

Surface Impregnation of Concrete Bridge Decks with Polymers*

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Synopsis

Polymer-impregnated concrete has proven to be a strong and environmentally resistant material with many potential uses. One such application is to impregnate the surface of highway bridge decks to improve their durability. This paper reports on various aspects of research directed toward the objective of developing a practical and economical process for surface treating bridge decks with liquid monomers which subsequently are polymerized. This work has included (1) selection and tailoring the monomer-initiator system, (2) development of application and curing systems, and (3) evaluation of the resulting treatments by many different testing procedures. Considerable progress has been made toward increasing the durability of concrete slabs as shown by laboratory and small-scale field tests and toward developing a practical method of application. Selected aspects of the fundamentals of surface treatments of highway bridge decks and details of the process and product as they have been developed to date will be presented here.

INTRODUCTION

Several years ago at the Brookhaven National Laboratory and the Bureau of Reclamation, the idea of impregnating the pores of concrete with polymer was originated.¹⁻⁸ Numerous applications of this concept to generate improved and new materials have been proposed and studied.⁹ A very exciting example of these applications is the impregnation of the surface of concrete bridge decks since the filling of these pores promises to improve the durability of the deck. Once the pores are plugged by solid polymer, the deck should be impermeable to water. This may greatly reduce the damage produced by expansion of water in pores during freezing and thawing and help eliminate the serious corrosion of the steel reinforcing bars that occurs because of ingress of salt added to the bridge surface to reduce the hazards of ice formation. The annual cost for repairing freeze-thaw and corrosion damage to bridge decks¹⁰⁻¹⁷ in the U.S. is several million dollars, which provides a great incentive to explore this possibility. In 1969, a research effort was initiated at the University of Texas to develop a practical process for producing surface impregnation on bridge decks and to

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evaluate their efficiency for improving durability. It was our objective to develop a process which did not require evacuation of air from the concrete pores, application of pressure to aid monomer penetration, or radiation-initiated polymerization which are convenient for fully impregnating precast elements but are regarded as impractical for large-scale use on bridge decks. Process development work recently described^{18,19} has progressed through the stages of small-scale laboratory experiments, larger-scale field trials, and finally demonstrations on actual bridge decks under field conditions. Several options for executing each step have been considered and overall optimization of the process is underway. A wide range of laboratory tests have been conducted to evaluate the effectiveness of surface impregnation for improving durability.^{18,19} The purpose of this paper is to give a brief review of this process and the benefits it produces and then to delve more deeply into some of the fundamental aspects of surface impregnation, especially those involving the physicochemical considerations of the monomer system and its conversion to polymer.

PROCESS DESCRIPTION

The process mentioned above for producing polymer-impregnated surface treatments on bridge decks involves three essential steps: drying the concrete, penetration of monomer, and curing. There are a variety of approaches that can be taken to accomplish each step, and there are a large number of variables for each method. A number of these have been considered and studied as described in some detail by earlier publications.^{18,19} It is not the purpose here to discuss the kinds of hardware or conditions which are optimal for executing a given step, but to review in general terms that should be accomplished and to indicate some ways that have been used to do this. As implementation of surface treatments evolves, it is probable that a single process will not emerge as optimal but that different application situations will find advantages with different equipment and procedures.

The first step is to dry the moisture from the concrete pores. This is necessary in order to get monomer to occupy these same pores. The amount of water present and its spatial distribution will depend on the detailed history of the concrete specimen; however, in general it may be assumed that sufficient moisture will always be present so that drying is necessary. Moisture removal can only be accomplished by exposing the concrete surface to an environment of lower relative humidity than the effective relative humidity of the water held in the concrete pores but will be greatly facilitated by elevated temperatures. Small specimens can be dried conveniently by putting them in a circulating air oven for extended periods of time. We have often used one week at 115°C for thorough drying of 3 in. × 6 in. cylinders and 1-ft² slabs (2 to 6 in. thick). This will reduce the moisture content to very low levels with a rather uniform distribution.

Much of our laboratory development work has employed this method of drying simply because we wished to eliminate the degree of drying as a factor when other variables were being studied. Oven drying is, of course, not possible for bridge decks nor is it practical for the larger slabs, $86 \times 40 \times 5\frac{1}{2}$ in., used in this work. The most likely way to dry such a large planar slab is to apply heat to the upper surface by a suitable method for an appropriate period of time. The amount of time heat can be applied to bridge in use is limited by traffic control considerations and may not be very long in high-use areas. Since heat is applied to only the upper surface, drying is limited to this one side, and the final moisture distribution will not be uniform through the slab thickness. The moisture content will be lowest at the upper surface and then increase with depth into the concrete with the depth of dried concrete as a function of the surface temperature and humidity and the time duration over which these conditions are maintained. Generally, the higher the temperature, the faster and more effective is the drying; however, there are upper limits placed on the drying temperature by the choice of equipment and ultimately by the concrete itself since damage can result at excessively high temperatures. At the current time the state of dryness required for satisfactory treatments has not been quantitatively established nor is the state of dryness completely known as a function of drying conditions. Present research is directed at answering these questions since drying is likely to be the most critical step in obtaining good treatments.

In order to proceed with the development of other steps in the process, we have generally dried the concrete more than that necessary as a minimum. Large-scale slabs have been dried by prolonged heating with an electric heating blanket; however, a more practical route for field use has been a heated forced-air system. In the latter, a tarpaulin is placed about 2 ft above the slab surface, and air heated by a fuel burner is forced into this space. To be safe, the slab surfaces have not been allowed to exceed $\approx 100^\circ\text{C}$. In order to ensure good treatments, slabs were dried for at least 72 hr, however, it appears that this is a longer time than is really necessary. Even shorter drying times can be achieved by using higher surface temperatures generated by, say, infrared heaters. Variation in drying affects both depth of impregnation and polymer loading of the pores in the impregnated zone.

After drying, the next step is to get the monomer into the pores. The approach we have found most effective is to spread a layer of sand or other fine aggregate over the deck surface to a depth of about $\frac{1}{4}$ in. The sand is then saturated with monomer (to which all necessary additives for polymerization have been included). The sand serves as a wick to hold the liquid monomer next to the concrete surface and to prevent it from running off the normally sloped surface. As shown later, the monomer is sucked into the concrete pores by rather large capillary forces. The amount of monomer imbibed is a function of soaking time as discussed later. Generally, soaking times from 4 to 12 hr give good depths of polymer. During the soaking

TABLE I
 Monomer Properties

Name	Abbrev.	Boiling point, °C	Viscosity at 25°C, cp	Polym. rate ^a k_{sp} at 44°C	Polymer T_g , °C
Methyl methacrylate	MMA	100	0.55	27	105
Isobutyl methacrylate	IBMA	155	0.83	—	48
Butyl methacrylate	BMA	163	0.86	41	20
Isodecyl methacrylate	IDMA	high	2.9	44	-41
Stearyl methacrylate	—	high	9.4	—	38 ^b
Isobornyl methacrylate	—	high	5.7	50	170
Butyl acrylate	BA	147	0.80	324	-54
Isobutyl acrylate	IBA	145	0.77	228	-43
Styrene	S	145	0.71	6	100
<i>t</i> -Butylstyrene	TBS	219	1.46	—	134

^a Defined as % polymerization/hr = $k_{sp} \sqrt{[AIBN]}$ where AIBN = azodiisobutyronitrile. Units are l.^{3/2}/moles^{1/2} hr.

^b Side-chain crystallization.

period, it is convenient to cover the monomer-wet sand with a polyethylene film to reduce monomer evaporation which causes material losses and fire and health hazards. In some cases it is desirable to rewet the sand periodically with monomer. For relatively small-scale field tests, it is adequate to batch mix the ingredients of the monomer system; however, as the volume of monomer required increases, safety considerations will require use of in-line mixing devices.

After monomer penetration into the concrete slab, it is necessary to polymerize, or cure, the monomer in some manner. An effective way to do this is to heat up the system to a temperature at which the initiator in the monomer generates free radicals at a rate to give a significant polymerization rate. For small slabs or specimens, this can be done by immersion in hot water or in a hot-air oven. But again, for large planar surfaces it is practical to apply heat from only one surface. Several methods for doing this have been described,^{18,19} with the use of hot water ponded on the slab surface appearing to be most useful. Since that time, steam has also proved to be very useful and is easier to apply under field conditions. Very good cures have been obtained by injecting steam from a portable steam generator into the space between the tarpaulin and the slab. The polyethylene barrier may or may not be left in place. The important factor is the surface temperature developed and the time it is maintained. Good results have been obtained with temperatures as low as 55°C for times as short as 1 hr.

The process described above involves a complex interaction of many phenomena. The physical and chemical characteristics of the monomer system used are very critical to the successful implementation of the surface impregnation concept as well as the mechanical considerations described above. Specific factors that are important are the polymerization

rate, the evaporation rate, viscosity, and polymer properties, as will be made evident in subsequent sections. Table I shows a list of monomers which have been used in this work and some properties which characterize the four factors mentioned above. The combination of these properties is unique for each monomer and to a large measure determines the suitability of that monomer for this application. In general, we have found methyl methacrylate (MMA) to have one of the best combinations of characteristics. As a result, the bulk of our work has used MMA; however, many others have been studied and some do offer unique advantages.

In addition to monomer, an initiator is required, and a wide variety of types are suitable for use. Benzoyl peroxide (BP) has been used primarily in this work, although several other initiator systems have been considered but none seems to offer clear advantages for the process at its current state of development. It has also been necessary to include a crosslinking agent into the monomer system for reasons to be made clear later. Again several agents have been examined, but trimethylolpropane trimethacrylate (TMPTMA) serves this function as well as any. The type and amount of both agents mentioned above have a significant effect on the polymerization rate, as does the monomer itself.

Surface impregnation involves various rate processes and their interaction. This is made clear by some simple examples. The monomer should flow into the pores in a reasonable period of time. It should not be polymerizing during this time but should do so rather rapidly once the desired depth of penetration has been achieved. The monomer should not completely evaporate from the sand before it has a chance to enter the concrete nor should it evaporate from the pores before it polymerizes. Subsequent sections will discuss experimental results related to rate processes and how they must be regulated through monomer system selection and process variables.

LABORATORY EVIDENCE FOR INCREASED DURABILITY OF SURFACE-IMPREGNATED CONCRETE SLABS

Using the procedures outlined in the previous section, surface-impregnated concrete depths of 2 in. or more can be obtained in the laboratory (see, for example, Fig. 1). Under field conditions, depths of up to 1 in. have been obtained. The shallower depths for field conditions are attributed to less drying of the concrete. The minimum impregnated depth required to provide adequate long-term durability has not been fully established. However, tests have been performed^{18,19} to determine the durability, skid resistance, and wear properties of surface-impregnated concrete slabs. A brief summary of these findings is presented here.

Freeze-thaw tests on the surface were performed on 6 × 10 × 10 in. surface-impregnated laboratory slabs. The slabs were subjected to a maximum of 120 freeze-thaw cycles. The air-entrained, good-quality slabs were the only untreated slabs capable of completing the freeze-thaw tests, but



Fig. 1. Fracture surface of surface-impregnated slab. Dark area at top is polymer-impregnated zone. Monomer is MMA.

more surface pitting was in evidence than on the treated slabs. Nonair-entrained untreated slabs failed by splitting in the range of 35 to 40 cycles, while nearly all of the treated slabs underwent 120 cycles with very little surface deterioration.

Freeze-thaw tests were performed on $5\frac{1}{2} \times 12 \times 12$ in. slabs cut from larger nonair-entrained slabs placed and treated under field conditions. The untreated slabs failed in the range of 30 to 40 cycles. The treated slabs had impregnated depths of $\frac{1}{4}$ in. to $\frac{3}{4}$ in. which in some cases were faint in color indicating a low polymer loading. However, nearly all of the slabs treated with MMA were able to complete the freeze-thaw tests although several did show signs of cracking. These results seem to indicate that a deep impregnation may not be essential to obtaining increased durability.

Water tightness tests were performed on treated and untreated slabs, before and after freeze-thaw tests. After the sides were coated with epoxy, the slabs were immersed for 24 hr in 5 in. of water with the treated surface down. The slabs were then broken open to determine the depth of water penetration. The treated slabs had no measurable water penetration prior to freeze-thaw testing as compared to two to 3 in. for the impregnated slabs. After freeze-thaw, the water tightness of the nonair-entrained control specimens was completely destroyed since they failed during testing; the air-entrained control specimens usually showed a slight increase in penetration. The treated slabs remained essentially water tight after freeze-thaw tests except in those cases where cracking had developed.

Since this research had the goal of developing practical applications for bridge decks, it was very desirable to determine the skid resistance of the impregnated surfaces subjected to vehicular wear. Untreated and treated slabs were placed on a wear track with a 10-ft diameter. Weighted tires at each end of a cross-beam were driven at 10 mph. For the first 70,000 revolutions (140,000 wheel passes), the specimens were tested dry. Afterward, the surface was wetted, and a silicone carbide grit was placed on the surface to accelerate the wear and to increase the polishing of the surface. Periodically, the skid resistance and wear were measured by a British Portable Testor and a linear potentiometer, respectively. Under dry conditions, the skid resistance of the slabs treated with MMA was significantly higher (20% to 40%) than that of the untreated slabs. Under wet conditions, and with the polishing by the grit, the skid resistance of the treated surfaces was reduced, but generally remained at least 5% to 10% higher than the control slabs. Wear measurements indicated that the impregnated concrete surfaces had about the same or slightly higher wear resistance.

The tests show that generally the freeze-thaw resistance and water tightness of the surface-impregnated slabs were significantly improved, while the skid resistance and wear resistance were not lowered and, in fact, were slightly improved.

Most of the above observations were made using MMA. However, several other monomers were included in these evaluations and appear to produce advantages when adequate treatments are obtained.^{18,19} To date, there is very little information in the literature on the relationship between the properties of polymer-impregnated concrete and the nature of the polymer in the pores. In most instances, the monomers which have been used give hard, glassy polymers with glass transition temperatures (T_g) well above ambient temperature. These monomers produce considerable increases in strength and modulus in the PIC. Since in surface impregnation there is a definite zone of impregnated concrete overlaying unmodified concrete, a sharp discontinuity in mechanical properties occurs at this boundary which, during thermal or mechanical stressing, could cause some problems although no evidence of this has been observed to date.

There might be some advantage to using a monomer that produces a polymer, e.g., a rubber, which does not greatly alter the concrete mechanical properties since apparently the main factor in increased durability is to reduce the concrete permeability. Monomers which produce polymer T_g 's less than ambient should have this effect. Figure 2 shows the ratio of modulus and compressive strength of fully impregnated cylinders (constant volume loading) to those of unimpregnated cylinders versus the polymer T_g for a number of the monomers shown in Table I. The tests were conducted at $\approx 25^\circ\text{C}$, so all polymers with T_g 's well below this temperature were soft while those with T_g 's well above were hard. Soft rubbers do produce some strengthening and stiffening but the effect is much smaller than for hard polymers. All of the monomers were copolymerized with 10% TMPTMA, so they are crosslinked. Use of rubbery polymers in surface

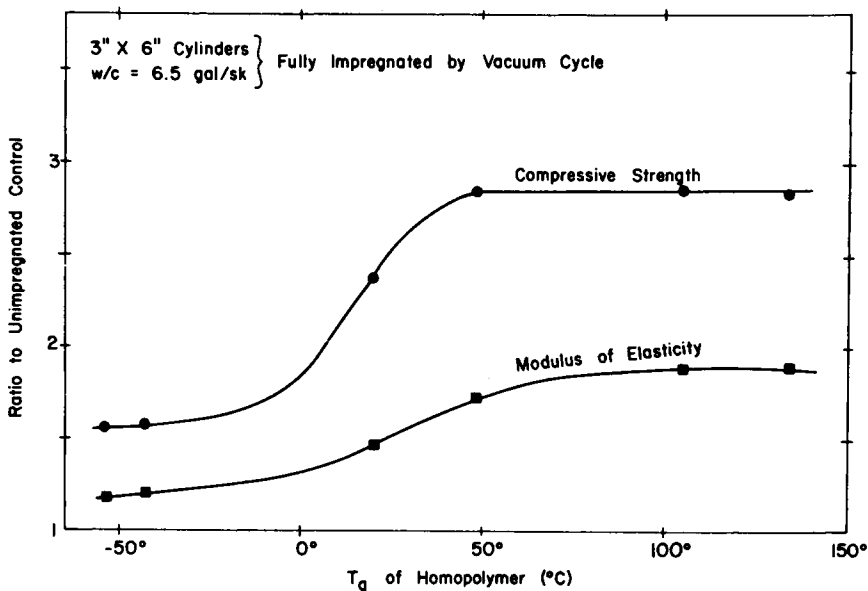


Fig. 2. Mechanical properties with concrete cylinders fully impregnated with various polymers.

impregnations when increased strength is not an objective may prove beneficial in some instances.

MECHANISM OF MONOMER PENETRATION

The resistance to the rate process of filling the concrete pores with monomer is viscous flow; therefore, monomer viscosity μ should be an important factor. This is made clear by some experimental observations on full impregnation of 3 in. X 6 in. cylinders shown in the lower half of Figure 3. In these tests, thoroughly dried cylinders were impregnated with various monomers listed in Table I, using a standard procedure which was to apply a vacuum to the cylinders for 4 hr to remove the air and then to immerse the cylinders in monomer for 5 hr with no overpressure except atmospheric. Polymerization was effected by immersion in hot water. The polymer loading was determined gravimetrically and is plotted here versus monomer viscosity. As can be seen, the loading achieved depends on the monomer viscosity. For some of the higher viscosity monomers, an unimpregnated core was visibly evident when the cylinders were broken open. Methyl methacrylate (MMA) has the lowest viscosity of all of these used, and the present data suggest that even in this case viscosity is still a factor using this procedure.

In the above experiment, the difference in pressure on the monomer outside the cylinder and that of the air in the void space acts as a driving force for monomer penetration. In this procedure, the pressure difference is 1 atm at most, but it can be made considerably larger by applying pressure to

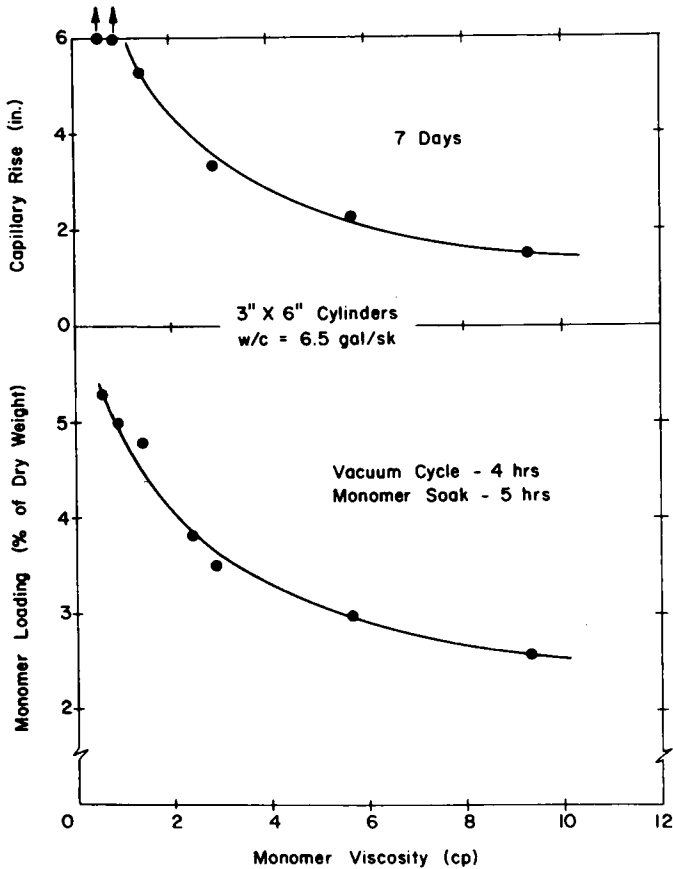


Fig. 3. Effect of Monomer Viscosity on penetration.

the monomer. However, in the application of monomer to flat bridge decks as described earlier, there is no vacuum in the pores, and the only overpressure is that provided by the approximately $\frac{1}{4}$ -in. head of monomer in the sand which may be assumed negligible. Since the monomer wets the concrete pores, there is a surface tension or capillary force to draw the monomer into the pores which is the main driving force in the current process.

It was therefore of some interest to examine experimentally this force and the penetration rate it causes. This was studied conveniently by measuring the rate of penetration of monomer into the end of 3 in. X 6 in. cylinders. It is important to coat the side of the cylinders with some barrier such as an epoxy resin to avoid evaporation of monomer. The experiments were conducted in two modes. In one, the cylinder face was immersed just below the surface of a monomer pool whereby the monomer was sucked up (against gravity) by capillary forces as in a capillary rise experiment. In the other, the monomer was ponded on top of the cylinder to a level of

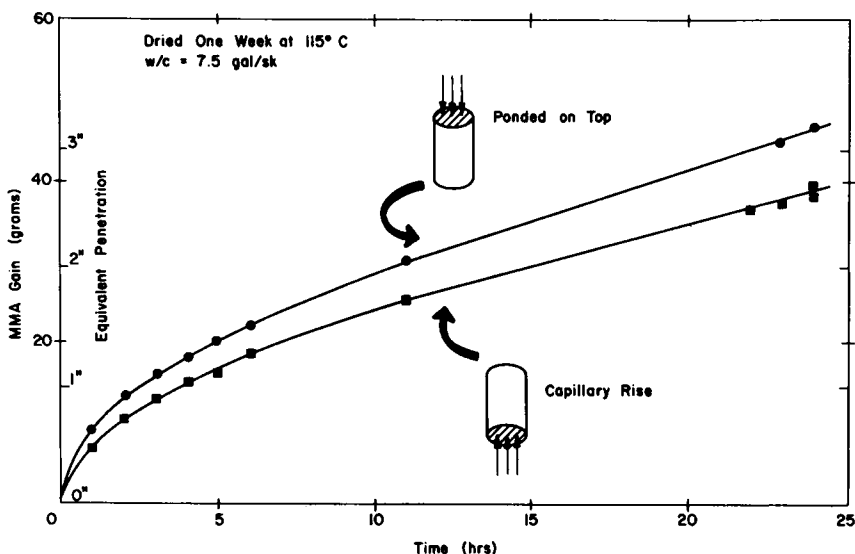


Fig. 4. Effect of cylinder orientation on rate of MMA penetration.

about $\frac{1}{4}$ in. and monomer penetrated downward (with gravity) into the cylinder. Progress of the experiment could be tracked approximately by noting visually the wetted depth or more accurately by gravimetrically monitoring the weight of monomer which entered the concrete. Owing to the variability of concrete from one cylinder to the next, experiments were run in duplicate or triplicate.

Figure 4 shows results for the two experimental modes for identical concrete specimens. Each data point is the average of three tests using MMA. As can be seen, penetration is faster when monomer is ponded on top than in the capillary rise mode. Intuitively, the difference might be attributed to the helping and opposing effects of gravity; however, the explanation may not be so simple. Both curves are similar in shape, with the rate declining with increased penetration. The details of the shape will be explored later. The mass of monomer which has penetrated can be converted into an equivalent depth of penetration by assuming that there is a front (which can be seen visibly) with no monomer beyond it while behind it there is an equilibrium loading of monomer. For the concrete used in these tests and MMA, the equilibrium loading was 5.5 g MMA/100 g of dry concrete based on weight gains of fully impregnated cylinders. The ordinate in Figure 4 shows the position of this front in inches calculated from the weight gain. These results compare well with visual observations.

In the capillary rise mode, there should be an equilibrium height to which monomer will rise that corresponds to the condition when the capillary forces are exactly balanced by gravity forces. This height would serve as a good measure of the strength of the capillary forces. Some information about this can be gained from the upper half of Figure 3, where capillary

rise experiments were performed on cylinders with various monomers. The rise was visually noted after one week. The two lowest viscosity monomers, MMA being the lowest, had wetted the entire length of the cylinders, which shows that the equilibrium rise is in excess of 6 in. The others had climbed to some fraction of the full length which decreased with the viscosity of the monomers in question, showing that they had not yet reached their equilibrium position and would likely rise the full 6 in. also. No experiments have been run with cylinders longer than 6 in. By comparison with similar porous materials, it is likely that the equilibrium height is quite large and cannot be measured in this fashion for practical reasons of sample preparation and the experimental time scale.

The imbibition of monomer into concrete is a complex problem of two-phase flow (monomer and air) in a porous medium similar to that of interest in many other areas.^{20,21} A single capillary model, while greatly oversimplified, serves to illustrate some of the salient features that operate in more complex porous media. Consider a capillary of uniform radius R , with one end immersed in a liquid which wets its wall and the other end open. A summation of all forces acting on the liquid combined with a Poiseuille-type resistance to flow gives the famous Washburn equation²² for the meniscus velocity, i.e.,

$$\frac{dh}{dt} = \frac{2\pi R\sigma \cos \theta + \pi R^2 P \pm \pi R^2 \rho g h}{8\pi\mu h} \quad (1)$$

if the resistance required to force the air out is ignored. The first term in the numerator is the capillary force arising from the surface tension of the liquid, σ , which wets the wall with an angle θ ; the second term is a possible force arising from a pressure P applied to the liquid (in excess of that in the air beyond the meniscus) at the capillary entrance via a hydrostatic head or other external means; and the last term gives the force of gravity on the liquid column which has penetrated a distance h into the capillary (ρ = liquid density, g = gravitational acceleration). The plus sign applies when the capillary is vertical and the meniscus is moving downward, i.e., the entrance is the top end. The minus sign applies when the capillary is vertical and the meniscus is moving upward, i.e., the entrance is the bottom end. The denominator is the resistance to flow which is proportional to liquid viscosity μ and the distance of penetration from the entrance, h .

If one neglects the gravitational force in comparison to the other forces, eq. (1) can be easily integrated to give (23-25)

$$h = \frac{R}{2} \sqrt{\left(\frac{2\sigma \cos \theta}{R} + P\right) \frac{t}{\mu}} \quad (2)$$

In this case, the depth of penetration increases in proportion to the square root of time. Equation (1) can also be integrated in general not neglecting gravity with the result for downward flow with gravity (plus sign):

$$\frac{h}{h_\infty} - \ln\left(1 + \frac{h}{h_\infty}\right) = \frac{R^2 \rho g}{8\mu h_\infty} t = Kt \quad (3)$$

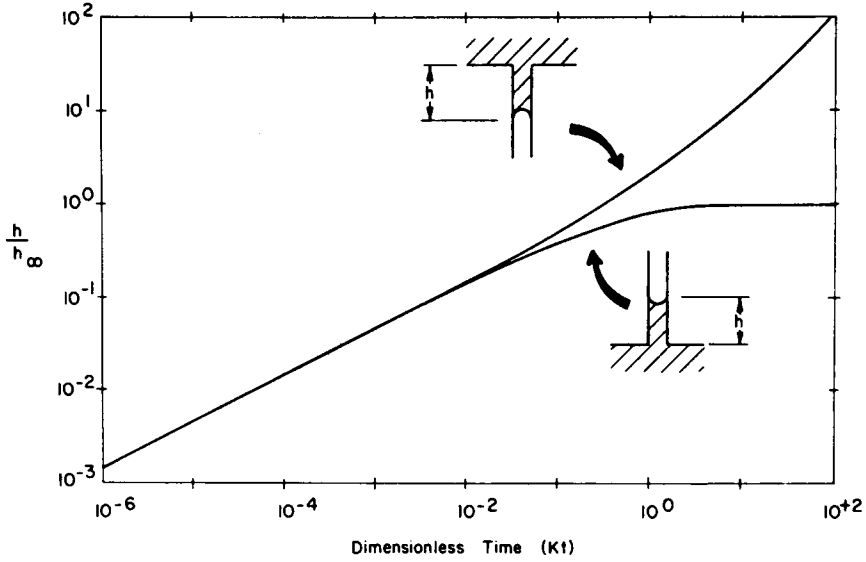


Fig. 5. Predictions by the single, uniform capillary model.

and for upward flow against gravity (minus sign):

$$-\frac{h}{h_{\infty}} - \ln\left(1 - \frac{h}{h_{\infty}}\right) = Kt. \quad (4)$$

In these equations, h_{∞} is defined as

$$h_{\infty} = \frac{2\sigma \cos \theta}{\rho g R} + \frac{P}{\rho g} \quad (5)$$

and has the meaning of the height the meniscus would rise to in infinite time in the case where flow is against gravity, i.e., it is the equilibrium capillary rise. Equations (3) and (4) are plotted in Figure 5 as dimensionless penetration h/h_{∞} versus dimensionless time Kt . In the region of h/h_{∞} less than about 0.1, both conditions give identical relationships with $h \propto \sqrt{t}$. Beyond this, the two results diverge, with the capillary rise case going to a plateau of $h = h_{\infty}$ in infinite time, while the other case goes on to achieve a constant velocity where $h \propto t$ with no bounds on the depth of penetration. This divergence marks the onset of the contribution of gravity being a significant factor occurring at an h of approximately 10% of h_{∞} .

The above analysis suggests plotting the monomer gain in the concrete cylinders versus the square root of time, which is done in Figure 6 for the same data shown in Figure 4. As can be seen, both sets of data conform to a linear relation. This would be expected if h_{∞} were such that $h/h_{\infty} < 0.1$; however, in this case, one would not expect to see any differences owing to gravity. It might be suggested that the current system is in the region where effects of gravity begin to appear, but that the data are not sufficiently accurate to detect departures from linearity in square root of time

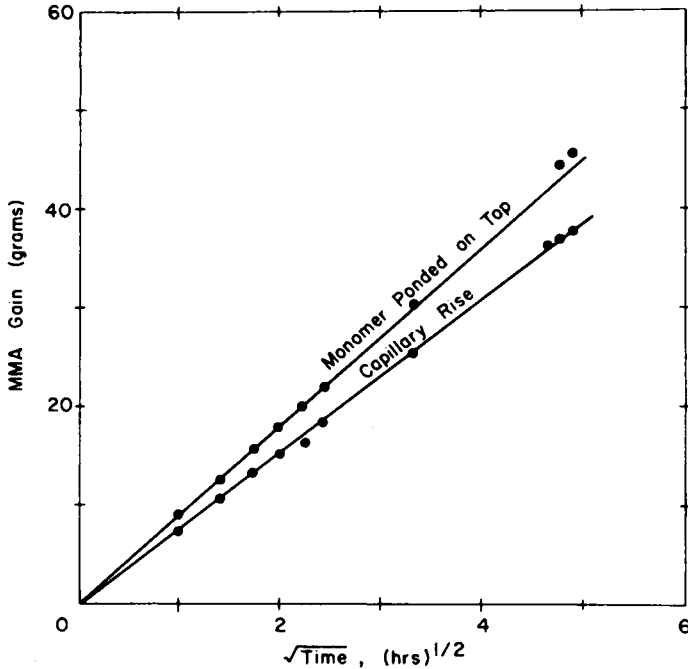


Fig. 6. Square root of time plots for data in Fig. 4.

plots. This would require a value of h_{∞} of the order of perhaps 3 to 30 in. Direct observation shows that h_{∞} is greater than 6 in. (note that in all cases here $P = 0$). The strict linearity with a slope of $1/2$ of h versus t on log-log plots for each of three individual sets of data for both modes and knowledge of h_{∞} in similar systems argue against this explanation. Oversimplification in the uniform capillary model cannot be ruled out. Clarification of this behavior requires further work.

The capillary rise mode offers some experimental advantages, and the studies on penetration kinetics described in subsequent sections employed this technique.

EFFECT OF MONOMER TYPE ON PENETRATION

According to the simple model that yields eq. (2), the rate of monomer penetration into a given type of concrete should depend on the surface tension and viscosity of the monomer and the wetting angle which is a function of both the concrete and monomer properties. Penetration experiments were conducted in duplicate by the capillary rise method for the monomers shown in Table II. All of the data conform to the relation

$$M = A \sqrt{t} \quad (6)$$

where M = mass of monomer imbibed into the concrete in time t . Values for the coefficient A determined from M -versus- \sqrt{t} plots are given in Table

TABLE II
Effect of Monomer Type on Penetration Rate^a

Monomer	$A,^b \text{ g/hr}^{1/2}$	$A/\rho, \text{ cc/hr}^{1/2}$	$\frac{A\sqrt{\mu}/\rho, \text{ cc}\sqrt{\text{cp}}}{\text{hr}^{1/2}}$
MMA	8.10	8.63	6.40
IBMA	7.46	8.45	7.70
BMA	7.30	8.21	7.63
BA	7.00	7.83	7.03
IBA	6.90	7.81	6.87

^a Concrete: 3 × 6 in. cylinders, nonair-entrained, $w/c = 7.5 \text{ gal/sk.}$

^b $M = A\sqrt{t}.$

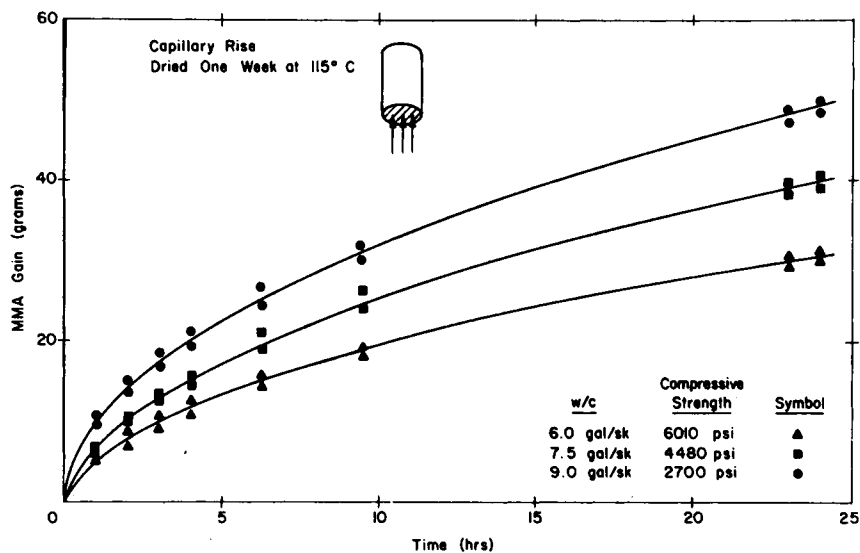


Fig. 7. Effect of concrete quality on MMA penetration rate.

II. As can be seen, MMA shows the fastest rate on a mass basis. However, to compare results with eq. (2), it would be more appropriate to express the loading on a volumetric basis, which can be done by dividing A by the monomer density ρ . Converting to a volumetric basis does not change the relative rates for the various monomers owing to their similar densities. Also according to eq. (2), the coefficient A is inversely proportional to $\sqrt{\mu}$, so that the combination $A\sqrt{\mu}/\rho$ shown also in Table II should be more nearly an indicator of the remaining term which is unknown, i.e., $\sigma \cos \theta$. Table II shows that the combination $A\sqrt{\mu}/\rho$ does not vary more than 20% within this group of monomers but would indicate a 40% variation in $\sigma \cos \theta$. Interestingly, MMA has the lowest value for this viscosity

normalized rate, which suggests that its superior penetration rate is due to its very low viscosity.

EFFECT OF CONCRETE QUALITY ON PENETRATION

The kinetics of monomer uptake should depend very critically on the nature of the concrete and especially such factors as porosity and pore size distribution. Concrete is, of course, a heterogeneous material composed of regions where these factors differ significantly; however, the nature of the mortar phase should be one of the most dominant factors. To examine this effect, capillary rise experiments were run using MMA on three grades of concrete that differed only in water-to-cement ratio (w/c). These mixes were nonair-entrained with slumps in the range of $4\frac{1}{2}$ to 5 in. The capillary rise results are shown in Figure 7 as MMA weight gain versus time. Duplicate points are shown to illustrate the magnitude of specimen-to-specimen variation. The key in Figure 7 lists the compressive strengths for these mixes which decrease as the water-to-cement ratio increases as normally observed. It is quite interesting to note that the rate of monomer imbibition is greatest for the higher water-to-cement ratios or the poorer-quality concrete.

The average of the duplicate data points in Figure 7 are plotted versus the square root of time in Figure 8. Again very good linear relations are evident. Table III lists the coefficients A that represent these results. As

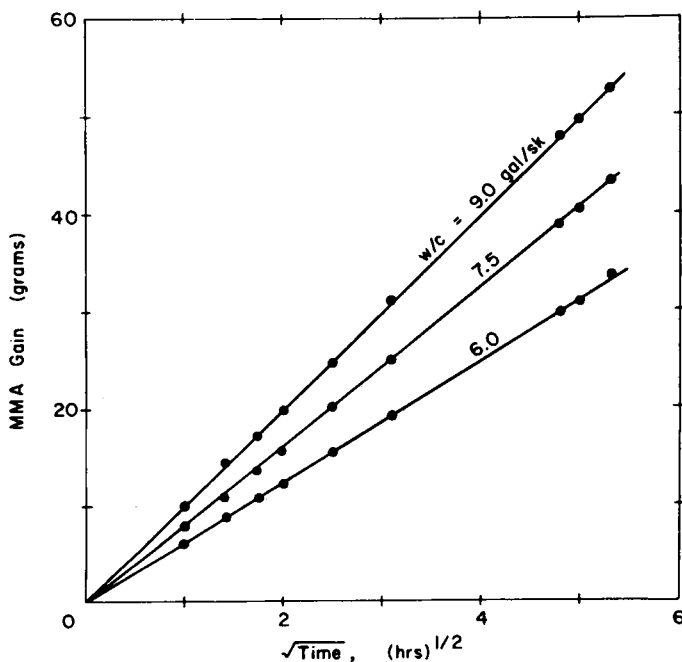


Fig. 8. Square root of time plots for data in Fig. 7.

TABLE III
Effect of Concrete Quality on Penetration Rate^a

Water/cement ratio <i>w/c</i> , gal/sk	<i>A</i> , ^b g/hr ^{1/2}	<i>B</i> , ^c in/hr ^{1/2}	Maximum monomer loading, % of dry concrete weight
6.0	6.3	0.472	5.00
7.5	8.1	0.562	5.39
9.0	10.0	0.636	5.90

^a Monomer = MMA.

^b $M = A\sqrt{t}$.

^c $h = B\sqrt{t}$.

discussed earlier, the mass gain M can be converted into an equivalent height h by use of the measured maximum monomer loadings shown in Table III so that a new coefficient, B , can be defined as follows:

$$h = B \sqrt{t} \quad (7)$$

which is also given in Table III for each type of concrete used.

Both the maximum loading and the rate constants A and B increase as the quality of the concrete decreases, i.e., as the water-to-cement ratio increases.²⁶ The higher loading is simply a result of the higher mortar porosity that results when the amount of water in the mix is increased. The rate of mass gain increases dramatically with an increased w/c ratio, as the values of A in Table III show. However, owing to the increase in porosity in this same direction, the differences in depth of penetration as judged by the B values are not as great. The model eq. (2) predicts that B should be proportional to \sqrt{R} , where R is the average pore radius. If this relationship is valid, the pores must get larger as the water-to-cement ratio increases. By this relation the pores in the lowest quality concrete, $w/c = 6$ gal/sk, are some 80% larger in diameter than those in the highest-quality concrete shown here.

The above observations are interesting because they help explain the leveling characteristics often observed in polymer-impregnated concrete, i.e., the properties of the impregnated material are about the same regardless of the initial quality of concrete. This is evidently true in part because the lower-quality concrete is more porous and accepts more monomer. It is interesting to see that this also applies to the rate of penetration. This means in surface impregnation that those zones which need help the most will imbibe monomer the most rapidly.

THE COMPETITION BETWEEN POLYMERIZATION AND EVAPORATION DURING CURING

Once the monomer has penetrated into the concrete to an adequate depth, the monomer must be converted into polymer, which involves three separate rate processes: heat transfer to build up an adequate temperature at each depth to cause polymerization; the rate of polymerization; and the

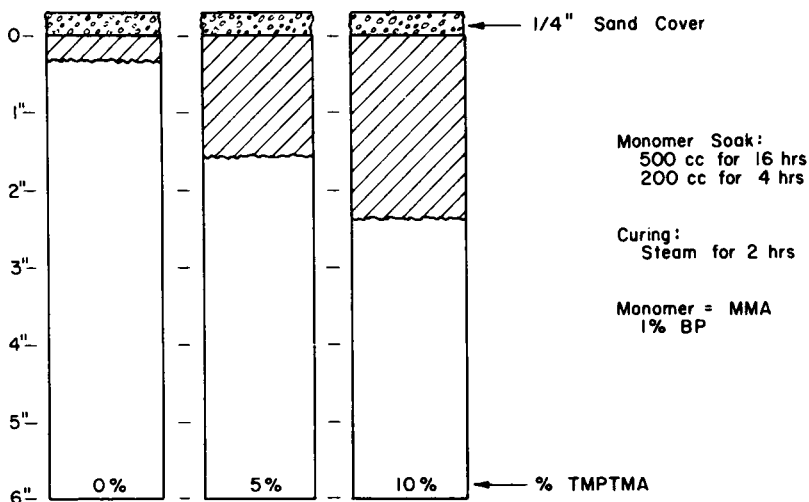


Fig. 9. Bar graphs showing depth of polymer-impregnated zone as a function of TMPTMA content in monomer mixture.

evaporation of monomer from the pores. The rates of these processes are highly interrelated and must be carefully regulated to obtain the desired depth of polymer-impregnated concrete.

The delicate balance required is illustrated here in a series of experiments using laboratory slabs which were 10 in. square and 6 in. thick. The depth of monomer penetration was held the same by using a standard soak cycle in all cases. This involved wetting the $\frac{1}{4}$ -in. sand layer with 500 cc monomer solution which was allowed to soak in for 16 hr. At this point, an additional 200 cc monomer mix was poured onto the sand, and soaking was continued for 4 more hours. According to Figure 4, this should produce a depth of penetration of about 2.8 in. in all cases. Immediately following impregnation, the slabs were placed under a steam curtain for 2 hr to cure. This gives a fixed heat transfer situation for all slabs. After curing, the slabs were broken open and the depth of the polymer impregnated zone observed visually. Some results are shown in Figure 9, where bar graphs indicate the depth of the polymer-impregnated zone. The soak and cure conditions were selected to give a very good impregnation. The only variables in this experiment were the polymerization rate and the amount of monomer evaporation which are now invoked to explain these results.

In this series of experiments, the monomer was MMA to which a constant level of BP, 1%, had been added. However, the amount of the crosslinking agent trimethylolpropane trimethacrylate (TMPTMA) was set at levels of 0%, 5%, and 10% based on the weight of MMA. The level of TMPTMA has a dramatic effect on the polymerization rate,²⁷ which can be seen by a simple technique devised here to obtain information on polymerization rates. In this technique, a test tube (see insert in Fig. 10) filled about three-fourths full of sand (≈ 70 g) is immersed in a liquid bath thermostated at

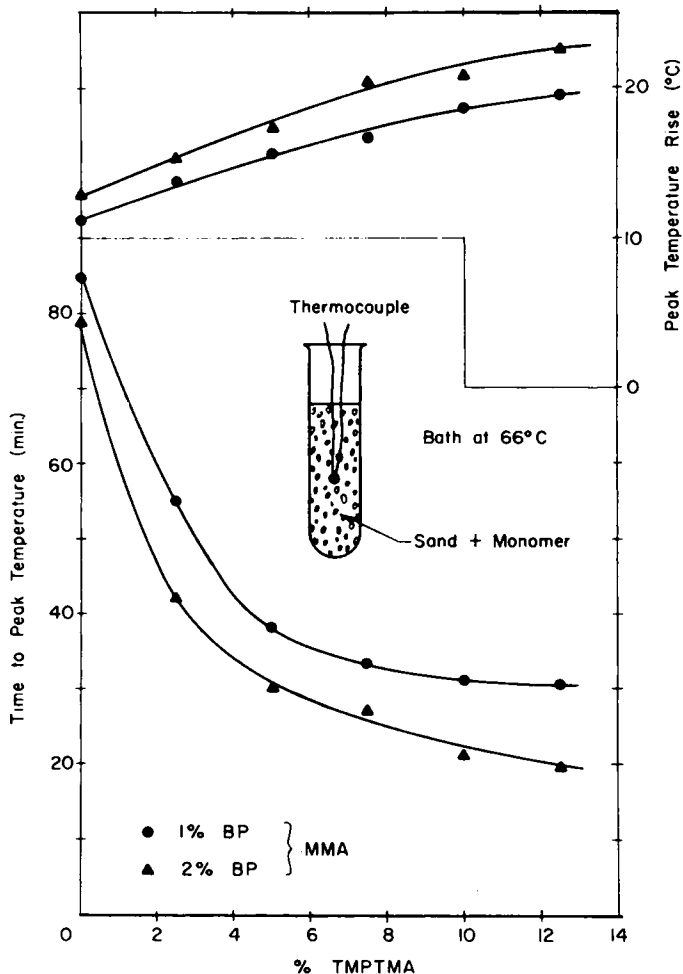


Fig. 10. Polymerization rate data.

150°F (66°C). The thermocouple shown is attached to a recorder, and when it indicates that thermal equilibration has been achieved, monomer mixture is poured over the sand to just fill up the pore space (≈ 12 g). As polymerization proceeds, heat is evolved by the exothermic reaction, so that the temperature rises. When polymerization is nearly complete, the temperature reaches a maximum and then declines. The temperature rise is greatly suppressed by the heat sink the sand provides. A similar heat absorption occurs during polymerization in concrete so that the temperature never rises to the level it would in the absence of the concrete or sand.²⁷ The magnitude of the temperature rise greatly affects the polymerization rate, so that it is very important to use the sand to simulate the time-temperature relationship in concrete.

The temperature rise can be used as a convenient way to follow polymerization progress. In fact, the time to the peak temperature rise is very

nearly the time required to complete polymerization, and it is therefore used here as a measure of rate. The time required to develop the peak temperature is shown in the lower half of Figure 10 for 1% and 2% BP as a function of the % TMPTMA. As can be seen addition of TMPTMA greatly increases the polymerization rate (27). The upper half of Figure 10 shows the maximum temperature rise above 66°C, which never exceeded about 22°C. This is a little higher than the rise observed in concrete since the monomer content there is less than one half that in the sand. The effect of BP is in the direction expected.

Now we will consider what the fate of the monomer which has penetrated into the concrete pores would be when the slab is heated from above if polymerization did not occur. MMA is volatile but it cannot evaporate from the top surface owing to the monomer held in the sand cover and the polyethylene barrier employed here. MMA can evaporate from the front inside the concrete and then diffuse or flow on through to the bottom of the slab. How rapidly this occurs will depend on the temperature at the front and the condition of the lower portion of the slab, e.g., its moisture content. However, if polymerization occurs, the monomer cannot migrate and eventually it will become a solid polymer. At low TMPTMA contents, the reaction is slow, so considerable monomer can evaporate before the front retracts to a position where the concrete temperature causes a polymerization rate that is sufficient to check additional evaporation; therefore shallow depths of impregnation result. As the TMPTMA level is raised, the reaction rate increases and solidification occurs before a great deal of monomer evaporates. There is some lowering of the volatility by adding TMPTMA, but the main effect seems to be the polymerization rate characteristics shown in Figure 10. The depth of polymer achieved here with 10% TMPTMA is about 2.4 in., which is only slightly less than the original depth of monomer before heating.

This series of experiments clearly shows the need to adjust the polymerization rate in the surface impregnation process. Use of TMPTMA in the monomer formulation is one way to do this. It could also be done by increasing the amount of benzoyl peroxide or using a more active initiator, but this is a less desirable approach. Alternately, one could select a less volatile monomer, but this is generally accompanied by a high viscosity which is self-defeating. Other monomers have different polymerization characteristics and produce impregnated concrete with different properties all of which had to be considered. In balance, MMA has proved to be a good choice for this application; however, several others may find use in this field.

SUMMARY

Successful surface impregnation requires the careful control and recognition of the rate processes: penetration, heat transfer, evaporation, and polymerization. In the process discussed here, monomer penetration into the concrete is accomplished by utilizing the capillary forces to imbibe monomer

into the concrete pores. This requires 4 to 12 hr under ambient conditions to develop the desired depth of penetration; however, it does not involve much capital expense. Monomer is supplied to the concrete surface by saturating a thin layer of sand or fine aggregate spread over the slab with monomer. This wick action prevents run-off on sloped decks. This layer also minimizes evaporation of monomer from the concrete during polymerization. After penetration, the concrete slab is heated to cause polymerization to occur at a reasonable rate. Various processes for providing this heat have been investigated. This procedure consistently gives a layer of polymer-impregnated concrete of $1/2$ to $1\frac{1}{2}$ inches thick when all factors in the process are properly regulated. The major advantage of filling the pores with polymer is to make the bridge deck impermeable to water. Other advantages include higher strength, better abrasion resistance, and more resistance to chemical attack. However, many other aspects of this treatment depend on the nature of the polymer in these pores.

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References

1. M. Steinberg, J. T. Dikeou, L. E. Kukacka, J. E. Backstrom, P. Colombo, S. Rubenstein, J. J. Kelsch, and B. Monowitz, *Concrete-Polymer Materials, First Topical Report*, BNL 50134 (T-509) and USBR General Report No. 41, December 1968.
2. M. Steinberg, J. T. Dikeou, L. E. Kukacka, J. E. Backstrom, P. Colombo, K. B. Hickey, A. Auskern, S. Rubenstein, B. Monowitz, and C. W. Jones, *Concrete-Polymer Materials, Second Topical Report*, USBR REC-OCE-70-1 and BNL 50218 (T-560), December 1969.
3. J. T. Dikeou, M. Steinberg, W. C. Cowan, L. E. Kukacka, G. W. DePuy, A. Auskern, W. G. Smoak, P. Colombo, G. B. Wallace, J. M. Hendrie, and B. Monowitz, *Concrete-Polymer Materials, Third Topical Report*, USBR REC-ERC-71-6 and BNL 50275 (T-602), January 1971.
4. J. T. Dikeou, W. C. Cowan, G. W. DePuy, W. G. Smoak, G. B. Wallace, M. Steinberg, L. E. Kukacka, A. Auskern, P. Colombo, J. M. Hendrie, and B. Monowitz, *Concrete-Polymer Materials, Fourth Topical Report*, USBR REC-ERC-72-10 and BNL 50328, January 1972.
5. J. T. Dikeou, L. E. Kukacka, J. E. Backstrom, and M. Steinberg, *J. Amer. Concrete Inst. Proc.*, **66**, 829 (1969).
6. L. Kukacka, P. Colombo, M. Steinberg, and B. Monowitz, *Concrete-Polymer Composites for Underwater Applications*, BNL 14267.
7. M. Steinberg, L. E. Kukacka, P. Colombo, A. Auskern, M. Reich, and R. Pike, *Concrete-Polymer Materials for Highway Applications*, Progress Report No. 1, BNL 15395, September 1970.
8. M. Steinberg, P. Comombo, and L. E. Kukacka, (to USAEC), U.S. Pat. 3,567,496 (March 2, 1971).

9. A. M. Lizzio, *Public Roads*, **37**, 129 (1973).
10. *Durability of Concrete Bridge Decks*, Report No. 5, Portland Cement Association, 1969.
11. P. Callahan, P. Siess, and C. E. Kesler, *Effect of Stress on Freeze-Thaw Durability of Concrete Bridge Decks*, National Cooperative Highway Research Program Report 101, 1970.
12. J. Murata, *Studies on the Permeability of Concrete*, RILEM Bulletin 29, December 1965.
13. C. G. Giles, *Proc. Inst. Civ. Eng.*, **6**, 216 (1957).
14. J. P. Callahan, *J. Structural Div., ASCE*, **96**, ST10, 2021 (1970).
15. D. L. Spell and W. H. Ames, *Highw. Res. Rec.*, **196**, 41, (1967).
16. H. B. Britton, *Roads and Streets*, **103**(5), 92 (1960).
17. G. Dallaire, *Civil Engineering-ASCE*, 80 (October 1973).
18. D. W. Fowler, J. T. Houston, and D. R. Paul, "Polymer-Impregnated Concrete for Highway Applications," Research Report 114-1, Center for Highway Research, The University of Texas at Austin, Feb. 1973.
19. D. W. Fowler, J. T. Houston, D. R. Paul, in *Polymers in Concrete*, Publication SP-40, American Concrete Institute, Detroit, 1973, pp. 93-117.
20. A. E. Scheidigger, *The Physics of Flow Through Porous Media*, Macmillan, New York, 1960.
21. A. M. Schwartz, *Ind. Eng. Chem.*, **61**, 10 (1969).
22. E. W. Washburn, *Phys. Rev.*, **17**, 273 (1921).
23. C. F. Heins, *ACS Polym. Preprints*, **14**, 1130 (1973).
24. J. W. Vanderhoff, J. D. Hoffman, and J. A. Manson, *ACS Polym. Preprints*, **14**, 1136 (1973).
25. E. Tazawa and S. Kobayashi, in *Polymers in Concrete*, Publication SP-40, American Concrete Institute, Detroit, 1973, pp. 57-96.
26. R. S. Mikhail and S. A. Selim, Symposium on Structure of Portland Cement Paste and Concrete, HRB Special Report No. 90, 1966, pp. 123-134.
27. D. R. Paul, D. W. Fowler, and J. T. Houston, *J. Appl. Polym. Sci.*, **17**, 2771 (1973).

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