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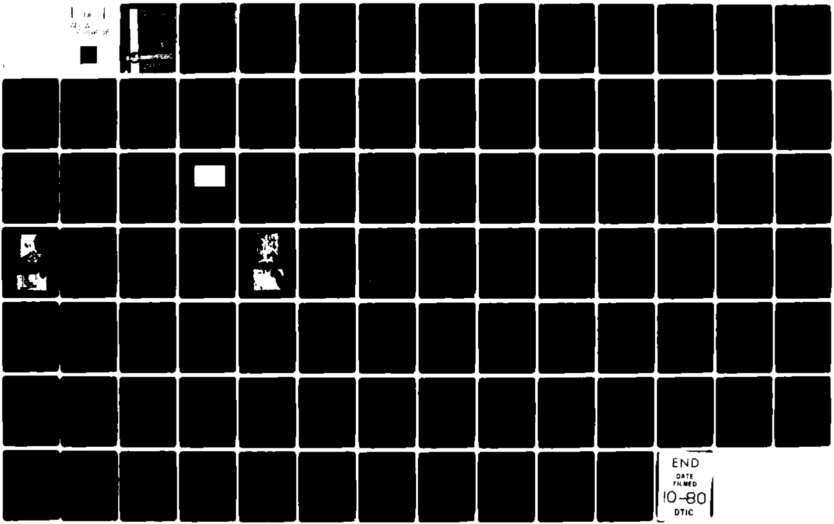

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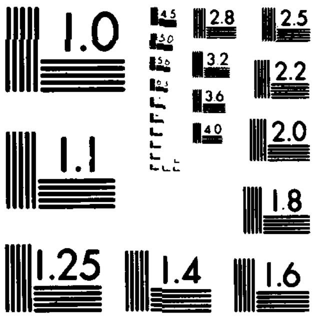

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POLYMER RESEARCH IN RAPID RUNWAY REPAIR MATERIALS

BATTELLE COLUMBUS LABORATORIES
COLUMBUS, OHIO 43201

NOVEMBER 1979

FINAL REPORT
JANUARY 1979 - OCTOBER 1979

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Low viscosity, two-component epoxy resins were formulated for airless spray application over quartz or dolomite aggregates. The formulation selected for full evaluation was based on mercaptan curing systems. Trifunctional acrylate monomers were used in some formulations as modifiers. The resulting polymer concrete set up within 3 to 4 minutes after mixing at temperatures around 73° F. Good cures within 1/2 hour of mixing can be obtained in wet environments down to 5° C and in dry environments down to -25° C. Good adhesion to wet aggregates requires the use of coupling agents, organofunctional silanes

being preferred. Good bonding to asphalt and Portland cement concrete and good wear characteristics were demonstrated. Flexural strength properties are satisfactory after cool down both under dry and wet application conditions. While the polymer concrete is hot due to the exotherm of the curing reaction, flexural strength properties are low.

PREFACE

This report was prepared by Battelle Columbus Laboratories, 505 King Avenue, Columbus, Ohio, 43201, for the Air Force Engineering and Services Center (formerly Air Force Civil and Environmental Engineering Development Office, Air Force Systems Command), Tyndall Air Force Base, Florida, 32403, under Contract No. F08635-79-C-0040. Mr. Richard G. Sinclair was project manager; Mr. Manfred Luttinger was principal investigator; and Mr. Charles W. Kistler, Jr., and Mr. Henry M. Grotta were coinvestigators. D. Mangaraj contributed to the analysis of factors contributing to heat build-up and dissipation during curing of epoxy resins. This report summarizes work done between January and October 1979. Captain Michael T. McNerney (AFESC) was project officer.

This report discussed the use of many name brand epoxy resins and components. This report does not constitute an endorsement of these products by the Air Force nor can it be used to advertise the products.

This report has been reviewed by the Public Affairs Office (PA) and is releaseable to the National Technical Information Service (NTIS). At NTIS it will be available to the general public including foreign nations.

This report has been reviewed and is approved for publication.

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SECTION I

INTRODUCTION

The need for rapid runway repair to restore operational capability following an enemy attack has been well recognized, and provisions for such contingencies in the NATO theatre are in effect in accordance with AFR 93-2. Repair methods are based on the use of AM-2 matting anchored over backfilled craters and have been designed primarily for damage caused by 750-lb bombs leaving large bomb craters of about 50-foot diameter.

Diversification of repair methods is required to meet the threat of new weapons technology which has the capability of producing a large number of smaller craters (about 20-foot diameter). Existing repair methods are inadequate under the changed circumstances, leaving a flight surface of excessive roughness. Inorganic binders which were evaluated were also unacceptable from a performance standpoint. Several research programs investigating the use of organic resin binders reported promising results. However, shortcomings such as limited shelf life, complexity of application, moisture sensitivity, and insufficient adhesion still remain in the most promising candidates which include acrylics, polyesters, and epoxy resins.

The contractor approach has involved a systematic study of epoxy resin technology to identify polymer-concrete systems for use in rapid runway repair under the extreme conditions of temperature and moisture prevalent in the North Atlantic Treaty Organization (NATO) theatre. The present program has focused on the following three technical problems that must be overcome to develop a satisfactory repair system:

(1) Adhesion to wet aggregates.
(2) Cure rate control for low temperature service.
(3) Control of resin viscosity.

In addition, resin bonding to asphalt and Portland cement concrete was studied, durability and flexural strength properties of the polymer-concrete were determined, and accelerated shelf life stability of the resin components was evaluated.

SECTION II

OBJECTIVE

This research and development program had the objective of investigating a broad range of epoxy resin and curing systems for development of a satisfactory repair method for bomb-damaged runways. An optimized resin-aggregate system was sought for use under a wide range of environmental temperature and moisture conditions, particularly as may be encountered in the NATO theatre. To this end, it was desired to accommodate temperature extremes of -25° to 125° F under wet and dry conditions. Flexural strengths of 400 psi needed to be developed in the resin-aggregate system. Bond strengths of at least 40 psi were required between resin and either Portland cement concrete or asphalt. The cure time of the resin-aggregate cap over the repaired crater should be held to within 30 minutes after application. Minimum shelf life of the resin system of one year at 72° F was required.

SECTION III

SUMMARY

3.1 Resin and Curing System Evaluation

The present program included an evaluation of a broad range of epoxy resins and curing systems. Initially, specialty resins were investigated because of their reportedly higher reactivity in order to meet the rapid cure requirements of the program. It was eventually demonstrated, however, that the DGEBA (diglycidyl ether of bisphenol-A) type resins could also meet the rapid cure requirements, both under cold and wet conditions, provided the appropriate curing system was utilized. In short, the curing system was the rate determining factor, and the particular epoxy resin usually played only an insignificant role. The viscosity and cost penalties imposed by most of the specialty epoxy resins could therefore not be justified.

Another important consideration in the selection of epoxy resins was their viscosity, since both the spray application and the penetration through potentially cold or wet aggregates require highly fluid resin combinations. A number of low-viscosity resins were included, therefore, in the study, as well as a variety of diluents. The latter included such nonreactive diluents as hydrocarbon resins as well as reactive diluents of both the epoxy-functional and nonepoxy variety. As might be expected, the best viscosity reduction with minimum compromise of hardness and strength properties was achieved with epoxy-functional (especially difunctional) diluents.

The resin system selected for full-scale evaluation was based on a combination of a standard DGEBA resin of 11,000 to 15,000 cps viscosity (Epon 828) and a resorcinol-di-glycidyl ether diluent (Heloxy 69). Also of potential interest for future study was a compounded DGEBA mixture with Epoxide No. 7 (Araldite 509). Three low-viscosity epoxy resins of proprietary composition were Capcure WR Epoxide and Epi-Rez 5027 and 50727. The latter two resins, however, were limited in their reactivity to amino-functional curing systems.

A very effective diluent type for admixture with epoxy resins was found to be polyfunctional acrylic monomers which combined low viscosity and nonreactivity with the epoxides with fast reaction rates with mercaptan curing agents. Acrylate diluents are limited, however, for use with this curing system and constitute a dual cure: acrylate-mercaptan and epoxy-mercaptan. An interpenetrating network, with the mercaptan resin forming the bridge between the epoxy and the acrylic constituents, may be postulated. The most effective acrylate monomer which was selected for full-scale evaluation was trimethylolpropane triacrylate.

A variety of curing agents were evaluated in the course of this program including several examples of polyamides, amido-amines, amines, mercaptans, and Lewis acids. In addition, several combinations of these curing agents were evaluated. The screening criteria used for this evaluation were (1) ambient temperature cure rate and hardness, (2) cure rates under cold and wet conditions, and (3) considerations relating to field application such as viscosity and mix ratio of epoxy resin and curing agent. An overview of the results of this screening study is given in the following tabulation.

Curing Agents	Fast Cure Rates			Fast Development of Hardness	Low Viscosity	Equal Mix Ratio
	Ambient	Cold	Wet			
Polyamides	-	--	+	-	-	++
Amines and Amido-Amines	++	-+	-	++	++	-
Mercaptans	+++	++	++	+	-+	+++
Mercaptans/Acrylics	+++	++	++	-+	-+	+++
Mercaptans/Amines and Amides	++	+	-+	++	-+	++
Lewis Acids	+++	++	-+	+++	+	--

\- poor performance or disadvantage.
\+ good performance or advantage.

Polyamides were eliminated because of their relatively slow cure rates. Amines and amido-amines did not usually perform well under very cold or wet conditions and had the disadvantage of unequal mix ratios. The best overall results were obtained with mercaptans and mercaptan/acrylic monomer combinations. The designation -+ in the above tabulation indicates wide variations between different formulations. Combinations of mercaptan resins and amines or amides lagged behind the all-mercaptan cure system with respect to cure rate and viscosity considerations. Some of the Lewis acid cures appeared quite promising, but adhesion under wet conditions was a major problem and large disparities in mix ratios was a disadvantage.

3.2 Coupling Agent Evaluation

It was shown during the adhesion studies of resin systems to wet silica and limestone aggregates that the use of coupling agents was essential. Coupling agents were employed as a pretreatment for the aggregates, which is believed to be the most effective method of use, given the rapid gellation of the curing system. Several silanes with varying organofunctional reactive groups and a titanate coupling agent were investigated. A mercapto-functional silane was selected for full-scale evaluation in keeping with the choice of curing system. Addition of low levels of silane coupling agent directly to the resin system was found to aid the bonding to wet asphalt and Portland cement concrete.

3.3 Performance Evaluation of Selected Resin Systems

The two mercaptan-cured resin systems were subjected to more extensive performance evaluation. These systems performed well during spray application and in fast-curing performance under ambient and adverse temperature conditions and with wet aggregates. Adhesion tests to asphalt and Portland cement concrete were also quite satisfactory, far exceeding the performance requirement of 40 psi both under dry and wet conditions, even without the aid of coupling agents. Excellent results were also obtained in the durability tests. The polymer-concrete was shown to be far superior in wear resistance to the traditional concrete surfaces generally encountered.

Flexural strength data were obtained under a variety of conditions of temperature and dryness or wetness. The short-term flexural strengths were quite disappointing, generally falling in the range of 200 to 400 psi. It was shown that these relatively low values were attributable to the high temperature of the polymer concrete at the time of testing which was caused by the high exotherm of the reaction. Flexural strength data after cooldown (tested at 24 hours) were about 1500 psi under dry conditions and 1200 psi under wet conditions. Similarly high flexural strength values were also obtained within 1 hour of application when the test beam was briefly quenched in ice water. Under application conditions employing cold aggregates, substantially higher flexural strengths were obtained (in the 400 to 600 psi range) than under ambient conditions as a result of the heat-sink effect of the aggregates.

Since storage stability tests could only be started after the resin selection for full-scale evaluation had been made, accelerated aging conditions were used to obtain short term data. Under these severe, accelerated conditions (60° C), considerable viscosity drift with time was encountered with several components. The component containing Mercaptate Q-43 ester also exhibited strong discoloration in the presence of oxygen. It will be necessary to establish whether similar observations hold true under more moderate storage conditions, and perhaps a switch to more stable components will be required.

SECTION IV

RESEARCH APPROACH

The review of the literature had indicated that many approaches to the rapid runway repair problem have been investigated with mixed results. The use of epoxy resin binder has been identified as among the more promising system by several investigators. The present program concentrated exclusively on epoxy compositions and investigated a variety of resin and curing system as part of a broad formulation study.

The overall approach of the program was to concentrate on those end use requirements that apparently were the most serious obstacles to the objective of rapid runway repair of bomb damage. These include:

(1) Rapid gel time
(2) Low temperature curing
(3) Curing under wet conditions
(4) Adhesion to wet aggregates
(5) Low resin viscosity for application purposes.

For a resin system to have any chance to cure at a low temperature such as -25° C, it was felt that a rapid gel time at ambient conditions was a minimum requirement. Laboratory effort was therefore devoted extensively to screening of the ambient gel time of two-component resin systems in the absence of aggregates. Hardness measurements were routinely monitored as an approximate indication of the strength properties that may be potentially achievable. While such a correlation does not hold across different polymer systems, in the highly crosslinked, tough epoxy resins an approximation between potential strength properties and hardness or rubberyness can be made.

The most successful candidates from the above screening program were then evaluated under cold and wet conditions. Most of the formulations were deficient in one or the other of these tests. Any resin system that showed promise under these severe curing conditions was suitable for optimization and further evaluation with regard to adhesive and strength characteristics.

Another major consideration for the successful utilization of a resin system was its viscosity characteristics. Low viscosity is essential for spray application and for penetration into the aggregate mix at low temperatures. Low viscosity also tends to aid the wetting of the aggregates which is a major requirement for the development of good adhesion.

While epoxy resins as a class are generally recognized for their good adhesion to a broad range of inorganic substrates, and while some epoxy formulations have been specifically formulated for adhesion to wet concrete, it was nevertheless considered advisable to investigate the use of coupling agents to enhance the bonding of resin to aggregates. Two methods of utilizing coupling agents are widely practiced:

(1) Pretreatment of the bonding surface.
(2) Addition of the coupling agent to the resin.

The latter method is frequently employed because of its simplicity and because it saves the extra pretreatment step. However, higher adhesive strengths (or reinforcement in the case of filled plastics) are usually obtainable by pretreatment methods. For the present application, pretreatment is considered highly desirable because the time for migration of the coupling agent to the interface is very short due to the fast gel time of the resin, and because the presence of coupling agent on the aggregates could aid wetting of the surface by the resin, especially under wet application conditions.

In order to achieve the speed of the repair required by the circumstances, airless spray application of the two-component resin system is considered the most feasible approach. This permits the use of highly reactive systems with fast gel times, because the reactive components are not in contact until they are mixed in the spray gun. The only open time or fluidity demanded by these conditions is the time required for the resin mixture to penetrate through the aggregate to the desired depth. The latter (flow-depth) can be limited by the placing of a barrier to resin flow (a sheet of nonwoven fabric, fine aggregate, or sand, etc.) at the time the crater is backfilled.

Spray application has the further advantage of permitting the heating of the resin components (if the appropriate spray equipment is available) to compensate for any prevailing low temperature conditions. In this manner, flow into the cold aggregate can be enhanced, and the cure rate can be boosted by giving the exothermic reaction an opportunity to start before it can get quenched by the heat sink represented by the cold aggregate.

SECTION V

EXPERIMENTAL PROGRAM

5.1 Resin Formulation and Screening

To fulfill the objectives set for this program, it was necessary to investigate a large number of combinations of epoxy resins, curing agents and accelerators in order to identify leads for compositions that could be cured both at low temperatures and under wet conditions. Resin systems with fast gel times under dry, ambient conditions were considered good candidates for further testing.

5.1.1 Testing Method

Screening of the cure rates of epoxy resin systems was conducted on draw downs of thick films (approximately 60 to 70 mils) on glass plates and on castings of approximately 40 g samples in aluminum weighing dishes (about 2-1/2 inches in diameter, 1/2 inch deep).

The progress of the cure was followed by monitoring the tack-free time and later the Shore hardness of both the films and the castings. Noticeable differences were observed due to the mass effect and correspondingly higher exotherm obtained in the more compact castings. The latter probably more closely simulate the actual field conditions. However, both films and castings continued to be tested throughout the program, because the differences in sensitivity to the mass effect exhibited by various formulations was a valuable clue for comparing their exotherming behavior. It is expected that, in the field, the exotherm and overall cure rate will depend on the application temperature of the resin system, the ambient temperature of the aggregates (heat sink), the heat transfer rate to the aggregates, and the size of the interstitial spaces between the aggregates or void volume.

5.1.2 Epoxy Resin Selection

In the initial stages of the program, major emphasis was placed on selecting epoxy resins that are known for their fast curing characteristics. One of these was a specialty resin called Apogen 101 which is supplied by Schaefer Chemicals, Inc. This material tends to produce fast gel and cure rates because of the activating effect of methylol groups adjacent to the glycidyl ether functionality of the bisphenol A structure. It was hoped that a small increase in water sensitivity due to the methylol group would be inconsequential for the present application in a highly cross-linked structure. Moreover, the presence of the methylol groups on the resin might improve wetting and adhesion to the aggregates. A major drawback of this resin is its very high viscosity (quoted as 7,000 to 11,000 cps at 50° C), which makes major dilution with other resins and diluents mandatory.

Apogen 141 is another member of this family of resins. This is a modified lower viscosity resin with somewhat diminished, but still fast, cure rate. Its viscosity, however, is still substantial at 16,000 to 19,000 cps at 25° C.

A resin of known fast reactivity and of low viscosity (900 to 1500 cps) * is Shell Chemical's former Epon 812. This triglycidyl ether of glycerine produces highly crosslinked structures and fast reaction rates. Its production has been discontinued, reportedly because of the presence of free epichlorohydrin, which is toxic. However, some initial experiments were found to be instructive.

Similar to Epon 812 structurally, but of lower molecular weight and lower functionality as well as without the same toxic hazard, are three epoxy-functional diluents, including Dow's D.E.R. 732 (55 to 100 cps) and D.E.R. 736 (300 to 60 cps) based on polyglycols, and Ciba Geigy's Araldite RD-2 (15 to 25 cps) based on 1,4-butanediol diglycidyl ether. Another aliphatic diluent is Epoxide No. 7 (5 to 15 cps) based on predominantly C^8 and C^{10} alkyl groups. This diluent exhibits low volatility and a very low order of toxicity and is manufactured by Procter and Gamble and marketed by Ciba-Geigy.

Two aromatic diluents were also included in the investigation. One of these is the diglycidyl ether of resorcinol (300 to 500 cps), exhibiting a high degree of reactivity and marketed by Wilmington Chemical Corporation as Heloxy 69 (formerly Ciba Geigy's Araldite ERE-1359, now discontinued). The other one is phenyl glycidyl ether (10 cps maximum), a monofunctional product of Shell Chemical Company.

A major effort in this program involved standard bisphenol A type epoxy resins such as Epon 828 and Araldite 509. The former is Shell's liquid epoxy resin of 11,000 to 15,000 cps viscosity. The latter is a compounded resin coupling Araldite 6010 (similar to Epon 828) and Epoxide No. 7 diluent with a viscosity of 500 to 700 cps.

Exceptionally fast reactivity is claimed for two low-viscosity, compounded epoxy resins of unspecified structure offered by Celanese Polymer Specialties Company. The resins are Epi-Rez 5027 (90 to 140 cps) and Epi-Rez 50727 (800 to 1100 cps) and are specifically designed to be cured with aliphatic amines. They are claimed to have excellent wetting characteristics and good low temperature curing properties.

A specialty, moderate viscosity resin from Diamond Shamrock's Process Chemicals Division, Capcure Epoxide WR (5300 cps), is recommended for fast- and low-temperature cures. Special mercaptan-based curing agents are available for this resin.

A novalac type epoxy resin, D.E.N. 431 (1100 to 1700 cps at 125 F), by Dow Chemical Company was included in the early experimental program. Epoxy novolacs are noted for their higher functionality and great strength and toughness when properly cured. However, their high viscosity requires substantial dilution for the purpose of the present application.

A two-part epoxy resin system with curing agent, Epibond 1217A/B from M and T Chemicals, Inc., was briefly investigated and its fast cure rate at room temperature verified. However, the paste-like viscosity renders its use impractical in this application.

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* All viscosity data at 25° C unless noted otherwise.

Limited, exploratory work was also carried out with two cycloaliphatic epoxides from Ciba Geigy: Araldite CY-179 (350-450 cps) and Araldite CY-183 (350 to 800 cps). The former is an alicyclic diepoxy carboxylate, and the latter is glycidylated difunctional hexahydrophthalic acid.

5.1.3 Polyamide Cures

Polyamide resins are widely used for the room temperature cure of epoxy resins. Most commonly, their structures are based on fatty acid-polyamine condensates, and the curing reaction with epoxides proceeds mainly by means of the remaining amine functionality. Their distinguishing features in comparison to polyamines are:

(a) Lower toxicity and skin sensitization.
(b) Lower exotherms in large castings.
(c) Greater lattitude in stoichiometry.
(d) Improved flexibility.

Depending on the specific structure, their water sensitivity is somewhat less than that of amines, especially before cure. However, since larger proportions of polyamides than polyamines are required in relation to the epoxy functionality, this difference tends to be minimized. Moreover, after cure, the flexibilizing capacity of the polyamides may actually bring about somewhat greater water sensitivity than is the case for the highly crosslinked amine-cured structures.

Two of the standard polyamide curing agents were used in the early work on this program, as shown in Table A-1 in Appendix A. Those are Epon V-40 (200 to 600 cps at 75° C) and Versamid 125 (7000 to 9000 cps at 75° C) from Shell Chemical Company and General Mills, Inc., respectively (equivalent products also available from other companies). A modified amine adduct from Schaefer Chemicals, Inc., Apogen 256 (300 to 600 cps), was included in this work for comparison.

The laboratory studies were conducted with and without the addition of an accelerator (DMP-30, Rohm and Haas' tridimethyl aminomethyl phenol). The use of this accelerator was clearly beneficial in formulations containing the polyamides. Without DMP-30, the amine adduct gave generally faster cure rates than the polyamides. However, the gel times of all of these compositions were too slow for the present application in spite of the fact that highly reactive epoxy resins were being used.

This trend continued to hold true for similar compositions shown in Table A-2, but employing D.E.R. 732 and 736 as diluents to reduce the high viscosity of Apogen 101. The three experiments at the top of that table employed Capcure 38 (450 cps) from Diamond Shamrock, an amido-amine type curing agent which improves wettability and imparts good adhesion to fresh or old concrete. Since this curing agent could not be conveniently compounded with the Apogen 101 at room temperature, mixing was accomplished after heating each of the components to 170 F. Under these conditions, very fast cure rates were obtained. However, these findings could not be directly translated to a practical system for use in the field without considerable reformulating to obtain a sprayable product viscosity under ambient conditions.

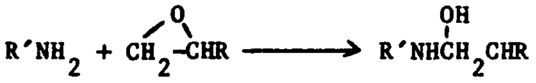
The experiments described in Table A-3 are based on another reactive, high viscosity resin, the epoxy novolac D.E.N. 431. The same type of curing agents discussed above were again investigated, with some of the room temperature cures coming within the desired 1/2 hour tack-free time (see formulation 10-6 in Table A-3). However, the difference in cure rate between the film and the casting illustrates how much the cure of this composition is dependent on the exotherm of the reaction. It may be anticipated, therefore, that the low temperature cure would be inadequate.

In the lower part of Table A-3, the effect of elevated application temperatures on one of the more reactive compositions is illustrated. Although cure times at 50° to 77° C were quite good for the cast samples and high hardnesses were achieved after aging, these compositions did not perform satisfactorily in wet and in lower temperature environments.

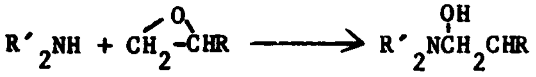
In Table A-4, the effectivenesss of Capcure 38 in Epon 828 compositions were explored. While the cure rates were generally inadequate, they were of a similar order of magnitude as those achievable with the more reactive specialty resins such as Apogen 101, Epon 812, and D.E.N. 431. Based on these and similar observations, it was concluded that major improvements in cure rate will need to be obtained from changes in the curing system rather than from any advantages that the more reactive epoxy resins can offer. Consequently, the viscosity and cost penalties associated with these more reactive resins would probably not be justifiable.

5.1.4 Amine Cures

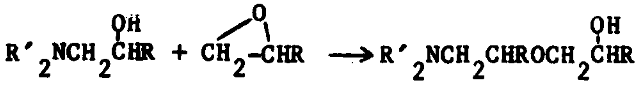
The reaction between amines containing active hydrogens and epoxides constitutes one of the major branches of epoxy technology. The basic reactions according to May and Tanaka * can be summarized by the following three equations:



$$R'NH_2 + CH_2\overset{O}{-}CHR \longrightarrow R'NH\overset{OH}{C}H_2CHR \qquad (1)$$



$$R'_2NH + CH_2\overset{O}{-}CHR \longrightarrow R'_2N\overset{OH}{C}H_2CHR \qquad (2)$$



$$R'_2NCH_2\overset{OH}{C}HR + CH_2\overset{O}{-}CHR \longrightarrow R'_2NCH_2CHROCH_2\overset{OH}{C}HR \qquad (3)$$

---

* Clayton A. May and Yoshio Tonaka, editors "Epoxy Resins, Chemistry and Technology", Marcel Dekker Inc., New York, 1973, p. 144.

Much evidence has been adduced to show that in the reaction between a primary or secondary amine and an epoxide, reactions (1) and (2) account for all of the facts and that, in effect, the sum of glycidyl ether and hydroxyl groups remains constant. These conclusions appear to hold true under certain conditions for polyfunctional amine curing agents such as polyethyleneamines, for instance.

Other work, on the other hand, has demonstrated that etherification by means of reaction (3) can play a major part in the network formation of amine cured epoxy resins, and that etherification is favored by certain amine structures and especially under conditions where less than stoichiometric quantities of amine hydrogens are present. Other factors favoring reaction scheme (3) are the presence of phenol or acid and high reaction temperatures.

Also significant for the present investigation is the observation that hydroxyl groups from either water or alcohol accelerate the reaction between amines and glycidyl ethers. Moreover, the accelerating effect of a specific alcohol structure is proportional to its concentration. Not only do most starting formulations of epoxy resins contain some hydroxyl functionality, but some moisture will almost always be present on the aggregates and additional hydroxyl functionality is constantly being introduced during the amine-epoxide cure in accordance with reactions (1) and (2). This factor together with the gellation effect and the consequent reduction in heat dissipation account for the exotherm observed with almost all epoxy cures.

Little emphasis was originally put on amine cures, because some of the most effective curing agents were thought to be too water sensitive. However, as the unsatisfactory performance of polyamides became obvious, experiments with amine cured compositions were initiated, as shown in Table A-5.

All of the curing agents are aliphatic amines except for D.E.H. 39 (20 cps) which is Dow Chemical Company's technical grade of aminoethylpiperazine (AEP, also available from other suppliers). Ciba Geigy's DP 152 was more recently known as HY 9517 (4000 to 5000 cps) and is a proprietary modified aliphatic amine which has been discontinued. Diamond Shamrock's Capcure EH-30 accelerator is 2,4,6-tri(dimethylaminomethyl) phenol and is functionally equivalent to DMP 30. Furfuryl alcohol (FA) was used to solubilize hexamethylene diamine and was then also included in other formulations as a control. It apparently also had a significant accelerating effect. In this group of curing agents, AEP was most effective, followed by the hexamethylene diamine/FA combination and by diethylene triamine (DETA). Under wet conditions, however, the cure rate of the AEP/FA combination dropped by an order of magnitude, as had been speculated.

In Table A-6 experiments are summarized with Ciba Geigy's modified aromatic amines, Hardener HY 2969 and Hardener 850 (20,000-26,000 cps). Each of these curing agents was further modified by forming an adduct with 5 percent by weight of salicylic acid. The acid adduct is reported to increase the cure rate of epoxy resins, but it unfortunately also increases the viscosity of the amines. The adduct of Hardener 850 was somewhat effective under ambient conditions, although there remained a large spread between the cure rate of the film and of the casting.

As indicated in the earlier section on epoxy resins, Celanese's Epi-Rez 5027 and 50727 are quite low in viscosity and are recommended for fast cures and for good adhesion to damp concrete. The manufacturer's recommendations to achieve the fastest cures was to use his proprietary, accelerated aliphatic amine, Epi-Cure 874 (75-175 cps). According to the data summarized in Table A-7, fast cures were recorded at ambient conditions with castings of both resins. At the lower temperatures, Epi-Rez 5027 failed to perform satisfactorily, while Epi-Rez 50727 performed better but not fully as required. In particular, when the resin and curing temperature was at 5° C, immersion in water at 5° C and dry-curing at -25° C left the samples partially soft or tacky.

A number of aliphatic and aromatic amine curing agents are offered by Pacific Anchor Chemical Corporation. Several of these were investigated in conjunction with Epon 828 in accordance with the data shown in Table A-8. Little description of the chemical structure of these curing agents is provided by the supplier, but some of the recommended end use applications appeared most relevant to the present study. Thus, Ancamine 1767 (aliphatic) is considered suitable for fast-setting adhesives and cold weather patching compounds; Ancamine AD (aliphatic 1000 to 1200 cps) is recommended for fast-setting civil engineering applications, since it is claimed to provide good bonds to concrete under cold and damp conditions; Ancamine LT (aromatic 1200 to 1400 cps) is claimed to be effective under water and at temperatures down to -5° C; Ancamine XT (aliphatic; 74 cps) can accelerate other amine cures and is effective at low temperatures; Sur-Wet R (polyamine; 4000 to 6000 cps) provides good adhesion to wet surfaces by displacing the water on the substrate, but its cure rate is not very fast (a similar product is available from 3M Company).

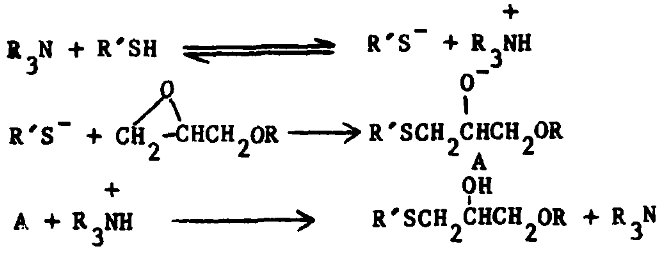
According to the results given in Table 8, fast cure rates (under 10 minutes tack-free time in castings) were obtained at ambient conditions with Ancamine 1767, mixtures of Ancamine 1767 and AD, Ancamine AD, and Ancamine XT. Cure rates of 15 to 20 minutes in castings were achieved under ambient conditions with mixtures of Sur-Wet R and Ancamine 11767 or AD.

At cold dry conditions at -25° C, Ancamine AD performed best followed by Ancamine 1767. Cure rates of 28 minutes and 38 minutes were obtained, respectively, with these two curing agents at 23° C and wet conditions. However, at 5° C and wet conditions, these compositions had not yet cured even though they had been mixed at room temperature. While not fulfilling all the requirements completely, these two curing agents, and especially Ancamine AD, showed considerable promise.

5.1.5 Mercaptan Cures

Because of the unavailability in the past of polymercaptans of relatively low molecular weight and high functionality, combinations of such resins with epoxy materials always required additional curing agents to form fully reacted networks. Indeed, without any accelerator, the reaction proceeds very slowly. However, in the presence of a tertiary amine catalyst, the epoxy-mercaptan reaction can proceed several times faster and at lower temperatures than the epoxy-amine reaction.

The amine-catalyzed epoxy-mercaptan cure may be considered either a general base catalysis or a nucleophilic catalysis. The reaction scheme according to the former proceeds through the initial reaction of the mercaptan with the amine as in reaction (4) followed by reaction with the epoxide in accordance with (5):

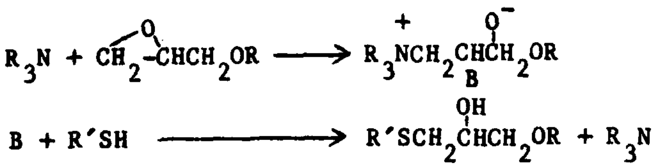


$$R_3N + R'SH \rightleftharpoons R'S^- + R_3\overset{+}{N}H \qquad (4)$$

$$R'S^- + \overset{O}{CH_2\text{-}CH}CH_2OR \longrightarrow R'SCH_2\underset{A}{\overset{O^-}{C}}HCH_2OR \qquad (5a)$$

$$A + R_3\overset{+}{N}H \longrightarrow R'SCH_2\overset{OH}{C}HCH_2OR + R_3N \qquad (5b)$$

The nucleophilic catalysis postulates an initial reaction between the amine and the epoxide followed by a nucleophilic displacement by the mercaptan in accordance with (6):



$$R_3N + \overset{O}{CH_2\text{-}CH}CH_2OR \longrightarrow R_3\overset{+}{N}CH_2\underset{B}{\overset{O^-}{C}}HCH_2OR \qquad (6a)$$

$$B + R'SH \longrightarrow R'SCH_2\overset{OH}{C}HCH_2OR + R_3N \qquad (6b)$$

The investigation of mercaptan curing agents in the laboratory phase of this program proceeded primarily with the aid of a Diamond Shamrock mercaptan-terminated liquid polymer, Capcure 3-800 (15,000 cps). In the presence of an amine catalyst, combinations of this reactant with an epoxy resin cure rapidly even at low temperatures, according to the manufacturer.

In early experiments, still using Epon 812 and Apogen 101, tackfree times of 2 minutes and 3.5 minutes were obtained in castings and films respectively (see Table A-9). Even at -20°C, curing within 5 and 10 minutes was obtained. Moreover, it was shown by the experiments in Table A-10 that compositions based on Epon 828 could be cured nearly as quickly. Under water, films of these compositions cured within 12 minutes and developed appreciable hardness on aging.

Based on these results, considerable effort was devoted to the mercaptan curing system. The next step, illustrated by the experiments in Table A-11, was to develop formulations of lower viscosity with the aid of reactive epoxy diluents. The fastest cures were obtained with the resorcinol diepoxide (Heloxy 69). However, while the viscosities of Epon 828 and of Capcure 3-800 were well matched for mixing, the addition of Heloxy 69 to the epoxy component brought the viscosity into imbalance.

Efforts to correct this viscosity imbalance initially took two directions, as shown in Table A-12. One of these was to resort to diluents such as furfuryl alcohol, p-nonylphenol and benzyl alcohol which do not react with the mercaptan resin and which can be used to reduce its viscosity. However, while the fast cure rates were maintained, substantial reductions in hardness resulted.

The other direction for viscosity adjustment shown in Table A-12 made use of Diamond Shamrock's formulated epoxy resin Capcure WR (5300 cps) and its low viscosity mercaptan reactant Capcure WR-6 (250 cps). The results with this system appeared promising.

An alternative direction for viscosity control was to use Araldite 509 epoxy resin which is a combination of Araldite 6010 and Epoxide No. 7 diluent (see Table A-13). Some reduction in hardness as compared to Epon 828 was noted, and some residual tackiness at low temperature curing conditions was obtained. Further dilution of Araldite 509 with low molecular weight epoxides reduced the hardness considerably, although the cure rate was substantially maintained.

Still another approach to viscosity control was the use of low-viscosity, polyfunctional mercaptans, as summarized in Table A-14. The curing agents selected for this work were Cincinnati Milacron's mercaptate Q-43 ester, pentaerythritol tetrakis (mercaptoproprionate) and mercaptate Q-42 ester, pentaerythritol tetrakis (thioglycolate). Both of these are also available from Evans Chemetics, now a W. R. Grace and Company subsidiary. Fast cures of Epon 828 resin was obtained both with the mercaptate ester by itself or in combination with the mercaptan resin Capcure 3-800. Hardness appeared satisfactory upon aging. Combinations with various epoxy resins as well as epoxy resin mixtures were cured with Capcure 3-800 and mercaptate Q-43 ester with generally good results (Table A-15). Also illustrated in this table is the use of Epodil L (100-150 cps), an inert nonreactive liquid hydrocarbon resin diluent. When used in moderation, this diluent did not significantly affect either the cure rate or the hardness.

The resin screening program had indicated the versatility of the mercaptan cure with a variety of resin and diluent combinations. This cure system had also given very promising results at low temperatures, under wet curing conditions at 23° C and 5° C and under elevated temperature application conditions at 50° C (see Table A-16). Resin components were further adjusted, as shown in this table, to provide low-viscosity mixtures of approximately equal volume of epoxy resin to mercaptate curing components for spray application. Formulation 122-1 of Table A-16 was selected for further evaluation with aggregates as described more fully below.

5.1.6 Mercaptan/Acrylic Monomer Cures

As a result of the search for diluents for the mercaptan cured formulations, it was found that unsaturated acrylic monomers reacted quickly with the mercaptan resins. It was found feasible, therefore, to use polyfunctional low viscosity acrylic monomers as diluents for the epoxy resin when the mercaptan curing system was employed. Under these conditions a dual cure takes place between the mercaptan resin and the epoxide and between the mercaptan resin and the acrylic unsaturation.

Table A-17 summarizes the results of experiments using trimethylolpropane triacrylate (TMPTA) and tetraethyleneglycol diacrylate (TEGDA) in systems based on Epon 828 and using Capcure 3-800 with or without mercaptate esters as the curing agents. The tack-free times indicated very fast cure rates which appeared unaffected by application conditions of -25° C dry and 5° C wet.

Additional variations in the ratios of the curing system were examined and low temperature tests performed as shown in the top portion of Table A-18. Viscosity adjustment and weight equalization of the components was carried out as shown in the lower part of this table and formulation 116-2 was selected for spray application evaluation on aggregates.

5.1.7 Polyamide and Amine/Mercaptan Cures

Attempts were also made to harness the rapid-cure characteristics of the mercaptan resins to boost the performance of epoxy/amide and epoxy/-amine systems. These experiments were conducted in case the good wetting properties of the amines or polyamides should be required, depending on the results of the bonding studies.

As can be seen from the experiments shown in Table A-19, in the case of the castings, the fast cure rates obtainable with mercaptans were maintained even when a substantial fraction of the curing system was substituted with Apogen 256 or Versamid 125. Some reduction of cure rate was discernible in the case of the films. In several of the experiments using Mercaptate Q-43, the hardness of the resins fell well below the Shore D 80 range that may be expected. This probably indicates that too high a ratio of coreactants to epoxy resins was being used.

Table A-20 describes the continuation of this line of inquiry, using Capcure 38 amido-amine resin. Some decrease in cure rate was observed as the Capcure 38 ratio was raised, but the faster rates attributable to the mercaptan generally dominated, especially in the case of the castings. At equal levels, Mercaptate Q-43 ester was more effective than Capcure 3-800 in conjunction with amido-amine curing agent (compare 94-2 and 79-1).

5.1.8 Lewis Acid Cures

Two Lewis acid or cationic catalysts were introduced into the investigation, and the experiments are described in Tables A-21, A-22, and A-23. The catalysts were DP-116 (now renamed XU 195) from Ciba-Geigy and Resicure 30 from Ozark-Mahoning Company, a Pennwalt subsidiary. Both of these catalysts gave extremely fast cure rates with Araldite 509. Formulations with DP 116 cured in 1 to 1.5 minutes on glass plates at room temperature. Shore D hardness was 78 after 10 minutes and 85 after 15 minutes. There was no further increase in hardness with time.

Resicure 30 was even faster than DP 116. As a consequence of the high exotherm of the cure, many of the samples became charred. This was the case in combinations of Resicure 30 and Araldite 509 or Apogen 141, respectively. Epon 828 formulated with 10 phr Resicure 30 cured within 1 minute without charring. Shore D hardness was up to 85 within 15 minutes.

Experiments with the above systems were also conducted with furfuryl alcohol as a reactive diluent. Such formulations are of interest because furfuryl alcohol remains very fluid at -25° C. At 25 phr the cure rate with either DP 116 or Resicure 30 was unaffected when compared to the unmodified formulations. However, the cured formulations were noticeably rubbery when the diluent was present and remained that way on aging.

Araldite DP 116 is used at relatively high levels (25 parts by weight based on epoxy resins). Immersed in water, the upper layer of the film which was in direct contact with the water remained tacky and soft for a long time, while the layer near the glass surface had hardened. The effect was evident in formulations with and without furfuryl alcohol, but was more pronounced in the presence of this water-miscible diluent. Similar results were also obtained with experiments carried out at low temperatures.

Resicure 30 is used at a level of 10 phr. Hard, tack-free samples were obtained within 1 minute on immersion in water as well as in the freezer. Additional experiments were then run at 5 phr and 2.5 phr based on the weight of epoxy resin. Full cures were also obtained with 5-phr Resicure 30 both in water and at low temperatures. Cure times were only a little slower (1.5 to 2 minutes). But the 2.5 level of Resicure 30 was insufficient to provide good cures, leaving tacky films after 2 hours under water and in air.

Attempts were also made to use Resicure 30 as an accelerator of polyamide or amido-amine resin cures. The results shown at the bottom of Table A-23 indicate that this was not successful. Very likely the Lewis acid was deactivated or so strongly complexed by the amine functionality that it was not available for cure at room temperature.

Resicure 30 was carefully considered as one of the curing systems for further evaluation. The final decision against its use was based on the following considerations:

(1) The reactivity is too fast even for spray application, and there may not be enough time for the resin to flow out and fill the interstices between the aggregate to the desired depth.

(2) The application ratio of the two-component system is in the range of 10:1 to 20:1 epoxy resin to curing agent. This is inconvenient to spray, and the system is very likely to be unforgiving of variations in spray application that might well occur in the field.

(3) Although good underwater cures have been obtained, there was some evidence that the cure in the very thin surface layer next to the water may have been incomplete. While this would not detract from the bulk properties of the resin, it was a serious detriment to the adhesion of the resin to the wet aggregate (see Resin Bonding to Aggregates, Section 5.3).

Work had not originally been planned with cycloaliphatic epoxies because of their greater sensitizing tendency as compared to more conventional epoxy resins. However, a number of cycloaliphatic epoxy resins have found acceptance in commerce for special applications. Moreover, the work described above with Lewis acid catalysts raised the question whether this curing system in combination with cycloaliphatic epoxides might be suitable for the present application.

Cycloaliphatic epoxy resins are mainly attractive because of their low viscosity. The two products selected for this screening study were Ciba-Geigy's Araldite CY 179 (350-450 cps), an alicyclic diepoxy carboxylate, and Araldite CY 183 (350-800 cps), a cycloaliphatic diglycidyl ester resin. Reactions with Resicure 30, with and without methyl nadic anhydride and with dibutyltin dilaurate, were attempted with widely varying results (see Table A-24). With the exception of 73-2, Araldite CY 183 did not cure in these trials. In experiment 73-2 a 10-minute quiescent initiation period was followed by a sudden exotherm which charred the resin as it cured. Araldite CY 179 cured very quickly in most of the experiments tried, but the reaction proceeded too quickly and was difficult to control.

5.2 Selection of Coupling Agents for Use in Polymer Concrete

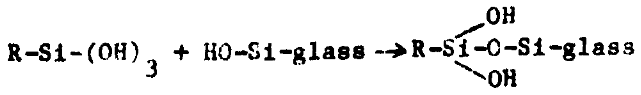
The strength of a filled polymer, including polymer concrete, depends to a considerable extent upon the formation of bonds between the filler (aggregate) and the bulk of the polymer. If this were not so, a filled polymer would be little more than a polymer containing voids, albeit occupied voids. On the other hand, if effective bonding is achieved, the strength of the final product is typically greater than that of the polymer alone. If the polymer does not spontaneously bond to the filler, use of a coupling agent can be helpful. An effective coupling agent should bond, either by reaction or other attractive mechanism (e.g., solubility in the polymer) to both aggregate and polymer. In the case of a polymer concrete, this requires that the coupling agent have two different functionalities.

Among the most widely used coupling agents for filled (reinforced) polymer compositions are the silanes. In addition, certain titanates are used for the same purpose. Both of these classes of compounds react in a comparable way with appropriate substrates (aggregates) to permit bonding of polymer since both contain organic and inorganic functionality. For example, the silane coupling agents typically have the structure

$$\text{R-Si(OR')}_3$$

where the R-group will be reactive toward the organic polymer molecules while the -OR' groups on hydrolysis at the appropriate pH will permit the formation of Si-O-M bond to the oxide functionality of the aggregate. Thus, with glass-fiber reinforced polymers, the coupler would react with the hydrated silaceous substrate as follows:

$$\text{R-Si(OR')}_3 + \text{H}_2\text{O} \longrightarrow \text{R-Si(OH)}_3 + 3\text{ROH}$$



$$\text{R-Si-(OH)}_3 + \text{HO-Si-glass} \rightarrow \text{R-}\overset{\text{OH}}{\underset{\text{OH}}{\text{Si}}}\text{-O-Si-glass} \qquad (7)$$

thus anchoring the silane to the glass and leaving the R group available for reaction with the polymer system. Titanium may be substituted for silicon in the above representation without materially altering the process except for reaction rates and conditions. Both the silica and the limestone or dolomite aggregates considered for use in the present study should be reactive toward these coupling agents.

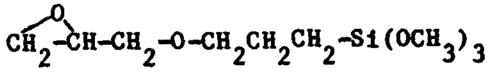
The R-group must be compatible with (i.e., soluble in) or preferably reactive toward the polymer. Since epoxy resins have been selected for use in this program, appropriate materials can readily be chosen from among commercially available materials. The following coupling agents were selected for evaluation based on the criteria noted above.

5.2.1 Union Carbide Silanes

A-1100 $H_2N\text{-}CH_2CH_2CH_2\text{-}Si(OCH_2CH_3)_3$

λ-aminopropyl triethoxysilane

A-187



$CH_2\text{-}CH\text{-}CH_2\text{-}O\text{-}CH_2CH_2CH_2\text{-}Si(OCH_3)_3$

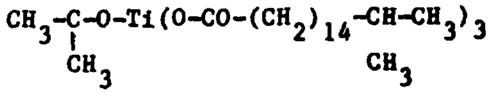
λ-glycidoxypropyl trimethoxysilane

A-189 $HS\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}Si(OCH_3)_3$

λ-mercapto-propyl trimethoxysilane (8)

Each of these compounds contains the requisite silyl ether functionality for reaction with the aggregate and a hydrolytically stable organic function, amino, epoxy, and mercapto, respectively, capable of reacting with the polymerizing epoxy function. In addition, a single titanium derivative from Kenrich Petrochemicals, Inc., was chosen, namely

Ken-React TTS



$CH_3\text{-}\underset{CH_3}{C}\text{-}O\text{-}Ti(O\text{-}CO\text{-}(CH_2)_{14}\text{-}\underset{CH_3}{CH}\text{-}CH_3)_3$

Isopropyl triisostearic titanate

This material differs significantly from the silane couplers in two ways: there is only one potential bond forming site for reaction with the aggregate (the single isopropoxy group) while the silanes have three, and there are three isostearic acid groups to provide compatibility with the polymer rather than the single one of the silanes. However, this titanate is not reactive toward the epoxy resin as are the silanes and would thus provide bonding only by virtue of compatibility with solubility in the resin.

These coupling agents can be applied in two ways: by pretreating the aggregate or by combining the coupling agent with the monomer-curing agent mixture. As a matter of convenience to permit controlled hydrolysis at adjusted pH and thus insure reaction with the aggregate, the former method seems preferable for the present work. It is also to be expected that aggregate pretreatment would make more effective use of the coupling agents, since only a limited time is available before gellation of the resin for the coupling agent to migrate and bond to the aggregate surface.

Based largely upon the manufacturer's recommendations, the silane coupling agents were applied to test blocks from 5 volume percent aqueous solutions adjusted to pH 4.5-5 with acetic acid and used within 1 hour of preparation. The blocks were immersed in the solution for one minute, allowed to drain and air dry, and finally cured by heating for 1 hour at 100° C. Couplers A-1100 and A-187 dissolved readily in the dilute acetic acid while A-189 dissolved only very slowly and required considerable agitiation to achieve complete solution. A similar procedure was also followed for treatment of aggregates used in the preparation of polymer concrete. Experimental results are presented in the sections on Resin Bonding to Aggregates and Flexural Strength of Polymer Concrete. Only A-189 was used for treating aggregate based on the preliminary findings with test blocks and was applied in the same manner.

The titanate complex is not water soluble. Solutions of it in petroleum ether (5 volume percent) were used for treating the test blocks for 1 minute followed by drying and curing in the same way as that by which the silane treated blocks were processed.

5.3 Resin Bonding to Aggregates

5.3.1 General Procedure

For obtaining property data on candidate resin systems, a rapid testing technique was desirable to facilitate testing multiple samples at close to one time period. In addition, a technique which would (1) use a minimum amount of hand-mixed resin to avoid exotherm problems, (2) avoid mold stripping problems (adhesion), and (3) provide meaningful engineering data was desirable. To meet these objectives, a tensile testing technique modeled after that described in ASTM C321 (Bond Strength of Chemically Resistant Mortars) was devised. Figure 1 illustrates the adhesively bonded cross-blocked tensile set-up which was used.

In preparing the sample, masking tape was applied to the ends of each block to keep resin off the loading areas. After the resin was hand-mixed and applied, the specimens were placed in pin alignment fixture to hold them in proper alignment while the epoxy adhesive cured. The samples were then placed on the lower U-shaped fixture, the upper fixture was placed above the sample, and the assembly was loaded in an Instron testing machine at a loading rate of 0.1 in/m in. To reduce the number of specimens required, specimens which failed at the bond line were rotated 90 degrees to expose another surface for evaluating another resin or for testing at another temperature. Using this technique, four tests could be conducted with most sets of test blocks.

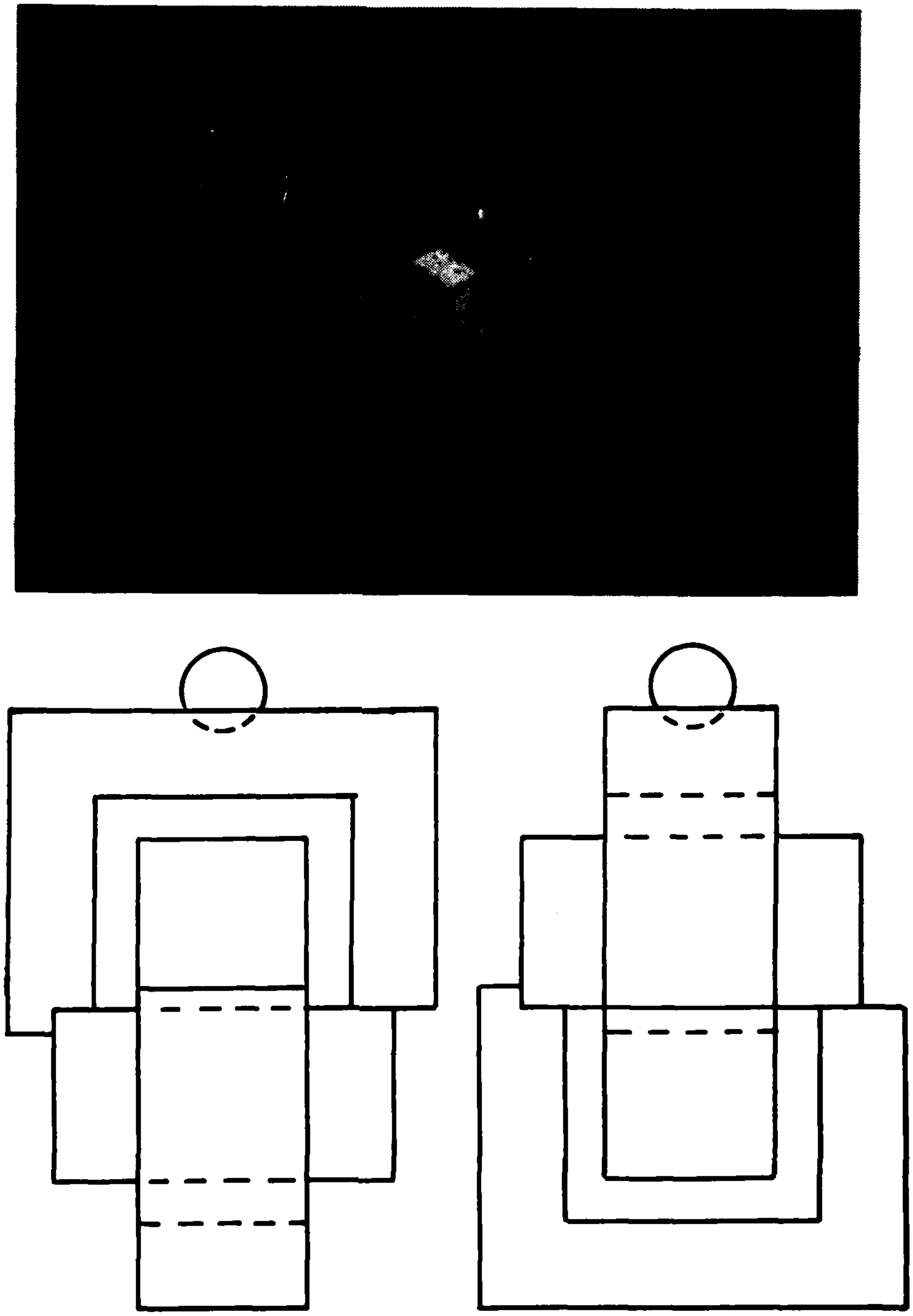


Figure 1. Adhesively Bonded Crossed-Block Tensile Test Specimen in Testing Rig (Each Block 1x1x2 Inches)

5.3.2 Substrate Selection

Substrate test block materials chemically similar to the concrete aggregates were used for these screening tests. Silica blocks were cut * from North American Refractories "Narsil" silica bricks which are made from the same round silica aggregate deposit (Sharon Conglomerate) used in the concrete evaluations. These bricks are about 95.5 SiO_2, 2.6 CaO, 1.0 Fe_2O_3, and 0.25 Al_2O_3, have a flexural strength of about 1000 psi, a bulk density of 116 to 121 pcf (actual block data), and an apparent porosity of 16.5 to 20.5 percent (actual block data equivalent to an absorption of 8.5 to 11.0 percent. Due to the heterogeneous nature of the locally available dolomite aggregate (fossil deposits), a building stone grade limestone (97.4 $CaCO_3$, 1.2 $MgCO_3$) with a fine uniform texture was selected to minimize porosity variations. All limestone test blocks were cut from the same piece of material, which had a bulk density of 141 to 146 pcf (actual block data) and an apparent porosity of 15.9 to 16.4 percent (actual block data equivalent to an absorption of 7.0 percent).

5.3.3 Results of Bonding Study

An initial test was conducted using an Epon 828 resin formulation diluted with acrylic monomer and cured with mercaptan resins (71-3, Table A-18). Adhesive bonds were tested ∿30 minutes after application at room temperature. Dry untreated blocks broke in the range of 275 to 360 psi (quartz) and 235 to 270 psi (limestone), which is below the adhesive strength of the resin bond to the surface. These results verified our expectations that epoxy resins would give good bond strengths to dry aggregates.

Adhesion to wet test specimens was of much poorer quality, as might be expected. A somewhat wider range of formulations was evaluated on wet silica and limestone blocks in order to discover possible differences in their adhesion performance to wet aggregates. As can be seen from Table 1, none of the formulations were satisfactory. The resin cured with the Lewis acid catalyst, however, had exceptionally poor adhesion, as had been anticipated (see Resin Formulation and Screening, Lewis Acid Cures, Section 5.1.8).

Three silane and one titanate coupling agents were used to treat silica and limestone blocks in accordance with procedures described earlier, and two epoxy/mercaptan formulations, one with and one without trifunctional acrylate monomer, were employed to evaluate adhesion to treated, wet silica and limestone surfaces. From the data in Table 2, it can be seen that significant improvement in bond strength is achievable with several of the coupling agents. The best results were obtained with the mercaptate-functional silane (A-187) and the epoxy-functional silane (A-189). When epoxy composition 71-3 was used on wet substrates pretreated with A-187, the bond strength was greater than the breaking strength of the blocks. A significant improvement in bond strength was also obtained with the titanate when Formulation 58-1 was used, but not in the tests employing Formulation 71-3. The aminofunctional silane was ineffective in all instances.

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* To avoid contamination all test block materials were cut with a diamond saw and then surface ground flat and paralleled using only tap water as a lubricant.

TABLE 1. ADHESIVE PERFORMANCE OF EPON 828-BASED EPOXY RESIN FORMULATIONS TO UNTREATED WET SILICA AND LIMESTONE SURFACES

Formulation	Reference Table	Reactive Diluent	Curing System	Adhesive Strength, psi	
				Silica Blocks	Limestone Blocks
48-2	A-22	--	Resicure 30	(a)	(a)
55-4	A-19	- --	Capcure 3-800 Versamid 125	30	16
58-1	A-11	Araldite RD-2	Capcure 3-800	18	21
58-1M(b)		Heloxy 69	Capcure 3-800	69	22
71-3	A-18	TMPTA	Capcure 3-800 Mercaptate Q-43	16	4

(a) Bond broke on loading; essentially 0 strength.

(b) Formulation 58-1 modified by substituting Heloxy 69 (diglycidyl ether of resorcinol) for Araldite RD-2 (1,4-butanediol diglycidyl ether).

TABLE 2. ADHESIVE BOND STRENGTHS (PSI) OF EPOXY COMPOSITIONS TO TREATED AND UNTREATED SILICA AND LIMESTONE SUBSTRATES UNDER WET CONDITIONS AT 73° F

	Silica Blocks	Limestone Blocks
Epoxy Formulation 58-1(b)		
Untreated, wet, 73° F	69	22
Treated(a), wet, 73° F		
Silane A-1100	35	17
Silane A-187	112	125
Silane A-189	264	150
Ken React TTS	64	191
Epoxy Formulation 71-3(c)		
Untreated, dry	> 316	> 247
Untreated, wet, 73° F	16	4
Treated(a), wet, 73° F		
Silane A-1100	13	31
Silane A-187	> 242	> 117
Silane A-189	242	101
Ken React TTS	15	30

(a) Silane A-1100 = Union Carbide's gamma-aminopropyltriethoxysilane

Silane A-187 = Union Carbide's gamma-glycidoxypropyltrimethoxysilane

Silane A-189 = Union Carbide's gamma-mercaptopropyltrimethoxysilane

Ken React TTS = Kenrich Petrochemicals' isopropyltriisostearic titanate.

(b) Bisphenol-A/epichlorophydrin diluted with 1,4-butanediol diglycidyl ether and cured with mercaptan-functional resin (see Table A-11).

(c) Combination of bisphenol-A/epichlorohydrin epoxy resin and trifunctional acrylate monomer cured with mercaptan-functional resin (see Table A-18).

Similar tests were also conducted with the wet substrates conditioned at 40° to 45° F. The data shown in Table 3 lead to very similar conclusions as those reached with the tests conducted at room temperature. The epoxide- and mercaptan-functional silanes were again among the most effective coupling agents. Also consistent with the previous findings, the titanate coupling agent was effective only with formulation 58-1 and only on limestone blocks. Variations between the two sets of data do not appear to follow a discernible pattern and are probably attributable to data scattering perhaps due to nonuniformity of resin application.

5.4 Adhesive Strength to Asphalt and Concrete

5.4.1 Substrate Selection

Adhesive strength of the resin to asphalt and Portland cement concrete was evaluated using the tensile bond strength test procedure described in the preceding section for screening resins, except that asphalt and Portland cement concrete test block materials were used. The asphalt concrete test material was a paving block manufactured by Hastings Pavement Company, Lake Success, New York, and used for industrial flooring. It has an asphalt content in the 5-7 weight percent range of normal asphalt road mixes and contained limestone aggregate graded to provide a void content of about 0.5 percent (not verified) compared to 3 to 9 percent in typical road mixes. The asphalt used in these blocks had a higher softening point than most road mixes, having less than 30 mm penetration at room temperature (ASTM D-946) compared to 70 to 80 mm for road mixes. The Portland cement concrete test material was a patio block mix containing a local dolomite aggregate. Since it was obtained from a local building supply yard, its exact source and properties were unknown.

5.4.2 Results of Adhesion Tests

The adhesion evaluation was carried out with formulation 71-3 which is based on Epon 828 diluted with trimethylolpropane triacrylate and cured with mercaptan resins (see Table A-18). The results are summarized in Table 4.

Under dry application conditions, both at 73° F and at 14° F, the test blocks broke before the resin/substrate bond gave way. It was encouraging to find that a thin resin layer could be cured in 1/2 hour at 14° F to an adhesive and cohesive strength greater than the breaking strength of either asphalt or Portland cement concrete.

Under wet application conditions adhesive failure occurred in all of the samples, although the strength developed within 1/2 hour was about twice the minimum strength of 40 psi which had been specified. A further improvement of about 50 percent of the adhesive strength under wet conditions could be obtained by incorporating 0.2 percent of a mercaptan-functional silane coupling agent into the resin mixture. Such a coupling agent could be added to the mercaptan curing component and may be expected to have good stability provided water was excluded. Alternatively, an epoxy-functional silane coupling agent could be incorporated in the epoxy resin component under exclusion of moisture.

TABLE 3. ADHESIVE BOND STRENGTHS (PSI) OF EPOXY COMPOSITIONS TO TREATED AND UNTREATED SILICA AND LIMESTONE SUBSTRATES UNDER WET CONDITIONS AT 40° TO 45° F

	Silica Blocks	Limestone Blocks
Epoxy Formulation 58-1(b)		
Untreated, wet, 73° F	69	22
Treated(a), wet, 40-45° F		
Silane A-1100	87	90
Silane A-187	> 338	120
Silane A-189	172	192
Ken React TTS	55	193
Epoxy Formulation 71-3(c)		
Untreated, dry, 73° F	> 316	> 247
Untreated, wet, 73° F	16	4
Treated(a), wet, 40-45° F		
Silane A-1100	38	30
Silane A-187	90	98
Silane A-189	130	113
Ken React TTS	15	30

(a) Silane A-1100 = Union Carbide's gamma-aminopropyltriethoxysilane

Silane A-187 = Union Carbide's gamma-glycidoxypropyltrimethoxysilane

Silane A-189 = Union Carbide's gamma-mercaptopropyltrimethoxysilane

Ken React TTS = Kenrich Petrochemicals' isopropyltriisostearic titanate.

(b) Bisphenol-A/epichlorophydrin diluted with 1,4-butanediol diglycidyl ether and cured with mercaptan-functional resin (see Table A-11).

(c) Combination of bisphenol-A/epichlorophydrin epoxy resin and trifunctional acrylate monomer cured with mercaptan-functional resin (see Table A-18).

TABLE 4. ADHESIVE BOND STRENGTH (PSI) OF EPOXY COMPOSITION 71-3 TO ASPHALT AND PORTLAND CEMENT CONCRETE

		Adhesive Strength[a]			
		Asphalt		Concrete	
Application	Conditions	psi	Failure Mode	psi	Failure Mode
Dry	73° F	204	Block failure	365	Block failure
Dry	14° F	204	Block and cohesive failure	362	Block failure
Wet	73° F	83	Adhesive failure	80	Adhesive failure
Wet + A-189[b]	73° F	115	Adhesive failure	135	Cohesive failure

(a) Tested on the Instron in a tensile mode at 0.1 in/min crosshead speed 30 minutes after application.

(b) 0.2 percent by weight added to the resin.

5.5 Flexural Strength of Polymer Concrete

5.5.1. Aggregate Selection/Characterization

Round quartz pebbles and crushed dolomite ($CaCO_3 \cdot MgCO_3$ mineral) aggregates obtained from local sources (Parry Company, Chillicothe, Ohio, and Marble Cliff Quarries, Columbus, Ohio, respectively) were selected for this program as being representative of two types of natural aggregates with different physical and chemical characteristics. Three size ranges (3/4-inch x 1/2-inch, 1/2-inch x 4-mesh, and 4- x 8-mesh) were prepared, but based on permeability considerations, only the coarsest one (3/4-inch x 1/2-inch) was used in actual specimen fabrication work.

Permeability coefficient of the aggregate blend used was believed to be the key factor in determining how rapidly the epoxy resin would penetrate the voids. Since epoxy formulations with viscosities in the 10^3 cp range were being developed which gelled in about 2 minutes, a target penetration rate (flux) of 4 inches/minute was assumed necessary for preparation of an 8-inch-thick slab. For the special case of free downward flow of a liquid column, * Darcy's law relating permeability coefficient and fluid flow parameters becomes:

$$k = \text{permeability coefficient (darcys)} = \frac{\mu\nu}{\rho g} \qquad (1)$$

where

μ = viscosity (cp = $\frac{10^{-7}\ \text{N sec}}{\text{cm}^2}$)

ν = flux (cm/sec)

ρ = fluid density (g/cc)

$g = 9.8\ \text{m/sec}^2$

Substituting a viscosity of 10^3 cp, a flux of 4 inches/minutes, and a density of 1 g/cc yields a required permeability coefficient of about 1.7×10^5 darcys. Permeability coefficient data reported by Bo, et al** for various sized aggregates have been plotted in Figure 2 and extrapolated to the range of interest to aid in selecting an aggregate size with an appropriate permeability coefficient. Based on the above calculation, an aggregate size of about 1 inch is required to obtain penetration rates compatible with resin characteristics. Preliminary epoxy penetration experiments indicated the 3/4 x 1/2-inch aggregate size could be readily penetrated by the resin, but that the 1/2 x 4 mesh size caused puddling and air entrapment. This observation is consistent with the dramatic change in permeability coefficient with size shown in Figure 2.

The 3/4- x 1/2-inch aggregates selected had void contents of 35 to 36 percent (quartz) and 42 percent (dolomite) after consolidation by table vibration (Table 1). Minor reductions in void volume (about 2 percent) were obtained by blending this size with the 1/2- x 4-mesh fraction, but this

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* <u>Recommended Practice for Determining Permeability of Porous Media</u>, American Petroleum Institute, RP 27, 3rd edition, August 1956.

** Bo, M K., Freshwater, D. C., and Scarlett, B., "The Effect of Particle Size Distribution on the Permeability of Filter Cakes", Trans. Inst Chem Engrs., 43, T228 (1965).

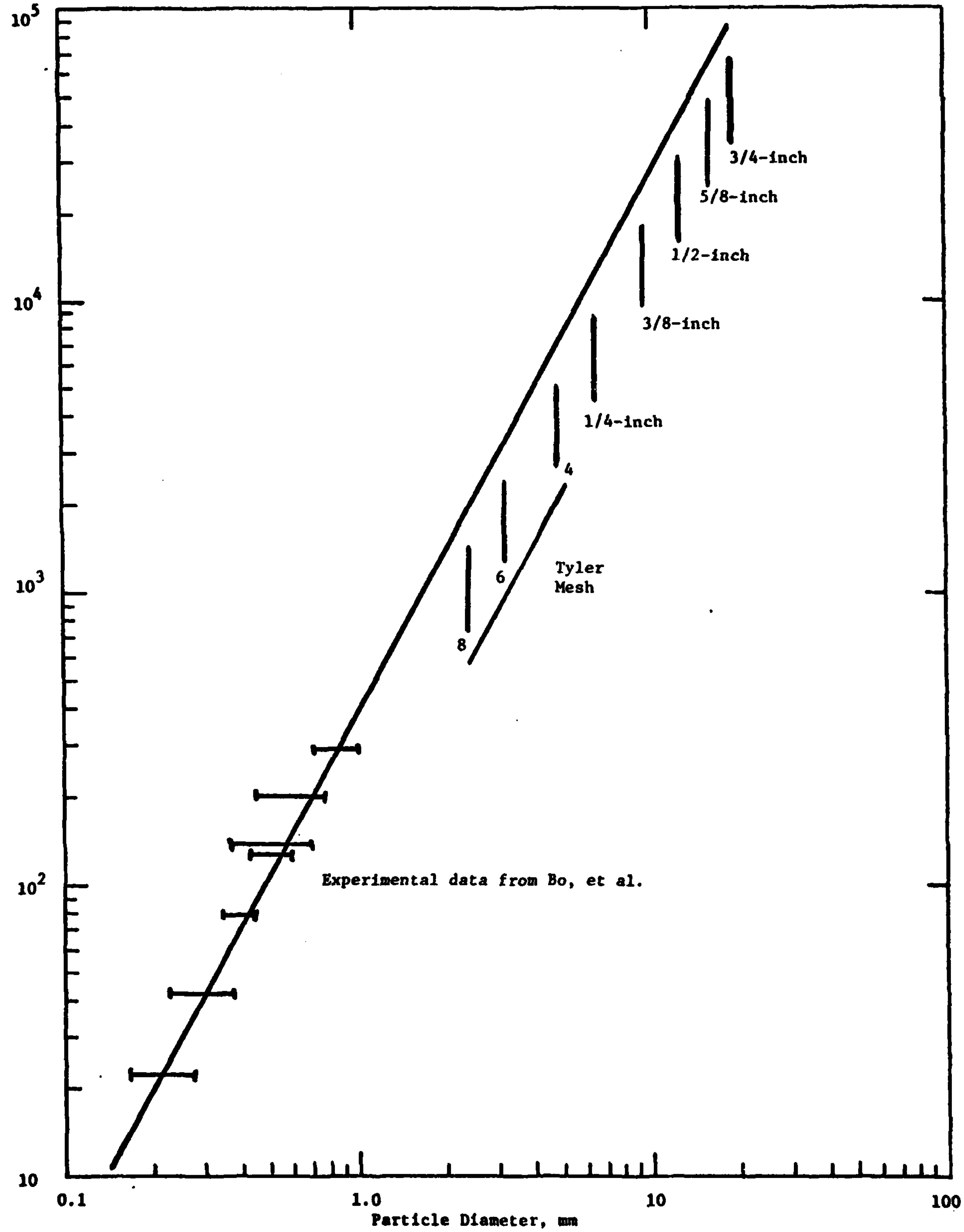

Figure 2. Effect of Aggregate Diameter on Permeability

amount was not considered beneficial enough to compensate for penetration penalties. Similar improvements should be obtainable through the use of slightly coarser aggregates (1-1/2 inches x 3/4 inch), but significant reductions in the void volume (e.g., 20 percent range) would require a 1:10 aggregate size ratio. * The use of aggregates in the 5-inch size range (to get minimal voids) was beyond the scope of this program but appears to be a feasible method of minimizing resin requirements in the field.

5.5.2 Specimen Preparation Procedure

Beam specimens 4x4x14 inches were used to evaluate the resin-concrete system. The beam molds were lined with polyethylene sheet and the 3/4x1/2-inch aggregates were vibratory compacted about 10 seconds to obtain a low void volume (see Table 5). The molds were then conditioned at the desired test temperature, removed from the conditioning chamber, and sprayed with a stream of resin applied to one edge of the beam to allow venting of air from the other edge. Mixing and application of the two-component resin system was accomplished with the aid of a Graco Bulldog Hydra Cat airless spray unit. After stripping the sample from the molds, the sprayed edge was placed down in the test fixture such that it was loaded in tension. Figure 3 shows a sample being prepared, and Figure 4 shows a sample being tested in third point loading. **

5.5.3 Results of the Flexural Strength Tests

Both of the two resin systems selected for this evaluation were based on Epon 828 resin and cured with a mixture of mercaptate resins (Capcure 3-800 and Mercaptate Ester Q-43 for viscosity control of the curing resin component). The two resin systems differed primarily in the diluent used for the epoxy resin component: (a) a difunctional resorcinol diglycidyl ether, in accordance with formulation 58-1M (Table 1 and Table A-11), and (b) a trifunctional acrylate, in accordance with formulation 71-3 (Table A-18). Some additional formulation adjustments were made to equalize the volumes of the epoxy resin and the curing resin components more closely. The final formulations used in the flexural strength evaluations were 122-1 and 116-2 (in Tables A-16 and A-18, respectively). Their compositions, by weight, were as follows:

	122-1	116-2
Part I		
Epon 828	33.3	35
Trimethylol propane triacrylate	--	15
Heloxy 69	16.7	--
Part II		
Capcure 3-800	27.2	22.5
Mercaptate Q-43	18.1	22.5
Capcure EH-30	4.7	5.0
	100.0	100.0

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* Powers, T. C., "Geometric Properties of Particles and Aggregates", PCA Bulletin 174, pp. 4-17 (1964).

** ASTM C78 except that the inner span length was reduced to 3 inches to facilitate uniform loading at the outer span, strength calculations were made by the general equation $\frac{3Pa}{bd^2}$ for these beams.

TABLE 5. PROPERTIES OF AGGREGATES EVALUATED

Aggregate	Size	Compaction	Pounds(a)		Unit Weight, pcf(b)	Bulk Specific Gravity(c)		Void Volume, o/o(b)	Apparent Sp. Gravity, g/cc(c)	Absorption, o/o(c)
			Gross	Net		g/cc	pcf			
Parry Quartz (round)	3/4 x 1/2(c)	loose(d)	29.50	23.90	97.15	2.61	162.9	40.4	2.63	0.28
Parry Quartz (round)	1/2 x 4 (M)	loose(d)	29.50	23.90	97.15	2.61	162.9	40.4	2.63	0.28
Parry Quartz (round)	60 C, 40 M	loose(d)	30.20	24.60	100.0	2.61	162.9	38.6	2.63	0.28
Parry Quartz (round)	3/4 x 1/2(c)	loose(e)	29.2	23.6	95.9	2.61	162.9	41.1	2.63	0.28
Parry Quartz (round)	1/2 x 4 (M)	loose(e)	29.4	23.8	96.7	2.61	162.9	40.6	2.63	0.28
Parry Quartz (round)	3/4 x 1/2(c)	vibrated(d)	31.25	25.65	104.3	2.61	162.9	36.0	2.63	0.28
Parry Quartz (round)	1/2 x 4 (M)	vibrated(d)	31.55	25.95	105.5	2.61	162.9	35.2	2.63	0.28
Parry Quartz (round)	60 C, 40 M	vibrated(d)	32.40	26.8	108.9	2.61	162.9	33.1	2.63	0.28
Parry Quartz (round)	3/4 x 1/2(c)	vibrated(e)	31.6	26.0	105.7	2.61	162.9	35.1	2.63	0.28
Parry Quartz (round)	1/2 x 4 (M)	vibrated(e)	31.8	26.2	106.5	2.61	162.9	34.6	2.63	0.28
Marble Cliff Dolomite (crushed)	3/4 x 1/2(c)	loose(e)	25.0	19.4	78.9	2.48	154.7	49.0	2.71	3.3
Marble Cliff Dolomite (crushed)	1/2 x 4 (M)	loose(e)	25.4	19.8	80.5	2.48	154.7	48.0	2.71	3.3
Marble Cliff Dolomite (crushed)	60 C, 40 M	loose(e)	26.4	20.8	84.6	2.48	154.7	45.3	2.71	3.3
Marble Cliff Dolomite (crushed)	3/4 x 1/2(c)	vibrated(e)	27.7	22.1	89.8	2.48	154.7	41.9	2.71	3.3
Marble Cliff Dolomite (crushed)	1/2 x 4 (M)	vibrated(e)	28.2	22.6	91.9	2.48	154.7	40.6	2.71	3.3
Marble Cliff Dolomite (crushed)	60 C, 40 M	vibrated(e)	29.1	23.5	95.5	2.48	154.7	38.3	2.71	3.3

(a) Weight of container having a factor of 4.065/ft^3 per ASTM C29

(b) ASTM C29 except for compaction procedure

(c) ASTM C127

(d) Operator A (10 seconds vibration)

(e) Operator B (15 seconds vibration)

Figure 3. Application of Resin With Airless Spray Equipment on Aggregate-Loaded Test Trays

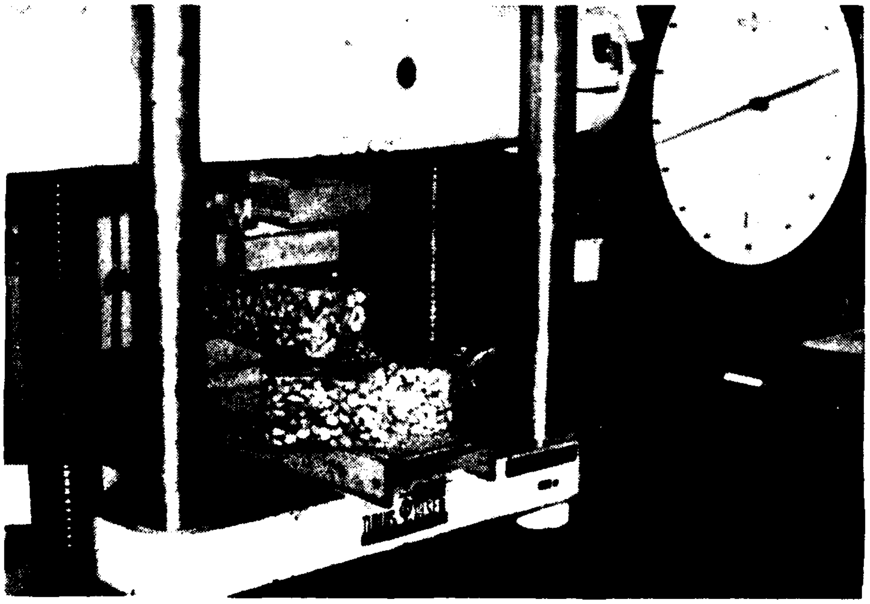

Figure 4. Flexural Testing of Beams

After initial adjustments were made on the Graco spraying equipment, both of these formulations could be applied at room temperature without heating. It was necessary, however, to insert a static mixer in front of the spray gun to assure that the two components were well mixed. Attempts to spray without the static mixer resulted in inadequate blending of the components as evidenced by slow cure and poor hardness properties. Filling of the beam mold required about 3 to 3-1/2 minutes which is close to the gellation time of these resin systems. Thus, the resin that had been sprayed first and had sunk to the bottom of the mold was about to gel when the filling of the mold was completed. Timing for testing purposes, however, was started when the first resin stream was applied to the aggregates in the molds.

The results of the flexural strength tests are given in Table 6. The initial tests were run on untreated aggregates. All subsequent runs were carried out with aggregate treated with Union Carbides A-189, mercapto functional silane, in accordance with the procedure described in section 5.2 on Selection of Coupling Agents for Use in Polymer Concrete.

The rapid gellation and curing of the resins resulted in a high exotherm which reached its peak from 45 minutes to 1 hour after spraying. Both the 1/2 hour and the 1 hour tests fell into this time region when the resin concrete was at high temperatures and its strength well below the optimum that could be reached after cool-down. Temperature measurements obtained with a surface pyrometer ranged from 110° to 140° F within this time interval. Internal temperatures were undoubtedly higher.

To illustrate the temperature effect on the flexural strength of the resin concrete, measurements were obtained on several test bars 24 hours after spraying. The data near the bottom of Table 6 illustrate that flexural strengths around 1500 psi can be obtained with dry treated quartz aggregate and around 1200 psi with similar wet aggregate. Moreover, when similar test bars were quenched in ice water starting 45 minutes after resin application (see Runs 38 and 39), the flexural strength again fell near 1500 psi.

It is concluded from this that the low flexural data are attributable to the high exotherm and the heat retention of the test bars rather than to incomplete cure. This is further supported by the observation that test bars prepared with aggregate at 40° F and others at 10° F had higher flexural strengths than comparable samples prepared at room temperature. Clearly, the greater heat sink provided by the cold aggregates lowered the temperature of the bars at the time of testing and thus resulted in higher flexural strength measurements. In fact, the flexural strength measurements at the 10°F conditions might have been higher, since penetration of the resin into the cold aggregates was incomplete, that is, the lower regions of the test bars were incompletely covered with resin.

Other observations which emerge from the data in Table 6 include:

(1) Flexural strengths of resin concrete based on quartz are higher than those of bars prepared with dolomite (in all but one instance, where the difference is essentially negligible).

TABLE 6. RESULTS OF FLEXURAL STRENGTH MEASUREMENTS

Test No.	Aggregate	Application Conditions	Application Temperature, °F	Testing Time, hr	Flexural Strength, psi
			Formulation 116-2		
1(a)	Dolomite	Dry	RT	1	146
2(a)	Dolomite	Dry	RT	1	176
3(a)	Quartz	Dry	RT	1	264
6	Dolomite	Dry	RT	1	281
7	Dolomite	Dry	RT	1	285
5	Quartz	Dry	RT	1	272
			Formulation 122-1		
8	Dolomite	Dry	RT	1	184
9	Dolomite	Dry	RT	1	206
10	Quartz	Dry	RT	1	352
11	Quartz	Dry	RT	1	387
12	Dolomite	Dry	10	1	406
13	Dolomite	Dry	10	1	364
14	Quartz	Dry	10	1	621
15	Quartz	Dry	10	1	590
16	Dolomite	Wet	RT	1	35
18	Dolomite	Wet	RT	1	45
17	Quartz	Wet	RT	1	230
19	Quartz	Wet	RT	1	238
30	Dolomite	Dry	RT	1/2	148
31	Dolomite	Dry	RT	1/2	138
28	Quartz	Dry	RT	1/2	187
29	Quartz	Dry	RT	1/2	194
34	Dolomite	Wet	RT	1/2	29
35	Dolomite	Wet	RT	1/2	38
32	Quartz	Wet	RT	1/2	354
33	Quartz	Wet	RT	1/2	220
24	Quartz	Dry	RT	1	309
25	Quartz	Dry	RT	1	429
26	Quartz	Dry	40	1	626
27	Quartz	Dry	40	1	468
36	Quartz	Wet	40	1	354
37	Quartz	Wet	40	1	220
38	Quartz	Dry	RT	1(b)	1568
39	Quartz	Dry	RT	1(b)	1438
20	Quartz	Dry	RT	24	1638
21	Quartz	Dry	RT	24	1298
22	Quartz	Wet	RT	24	1147
23	Quartz	Wet	RT	24	1263

(a) Untreated aggregates; all other aggregates treated with mercaptofunctional silane, A-189.

(b) Samples were quenched in ice water for 15 minutes before testing.

(2) Flexural strengths obtained with wet quartz are only moderately lower than comparable data obtained with dry quartz. In contrast, flexural strengths decline drastically between wet and dry dolomite.

The hypothesis that can best support these observations is that the coupling agent treatment was successful with the quartz aggregates, but not with the dolomite. However, it was established during the bonding studies of resin to silica and limestone blocks that silane A-189 was beneficial for both surfaces. It would appear to be necessary, therefore, that the coupling agent treatment be optimized separately for each substrate.

5.6 Durability

5.6.1 Background

A method of evaluating the relative resistance of the resin concrete to rutting raveling and/or wear from aircraft wheel traffic was required in this program. ASTM methods for abrasion testing of concrete considered for this purpose included a sand blast test (C 418), a rotating abrasive disc (C799, procedure A), a rotating cutter wheel (C779, procedure BO), and a rotating ball-bearing test (C779, procedure C). However, none of these test facilities were available at the contractor facilities or at the Portland Cement Association Laboratories. Contacts with the Army Corps of Engineers Waterways Experiment Station revealed two somewhat simpler abrasion test methods (a rotating slurry of steel balls and a single rotating cutter wheel), neither of which imposed high shear forces associated with landing or braking aircraft. A rotating abrasive cup wheel (a test used previously by the contractor in comparing the wear resistance of various orthotropic bridge deck pavements) was considered but was rejected on the basis that the continuous contact area of the wheel would not provide localized impact forces to the coarse textured resin concrete mix. A rolling grinding wheel technique was considered attractive in that it would more closely duplicate the type of stress actually imposed. However, this technique would have required a rather elaborate experimental set-up to maintain a constant wheel load using wheels of reasonable size (1-inch x 6-inch diameter), and miniature rotating wheel test equipment available at the contractor facility (Taber Abrasive Tester) was not compatible with the 3/4-inch x 1/2-inch aggregate in the concrete.

5.6.2 Test Procedure

Due to the lack of available standard test equipment, and/or concern for the appropriateness of these techniques, a rotating rod abrasion test procedure was devised for this program. The concept provides for relatively large contact area of a sliding abrasive material (similar to ASTM C779, procedure A), but utilizes simpler equipment and imposes impact forces (similar to ASTM C779, procedure C). Figure 5 illustrates the device, which is simply three 1-inch diameter hardened tool steel rods welded to the periphery of a threaded adapter fitting a commercial diamond core drill motor. The rods form a circular tract about 3-1/2 inches outside diameter and 1-inch wide, permitting tests to be run on portions of 4x4x14-inch beam specimens. The drill motor rotates at 500 RPM (no load) and provides a total dead weight of 47 pounds.

Figure 5. Device for Durability Tests

Figure 6. Asphalt Concrete Sample
After Durability Testing

Initial experiments with the rods revealed that little (<0.1 inch) or no wear but considerable heat build-up occurred in a 30-minute test period when the rods were run dry and without abrasive material feed. To accelerate the test and keep the specimens from heating up, a 7-inch-diameter bottomless plastic beaker about 7 inches high was cemented to the specimen with silicone rubber to contain a 1/2-inch layer (dry) of ASTM C109 sand and sufficient water to give a one-inch deep slurry. With the wet sand slurry, significant wear data could be obtained in 5-minute test periods, at which time the used sand was removed and a fresh sand slurry introduced. Figure 5 illustrates the entire test rig, showing the core drill apparatus and the plastic beaker in position. Figure 6 shows an asphalt concrete specimen (with beaker removed) after being tested several times.

5.6.3 Control Materials

In addition to the epoxy mixes, several control materials were tested to provide comparative data. The asphalt paving brick and Portland cement patio block materials used for adhesive tests were also evaluated for durability. (These materials are described in a previous adhesive test section of this report.) In addition, a Portland cement concrete test beam made from the same strength of Marble Cliff dolomite aggregate (w/c = 0.45 and 28-day flexural of 675 psi) was also evaluated. The epoxy concrete specimens were about one week old at the time the abrasion tests were conducted. All of the materials evaluated wore smoothly, and no evidence of aggregate pull out was noted.

5.6.4 Results

Figure 7 is a plot of the abrasive wear results obtained from the various materials tested. A total of 6 tests were run on 4 epoxy concrete test specimens, but the wear rates of the 3 quartz and 3 dolomite aggregate samples were essentially so similar that the data is simply shown as a band representing the widest data spread. Compared to either the asphalt block or a conventional Portland cement concrete mix (both with dolomite aggregate), the epoxy concrete mixes wear only about one-fourth as fast. The poor agreement between the two asphalt specimens tested may be due to the edges of the steel rods being flatter, and possibly sharper, during the first few tests of the series, * but the two concrete patio slabs were the second and second last specimens tested, yet gave excellent agreement. Material variability is another possible cause for this discrepancy.

Although only a limited number of tests were conducted with each material, the results clearly show that the wear resistance of epoxy concrete made from the preferred epoxy formulation (122-1) is at least twice that of asphalt or Portland cement concrete control materials after being fully cured. Time constraints imposed near the end of the program precluded abrasion testing beams only 30 to 60 minutes old, but somewhat similar data might be expected since the water slurry would tend to cool the beam surface somewhat. Although the relative performance of the epoxy concretes appears promising,

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* The leading edges were rounded back about 1/16-inch at the conclusion of the test sequence.

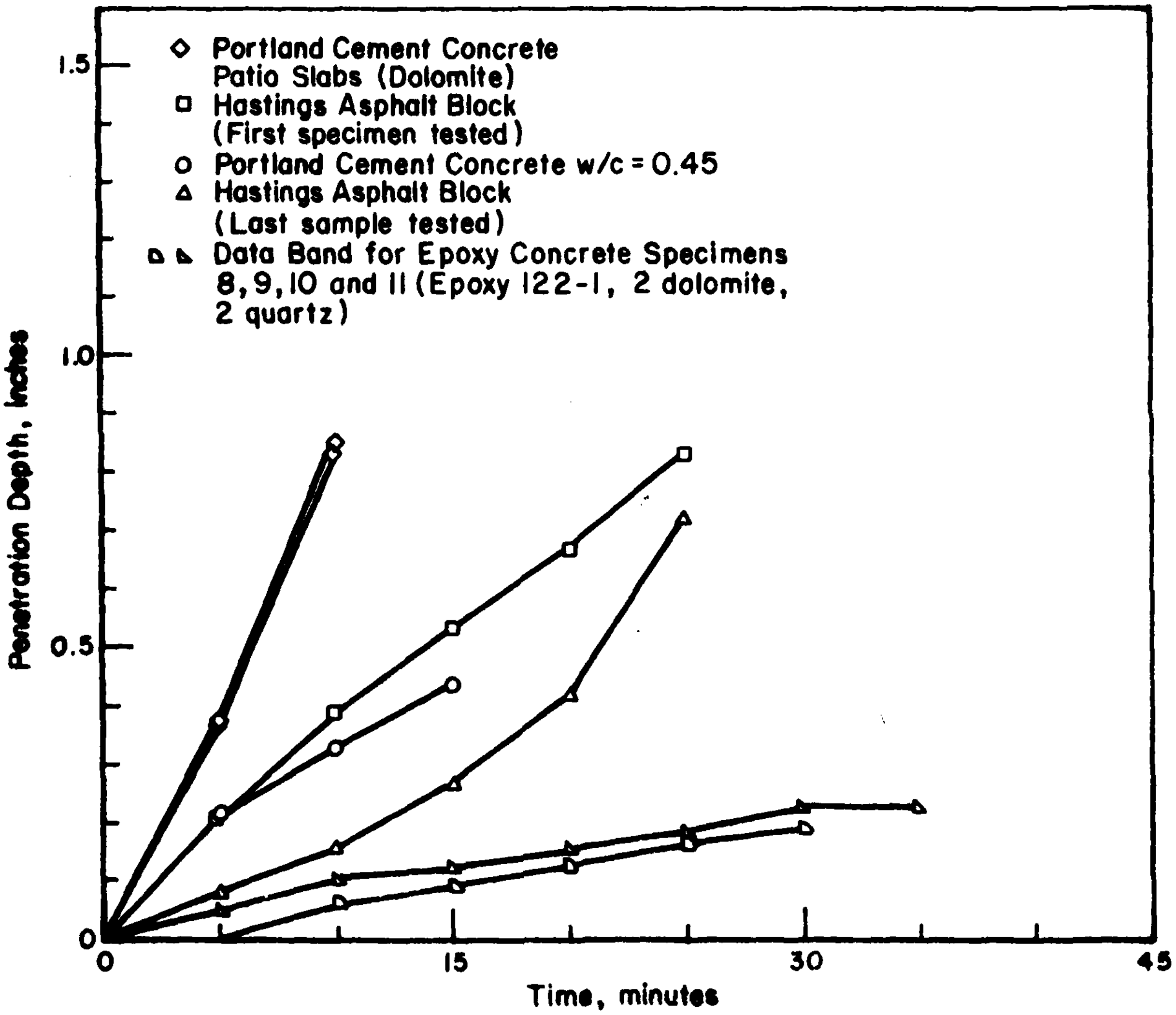

Figure 7. Abrasive Wear of Concrete Materials Versus Time

full-scale rolling wheel field tests would be required to properly assess the durability of any material ultimately developed.

5.7 Storage Stability of Resin Systems

Epoxy resin components and mercaptan components corresponding to the several formulations of interest were monitored for several weeks with respect to viscosity changes under various environmental conditions. Resins were stored at room temperature, at -20° C, and at 60° C. The latter condition will be rarely, if ever, encountered in the field. It represents an accelerated aging test and may indicate the storage stability over a longer time period at more moderate temperatures. Such extrapolations, however, are always risky, since reactions may be initiated at the higher temperatures which, under more modest temperature conditions, may not occur. The accelerated aging data can be used, however, as an alert to possible storage problems and to indicate the need for more extensive storage stability evaluations.

Resin mixtures were stored in glass jars. No effort was made to exclude oxygen from the head space. Periodically, the containers were brought back to room temperature, and their viscosity was determined with a Brookfield viscometer. The high sensitivity of these measurements to small temperature fluctuations was not at first recognized, which accounts for the scattering of the data in some of the experiments. Overall trends can still be recognized, however.

The epoxy formulations in Table 7 appear to be stable under the accelerated aging conditions. No trend of viscosity increase can be detected with the Epon 828/acrylic monomer mixture. There may be a very slow viscosity rise in the case of the Epon 828/Heloxy 69 mixture. However, using the rule of thumb that every 10 C in reaction temperature approximately doubles the rate of reaction, the viscosity change in this resin mixture does not appear alarming and a useful resin life in excess of 1 year appears likely.

The observed increase in viscosity in the mercaptan components is of real concern. It is especially high in formulations containing Mercaptate Q-43 Ester but is also significant in the case of the Capcure 3-800/EH-30 mixture. There is no indication that Capcure 3-800 has a storage stability problem, and it must be concluded that the presence of the tertiary amine, Capcure EH-30, creates the problem. *

In the relatively short temperature storage tests no clearly definable trend of viscosity increase could be identified, and it remains to be established whether the instability found at 60° C corresponds to a shelf life stability problem under more moderate temperatures. If this is the case, an alternative accelerator may need to be identified or a means to stabilize the mixture may need to be devised.

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* Recent information received from the manufacturer claims good shelf life stability of Capcure 3-800/EH-30 mixtures up to 50° C.

TABLE 7. ACCELERATED AGING TEST OF RESIN COMPONENTS AT 60° C

Reference Table Formulation	A-16 116-1		A-18 116-2	
	Part I	Part II	Part I	Part II
Epon 828	66.7		70	
Heloxy 69	33.3			
Trimethylolpropane triacrylate			30	
Capcure 3-800		90		43.5
Mercaptate Q43				43.5
Capcure EH-30		10		13

Day of Test	Measurement Temperature, °F	Brookfield Viscosity Data, cps			
0	--	2870	18,840	1896	3,470
7	--	3040	19,760	1919	6,630
14	73	2370	14,200	1552	8,930
21	72	3200	24,600	2008	--
28	71	4100	28,720	2168	18,080
35	72	3880	29,200	2140	20,400
42	72	4080	29,520	2072	23,000
49	76	3140	20,280	1388	18,720
56	73	3960	34,880	2024	28,320

SECTION VI

EQUIPMENT REQUIREMENTS

Assuming that the repair effort with polymer concrete is directed towards damage of craters about 20-foot diameter and assuming that up to 10 craters may need to be repaired, some general conclusions can be reached regarding equipment needs. The following analysis illustrates situations requiring either a 12-inch or a 6-inch deep repair cap:

Depth of repair cap, inches	12	6
Volume of repair cap, ft^3	314	157
Required resin volume, (a) ft^3	110	55
gal	822	411
Required resin flow rate, gal/min		
Resin application, 5 minutes	164	82
10 minutes	82	41
15 minutes	55	28
30 minutes	28	14

(a) Assuming 35 percent void volume.

If airless spray equipment of the type used in this project is to be employed, custom-made units will most likely be required to handle the necessary flow rates. The supplier of the equipment used in this study, Graco, Inc., of Minneapolis, Minnesota, has supplied units up to 20 to 30 gallons/minute capacity in the past by special request. Cost of such units, without heaters, is estimated in the $8,000 to $20,000 range, but economies are undoubtedly possible in the construction of large numbers of such units.

While the 20 to 30 gallon/minute application unit is the largest that was supplied in the past, units of greater capacity can undoubtedly be designed. Moreover, it is quite feasible to use two or more units in tandem, either feeding into a single hose or running multiple hoses into as many nozzles and letting the streams blend on the repair cap. Static mixers (similar to the one used in this effort) are recommended in favor of mechanical mixers because of their better wear and low maintenance characteristics and substantially lower costs. Large static mixers are readily available and are not expected to pose any flow limitations.

In addition to the airless spray units, a power supply must be available to provide about 100 psi compressed air to the air pumps. Higher pressures are not necessarily desirable, since the equipment typically works on a 34:1 fluid-to-air ratio (compression ratio). Other supportive equipment must include a supply truck with dual tanks of a minimum of 200 or 400-gallon capacity each, depending on depth of repair cap, to repair one crater, and stationary storage tanks of 2000- or 4000-gallon capacity for each resin component to service 10 craters. Provisions must also be made to lay down a fluid barrier (sand, nonwoven fabric, plastic film) underneath the graded aggregates of the repair cap.

It is assumed that appropriate quantities of aggregates (38 to 76 cubic yards for the 10 craters in the above example) will have been pretreated with coupling agent and will be stored outdoors under tarpolines. Resin storage should be near 70° F to avoid excessive viscosity increases in cold weather and to assure maximum storage life in hot weather. Underground storage may be advisable.

SECTION VII

CONCLUSIONS AND RECOMMENDATIONS

This research program has succeeded in identifying two-component epoxy resin formulations of low viscosity that can be applied in equal ratio of resin to curing agent components by means of commercially available airless spray equipment. The formulations selected for full evaluation are based on mercaptan curing systems and can utilize a variety of diluents for viscosity control.

These resin systems typically set up within 3 to 4 minutes after mixing at temperatures around 73° F. Good cures can be achieved within 1/2 hour of mixing in wet environments down to 5° C and in dry environments down to -25° C. Good adhesion to silica or limestone aggregates is obtained under dry conditions without the aid of coupling agents. Under wet conditions, the use of coupling agents is necessary to obtain good adhesion.

On test blocks in the laboratory, several organofunctional silane coupling agents worked well on both substrates. A mercaptan functional silane was selected for further evaluation. However, good adhesion with this coupling agent on spray application under wet conditions was only achieved in the case of quartz aggregates. In the case of dolomite aggregates results were not satisfactory, and either a different application method or a different coupling agent should be employed.

Adhesion performance of the resin systems to asphalt and Portland cement concrete was several times greater than the minimum requirement of 40 psi when applied under dry conditions. Under wet application condition, the adhesion was still twice the minimum requirement without the aid of coupling agents. When 0.2 percent of a silane coupling agent was added to the resin, an improvement of approximately 50 percent was obtained in adhesive strength to the wet substrates.

Durability tests were performed with the aid of a specially devised procedure which had been approved by the project monitor. The performance of polymer concrete samples to this severe wear test was far superior to that of asphalt and Portland cement concrete reference surfaces.

Two problems were encountered towards the end of the program which remain unresolved: (a) accelerated storage stability tests at 60° C pointed to a stability problem with mixtures of mercaptan resins and the tertiary amine accelerator, Capcure EH-30, and (b) the flexural strength tests were quite low under the majority of application conditions encountered.

As a follow-up of the present program, it is recommended that the stability problem be more carefully examined to determine:

(1) Its severity under lower temperature conditions.

(2) The possibility of substituting alternative tertiary amines or other accelerators for Capcure EH-30.

(3) The effect of substituting alternative diluents for the Mercaptate Q-43 Ester (either reactive or nonreactive types).

(4) The possibility of adding stabilizers to the resin/accelerator mix.

The results of the flexural strength tests demonstrated that the low values obtained within one hour of application are attributable to the high exotherm of the curing reaction which requires a long cool-down period. When let to cool down slowly or when quenched with ice water just prior to testing, flexural strength values of about 1500 psi were obtained with beams prepared under dry conditions and values of 1200 psi with beams prepared with wet aggregates.

Two possible approaches may be considered to address the problem of the exotherm and the heat content of the repair cap shortly after preparation:

(1) Physical cooling of the repaired cap with dry ice or other suitable coolant; this is technically a simple matter and would probably be successful, but must be examined from a logistics standpoint.

(2) Reformulation of the epoxy-curing system to minimize the exotherm problem and to build rigidity into the polymer-concrete within 1 hour of its preparation.

A follow-up effort is recommended to examine the feasibility of these approaches. A discussion of the theoretical considerations for achieving the necessary chemical modifications is provided in the next section.

7.1 Discussion of Theoretical Considerations

It has been shown earlier that using a mercaptan type curing agent, bisphenol-A based epoxy resins can be cured within a half hour, as desired. However the excess accumulation of heat takes time to dissipate, and the resin-aggregate mix is kept hot and relatively soft. This makes the runway unsuitable for landing. It would be desirable, therefore, not only to achieve the necessary state of cure of the epoxy compound but to get it in reasonably rigid condition within the scheduled time.

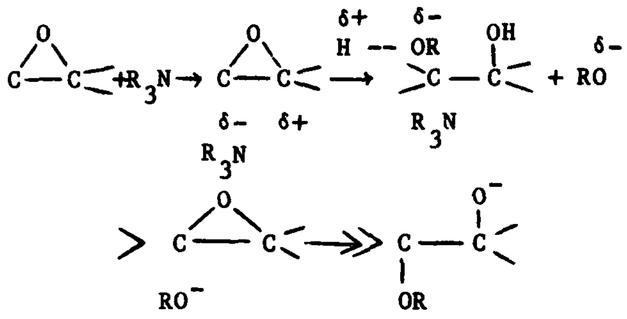
The accumulation of heat is brought about by:

(1) A high heat of polymerization (ΔHp).
(2) Increased rate of polymerization (Rp).
(3) Slow rate of heat transfer, (Rt), through the organic medium.

7.1.1 Rate of Polymerization (Rp)

It has to be kept in mind that the high rate of polymerization (curing) is essential to achieve a good state of cure in a short time. The sharp rise in temperature at the beginning accelerates the process. But once the state of cure is achieved, the heat should be dissipated faster. In other words, a short time-temperature peak is ideal for this process. Alternatively an optimum temperature for the exotherm may be worked out where the temperature rise is moderate but high enough to carry out the polymerization and low enough to ensure rigidity of the finished product. This can be achieved by selecting an appropriate resin system.

The mechanism of epoxide reaction with amines, phenols (oxey and thio), anhydrides, etc., has been well described by Lee and Neville *. Although the rate of reaction depends on the molecular structure of the epoxide and the curing agent, it is mainly controlled by the accesibility or steric factor. Table 8 lists the time required for gelling of diglycidyl ether of bisphenol A (DGEP) by a number of substituted amines, and it is clear that the curing agent having the smallest substituent (Benzyl dimethyl aniline) reacts faster than curing agents with large substituents. This is obvious from the scheme of the reaction given below:



Thus, the tertiary amine has to get adequate space to approach C atom 1 to initiate the reaction. The accessibility of the hydrogen donor H..OR is equally important. Since primary and secondary amines, after donating their hydrogen in successive steps become converted to tertiary amines, the mechanism of their reaction remains quite similar to that of the tertiary amine. It is important to note that the availability of active hydrogen is part of the curing process. The reactivity of the hydroxylic group and the crowding in its vicinity determine the rate of the reaction. Similar correlations between the rate and the structure of other curing agents, such as acids and phenols, have been established. The reactivity of the epoxy resin is also important. This again is basically determined by the accessibility of the epoxy group and the electronic-nature of the epoxy oxygen. Given good accessibility, electron attracting substituents such as methylene and vinyl improve the rate of reaction with acid type electrophilic curing agents. On the other hand, in the presence of a base catalyst glycidyl ether will act faster compared to epoxidized cyclohexene or vinyl cyclohexene. Finally, the rate of reaction also depends on the number of epoxy groups in a resin molecule, and this can be varied widely. It may therefore be possible to control the rate of the reaction by proper choice of epoxides and curing agents.

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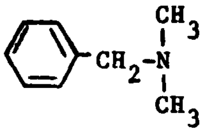
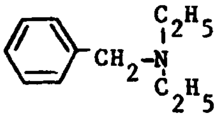
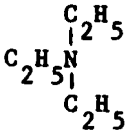
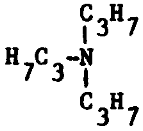
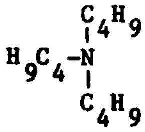
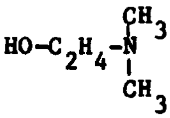
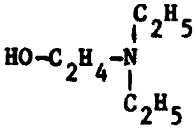
* Lee, H., Nelville, K. "Handbook of Epoxy Resins", McGraw-Hill, inc., 1967.

TABLE 8. EFFECT OF SUBSTITUENTS ON TERTIARY AMINE ON REACTIVITY OF DGEBA

Amine		Gel time, min
Benzyl dimethyl amine		5.3
Benzyl diethyl amine		7300.0
Triethyl amine	 $C_2H_5\overset{\displaystyle C_2H_5}{\underset{\displaystyle C_2H_5}{N}}$	11.2
Tripropyl amine	 $H_7C_3{-}\overset{\displaystyle C_3H_7}{\underset{\displaystyle C_3H_7}{N}}$	29.0
Tribuhyl amine	 $H_9C_4{-}\overset{\displaystyle C_4H_9}{\underset{\displaystyle C_4H_9}{N}}$	33.0
Dimethyl ethanolamine	 $HO{-}C_2H_4{-}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{N}}$	4.3
Diethyl ethanolamine	 $HO{-}C_2H_4{-}\overset{\displaystyle C_2H_5}{\underset{\displaystyle C_2H_5}{N}}$	17.2

7.1.2 Heat of Polymerization (ΔHp)

The heat of polymerization depends on the chemical nature of the curing agent. Some of the measured values of ΔHp with diglycidyl ether of bisphenol A are given in Table 9. It would appear that the maximum heat is generated when curing is carried out with the primary amine and the minimum in the case of a combination of a highly substituted tertiary amine and a carboxylic acid. Hence the heat evolved and accumulated during polymerization can be adjusted by choosing proper catalysts or combinations of catalysts.

7.1.3 Temperature Profile

The exotherm, which is a measure of the highest temperatures reached during curing of an epoxy compound, is also a function of the temperature of mixing. The exotherm profile of DGEBA and DMP salt is shown in Lee and Neville. * It will be seen that whereas mixing at 23° C and curing at 46° C give highest exotherm it lasts only for a short time compared to the one which is cured at 30° C. On the other hand, mixing at higher temperatures and curing at 23° C make the exotherm peak around 80° C and cool-down quickly. Thus suitable combinations of mixing and curing temperatures can be used to control the peak temperature and the life of the exotherm.

7.1.4 Heat Transfer

The heat transfer coefficient of the compound depends on the nature of the resin, the state of aggregation, and the macroscopic structure. Usually metallic and ceramic materials transfer heat much more quickly than the organic compounds. A number of fillers can be used with epoxy resins to assist the transfer of heat from the finished product. Again fine particles, because of their greater surface area, may transfer heat better than coarse particles, and metallic fibers in particular may be well suited for this purpose.

7.1.5 Temperature Rigidity

The temperature where the the polymeric product becomes rigid (glass temperature) again depends on the rigidity of the backbone chain of the polymer and intermolecular force density. Epoxides with bulky groups on the side chain have higher glass temperatures compared to the linear ones. Polymeric epoxides, particularly the ones based on Novolacs, tend to have higher Tg. Although a finished epoxy product is a thermoset and the concept of glass temperature does not apply, the principles can still be used to design the base materials and, by suitable choice of epoxy materials, products can be obtained which are rigid at higher temperature.

Whereas epoxy resin with mercaptan type curing agent has demonstrated the possibility of repairing the runway within an half hour, the residual problem of achieving rigidity within that time can be solved by adjusting the molecular and physical parameters as outlined above.

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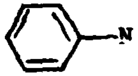
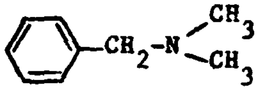
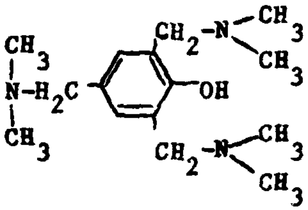
* Lee, H., Nelville, K., "Handbook of Epoxy Resons", McGraw-Hill, Inc., 1967.

TABLE 9. HEAT OF POLYMERIZATION OF DGEBA WITH VARIOUS CURING AGENTS

Curing Agent	Structure	Mole of curing agent per epoxy equivalent	ΔH(K cal/mole) Heat evolution
Benzyl amine		0.53	26.83
Pyridine		0.37	26.98
Benzyl dimethyl amine		0.19	22.14
2.4.6 Tris (dimethyl aminomethyl) phenol Tri 2 ethyl hexoic acid		0.028	19.88

APPENDIX A

SUMMARY OF TABLES OF EPOXY FORMULATIONS

TABLE A-1. POLYAMIDE CURED FORMULATIONS BASED ON EPON 812 AND APOGEN 101 EPOXY RESINS

Formulation	Epoxy Resin	%	Curing Agent	phr	Accelerator	phr	Components Temperature at Application, C	Application Conditions		Cure Rate(a)		Hardness of Casting,(b) Shore D
								Temperature, C	Environment	Film	Casting	
2-1	Epon 812		Epon V-40	50.2	--		23	23	Dry	24 hrs	24 hrs	20 (3)
2-2	Epon 812		Versamid 125	71.7	--		23	23	Dry	24 hrs	24 hrs	45 (3)
2-3	Epon 812		Apogen 256	31.4	--		23	23	Dry	4 hrs	45 min	65 (3)(c)
3-1	Epon 812 Apogen 101	50 50	Epon V-40	42	--		23	23	Dry	4 hrs	4 hrs	82 (3)
3-2	Epon 812 Apogen 101	50 50	Versamid 125	60	--		23	23	Dry	4 hrs	4 hrs	82 (3)
3-3	Epon 812 Apogen 101	50 50	Apogen 256	26.4	--		23	23	Dry	2 hrs	30 min	89 (3)
6-1	Epon 812 Apogen 101	50 50	Epon V-40	42	DMP 30	10	23	23	Dry	1.5 hrs	1.25 hrs	87 (3)
6-2	Epon 812 Apogen 101	50 50	Versamid 125	60	DMP 30	10	23	23	Dry	1.5 hrs	1 hr	85 (3)
6-3	Epon 812 Apogen 101	50 50	Apogen 256	26.4	DMP 30	10	23	23	Dry	1.25 hrs	1.25 hrs	88 (3)
6-4	Epon 812 Apogen 101	50 50	Apogen 256	26.4	DMP 30	10	23	5	Dry	4 hrs	--	79 (3)(c)

(a) Expressed as tack-free time. Data in air and in water are not strictly comparable.

(b) Numbers in parenthesis express time of testing in days following casting.

(c) Measurement obtained on film.

TABLE A-2. POLYAMIDE CURED FORMULATIONS BASED ON APOGEN 101 AND DER 732 EPOXY RESINS

Formulation	Epoxy Resin	%	Curing Agent	phr	Accelerator	phr	Components Temperature at Application, C	Application Conditions: Temperature, C	Application Conditions: Environment	Cure Rate(a): Film	Cure Rate(a): Casting	Hardness of Casting,(b) Shore D
12-1(c)	Apogen 101		Capcure 38	50	--		77	23	Dry	30 min	1 min	87 (3)
12-2(c)	Apogen 101		Capcure 38	100	--		77	23	Dry	1 hr	2 min	(d) (3)
12-3(c)	Apogen 101		Capcure 38	100	DMP 30	10	77	23	Dry	(e)	(e)	--
17-1	DER 732 Apogen 101	50 50	Epon V-40	28	DMP 30	10	23	23	Dry	3.5 hrs	2 hrs	78 (3)
17-2	DER 732 Apogen 101	50 50	Versamid 125	50	DMP 30	10	23	23	Dry	4.5 hrs	4.5 hrs	76 (3)
17-3	DER 732 Apogen 101	50 50	Apogen 256	22	DMP 30	10	23	23	Dry	4.5 hrs	1.5 hrs	71 (3)
18-1	DER 736 Apogen 101	50 50	Epon V40	39.6	DMP 30	10	23	23	Dry	4 hrs	4 hrs	83 (3)
18-2	DER 736 Apogen 101	50 50	Versamid 125	56.6	DMP 30	10	23	23	Dry	4.5 hrs	4.5 hrs	83 (3)
18-3	DER 736 Apogen 101	50 50	Apogen 256	24.8	DMP 30	10	23	23	Dry	1 hr	3 hrs	83 (3)

(a) Expressed as tack-free time. Data in air and in water are not strictly comparable.

(b) Numbers in parenthesis express time of testing in days following casting.

(c) Components were heated to 170 F before mixing.

(d) Surface tacky after 3 days.

(e) Too fast to be mixed.

TABLE A-3. POLYAMIDE CURED FORMULATIONS BASED ON DEN 431 EPOXY NOVOLAC RESIN

Formulation	Epoxy Resin	Curing Agent	phr	Accelerator	phr	Components Temperature at Application, C	Application Conditions: Temperature, C	Application Conditions: Environment	Cure Rate(a): Film	Cure Rate(a): Casting	Hardness of Casting,(b) Shore D
10-1	DEN 431	Epon V40	42	--		23	23	Dry	--	--	78 (4)
10-4	DEN 431	Epon V40	42	DMP 30	10	23	23	Dry	3 hrs	Sl. tacky at 3 hrs	86 (4)
10-2	DEN 431	Versamid 125	61.3	--		23	23	Dry	--	--	76 (4)
10-5	DEN 431	Versamid 125	61.3	DMP 30	10	23	23	Dry	3 hrs	3 hrs	80 (4)
10-3	DEN 431	Apogen 256	27	--		23	23	Dry	4 hrs	35 mins	90 (4)
10-6	DEN 431	Apogen 256	27	DMP 30	10	23	23	Dry	3 hrs	25 mins	90 (4)
28-1	DEN 431	Arogen 256	27	--		50	23	Dry	140 mins	5 mins	86 (3)
28-2	DEN 431	Apogen 256	27	--		60	23	Dry	120 mins	4 mins	88 (3)
28-3	DEN 431	Apogen 256	27	--		77	23	Dry	75 mins	2 mins	85 (3)
31-1	DEN 431	Apogen 256	27	--		77	23	Wet	(c)	(c)	--
31-2	DEN 431	Arogen 256	27	--		77	-25	Dry	(d)	(d)	--

(a) Expressed as tack-free time. Data in air and in water are not strictly comparable.

(b) Numbers in parenthesis express time of testing in days following casting.

(c) Separation of phases was observed after immersion in water.

(d) Remained tacky after 2 hours.

TABLE A-4. POLYAMIDE CURED FORMULATIONS BASED ON EPON 828 EPOXY RESIN

Formula-tion	Epoxy Resin	Curing Agent	phr	Accelerator	phr	Diluent	phr	Components Temperature at Application, C	Application Conditions		Cure Rate(a)		Hardness of Casting,(b) Shore D
									Temperature, C	Environment	Film	Casting	
22-1	Epon 828	Capcure 38	51	DMP 30	10	--		23	23	Dry	5 hrs	5 hrs	83 (3)
22-2	Epon 828	Capcure 38	75	DMP 30	10	--		23	23	Dry	5 hrs	5 hrs	82 (3)
22-3	Epon 828	Capcure 38	100	DMP 30	10	--		23	23	Dry	--	--	76 (3)
22-4	Epon 828	Capcure 38	100	DMP 30	10	p-Nonyl Phenol	20	23	23	Dry	--	--	80 (3)
22-5	Epon 828	Capcure 38	100	DMP 30	10	p-Nonyl Phenol	10	23	23	Dry	--	2.5 hrs	55 (3)
26-1	Epon 828	Capcure 38	50	DMP 30	10	Furfuryl Alcohol	10	23	23	Dry	3.5 hrs	90 mins	84 (3)
26-2	Epon 828	Capcure 38	50	DMP 30	10	Furfuryl Alcohol	20	23	23	Dry	3.5 hrs	40 mins	83 (3)

(a) Expressed as tack-free time. Data in air and in water are not strictly comparable.

(b) Numbers in parenthesis express time of testing in days following casting.

TABLE A-5. AMINE CURED FORMULATIONS BASED ON ARALDITE 509, CAPCURE WR AND EPON 828 EPOXY RESINS

Formula-tion	Epoxy Resin	Curing Agent	phr	Accelerator	phr	Components Temperature at Application, C	Application Conditions Temperature, C	Application Conditions Environ-ment	Cure Rate[(a)] Film	Cure Rate[(a)] Casting	Hardness of Casting,[(b)] Short D
32-3	Capcure WR Epoxide	Araldite DP152	20.5	--		23	23	Dry	(d)	(d)	--
32-5	Araldite 509	Araldite DP152	18	--		23	23	Dry	(d)	(d)	--
53-1	Epon 828	DEH 39	14.3	Capcure EH30	10	23	23	Dry	2 hrs	25 mins	85 (2)
53-2[(c)]	Epon 828	DEH 39	14.5	Capcure EH30	10	23	23	Dry	60 mins	7 mins	83 (2)
53-3[(c)]	Epon 828	Hexamethylene Diamine	18	Capcure EH30	10	23	23	Dry	1.5 hrs	20 mins	80 (2)
54-1[(c)]	Epon 828	DEH 39	14.5	Capcure EH30	10	23	23	Wet	2 hrs	1 hr	83 (4)
57-1	Epon 828	Diethylene-triamine	13.3	--		23	23	Dry	146 mins	38 mins	84 (3)
57-2	Epon 828	Diethylene-triamine	13.3	Capcure EH30	10	23	23	Dry	120 mins	39 mins	84 (3)

(a) Expressed as tack-free time. Data in air and in water are not strictly comparable.

(b) Numbers in parenthesis express time of testing in days following casting.

(c) Furfuryl alcohol added as diluent at 17.8 phr.

(d) Did not fully cure.

TABLE A-6. AMINE CURED FORMULATIONS USING SALICYLIC ACID/AMINE ADDUCTS AS CURING AGENTS

Formulations	Epoxy Resin	Curing Agent	phr	Accelerator	phr	Components Temperature at Application, C	Application Conditions		Cure Rate(a)		Hardness of Casting,(b) Shore D
							Temperature, C	Environment	Film	Casting	
38-1	Araldite 509	Araldite HY 2969	60	--		23	23	Dry	(c)	(c)	80 (3)
97-4	Araldite 509	Adduct A(d)	60	--		23	23	Dry	7120 mins	96 mins	77-80 (4)
97-1	Epon 828	Adduct A(d)	60	--		23	23	Dry	115 mins	40-48 mins	83 (4)
97-2	Epon 828	Adduct A(d)	60	Capcure EH-30	10	23	23	Dry	160 mins	124 mins	85 (4)
38-2	Araldite 509	Araldite 850	60	—		23	23	Dry	2 hrs	2 hrs	81 (3)
97-5	Araldite 509	Adduct B(e)	60	--		23	23	Dry	>120 mins	12.5-14.5 mins	76-80 (4)
97-3	Epon 828	Adduct B(e)	60	--		23	23	Dry	72 mins	12-13.5 mins	85 (4)

(a) Expressed as tack-free time. Data in air and in water are not strictly comparable.

(b) Numbers in parenthesis express time of testing in days following casting.

(c) Tacky after 5 hours.

(d) Adduct A - 200/10 Araldite HY 2969/Salicylic acid reacted at 60 C.

(e) Adduct B - 200/10 Araldite 850/Salicylic acid reacted at 60 C.

TABLE A-7. ' AMINE CURED FORMULATIONS BASED ON EPI-REZ/EPI-CURE COMBINATIONS

Formulation	Epoxy Resin	Curing Agent	phr	Components Temperature at Application, C	Application Conditions		Cure Rate(a)		Hardness of Casting,(b) Shore
					Temperature, C	Environment	Film	Casting	
68-1	Epi-Rez 50727	Epi-Cure 874	22	23	23	Dry	6 hrs(c)	1.5 min	84 (2)
72-1A	Epi-Rez 50727	Epi-Cure 874	22	5	5	Dry	49 mins	6 mins	85 (3)
72-1B	Epi-Rez 50727	Epi-Cure 874	22	5	5	Wet	8 mins(d)	8 mins(d)	82 (3)
72-1C	Epi-Rez 50727	Epi-Cure 874	22	5	-25	Dry	40 mins (c)	12 mins (c)	85 (3)
68-2	Epi-Rez 5027	Epi-Cure 874	21	23	23	Dry	1.5 hrs (c)	3 mins	82 (2)
72-2A	Epi-Rez 5027	Epi-Cure 874	21	5	5	Dry	>2 hrs	>2 hrs	82 (3)
72-2B	Epi-Rez 5027	Epi-Cure 874	21	5	5	Wet	(e)	(e)	78-82 (3)
72-2C	Epi-Rez 5027	Epi-Cure 874	21	5	-25	Dry	(f)	(f)	81 (3)

(a) Expressed as tack-free time. Data in air and in water are not strictly comparable.

(b) Numbers in parenthesis express time of testing in days following casting.

(c) Hard, but tacky after 6 hours.

(d) Soft, but not tacky.

(e) Cured overnight.

(f) Not cured overnight.

TABLE A-8. AMINE CURED FORMULATIONS BASED ON COMBINATIONS OF EPON 828 AND VARIOUS ANCAMINE CURING AGENTS

Formulation	Epoxy Resin	Curing Agent	phr	Accelerator	phr	Components Temperature at Application, C	Application Conditions Temperature, C	 Environment	Cure Rate$^{(a)}$ Film	 Casting	Hardness of Casting,$^{(b)}$ Shore D
99-1	Epon 828	Ancamine 1767	100	--		23	23	Dry	58 mins	7.5 mins	80-82 (3)
99-2	Epon 828	Ancamine 1767	100	Capcure EH-30	10	23	23	Dry	57 mins	5.5 mins	80 (3)
106-1	Epon 828	Ancamine 1767	100	Capcure EH-30	10	23	23	Wet	—	58 mins	79-82 (3)
106-3	Epon 828	Ancamine 1767	100	Capcure EH-30	10	23	5	Wet	—	>48 mins	80-82 (1)
106-5	Epon 828	Ancamine 1767	100	Capcure EH-30	10	23	-25	Dry	—	19 mins	82 (3)
99-3	Epon 828	Ancamine 1767 Ancamine AD	50 30	Capcure EH-30	10	23	23	Dry	25 mins	6 mins	78-82 (3)
99-4	Epon 828	Ancamine 1767 Ancamine AD	50 12.5	Capcure EH-30	8	23	23	Dry	37 mins	7 mins	84-85 (3)
100-1	Epon 828	Ancamine LT	50	—		23	23	Dry	<107 mins	34 mins	85 (3)
100-2	Epon 828	Ancamine LT	50	Capcure EH-30	7.5	23	23	Dry	140 mins	40 mins	85 (3)
100-3	Epon 828	Ancamine AD	60	--		23	23	Dry	27 mins	5 mins	80 (3)
100-4	Epon 828	Ancamine AD	60	Capcure EH-30	8	23	23	Dry	19 mins	4 mins	80 (3)
106-2	Epon 828	Ancamine AD	60	Capcure EH-30	8	23	23	Wet	—	28 mins	83 (3)
106-4	Epon 828	Ancamine AD	60	Capcure EH-30	8	23	5	Wet	—	>45 mins	85-86 (4)
106-6	Epon 828	Ancamine AD	60	Capcure EH-30	8	23	-25	Dry	—	6-6.5 mins	78-81 (2)
100-7	Epon 828	Ancamine XT	25	--		233	23	Dry	<50 mins	8 mins	85 (3) Film
100-6	Epon 828	Ancamine XT	25	Capcure EH-30	6.3	23	23	Dry	<55 mins	7 mins	85 (3) Film

TABLE A-8. (Continued)

Formulation	Epoxy Resin	Curing Agent	phr	Accelerator	phr	Components Temperature at Application, C	Application Conditions		Cure Rate[(a)]		Hardness of Casting,[(b)] Shore D
							Temperature, C	Environment	Film	Casting	
110-1	Epon 828	Sur-wet R	100	--		23	23	Dry	>110 mins	>110 mins	55-60 (3)
110-2	Epon 823	Sur-wet R	100	Capcure EH-30	10	23	23	Dry	>104 mins	45-65 mins	78 (3)
110-3	Epon 828	Sur-wet R	133	Capcure EH-30	11.7	23	23	Dry	>98 mins	39-59 mins	50-53 (3)
110-4	Epon 828	Sur-wet R Ancamine 1767	50 50	Capcure EH-30	10	23	23	Dry	75 mins	15-17 mins	77 (3)
110-5	Epon 828	Sur-wet R Ancamine AD	50 30	Capcure EH-30	9	23	23	Dry	81 mins	15-20 mins	82-83 (3)
110-6	Epon 828	Sur-wet R Ancamine XT	50 14.5	Capcure EH-30	8	23	23	Dry	>76 mins	27-44 mins	83-84 (3)

(a) Expressed as tack-free time. Data in air and in water are not strictly comparable.

(b) Numbers in parenthesis express time of testing in days following casting.

TABLE A-9. MERCAPTAN CURED FORMULATIONS BASED ON EPON 812 EPOXY RESIN AND MIXTURES OF EPON 812 WITH EPON 828 AND APOGEN 101

Formulation	Epoxy Resin	%	Curing Agent	phr	Accelerator	phr	Components Temperature at Application, C	Application Conditions		Cure Rate$^{(a)}$		Hardness of Casting,$^{(b)}$ Short D
								Temperature, C	Environment	Film	Casting	
14-1	Epon 812		Capcure 3-800	100	Capcure EH-30	10	23	23	Dry	4 mins	2 mins	60-65 (2)
21-1	Epon 812		Capcure 3-800	100	Capcure EH-30	10	23	-20	Dry	5 hrs	10 mins	60 (3) still cold
14-2	Apogen 101 Epon 812	50 50	Capcure 3-800	100	Capcure EH-30	10	23	23	Dry	3.5 mins	2 mins	73 (2)
21-2	Apogen 101 Epon 812	50 50	Capcure 3-800	100	Capcure EH-30	10	23	-20	Dry	10 mins	5 mins	82 (3) still cold
14-3	Epon 812 Epon 828	50 50	Capcure 3-800	100	Capcure EH-30	10	23	23	Dry	5 mins	2 mins	78 (2)
21-3	Epon 812 Epon 828	50 50	Capcure 3-800	100	Capcure EH-30	10	23	-20	Dry	10 mins	5 mins	85 (3) still cold
24-2	Epon 812 Epon 828	50 50	Capcure 3-800	100	Capcure EH-30	10	23	23	Dry	5 mins	2 mins	67 (3)
14-4	Epon 812		Capcure 3-800	125	Capcure EH-30	10	23	23	Dry	3.5 mins	2 mins	30 (2)

(a) Expressed as tack-free time. Data in air and in water are not strictly comparable.

(b) Numbers in parenthesis express time of testing in days following casting.

TABLE A-10. MERCAPTAN CURED FORMULATIONS BASED ON EPON 828 EPOXY RESIN

Formulation	Epoxy Resin	Curing Agent	phr	Accelerator	phr	Components Temperature at Application, C	Application Conditions		Cure Rate$^{(a)}$		Hardness of Casting,$^{(b)}$ Shore D
							Temperature, C	Environment	Film	Casting	
13-1	Epon 828	Capcure 3-800	100	DMP 30	10	23	23	Dry	4 mins	2 min	86 (3)
13-2	Epon 828	Capcure 3-800	100	Capcure EH-30	10	23	23	Dry	3 mins	3 mins	80-84 (3)
15-1	Epon 828	Capcure 3-800	100	Araldite Accelerator 062	10	23	23	Dry	7 mins	4 mins	85 (2)
24-1	Epon 828	Capcure 3-800	100	Capcure EH-30	10	23	23	Dry	2.5 mins	1.5 mins	83 (2)
24-4	Epon 828	Capcure 3-800	100	BDMA	10	23	23	Dry	8 mins	2 mins	83 (3)
20-1	Epon 828	Capcure 3-800	100	Capcure EH-30	10	23	23	5 mins in water	7 mins	--	76-78 (3)$^{(c)}$
20-2	Epon 828	Capcure 3-800	100	Capcure EH-30	10	23	23	15 mins in water	12 mins	--	75 (3)$^{(c)}$
20-3	Epon 828	Capcure 3-800	100	Capcure EH-30	10	23	23	30 mins in water	12 mins	--	76 (3)$^{(c)}$
34-1	Epon 828	Capcure 3-800	100	Capcure EH-30	10	23	A-23	Wet	15 mins	--	70$^{(d)}$
							B-25	Dry	15 mins	--	72$^{(d)}$

(a) Expressed as tack-free time. Data in air and in water are not strictly comparable.

(b) Numbers in parenthesis express time of testing in days following casting.

(c) On film, 3 days after application.

(d) On film, 2 hours after application.

TABLE A-11. MERCAPTAN CURED FORMULATIONS BASED ON LOW VISCOSITY EPOXY RESINS AND MIXTURES

Formulation	Epoxy Resin	%	Curing Agent	phr	Accelerator	phr	Components Temperature at Application, C	Application Conditions		Cure Rate$^{(a)}$		Hardness of Casting,$^{(b)}$ Shore D
								Temperature, C	Condition	Film	Casting	
24-3	Epon 828 DER 732	50 50	Capcure 3-800	100	Capcure EH-30	10	23	23	Dry	30 mins	17 mins	20 (3)
30-1	Epon 828 Araldite ERE 1359	50 50	Capcure 3-800	100	Capcure EH-30	10	23	23	Dry	8 mins	1 min	82 (3)
30-2	Araldite ERE 1359		Capcure 3-800	100	Capcure EH-30	10	23	23	Dry	10 mins	1 min	82 (3)
34-4A	Araldite ERE 1359		Capcure 3-800	100	Capcure EH-30	10	23	23	Wet	20 mins	--	60$^{(c)}$
34-4B	Araldite ERE 1359		Capcure 3-800	100	Capcure EH-30	10	23	25	Dry	Froze, tacky	--	65$^{(c)}$
42-1	Epon 828 Epoxide No. 7	50 50	Capcure 3-800	100	Capcure EH-30	10	23	23	Dry	30 mins	13 mins	55 (3)
42-2	Epon 828 Araldite RD-2	50 50	Capcure 3-800	100	Capcure EH-30	10	23	23	Dry	20 mins	4 mins	70-72 (3)
42-3	Epon 828 Heloxy 69	50 50	Capcure 3-800	100	Capcure EH-30	10	23	23	Dry	3 mins	1 min	86 (3)
52-1	Epon 828 Araldite RD-2	50 50	Capcure 3-800	100	Capcure EH-30	10	23	23	Dry	--	5 mins	65 (2)
52-2	Epon 828 Araldite RD-2	66.7 33.3	Capcure 3-800	100	Capcure EH-30	10	23	23	Dry	--	4 mins	78 (2)
52-3	Epon 828 Araldite RD-2	75	Capcure 3-800	100	Capcure EH-30	10	23	23	Dry	--	5 mins	80 (2)
58-1	Epon 828 Araldite RD-2	66.7 33.3	Capcure 3-800	100	Capcure EH-30	10	23	23	Dry	7 mins	--	15 (3)
58-1B	Epon 828 Araldite RD-2	66.7 33.3	Capcure 3-800	100	Capcure EH-30	10	23	23	Wet	11 mins	--	70 (3)
59-1	Epon 828 Araldite RD-2	66.7 33.3	Capcure 3-800	100	Capcure EH-30	10	23	-25	Dry	>55 mins	--	62 (3)

TABLE A-11. (Continued)

Formulation	Epoxy Resin	%	Curing Agent	phr	Accelerator	phr	Components Temperature at Application, C	Application Conditions		Cure Rate[a]		Hardness of Casting,[b] Shore D
								Temperature, C	Condition	Film	Casting	
77-1	Epon 828 Phenyl-Glycidyl Ether	50 50	Capcure 3-800	100	Capcure EH-30	10	23	23	Dry	>>1 hr	5 mins	65-75 (5)[d]
77-2	Epon 828 Phenyl-Glycidyl Ether	75 50	Capcure 3-800	100	Capcure EH-30	10	23	23	Dry	11 mins	4.5 mins	65-67 (5)
77-3	Epon 828 Phenyl-Glycidyl Ether	85 15	Capcure 3-800	100	Capcure EH-30	10	23	23	Dry	9 mins	4.5 mins	72-75 (5)

(a) Expressed as tack-free time. Data in air and in water are not strictly comparable.

(b) Numbers in parenthesis express time of testing in days following casting.

(c) On film, 2 hours after application.

(d) Shore A hardness.

TABLE A-12. MERCAPTAN CURED FORMULATIONS BASED ON CAPCURE WR AND EPON 828 EPOXY RESINS

Formulation	Epoxy Resin	%	Curing Agent	phr	Accelerator	phr	Diluent	phr	Components Temperature at Application, C	Temperature, C	Condition	Cure Rate,$^{(a)}$ min		Hardness of Casting,$^{(b)}$ Shore D
												Film	Casting	
32-1	Capcure WR		Capcure WR-6	81	--		--		23	23	Dry	7	4	82 (2)
33-1A	Capcure WR		Capcure WR-6	81	--		--		23	23	Wet	20	--	80$^{(c)}$
33-1B	Capcure WR		Capcure WR-6	81	--		--		23	-25	Dry	50	--	78$^{(c)}$
32-2	Capcure WR		Capcure WR-6	81	Capcure EH-30	5	--		23	23	Dry	7	4	80 (2)
52-4	Epon 828 Araldite RD-2	50 50	Capcure WR-6	100	Capcure EH-30	10	--		23	23	Dry	--	7	--
47-1	Epon 828		Capcure 3-800	200	Capcure EH-30	20	Furfuryl alcohol	100	23	23	Dry	10-12	6-7	12-15$^{(d)}$
47-2	Epon 828		Capcure 3-800	100	Capcure EH-30	10	Furfuryl alcohol	31	23	23	Dry	8	3	43-49$^{(e)}$
47-3	Epon 828		Capcure 3-800	100	Capcure EH-30	10	p-Nonyl phenol	31	23	23	Dry	7-8	3	75-80$^{(e)}$
76-1	Epon 828		Capcure 3-800	100	Capcure EH-30	10	Benzyl alcohol	31	23	23	Dry	12.5	6.5-7	80-85 (5)

(a) Expressed as tack-free time. Data in air and in water are not strictly comparable.

(b) Numbers in parenthesis express time of testing in days following casting.

(c) Measurement obtained on film 3.5 hours after application.

(d) On Shore A-2 scale, 20 hours after casting.

(e) 20 hours after casting.

TABLE A-13. MERCAPTAN-CURED FORMULATIONS BASED ON ARALDITE 509 EPOXY RESIN

Formulation	Epoxy Resin	%	Curing Agent	phr	Accelerator	phr	Components Temperature at Application, C	Application Conditions: Temperature C	Application Conditions: Environment	Cure Rate(a): Film	Cure Rate(a): Casting	Hardness of Casting,(b) Shore D
51-1	Araldite 509		Capcure 3-800	100	Capcure EH-30	10	23	23	Dry	10 mins	5 mins	76 (2)
96-1A	Araldite 509		Capcure 3-800	100	Capcure EH-30	10	23	23	Wet	12.5 mins	--	55-60 (3)(d)
96-1B	Araldite 509		Capcure 3-800	100	Capcure EH-30	10	23	-25	Dry	(c)	--	72-73 (3)(d)
51-2	Araldite 509		Capcure 3-800 Mercaptate Q-43	75 25	Capcure EH-30	10	23	23	Dry	6 mins	4 mins	72 (3)
52-5	Araldite RD-2 Araldite 509	50 50	Capcure 3-800	100	Capcure EH-30	10	23	23	Dry	--	5 mins	45 (3)
56-1	Araldite 509 Araldite RD-2	66.7 33.3	Capcure 3-800	100	Capcure EH-30	10	23	23	Dry	--	6 mins	62 (3)
56-2	Araldite 509 Araldite RD-2	66.7 33.3	Capcure 3-800	100	Capcure EH-30	10	23	23	Dry	--	6 mins	55-70 (3)
58-2A	Araldite 509 Araldite RD-2	66.7 33.3	Capcure 3-800	100	Capcure EH-30	10	23	23	Dry	9 mins	--	70 (3)(d)
58-2B	Araldite 509 Araldite RD-2	66.7 33.3	Capcure 3-800	100	Capcure EH-30	10	23	23	Wet	12 mins	--	15 (3)(d)
59-2	Araldite 509 Araldite RD-2	66.7 33.3	Capcure 3-800	100	Capcure EH-30	10	23	-25	Dry	>45 mins	--	62 (3)(d)
32-4	Araldite 509		Capcure WR-6	71	Capcure EH-30	4.4	23	23	Dry	18 mins	8 mins	80 (2)
33-2A	Araldite 509		Capcure WR-6	71	Capcure EH-30	4.4	23	23	Wet	50 mins	--	72 (3.5 hrs) (d)
33-2B	Araldite 509		Capcure WR-6	71	Capcure EH-30	4.4	23	-25	Dry	(e)	--	75 (3.5 hrs) (d)
56-3	Araldite 509 Araldite RD-2	66.7 33.3	Capcure WR-6	100	Capcure EH-30	10	23	23	Dry	--	10 mins	(f)
56-4	Araldite 509 Araldite RD-2	75 25	Capcure WR-6	100	Capcure EH-30	10	23	23	Dry	--	15.5 mins	(f)

TABLE A-13. (Continued)

Formulation	Epoxy Resin	%	Curing Agent	phr	Accelerator	phr	Components Temperature at Application, C	Application Conditions		Cure Rate(a)		Hardness of Casting,(b) Shore D
								Temperature, C	Environment	Film	Casting	
49-1	Araldite 509		Thiokol LP-3	100	Capcure EH-30	10	23	23	Dry	24 hrs	24 hrs	50 (3)
49-2	Araldite 509		Thiokol LP-3	50	Capcure EH-30	10	23	23	Dry	24 hrs	24 hrs	77 (3)
49-4	Araldite 509		Thiokol LP-3 Resicure 30	50 5	--		23	23	Dry	Did not cure		--

(a) Expressed as tack-free time. Data in air and in water are not strictly comparable.

(b) Numbers in parenthesis express time of testing in days following casting.

(c) Hard, but tacky surface after 75 minutes.

(d) On film, 3.5 hours after application.

(e) Did not harden till temperature was raised up to ambient.

(f) Could not be removed from aluminum casting dish.

TABLE A-14. MERCAPTAN CURED FORMULATIONS BASED ON EPON 828 EPOXY RESIN AND LOW VISCOSITY MERCAPTATE ESTERS

Formulation	Epoxy Resin	Curing Agent	phr	Accelerator	phr	Components Temperature at Application, C	Application Conditions		Cure Rate(a)		Hardness of Casting,(b) Shore D
							Temperature, C	Environment	Film	Casting	
25-1	Epon 828	Mercaptate Q-43	10	--		23	23	Dry	Did not cure		--
25-2	Epon 828	Mercaptate Q-43	20	--		23	23	Dry	Did not cure		--
25-3	Epon 828	Mercaptate Q-45	40	--		23	23	Dry	Did not cure		--
27-3	Epon 828	Mercaptate Q-43	10	Capcure EH-30	10	23	23	Dry	15 mins	8 mins	85 (3)
27-4	Epon 828	Mercaptate Q-43	20	Capcure EH-30	10	23	23	Dry	8 mins	5 mins	85 (3)
27-1	Epon 828	Mercaptate Q-43	52.3	Capcure EH-30	10	23	23	Dry	5 mins	5 mins	85 (3)
27-2	Epon 828	Mercaptate Q-43	75	Capcure EH-30	10	23	23	Dry	20 mins	19 mins	80 (3)
27-5	Epon 828	--		Capcure EH-30	10	23	23	Dry	70 mins	70 mins	80 (3)
70-1	Epon 828	Capcure 3-800 Mercaptate Q-43	50 50	Capcure EH-30	10	23	23	Dry	9.5 mins	7.5-8 mins	77 (3)
70-2	Epon 828	Capcure 3-800 Mercaptate Q-43	75 25	Capcure EH-30	10	23	23	Dry	7 mins	6 mins	80 (3)
67-1	Epon 828	Capcure 3-800 Mercaptate Q-42	50 50	Capcure EH-30	10	23	23	Dry	4 mins	3 mins	80 (2)
67-2	Epon 828	Capcure 3-800 Mercaptate Q-42	75 25	Capcure EH-30	10	23	23	Dry	5.5 mins	4 mins	83 (2)

(a) Expressed as tack-free time. Data in air and in water are not strictly comparable.

(b) Numbers in parenthesis express time of testing in days following casting.

TABLE A-15. MERCAPTAN CURED FORMULATIONS BASED ON APOGEN 101, D.E.N. 431 AND EPI-REZ AS THE MAIN EPOXY RESIN COMPONENTS

Formulation	Epoxy Resin	%	Curing Agent	phr	Accelerator	phr	Diluent	phr	Components Temperature at Application, C	Application Conditions		Cure Rate(a)		Hardness of Casting,(b) Shore D
										Temperature, C	Environment	Film	Casting	
113-1	Apogen 101		Capcure 3-800 Mercaptate Q-43	100 100	Capcure EH-30	20	Epodil L	100	23	23	Dry	Did not cure		--
113-2	Apogen 101		Capcure 3-800 Mercaptate Q-43	50 50	Capcure EH-30	10	Epodil L	100	23	23	Dry	11 mins	11 mins	35-40 (2)(c)
113-3	Apogen 101 Heloxy 69	50 50	Capcure 3-800 Mercaptate Q-43	50 50	Capcure EH-30	10	--		23	23	Dry	4.5 mins	4 mins	75 (2)
114-7	Apogen 101 Heloxy 69	66.7 33.3	Capcure 3-800 Mercaptate Q-43	33.3 33.3	Capcure EH-30	6.67	Epodil L	33.3	23	23	Dry	4.5 mins	3 mins	80 (5)
113-4	Den 431		Capcure 3-800 Mercaptate Q-43	100 100	Capcure EH-30	20	Epodil L	100	23	23	Dry	30 mins	28 mins	17-19 (2)(2)
114-5	Den 431		Capcure 3-800 Mercaptate Q-43	50 50	Capcure EH-30	10	Epodil L	100	23	23	Dry	29 mins	29 mins	350 (2)
114-6	Den 431 Heloxy 69	50 50	Capcure 3-800 Mercaptate Q-43	50 50	Capcure EH-30	10			23	23	Dry	6 mins	4.5 mins	83 (2)
114-8	Den 431 Heloxy 69	66.7 33.3	Capcure 3-800 Mercaptate Q-43	33.3 33.3	Capcure EH-30	6.67	Epodil L	33.3	23	23	Dry	10.5 mins	8 mins	80 (5)
133-1	Epi-Rez 50727		Capcure 3-800	100	Capcure EH-30	10	--		23	23	Dry	45-60 sec	45-60 sec	73-75(d)
133-2	Epi-Rez 50727		Capcure 3-800 Mercaptate Q-43	60 40	Capcure EH-30	10	--		23	23	Dry	1-1.5 mins	1-1.5 mins	65-68(d)
133-3	Epi-Rez 5027		Capcure 3-800	100	Capcure EH-30	10	--		23	23	Dry	1-1.5 mins	1-1.5 mins	57(d)
133-4	Epi-Rez 5027		Capcure 3-800 Mercaptate Q-43	60 40	Capcure EH-30	10	--		23	23	Dry	--	3.5-4 mins	33(d)

(a) Expressed as tack-free time. Data in air and in water are not strictly comparable.

(b) Numbers in parenthesis express time of testing in days following casting.

(c) On Shore A-2 scale.

(d) 20 hours after casting.

TABLE A-16. MERCAPTAN CURED FORMULATIONS BASED ON EPON 828/HELOXY 69 EPOXY RESIN MIXTURES

Formulation	Epoxy Resin	%	Curing Agent	phr	Accelerator	phr	Components Temperature at Application, C	Application Conditions Temperature, C	Application Conditions Environment	Cure Rate(a) Film	Cure Rate(a) Casting	Hardness of Casting,(b) Shore D
103-1	Epon 828 Heloxy 69	66.7 33.3	Capcure 3-800	100	Capcure EH-30	10	50	23	Dry	3.5 mins	1.5 mins	74-76 (2)
112-1	Epon 828 Heloxy 69	66.7 33.3	Capcure 3-800	100	Capcure EH-30	10	23	5	Wet	—	7.5 mins	77-80 (2)
104-1	Epon 828 Heloxy 69	66.5 33.5	Capcure 3-800 Mercaptate Q-43	60 40	Capcure EH-30	10	23	23	Dry	5-6 mins	4-4.5 mins	65-68 (2)
112-3	Epon 828 Heloxy 69	66.5 33.5	Capcure 3-800 Mercaptate Q-43	60 40	Capcure EH-30	10	23	5	Wet	—	22 mins	70-76 (2)
116-1	Epon 828 Heloxy 69	66.7 33.3	Capcure 3-800	90	Capcure EH-30	10	23	23	Dry	4-4.5 mins	2.5-3 mins	84 (3)
122-1	Epon 828 Heloxy 69	66.7 33.3	Capcure 3-800 Mercaptate Q-43	54.4 36.2	Capcure EH-30	9.2	23	23	Dry	6-6.5 mins	5 mins	72-74 (3)
134-1	Epon 828 Heloxy 69	66.7 33.3	Capcure 3-800 Mercaptate Q-43 NMA	27.2 18.1 54.1	Capcure EH-30	4.7	23	23	Dry	Did not cure		—
134-2	Epon 828 Heloxy 69	66.7 33.3	Capcure 3-800 Mercaptate Q-43 NMA BTDA	27.2 18.1 27 24.4	Capcure EH-30	4.7	23	23	Dry	Did not cure		—
134-3	Epon 828 Heloxy 69	66.7	Capcure 3-800 Mercaptate Q-43 NMA BTDA	27.2 18.1 35.8 16.4	Capcure EH-30	4.7	23	23	Dry	Did not cure		—

(a) Expressed as tack-free time. Data in air and in water are not strictly comparable.

(b) Numbers in parenthesis express time of testing in days following casting.

TABLE A-17. EVALUATION OF POLYFUNCTIONAL ACRYLIC MONOMER AS DILUENTS IN MERCAPTAN CURED EPOXY FORMULATIONS

Formulation	Epoxy Resin	Curing Agent	phr	Accelerator	phr	Monomer	phr	Components Temperature at Application, C	Application Condition		Cure Rate,[a] min		Hardness of Casting,[b] Shore D
									Temperature, C	Environment	Film	Casting	
63-1	Epon 828	Capcure 3-800	100	Capcure EH-30	20	TMPTA	66.7	23	23	Dry	<2	<2	75 (3)
63-2	Epon 828	Capcure 3-800	100	Capcure EH-30	20	TEGDA	66.7	23	23	Dry	<1.5	<1.5	55 (3)
63-3	Epon 828	Capcure 3-800	100	Capcure EH-30	20	TEGDA	33.3	23	23	Dry	1.5	1.5	75 (3)
67-2	Epon 828	Capcure 3-800 Mercaptate Q-42	75 25	Capcure EH-30	10	--	--	23	23	Dry	5.5	4	83 (2)
67-4	Epon 828	Capcure 3-800 Mercaptate Q-42	75 25	Capcure EH-30	10	TMPTA	50	23	23	Dry	<1	<1	76 (2)
67-1	Epon 828	Capcure 3-800 Mercaptate Q-42	50 50	Capcure EH-30	10	--	--	23	23	Dry	4	3	80 (2)
67-3	Epon 828	Capcure 3-800 Mercaptate Q-42	50 50	Capcure EH-30	10	TMPTA	50	23	23	Dry	1	1	82 (2)
69-1A	Epon 828	Capcure 3-800 Mercaptate Q-42	75 25	Capcure EH-30	10	TMPTA	50	23	-25	Dry	1.5	--	--
69-1B	Epon 828	Capcure 3-800 Mercaptate Q-42	75 25	Capcure EH-30	10	TMPTA	50	5	-25	Dry	2.75	--	--
69-1C	Epon 828	Capcure 3-800 Mercaptate Q-42	75 25	Capcure EH-30	10	TMPTA	50	23	23	Wet	0.75	--	--
69-1D	Epon 828	Capcure 3-800 Mercaptate Q-42	75 25	Capcure EH-30	10	TMPTA	50	5	5	Wet	1	--	--

(a) Expressed as tack-free time. Data in air and in water are not strictly comparable.

(b) Numbers in parenthesis express time of testing in days following casting.

TABLE A-18. ADDITIONAL FORMULATIONS WITH POLYFUNCTIONAL ACRYLIC MONOMERS AS DILUENTS IN MERCAPTAN CURED EPOXY FORMULATIONS

Formulation	Epoxy Resin	Curing Agent	phr	Accelerator	phr	Monomer	phr	Components Temperature at Application, C	Application Conditions Temperature C	Application Conditions Environment	Cure Rate,(a) min Film	Cure Rate,(a) min Casting	Hardness of Casting,(b) Shore D
71-1	Epon 828	Capcure 3-800 Mercaptate Q-43	100 66.7	Capcure EH-30	13.3	TMPTA	66.7	23	23	Dry	2	1.5	72 (3)
71-2	Epon 828	Capcure 3-800 Mercaptate Q-43	83.3 83.3	Capcure EH-30	13.3	TMPTA	66.7	23	23	Dry	2	1.5	72 (2)
71-3	Epon 828	Capcure 3-800 Mercaptate Q-43	71.4 71.4	Capcure EH-30	13.3	TMPTA	42.8	23	23	Dry	2	2	73 (2)
74-1A	Epon 828	Capcure 3-800 Mercaptate Q-43	71.4 71.4	Capcure EH-30	13.3	TMPTA	42.8	5	5	Dry	8	5	74 (5)
74-1B	Epon 828	Capcure 3-800 Mercaptate Q-43	71.4 71.4	Capcure EH-30	13.3	TMPTA	42.8	5	5	Wet	6	6	76 (5)
74-1C	Epon 828	Capcure 3-800 Mercaptate Q-43	71.4 71.4	Capcure EH-30	13.3	TMPTA	42.8	5	-25	Dry	11	5	76 (5)
86-1	Epon 828	Capcure 3-800	71.4	Capcure EH-30	11.4	TMPTA TMPTMP	42.9 71.4	23	23	Dry	2	1.5	42-50 (3)
86-2	Epon 828	Capcure 3-800 Mercaptate Q-42	71.4 71.4	Capcure EH-30	11.4	TMPTA	42.9	23	23	Dry	1.25	1.25	73-77 (3)
103-2	Epon 828	Capcure 3-800 Mercaptate Q-43	100 66.7	Capcure EH-30	13.8	TMPTA	66.7	50	23	Dry	0.5-1	0.5	55-60 (2)
112-2	Epon 828	Capcure 3-800 Mercaptate Q-43	71.4 71.4	Capcure EH-30	11.4	TMPTA	42.9	23	5	Wet	--	3.5	66-68 (2)
116-2	Epon 828	Capcure 3-800 Mercaptate Q-43	64.3 64.3	Capcure EH-30	14.3	TMPTA	42.9	23	23	Dry	2	2	77-79 (3)

(a) Expressed as tack-free time. Data in air and in water are not strictly comparable.

(b) Numbers in parenthesis express time of testing in days following casting.

TABLE A-19. THE USE OF APOGEN 256 AND VERSAMID 125 IN THE MIXED POLYAMIDE/MERCAPTAN CURE OF EPOXY COMPOSITIONS

Formulation	Epoxy Resin	Curing Agent	phr	Accelerator	phr	Components Temperature at Application, C	Application Conditions		Cure Rate,[a] min		Hardness of Casting,[b] Shore D
							Temperature, C	Environment	Film	Casting	
15-3	Epon 828	Capcure 3-800 Apogen 256	100 10	--		23	23	Dry	40	15	78 (2)
15-4	Epon 828	Capcure 3-800 Apogen 256	50 10	--		23	23	Dry	60	15	80 (2)
55-2	Epon 828	Capcure 3-800 Apogen 256	50 12.6	Capcure EH-30	10	23	23	Dry	15	3	85 (4)
61-2A	Epon 828	Capcure 3-800 Apogen 256	50 12.6	Capcure EH-30	10	23	23	Wet	15	--	--
61-2B	Epon 828	Capcure 3-800 Apogen 256	50 12.6	Capcure EH-30	10	23	-25	Dry	15	--	82 (3)[c]
78-4	Epon 828	Apogen 256	50	Capcure EH-30	10	23	23	Dry	≥122	115	81-82 (4)
78-5	Epon 828	Apogen 256 Mercaptate Q-43	25 25	Capcure EH-30	10	23	23	Dry	3.5	17	75-83 (4)
78-6	Epon 828	Apogen 256 Mercaptate Q-43	50 25	Capcure EH-30	10	23	23	Dry	35	5	62-65 (4)
79-2	Epon 828	Apogen 256 Mercaptate Q-43	50 25	Capcure EH-30	10	23	23	Dry	6	3	53-60 (2)
111-1	Epon 828	Apogen 256	50	Capcure EH-30	10	23	23	Dry	--	18	75 (2)
111-2	Epon 828	Apogen 256 Mercaptate Q-43	25 25	Capcure EH-30	10	23	23	Dry	15	4	76-83 (2)
111-3	Epon 828	Apogen 256 Mercaptate Q-43	50 25	Capcure EH-30	10	23	23	Dry	30	2	55-57 (2)
55-4	Epon 828	Versamid 125 Capcure 3-800	28.5 50	Capcure EH-30	10	23	23	Dry	18	5	85 (4)
61-1A	Epon 828	Versamid 125 Capcure 3-800	28.5 50	Capcure EH-30	10	23	23	Wet	<22	--	--
61-1B	Epon 828	Versamid 125 Capcure 3-800	28.5 50	Capcure EH-30	10	23	-25	Dry	<22	--	80 (3)[c]

(a) Expressed as tack-free time. Data in air and in water are not strictly comparable.

(b) Numbers in parenthesis express time of testing in days following casting.

(c) Measurement obtained on film.

TABLE A-20. THE USE OF CAPCURE 38 IN THE MIXED POLYAMIDE/MERCAPTAN CURE OF EPOXY COMPOSITIONS

Formulation	Epoxy Resin	Curing Agent	phr	Accelerator	phr	Components Temperature at Application, C	Application Conditions: Temperature, C	Application Conditions: Environment	Cure Rate,(a) min: Film	Cure Rate,(a) min: Casting	Hardness of Casting,(b) Shore D
29-1	Epon 828	Capcure 3-800 Capcure 38	75 12	Capcure EH-30	8	23	23	Dry	17	7	83 (3)
29-2	Epon 828	Capcure 3-800 Capcure 38	100 12	Capcure EH-30	8	23	23	Dry	8	4	80 (3)
94-1	Epon 828	Capcure 3-800 Capcure 38	75 25	Capcure EH-30	10	23	23	Dry	11.5	5	75 (3)
94-2	Epon 828	Capcure 3-800 Capcure 38	50 50	Capcure EH-30	10	23	23	Dry	60	10	71 (3)
94-3	Epon 828	Capcure 3-800 Capcure 38	75 50	Capcure EH-30	10	23	23	Dry	45	~8	45 (3)
78-1	Epon 828	Capcure 38	50	Capcure EH-30	10	23	23	Dry	230	120	83-84 (4)
78-2	Epon 828	Capcure 38 Mercaptate Q-43	25 25	Capcure EH-30	10	23	23	Dry	≥123	7	83-85 (4)
78-3	Epon 828	Capcure 38 Mercaptate Q-43	50 25	Capcure EH-30	10	23	23	Dry	62	7	79-81 (4)
79-1	Epon 828	Capcure 38 Mercaptate Q-43	50 50	Capcure EH-30	10	23	23	Dry	16	4	71-75 (2)

(a) Expressed as tack-free time. Data in air and in water are not strictly comparable.

(b) Numbers in parenthesis express time of testing in days following casting.

TABLE A-21. DP116 CURE OF ARALDITE 509 EPOXY RESIN

Formulation	Epoxy Resin	Curing Agent	phr	Diluent	phr	Components Temperature at Application, C	Application Conditions Temperature, C	Application Conditions Environment	Cure Rate,[a] min Film	Cure Rate,[a] min Casting	Hardness of Casting,[b] Shore D
36-1	Araldite 509	DP116	50	—		23	23	Dry	1	1	85 (3)
39-1	Araldite 509	DP116	50	Furfuryl alcohol	25	23	23	Dry	1	—	40-50 (3)[c]
40-1	Araldite 509	DP116	25	—		23	23	Dry	1	1	80-70 (3)
40-2	Araldite 509	DP116	25	Furfuryl alcohol	25	23	23	Dry	2	1	55-60 (3)[c]
43-1	Araldite 509	DP116	25	—		23	23	Wet	>10	—	—
43-2	Araldite 509	DP116	25	Furfuryl alcohol	25	23	23	Wet	>10	—	—
44-1	Araldite 509	DP116	25	—		23	-25	Dry	40[d]	—	—
44-2	Araldite 509	DP116	25	Furfuryl alcohol	25	23	-25	Dry	>10	—	—

(a) Expressed as tack-free time. Data in air and in water are not strictly comparable.

(b) Numbers in parenthesis express time of testing in days following casting.

(c) Measurement obtained on film.

(d) Frozen hard, but not cured.

TABLE A-22. RESICURE 30 CURE OF EPON 828 EPOXY RESIN

	Epoxy Resin	%	Curing Agent	phr	Additive	phr	Components Temperature at Application, C	Application Conditions		Cure Rate,(a) min		Hardness of Casting,(b) Shore D
								Temperature, C	Environment	Film	Casting	
1	Epon 828		Resicure 30	10	--		23	23	Dry	1	1	85 (3)
45-1A	Epon 828		Resicure 30	10	--		23	23	Wet	--	1	--
-5-1B	Epon 828		Resicure 30	10	--		23	-25	Dry	--	1	--
61-5A	Epon 828		Resicure 30	10	--		23	23	Wet	1	--	77 (3)
61-5B	Epon 828		Resicure 30	10	--		23	-25	Dry	1	--	75 (3)
48-2A	Epon 828		Resicure 30	5	--		23	23	Wet	1.5	--	--
48-2B	Epon 828		Resicure 30	5	--		23	-25	Dry	2	--	--
48-1	Epon 828		Resicure 30	2.5	--		23	23	Wet	>120	--	--
92-1	Epon 828 Araldite RD-2	75 25	Resicure 30	5	--		23	23	Dry	--	1.5	85 (3)
92-2	Epon 828 Epoxide #7	75 25	Resicure 30	5	--		23	23	Dry	--	2.5(c)	80-85 (3)
92-3	Epon 828 Heloxy 69	75 25	Resicure 30	5	--		23	23	Dry	--	1.25	86 (3)
66-1	Epon 828		Resicure 30	10	THF	30	23	23	Dry	--	3	73 (3)
66-2	Epon 828		Resicure 30	12.5	THF	29.5	23	23	Dry	--	2.5	73 (3)

(a) Expressed as tack-free time. Data in air and in water are not strictly comparable.

(b) Numbers in parenthesis express time of testing in days following casting.

(c) Hard, but slightly tacky.

TABLE A-23. RESICURE 30 CURE OF VARIOUS EPOXY AND EPOXY/POLYAMIDE RESIN COMPOSITIONS

Formulation	Epoxy Resin	Curing Agent	phr	Accelerator	phr	Diluent	phr	Components Temperature at Application, C	Application Conditions Temperature, C	Application Conditions Environment	Cure Rate,(a) min Film	Cure Rate,(a) min Casting	Hardness of Casting,(b) Shore D
37-2	Araldite 509	Resicure 30	10	--		--		23	23	Dry	1	1	80 (3)
61-4A	Araldite 509	Resicure 30	10	--		--		23	23	Wet	<1	--	77 (3)
61-4B	Araldite 509	Resicure 30	10	--		--		23	-25	Dry	<1	--	80 (3)
61-3A	Araldite 509	Resicure 30	5	--		--		23	23	Wet	>35	--	60 (3)
61-3B	Araldite 509	Resicure 30	5	--		--		23	-25	Dry	>35	--	70 (3)
39-2	Araldite 509	Resicure 30	10	--		Furfuryl alcohol	25	23	23	Dry	<1	--	55-75 (3)
37-3	Apogen 141	Resicure 30	10	--		--		23	23	Dry	<1	<1	85 (3)
93-1	Epon 828	Versamid 125 Resicure 30	75 2.5	Capcure EH-30	10	--		23	23	Dry	≤130	≤130	80-82 (3)
93-2	Epon 828	Versamid 125 Resicure 30	75 2.4	--		--		23	23	Dry	≤130	≤130	76 (3)
93-3	Epon 828	Capcure 38 Resicure 30	75 10	Capcure EH-30	10	--		23	23	Dry	~200	<70	81 (3)
93-4	Epon 828	Capcure 38 Resicure 30	75 2.4	--		--		23	23	Dry	--	70	79 (3)

(a) Expressed as tack-free time. Data in air and in water are not strictly comparable.

(b) Numbers in parenthesis express time of testing in days following casting.

TABLE A-24. LEWIS ACID CURES OF CYCLOALIPHATIC EPOXIDES

Formulation	Epoxy Resin	Curing Agent	phr	Cure Rate of Casting
73-1	Araldite CY179	Resicure 30	10	(a)
73-2	Araldite CY179	Resicure 30	10	10 min (b)
81-1	Araldite CY179	Dibutyltin Dilaurate	10	Did not cure
81-2	Araldite CY183	Dibutyltin Dilaurate	10	Did not cure
75-1(c)	Araldite CY179	NMA Resicure 30	127.2 10	Did not cure
75-2(d)	Araldite CY179	NMA Resicure 30	127.2 10	(a)
80-1	Araldite CY183	NMA Resicure 30	115.8 10	Did not cure
80-2	Araldite CY183	NMA Resicure 30	115.8	Did not cure

(a) Set up in less than 25 seconds; could not be cast.

(b) Strong exotherm; resin charred.

(c) CY179 and NMA premixed and Resicure 30 added.

(d) NMA and Resicure 30 premixed and CY179 added.

APPENDIX B

SELECTED POLYMER CONCRETE LITERATURE REVIEW

A comprehensive literature review of polymer concretes or of runway repair methods was not within the scope of this program, but a number of relevant reports were reviewed to give perspective to the present study.

The problem of rapid runway repair has been addressed by various investigators for 10 years with varying results and with differing conclusions being drawn. The approaches to the problem varied, since the objectives were not uniform: some sought repair methods only for temperatures above freezing, others limited investigation to dried aggregate only, while the durability of the rapid repair was of importance to some, not to others. In a general sense, there appears to be a preference throughout for polyester resin binders for polymer concretes. Some of the salient features and reported results of a number of these studies are reported below.

1. Leitheiser, R. H., R. J. Hellmer, and E. T. Clocker; Technical Report AFAPL-TR-67-146. The objective of 300 psi flexural and 1000 psi compressive strength was exceeded using polyester-styrene emulsions. Flexural strengths of 500-2500 psi were achieved depending upon water content. However, these measurements were typically made many hours after the resin was applied. High temperatures gave poor results because of too rapid gelation. The use of aggregate (unspecified) was unsuccessful since it did not bond to the resin even when a silane coupling agent was added. Although not stated in the report, it is obvious that an aqueous emulsion is of no possible use at temperatures below 32° F because of freezing.

2. Hickman, B. R., et al.; Technical Report AFML-TR-66-141. A wide variety of approaches to the rapid repair problem are considered in this report, including:

   a. Graded density polyurethane foam applied over a base to a depth of three feet. A compressive strength of 440 psi was achieved, but no flexural strengths are reported. An isocyanate containing formulation is clearly unsuitable for wet aggregate (no aggregate was used here) due to its reactivity with water.

   b. Molten sulfur with gravel provided a compressive strength of 1500-2100 psi, but the temperature required for penetration of the aggregate proved to be too high for practicality.

   c. Several inorganic soil binders were examined including sodium silicate-calcium chloride, but the product strength was poor and the method of application too complicated.

d. Similarly, calcium acrylate-soil mixtures were evaluated, but low compressive strength, slow cures, and water sensitivity made this approach unattractive.

e. Epoxy resins were evaluated, premixed with aggregates of various sorts of which sand proved to be best; stone was not evaluated as an aggregate. Flexural strengths up to 3750 psi were obtained using Epon 828, triethylenetetramine and boron trifluoride-diethyl amine complex blended with sand, then poured. However, only Epon 812 bonded to wet sand, and the strength of this product was poor. In spite of deficiencies, this work lends encouragement to the epoxy resin approach, since better results were achieved under certain conditions than with the other systems studied.

3. Nielson, J. P. and V. Cassino; AFCEC-TR-75-25. An objective of this study was attainment of a flexural strength of 1200 psi. Effects of temperature and wetness were not studied. Liquid resins were applied to a 10-inch bed of gravel on a sand base, but the 10-inch depth was not filled so that gravel particles were simply coated. A variety of binders were evaluated. Objections to the polyester-type binder included cooling by evaporation of styrene and residual tack. These objections did not apply to the epoxy resins. However, flexural strengths measured several hours after the test beams were formed were only about half that desired using 3/4-inch gravel.

4. McClain, R. R., in "Polymers in Concrete", Second International Congress on Polymers in Concrete; University of Texas, Austin (1978). This work is not directly applicable to runway repair but does indicate that improved properties can be achieved when epoxy resins are blended into cement concrete (wet) mixes for use in patching bridge decks. Strength is slow to develop, but the concrete is significantly strengthened by using an amine-cured epoxy in the mix.

5. Peasley, J. A., Air Force Aero Propulsion Laboratory TR-65-120. The objectives of this study were to achieve satisfactory runway repair within 4 hours to support wheel loads of 25,000 pounds. Application should be possible within the 0° to 110° F range (minimum) and from dry weather to rainfall. The report recommends polyester with dry aggregate. Epoxies are reviewed as imposing too exacting demands to be practical. Silica aggregate was used, but no coupling agents were evaluated.

6. American Concrete Institute, "Polymers in Concrete", State-of-the-Art Report, 1977. This report is not directly applicable to the current work and is rather general in nature. Polystyrene is cited as the most commonly used organic material, but furan, epoxy and polyester compositions are also noted. The use of coupling agents is noted, and only silanes are identified. These produce the best strength enhancement when the aggregate is pretreated rather than when the coupler is blended with the monomer.

7. Keeton, J. R. and R. L. Alumbaugh, U.S. Navy Civil Engineering Laboratories, TN-1479 (1977). This report deals with polymer additions for concrete rather than the use of polymers as the concrete binder. Only two resins were examined. an epoxy and a Saran latex. The epoxy modified concrete developed flexural strength more rapidly than the Saran and had greater ultimate (one-year) strength as well. The use of coupling agents was not mentioned.

8. McNerney, M.T., Air Force Civil and Environmental Engineering Development Office. TR-78-10. This study was confined to the use of acrylic monomers polymerized with gravel aggregate. Any significant amount of moisture reduced the strength of the finished product; rainfall precluded use of this system. Use of a silane coupling agent (Dow: DC-7-3060) increased the compressive but not the flexural strength of the samples. The polymer concrete proved to be significantly stronger than ordinary cement concrete.

9. Setser, W. G., et al., Air Force Aero Propulsion Laboratory TR-67-165. This study is notable for the large number of polymer systems which were screened experimentally: 170 polyester and vinyl ester materials and 61 epoxy resin formulations. The objectives include: cure in 30 minutes or less, rapid cure at -5 °F and a working range of -5 ° to 110 °F, curing in the presence of water and high tensile strength when hot so that the repair would be functional during the long cooling period. Epoxy systems were disqualified early in the program because of high viscosity and high cost. Of the organic systems only one polyester and one vinyl ester formulation were selected for final testing. Fine particle filler was used to enhance product strength and reduce the exotherm. Addition of a silane coupling agent enhanced the flexural strength of silica filled resin formulations. The overall approach was directed more toward preparation of surfacing formulations than the use of a resin as a binder for aggregate. The final selection was an inorganic cement which produced a flexural strength of 600 psi and compressive strength of 3600 to 4000 psi within 30 minutes of pouring. The success of this approach in use was greatly dependent on the preparation of the base.

10. Smith, A., Air Force Civil and Environmental Engineering Development Office TR-77-53. The goals of this study included a 30-minute cure in the 35 ° to 125 °F range using polymer poured on wet aggregate so as to fill the void space. Laminac 4128 polyester most closely met these requirements. Epoxy resins and urethanes were also evaluated. However, fiberglas reinforcement was required and dry aggregate was specified. With these limitations the resin at 50 °F could be applied to aggregate in the range -22 ° to 122 °F and produce a product with a flexural strength of 815 psi in 20 minutes, 1057 psi in 45 minutes.

APPENDIX C

PRICE, HANDLING, AND SAFETY INFORMATION OF FORMULATION COMPONENTS

All resins and additives used in the two formulations selected for full evaluation (116-2 and 122-1) are commercially available. Descriptions of the chemical characteristics are given in the section on Resin Formulation and Screening. Following are the price, safety, and handling information provided by the manufactuers of the products used in this study. It must be borne in mind, however, that equivalent products may be available from more than one supplier.

This information is only provided as a general guideline. For complete information, the manufacturers' data sheets and recommendations should be consulted.

Capcure EH-30

2,4,6-Tri (dimethylaminomethyl) phenol

Diamond Shamrock Corporation
Process Chemicals Division
P.O. Box 2386 R
Morristown, N.J. 07960

Specific Gravity	0.97
Flash Point, Open Cup	300° F

Price:	2000-5999 lb	\$1.49/lb
	6000-29,999 lb	\$1.37/lb
	30,000 lb to TL	\$1.35/lb

Storage and Handling: Capcure EH-30 is shipped in lined openhead steel drums. Temperature changes have no adverse effect on the properties of the product.

Safety Information. The acute oral LD_{50} is 1.7 g/kg body weight in rabbits. Slightly toxic through skin absorption and inhalation but not a sensitizer. Potentially can cause severe burns on contact with skin and may act as a corrosive on prolonged contact with skin. Prolonged overexposure can produce irritation of skin and mucous membranes, eye injury, delayed lung injury, and chemical pneumonia.

Splash goggles, protective gloves, and NIOSH-approved respirators for organic vapors are recommended.

Capcure 3-800

Mercaptan terminated liquid polymer

Diamond Shamrock Corporation
Process Chemicals Division
P.O. Box 2386 R
Morristown, New Jersey 07960

Specific Gravity		1.15
Price:	2000-5999 lb	\$2.32/lb
	6000-29,900 lb	\$2.21/lb
	30,000 lb to TL	\$2.13/lb

Storage and Handling: Capcure 3-800 is shipped in 55 gallon lined tighthead steel drums. Neither chemical nor physical properties of this product are adversely affected by temperature changes.

Safety Information: The oral LD_{50} is over 2.6 g/kg body weight in rabbits. The dermal LD_{50} is over 10.6 g/kg body weight in rabbits. Mildly irritating to eyes and skin. On ingestion, call physician immediately. On contact with eyes, wash with water and call a physician. On contact with skin, wash with soap and water.

Splash goggles, protective gloves, and NIOSH-approved respirator for organic vapors are recommended.

Epon 828

Dilycidyl ether of bisphenol-A type epoxy resin

Shell Chemical Company
P.O. Box 2463
Houston, Texas 77001

Specific Gravity		1.16
Price:	Truck load drums (delivered)	\$0.98/lb
	Tank truck (delivered)	\$0.93/lb

Storage and Handling: Shipped in 55 gallon steel drums.

Safety Information:

LD_{50} oral = 11.4 g/kg body weight in rats
= 19.8 g/kg body weight in rabbits
= 15.6 g/kg body weight in mice

LD_{50} derual = >20 g/kg body weight in rabbits

Contains 1-2 ppm epichlorohydrin, a cancer suspect agent. Irritating to eyes and primary irritation to skin on prolonged or repeated contact.

Eye protection, rubber gloves protective clothing and respirators are recommended to prevent body contact and inhalation.

Heloxy 69

Resorcinol diglycidyl ether

Wilmington Chemical Corporation
Pyles Lane, Hamilton Park
Wilmington, Delaware 19899

Specific gravity	1.20-1.22
Flash Point, Open Cup	Exceeds 300° F
Price: truck load, 55-gallon drums	\$3.25/lb

Storage and Handling: Heloxy 69 may crystallize on standing. If this should occur, warming the resin will melt it. No change in properties occurs during crystallization and melting. Storage is recommended in tightly sealed containers in a dry place at ambient temperatures.

Safety Information: Short-term exposure to vapors may cause eye, nose, and throat irritation. Prolonged and/or repeated contact may cause sensitization and dermatitis. Avoid fumes from material. If hot, over 180 F, wear a respiration mask for organic vapors. Eye protection with side shields and rubber gloves are recommended.

In case of skin contact, wash contaminated skin with soap and water. In the event of eye contact, flush well with water and consult a physician. If ingested, induce vomiting if the patient is conscious and then call a physician.

Mercaptate Q-43 Ester

Pentaerythritol tetrakis (mercapto propionate)

Cincinnati Milacron Chemicals, Inc.
West Street
Reading, Ohio 45215

Specific Gravity	1.28
Flash Point, Open Cup	490° F

Price: 500-4000 lb	\$2.35/lb
4,000-10,000 lb	\$2.30/lb
10,000-24,000 lb (truck load)	\$2.25/lb

Storage and Handling. Mercaptate Q-43 is shipped in polylined steel drums. Excessive contact with iron and non-ferrous metals should be avoided.

Safety Information: The acute oral LD_{50} is 872 mg/kg body weight of male albino rats. Mercaptate is considered toxic but not highly toxic by oral ingestion. Exposure of the eyes and skins of rabbits indicated that Mercaptate Q-43 ester is considered nonirritating.

Safety glasses and protective gloves are recommended.

TMPTA

Trimethylolpropane triacrylate

Celanese Chemical Company
1211 Avenue of the Americas
New York, New York 10036

Specific Gravity	1.1
Flash Point, Open Cup	280° F

Price:	Truck load, 30,000 lb	\$1.15/lb
	Tank wagon, 40,000 lb	\$1.10/lb

Safety Information. Acute oral LD_{50} is 500 to 5000 mg/kg body weight in rats. Acute dermal LD_{50} is 2000 to 20,000 mg/kg body weight in rabbits. Harmful if swallowed, inhaled or absorbed through the skin. Mild skin irritation at 72 hours. On contact with eyes, corneal opacity reversible within 7 days.

In case of contact, immediately flush eyes with water for at least 15 minutes. Call a physician. Wash clothing before reuse.

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293rd Engr Combat Battalion	1
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Etat-Major Force aerienne	1
Defense Equipment Staff	1
HQ AFESC/RDCR	15
AFIT, Tech Library	1
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