between the two types. The thinning method, using water, will indicate an oil-in-water emulsion if the viscosity is reduced. If viscosity is increased, it would indicate a water-in-oil emulsion.

There are many types of emulsifying agents which are used in preparing emulsions. As indicated, they facilitate the emulsification and impart stability to the prepared emulsion. Chemically, they belong to different classes of compounds among which are salts, acids, bases, and esters. Physically, they are substances of medium molecular weight (above 300), and the molecules are of elongated shape and belong to the mixed polar:non-polar type. These emulsifying agents have a very definite bearing on the type of emulsion produced and the particle size of the dispersed droplets.

The emulsions which are generally utilized in cementitious compositions are of the oil-in-water type, having at least 50% water in the composition, although some have less than 50% water, and are still

oil-in-water emulsion, and are stable in the presence of the various salts and oxides comprising the make-up of cement. Not all emulsions are compatible with cement and it would be a mistake to select an emulsion which is primarily intended for production of paint or adhesives to act as an admixture for a cementitious mortar.

PART B - BUTADYENE STYRENE LATICES

As a result of the synthetic rubber program instituted during World War II, because of the lack of natural rubber, methods for producing synthetic rubber were developed which were based on the emulsification of different types of latices. Butadyene was, of course, the basis for the synthetic rubber industry as a result of these programs. Styrene was a material in plentiful supply and was low in cost. Polystyrene, which is a polymerized styrene, is a hard material which requires plasticizing. It may be plasticized by one of three ways: Internally, where the plasticizer is part of the copolymeric molecule; pre-plasticized, where the plasticizer is added during the polymerization; post-plasticized, where the plasticizer is emulsified separately and added to the latex. Polystyrene may be plasticized internally by copolymerizing with a reactive monomer, such as butadyene. In the various emulsions available, styrene content may be as high as 85% with the butadyene about 15%. The use of butadyene introduces a small amount of unsaturation in the polymer which is subject to oxidation on aging, with possible hardening and yellowing.

The butadyene styrene latices which are compatible with cementitious compounds are copolymers. Typical physical properties are given in Table 1.

For purposes of simplicity, the butadyene styrene latices will be referred to as SBR latices. Those which are compatible with cement, show excellent stability in the presence of such multivalent cations as calcium and aluminum. They are unaffected by the addition of relatively large amounts of electrolytes, such as sodium chloride, calcium chloride and hydrochloric acid. The SBR latices may coagulate if subjected for

long periods of time to high temperatures, freezing temperatures or severe mechanical action. They are not stable to most air-entraining agents, and they should not be used in combination with air-entraining cements.

Table 1. Properties of Butadyene Styrene Latex

Percent Solids	48
Specific Gravity	1.01
Weight per gallon (pounds)	8.4
pH	10.5
Particle Size Range (angstroms)	1900-2100
Viscosity at 25°C (centipoise)	10-12
Surface Tension at 25°C (dynes/Square cm.)	30-32
Tensile Strength (psi)	745
Elongation (percent)	650

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Suggested formulations have been given for latex fortified cement mortars, used for toppings and patching compounds,

The ratios of sand to Portland cement are generally 3:1; the percentage of latex solids to cement may range from 5%-20%, and the water/cement ratio may range from 0.35-0.50. If the water/cement ratio is too high, flotation of latex solids may occur, causing the latex particles to be unevenly distributed through the mix. There is a definite difference in results between wet cure and air-dry cure. Generally, wet cures of unmodified mixes give best properties, and air-dry cures of latex-modified mixes give best properties.

Setting time of an SBR modified cement composition is delayed. However, in actual use, such mortar toppings may often be walked on in 12 to 18 hours, and may take light rubber tire traffic in 48 hours. These times will vary, depending upon the temperature, humidity and the percentage of latex in the mix. Table 2 shows the setting time for SBR latex/cement compositions.

Table 2. Setting Time for SBR Latex/Cement

<u>Latex/Cement</u> <u>Ratio</u>	<u>Water/Cement</u> <u>Ratio</u>	<u>Initial Set</u> <u>(Hours)</u>	<u>Final Set</u> <u>(Hours)</u>
0.10	0.45	6	9
0.20	0.45	5.5	10
No Latex	0.45	2	5

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Water in the latex is always included in the water/cement ratio. When the water/cement ratio is raised and the latex/cement ratio remains constant, the initial and final set times are further delayed.

In compressive strength development, the latex modified mortars always have higher compressive strengths than the unmodified mortars, in dry cure. Additions of latex to a ratio greater than 0.20 reduces compressive strength and is expensive.

Tensile strength for SBR latex modified mortars may average about 570 psi. The tensile strength for wet cured unmodified mortars is about 410 psi. In general, tensile strength is higher for the SBR modified mortar than for the unmodified mortar under any conditions of cure. The highest tensile strength is obtained at the 0.20 latex/cement ratio.

Flexural strength for an SBR latex modified mortar may average 1650 psi. Flexural strength for wet cured unmodified mortar is about 810 psi. These are figures for a 0.20 latex cement/ratio. At a 0.10 ratio, the flexural strengths are about equal. Bond strength for an SBR latex modified mortar is about 580 psi. Bond strength for an unmodified Portland cement mortar is about 250 psi. The bond strength of the modified mortars is always higher than that for the unmodified mortar under any curing conditions.

Anti-foam agents are almost always used in SBR latex modified cement compositions because they increase mix density by minimizing air-entrainment, thereby upgrading physical properties. Anti-foam agents may be added to the SBR latex by the manufacturer of the latex and additional amounts may be added by the formulator of the final cementitious mortar composition. The amount of anti-foam added may range from 0.1% anti-foam solids on latex solids up to 3.5%.

Some anti-foam materials are based on silicone resins, others are based on petroleum oils, and all of them are intended to depress the surface tension of the latex emulsion. The anti-foam agents delay the entrapment of air in mixes which is always a possibility when mixing liquids and solids, such as a mortar in a cement mixer. This results in a denser mortar which has better abrasion resistance, better resistance to water absorption, and higher compressive, tensile and bond strengths.

Mixing of all latex modified cement compositions should be held to a minimum, in any circumstance. Anti-foam agents can lose their efficiency if they are over-mixed. They tend to become emulsified after continuous shear action and they no longer give adequate performance.

It has already been indicated that SBR latices are stable and are unaffected by the addition of large amounts of calcium chloride. This is an indication that calcium chloride may be used with an SBR latex modified mortar in the same way that it is used with an unmodified cement mortar. In general, the addition of 2% calcium chloride, based on the Portland cement, improves the early compressive strength development, from 24 hours to 7 days.

The water vapor transmission characteristics of an SBR latex modified mortar are twice as good as those of an unmodified mortar. The water vapor transmission rate, as measured in grains/square foot/hour/inches mercury is as follows:

Unmodified Cement Mortar	WVTR = 9.9
SBR Latex/Cement Mortar (0.20 ratio)	WVTR = 4.1

PART C - POLYVINYL ACETATE LATICES

The vinyl radical is designated chemically as $\text{CH}_2=\text{CH}\cdot$; therefore, the term "vinyl resins" could be applied to substituted ethylenes and their many copolymers. Among these can be included polyethylene, polystyrene, polyvinyl chloride, polyvinyl acetate, acrylic esters, methacrylic esters and even some of

the synthetic rubbers, such as isoprene. Vinyl resins are chiefly copolymers rather than homopolymers. Homopolymers are polymers in which the monomeric units are all identical. Typical examples are polyvinyl chloride, polyvinyl acetate and polystyrene. Copolymers are polymers in which the monomeric units are different. Typical examples are polyvinyl chloride - polyvinyl acetate resins, polyvinyl chloride-acrylonitrile resins, and polystyrene-butadiene resins. However, commercial vinyl resins usually contain a small percentage of a modifying resin, such as an acid or an acid anhydride, which is distributed randomly in the polymer chains. The amount of these modifying materials is relatively small so they may be considered copolymers. The particular value of the copolymerization technique is that the properties of the copolymer resins may be varied over a wide range by adjusting the type and amount of the various monomers used in their formulation.

Vinyl resins are polymerized and copolymerized commercially by four different processes: bulk, solvent, suspension and emulsion. The emulsion polymerization process is widely used in the manufacture of vinyl resins. In this process, the monomer is emulsified in water, using a suitable emulsifying agent. Of course, the monomer must be substantially insoluble in water in order to obtain a good emulsion. After polymerization is essentially complete, the emulsion may be broken and the resin coagulated, washed and dried; or suitable protective colloids, buffers, corrosion inhibitors, fungicides, etc. may be added to produce a stable latex of the polymeric resin.

Non-Reemulsifiable Polyvinyl Acetate Latex

In producing a polyvinyl acetate latex for use with cement, the emulsion polymerization process is utilized. A small percentage, about 1%, of a substance like maleic acid is added in the polymerization reaction so that a copolymer is formed. Maleic acid, itself, has an ethylenic type of unsaturation, but it does not form homopolymers. Since the amount introduced is so small, the resultant polymer is a copolymer. The introduction of the highly polar carboxyl

groups on maleic acid improves the adhesion characteristics of the polyvinyl acetate. Just as the polystyrene-butadiene resins are generally referred to as SBR resins, the polyvinyl acetate resins are generally referred to as PVA resins.

Typical physical properties of a polyvinyl acetate copolymer emulsion suitable for use with cement are given in Table 3.

Table 3. Properties of Polyvinyl Acetate Latex

Percent solids	52
pH	4.0-6.5
Weight/gal. Emulsion (lbs.)	8.9
Weight/gal. Solids (lbs.)	9.76
Average Particle Size	Less than 2 Microns
Free Monomer Content	Less than 1%
Odor	Slight
Borax Compatible	No
Particle Charge	Negative

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This PVA latex leaves a dried film which is flexible without the addition of a plasticizer. The film has excellent water resistance, light stability, good aging characteristics and good film consolidation. This particular PVA latex may be used as a film forming binder in a water-based emulsion paint. Its particular characteristics of compatibility with cement have led to wide uses of this latex as an adhesive and an admixture for cementitious mortars and concrete.

There are a variety of different applications for all latex emulsions as bonding agents and admixtures. Some types have a greater degree of water resistance than others; and, of course, there is a wide range of cost factors. For purposes of presentation, it is assumed that all types are utilized at about 45-50% solids content.

Re-emulsifiable Polyvinyl Acetate Latex

In the descriptions of PVA latices, all the properties described are based on the fact that these latices, as well as the SBR latices, and the acrylic latices, are essentially non-reemulsifiable. When

latices were first developed and used in formulating paints, one of the characteristics that was objectionable was the long period of time which had to elapse before paint films, cast from the original SBR latices, had coalesced or dried enough to be "washable." Sometimes, this period lasted for as long as six weeks. As progress was made in producing these latices, products were soon available on the market which produced films which could be washed in very quick order.

Where latices are used as bonding agents in themselves, an obvious problem develops. This involves the rapid drying of a film cast from a latex creating a situation whereby a subsequent placement of a cement mortar or concrete would not bond to a dried film of latex. As an example, should a floor area be treated with a latex bonding agent in its entirety before the application of a new cementitious topping, the latex film would have dried in the first part of the area before the last part of the area had been coated. Since the latex film becomes comparatively hard, smooth and glossy, the adhesion of the subsequent topping would be less than adequate.

Other than by the method of preparing a neat cement slurry, utilizing the latex as part of the gauging water, to provide a bonding medium, there was one method available by which a latex could be modified to be useful as a film-forming bonding agent. This involved modifying a latex so that it would be reemulsifiable, i.e., able to be softened and retackified upon contact with a water-containing medium. Such a latex would permit application of a film to a surface long before the subsequent application of a water-based overlay. This film, of course, would dry, and resemble a dried film of a non-reemulsifiable latex. However, the difference would be that this film would be resoftened upon contact with water, whereas the film cast from the non-reemulsifiable latex would be affected very slightly, if at all.

A film cast from a reemulsifiable latex would have a thickness of about one mil, or one thousandth of an inch. A film of this thickness would almost, of necessity, have to be applied to a smooth surface in order to leave a visible film. Application to a rough and/or porous surface would result in the absorption

of most of the film, leaving very little in the glue line as an adhesive. Of course, a first coat application could be used as a primer, followed by one or more succeeding coats which would not be absorbed. This, of course, is laborious and costly. Therefore, a reemulsifiable latex bonding agent is not recommended for repair and maintenance, unless the surface to which it is applied is smooth.

The most widely used application of a reemulsifiable PVA latex is as a bonding agent for plaster. It is used to bond finish or base coat gypsum, accoustical or Portland cement plaster to interior surfaces of cured concrete cast in place, stone, unglazed tile, metal, plywood, rock lath, painted surfaces and even glass. The latex bonding agent dries quickly to form a thin, flexible film with outstanding adhesive properties, providing a permanent bond for plaster. It is generally unaffected by the alkalinity of gypsum, lime putty, or Portland cement mixes. It is resistant to acids, vibration, freezing and thawing. The tensile and shear strengths far exceed those of the materials which are bonded together. This type of bonding agent found wide use in the application of thin film, white finish plaster to ceilings of high rise buildings, eliminating the need for scratch coats and brown coats. The adhesive replaced the intermediate coats and provided a stronger bond for the white finish plaster. Unfortunately, the use of plaster in new construction has dwindled to the point where the plastering trades have almost disappeared. Dry wall board is being used almost exclusively for wall surfaces. Ceilings are now being painted, tiled, sprayed with accoustical materials, or are constructed as hung ceilings. About the only members of a structure which are still being finished in white plaster are columns and beams.

The surface to be coated with a reemulsifiable PVA bonding agent should be thoroughly clean, free of grease, dirt and efflorescence. If the area is coated with water-sensitive materials, such as whitewash, calimine, or poorly bonded cement paint, these must be removed. The adhesive is applied at the rate of 300 to 400 square feet per gallon. It is generally colored to enable the applicator to see what has been

sprayed. The film which is applied has a low sheen which can be used as an indication of adequate film thickness. This film will dry and may be plastered in as little time as one hour. It will also retain its adhesive characteristics and ability to be re-emulsified for a period as long as 60 days, in many cases. However, it is advisable to apply plaster within the first week after application of the bonding agent. With each succeeding period of time after this first week, the adhesive qualities are reduced.

Even though there is a reaction between the lime in the plaster and the latex film, causing it to set, the film still retains a degree of sensitivity to water. Therefore, it is indicated that these bonding agents not be used in exterior applications where water might resoften the film and loosen the plaster. The same precautions would apply in using these adhesives in areas which might be subject to water damage, such as ceilings in bathrooms or kitchens where leaks might occur from above.

Figure 1 presents a typical formulation for a re-emulsifiable PVA latex bonding agent. This formulation is based on a medium to low molecular weight polyvinyl acetate homopolymer which is plasticized externally to contribute to its re-emulsification properties. There are companies which make available a complete latex vehicle which can be used directly with little or no modification, except the addition of color and, possibly, reduction of solids content for cost reasons. Generally, a coalescing agent, in the form of a solvent, is added to the formula so that there will be minimum difficulties in forming a continuous film at low temperatures.

<u>Materials</u>	<u>Pounds/100 Gallons</u>
PVA Latex-homopolymer (NVM=55%)	780
Chlorinated biphenyl	13
Dipropylene glycol dibenzoate	8
Ammonium acetate	7
Color in water dispersion	3
Water	65
Toluene	<u>60</u>
	936

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Figure 1. Reemulsified PVA latex bonding agent

This formulation has a total solids content of 49% and is applicable (in its viscosity) by spray. Of course, it can also be applied by brush and roller.

Table 4 presents some typical properties of this bonding agent as tested in accordance with Military Specification MIL-B-19235 (Docks) Bonding Compound, Concrete.

Table 4. Properties of PVA Latex Bonding Agent

Tensile Strength

<u>Specimens</u>	<u>P.S.I.</u>	<u>Failures</u>
Neat cement	600	Failed in bond
Ottawa sand mortar, 1:3	420	Failed in bond
Perlite plaster, 1:3	100	Failed in plaster
Accoustical plaster	160	Failed in plaster
Base coat plaster, 1:3	270	Failed in plaster
Finish plaster	65	

Shear Strength

Cement mortar 398

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PART D - ACRYLIC LATICES

The acrylic ester resins are polymers and copolymers of the esters of acrylic and methacrylic acids. These resinous materials range in physical properties from soft elastomers having more than 1000% elongation to hard plastics which can be sawed and machined. These hard plastics are commonly known under the trade names Plexiglass and Lucite. They have excellent initial color, actually water-white, they are stable to light, do not discolor or degrade on aging or outdoor exposure. These resins are available for many purposes as solutions in organic solvents and as oil-in-water emulsions.

A wide range of physical and chemical properties may be obtained by changing the side chains on the monomer in making homopolymers, and also by mixing the various monomers before polymerization to form copolymers. There are many variations of combinations possible as well as many variations in molecular weight. The acrylic esters may be polymerized by one of the four methods described in previous sections; namely,

bulk, solution, suspension, or emulsion. The bulk method is generally used to produce the hard polymethyl methacrylate, the solution method for the polymers which are ultimately dissolved in solvents, and the emulsion method for those polymers which are used as latices. In the emulsification process, a water soluble peroxide, such as hydrogen peroxide or ammonium persulfate, is used as the catalyst. The emulsifying agent may be anionic, cationic or non-ionic. Each will have a different effect on the type of latex produced.

Typical physical properties of an acrylic latex emulsion suitable for use with cement are given in Table 5.

Table 5. Properties of Acrylic Latex

Percent solids	45%	
pH	9.4-9.9	
Specific gravity	1.054	
Pounds per gallon	8.8	Structures Publishing Company

The uses made of this emulsion as an admixture in cementitious compounds are similar to those made with SBR and PVA latices. Among these, of course, we can include patching and resurfacing work, floor underlayments, terrazzo tile flooring, spray coat and fill coat applications, cement plaster and stucco, tile grouts, crack fillers and precast panel surfacing. The addition rates of acrylic latices are comparable to those for the SBR and PVA latices, ranging from 0.10 to 0.20 latex solids:cement. There are indications that the acrylic resins may be added at a ratio as low as 0.05. The usual indications about the variations in strength characteristics which depend on addition rates apply to the acrylic resins as well. The same is also true for water/cement ratios and method of curing.

The generally recommended addition rates fall in the range of 0.10 to 0.20. Above this level, some properties actually begin to drop. Below this level, many properties are still more than adequately higher than for unmodified mortars. Many commercial formulations are based on an addition rate at this level for price reasons.

Among the various applications which have not been treated in greater detail are the spray coat applications and the underlayment applications. The spray coat applications are based on combinations of cement and other fillers, together with a latex binder. These applications may be applied by brush, roller and trowel, as well as by spray. They are often promoted as a substitute for "rubbing" concrete.

Floor underlayments are utilized to produce a level and smooth surface before placing vinyl tile, asphalt tile, rubber tile, or other resilient flooring materials. Acrylic latex modified underlayments are ideally suitable for leveling floors prior to the installation of these surfacing materials, since these underlayments provide an excellent substrate for bonding purposes, as well as offering good chemical resistance to tile adhesives and solvents which some of them contain.

PART E - DRY ACRYLIC ADMIXTURES

There have been a number of methods utilized for improving the physical properties and working characteristics of cement mortars by means of dry powder additions to the cement:sand mixtures. One of these dry powder admixtures is a synthetic polymer derived from cellulose. There are several variations of this polymer, two of which have been widely used for this purpose, namely, methylcellulose and hydroxyethyl cellulose. Both of these are available in different viscosity ranges, when dissolved in water, and both are soluble in water. When they are blended into a cementitious mix at addition rates of 3% to 5% on the cement content, the resultant product achieves improved characteristics when mixed with water. The plastic mortar is more readily workable and retains water more completely. Retention of water is important, especially in mortars which are used to bond porous bricks or other building materials. In addition, greater bonding characteristics are obtained. The use of these cellulosic materials in various applications has been covered by many patents in the United States and in Europe. Among the uses for these admixtures are the compounding of grouting systems, cement base paints,

stuccos, patching and repair formulations, cellular concrete blocks, sound insulating materials, refractories, and even dental preparations. One of the major disadvantages of these admixtures is that they are water resolvable and they may leach out of a cured cement mortar.

Other attempts have been made to utilize dry powder polyvinyl alcohol and polyvinyl acetate as admixtures for the same purpose. The polyvinyl alcohol is readily soluble in water, and it requires significant amounts in addition to achieve any distinct advantages. Significant amounts of any viscosity range of polyvinyl alcohol contribute to an undesirable increase in viscosity in the cement mortar. Polyvinyl acetate in powder form has been used for this purpose with consequent improvements in working characteristics and physical properties. However, dry powder polyvinyl acetate does not form a true polymer emulsion when dissolved in water. It, therefore, may also be dissolved out of a cement mortar.

The acrylic resins may be so polymerized that a resultant product may be obtained which can be dispersed in water to form a true polymer emulsion. Such a product is now available as a cement mortar modifier. By dry blending this resin with appropriate cementitious materials, it is possible to formulate a one-package acrylic modified cement mortar. Addition of water to the dry blend will produce a mortar with superior adhesion and physical strength properties.

<u>Materials</u>	<u>Pounds</u>
Silica sand No. 80 Mesh dry	250
Portland cement, white	100
Acrylic powder, dry	10
Sodium citrate	0.5
Sodium carbonate	1.0
Dry wetting agent	2.0
Hydroxyethyl cellulose	0.5
Water	70
	<hr/> 434.0

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Figure 2. Dry acrylic cement mortar

Water is added at the time of use on the job site.

In addition to the use of dry acrylic powders in cement mortars, other typical uses for these modifiers are in cement toppings, ceramic tile adhesives, ceramic tile grouts, white masonry paints and cement block fillers. It is obvious that these compounds are more convenient to use with the simple addition of water, than those compounds requiring the addition of a latex emulsion. As improvements are made in these dry powders, there will be more emphasis on this type of compound. At the present time, the dry powder acrylics are more costly than the latex emulsions on a dry solids basis.

PART F - EPOXY LATICES

There has always been a desire for water-soluble epoxy resin systems. Although epoxy resins were introduced a good many years ago, all attempts at water systems have met with general failure. The investigations into epoxy systems as emulsions for use with concrete have been roughly divided into three general classifications. The first attempts were in the emulsification of the epoxy resins themselves. The problems and failures in this approach may be generalized as follows:

- (a) The polarity of the epoxy resin makes the choice of surfactant or emulsifying agent very limited and difficult;
- (b) Poor compatibility of the epoxy resin with protective colloid;
- (c) All surfactants, emulsifying agents and compatible protective colloids promote hydrolysis of the epoxy groups in water systems;
- (d) Poor emulsion stability and poor freeze-thaw stability at best;
- (e) Phase inversion with all curing agents;
- (f) High levels of resin required.

The second approach to water systems has been the development and investigation of water-soluble epoxy systems. The failure in these attempts may be summarized as follows:

- (a) All known water-soluble epoxy resins are ali-

phatic poly-epoxides which exhibit little or none of the strength properties normally expected of the epoxy resins;

(b) All water-soluble epoxy resins hydrolyze in water;

(c) Reaction, if at all, with curing agents, is slow and still exhibits the shortcomings of low strength characteristics.

The third approach has been the direct addition of epoxy resin and curing agent to cement. This can be accomplished, but generally requires the addition of 20% to 50% of the resin:curing agent combination to obtain the desired properties. This approach is a compromise, resulting in a system which is economically impractical.

Because of the generally bad to poor results of past attempts, it became apparent that an entirely new and different approach to the water dilutable epoxy system had to be followed, whereby the resin emulsion could be added to cement in small quantities and still affect the desired increase in properties. The properties desired would be as follows:

(a) Emulsion stability and water dilutability from the time of mixing the resin and curing agent until gellation;

(b) A set time equivalent, or nearly equivalent, to a cement system itself;

(c) High strength properties;

(d) Good freeze-thaw stability;

(e) Retention of strength on rewetting;

(f) Troweling and finishing properties equivalent, or nearly equivalent, to an unmodified mortar system;

(g) As low a resin content as possible for economic reasons.

It becomes obvious that many of these properties could be obtained by using a straight epoxy resin, typically, one of the liquid types, as one of the components which would be emulsified at the time of mixing with the curing agent. The curing agent, therefore, would have to be an emulsifying agent, wetting agent and surfactant, as well as a curing agent. Such

an agent is now available commercially for producing epoxy emulsions.

These curing agents are polymeric compounds which are water soluble, forming excellent emulsions with epoxy resins. Pot life may be varied, depending upon the choice of curing agent. Pot life may also be extended by the addition of higher amounts of water.

The basic principle involves the preparation of an epoxy emulsion just prior to use. Previously, in pre-emulsifying the epoxy resins and the curing agents, and packaging them separately, the emulsions would break and separate into phases, in the package, or upon mixing.

This latest approach of preparing the emulsion on job site eliminates these problems. Upon preparing the emulsions in the field, and blending, the blend is already in the process of polymerization, and there is no time for phase separation, especially, since the blend is added to a cementitious composition in the same way that a previously described latex is added. The user is aware that the base material is 100% solids. The amount of water which is added determines the solids content of the emulsion. The user knows exactly what the resin:cement ratio is.

In preparing the emulsion in the field, equal parts of a liquid epoxy resin having an epoxide equivalent of 175-210 are mixed with equal parts of the emulsifying curing agent. The mixture is blended and allowed to sweat in for 15 minutes for polymerization to begin. Water is then added slowly, mixing continuously, to form the emulsion. The amount of water added determines whether it is a water-in-oil type, or an oil-in-water type. This has a definite bearing on the rate of polymerization.

When the epoxy resins are emulsified by this method, and the emulsion is added to a cementitious mix, there is an immediate surface acting effect which greatly reduces the water requirements of cement. This water-reducing characteristic, of approximately 15%, is developed with low addition rates of the epoxy emulsion. The addition rate may be as low as 0.1 parts of emulsion solids per 100 parts cement. The addition of 2 parts of emulsion solids to 100 parts cement produces slightly lower water requirements, but not below

LATEX AND EPOXY ADHESIVES
COMPARATIVE

A. Latexes

	Appearance	Solids Content	Primary Use	Application Methods	Applications	Specifications	Cleaning Surface Preparation	Finishing Procedures	Chemical Resistance of Mortar ASTM-C-287-811
A. Acrylic	Milky White	45.0%	Bonding fresh concrete to old concrete. Concrete admixture. Thin layer toppings.	Brush, broom spray, roller as adhesive. Trowel as topping.	Underlayments Stucco Grouting-mortar Terrazzo Home Kits Crack Fillers	MIL-B-19235	A. Remove oil, grease. Wet surface.	Steel trowel, wood float. No excessive trowelling.	Acids—Fair Alkalis—Very Good Salts—Very Good Solvents—Fair-Good
B. Polyvinyl-Acetate Non- Re-Emulsifiable	Milky White	55.0%	Bonding fresh concrete to old concrete. Concrete admixture. Thin layer toppings.	Brush, broom spray, roller as adhesive. Trowel as topping.	Underlayments Stucco Grouting-mortar Terrazzo Home Kits Crack Fillers	MIL-B-19235	B. Remove oil, grease. Wet surface.	Steel trowel, wood float. No excessive trowelling.	Acids—Fair Alkalis—Very Good Salts—Very Good Solvents—Fair-Good
C. Butadiene-Styrene	Milky White	48.0%	Bonding fresh concrete to old concrete. Concrete admixture. Thin layer toppings.	Brush, broom spray, roller as adhesive. Trowel as topping.	Underlayments Stucco Grouting-mortar Terrazzo Home Kits Crack Fillers	MIL-B-19235	C. Remove oil, grease. Wet surface.	Steel trowel, wood float. No excessive trowelling.	Acids—Fair Alkalis—Very Good Salts—Very Good Solvents—Fair-Good
D. Polyvinyl-Acetate Re-Emulsifiable	Milky White or Pink	50.0%	Bonding of plaster. Not used as an admixture.	Brush, spray roller.		MIL-B-19235	MIX — Cement: Sand :: 1:3 Latex Solids on Cement = 10-20%, Water: Cement Ratio = 0.45		

B. Epoxies

	Mix Ratio	Appearance	Solids Content	Working Life	Covering Rate	Uses and Applications	Specifications	Chemical Resistance
I. Epoxy — a. Unfilled Binder b. Filled	1:1 by volume Part A and Part B	Light straw to amber	100%	a. 30-60 min. b. 30-60 min.	a. 100 sq. ft. per gal. as mortar 25 sq. ft. 1/8" thick, containing sand. b. 25-38 sq. ft. per gal.	a. Bonding hardened concrete and other materials to hardened concrete. Setting, dowels. Type Ib, Iib. b. Filling cracks in concrete to bond both sides of crack into an integral member. Type Ia and Iia.	I. a. MWM-B-350A b. MWM-G-650A New Jersey Turnpike Section 4.3.3 Standard Specifications 1965 AASHTO Specification Designation M-200-631	Excellent to acids, alkalis, solvents, salts with maximum properties. Also maximum resistance to hydro- static water pressure.
II. Epoxy — a. Unfilled Binder b. Filled	1:1 by volume Part A and Part B	Light straw to amber	95-100%	a. 1-3 hours b. 1-3 hours	a. 100 sq. ft. per gal. as mortar 25 sq. ft. 1/8" thick, containing sand. b. 100-150 sq. ft. per gal.	c. Bonding plastic concrete to hardened concrete. Type Ib and Iib. d. Preparation of epoxy mortars by adding sand. Types Ia, Iia, III.	II. Virginia Dept. of Highways AASHTO Specification Designation M-200-631	
III. Epoxy — a. Unfilled	1:1 by volume Part A and Part B	Part A — Light straw Part B — Black Combined — Black	100%	30-60 min.	a. 30-50 sq. ft. per gal.	e. Bonding skid-resistant materials to hardened concrete. Types Ib, Iib, III. f. Membrane between asphalt and concrete. Type III.	III. AASHTO Specification Designation M-200-631 New Jersey Turnpike Section 4.8.2. Standard Specifications 1965 N. Y. State Dept. of Public Works Item # 600B	

the stoichiometric amounts of water required to hydrolyze the cement. This low addition rate is in contrast to the recommended addition rate for other latex emulsions of 10% to 20%.

The addition of small amounts of epoxy emulsion to a cementitious mixture improves trowelability of the resultant product tremendously, in contrast to a typical latex admixture mortar where the high addition rate creates difficulty in troweling, because the latex solids are brought to the surface, exerting a drag on the trowel. The initial set time of an epoxy admixed mortar is considerably reduced, and the final set time is also accelerated. This rapid setting of an epoxy emulsion admixed cement mortar may be attributed to the polymerization of the epoxy resin, as well as to the acceleration in the rate of hydration of the cement.

The physical properties of these mortars show phenomenally high flexural and tensile strengths, with little or no loss in compressive strength. For all practical purposes, a level of 2% as an addition rate, produces results which are outstanding, without excessive cost. Cured mortar specimens have been exposed to continuous water immersion with no loss in properties.

Additional possibilities for using these epoxy emulsions are apparent. A water-based epoxy system could certainly be used as a curing compound for freshly placed concrete. There would be no incompatibility because both are in a water phase. Another possibility is to use the epoxy emulsions systems as bonding agents for placing fresh concrete onto hardened concrete. Even though most epoxy bonding agents are 100% solids, they do present a problem of fast setting, so that fresh concrete must be placed quickly while the bonding agent is still tacky. In using an epoxy emulsion system, a film could be applied far in advance of placing concrete, the presence of water would prolong the setting time, and if concrete should be placed too soon, there would be no problem of entrapping solvent, such as might be present in other bonding agents. Another advantage of the epoxy emulsions is that they do not present fire or health hazards. With stress being laid by governmental agencies on problems of air pollution, water based epoxy systems provide an alternative answer.

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Sealing and Caulking Compositions

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Since the use of sealants and caulking compositions is essential for energy conservation in the construction of modern buildings, large quantities of hot melt and room temperature curing sealants and caulking compounds were used worldwide in 1978.¹ This segment of the organic coatings polymer industry is diffuse and complex and usually considered as part of the one million tons adhesives industry.² The U.S. Putty, Caulk and Sealant Industry consumes \$15 million worth of acrylic and polyvinyl acetate latex annually.³

Sealants may be puttylike mastics, noncured tapes or cured gaskets. The widely used puttylike sealants which are emphasized in this and subsequent chapters are available as both one component and two component formulations. The term sealants is used to describe compositions used as load bearing joints and the term "caulks" is used to describe those used as nonload bearing compositions.

The original caulking compositions were bituminous or vegetable oil-based products but these have been supplemented by polybutene and butylrubber, natural and synthetic rubber, polyvinyl acetate, acrylic resin, polyurethanes, polysulfides and silicones. The last two are discussed in detail in Chapters 11 and 12.

The life expectancy of polyurethane sealants has been considered to be 10 years while that of butyl rubber, acrylics, polysulfides and silicones has been stated to be 15 years.⁴ Additional information on application techniques⁵⁻¹⁴ and tests for sealants is readily available.¹⁵⁻¹⁶

Of course, bituminous caulking materials under the name of slime were mentioned in Genesis and Exodus and evidentially these

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compositions performed satisfactorily as sealants for Noah's ark. Caulking materials used during the 15th and more recent centuries were based on asbestos and limestone/filled drying oils. These putties which were used as glazing sealants have been upgraded to meet Class III requirements of Federal Specification TT-1-791 by the incorporation of a polybutene.

In addition to their use on highways and roofs, both hot poured and room temperature hardening bituminous compositions have been used as caulking materials and sealants in building construction. The classical asphalt/asbestos sealants contained volatile solvents and their resistance to solvents was increased by the incorporation of coal tar. These sealants have also been modified by the addition of elastomers, such as powdered rubber, and fillers, such as sawdust.¹⁷

Polybutenes have been used for almost a century and while they are still used, most of this type sealant contains butyl rubber, which is a copolymer of butene and isoprene. Most building specifications, including Federal Specification, TT-S-001637, require solutions of butyl rubber instead of oil-based caulking compositions. Self curing butyl rubber sealants may contain phenolic resins,¹⁸ resorcinol and hexamethylenetetramine.¹⁹

Liquid natural rubber, SBR, acrylonitrile elastomers, neoprene, and chlorosulfonated polyethylene are also used as sealant compositions. Filled depolymerized natural rubber and SBR latex are readily cured at room temperature by the incorporation of ultraaccelerators.²⁰

Filled liquid neoprene sealants are cured at room temperature by the addition of lead oxide, tertiary amines or epoxy resins. Neoprene sealants covered by a top coat of white chlorosulfonated polyethylene are being used on solar collectors.²¹ Mixtures of carboxyl terminated acrylonitrile elastomers (CTBN) and liquid epoxy resins cure readily at room temperature in the presence of bis phenol A and amines.²² Coal tar-epoxy resin, two component epoxy resin, and epoxy polyester resin systems have been used as sealants.²³

Chlorosulfonated polyethylene (Hypalon) has been used as a roofing composition and blends of this polymer and neoprene have been used as sealants. Block copolymers of styrene and butadiene (Kraton) have also been used as sealants.²⁴

Emulsions of polyvinyl acetate and polyalkyl acrylates have been used as tub caulking compositions, spackling compounds and as building sealants.²⁵ Acrylic sealants which harden in the presence of powdered iron or copper meet Federal Specifications TT-S-00230C.²⁶⁻²⁷ Liquid monomers, such as polyethylene glycol dimethacrylate and butyl alpha-cyanoacrylate have been used as room temperature curing sealants.²⁸⁻²⁹

Two component acrylic systems which are known as second generation acrylics in the U.S. and as "honeymoon adhesives" in Europe are discussed in Chapter 10. Acrylic resins have been

used with silicones.³⁰ Of course, as discussed in Chapter 11, the latter as well as fluorosilicones are widely used as sealants.³¹

Room temperature cured (RTV) silicones are used as potting compounds and as in situ formed gaskets. These compositions are toughened by the addition of styrene or butyl acrylate which form minute strands of fiber in situ when they polymerize.³² Silicone sealants and coatings are being used in the NASA space shuttles.³³ Paintable, fast curing-octoate-cured silicone sealants are also available.³⁴ Simple tests for utility, based on a filled glass tube, have been described.³⁵

Since their introduction less than a century ago, the use of polyurethane sealants has grown tremendously. The use of polyurethane sealants³⁶⁻³⁷ and ways of minimizing toxicity hazards characteristic of these materials have been outlined.³⁸

Polyethylene sulfide (Thiokol) was discovered serendipitiously by Dr. Patrick who was attempting to synthesize an antifreeze. This elastomer which was introduced commercially in 1929, had limited use until liquid polymers with reactive thiol end groups were obtained by the reduction of this elastomer. The liquid polyethylene sulfides are readily oxidized and cured by the addition of oxidants, such as lead peroxide.³⁹

These sealants, which are, by far, the most important application of polysulfides are described in detail in Chapter 12. These sealants which are available as both one and two component compositions⁴⁰⁻⁴¹ are also used as sealants for ammonium nitrate in rocket fuel. The annual sales for the latter are about \$150 million.⁴²

Regardless of their composition, these sealants are used to prevent the penetration of waterborne salts into cracks in concrete surfaces, to prevent leakage of fuel tanks, and to seal crevices in residential and commercial buildings. These sealing and caulking compositions not only conserve energy in these applications but they save energy by functioning as thermal insulators. Because of the emphasis on energy conservation, the use of these materials will increase but since they perform a vital sealing function in solar energy equipment, their use will increase at a much greater than anticipated rate.⁴³

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Reactive Adhesives

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A variety of two component adhesives and sealants are currently available for applications requiring the ultimate in bonding and sealing efficiency and performance. Included among these conventional systems are: epoxies, urethanes, polyesters, silicones, polysulfides and some modified phenolics and acrylics. Although their performance can be and usually is quite satisfactory, most are limited by pot life and fixturing requirements - and the need for thorough substrate treatment and cleanliness.

An unusual type of two component system has recently been introduced in the adhesive industry (1). These are called reactive adhesives, second generation acrylics, toughened acrylics, modified acrylics (2) or "honeymoon adhesives" (in Europe).

Basically, the system is comprised of two liquid components - an oligomeric liquid blend (usually acrylic), and a dilute solution of an often proprietary free radical initiator or activator. Application methods are similar to those used for contact adhesives; the oligomeric portion is applied by brush, roller or spray to one surface, and the initiator solution is applied in a thin (quasi-monomolecular) film to the other surface. The two films are non-air inhibited and may be left open, unbonded for many hours with no adverse effect on subsequent bonding operations.

After mating, the surfaces may be positioned for up to two minutes before the reaction starts and the bond forms. Mild contact pressure is maintained for 5-10 minutes; 75% of the ultimate bond strength is reached within one hour. Lap shear strengths of 3500 psi and peel strengths of 20 pli have been achieved in model systems.

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Compositions of these adhesives are suggested in a number of recent patents (3-12). All of these reactive adhesive patents indicate essentially the same concept: an elastomer is colloiddally dispersed in a monomer, or a monomer/oligomer/polymer solution. The system is then polymerized using a free radical mechanism. What occurs is a rapid, "in situ" polymerization of a (typically) methyl methacrylate system, toughened by elastomeric domains which have been incorporated into the structure by grafting.

Many variations are possible in the nature of the elastomer, polymer, monomer (or monomers), stabilizers, activators and initiators (redox, Schiff's base, etc.) - and in the distribution of the components between the adhesive base and the accelerator portion. Monomers are fairly standard - mostly methyl methacrylate (and methacrylic acid), with softer monomers such as butyl acrylate sometimes used for T_g control. Some systems may use small amounts of polyfunctional acrylates to reduce vapor pressure; however, this can lead to brittle glue lines. Four different elastomer domain materials have been reported: polychloroprene, chlorosulfonated polyethylene, nitrile rubber and urethane (13).

One composition for a reactive adhesive is shown in ref. (9). This patent describes both a conventional two-part, pre-catalyzed adhesive system - and an adhesive/activated primer system. In the latter system, a primer (containing the polymerization catalyst) is first applied to one or both of the surfaces to be joined. Following this, a solution of oligomer/polymer in a vinylic monomer is applied to at least one of the surfaces. The two compositions follow:

<u>US Patent 3,890,407</u>	<u>Examples (weights in grams)</u>	
	1	2
Methyl methacrylate	85	85
Methacrylic acid, glacial	15	15
Ethylene glycol dimethacrylate	2	2
Chlorosulfonated polyethylene*	100	100
	<u>(202)</u>	<u>(202)</u>
Cumene hydroperoxide	6	0.4
N,N-dimethylaniline	2	-
	<u>210</u>	<u>202.4</u>
Accelerator 808**	-	***

- Notes: * Contains 43% Cl and 34 millimoles of sulfonyl chloride per 100 g. polymer
- ** A mixture of butyraldehyde and aniline condensation products
- *** Example 2 is a reactive adhesive system. The accelerator is applied as a primer with a cotton swab to the steel test substrate, and then wiped to a thin film with a piece of cloth.

Another reference (11) describes acrylic/urethane systems - with optional epoxy content (for improved heat resistance). Typical compositions from the patent follow:

<u>US Patent 3,994,764</u>	<u>Examples</u> (parts by weight)	
<u>Component A</u>	I	IV
Polyester-based polyurethane*	<u>33</u>	<u>33</u>
Acrylic acid	33	10
Methyl methacrylate	34	46
Diglycidyl ether of Bisphenol A**	-	6
Benzoyl peroxide	5	5
Hydroquinone	<u>0.1</u>	<u>0.1</u>
	105.1	100.1
 <u>Component B</u>		
Dimethyl aniline	10	10
Methanol	<u>90</u>	<u>90</u>
	100	100

- Notes: * e.g. Estane 5712 (B.F. Goodrich)
- ** e.g. Epon 828 (Shell Chemical Co.)

Component B is sprayed as a very thin film on clean (or oily) steel and allowed to evaporate for 2 minutes. Component A is applied to the other steel substrate in a film thickness of 3-10 mils. The two surfaces are mated under contact pressure. Shear strengths of 3200 psi were achieved, with peel strengths on the order of 25-30 pli.

Most current applications for reactive adhesives are as structural adhesives (16). They compete with high performance epoxies and urethanes and, in certain cases, with anaerobics and cyanoacrylates - in stringent aerospace, aircraft, electrical, electronic, marine, instrument and other uses (1,2,14). The reactive adhesives do not require the sophisticated fixturing usually needed

by the epoxies and urethanes, nor the need for heat cure. Reactive adhesives have the following combination of advantageous properties:

- Simple no-mix application
- Broad applicability to a wide variety of substrates (metal, plastic) with minimal surface preparation
- Tolerance for oil-contaminated surfaces
- Rapid bonding at room temperature
- Excellent bond flexibility
- High peel strength, lap shear strength and impact resistance
- Long open time
- Wide latitude in cure rate
- Ability to bond heat-sensitive substrates
- Low shrinkage during polymerization
- Excellent reproducibility and reliability
- Good heat resistance
- Excellent solvent resistance
- Good low- and high-temperature properties
- Formulating flexibility for specific end use requirements

To date, other than high unit cost, the limitations of reactive adhesives are few; however, these may be critical for certain applications:

- Storage and shipping stability is poor over 20°C. Many of the current products on the market are handled in refrigerated containers, under 4°C.
- Bond line thickness is limited, e.g. 3-10 mils is common, with poor cure over 50-60 mils - because of reduced activator diffusion. However, at high thicknesses, the cost of the adhesive is already excessive.
- Surfaces must be flat; the low viscosity adhesive system has poor gap-filling properties
- Potential (and actual) toxicity problems, due to monomers and activators.

Toxicity. One of the principal deterrents to the growth of reactive adhesives has been the toxicity (and potential carcinogenic nature) of the ingredients:

1. Monomers. Methyl methacrylate and methacrylic acid have well recognized toxicity characteristics as regards inhalation, ingestion and skin contact. Compositions containing large quantities of these materials have been rejected for use on certain production lines, e.g. automotive assembly. (Interestingly, the use of dimethacrylates, as in ref. (4), which have lower vapor pressure, may ease this situation, at the expense of

wetting and oil penetration.)

2. Initiators, Activators, Accelerators. Dimethylaniline, the preferred activator in most patents, is strongly suspected to be a carcinogen. As such, it will be under scrutiny by TSCA - Toxic Substances Control Act. Generically similar materials, e.g. dimethyl-p-toluidine, diisopropanol-p-toluidine, also mentioned in patents, may also subject to similar restrictions. Schiff's bases (such as the Accelerator 808 previously described) are apparently less toxic.

Considerable activity is underway to develop non-toxic activator and accelerator systems for these room temperature curing reactive adhesives. It is of interest to note that progress in analogous systems has been made in dental research - in work on acrylic adhesives for repair and for acrylic dentures. In one of several papers (15), workers describe compositions of complex, exotic acrylic monomers cured with standard and modified Schiff's bases and with complex aromatic amines. Two of the latter are: N,N-dimethyl-sym-m-xylylene and N,N-dimethyl-p-t-butylaniline. Toxicity of these materials is believed to be significantly lower than that of dimethylaniline.

Broad acceptance of reactive adhesives will be contingent upon the development of systems with acceptable toxicity limits. Until then, applications will be limited to those in selected, high performance adhesive markets. However, their technology has important implications for adhesives of the future.

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The Chemistry of Silicone Room Temperature Vulcanizing Sealants

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The first silicone sealants were developed in the early 1940's. These early sealants resembled putties. They contained only a filler and a polydimethylsiloxane fluid; they did not cure to an elastomeric solid. Nevertheless, they offered one main advantage over organic sealants: painting was not required to prevent hardening and weathering.

Elastomeric silicone sealants first appeared in the early 1950's. The first of these, patented by J. F. Hyde of Dow Corning Corporation, was a two-part system consisting of an acid-ended polysiloxane and polysilicate.¹ With this system, materials which cured at room temperature were possible and the term "RTV" (Room Temperature Vulcanizing) was coined. These two-part systems required premixing in appropriate ratios before application and curing.

In the early 1960's two patents were issued on one-component RTV elastomers, one to Rhone-Poulenc (France)² and one to L. B. Bruner,³ Dow Corning (U.S.A.). These patents described a silicone sealant using hydroxy-ended polydimethylsiloxane and acetoxy-silanes. The sealant cured when exposed to moisture in the air. Metal salts of carboxylic acids were added to promote surface cure, eliminating the "tacky" feel of the early materials. This technology set the stage for large-scale commercialization and utilization of silicone sealants. The one-component materials required no mixing before use and could be stored for several months as long as moisture was absent. Although two-component silicone RTV sealants are important in certain applications, one-component sealants account for the greatest share of the silicone sealant market.

Silicone sealants are used today in adhesive, encapsulating, impregnating, mold-making, sealing and other applications. Market growth has been rapid.

The increasing acceptance of silicone RTV sealants is due to their cost effectiveness and proven performance in building construction and OEM (original equipment manufacturer) applications. This performance has won these sealants a reputation as top-of-the

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line materials in the eyes of many architects, designers, contractors, and equipment engineers. This premium status is due to the unique, but uncomplicated, chemistry of their components, especially the chemistry of the silicone polymer backbone.

Generally, silicone sealants possess the best combination of physical strength, cure rate, performance over a wide temperature range, adhesion, sealability and weatherability of any available material.

Many new sealants have surfaced over the past few years with claims of being "siliconized" or being "silicone-like" or "has silicone added", etc. Usually, these "siliconized" sealants contain but a few parts of silicon in the form of silica, silicone fluid or silane coupling agent; therefore, the "new" "siliconized" sealant differs, but slightly from a regular organic sealant and generally in only one performance area. Their overall performance is still inferior to typical silicone sealants. The only way known to gain the unique silicone sealant properties is to use a silicone sealant.

Silicone sealants derive their unique properties from their components. Silicone sealants are generally based on a polydimethylsiloxane fluid or gum. These fluids and gums consist of long-chain siloxane molecules with alternating Si-O bonds, the basic chemical bonds of quartz or sand. These bonds are quite strong⁴ and the barrier of rotation around the Si-O-Si bond is low.⁵ This low barrier of rotation, unmatched in organic chemistry, produces the excellent high and low temperature flexibility of cured silicone sealants as well as their unusual cure characteristics. Alkyl siloxane polymers are generally transparent to ultra-violet radiation, and this transparency contributes to the excellent long-term weatherability of silicone sealants. More detail on all of these properties is summarized later.

The various silicone sealants now available provide a broad spectrum of physical properties. For example, ultimate elongation (as measured by ASTM-D-412) varies from 50% to 1200%; and one commercially available silicone sealant⁶ has a typical value of >1200% with almost 100% recovery. Tensile strengths vary from 100 to 1000 psi, while moduli at 100% extension range from <50 to >500 psi. Durometer hardnesses can range from 15 to 80 (Shore A).

Adhesion characteristics depend on the chemistry of the specific sealant and the substrate to be bonded. For example, acid-liberating (acetoxo) sealants bond quite well to glass and to many aluminums, but should not be used against porous cementitious substances because, with time, a thin powdery film of

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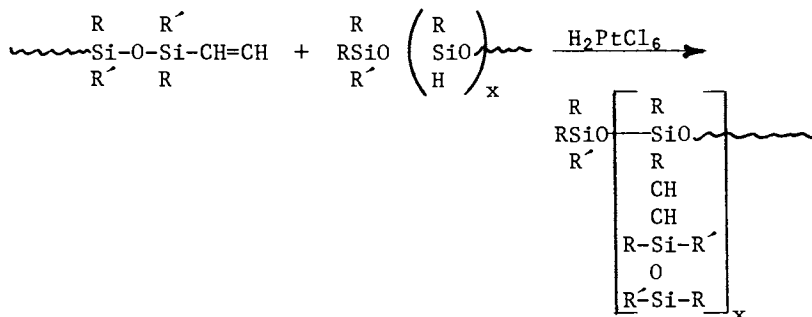
Ca(OCCH₃)₂ may form (see Equation 1) and cause adhesion failure. Neutral and base-liberating sealants bond well to these cementitious substrates with no loss of adhesion with time. Some of the more recent non-acid-curing silicone sealants bond effectively to most common substances. However, the 100% modulus of these sealants tends to be lower than typical acid-curing silicone sealants.

Eq. 1



In both one-component and two-component silicone sealants, the system is crosslinked by using molecules with multi-reactive sites. Either displacement/condensation or addition reactions are used in commercially important sealants. In addition reactions, (Equation 2), a silyl-hydride, $\equiv\text{SiH}$, reacts with an unsaturated site with no evolved by-product. These reactions are catalyzed by a transition metal complex (i.e., H_2PtCl_6). One-component addition systems are technically feasible, but generally require a cure retarder⁷ and heat activation for cure, and are not considered RTV sealants. In these sealants a C-C bond is introduced into the backbone of the system and this could decrease the thermal oxidative stability.

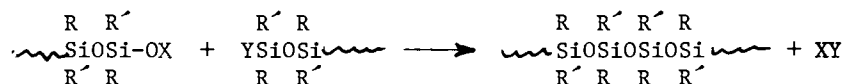
Eq. 2



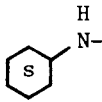
R, R' are generally CH_3 , C_6H_5 , etc.

In sealants using a condensation/displacement cure, a small molecule such as water, alcohol, amine, amide, or acetic acid is released as in Equation 3. These small molecules eventually vaporize leaving only the stable $\equiv\text{SiOSi}\equiv$ bonds formed from the crosslinking, reinforcing and polymerization reactions.

Eq. 3



X is generally H, CH_3 , CH_2CH_3

Y is generally $-\text{OC} \overset{\text{O}}{\parallel} \text{CH}_3$, $-\text{N} \overset{\text{CH}_3}{\overset{\text{O}}{\parallel}} \text{C} \emptyset$, OH, $-\text{N} \overset{\text{CH}_3}{\overset{\text{O}}{\parallel}} \text{C}-\text{CH}_3$, $-\text{OC}=\text{CH}_2$, 

R, R' are generally CH_3 , CH_3CH_2 , \emptyset

It is not practical to attempt to detail the complete chemi-

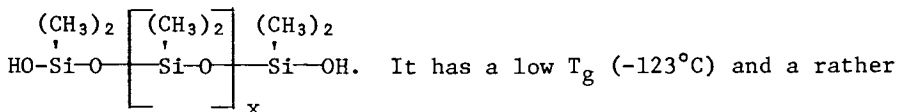
stry of all available silicone RTV sealants. Therefore, we will concentrate on the properties and chemistry of the highest volume products, the one-component silicone sealants.

Composition

A silicone sealant can be as simple as a mixture of polymer, filler and crosslinker. It can be a bit more complex with polymer variations for even greater thermal stability or even lower T_g (glass transition temperature); with a catalyst added to give a drier surface or speed the cure; with a combination of fillers added to enhance elongation or durometer or lower the cost; with other additives for retarding fungus growth or increasing adhesion or making them fire resistant, etc. But, regardless of the additives, the basic performance is derived from the combination of polymer, filler and crosslinker.

Polymer

The basic polymer for the vast majority of the silicone sealants is hydroxy-ended polydimethylsiloxane.



small viscosity change with temperature⁸ as is seen in Figure 1. Typical organic or carbon backbone polymers are affected more by temperature changes because of the higher barrier of rotation around the C-C-bond.²

Sealants made with this silicone polymer are extrudable over a wide temperature range; they can be applied in winter on the Alaskan North Slope or in the heat of an Egyptian summer. When the polymer is then crosslinked into a three-dimensional network to form the cured sealant, the rubberiness, or extensibility, does not change significantly with temperature. A sealant used in Alaska will continue to stretch easily and seal when temperatures are far below freezing.

The silicone polymer backbone is composed of Si-O-Si bonds. This bond is very strong and stable with a bond energy of 87 Kcal/mole. The polymer can tolerate 250°C to 300°C without decomposing.¹⁰ The fully compounded silicone sealant, when cured to a rubber, can withstand 200°C for sustained periods of time with no special additives; and even higher temperatures with polymer modifications and/or heat stability additives.¹¹ The Si-O-Si molecular structure is also transparent to U.V., so silicone sealants are virtually unaffected by weather. Samples of silicone sealants used in exterior construction applications have been tested after 20 years of actual performance. These samples exhibited essentially no change in physical properties or adhesion during that time period.

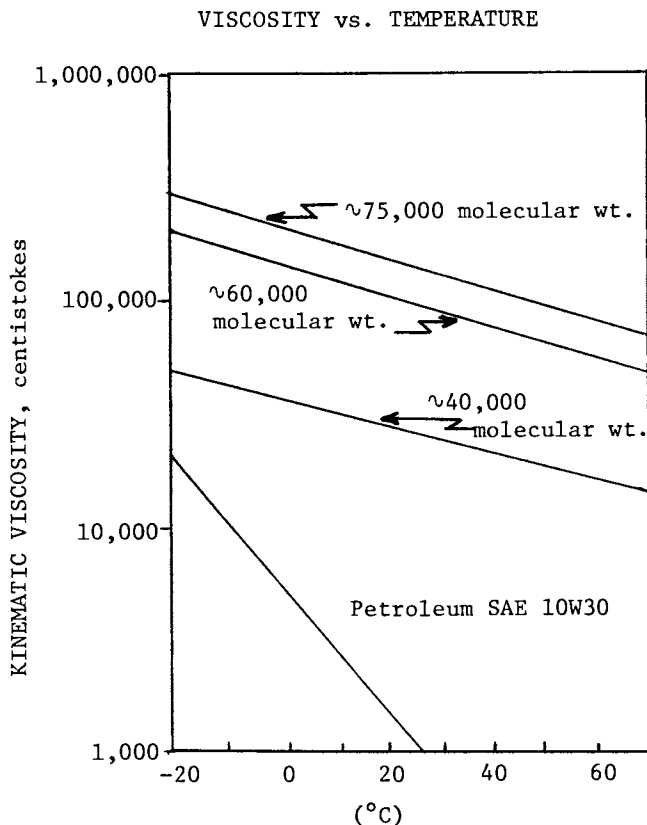
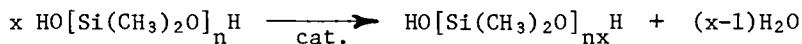


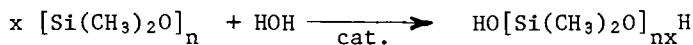
Figure 1. Viscosity vs. temperature

Siloxane polymers are made by condensation (Equation 4) or cyclic polymerization (Equation 5). Low viscosity fluids, higher molecular weight polymers and even very high molecular weight gums may be produced from these reactions. This range of reaction products allows for flexibility in designing the molecular architecture of the sealant.

Eq. 4



Eq. 5



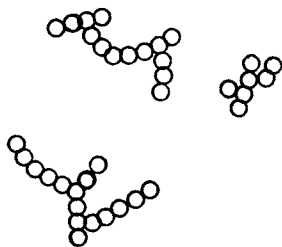
The molecular weight of a polymer chosen for a sealant will influence the tensile and elongation (stress and strain) characteristics of the sealant. Therefore, a sealant formulator can

match polymer molecular weight to the stress-strain performance values he seeks. The molecular weight of a polymer in a sealant will not change the sealant's weatherability or characteristics. Those properties are a consequence of the Si-O-Si backbone structure and exist regardless of molecular weight.

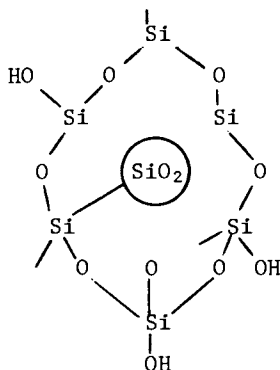
Fillers

Almost all silicone sealant compounds use some percentage of a silica filler for achieving desired tensile strength. Most use a fumed silica which can be illustrated as follows:

MACRO SCALE



MOLECULAR SURFACE OF SILICA



A significant part of the reinforcing nature of fumed silica comes from the particle shape and size but some of the reinforcement comes from the molecular reactions on the surface.

The general molecular structure is SiO_2 , that of sand, with the surface partially covered with SiOH , the same functional group that is on the ends of the polymer. This means that the filler can be incorporated into the polymer network by the same chemistry that ties the polymer ends together.

The tensile strength of a nonfilled, but crosslinked polydimethylsiloxane fluid is about 20 psi. The same polymer/crosslinker mixture with 15% highly functional silica filler could have a tensile strength of >600 psi or a 30-fold increase.

Thus, silica or fumed silica is truly the work-horse filler of the silicone industry. One attribute of silica fillers, when of the proper particle size and properly dispersed, is their transparency in the polymer. This allows the preparation of the clear silicone sealants commonly used. The silicas can either be untreated or treated by any of several methods.^{12,13} This treat-

ment can impart reinforcement with minimum increase in thixotropy.

The filler technology described here is not really unique to silicone sealants but holds true for a variety of sealants. The silica, however, serves a dual purpose in that in addition to reinforcement it also imparts thixotropy (flow control) to prevent the sealant from flowing out of the joints before cure.

Silica, then, is an important part of all or nearly all silicone sealants. If the sealant is clear, silica's probably the only filler. If the sealant is opaque, silica may or may not be present for reinforcement but it's almost always present for flow control. The single drawback to fumed silica is cost; therefore, only a minimum quantity is used and there is a continual search for ways to use less.

Other silica fillers can be used as well. One such filler is ground quartz. This also has SiOH on the surface and it also ties in, but has a much larger particle size, lower surface area and lower relative density of SiOH. Because of this, it gives much less reinforcement on an equal weight basis when used as a replacement for fumed silica.

Non-reinforcing extending fillers are used in many silicone RTV sealant formulations. These include calcium carbonate, carbon blacks, talcs and other inorganic fillers.

The semi-reinforcing fillers and extending fillers are often used to provide bulk and impart desirable handling characteristics.

The filler then contributes to reinforcement, thixotropy, and bulk. Since most of the fillers are mineral-like inorganic materials, they generally don't add or detract from the intrinsic silicone properties for which the sealants are most often sold, such as good electrical insulating properties, weather resistance, heat stability and low temperature serviceability. Organic fillers (polymers, resins, rubbers) have been added to some silicones and indeed enhance certain properties or reduce cost but always at the expense of another property. The property most often sacrificed is thermal stability.

Putting together the proper polymer-filler combination to achieve the desired durometer, tensile, elongation and modulus while keeping the cost as low as possible is one of the proprietary features of each sealant formula.

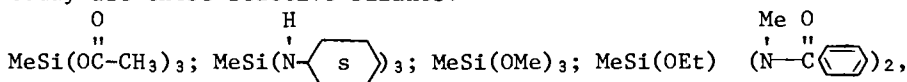
Crosslinkers

The exceptional intrinsic performance of silicone sealants is due to the silicone polymer, the filler, and the unique crosslinking systems.

In this section we will focus on crosslinking systems used in one-part RTV silicone sealants. Most of these systems involve condensation reactions in which a by-product is produced and the by-products are important to final sealant properties. Two-part silicone sealants which are cured by addition reactions, with no by-products, and two-part silicone sealants that cure by condensation are also available, but they are not as commercially

important today as the one-part silicone RTV's and are generally more expensive.

The most common crosslinkers employed in silicone sealants today are these reactive silanes:



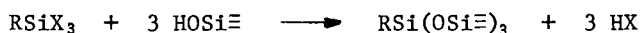
and $\text{MeSi}(\text{O-N=CEtMe})_3$.

All of the above crosslinkers are tri-functional (3 reactive sites) monomers. Patent literature also describes several cure systems which employ tetrafunctional crosslinkers such as

$(\text{EtO})_4\text{Si}$ or $(\text{CH}_3\text{CO})_4\text{Si}$. And finally, there are short polymeric crosslinkers such as $(\text{EtO})_3\text{SiOSi}(\text{OEt})_3$, $\text{X}_3\text{SiOSiRX}_2$, $\text{X}_2\text{RSiOSiX}_2\text{R}$ or $\text{X}_2\text{SiOSiX}_2\text{OSiX}_3$ where R is generally an alkyl and X is any of the functional groups on the crosslinkers mentioned above.

The first crosslinker, $\text{MeSi}(\overset{\text{O}}{\parallel}\text{OCCH}_3)_3$, is the one most commonly used throughout the world today, due to its availability and fast reactivity. It's a good crosslinker producing higher modulus silicone sealants useful in structural applications where acid-induced corrosion is not a problem. (Modulus variations will be discussed later). In all condensation cures the functional group on the crosslinker is released in its protonated form. This has been grossly oversimplified in Equation 6 to illustrate that point:

Eq. 6



(R = alkyl, aryl, etc.; x = functional group such as

$\overset{\text{O}}{\parallel}\text{OCCH}_3$, OMe, etc.).

This correctly implies that all the acetoxy functionality present on the crosslinker will be released during the cure as acetic acid. The acetic acid corrodes copper and some other metals, and also reacts with concrete forming a layer of $\text{Ca}(\text{OAc})_2$, which interferes with the stability of the bond between the sealant and the calciferous surface. Acetic acid also has a pungent odor which some find offensive. Thus, sealants containing this most common crosslinker are not desirable for all applications.

The second crosslinker listed above, $\text{MeSi}(\overset{\text{H}}{\mid}\text{N}-\langle \text{s} \rangle)_3$ is relatively inexpensive and fast to react. It releases cyclohexylamine when it cures. Cyclohexylamine doesn't react with concrete,

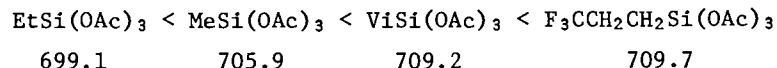
but it does react with and corrode many metals, and some people find the heavy, musty amine odor objectionable.

The third crosslinker listed above, $\text{MeSi}(\text{OMe})_3$, is also readily available. It releases methanol as a by-product, which is non-corrosive to most substrates and is not particularly offensive in odor. This crosslinker is, however, relatively slow to react, and sealants using it as a crosslinker require high concentrations of a special catalyst to hasten cure. Finally, the last two crosslinkers have been recently developed. They present fewer problems, but they are quite expensive.

Each of the above crosslinkers offers certain advantages and disadvantages, and these must be weighed when choosing a cure system. In the silicone sealant market, with its diversity of applications, a single, universal crosslinker is unlikely. Instead a knowledge of market applicability and acceptance, along with cost considerations, determines the cure system for each sealant introduction.


Crosslinker reactivity is a function of the size of the R group on the silane and its electron withdrawing nature.

A few acetoxy-based crosslinkers are listed below in increasing order of reactivity with water or silanols. This reactivity correlates with the electronegativity of the substituents.



Electronegativity or E values¹⁴

The same order exists when acetoxy is replaced by $-\text{ON}=\text{CEtMe}$ or

$-\text{OMe}$ or $-\text{N}-\overset{\text{O}}{\parallel}{\text{C}}-\text{Me}$ . While the data are not available, it can be assumed that the other leaving groups would follow a similar trend.

Other than cure rate, the effect on the sealant performance of changes in the R group on the silane crosslinker is quite small. When R is changed for a 4th functional group [e.g., $\text{MeSi}(\text{OAc})_3$ replaced with $\text{Si}(\text{OAc})_4$ (both commonly used)] the reactivity increases dramatically but so does the crosslink density.

The crosslink density is dependent on the crosslinker functionality and concentration, the chain length of the polymer and the concentration of functional, crosslinkable filler (silica).

The key feature in these reactions is that silane crosslinkers form siloxane bonds, the same as the polymer backbone. Thus, the stability and uniqueness of the silicone polymer has not been significantly disturbed by the crosslinking system. The crosslink density of a sealant system is often modified to achieve a desired stress-strain performance profile.

As this reaction proceeds, the system begins to crosslink. Subsequent sites react and are tied together as more water from the air enters the system. Deep section cure is relatively slow because it is dependent on the diffusion rate of water, and a half inch bead of sealant will take several days to develop full rubber properties.

During the cure (or vulcanization) process, Si-O-Si bonds are formed, and these are the same stable bonds present in the silica filler and polymer backbone. The result is a 3-dimensional network of polymer and silica consisting exclusively of siloxane bonds.

Thus, the stability of the silicone is assured. The $\text{MeSi}(\overset{\text{O}}{\parallel})\text{CCH}_3)_3$ crosslinker in this example can be replaced with any of the crosslinkers mentioned earlier. The result is the same crosslinked network.

The sealants cure from the outside in as the moisture in the air contacts the sealant and promotes crosslinking. A "skin" will form on the sealant surface, and this skin will proceed to become tack-free with soft, pliable, uncured sealant below it. The cure rate will then slow, since it is dependent on moisture permeation through the exterior skin. The skin will increase in thickness until the entire sealant bead has cured.

Silicone polymers have a naturally high degree of free rotation and a large void volume. This allows for a cured elastomer material which is very permeable to water in the vapor form, yet completely hydrophobic to liquid water. Cure proceeds rapidly under most conditions. Water vapor will readily penetrate the skin so that a $\frac{1}{4}$ inch bead develops approximately 80% of its properties (in its cured state) in 24 hours.

The statements made above apply regardless of the crosslinking system used. When the crosslinker is changed, the skin formation time and the tack free time may change but the effect on the deep section cure rate is minimal, since the rate of water permeation through the cured skin is generally the rate-controlling factor in the cure of one-component RTV silicone sealants.

In terms of environmental conditions, the cure rate is dependent on the temperature and relative humidity during the cure process. A silicone sealant used at -45°C will take several days to become tack free, while the same sealant takes 30 minutes at 23°C , 50% relative humidity and 8 minutes at 38°C , 100% relative humidity. The time it takes to develop a tack-free surface will also vary with the type of crosslinker utilized. With other crosslinkers mentioned earlier, sealants may develop a tack free surface in as little as six minutes or as long as one hour, given similar cure conditions.

An interesting note in the development of silicone sealants is that their high rate of water vapor transmission has been exploited to make a vapor permeable (breathable) coating for roofs and other surfaces. This sealant is applied in the form of a solvent dispersion to attain the necessary consistency for easy application.

The chemistry just outlined produces silicone sealants which cure to a fairly tough, resilient rubber. Generally, sealants made by the above route are the higher modulus, strong silicone sealants used in products like silicone glazing sealants, silicone adhesives and silicone bath tub caulk.

For many applications these sealants are too high in modulus. For places sealed with silicone sealants that see tremendous movement (>25% expansion and contraction), like expansion joints in highways or buildings, the toughness of the above sealant results in undue stress on the bond line at high elongation. In these applications, either the sealant will fail adhesively or the sealant will pull the concrete surface (or similar surface) apart.

Low and Very Low Modulus Sealants

The way chosen by most compounders to produce low modulus sealants is to increase the length of the polymer chain, but this approach presents problems. When the fluid polymer is changed to a viscous polymer and again mixed with a filler, the sealant is very thick and stiff and doesn't extrude easily from the tube. This problem is remedied through the addition of low molecular weight, nonreactive fluid softeners. This works quite well and the resultant sealant has a lower crosslink density and stretches easily, failing cohesively when the stress is great. Ultimate elongation in an ASTM tensile bar increases from 400% or 500% to 600% or 800%. This solution has a serious drawback, however. No softener has yet been invented for silicones that doesn't bleed and cause staining on some building surfaces.

Recently Dow Corning Corporation developed a one-package sealant (the familiar cartridge) and General Electric developed a two-package sealant (mix in pails on site) which skirts these problems. The approach is basic: compound with relatively low molecular weight polymer, so that the extrusion rate is satisfactory and add a chain extender to the system. The chain extender chosen must be one which builds the polymer chain length during the cure and before the crosslinker ties into the system. The result is a sealant with very long polymer chains between crosslinks and no softener.

The chemistry of such a chain extended system is very complex. The key to success is utilization of a chain extender which closely matches the reactivity of the crosslinker. Both must be sufficiently sensitive to react with water from the air and then condense silanols so that a dry surface cure results.

If the chain extension is faster than the crosslinking activity, the system builds to a gum with very low crosslink density and a gummy, sticky product results. If the crosslinking is faster than the chain extension, then a tough, high modulus, low elongation sealant results.

The details of these systems are still quite proprietary but it's sufficient to say that controlled crosslinking is possible. Very low modulus, high elongating sealants are available which

have all the performance expected of a silicone in terms of weathering and stability. The previous 800 to 1000% extension limit for sealants has been surpassed.

The sealants made by chain extension have a typical elongation in the ASTM tensile bar of 1600%. This translates to 50% compression and >50% extension in an expansion joint with no bleed. This offers tremendous design flexibility to the architect or construction engineer.

The bottom line is this: the building owner or other sealant user can now choose the modulus of silicone he needs. He can have high modulus for an adhesive application, medium modulus for general sealing and glazing, and low modulus with very high elongation for applications such as expansion joints and highway joints. Each class of silicone sealant has the typical durability characteristics of silicones since the crosslinking and/or chain extension forms only stable siloxane bonds.

Long Term Value of Silicone Sealants

Thus far we have addressed many of the initial properties of silicone sealants and the chemistry that leads to those properties. Many of the long term properties of silicone sealants can be summed up in the general term, weatherability.

Weatherability implies:

Resistance to Oxidation, Especially Ozone Attack. Silicone sealants maintain their performance after 50,000 hours in an ozone rich atmosphere, surpassing all other sealants.¹⁵ This property results from the inorganic character of the basic chemical bonds. This inherent inertness is one reason that silicone sealants excel in outdoor applications.

Resistance to Water Damage. Water repellency is not unique to silicone sealants. Many organic materials exhibit similar contact angles with water; but, silicones have the ability to maintain this property longer due to a molecular orientation of the siloxane molecule to a particular substrate. Essentially, the hydroxy groups on the substrate either bond to the residual hydroxy-ends of the siloxane system or hydrogen-bonds are formed with the siloxane units. This can cause the molecule to orient itself such that the organic side groups (i.e., methyl) are displaced toward the outer surface, thereby exposing the hydrophobic portion. This orientation is made possible by the low barrier of rotation around the siloxane, =Si-O-Si= bond.

Resistance to Photochemical Reaction Initiated by U.V. Light (the sun). With the introduction and acceptance of silicone sealants the stress tests have had to be made more stringent. Filters are removed from the Weather-O-Meter tests so some change can be noted in 6000 hours.¹⁶ Previously, sealants were considered good if performance changes were not significant after 250 hours. In fact, silicone sealants are now used to seal the test chamber of weather-simulating machines.¹⁵

Resistance to Hardening or Cracking. Fully cured sealants

made soft and pliable by the addition of solvent-like plasticizers crack and harden as the solvent evaporates. This hardening and cracking can also be a consequence of U.V.-induced free-radical polymerization at the surface. More crosslinks are introduced and the sealant hardens, becomes less rubbery and cracks when stress is applied. Silicones contain little or no volatile plasticizer and don't easily react to U.V. radiation. Twenty years of outdoor tests in Florida shows no hardening or cracking.¹⁷

Usable in Cold Temperatures. Silicones are extrudable from the pail or cartridge at temperatures down to -45°C with no special heating required. After it cures, the rubber seal formed is flexible, will expand and contract and continue to seal at -45°C . Most other sealants become stiff and brittle before -30°C is reached. This means when joints have moved to their ultimate dimensions and stress is maximum, silicone sealants will still perform.

Usable in Hot Climates. Most organic sealants perform satisfactorily when temperatures are warm. But silicones remain effective in such hot locations as the sandwich panel of a solar collector or around heat ducts or hot pipes. However, the designer must choose the right silicone, since some perform up to 150°C , some to 200°C and 250°C . These temperatures can be contrasted to the 70°C to 120°C operating maximum of nonsilicones.

In addition to their excellent weatherability and the benefits that implies, silicones are sometimes the sealant of choice because of their controllable cure rate (it can be fast or slow), or adhesion qualities (silicones can bond glass together to form an aquarium with no other support or reinforcement necessary or bond glass in a building with no other supports necessary), or its nontoxicity (many silicones have FDA, USDA clearance), or its non-conductive electrical qualities.

Silicone sealants retain their excellent adhesion properties and their excellent nonconductive or insulation properties upon aging under heat and in harsh environments, again because of the stable bonds formed internally and to the substrate. The limits have not been fully established, but actual in-use applications have surpassed 15-20 years without a significant change.¹⁷ This results in a confidence factor that is very important to the quality specifier, engineer or owner who is interested in cost-effective construction with long-term usability.

All the properties mentioned above are the result of the intrinsic qualities of the silicone or silane components of the sealant and the chemistry of the formulation. These intrinsic qualities cannot be duplicated in organic sealants with or without silicon-containing additives. The chemistry of silicone sealants is, to a large degree, a balance between the chemistry of sand or quartz and the chemistry of hydrocarbon side groups. This unique balance of chemistries has resulted in a well-deserved "top-of-the-line" reputation for silicone sealants.

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Technology of Polysulfide Sealants

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Polysulfides, in the liquid polymer form, have been used in sealants since the early fifties. Compounders have been able to devise many uses for these highly versatile reactive liquid polysulfides. Systems based liquid polysulfides have properties of solvent resistance, predictable cure, and excellent adhesion to many substrates. Polysulfide polymers are easily formulated to provide properties and application qualities that allow the compounds to be used as sealants, adhesives and coatings. In addition, compounds based on polysulfides have shown lasting durability in exposure to many environments. They are the oldest, high-performance building sealants used in the world. A property of polysulfide polymers of interest to compounders and end-users alike is their ability to stress-relax, thereby maintaining adhesion to substrates and minimizing stresses. The long lasting performance of polysulfide compounds is attributed to the physical and chemical properties of the polymer.

Today, compounds based on liquid polysulfide polymers are used as sealants to seal moving joints. Polysulfide compounds are the standard of performance of the edge seal used in insulating glass. Outstanding solvent resistance has made them the choice for sealing integral wing gas tanks on commercial and military aircraft. In combination with epoxies, polysulfides produce tough casting and potting compounds. They have been used to seal automotive windshields and are still called upon to seal many sidelights and backlights.

In addition to the liquid polysulfides, polysulfide millable gum elastomers have been used for many years with conventional rubber processing equipment. Compounds based on solid elastomers are being used in the manufacture of paint spray hose, rollers, and printing blankets for the graphic arts industry. New applications for these versatile materials are still being developed.

The first polysulfide elastomers were developed in 1927 by Dr. J.C. Patrick, who, in search for a means to make anti-freeze, reacted an organic dichloride with sodium polysulfide, and produced the first synthetic rubber manufactured.

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The original material, which was based on the reaction of ethylene dichloride with sodium polysulfide, was a solid elastomer. Generally, this chemistry yields products that tend to be difficult to process and the high temperatures needed to band and compound them result in a foul smelling material.

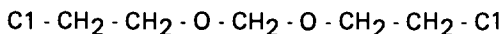
A process was developed in 1943 to make polysulfides as a reactive liquid polymer with mercaptan-end groups. These terminals lend themselves readily to oxidation to high molecular weight elastomeric compounds. As a result, the liquid polymers could be compounded with greater facility than the solid elastomers.

After examining many potential dichloride monomers, *bis*-2-chloroethyl formal was selected for the manufacture of the liquid polymers; the result was a polymer with great versatility at reasonable cost. The liquid polymer when reacted with oxidizing agents displays outstanding resistance to solvents and ozone, and maintains its flexibility at temperatures as low as -65° F (-54°C). As this technology evolved, a family of polymers was developed that provided compounding flexibility by giving different viscosity and modulus properties to meet the specific needs of the marketplace. This was accomplished by introducing a small mole fraction percent of 1,2,3-trichloropropane.

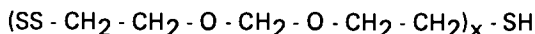
The liquid polymer is reacted as a suspension or emulsion; the high molecular polymers are then split using sodium sulfahydrate and sodium sulfite to produce polymers of controlled molecular weight and viscosity.

Liquid polysulfide polymers range from a molecular weight of 1000 to 8000 with crosslinking ranging from 0 to 2%.

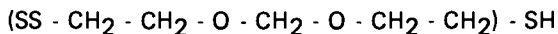
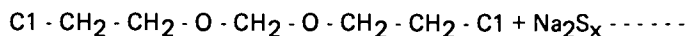
The monomer of greatest utility is *bis* chloroethyl formal.



This is reacted with sodium polysulfide (Na_2S_x) resulting in the polymer represented by the structure:



The equation showing the reaction to produce polysulfide is as follows:



x is the sulfur content or rank of the polymer which varies from 2 to 4; (the most useful rank for liquid polysulfides is 2).

PROPERTIES OF LIQUID POLYMERS

Liquid polysulfide polymers as manufactured by THIOKOL CORPORATION under the tradename LP are available in a series of viscosities and cross-link densities that influence the application areas for each polymer type. See Table 1.

TABLE I
PROPERTIES OF LP LIQUID POLYSULFIDE POLYMERS

Specification Requirements	LP-31	LP-2	LP-32	LP-12	LP-3	LP-33
Color—MPQC-29A	150 max.	150 max.	100 max.	80 max.	50 max.	30 max.
Viscosity—poises 77°F (25°C)	950 to 1550	410 to 525	410 to 525	410 to 525	9.4 to 14.4	15 to 20
pH range	6.5 to 7.5	6.5 to 7.5	6.5 to 7.5	6.5 to 7.5	6.0 to 8.0	6.0 to 8.0
Moisture content, %	0.12 to 0.22	0.12 to 0.22	0.12 to 0.22	0.12 to 0.22	0.1 max.	0.1 max.
Mercaptan content, %	1.0 to 1.5	1.50 to 2.00	1.50 to 2.00	1.50 to 2.00	5.9 to 7.7	5.0 to 6.5
General Properties						
Sp.G at 25°/25°C	1.31	1.29	1.29	1.29	1.27	1.27
Average molecular weight	8000	4000	4000	4000	1000	1000
Refractive index D_D^{20}	1.5728	—	1.5689	—	1.5649	—
Pour point, °F (°C)	50 (10)	45 (7)	45 (7)	45 (7)	-15 (-26)	-10 (-23)
Flash Point (Pensky-Marten CC), °F (°C)	437 (225)	406 (208)	414 (212)	406 (208)	345 (174)	367 (186)
% Cross-linking agent	0.5	2.0	0.5	0.2	2.0	0.5
Low temp. flex., (G 10,000 psi), °F (°C) (703 kg/cm ²)	-65 (-54)	-65 (-54)	-65 (-54)	-65 (-54)	-65 (-54)	-65 (-54)

Polymers of approximately 400-500 poises are used most frequently in sealants and adhesives, while the lower viscosity polymers are most frequently used for flexibilizing epoxy polymer casting compounds.

Viscosities of liquid polymers range from 10 poises for LP-3 to 1100 poises for LP-31. A straight line relationship between viscosity and molecular weight can be drawn from the following equation:

$$\text{Log } N = \text{Log } K + N \log \overline{M}_n$$

$$n = 2.75 \pm .03 \quad K = 5 \pm 1 \times 10^{-8}$$

FIGURE 1 illustrates this relationship.

There is a sharp viscosity/temperature dependence.

Viscosity for a typical polymer, LP-32, as a function of temperature is illustrated in FIGURE 2.

Polysulfide polymers are unique in their ability to internally relieve stress in cured polymer systems by interchange reactions between the mercaptans and the disulfide linkages. The stress decay of crosslinked rubbers follows the equation:

$$F(t) = F(o) + \text{Exp}^{-t/\tau}$$

$$F(t) = \text{final stress} \quad \tau = \text{relaxation constant}$$

$$F(o) = \text{initial stress} \quad t = \text{time}$$

For polysulfides at 176°F (80°C) the relaxation constant is shown for different curative systems. (See Table II). This ability of polysulfides to relieve stress is valuable in maintaining adhesion in joints where movement must be accommodated. Polysulfide polymers which are based on *bis* chloroethyl formal show no evidence of crystallization at low temperatures and have a glass transition temperature of -74°F (-59°C).

COMPOUNDING OF POLYSULFIDES

Polysulfides are compounded with many materials to impart the properties required in a specific application.

FILLERS

Fillers increase the strength of the compound and impart useful rheological properties while reducing the compound cost. Table III and FIGURE 3 (using data based on LP-32 polymer) illustrate typical effects on the properties of filled compounds.

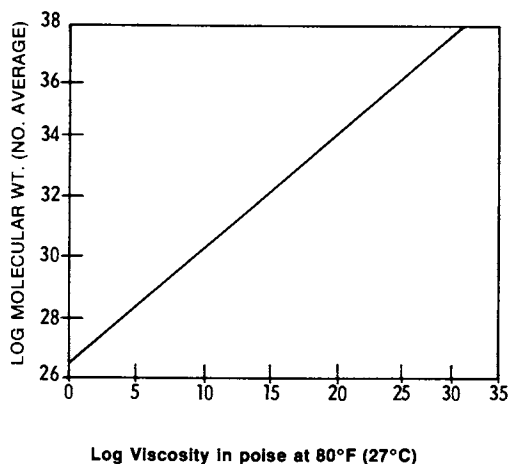


Figure 1. Viscosity-molecular weight relationship for bis-2-chloroethyl-formal derived products LP-3, LP-2, LP-33, LP-12, LP-32, LP-31 for which $\log \% SH = 3.82 - \log M_n$.

TABLE II

Chemical Relaxation Time τ_{ch} at 176°F (80°C) for
Polysulfide Rubber Cured with
Different Chemical Agents

CURING AGENT	Weight of Curing Agent per 100 parts of polymer	τ_{ch} , hours
Lead peroxide	7.3	0.68
Lead peroxide plus 5 days of heating at (176°C) 80°F	7.3	15
Manganese dioxide plus morpholine	18.9 ± 2.0	32
2,4-Toluene diisocyanate plus N-methyl-2-pyrrolidone	7.0 ± 0.5	200

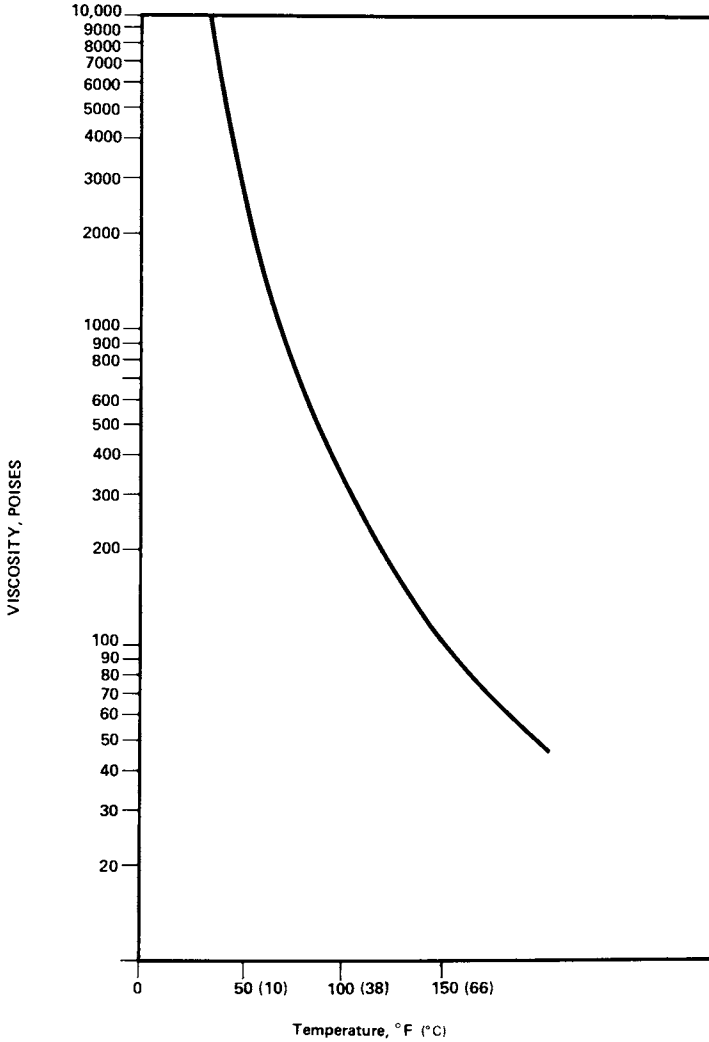


Figure 2. Change in viscosity of LP-32 polymer with temperature

Fillers significantly increase the tensile properties of polysulfides. This is related to the type of filler, its particle size and the type of cure. A balance of filler particle size and type is required to achieve the optimum wetting and rheology to produce the most cost effective compounds. Consideration must be given to the pH of the filler, since this affects shelf stability or well as cure properties of the compound. Fillers must be inert and insoluble in the sealants's environment. Care must be taken that the filler is adequately dispersed to ensure optimum thixotropy and barrier properties.

Classes of Fillers

The variety of fillers compared in Table IV are selected from various classes used in compounding liquid polysulfide polymers. It appears that particle size has the greatest effect on physical properties within a single type of filler. Other properties such as surface area and surface coatings will effect the viscosity and thixotropy of polysulfide polymer compound, while high pH fillers can result in increased viscosity after a period.

The best method for determining the effect of a filler on a compound is to study the change in viscosity and cure rate. If test results must be obtained quickly, testing can be expedited by storing the base of the compound for short periods of time at a temperature of 158°F (70°C). Test results can then be compared with the original test samples.

The classes of fillers used in formulating polysulfide sealants include:

Carbon Blacks - Two classes of carbon blacks most frequently used in compounding liquid polysulfide polymers are the furnace and thermal blacks. SRF#3 and Sterling MT are fillers typical of these two classes of carbon blacks. Channel blacks are not used in polysulfide compounds. Their low pH considerably retards the rate of cure and the very large surface area greatly restricts volume loading.

Calcium Carbonates - Calcium carbonate fillers are available in a wide range of particle sizes and can be obtained as wet or dry ground limestone, chalks, or precipitated carbonates. The carbonates with a coarse particle size reinforce slightly and increase viscosity slightly. However, they are used to adjust rheology and lower the cost of a compound. The coarse and fine carbonates are generally used together.

Use of fine particle size precipitated carbonate filler provides good reinforcing properties and also increases viscosity. Some fine particle size precipitated carbonates are coated with stearic acid to improve wetting. These fillers are desirable where a high pH is required in a compound. Fine particle size coated precipitated carbonates improve thixotropy of a compound.

Clays - Most commercial clays are classified as hydrous. They are undesirable for use in liquid polysulfide base compounds because of their low pH. However, calcined clays have been found to be satisfactory for use in polysulfide compounds because they are less acidic. The best use of calcined clay fillers is in conjunction with precipitated calcium carbonate fillers to produce a compound with a relatively neutral pH value. For example, calcined clay of the type similar to Iccap K has given good results.

TABLE III

Effect of Fillers on Cured Compositions Based on LP-32 Polymer
(Cast Sheets Cured 7 Days at 70-72°F (21-22°C) and 44-48% RH)

Type	Formulation	PbO ₂ Cure	CaO ₂ Cure	MnO ₂ Cure
Part A	LP-32 Polymer	100	100	100
	Filler	As noted	As noted	As noted
	Stearic Acid	0.5	---	0.5
	Sulfur	0.1	---	0.1
	Microcel E	---	3	---
	Water	---	6	---
Part B	PbO ₂	7.5	---	---
	TP-680	7.5	18	---
	CaO ₂	---	12	---
	Calcium Hydroxide	---	2.5	---
	MnO ₂	---	---	7.5
	Santicizer 278	---	---	7.5

Filler Level	Tensile psi (kg/cm ²)			100% Modulus psi (kg/cm ²)			200% Modulus psi (kg/cm ²)		
	0	30	50	0	30	50	0	30	50

Filler - Medium Thermal Carbon Black

PbO ₂ Cure	125 (8.8)	260 (18.3)	305 (21.4)	71 (5.0)	125 (8.8)	153 (10.7)	93 (6.5)	161 (11.3)	205 (14.4)
CaO ₂ Cure	120 (8.4)	185 (15.1)	215 (13.0)	68 (4.8)	82 (5.7)	86 (6.0)	90 (6.3)	117 (8.2)	125 (8.8)
MnO ₂ Cure	130 (9.1)	205 (14.4)	280 (19.6)	91 (6.4)	155 (10.9)	232 (16.2)	115 (8.1)	199 (13.9)	----

Filler - Semi Reinforcing Furnace Carbon Black

PbO ₂ Cure	125 (8.8)	470 (32.9)	505 (35.4)	71 (5.0)	170 (11.9)	210 (14.7)	93 (6.5)	236 (16.5)	305 (27.0)
CaO ₂ Cure	120 (8.4)	425 (29.8)	575 (40.3)	68 (4.8)	145 (10.2)	210 (14.7)	90 (6.3)	221 (15.5)	362 (25.3)
MnO ₂ Cure	130 (9.1)	390 (27.3)	445 (31.2)	91 (6.4)	218 (15.3)	355 (24.9)	115 (8.1)	335 (23.5)	----

Filler - Ultra-Fine Precipitated Calcium Carbonate

PbO ₂ Cure	125 (8.8)	180 (12.6)	270 (18.9)	71 (5.0)	104 (7.3)	138 (9.7)	93 (6.5)	120 (8.4)	150 (10.5)
CaO ₂ Cure	120 (8.4)	175 (12.3)	205 (14.4)	68 (4.8)	132 (9.2)	149 (10.4)	90 (6.3)	152 (10.5)	169 (11.8)
MnO ₂ Cure	130 (9.1)	145 (10.2)	165 (11.6)	91 (6.4)	105 (7.4)	115 (8.1)	115 (8.1)	125 (8.8)	130 (9.1)

300% Modulus psi (kg/cm ²)			400% Modulus psi (kg/cm ²)			500% Modulus psi (kg/cm ²)			Elongation %			Hardness Shore A		
0	30	50	0	30	50	0	30	50	0	30	50	0	30	50
112	195	248	----	227	276	----	250	293	360	550	620	34	45	50
(7.8)	(13.7)	(17.4)		(15.9)	(19.3)		(17.5)	(20.5)						
111	155	158	----	180	194	----	-----	-----	350	420	470	30	36	39
(7.8)	(10.9)	(11.1)		(13.6)	(12.6)									
----	----	----	----	-----	-----	----	-----	-----	290	260	190	39	49	58
112	298	385	----	342	440	----	378	477	360	750	620	34	53	61
(7.8)	(20.9)	(27.0)		(23.9)	(30.8)		(26.5)	(33.9)						
111	297	525	----	373	-----	----	425	-----	350	500	340	30	48	55
(7.8)	(20.8)	(36.8)		(26.2)			(29.8)							
----	----	----	----	-----	-----	----	-----	-----	290	280	180	39	55	68
112	135	165	----	149	180	----	167	195	360	500	800	34	43	49
(7.8)	(9.5)	(11.6)		(10.4)	(12.6)		(11.7)	(13.7)						
111	170	185	----	-----	201	----	-----	-----	350	330	420	30	48	53
(7.8)	(11.9)	(13.0)			(14.1)									
----	----	150	----	-----	-----	----	-----	-----	290	290	350	39	45	50
		(10.5)												

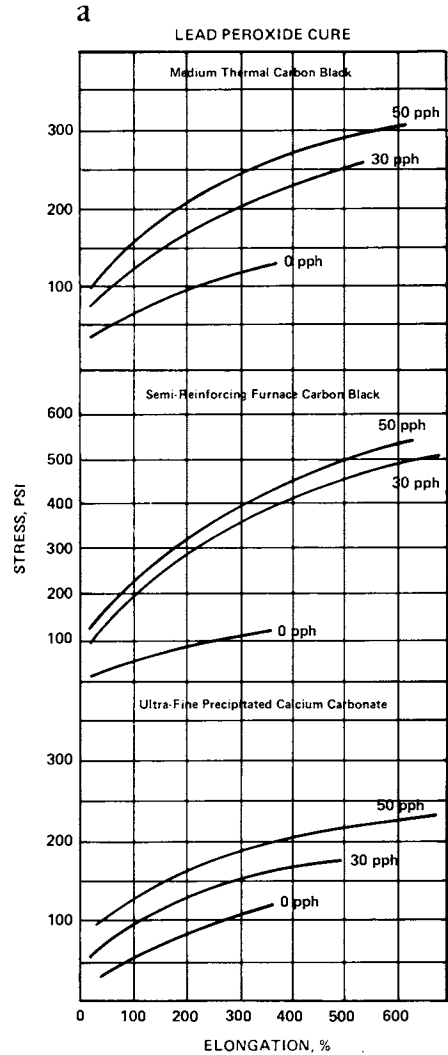


Figure 3. (a,b,c) Effect of fillers on cured compositions based on LP-32 polymer

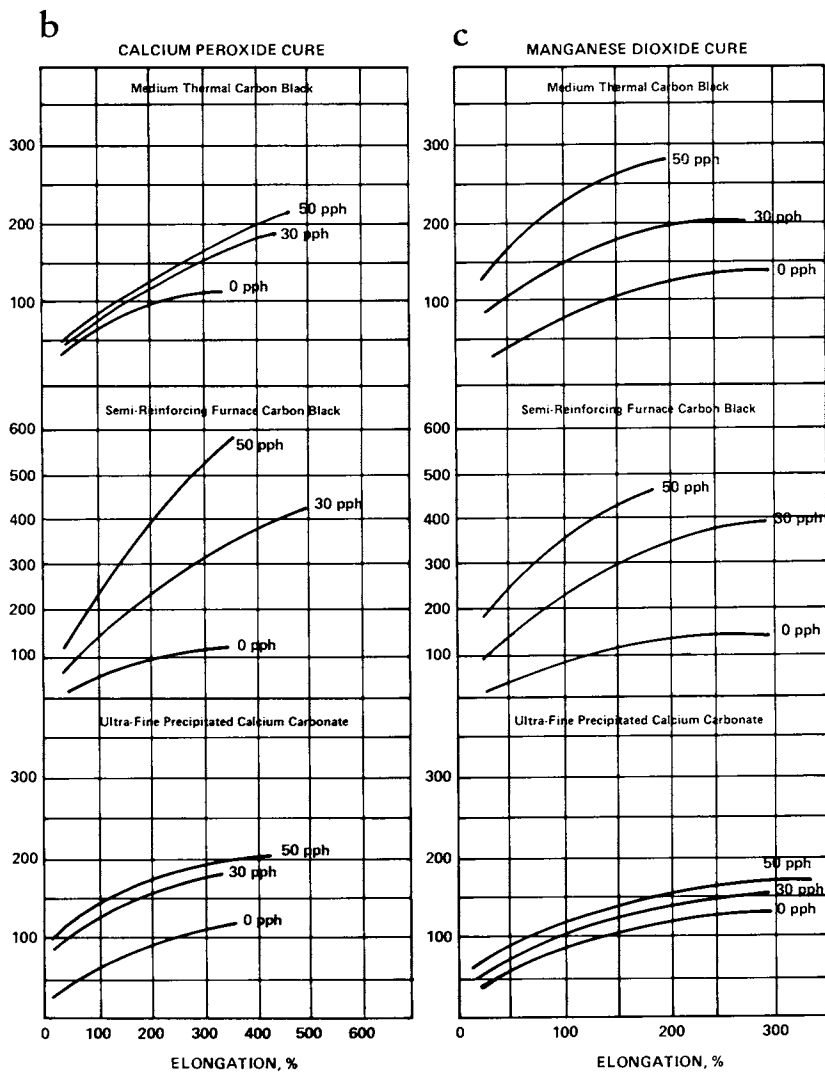


TABLE IV
Mineral and Black Fillers for LP Liquid Polysulfide Compounds

Filler	Composition	Spec. Gr.	Particle Size (Microns)	pH	% Free Moisture
Pelletex (SRF #3)	Pelleted semi-reinforcing furnace	1.80	0.08	8.5	1.0
Sterling MT	Medium thermal	1.80	0.46	9.5	0.5
Calcene TM	pp'td calcium carbonate (coated)	2.55	0.07	9.0-9.7	0.4
Multiflex MM	pp'td calcium carbonate	2.65	0.06	9.0	0.5
Witcarb RC	pp'td calcium carbonate (coated)	2.55	0.06	7.3-7.5	2.0
York White	Dry ground limestone	2.71	5-10	9.4-9.7	—
Calwhite	Wet ground calcium carbonate	2.71	5	9.0-9.5	—
OMYA BSH	Surface-treated chalk	2.70	1-3	7.0	0.1
	(1% stearic acid)				
Icecap K	Anhydrous calcine clay	2.63	1.0	5.0-6.0	0.5
Cabosil	Fumed silica-99% SiO ₂	2.2	0.015	3.5-4.2	1.0
HiSil 233	pp'td silica-87% SiO ₂	2.0	0.02	6.5-7.3	6.0
Permolith 40M (Lithopone)	29% Zinc sulfide	4.3	99.8% thru	8.0-9.0	—
	71% barium sulfate		325 mesh		
Bianc Fixe	pp'td barium sulfate	4.4	0.18	8.8-9.5	0.3
Titanox 2020	Titanium dioxide	4.1	0.3	7.0-8.0	0.7
Superlith XXXHD	Pure zinc sulfide	4.1		6.8-7.8	—

Miscellaneous Fillers. Silica and silicate fillers, such as Cabosil and Hi-Sil 233 are generally used as thickening agents in amounts of 2 to 10 parts per 100 parts of polysulfide polymer. When the silicate has a high pH value, care should be used in selecting this type of filler since it may affect package stability.

Titanium dioxide fillers of the rutile type are considerably better for polysulfide compounds than fillers of the anatase type. Titanium dioxide is generally used to impart whiteness or give better color stability to light colored compounds. These fillers, represented by Titanox 2020, are preferred for use in polysulfide compounds. Generally, the level for loading is in the range of 10 to 25 parts.

Other fillers which have been found to be satisfactory for use in polysulfide compounds are zinc sulfide, lithopone and barium sulfate. These fillers have the highest specific gravity and are higher in cost, but have been used in special compounds for dental impression and cold molding applications.

PLASTICIZERS

Plasticizers improve the working properties of the compound while lowering its modulus. Control of modulus is extremely important in an elastomeric sealant to ensure that the adhesive strength of the compound does not exceed the structural strength of the substrate to which it is applied.

The amount or type of plasticizer used must be compatible in the cured sealant and its volatility should be adequate for its intended use. Table V and FIGURE 4 show the effect of three typical plasticizers on the properties of a polysulfide compound.

CURATIVES

The mercaptan terminated liquid polymers are converted to high molecular weight disulfide elastomers using a variety of oxidizing agents. Cure rate can be controlled by the use of additives to the base compound or accelerator.

The most common compounds used are based on the higher valence metal oxides such as lead and manganese. Zinc peroxide, calcium peroxide or some chromates are also useful in curing polysulfide compounds and are generally used with higher molecular weight polysulfides, with mercaptan content of 2% or less. For the lower molecular weight polymers, except where specific properties are required, the metal oxides and chromates result in fast cures. A curative such as paraquinone dioxime gives a more controllable cure. The cure rate of liquid polymers is affected strongly by moisture; increasing the moisture content of the compound generally speeds the cure time. (Table VI). Though not normally considered a curative, amine catalyzed epoxy reactions result in very useful compounds.

Sulfur in some polysulfide compounds has a significant effect on the cure rate (Table VII) generally resulting in tougher, more resilient materials since the sulfur converts metal mercaptides to disulfide linkages.

A summary of the commonly used curatives is found in Table VIII.

TABLE V

Effect of Plasticizers on Calcium Carbonate Filled Compositions
(Cast Sheets Cured 7 Days at 70-72°F (21-22°C) and 44-48% RH)

Type	Formulation	PbO ₂ Cure	MnO ₂ Cure
Part A	LP-32 Polymer	100	100
	Ultra-Fine Precipitated CaCO ₃	50	50
	Stearic Acid	0.5	0.5
	Sulfur	0.1	0.1
	Plasticizer (Type and amount as noted in table below)		
Part B	PbO ₂	7.5	...
	MnO ₂	...	7.5
	TP-680	7.5	...
	Santicizer 278	...	7.5

Lead Peroxide Cure

Plasticizer in Part A Amount of Plasticizer, pbw	TP-680		Flx0012		Santicizer 261	
	15	30	15	30	15	30
Tensile, psi (kg/cm ²)	200 (14.1)	165 (11.6)	220 (15.4)	185 (13.0)	220 (15.4)	160 (11.2)
100% Modulus, psi (kg/cm ²)	85 (6.0)	60 (4.2)	100 (7.0)	75 (5.3)	88 (6.2)	64 (4.5)
200% Modulus, psi (kg/cm ²)	98 (6.9)	71 (5.0)	124 (8.7)	96 (6.7)	111 (7.8)	81 (5.7)
300% Modulus, psi (kg/cm ²)	106 (7.4)	80 (5.6)	136 (9.5)	111 (7.8)	125 (8.8)	92 (6.4)
400% Modulus, psi (kg/cm ²)	116 (8.1)	88 (6.2)	147 (10.3)	123 (8.6)	135 (9.5)	99 (6.9)
500% Modulus, psi (kg/cm ²)	126 (8.8)	96 (6.7)	158 (11.1)	132 (9.2)	145 (10.2)	108 (7.6)
Elongation, %	965	1060	880	920	985	995
Hardness, Shore A	40	34	40	36	40	34

Manganese Dioxide Cure

Plasticizer in Part A Amount of Plasticizer, pbw	TP-680		Flx0012		Santicizer 261	
	15	30	15	30	15	30
Tensile, psi (kg/cm ²)	115 (8.1)	70 (4.9)	175 (12.3)	165 (11.6)	142 (9.9)	130 (9.1)
100% Modulus, psi (kg/cm ²)	76 (5.3)	50 (3.5)	89 (6.2)	75 (5.3)	73 (5.1)	50 (3.5)
200% Modulus, psi (kg/cm ²)	87 (6.1)	57 (4.0)	100 (7.0)	85 (6.0)	87 (6.1)	61 (4.3)
300% Modulus, psi (kg/cm ²)	98 (6.9)	64 (4.5)	116 (8.1)	97 (6.8)	102 (7.1)	75 (5.3)
400% Modulus, psi (kg/cm ²)	105 (7.4)	68 (4.8)	135 (9.5)	110 (7.7)	123 (8.6)	89 (6.2)
500% Modulus, psi (kg/cm ²)	...	69 (4.8)	159 (11.1)	130 (9.1)	142 (9.9)	106 (9.4)
Elongation, %	460	805	570	680	500	625
Hardness, Shore A	41	32	43	37	39	31

NOTE: To obtain plasticizer control data, see Table III (50 pph Ultra-Fine Precipitated Calcium Carbonate) for PbO₂ and MnO₂ cures respectively.

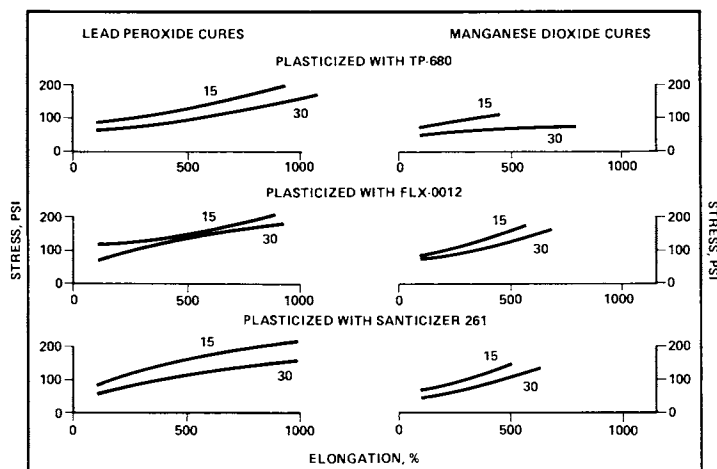


Figure 4. Stress-strain properties of plasticized LP-32 polymer based compositions (see Table V for formulations)

TABLE VI
Effect of Moisture on Cure Rate of an LP Polymer

Time (min.)	0% Water (sec.)	0.5% Water (sec.)	2.0% Water (sec.)
0	5	5	5
10	5	5	5
20	5	5	5
30	5	5	15
40	5	5	35
50	5	5	120
60	5	5	
70	5	5	
80	10	30	
90	25	120	
100	35		
110	120		

Cure rate measured in seconds of time in which a rod imbedded in a catalyzed control batch of LP polymer traverses a fixed distance. The time of 120 sec. is taken as the limit of working life of the batch.

TABLE VII
Effect of Sulfur on Cure Rate of LP -32

	Composition^a			
	No. 1	No. 2	No. 3	No. 4
SRF Black	30	30	30	30
Stearic acid	1	1	1	1
Sulfur		0.5	0.25	0.5
C-5 paste	15	15	15	15
	Working Life (min.)			
	75	60	40	32
Physical Properties of Sheets^b				
Tensile (psi)	350	400	500	500
Elongation (%)	750	720	700	650
Modulus, 300% (psi)	150	170	180	200
Hardness, Shore A	32	36	37	38

^aIn parts by weight per 100 parts LP-32.

^bCured 24 hrs. at 80°F (27°C) and pressed out 10 min. at 310°F (154°C).

TABLE VIII

Curing System for Compositions Based on LP Polymers			
Curing Agents	Accelerators	Retarders	Comments
Lead Peroxide	Sulfur, H ₂ O, 20% Magnesium acetate solution in H ₂ O, amines	Stearic acid, Isostearic acid, Lead stearate and other Metallic stearates	PbO ₂ (medium grade) provides an easily controllable curing rate. Amount recommended per 100 parts of polysulfide polymer: 7.5
Manganese Dioxide (active grade)	Amines, Inorganic Bases, H ₂ O, Tuads Meta-dinitrobenzene	Stearic acid, Isostearic acid	MnO ₂ (active grade) provides polysulfide compositions with heat resistance. Amount recommended per 100 parts of polysulfide polymer: 7.5
Calcium Peroxide	H ₂ O, Amines, Bases	Molecular Sieves	CaO ₂ requires moisture for activation and can provide a white cured system. Amount recommended per 100 parts of polysulfide polymer: 10.0
Zinc Peroxide	Amines	Molecular Sieves, Sulfur	ZnO ₂ can provide white polysulfide compositions. Amount recommended per 100 parts polysulfide polymer: 10.0
Ammonium Dichromate*	H ₂ O, Polar solvents such as DMF (dimethyl formamide), Sulfur	Stearic acid	Ammonium dichromate provides polysulfide compositions with high service temperatures for specialty applications. Amount recommended per 100 parts of polysulfide polymer: 2 to 7
Cumene Hydroperoxide	Copper Ions (cupric resinate), Amines	H ₂ O, Cupric resinate in excess of .07% by weight of LP polymer	Cumene hydroperoxide, in liquid form, is useful for pourable compositions with compression set resistance. Metallic oxides (ZnO or MgO) neutralize acid by-products. Amount recommended per 100 parts of polysulfide polymer: 8.0
p-Quinone Dioxime (GMF)	DPG (diphenylguanidine), Sulfur, Metallic oxides	None normally required	GMF reacts very slowly at room temperature and thus requires heat and diphenylguanidine (DPG) for activation. Amount recommended per 100 parts of polysulfide polymer: 2 to 5

*U.S. Patents: 2,787,608 2,964,503 2,940,958.

TABLE IX
THIOKOL PRIMER SYSTEM

Primer	Formulation	Parts by Weight
TPR-408	Solithane [®] 113 Resin	80
	Toluene	<u>20</u>
		100
TPR-409	Mondur CB-60	50
	Toluene	<u>50</u>
		100
TPR-414	Silane A-187	3.85
	Tyzor-TPT	1.15
	Isopropanol	<u>95.00</u>
		100.00
TPR-415E	Parlon S-10	38.0
	Toluene	57.1
	Silane A-189	4.8
	Chlorohydrin	<u>0.1</u>
		100.00
NOTE: Primer TPR-415E must be stored in phenolic lined cans or glass.		
TPR-417	Silane A-189	25
	Toluene	<u>75</u>
		100
TPR-421	Part A	
	Mondur CB-60	100
	Part B	
	Cellosolve acetate	60
	NIAX D-22	<u>0.4</u>
	160.4	
TPR-429	Silane A-187	5
	Isopropanol	<u>95</u>
		100
TPR-430	Parlon S-10	27.4
	Toluene	41.0
	Silane A-189	3.5
	FLX-0012	28.0
	Chlorohydrin	<u>0.1</u>
	100.0	
NOTE: Primer TPR-430 must be stored in phenolic lined cans or glass.		

(continued)

TABLE IX (continued)

Primer	Formulations	Parts by Weight
TPR-431	Parlon S-10	25
	Acryloid F-10	25
	Toluene	17.5
	Cellosolve acetate	17.5
	Santicizer 160	<u>15</u>
		100.0
TPR-432	Parlon S-10	25
	Mondur CB-60	25
	Paraplex G-60	10
	Toluene (dry)	17.5
	Cellosolve acetate	<u>17.5</u>
		95.0
TPR-433	Parlon S-125	20
	Benzoflex 9-88	8.9
	Toluene	<u>68</u>
		96.9
TPR-434	Parlon S-10	25
	Mondur CB-60	25
	TP-680 Plasticizer	11
	Toluene (dry)	17.5
	Cellosolve acetate	<u>17.5</u>
		96.0
TPR-435	Parlon S-125	20
	TP-680 Plasticizer	8
	Toluene	68
	Paraplex G-60	<u>2</u>
		98
TPR 437	Parlon S-10	30.5
	Paraplex G-60	9.2
	Toluene (dry)	17.5
	Cellosolve acetate	17.5
	Mondur CB-60	<u>23.3</u>
		98.0
TPR-439	Silane A-1100	5
	Isopropanol	<u>95</u>
		100

NOTE: Toluene, Isopropanol and Cellosolve acetate are urethane grade solvents.

ADHESION

Formulations must be adjusted to adhere to various substrates. This requires the addition of suitable plasticizers and adhesion promoters. It is necessary, in some cases, particularly for adhesion to masonry, that primers be used. Primers also are specific to the type of surface and the nature of the formulation. Some primer formulations appear in Table IX.

Some commonly used adhesion promoters are described in Table X.

Many environmental factors such as moisture and temperature determine the long term adhesion of polysulfide sealants. It is necessary that the substrates be properly prepared; surfaces must be clean and structurally sound. To wet the surface and permit the adhesion additives to migrate to the surface, the sealant must have the necessary rheology and cure properties.

It is critical that the plasticizers that are compatible in the liquid compound remain so when the compound cures to a rubber. Many adhesion failures have been the result of plasticizer migration that destroys the adhesive bond.

Achieving a balance of sealant properties is the most severe test of the formulator's skill.

RHEOLOGY

There are various uses requiring compounds with different flow characteristics. These range from a self-leveling material and one that must resist flow completely in vertical joints. A balance between fine and coarse fillers achieves the desired flow characteristics. Fine particle fillers build a network that result in thixotropic behavior. This must be balanced by the desired consistency and cost of the finished sealant. Care must be taken that the fillers are adequately dispersed to achieve the desired thixotropy. Specifically designed additives are available to impart thixotropy to a polysulfide sealant. These are listed in Table XI.

EPOXY MODIFIERS

Polysulfide polymers have been used successfully to improve the impact resistance of epoxy sealants and adhesives for 20 years. The polysulfide liquid polymers used for this application are the low molecular weight materials, LP-3 and LP-33. Formulations with epoxy generally utilize ratios of liquid polymer to epoxy of 1/2 to 1/1. Some amine catalyst is required to speed the reaction. The ratio of 10 to 15 parts of amine per 100 parts of epoxy is normally used. The most common amine for this application is DMP-30 or EH-330. Typical properties of compounds of epoxy/polysulfide liquid polymers are listed in Table XII.

The use of liquid polysulfides greatly enhances the impact strength without significantly reducing the chemical and solvent resistance of these systems.

TABLE X
Adhesion Additives

Cure System	Additive	Recommended pph of LP Polymer	Comments
PbO ₂	Durex 10694	5	Stains concrete, good adhesion to many plastics.
PbO ₂ , MnO ₂	Methylon 75108	5	Non-staining phenolic. May impart a greenish tint to white sealants. Slows MnO ₂ cure.
CaO ₂ , ZnO ₂	Epon 1001-B-80	5	Can slow cure or react slowly with LP. Good for glass and metals.
All	A-187 Silane	0.3-3*	Particularly good for glass.
All	A-189 Silane	0.3 max.*	Good for ceramic tiles.

*U.S. Patent No. 3,123,495.

NOTE:

These materials are reactive and should be thoroughly evaluated in specific formulations for adhesion.

TABLE XI
Thixotropy—Non-Sag Properties

Name	pph of LP Polymer In Formulation	Type	Comments
Thixatrol ST	3-5	Organic	Predisperse in solvent. Incorporated with high shear at 135°F (57°C)
Thixcin GR	10-12	Organic	Disperse with moderate shear or high speed mixing 95°-135°F. (35-57°C)
Bentone 34	2-5	Treated clay	Disperse with high shear. Predampen with polar liquids such as propylene carbonate. Thixotropy may be transient. (Treatment on clay may be reactive.)
Cabosil	2-5	Fumed silica	Disperse with high shear. Use polar additives to improve thixotropy.
Attagel 40 or 50	2-5	Attapulgu clay	Disperse with high shear.

LP/EP Ratio Determines General Properties

The basic determinant of the final properties of a cured polysulfide polymer/epoxy resin compound is the weight ratio of liquid polymer to epoxy resin. By varying this ratio, the formulator is able to develop the optimum properties for a specific application. The effect of varying LP/EP ratios on the properties of a typical compound is shown in the following table.

TABLE XII

Typical Properties Obtained with Various LP/EP Ratios

Note: Each compound cured with 10 pbw of EH-330 curing agent/100 pbw epoxy.

LP/EP ^(a) Ratio (pbw):	0/1	1/2	1/1
Working Properties at 80°F (27°C) ^(b)			
Viscosity, poises ^(c)	24	20	18.5
Working Properties at 80°F (27°C) ^(b)			
Pot Life, min.	25	17	20
Set Time, min.	35	19	20
Max Temp., °F	230 (110°C)	265 (129°C)	240 (116°C)
Mechanical Properties at 80°F (27°C)			
(Cured 7 days at 80°F (27°C))			
Tensile Strength, psi ^(d)	3500	6900	2750
Elongation, per cent ^(d)	0	10	30
Hardness, Shore D ^(e)	80	78	69
Impact Strength, ft-lbs. ^(f)			
at 80°F (27°C)	0.5	2.8	71.5
at -35°F (-37°C)	0.5	0.5	1.5
(Cured 7 days at 80°F (27°C) + 70 hrs. at 212°F (100°C))			
Tensile Strength, psi	3400	6000	850
Elongation, per cent	0	12	65
Hardness, Shore D	80	75	35
Electrical Properties			
(at 25°C, 50% R.H., 1 Kc.)			
Dielectric Constant ^(g)	3.8	4.2	5.1
Dissipation Factor ^(g)	0.004	0.011	0.016
Volume Resistivity, ohm-cm ^(h)	8 x 10 ¹⁴	1.5 x 10 ¹⁴	2.7 x 10 ¹³
Surface Resistivity, ohms ^(h)	5 x 10 ¹⁴	2.3 x 10 ¹³	1.5 x 10 ¹³
Chemical Resistance			
(Per cent volume swell after 30 days immersion at 80°F (27°C):			
10% HCl	0	0	1
20% H ₂ SO ₄	2	2	2
Conc. NH ₄ OH	3	3	1
10% NaOH	0	0	0
50% NaOH	0	0	0
Sat'd. NaCl	0	0	0
SR-6 Aviation Fuel (Aromatic)	0	0	1
Benzene	16	18	35
Carbon tetrachloride	0	-1	13
Methyl ethyl ketone	30	33	35
Ethyl acetate	13	17	15
Distilled H ₂ O	0	2	3

^(a)Epoxy resin: Epoxide Equiv., 180-200; Ave. mol. wt., 350-400; Viscosity at 25°C, 9,000-18,000 cps.

^(b)Determined on 50 gm. sample in a paper cup.

^(c)Brookfield Viscometer.

^(d)ASTM Spec. D 638-56T

^(e)ASTM Spec. D676-49T.

^(f)MIL-C-16923, Bureau of Ships

^(g)ASTM Spec. D 150-47T.

^(h)ASTM Spec. D 257-49T.

MANUFACTURING OF LP SEALANTS

The operations involved in producing sealants are basically mixing and dispersion. The equipment used is common to other industries, i.e., paints, inks, cosmetics. Since the viscosities of the finished compounds go to 60,000 poises, heavy duty equipment is generally required.

A change-can mixer with double acting agitation is used. This mixer has slow moving arms with scraper blades that move the compound from the walls to a fast moving set of blades in the center of the mixer that provide the shear for the dispersion of fillers. It is necessary at times that these mixers be jacketed to allow heating and cooling of the compound. The mixer must be covered to permit vacuum degassing or inert blanketing of the vessel.

Typical information on such mixing equipment is listed in Table XIII.

For fine dispersion of curatives and colorants a paint mill is commonly used. This equipment consists of 3 rolls turning at slightly different surface speeds relative to each other. The adjustable nip between the rollers allows dispersion with exceptional fineness of grind.

Paint mills are available in different sizes to meet production requirements for high viscosity. (See Table XIV) Other mixers available for high speed processing of sealants include the SIGMA blade type supplied by Hockmeyer Corp. or the high speed Meyers mixer. High speed dispersers are generally limited to compounds up to 600 poises in viscosity.

Transferring finished sealants requires the use of heavy duty positive displacement pumps or piston type pumps such as those manufactured by Grayco Corp., Pyles Corp., or Semco Corp. Removing sealant from a mixer often requires that the mixture be pressurized with an inert gas to force the sealant to the suction side of a pump. Cartridge filling equipment is available from a number of packaging machine manufacturers who supply fully engineered systems.

Processing Equipment

Change Can Mixers

This equipment is generally made with double planetary mixing action and the equipment comes in a broad range of sizes, varying from one gallon to 150 gallons, both at atmospheric and vacuum pressure. The final dispersion of filler is based on the viscosity of the binder; the power requirements of the motor; and the space tolerance between blades and wall of the container. If the tolerance is less than 1/16th", a good dispersion can be obtained. Where the tolerance is wide, the equipment can be used as a pre-mixer before passing the material through a paint mill.

The following table lists a number of representative change can mixers:

TABLE XIII

Change Can Mixers

Capacity Gallons	Motor, H.P.	Variable RPM	Single RPM	Batch Time, Minutes
1	1/4	0-170	—	15
3	1/2	0-133	—	15
15	2	20-55	25	30
32	3	24-48	25	30
80	7-1/2	17-50	20	30
146	15	14-42	20	45
175	20	14-42	23	45

Equipment available with or without jackets for use under vacuum, and in various alloys

Paint Mills

The optimum dispersion of a filler is obtained on a paint mill where all filler is subjected to a grinding action, and the various agglomerates are broken down. The setting of the rolls is dependent on the viscosity of the sealant and the fineness of grind desired.

The paint mills can turn out considerable volume when used in conjunction with a change can pre-mixer. The following table gives approximate sizes and production capabilities of various size paint mills when used in conjunction with pre-mixing equipment.

TABLE XIV

Various Sizes of Paint Mills

Size	Front Roll Speed	Motor	Estimated Output Gallons/Hour
4-1/2" x 10"	450 RPM	2 HP	2 Gal./Hr.
9" x 12"	350 RPM	10 HP	15 Gal./Hr.
10" x 20"	350 RPM	15-20 HP	35 Gal./Hr.
12" x 30"	300-350 RPM	20-25 HP	75 Gal./Hr.
14" x 32"	350 RPM	25-30 HP	125 Gal./Hr.
16" x 40"	250-350 RPM	30-40 HP	200 Gal./Hr.

Paint mills are available with pressure gauges for controlling film thickness; one or two speed operations; cold or hot water; change can holding and tilting devices; fixes or floating center roll, and other modifications.

APPLICATIONS

The unique functional properties of the polysulfide liquid polymers have been put to various demanding uses. In some areas of application the liquid polysulfide polymer compound continues to be the current choice after more than thirty years of use.

End-Use Applications and Related Features

1. **Building Sealants** - (Seals joints in exterior joints of curtain wall and other building exterior joints)
Resists weathering, bonds tenaciously, prevents air and water intrusion; provides excellent flexibility and long-term performance.
2. **Insulating Glass Sealant** - (Forms structural seal to bond pieces of glass and spacer; first high performance organic seal)
Provides long lasting seal against moisture vapor transmission.
3. **Airfield & Highway Joint Sealant** - Resists fuel spillage; resists softening in heat; withstands jet blast during "rotation".
4. **Canal Sealant** - Withstands constant immersion in the concrete aqueducts.
5. **Bridge Deck Joint Sealant** - Withstands sudden impact at bridge -to- grade joint; maintains flexibility at low temperatures.
6. **Swimming Pools & Reservoirs** - (Seal joints in concrete water containers)
Withstands pressure, immersion and water treatment chemicals.
7. **"Membrane"** - (Blends with coal tar to form fluid applied membrane)
Bonds to surface below (usually concrete) for long lasting service.
8. **Aircraft Wing Tank Sealant** - Low temperature flexibility, solvent resistance, adhesion to aluminum and other aircraft metal surfaces.
9. **Aircraft Electrical Potting Compound** - Low temperature flexibility, resistance to corona, resistance to hydraulic fluids and aircraft fuels.
10. **Aircraft Wing Faying Surface Compounds and Leading Wing Edge Protection** - Adheres to aircraft surfaces to reduce friction; protects leading edge of wing against hailstone cavitation (accommodates and recovers from hailstone impingement).
11. **Marine** - (Sealants for pleasure craft in wooden decks and fiberglass portions)
Resists UV light, salt spray, constant immersion.

12. Automobile Windshield Sealant - (Seals windshield into metal cavity)
Resists weathering; meets requirements for "pop-out" from internal impact.
13. Aircraft Carrier Wooden Deck Joint Sealant - (Between fir and teak planking)
Resists UV, fresh and salt water, fuel spills; repairs readily; resists arresting hook damage.
14. Mine Sweeper Double Planking - Bonds planking in hull and provides structural integrity; resists effects of salt water that might penetrate wood; forms a barrier against water intrusion.
15. Printing Rolls - Maintains durometer; resists solvents in printing inks and cleaning solutions; permits accurate embossing.
16. Dental Impression Compound - Reflects tooth, gum and cavity accurately, enabling corrective prosthesis; converts to rubbery state quickly; does not break if dropped.
17. Thread Seal for Artillery Items - Prevents water and dust intrusion; permits access to modify characteristics of unit.
18. Solid Rocket Fuel Binder - Low-temperature flexibility, long term aging qualities, castable fluid, accurate reflection of required configuration, adhesion to case, shock resistance.
19. Leather Impregnation - Permits adjustment of degree of void filling in leather; via fluid system provides solvent resistance in leather gasket applications; displays "breathing" qualities when used in "clothing" application, i.e., shoes and protective leather gloves and garments.
20. Relief Maps - (used to make "master" of geographical terrain)
Provides accurate topographical maps and radar training units.
21. Molding Compounds - Castable; reflects fine details; maintains flexibility; does not shrink.
22. Polyethylene Gas Tank Liner - (Lines polyethylene gas tanks for automobile use)
Fuel resistance, low temperature flexibility, fill and drain convenience for manufacture; becomes barrier to prevent vapor transmission through polyethylene and contain fuel where pin-holes may exist or appear in polyethylene.
23. Electrical Transmission Cable Plug - (To prevent water infiltration)
Excellent adhesion to some cable cover material, resistance to UV and solvents.

24. Polysulfide Polymer/Epoxy Applications
Telephone Cable Plug Compounds - Co-reacts with epoxy and amines to form dam in lead-sheathed cable and polyethylene covered cable. Prevents moisture intrusion and permits pressurization of cable. Does not interfere (electrically) with transmission with paper insulated conductors.
25. Polysulfide/Epoxy Setting Compounds for Tools -
Replaces steel wedges in axe and hammer handles.
26. Traffic "Buttons" - Adjustable hardness, resistance to traffic impact and distortion, readily bonded to concrete roadbed.
27. Coatings - Electrically conductive polysulfide/epoxy compounds for static dissipating areas; intumescent coating applications, holds crystals until gas is released.
28. Polysulfide/Epoxy Applications - (Bonding of new to old concrete; mortar replacement for rocket aprons; electrical applications; structural adhesive in trailer production; flexibilized coatings; bridge deck coatings to resist salt intrusion; aircraft metal forming jigs; insulating glass seals -- keeps out moisture.

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Development of Test Procedure for Predicting Performance of Sealants

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The outside envelope of a building undergoes cyclic movements in responding to changing temperature and moisture conditions. It may consist of building elements such as panels of various materials with joints between or large wall sections interrupted by expansion joints. These building elements or sections expand and contract as one unit with any change of temperature or moisture content and the resulting movements are accommodated at the joint. To prevent the passage of water, air or dust the joints must be sealed. Organic materials, called sealants, applied as viscous liquids are used for this purpose. To regulate the cross-section of the sealant bead, a solid back-up material that is most frequently a flexible closed-cell polyethylene foam rod of circular cross-section is first placed into the joint. It has to be wider than the joint and is forced into the opening in such a way as to allow the application of the sealant to an even depth. The liquid sealant is applied against the back-up material, to which it has no adhesion, but adheres to the edges of the building elements.

The sealant is so formulated that it keeps its shape as applied and hardens through chemical or physical processes to form a viscoelastic rubber-like material that withstands extension or compression. The sealant is extended at low temperatures and compressed at high temperatures because the building elements meeting at the joint contract with decreasing temperature and expand with rising temperature.

The demands on sealants are severe because of the large temperature changes imposed on the outside of buildings, especially in cold climates. To investigate their performance, a testing procedure is needed that provides a connection between laboratory and outdoor behavior. A great many factors influence sealant performance and systematic experimenting is needed to find a way of testing that defines the essential sealant properties and discards those that are secondary. Such a test procedure is based on complex relations between the different factors that govern polymer behavior, but it can be made easy to perform by means of

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various simplifying steps in the development of practical testing conditions.

Tensile Test

The factors that govern the behavior of sealants are: stress, strain, temperature, rate of deformation, humidity, air, light, type and condition of substrate, and presence of water or chemicals. Of these, stress, strain, deformation rate, and temperature are of primary importance. They have to be known simultaneously in describing a material at any given age, humidity, substrate condition, etc. Consequently, these four factors must be included in any test method devised to measure mechanical properties, while the other variables must be kept constant at values considered to be realistic.

Cyclic tests provide the best representation of the conditions to which sealants are subjected in practice. They are very complex tests, however, and can be designed satisfactorily only if the material properties are well known from the results of tests using simpler loading patterns and if the rates are related to those of actual joints. Tensile extension at constant rate, stress relaxation under constant strain, and creep under constant stress are three of the simpler tests used to obtain the material properties of polymers. Tensile extension is not the simplest of the three tests (of the four basic variables only temperature can be kept constant), but it has been chosen because it is this type of loading that occurs in the sealant in a joint when the chance of failure is most probable. There is less likelihood of failure when the sealant is compressed in summer than when it is extended in winter. In addition, the tensile test is the least time-consuming and most laboratories are equipped for it.

Model Specimens

After selecting the tensile test as the basic method for investigating sealant behavior, in both laboratory tests and outdoor performance, the size and shape of the specimen have to be considered. Tensile tests are usually carried out on dumbbell or ring-shaped specimens, stress fields of which remain parallel during extension. The true stress can be calculated, therefore, through the minimum cross-section at any time during the experiment. Sealant beads in building joints, however, have an extremely complicated stress field because the side of the bead curves in on extension and the stress changes direction, concentrating at the ends and edges as extension progresses. Consequently, the specimen chosen for the investigation is a model of the sealant bead used in building joints, i.e., it has a stress field similar to that of the sealant in a building joint. The model can fail either cohesively or adhesively, as does a sealant in a joint. This is a distinct advantage compared with dumbbell

or ring-shaped specimens that can fail only cohesively. The model also permits the study of adhesive properties of sealants on various substrates. Another advantage of the model specimen is that most standards call for it and many investigators use it, so that data are available for comparison of materials or conditions. The size of the sealant bead is $\frac{1}{2} \times \frac{1}{2} \times 2$ in. ($1.3 \times 1.3 \times 5.1$ cm), as illustrated in Figure 1, unextended and extended, the latter showing curved sides.

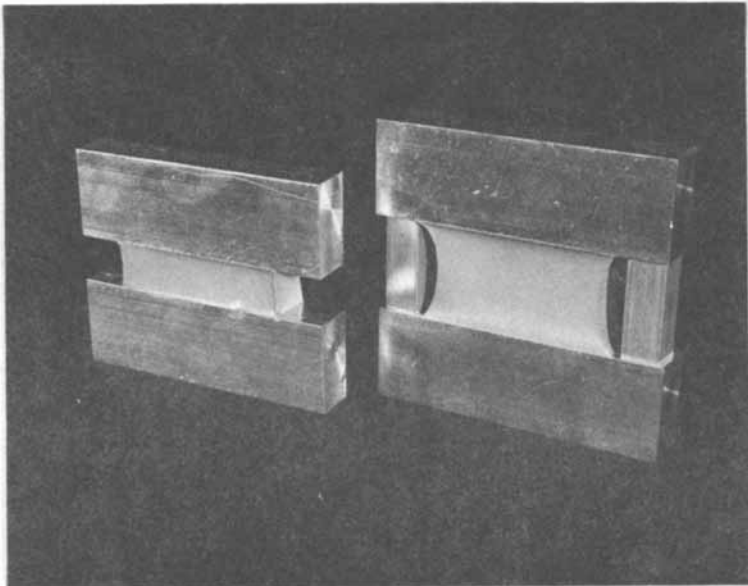
Deriving the Test Procedure

Three-Dimensional Representation. Whatever the configuration of the specimen, an infinite number of tensile curves can be obtained by changing either temperature or tensile extension rate. Figure 2, for one-part chemically cured silicone, and Figure 3, for two-part polysulfide model specimens, show a few examples that are obtained by varying the test conditions. The question arises, which of the tensile curves defines the mechanical properties of a sealant unambiguously?

It is known that for some polymers, and using specimens with parallel stress fields, all tensile curves can be reduced to a single one at a given temperature if the stress and strain at each point of the curve are divided by the strain rate (producing time as abscissa) and if an empirical correction factor, λ , the extension ratio, is applied to stress (1). This treatment of results has also been applied (2) to tensile curves obtained with the model specimens. The resulting single curves of unit strain rate are shown in Figures 4 and 5, derived from Figures 2 and 3, respectively. As may be seen, the fit of the individual tensile curves to the single curve of unit strain rate is excellent for silicone and within acceptable limits for polysulfide sealants. This proves that the model specimen can be used for an investigation intended to establish the interdependence of the tensile curves. It would permit the derivation of a simple and rational method for presenting the deformation characteristics of sealing materials.

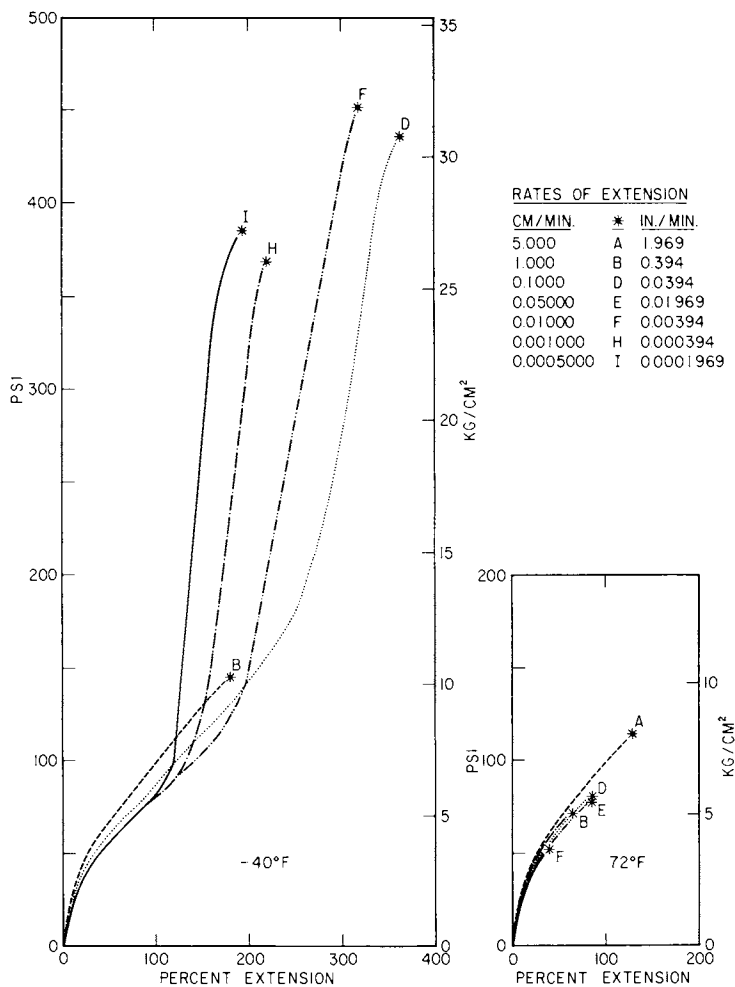
The unit strain rate curves are not fully suitable for describing the behavior of sealants, for they give little information on failure behavior because the failure points for given conditions fall at various points on them. To investigate failure properties as a function of the four basic variables a three-dimensional system has to be used: an example is shown in Figure 6 for two-part polysulfide sealant. Each line represents a tensile curve, calculated from the original curves, and the failure points form the upper curved edge of the three-dimensional representation.

There are several steps of calculation involved in arriving at the three-dimensional presentation. They are necessary in order to reduce the number of variables from four to three. The first step in obtaining the curves in Figure 6 is to recalculate



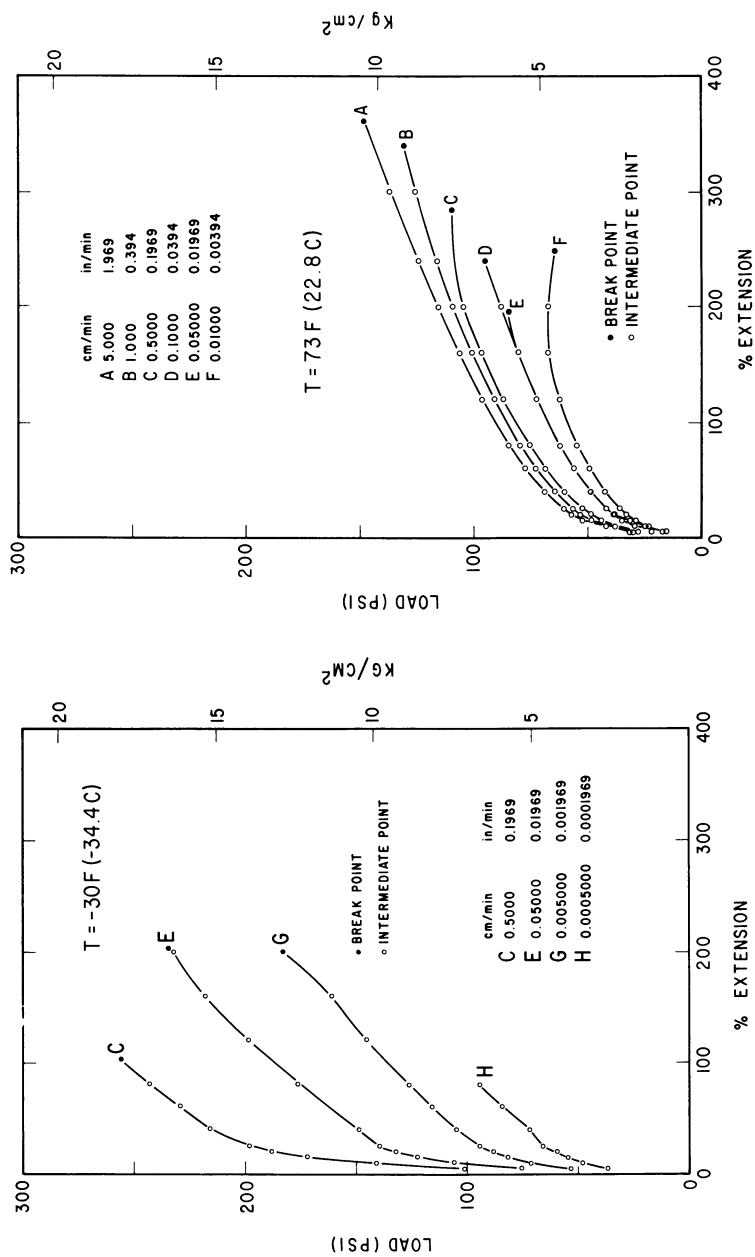
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Figure 1. Original and extended model specimens (4)

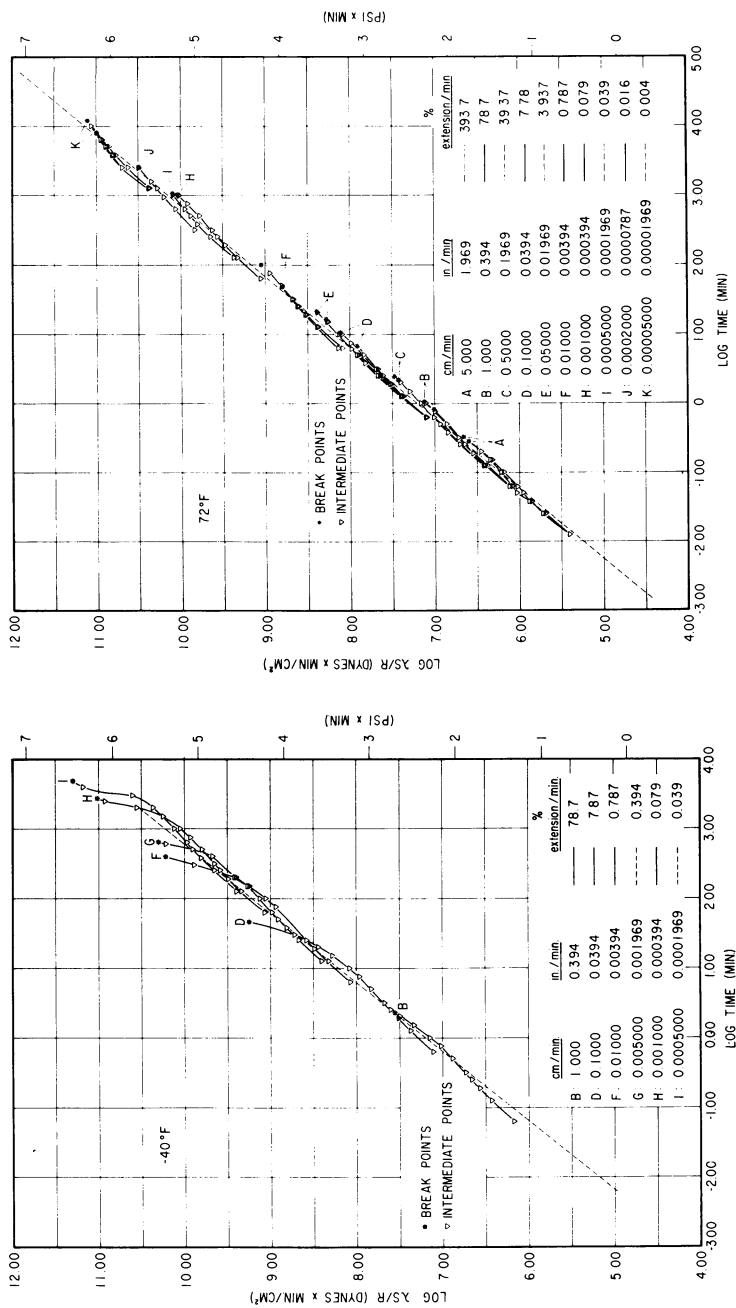


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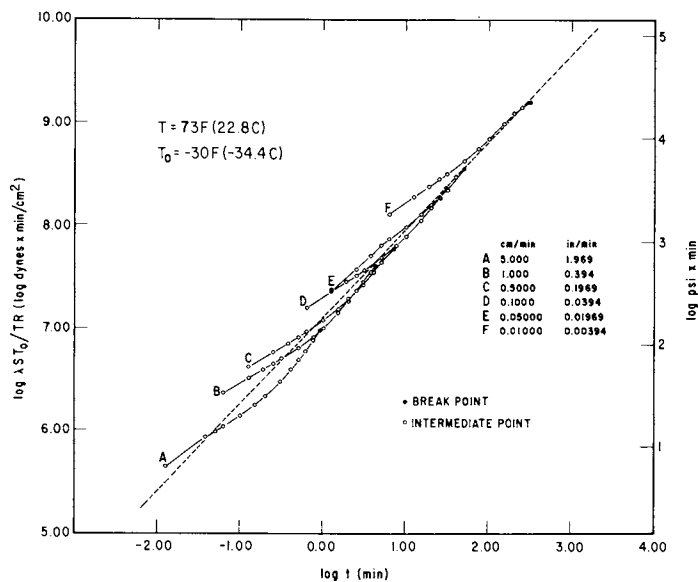
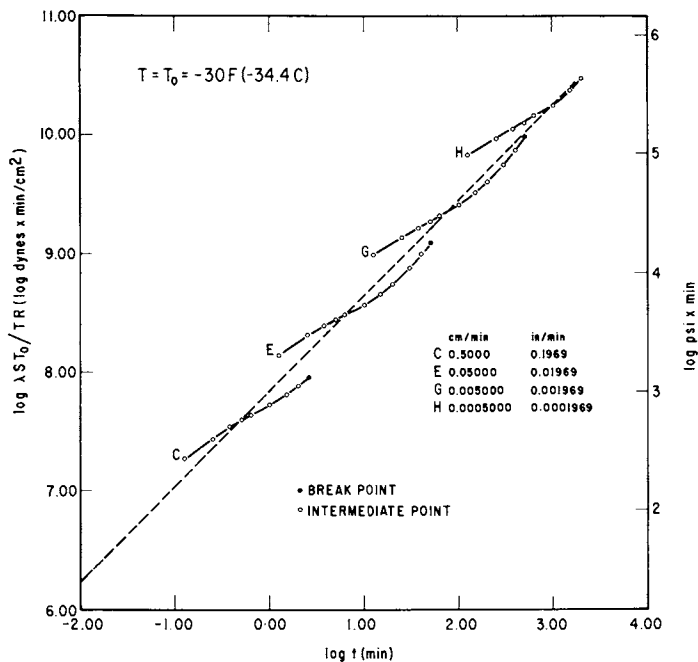
Figure 2. Tensile curves of silicone specimens at different extension rates and two temperatures (2)



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 Figure 3. Tensile curves of polysulfide specimens at different extension rates and two temperatures (4)

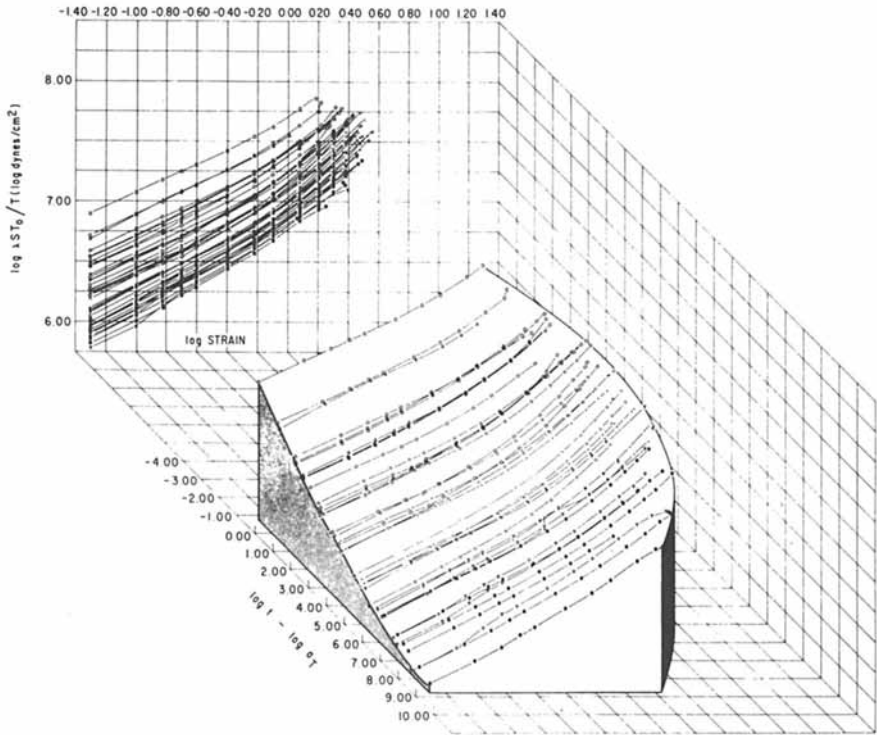


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 Figure 4. Tensile curves reduced to unit strain rate for silicone specimens at different temperatures (2); λ, extension ratio (empirical correction (2)); S, load; and R, strain rate.



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Figure 5. Tensile curves reduced to unit strain rate for polysulfide specimens at different temperatures (4); λ , extension ratio; R, strain rate; T, test temperature, degree Kelvin; T_0 , reference temperature, degree Kelvin; t, time; and S, load.



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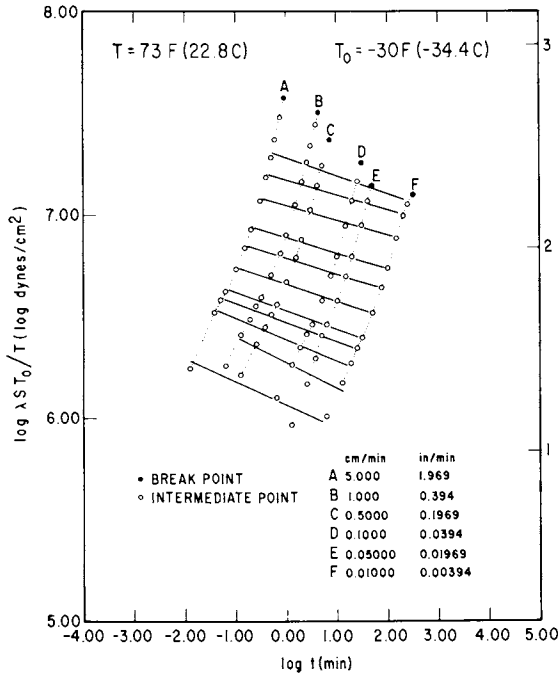
Figure 6. The property surface for polysulfide sealant (4); λ , extension ratio; S , load; T , test temperature, degree Kelvin; T_0 , reference temperature, degree Kelvin; t , time; and a_T , time-temperature shift factor.

each point of the original tensile curves for plots of the type shown in Figure 7. The abscissa is the logarithm of time, derived by dividing the strain by the strain rate, and the ordinate is the load corrected for "true stress" by λ , the extension ratio, and by T_0/T , the reference temperature divided by the test temperature, both in degrees Kelvin (2). The temperature correction is that required by the theory of rubberlike elasticity. Figure 8 is the projection of the original tensile curves on the stress versus time plane. These curves are shown as dotted lines in Figure 7. The continuous lines are the best fits connecting the tensile curves at 5, 10, 15, 20, 25, 40, 60, 80, 120, 160 and 200 per cent extensions. From this plot the isochronal stress-strain curves can be derived by reading values from the best fitting lines for a given time. The times chosen were those at which failure occurred for each specimen. The actual breaking stresses and associated scatter were thereby preserved. The isochronal curves are shown in the background of Figure 6 in the log stress-log strain plane. The third dimension is added by shifting the curves along the time axis, which is perpendicular to this plane, according to the time at which each curve was read. This procedure is followed for each temperature, and with the help of the WLF shift factor, a_T , curves obtained at all temperatures are incorporated in the one three-dimensional representation.

It must be recognized that for silicone sealants the time-temperature superposition was not necessary because the unit strain rate curves fell on the same cumulative single line at each temperature (Figure 4). In other words, the silicone sealant was insensitive to temperature changes within the temperature region observed and within experimental error.

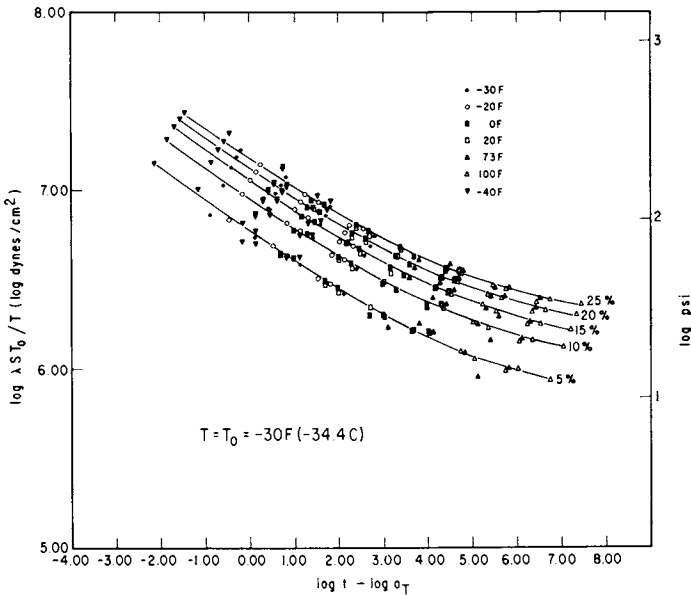
The WLF shift factor was also investigated and experimentally derived for polysulfide sealant using the model specimen (4). The best-fitting (continuous) lines of the various extensions (Figure 7) were used as guidelines for manually shifting the plots obtained at different temperatures along the time axis until the lines for each extension formed a smooth curve (Figure 8). From the measured shifts the constants of the WLF equation, often referred to as "universal constants," were calculated and compared with constants obtained for other polymers. The difference between those calculated here and the universal constants was small, but it was large enough to require use of the former in shifting the sealant data.

The surface formed by the calculated curves shifted along the $\log t - \log a_T$ axis (Figure 6) is the property surface of the polysulfide sealant. A similar surface could be derived for the silicone sealant. The three-dimensional system gives a complete and coherent description of sealant properties, i.e., from a single tensile curve any other can be calculated once this system is known. It is, however, too complex for everyday use and in the next phase of the investigation steps were taken to derive a simpler way of characterization.



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Figure 7. Time dependence of stress at 73°F (4)



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Figure 8. Determination of shift factors (4)

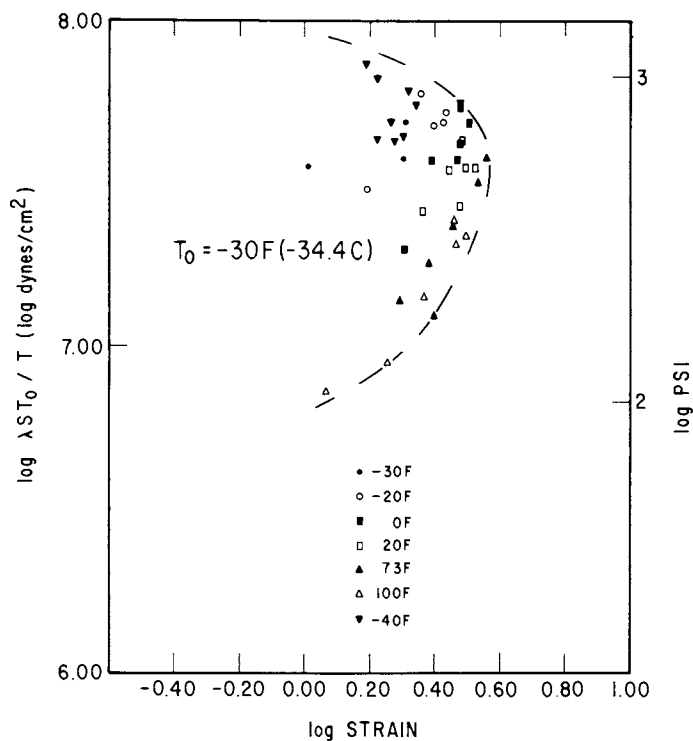
Projections of the Three-Dimensional System. To simplify the three-dimensional system, its projections into the various planes can be used. In particular, the projection of the break points is important because they define the limitations sealants have in practice. Their projection in the log stress-log strain plane is the failure envelope (5) shown for polysulfide sealant in Figure 9. The outer limit of the envelope is well defined and is drawn in with a dashed line, but the inner one disappears in the scatter. For the silicone sealant, Figure 10 gives the failure envelope where both the upper and lower limits are well defined.

The failure envelope is used in the literature to characterize polymers because it is independent of time and temperature, but its usefulness is limited with sealants. From the point of view of sealant performance, the projection of the failure points into the log strain-log time plane is the most important characterization; it is the strain that is imposed on the sealant by the movement of the joint and the stress develops as a consequence of the imposed strain. Consequently, the design of a sealed joint is usually based on an estimate of strain, not of stress, and the sealant is chosen according to its movement capability, that is, the \pm per cent movement the sealant can take without failure in a yearly movement. Stress has to be considered only in those rare cases where the substrate is a fragile, porous material whose tensile strength approaches that of sealants. In this case, a sealant with the lowest strength possible has to be chosen.

Projections of the failure points are shown in Figures 11 and 12 for silicone and polysulfide sealants, respectively. The points plotted in the curves represent the strain at break at the time needed to reach the break. For silicone sealants it was found that the break points obtained at room temperature are sufficient for a final analysis. For polysulfide, data obtained at seven different temperatures are used, reduced to -30°F (-34.4°C).

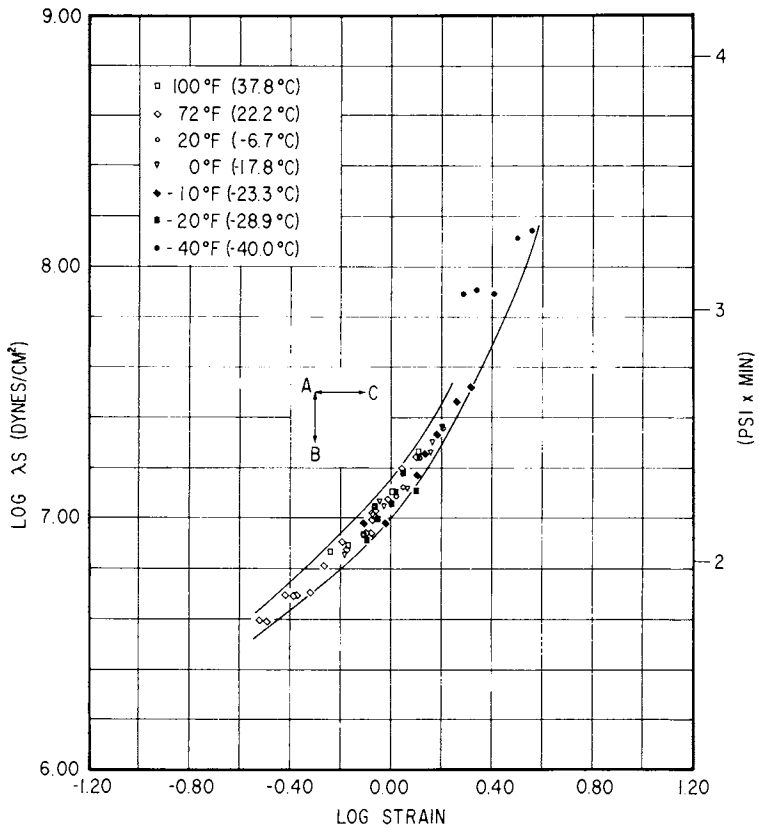
The time dependence of the strain at break is very different for the two types of sealant. The break points of the silicone data can be fitted by a straight line, and confidence limits at various levels can be drawn on the plot (Figure 11). The break points of the two-part polysulfide sealant form a broad band, the upper and lower limits of which are drawn qualitatively. The upper limit is better defined than the lower one (as for the failure envelope). Because of the difference between the plots for silicone and polysulfide sealants the further simplification of characterization is different for the two types of sealant.

Silicone Sealant. Failure of the silicone specimens occurred at increasingly longer times with decreasing strain rates, covering $4\frac{1}{2}$ time decades, measured in minutes. With an extrapolation of $1\frac{1}{2}$ time decade, the extension at failure at half a year can be estimated. In Figure 11 the value obtained is 28 per cent,



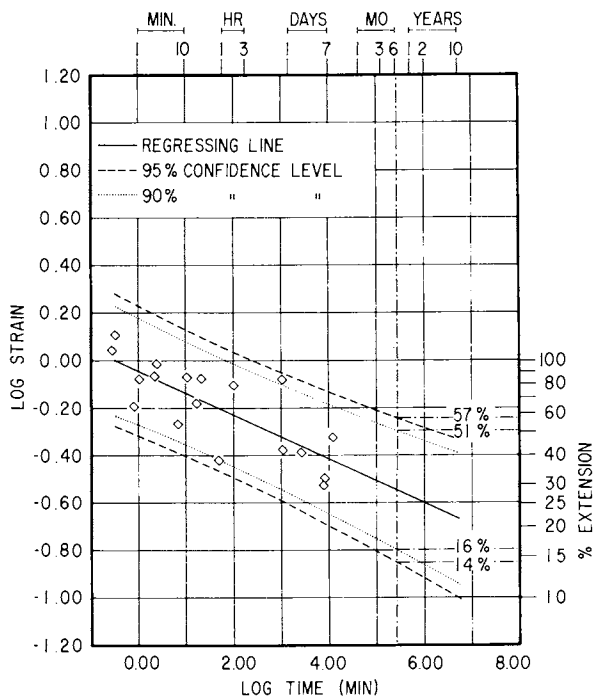
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Figure 9. Failure envelope of polysulfide sealant (4)



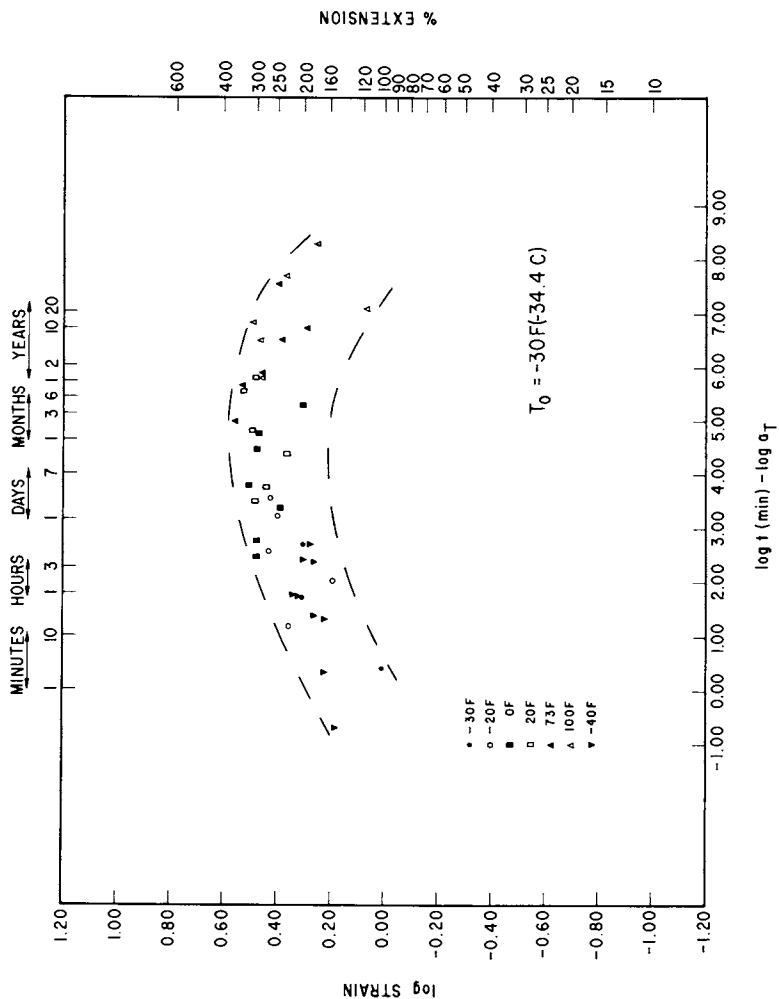
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Figure 10. Failure envelope of silicone sealant (2)



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Figure 11. Time dependence of strain at break; silicone sealant at 72°F (22°C)
(2)



with 95 per cent confidence limits of 57 and 14; that is, 95 out of 100 tests will give failure points inside this confidence interval. Although the characterization could be done at any time value, the choice of half a year has the advantage of being a critical time in the life of a sealant as, on average, half a year is reached in winter, at maximum extension. If a sealant does not fail during the first winter, there is a good chance that it will last for many years.

It has to be pointed out that the single value, 28 per cent, is based on one batch of a one-part chemically-cured white silicone sealant. This single value is presented only as an illustration of the testing procedure. One can expect variations from batch to batch and from manufacturer to manufacturer. Another important factor that may influence the characteristic single value is the aging process to which the sealant is subjected before testing (one month at 70°C in this case). It is only after investigation of all the above factors that a single extension value with its confidence limits can be derived to characterize all chemically-cured silicone sealants available on the market. Such work would need cooperation on the part of manufacturers, but it would remove much of the uncertainty involved in sealed joint design.

Polysulfide Sealant. The single value and its confidence limits have to be derived in a different manner for two-part polysulfide sealants because of the flat maximum formed by the break points. Another difference from the results obtained for silicone sealants is that the tensile properties change with temperature. To characterize extreme winter conditions when failure is most probable the extensibility is given for -30°F (-34.4°C) (Figure 12). According to the lower limit (drawn by dashed line), the sealant can last about 20 years at about 100 per cent extension at this temperature. This estimate is supported by only a few points in the neighborhood of this reading. A better way of characterizing the sealant is to consider that all the readings belong to the same "population" and calculate the mean of the logarithmic strain; this can be done because of the flat maximum. From the mean and its standard deviation one can calculate the extensibility at which only 1 per cent of the tests will fail; this was 119 per cent in the particular batch used. The same applies for polysulfide as for silicone sealants: several manufacturers' products and batches would have to be tested following the method described and the aging process investigated in order to derive an extensibility value that applies to all good quality two-part polysulfide sealants.

Cyclic Tests

Sealants undergo daily cycles superimposed on the yearly one as building movements follow weather conditions. To investigate

the connection between tensile and cyclical behavior, model specimens of one-part chemically-cured silicone sealant were strain cycled on a tensile tester (6). The amplitude and rate of the cycles occurring in practice were known from joint movement investigations (7, 8, 9, 10). The average daily movement is about ± 4 per cent of joint width for a joint that moves ± 25 per cent a year. The silicone sealant model specimen, the only sealant type used for the cyclical experiments so far, showed rubbery behavior when cycled at ± 4 per cent. To cause failure, the daily cycles had to be superimposed on the maximum yearly extension. For example, specimens were cycled between 25+4 and 25-4 per cent extensions. By choosing the cycles in this manner the laboratory strain rates were brought as close as practically possible to actual joint movement rates. It was also necessary to define the number of daily cycles to be imposed. Various considerations led to the selection of 120 cycles. It became clear from the experiments that a number of cyclical tests at identical conditions were needed in order to establish the probability of 50 per cent failure. Failures occur with a scatter, and if all tests pass or fail one does not know what the failure limit is.

In a series of experiments the initial extension, the superimposed cycles, and the rate of movement were varied. For the particular batch of silicone sealant used it was found that for a 25 per cent extension a cyclical movement of ± 8 per cent had to be superimposed at a rate of movement of 1.0 cm/min in order to achieve close to (but less than) 50 per cent failure in the number of specimens tested. Lower rates or higher extensions at the same rate of movement produced more failures. For example, the number of failures increased to four-fifths of the total number of tests when either the above ± 8 per cent to ± 12 per cent were increased or when the rate from 1.0 to 0.1 cm/min was decreased.

These results can be explained if they are examined in conjunction with Figure 13, which is similar to Figure 11 except that another batch of sealant was used. The strains and rates used in the cyclical tests can be located in this plot. The failure points at each rate form a line almost perpendicular to the best-fit line, the alignment of the points being indicated by arrows. Close to the intersection of a line formed by the break points and the lower confidence limit one may read the extension on which the daily cycle should be superimposed to obtain approximately 50 per cent failure in a cyclical experiment. The initially imposed strain with the superimposed daily cycles should reach less than half way to the best-fit line. The further one enters into the confidence limits by changing any of the cycling conditions, i.e., proceeding vertically on the plot by increasing the strain or horizontally toward decreasing strain rate, the greater the chances of failure.

If this correlation of tensile breaks and failures obtained from the cycling tests is valid at rates of the naturally occurring average daily cycles (0.00014 cm/min (6)), then failure in the joint can be predicted from the tensile data. From Figure

13 one reads approximately 13 per cent extension at 0.00014 cm/min rate at the lower confidence limit. This predicts a failure for this particular batch of silicone sealant at a much lower yearly extension than the ± 20 to ± 25 per cent claimed by manufacturers as movement capability. The batch used for obtaining the data published by Karpati (2) is, however, within the claimed values. Apart from the large variation from batch to batch, this shows that the correlation of tensile data with cycling tests should be experimentally verified. Laboratory cycling tests are impractical at this rate of one cycle per day and the cycling facilities used for exposure of sealants have to be utilized.

Weathering Sealants

Once a simple but effective means of characterizing the sealant by a laboratory test method was found, outdoor exposures were started. The resulting changes in sealant properties are being followed by this test procedure as well as by visual assessment of the degree of failure. Different methods of exposing sealant specimens to outdoor weathering are used: a strain cycling weathering rack, a rack that imposes no movement on the specimens, and vice-type devices where the movement is produced by manual adjustments.

A vertical weathering rack 12.5 m (41 ft) long and 1.1 m (3.5 ft) wide, accommodating 216 model specimens (11), was erected in a position facing south (Figure 14). The rack utilizes the difference in the thermal coefficients of expansion of steel and aluminum to produce cyclic movements in response to temperature changes. It has a rigid steel frame to which aluminum bars are attached at one end, leaving them free to move on the other end. Differential movement between the bar and the frame is transferred to the sealant specimens with the help of vertical aluminum plates attached to the steel or to the aluminum bars. Figure 15 shows the bolting of the specimens to the vertical plates. The frame is so constructed that on three quarters of the total area the yearly movement increases from about ± 9 to ± 30 per cent in 36 increments, the amount of movement being dependent on the weather of each year. On the remaining one quarter of the area movement is the same on all specimens, being about ± 13 per cent per year. With this arrangement the limiting movement above which a sealant starts to fail can be determined from a series of specimens exposed to various amounts of yearly movement. Specimens that do not fail can be subjected to the testing procedure described above at chosen time intervals. Visual assessment of the specimens provides information on their performance characteristics; the tensile tests made on the specimens provide a basis for the design of accelerated aging tests related to performance. The evaluation of the performance of various types of sealant during a three-year period is in progress and will be published in the near future.

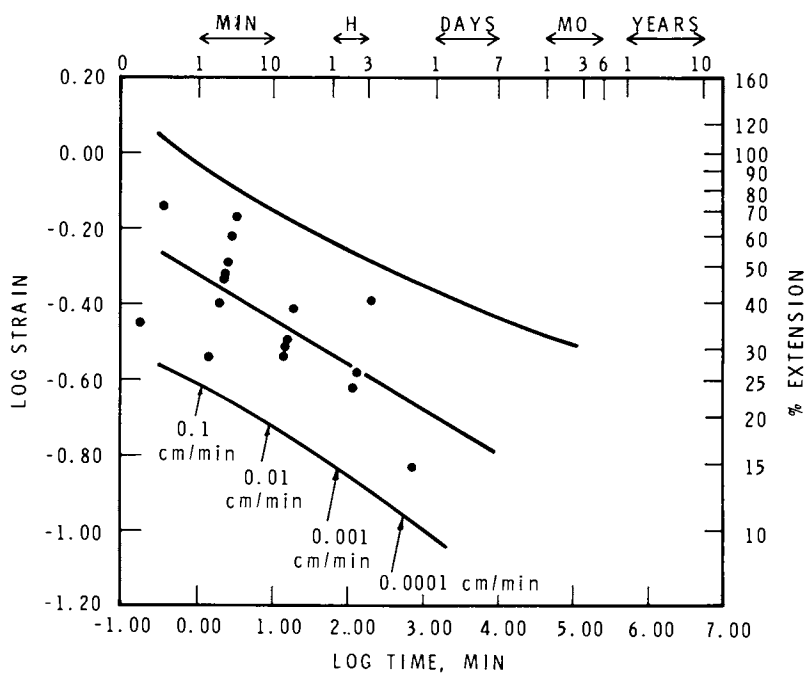
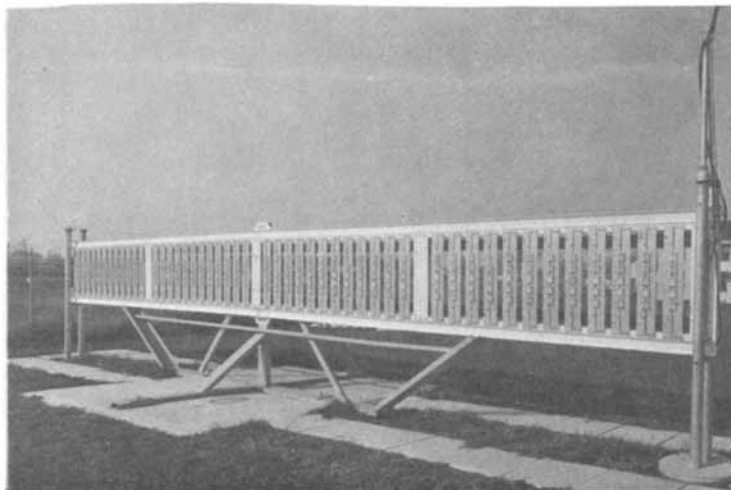


Figure 13. Time dependence of tensile strain at break for the batch of silicone sealant used in cyclical tests (13)



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Figure 14. Strain cycling weathering rack (11)

Sufficiently large differential movements can only be produced with a large size rack. Because few users or manufacturers can afford the construction of this relatively expensive rack, there is need for a simple, inexpensive device that can subject sealant specimens to extension and compression while exposed outdoors or to various imposed conditions. The device shown in Figure 16 was developed to meet these requirements (12).

The device is designed to hold a single specimen and to impose intermittent movement on the sealant by manual adjustment of width, in contrast with the cyclical movement on the weathering rack where it is continuous and automatic. The device resembles a vice; the distance between two aluminum blocks can be adjusted by a screw traversing the center of both blocks so that the distance between them can be varied between 0 and 5 cm (2 in.). The specimen is attached to the aluminum blocks. Tension or compression can be imposed on the sealant bead by varying the distance between the blocks. Up to 300 per cent extension can be produced on a standard 1.3 cm (0.50 in.) specimen. Exposure and evaluation of various types of sealant using this device are in progress.

Summary

The properties of high performance building sealants have been studied as a function of four variables: stress, strain, time and temperature, using tensile tests. By time-temperature superposition the number of variables can be reduced to three and the material properties characterized in a three-dimensional coordinate system. For sealants the projection of the failure points to this system in the log strain versus log time plane is sufficient for characterization. Further simplification can be made depending on the properties of the various types of sealant.

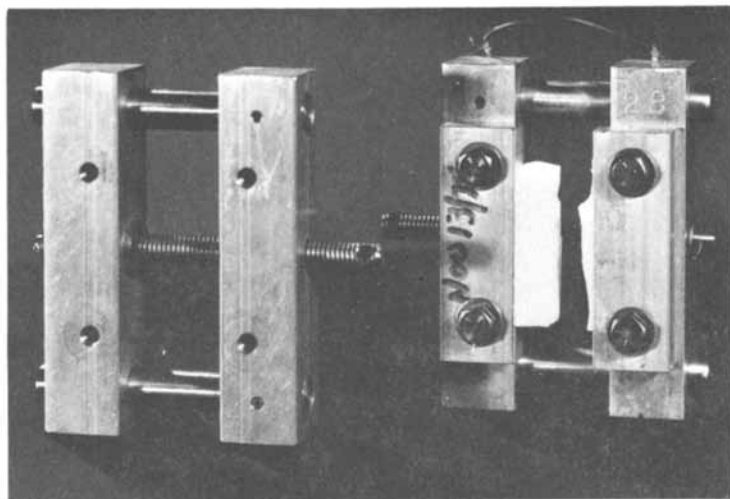
Silicone sealant tensile failure data can be fitted by a straight line in the log strain versus log time plot and the equation of the line characterizes the sealant. A possible further simplification is to specify as a characteristic of the sealant the strain of failure, with its confidence limits, for an arbitrarily chosen time.

The failure points of polysulfide sealants fall on a broad band with a flat maximum. This family of sealants is best characterized by the average of the log strain at failure and the associated confidence limits for a sufficient number of tests.

Cyclical movements are more difficult to analyse than tensile behavior and have been investigated for silicone sealants only. A connection between cyclical and tensile tests has been found by comparing the strain at failure for cycle testing on a log strain versus log time plot with that for failure in simple tension. This connection enables some degree of prediction of performance, i.e., behavior for cycling that occurs under natural conditions. The cyclical tests have shown that lowering the cycling rate or increasing the strain at a given rate increases the probability of



Figure 15. Bolting the specimens to the strain cycling weathering rack



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Figure 16. Cyclic movement device (12)

failure. If it can be shown that the relation between strain to failure for cyclical and tensile tests is also valid for cycling at a daily rate, then prediction of performance can be made based on tensile tests. The results suggest that failure of silicone sealant might occur under natural cycling conditions at a lower extension than the claimed extensibility. At slow rates (one cycle per day) laboratory cycling is not practical. An exposure rack and a hand-adjusted device have been developed for imposing daily cycles of strains on sealant specimens. This investigation of the effect of weathering and strain cycles on sealants is continuing and results will be published in the near future.

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