TECHNICAL REPORT STANDARD TITLE PAGE

1. Report No.
FHWA/TX-84/02+246-4F

2. Government Accession No.

3. Recipient's Catalog No.

4. Title and Subtitle
IMPLEMENTATION MANUAL FOR
POLYMER CONCRETE REPAIR

5. Report Date
December 1983

6. Performing Organization Code

7. Author(s)
David W. Fowler, Alvin H. Meyer,
and Donald R. Paul

8. Performing Organization Report No.
Research Report 246-4F

9. Performing Organization Name and Address
Center for Transportation Research
The University of Texas at Austin
Austin, Texas 78712-1075

10. Work Unit No.

11. Contract or Grant No.
Research Study 3-9-79-246

12. Sponsoring Agency Name and Address
Texas State Department of Highways and Public
Transportation; Transportation Planning Division
P. O. Box 5051
Austin, Texas 78763

13. Type of Report and Period Covered
Final

14. Sponsoring Agency Code

15. Supplementary Notes
Study conducted in cooperation with the U. S. Department of Transportation, Federal Highway Administration
Research Study Title: "Polymer-Concrete for Concrete Pavement Rehabilitation"

16. Abstract

Polymer concrete (PC) has been widely used for repairing concrete bridges and pavements. The primary advantages are its rapid curing and high strength. The materials include a monomer, a cross-linking agent, a promoter, an initiator, and an aggregate. Other materials can be added to improve the workability and to improve the ductility and toughness.

PC can be made by one of several methods: (1) preplaced aggregate saturated with monomer which is poured or sprinkled; (2) preplaced aggregate with monomer injected using in-line mixing systems; (3) conventional concrete mixers; (4) mobile concrete batching units. Finishing is accomplished by screeding or troweling.

Safety procedures must be maintained in mixing, handling, storing, and in construction. Safety requirements are outlined.

17. Key Words
polymer concrete, portland cement, repair, bridges, pavements, field applications, safety procedures

18. Distribution Statement
No restrictions. This document is available to the public through the National Technical Information Service, Springfield, Virginia 22161.

19. Security Classif. (of this report)	20. Security Classif. (of this page)	21. No. of Pages	22. Price
Unclassified	Unclassified	84	

Form DOT F 1700.7 (8-69)

IMPLEMENTATION MANUAL FOR
POLYMER CONCRETE REPAIR

by

David W. Fowler
Alvin H. Meyer
Donald R. Paul

Research Report Number 246-4F

Research Project 3-9-79-246

conducted for

State Department of Highways and Public Transportation

in cooperation with the

U.S. Department of Transportation
Federal Highway Administration

by the

CENTER FOR HIGHWAY RESEARCH
THE UNIVERSITY OF TEXAS AT AUSTIN

December 1983

PREFACE

The study supervisors sincerely appreciate the very valuable assistance and suggestions of many people in the Department of Highways and Public Transportation. In particular, John Nixon, Jon Underwood, Ralph Banks, Ray Brown, and Donald O'Connor have been very helpful. John Nichols of the Federal Highway Administration has been a very cooperative and interested representative.

Sincere thanks are due to the personnel in many districts in assisting us in making field repairs. The study would not have been possible without their help.

Many graduate research assistants contributed to the research which formed the basis for this report: M. Haddad, D. Shrikant, S. Masaki, M. Hsu, and B. Addada-Shlone were instrumental in the study. David Whitney, technical staff assistant, was a very important part of the research. Nancy Zett served as project secretary. Gloria Clay typed the manuscript.

David W. Fowler
Alvin H. Meyer
Donald R. Paul

ABSTRACT

Polymer concrete (PC) has been widely used for repairing concrete bridges and pavements. The primary advantages are its rapid curing and high strength. The materials include a monomer, a cross-linking agent, a promoter, an initiator, and aggregate. Other materials can be added to improve the workability and to improve the ductility and toughness.

PC can be made by one of several methods: (1) preplaced aggregate saturated with monomer which is poured or sprinkled; (2) preplaced aggregate with monomer injected using in-line mixing systems; (3) conventional concrete mixers; (4) mobile concrete batching units. Finishing is accomplished by screeding or troweling.

Safety procedures must be maintained in mixing, handling, storing and in construction. Safety requirements are outlined.

SUMMARY

This report describes materials used for making polymer concrete for the repair of portland cement concrete. Several methods are described for producing polymer concrete for field applications. Procedures suitable for small and large repairs are given. Safety procedures for mixing, handling, storing, and using the chemicals are outlined.

IMPLEMENTATION

Implementation of the use of polymer concrete has begun in several districts. Several contracts have been awarded for repair of concrete pavements in which large quantities of user-formulated and commercially-available polymer concrete were used. Polymer concrete appears to be a durable and cost-effective material for repairing portland cement concrete. The fast setting time permits the material to be used in urban areas where lane closing time must be kept to a minimum.

TABLE OF CONTENTS

Page

LIST OF TABLES

LIST OF FIGURES

CHAPTER 1

MATERIALS

1.1 Introduction

There are several materials used in the production of polymer concrete, including several chemicals. These materials are briefly described in this chapter. Additional information pertaining to safety and handling is presented in Chapter 5 of this Implementation Manual.

1.2 Monomer System

The monomer system consists of several chemicals which must be mixed in the correct proportions to produce a cure in the desired time (less than one hour).

1.2.1 Monomer

The basic monomer is methyl methacrylate (MMA). MMA is the monomer from which Lucite® and Plexiglas® are made. MMA is a clear, volatile liquid that looks like water and has about the same viscosity as water. It has a sharp, pungent odor; about one part per million can be detected by smell. MMA can be obtained in units of 5 gallons, 55 gallons, and/or in tank car lots. It should always contain an inhibitor, MEHQ, which is described in a subsequent paragraph. For long storage times, the inhibitor level should be monitored as described in the Appendix.

1.2.2 Cross-Linking Agent

A cross-linking agent, which is a special type of monomer, is added to the MMA in small quantities to increase the cure rate. The cross-linking agent is trimethylolpropane trimethacrylate (TMPTMA). TMPTMA is a slightly yellow liquid with the viscosity of light oil. It is not nearly as volatile as MMA and has little odor. It should always be inhibited with either MEHQ or HQ, described in a subsequent paragraph.

1.2.3 Inhibitors

Inhibitors are additives used in MMA or TMPTMA to prevent premature polymerization, which can be caused by excessive temperatures, contaminants, etc. The two most common inhibitors are methyl ester of hydroquinone (MEHQ) and hydroquinone (HQ). For MMA, MEHQ is added at the rate of from 10 to 100 parts per million. TMPTMA usually contains from 100 to 125 parts per million of MEHQ or 60 to 100 parts per million of HQ. The higher levels should be specified when long storage times and/or high storage temperatures are anticipated. The level of the inhibitor should be monitored at six-month intervals following the procedure outlined in Appendix A.

1.2.4 Promoter

A promoter is used, in very small quantities, to increase the decomposition rate of the initiator, which results in faster curing. The promoter, dimethyl-para-toluidine (DMT), is a liquid with a viscosity about the same as water. Either the distilled or the undistilled form, which is less expensive, can be used. If the promoter is stored separately in concentrated form, caution must be exercised to prevent contact between the DMT and the initiator, benzoyl peroxide, BzP. Mixture of the concentrated forms can result in an explosive reaction. When the DMT is already mixed in the MMA, the initiator can be added with no danger.

1.2.5 Initiator

The initiator, benzoyl peroxide (BzP), is required to begin the polymerization, or cure. The BzP is added in relatively small amounts to the monomer just prior to adding the monomer to the aggregate. BzP comes in several forms, but the recommended type is a 40 percent concentration (commonly referred to as 40 percent dispersion) manufactured by Reichhold Chemicals, Inc. (Superox 742 or Superox 744 for pumping). BzP of 40 percent concentration is available from other manufacturers, but the Superox 744 is the only material that has performed satisfactorily here for mixing equipment in which the BzP must be pumped. The BzP dispersion is white with the viscosity of a heavy motor oil and it readily dissolves in MMA. Under no circumstances should nearly pure BzP in a dry, granular solid form be used since it can react in an explosive manner to heat, shock, or contact with other chemicals. Even the 40 percent dispersion should not be mixed with concentrated DMT.

1.2.6 Thickening Agent

Finely granulated polymethyl methacrylate (PMMA), which is the solidified form of MMA, is sometimes added to the PC mix to make it more viscous and more cohesive thus preventing segregation of aggregate and evaporation of monomer. The PMMA, added in small amounts, absorbs some of the MMA and results in an improved workability more nearly like normal portland cement concrete.

1.3 Commercially Prepackaged Polymer Concrete Systems

Several two-component prepackaged PC systems are available. The brands include Silikal® and Concresive®. These systems contain a liquid component, primarily MMA, and a powder component which contains fine aggregate, colorants, initiator, and thickener. For PC depths of several inches and/or large volumes, coarse aggregate can be added to the PC to extend it. These materials must be mixed prior to placement. Most of the prepackaged systems have separate cold weather and hot weather formulas.

1.4 Steel Fibers

Steel fibers can be added to the PC mix to minimize the reduction in strength due to wet aggregate and/or to increase the ductility and toughness of the PC. The recommended fibers (Bekaert ZL 30/50) are hooked at each end to provide better bond (Fig. 1.1). The fibers are generally glued together in groups of 5 to 20 with a water soluble adhesive, which results in a more uniform dispersion throughout a portland cement concrete mix. If the fibers are for use with PC, however, it should be noted that the usual adhesive is not soluble in MMA. It is necessary to specify an adhesive which is soluble in MMA or to order loose fibers.

1.5 Mold Release Agents

Mold release agents should be used when PC is cast in molds or removable forms. Without mold release agents, the PC tends to develop a strong bond to most materials. There are many materials which will provide some degree of mold release, including vegetable oil, paraffin, and commercially available compounds. The recommended material is a buffered fluorocarbon (Mold-Whiz F57®) which can be painted or wiped onto the form or mold surface. About an hour after applying the mold release, a spray lubricant (LPS-3® or LPS-7®) can be sprayed onto the mold release surface for even better results when moisture is present in aggregate.

1.6 Caulking Compounds

Since the monomer has a very low viscosity, it is important to make the mold or form joints water-tight. Acrylic latex, or silicone caulking compound applied with a caulking gun is recommended for this application.

1.7 Methylene Chloride

Methylene chloride (MeCl) is a non-flammable solvent used to

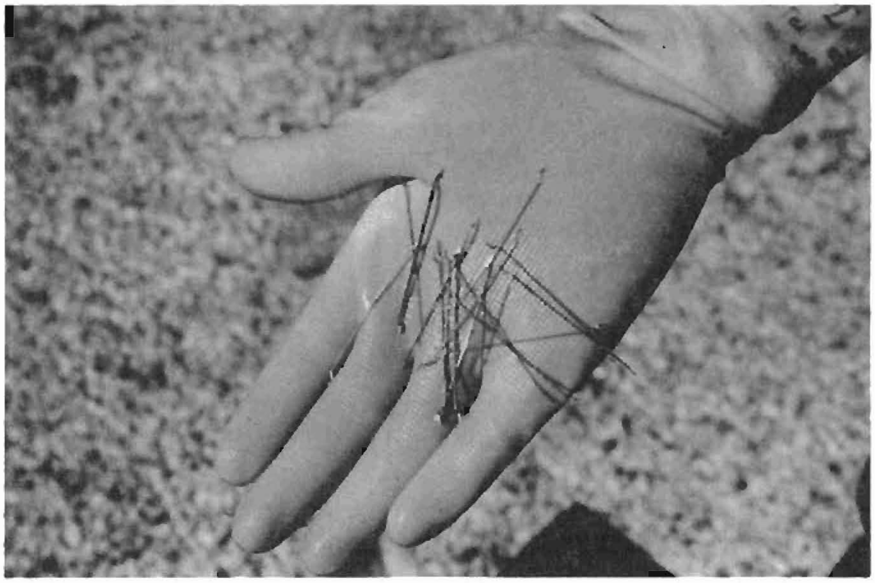


Fig. 1.1 Steel Fibers.

clean hoses, mixers, tools, and other equipment used for producing or finishing polymer concrete. It is readily available from many chemical supply stores.

1.8 Aggregates

1.8.1 Types

Any aggregate suitable for use in normal-weight structural portland cement concrete (PCC) may be used in polymer concrete (PC). Generally, higher strengths are obtained with crushed limestone coarse aggregates and well-graded silicious fine aggregates.

1.8.2 Gradation

Aggregates graded for structural PCC are suitable for use in PC. The basic mixture is 50 percent coarse aggregate (CA) and 50 percent fine aggregate (FA) by weight. Since most aggregates for structural PCC are similar in unit weight, a 50:50 mixture of CA and FA by volume is also suitable for use in PC. For large repairs (greater than 2 ft in diameter and 3/4 in. deep), a 1 1/2-in. maximum top size is recommended. For small or shallow repairs, a "pea gravel" and fine aggregate mixture will generally give the best results. For commercially-available PC, such as Silikal®, only coarse aggregate is required. The manufacturer's recommendations should be followed.

The following gradations have given excellent results in both the laboratory and field tests.

Coarse Aggregates

Retained on	Percent
1 1/2-in. sieve	0
3/4-in. sieve	30-65
3/8-in. sieve	70-90
No. 4 sieve	95-100

Fine Aggregates

Retained on	Percent
3/8-in. sieve	0
No. 4 sieve	0-5
No. 8 sieve	0-20
No. 16 sieve	15-30
No. 30 sieve	35-75
No. 50 sieve	70-90
No. 100 sieve	90-100
No. 200 sieve	97-100

It has been found that commercially-available bagged dried sand is adequate for the fine aggregate.

1.8.3 Storage and Handling

Aggregates should be stored in a well drained, protected area, in a dry condition. When such storage is unavailable, the aggregates should be stockpiled in a well-drained area, allowed to air dry as much as possible, and covered with plastic sheets or other moisture barrier until needed.

Aggregates for PC can be handled in the same manner as aggregates for PCC. Care should be exercised to avoid exposing the aggregates to moisture. Aggregates should have less than one percent moisture content at time of use.

CHAPTER 2

EQUIPMENT

2.1 Introduction

For small repairs in which preplaced aggregate is saturated with monomer solution, no equipment is required.

The primary items of equipment required for large polymer concrete repairs are in-line mixing systems and/or mobile concrete batching facilities. Some modifications and special supporting equipment are required. The equipment needs are summarized in this chapter.

2.2 Mixing and Batching Equipment

2.2.1 In-Line Mixing Systems

The recommended equipment is the Hydraulic Injection System (H.I.S.) (Fig. 2.1) manufactured by Venus Products, Inc., Kent, Washington. The high volume unit has a capacity of approximately 9 gallons per minute, which would permit up to 10 cubic yards per hour per pump for continuous operation; however, the actual intermittent operation of the gun would result in a production of not more than 5 cubic yards per hour per pump, or 10 cubic yards for two pumps. Another unit has a capacity of about 4 gallons per minute. It is recommended that the in-line H.I.S. units be trailer-mounted and include the following (Fig. 2.2).

1. one or two pumps equipped with
    a. an injector gun for each pump

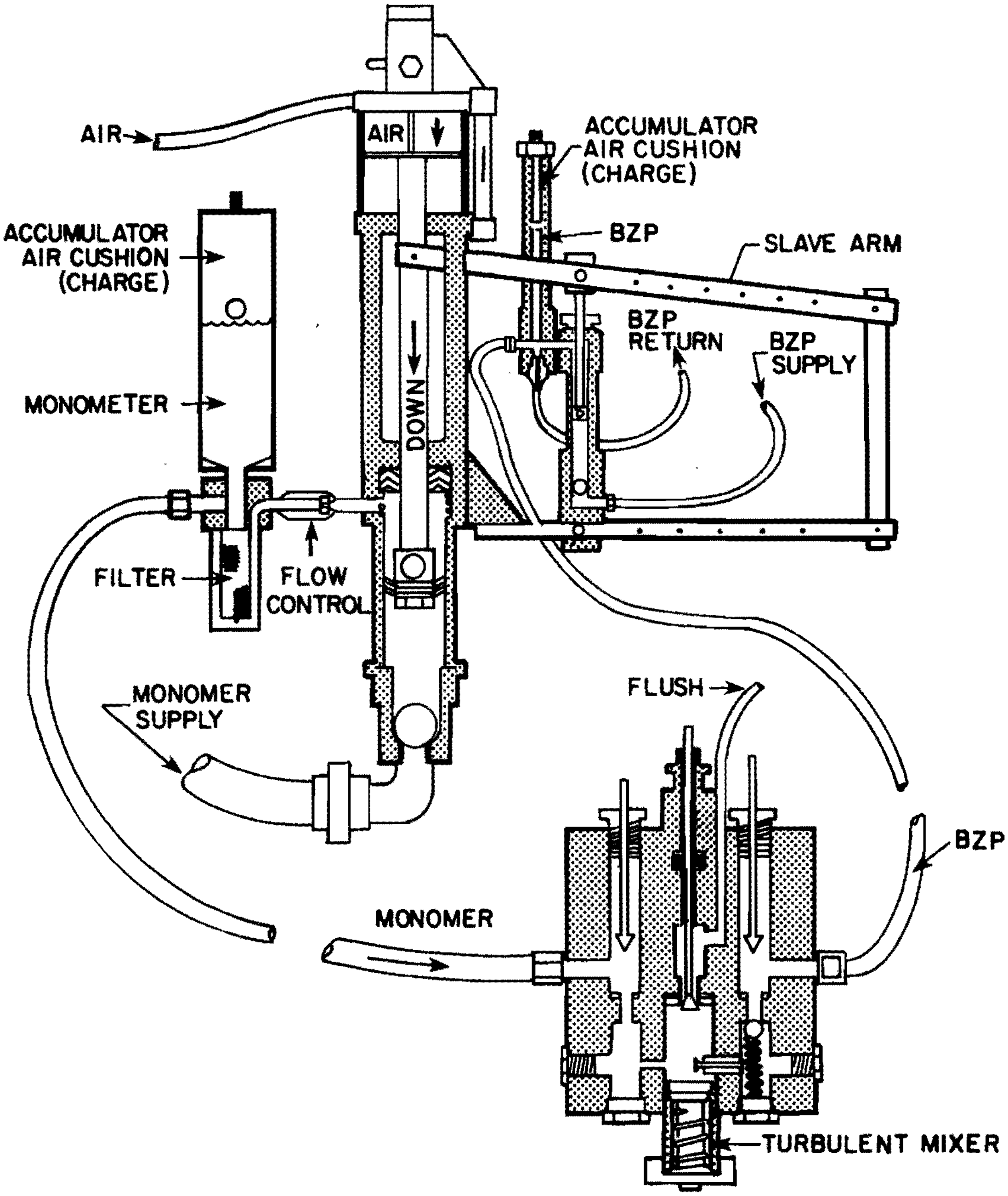


Fig. 2.1 In-Line Injection System

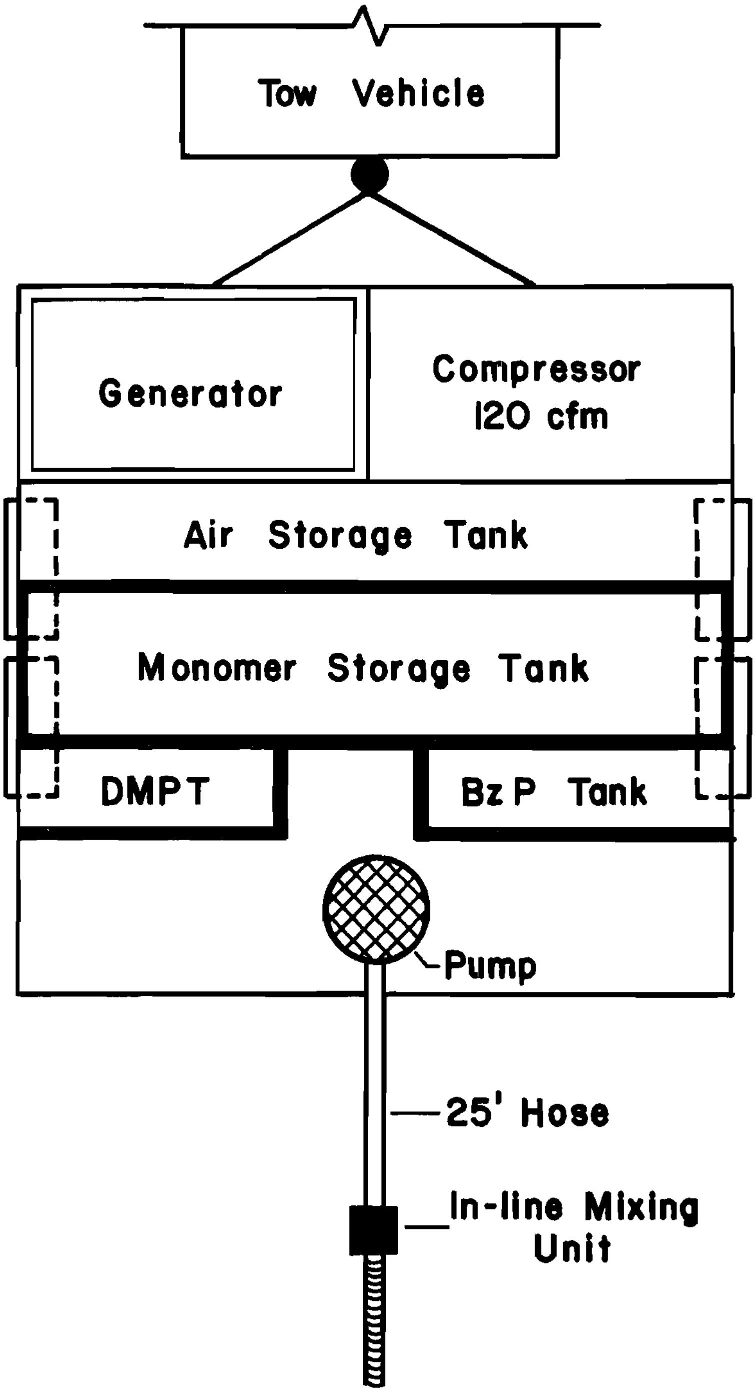


Fig. 2.2 Schematic of Trailer-Mounted In-Line Mixing System.

   b. 25-foot methylene chloride-resistant hose attached to each gun
   c. H.I.S. slave-pumps equipped for 8-percent BzP dispersion and 5-percent DMT
2. monomer storage tank
3. drum of 40-percent BzP dispersion
4. drum of DMT
5. 120-cubic-foot-per-minute air compressor/generator equipped with high efficiency water trap before air lines
6. air storage tank
7. safety equipment on or near the trailer, including
   a. large volume dry chemical type fire extinguishers
   b. fire-resistant clothing, goggles, respirators, boots and gloves
   c. eye wash station

2.3 Concrete Mobile Batching Facility

One recommended mobile batching facility is the Concrete Mobile®, manufactured by Daffin Mobile Products Division of Barber Greene, Lancaster, Pennsylvania. This unit is capable of producing up to 10 or more cubic yards per hour. The unit is designed for the production batching of portland cement concrete, and some modifications are required to accommodate batching of MMA based polymer concrete. Modifications should include

1. Making all gaskets, seals, and hose linings of Teflon®, silicone, or polyethylene.
2. A gear pump, without gaskets or seals in contact with monomer, should be provided for monomer transfer.
3. Provide a positive displacement pump that can be adjusted to pump different levels of DMT. An in-line static head mixer should be used to add DMT into the monomer line.
4. For BzP dispersion, provide a positive displacement pump

which is adjustable to add varying levels of BzP. Lined hoses and stainless steel or polyethylene contact materials are required.

5. Provide a flush system which includes an air-pressurized flush tank for cleaning initiated monomer-contact areas, e.g., mixing auger and chute, polyethylene-lined hoses, gaskets, and seals.
6. Using only non-sparking materials at the delivery end of the conveyor belt and in the mixing chamber.
7. A chamber for storing and adding steel fibers.
8. Including a storage chamber for adding PMMA powder in varying amounts for user-formulated systems.
9. Maintaining large chemical fire extinguishers on the unit near the monomer tank and near the mixing chamber.
10. Having portable eye wash stations readily available.
11. Wearing fire-resistant clothing, goggles, boots, gloves during repair operations.

CHAPTER 3

MONOMER SYSTEM

3.1 Introduction

The monomer system usually consists of four (4) components: methyl methacrylate (MMA), trimethylolpropane trimethacrylate (TMPTMA), dimethyl-para-toluidine (DMT) and benzoyl peroxide (BzP). Polymethyl methacrylate (PMMA) is sometimes used as a thickening agent to make the PC mix more cohesive.

3.2 Preplaced Aggregate Method

The monomer formulation is 95 percent MMA and 5 percent TMPTMA. Sufficient promoter (DMT) and initiator (BzP) must be added to polymerize (cure) the monomer. Figure 3.1 gives the percents of BzP and DMT as a function of initial material temperature. It should be noted that exact amounts of BzP and DMT do not have to be used for each temperature; the curves are not highly sensitive to small changes. Table 3.1 summarizes the BzP and DMT levels required at different temperatures.

It is important to note that the BzP generally comes in diluted form, and the amount of BzP to be used is the concentrated amount. For example, if a 40 percent BzP dispersion is used and one percent is required, the amount of dispersion to be used is 1.0/0.4 = 2.5 percent.

Example:

Determine the volumes of MMA, TMPTMA and DMT that would be

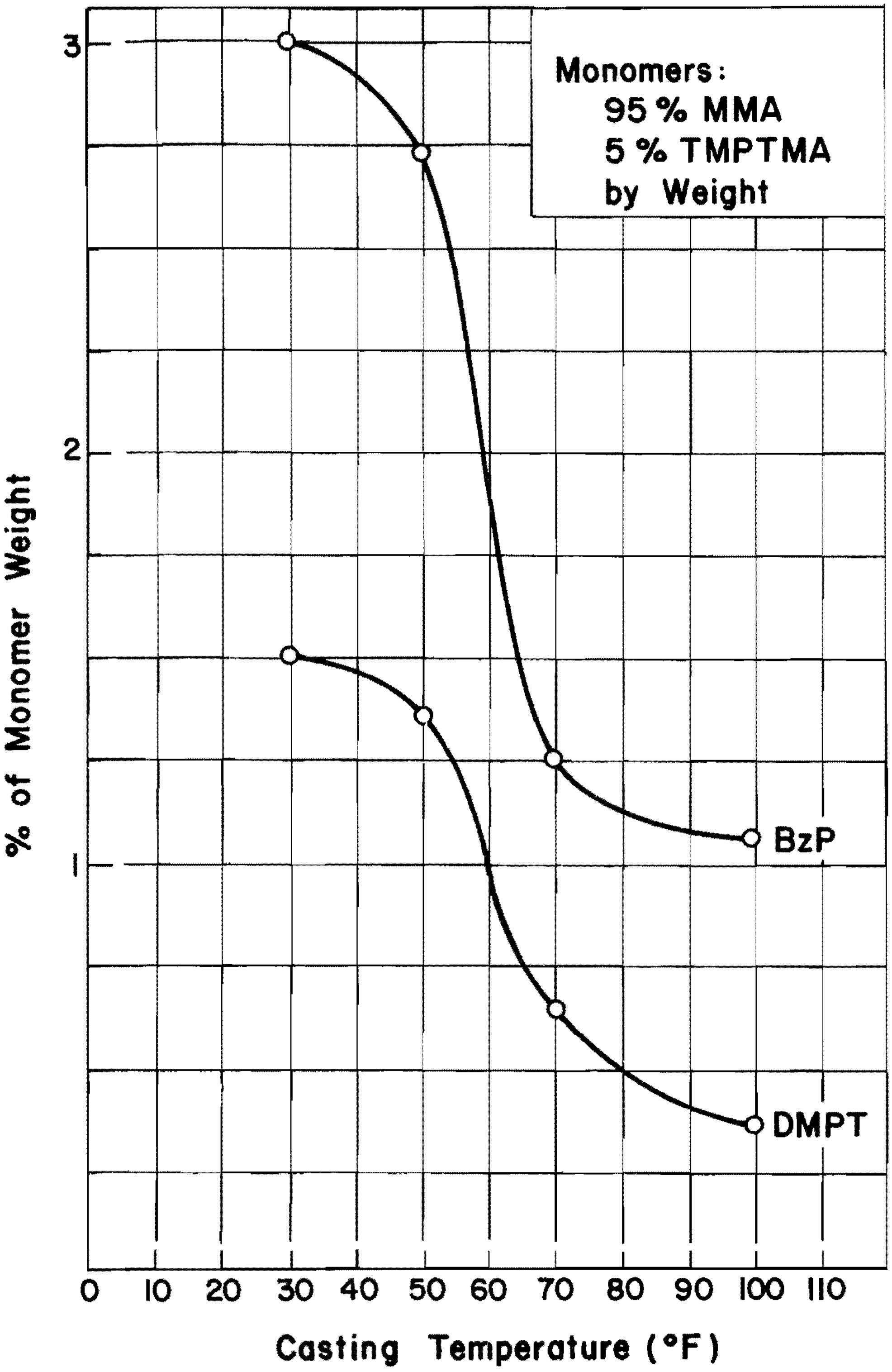


Fig. 3.1 BzP and DMT Levels in the Monomer Formulations Which Yielded the Highest Average Moduli of Rupture vs Casting Temperature.

Table 3.1 Recommended Levels of BzP and DMT as a Function of Initial Material Temperature.

Component	Temperature, °F			
	30	50	70	100
BzP, %	3.0	2.75	1.25	1.05
DMT, %	1.5	1.375	0.625	0.35

required to produce 55 gallons of monomer ready for initiator to be added. Find the required amount of initiator. Assume a temperature of 75°F.

1. Determine amount of DMT required for 75°F. From Fig. 3.1, use 0.60 percent.
2. Determine volume of MMA, TMPTMA and DMT to produce 55 gallons of monomer (the BzP is added later). Note that the volume percent is not the same as weight percent since the specific gravities (SG) of the components are not equal.

Component	SG	Weight Percent (WP)	WP/SG	Volume Percent (VP)[a]	Total Volume, gallons[b]
MMA	0.95	95	100.00	94.90	52.20
TMPTMA	1.06	5	4.72	4.48	2.46
DMT	0.925	0.6	0.65	.616	0.34
			Sum (A) 105.37		

[a] volume percent (VP) = $\dfrac{\text{WP x 100}}{\text{(SG)(Sum A)}}$

[b] total volume = $\dfrac{\text{55 gallons x VP}}{100}$

Component	Weight Percent (WP)	Percent of Total Weight[c]
MMA	95	94.43
TMPTMA	5	4.97
DMT	0.6	0.60
	Sum (B) = 100.6	

[c] percent of total weight = $\dfrac{\text{weight percent}}{\text{sum (B)}}$ x 100

3. Determine the amount of BzP to be added to 55 gallons of monomer. Assume 40 percent dispersion. From Fig. 3.1, use 1.15 percent.

Component	SG	Total Volume, gallons[d]	Weight, pounds[e]
MMA	0.95	52.20	413.0
TMPTMA	1.06	2.46	21.7
			Sum (C) = 434.7

[d] from previous table

[e] weight = total volume x SG x 8.33 lb/gal

$$\text{Weight of BzP} = \text{Sum (C)} \times \frac{1.15}{100} = 434.7 \times 0.0115 = 5.00/\text{lb}$$

$$\text{Weight of 40 percent dispersion} = \frac{5.00}{0.40} = 12.50 \text{ pounds}$$

3.3 Premixed Polymer Concrete

3.3.1 Monomer Formulation

The monomer formulation used in this method consists of 97 percent MMA and 3 percent TMPTMA by weight. The BzP and DMT levels are the same as those used in the preplaced aggregate (Fig. 3.1). Polymethyl methacrylate (PMMA) is usually added to the aggregate in the amount of 3 percent of the aggregate weight to make the PC mix more cohesive.

3.3.2 Colorant

A colorant consisting of a mixture of carbon black and titanium dioxide can be added to the PC mix to impart a grey color to the final product. The ratio of carbon black to titanium dioxide usually ranges between 1/300 and 1/500 by weight. The resulting mixture is added to the aggregate in the amount of 0.50 to 1.0 percent of the aggregate weight.

3.3.3 Calculations

Calculating the amount of monomers, initiator and promoter is similar to that outlined in Section 3.2 except that the MMA:TMPTMA ratio is 97:3 instead of 95:5 by weight. The PMMA and colorant quantities can be calculated as per the following example:

Calculate the amount of PMMA and colorant needed for one cubic foot of polymer concrete.

Solution:

The amount of aggregate needed for one cubic foot of polymer concrete is approximately 125 lb. The PMMA content is 3 percent of the aggregate weight.

$$\text{PMMA} = \frac{125 \times 3}{100} = 3.75 \text{ lb}$$

Assume the amount of colorant to be 0.75 percent of aggregate weight.

$$\text{Colorant} = \frac{125 \times 0.75}{100} = 0.9375 \text{ lb}$$

Assume the ratio of carbon black (CB) to titanium dioxide (TDO) to be 1:400.

$$\frac{\text{CB}}{\text{TDO}} = \frac{1}{400} \qquad \frac{\text{TDO}}{400} = \text{CB}$$

But CB + TDO = 0.9375 lb

$$\text{TDO} \quad 1 + \frac{1}{400} = 0.9375 \text{ lb}$$

TDO = 0.935 lb

$$\text{CB} = \frac{\text{TDO}}{400} = 0.0025 \text{ lb}$$

3.3.4 Packaging

Packaging user-formulated polymer concrete simplifies the application procedures. As indicated in Fig. 3.2, the materials can be prepackaged in two components: liquid and powder. The liquid component is a mixture of MMA, TMPTMA and DMT. The powder component is a mixture of PMMA, BzP and colorant. The two components can be mixed with dry coarse aggregate and sand to produce polymer concrete.

3.4 Sources and Costs of Chemicals

3.4.1. MMA (Methyl methacrylate) with MEHQ @ 10 ppm Monomer

SOURCE*	PRICE (PER POUND)	
	No. of Drums	Price
1. Rohm and Haas Company	30-53	0.71
Margaret Pursel, Rep.	15-29	0.72
214/233-1021	5-14	0.73
	3- 4	0.75
	1- 2	0.77

*Complete address and phone number of each chemical supplier are listed in alphabetical order in Appendix B.

2.	E.I. DuPont de Nemours & Co., Inc.	30-53	0.71
	Dr. Robert Feild, Rep.	15-29	0.72
	302/774-9888	5-14	0.73
		3- 4	0.75
		1- 2	0.81
3.	American Cyanamid	Call for current pricing	
	713/790-1500		

3.4.2 TMPTMA (Trimethylolpropane trimethacrylate) with HQ 100 ppm

Cross-linking Monomer

	SOURCE*	PRICE (PER POUND) + FREIGHT	
		No. of Drums	Price
1.	Rohm and Haas Company	10	1.78
	Margaret Pursel, Rep.	4- 9	1.83
	214/233-1021	1- 3	1.88
	Product Name: "Rocryl X-980"	5 gal	3.00
2.	Sartomer Company	10	1.83
	Linda Compton	4- 9	1.88
	215/692-8400	1- 3	1.93
	Product Name: SR-350	44	1.75
3.	Celanese Chemical Co., Inc.	1- 15	1.78
	Dwight D. Edman	T/L	1.72
	214/233-1021		
	Product Name: TMPTMA		

---

*Complete address and phone number of each chemical supplier are listed in alphabetical order in Appendix B.

3.4.3 BzP (Benzoyl peroxide)[a]

Initiator 40% Benzoyl Peroxide Dispersion

SOURCE*	PRICE (PER POUND)	
	No. of Drums	Price
1. U.S. Peroxygen Div. of Witco Chem. Co. Nancy Bentsen, Rep. 415/233-5911	380 lb drum	2.08/lb pay freight truckload shipment N.A in this size
2. Reichhold Chemical Company	< 10 pails	2.07/lb
Kathryn Gann, Rep.	> 10 pails	2.02/lb
512/836-1426		
Product Code Names: "46-742 or Superox 742" and/or Pumpable "46-744"		
3. Noury Chemical Corporation	> 500 lb	2.44/lb
716/778-8554	< 500 lb	2.69/lb
Product Notation: "40E"	> 500 lb	2.79
	< 500 lb	3.07

---

[a] Benzoyl Peroxide (BP, BPO, BzP)
Because of the need for safe and easy handling of this peroxide, our recommendations for most field applications are for "waterless" 40% dispersion of benzoyl peroxide. Other forms such as dry powders and pastes will work well, too, although they may be more difficult to handle or more hazardous in some cases. "Wet" (12% to 20% water) powders should be avoided since water affects the quality of the polymer.

*Complete address and phone number of each chemical supplier are listed in alphabetical order in Appendix B.

3.4.4 PMMA (Polymethylmethacrylate, powder)

Polymer Powder

SOURCE*	PRICE (PER POUND) No. of Drums	Price
1. E.I. DuPont de Nemours & Co.	CRYLCON EP 4160	
For Technical Information		
Dr. Robert Feild, Rep.	2000-4999 lb	1.53
302/744-9888	1000-1999 lb	1.55
(orders for Crylcon	- 50 lb	1.81
EP 4160 only)		
Bob Folts, Rep.		
800/441-9494		

3.4.5 DMT (Dimethyl-para-toluidine)

Promoter or Accelerator

SOURCE*	PRICE (PER POUND) No. of Drums	Price
1. RSA Corporation	1 qt	15.00
Robert Anthony, Rep.	1 gal (7.5 lb)	50.00
914/693-2493	5 gal (38 lb)	5.00/lb
	15 gal drum 110 lb net	4.60/lb
	1 415 lb drum	3.80/lb

3.4.6 Prepackaged Concrete Systems (Polymer concrete)

1. Adhesives Engineering Company
1411 Industrial Road
San Carlos CA 94070
(415) 592-7900
Telex 34-8459

---

*Complete address and phone number of each chemical supplier are listed in alphabetical order in Appendix B.

2. Silikal of North America, Inc.
   Type R7 - High Strength Overlay PC powder 0.77/lb plus liquid 1.72/lb
   Type R8 - Industrial Acid Resistant Floor PC (call for price)
   Type R9 - Thixotropic Vertical Application PC (call for price)
   Type R17 - General Patching PC (Surfaces Similar Concrete) powder 0.77/lb plus liquid 1.69/lb
   All materials approximately $0.50 to $1.00/lb
   Contact: Manfred Grove
   203/333-1013
   Licensed contractor or volume job receives 30% off price.

3. Superior Products Company, Inc.
   445 Coney Island Drive South
   Sparks NV 89431
   (702) 358-7870
   Telex 354484 Superior Spks
   Gary Farnes

4. Transpo Materials Inc.
   111 Cedar Street
   New Rochelle NY 10801
   (914) 636-1000
   Arthur Dinitz

3.4.7 <u>Colorants</u> (Titanium dioxide and carbon black and/or black iron oxide)

<u>SOURCE*</u>

1. American Cyanamid
   201/356-2000

*Complete address and phone number of each chemical supplier are listed in alphabetical order in Appendix B.

2. E. I. DuPont DeNemours & Co.
Jack Dellcex
302/999-3066
Product name TiPure R 900-28

3. Hilton Davis Chemical Company
2235 Langdon Farm Road
Cincinnati, Ohio 45237
513/351-1300

4. P.P.G.
Resin Products C&R Division
1 Gateway Center
Pittsburgh, Pennsylvania 15222
412/434-3920

5. Ferro Corp.
Cleveland, Ohio
216/641-8580

6. GAF Corp.
New York
212/582-7600

7. Pigment Dispersion Inc.
Edison, NJ
201/287-1930

3.4.8 In-Line Monomer Injection Systems

Venus Products Inc.
1862 Ives Avenue
Kent WA 98031
(206) 854-2660
Terry Nash

3.4.9 Small Mobile Batching Facilities

1. Daffin Products Division
   Barber-Greene Company
   400 North Highland Avenue
   Aurora IL 60507
   (312) 859-2200
   Jack Skinner

2. Shotcrete Plus Inc.
   10627 Sentinel
   San Antonio, Texas
   (512) 657-4901
   Paul Diemert

CHAPTER 4

REPAIR PROCEDURES

4.1 Preparation of Repair Area

Proper preparation of the repair area is important to insuring a usable repair (Fig. 4.1). All asphalt and unsound concrete must be removed. The depth of the repair area should extend below the top layer of reinforcement if possible. Delaminated concrete and deteriorated concrete should be removed to leave only sound concrete. Corrosion scale or asphalt on the reinforcing steel must be removed, preferably by sandblasting (Fig. 4.2). The concrete surface against which the polymer concrete is placed must be clean of asphalt, oil and other contaminants. The surfaces must also be dry, to develop good bond between the concrete and polymer concrete. If a surface is damp, a heater or torch should be used to thoroughly dry the surface. The surface should be allowed to cool prior to placing monomer.

Formwork must be used for full depth repairs, at expansion or construction joints, or to establish grade with asphalt overlays. Wooden forms should be treated with a release agent especially made for use with polymers (Section 1.5), with vegetable oil, or with paraffin. All joints in formwork must be watertight. All cracks in concrete or at expansion joints must also be sealed (Fig. 4.3). Polyester putty (used for repairing auto bodies) or silicone or latex caulking compound can be used to seal the joints. It is recommended that the form be pretested for leaks with a small amount of water the day prior to placement of the polymer concrete or with the monomer

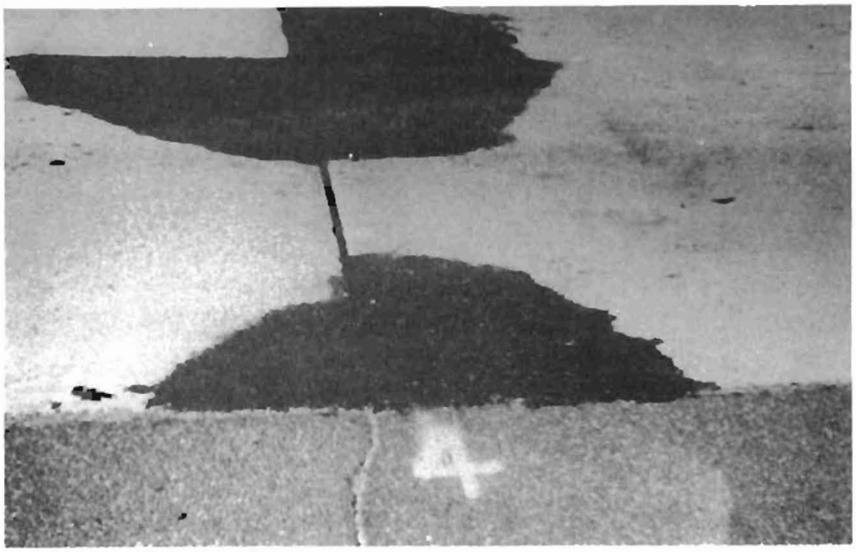


Fig. 4.1 Repair Area Prior to Removal of Asphalt.

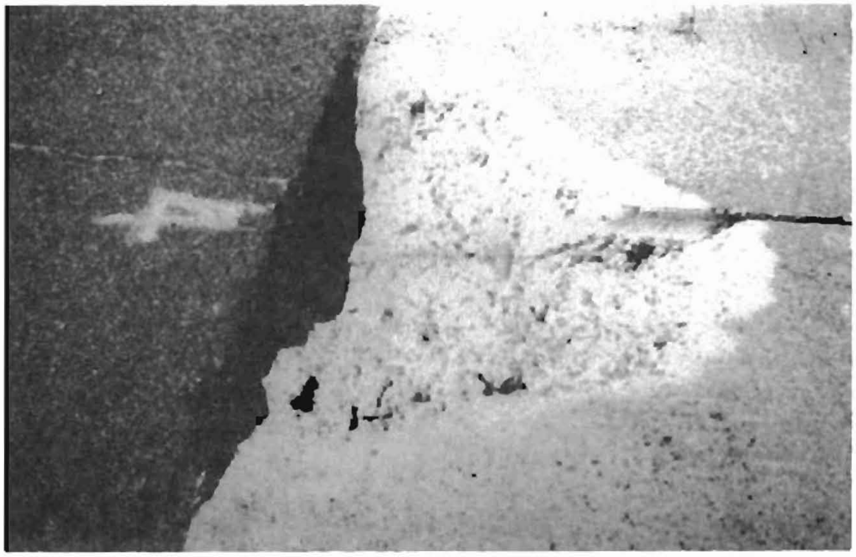


Fig. 4.2 Repair Area After Sandblasting.

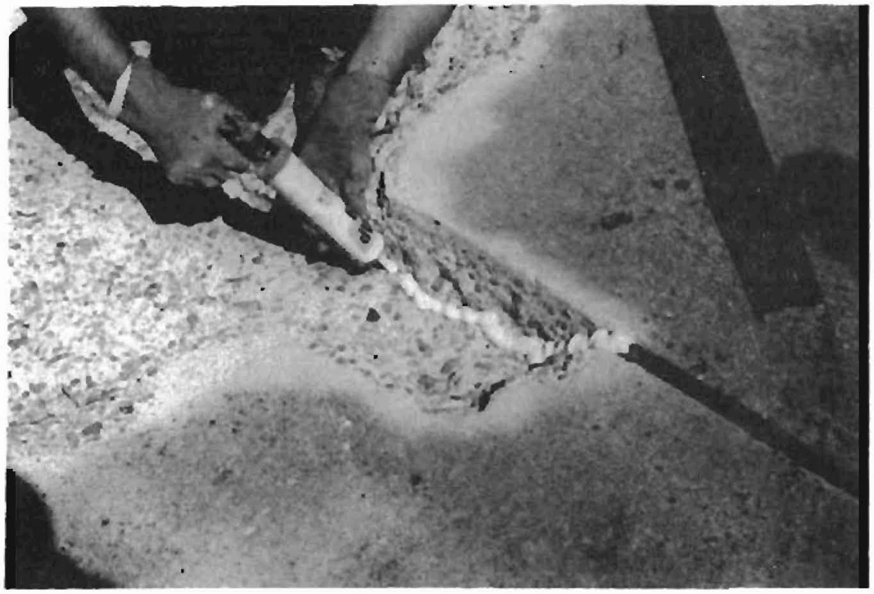


Fig. 4.3 Caulking Joints to Prevent Monomer Leakage.

formulation if the repair is to be made the same day.

For precast slabs used in repair, Research Report 246-1, "Polymer Concrete for Precast Repair of Continuously Reinforced Concrete Pavement on IH 30, Near Mt. Pleasant" (Ref 3) should be consulted for design recommendations. References 1 and 2 have additional information on polymer concrete repairs.

4.2 Mixing or Batching PC

Several methods are available for mixing or batching PC. Preplaced aggregate can be used with monomer poured or sprinkled over the aggregate, or monomer can be injected with an in-line mixing system. PC can be mixed prior to placing in the repair area using either ordinary concrete mixers or mobile concrete batching units.

The methods using only preplaced aggregate are appropriate only with user-formulated monomer system. The batching method can be used with either user-formulated or commercially-available systems.

4.2.1 Preplaced Aggregate Method

The aggregates, which are discussed in Section 1.8, are mixed dry and placed into the repair hole. For a repair 3/4-in. or less in depth, a well-graded concrete sand can be used. For a deeper repair, approximately 50 percent Grade 3 or Grade 4 coarse aggregate can be used.

The aggregate should be screeded to a relatively smooth finish prior to applying monomer.

1. Pouring or Sprinkling Monomer

   This method is appropriate for small repairs. The monomer system is mixed in clean vessels such as 5-gallon cans or 55-gallon drums. The TMPTMA and DMT can be added to the MMA several days prior to the repair, but the BzP should be added only a few minutes before the monomer is to be applied to the aggregate. The monomer system should be thoroughly mixed with a wooden paddle.

It should be noted that the DMT and the BzP should never be mixed directly together because of the danger of explosion.

The monomer system is mixed and poured or sprinkled over the aggregate (Fig. 4.4). For small or shallow repair, sprinkling with a sprinkler can is recommended to minimize erosion of the aggregate. For larger repairs, monomer can be poured from larger cans or applied by means of spray bars attached to larger drums or containers. Since the pot life of the monomer is usually less than 30 minutes, caution should be exercised to use all mixed monomer within 10 to 15 minutes after the initiator has been added. Consolidation of repairs with depths of 3 in. or more should be accomplished by tamping or vibration, although care must be taken to avoid segregation of the monomer and aggregate. After monomer ponds on the surface, the surface should be screeded with a straight edge to level and smooth the surface. The area of the ponded monomer should be filled with sand to prevent slick spots from occurring after the monomer polymerizes (hardens). The surface can be given a smooth finish with wooden floats or steel trowels (Fig. 4.5). Since the monomer is volatile, the surface should be protected during curing in one of two ways to minimize evaporation of monomer:

a. Polyethylene membrane can be placed over the repair and weighted down with sand or lumber around the edges. It may be necessary to add additional monomer with a sprinkler can if evaporation, leakage, or other losses cause depletion of monomer on the surface. Lack of sufficient monomer can result in insufficient binder for the aggregate on the surface, which will result in an abraded or worn surface after a few days of exposure to traffic.

b. A mixture of sand and PMMA (approximately 3 percent PMMA by

Fig. 4.4a Pouring Monomer.

Fig. 4.4b Sprinkling Monomer.

Fig. 4.5a Trowelling Surface.

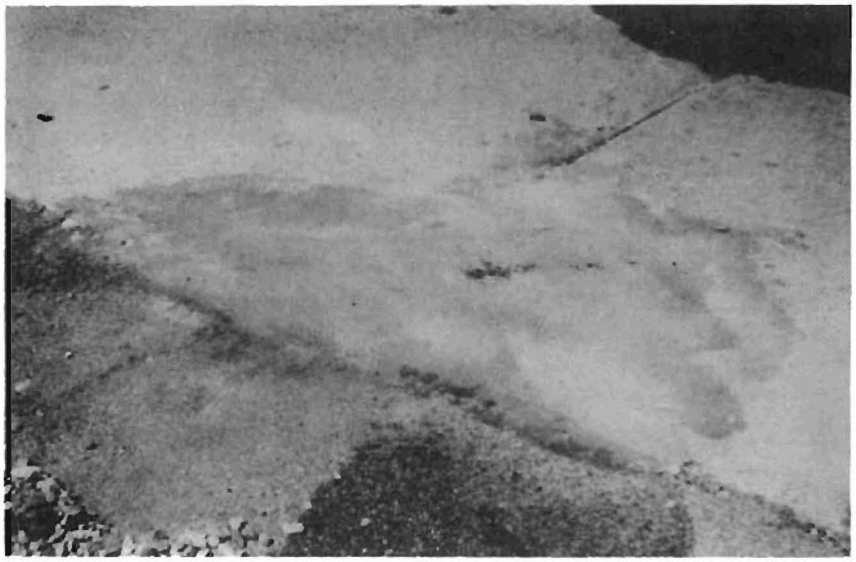


Fig. 4.5b Finished Surface.

weight of sand) can be added to the top of the repair prior to troweling or other finishing. The PMMA serves as a thickener and causes a surface skin to form, which helps to minimize evaporation.

2. Injecting Monomer

The in-line mixing system permits better control of curing rates for PC since the flow rate of BzP and sometimes DMT can be easily adjusted. Because the chemicals are mixed at the gun head and immediately injected, there is no waste due excess monomer being batched. The clean-up is minimal with only a 60-second flushing with methylene chloride.

The primary disadvantage is that when monomer is injected at maximum flow rates, there is a tendency to segregate the fine and coarse aggregate at the nozzle. It is recommended that the flow rate be adjusted to minimize the segregation.

After the repair area has been filled with aggregate, the gun nozzle should be inserted into the aggregate so that monomer is injected near the bottom of the repair (Fig. 4.6). The monomer is injected until ponding occurs on the surface. The nozzle may have to be moved to different locations to minimize segregation. Finishing of the surface should be performed as described in the previous section on "Pouring or Sprinkling Monomer."

4.2.2 Premixing Monomer and Aggregate.

For all premixed monomer and aggregate, PMMA should be added as discussed in Section 3.2. Colorant can also be added to result in a color more similar to portland cement concrete. Monomer in the weight of 10 to 12 percent by weight of aggregate is usually required, depending upon aggregate gradation and porosity: Additional monomer may be required if the surrounding concrete is porous or cracked. Improved bond may be obtained if the basic concrete is for preplaced

Fig. 4.6 In-Line Mixing System Gun.

aggregate (Section 4.2.1).

1. Conventional Concrete Mixers

Conventional concrete mixers can be used to mix PC. The fine and coarse aggregates are placed into the mixer and allowed to mix thoroughly (Fig. 4.7). The initiator can be placed in the monomer, which is then poured into the mixer, or the monomer can be placed into the mixer and followed by the BzP dispersion. After a few minutes of mixing, the PC is ready for placement (Fig. 4.8). Finishing is accomplished by screeding or trowelling.

2. Mobile Concrete Batching Units

PC can be effectively mixed in several kinds of mobile concrete batching units. These units, made for batching portland cement concrete, feed aggregates, cement (or PMMA), water (or monomer), and additives (BzP) into a mixing auger. The mixing usually requires less than a minute and produces a well-mixed, cohesive PC (Fig. 4.9).

It is important to note that most concrete batching equipment requires some modification for the use of MMA. MMA acts as a solvent on many types of seals and gaskets. Pumps must also be compatible with MMA. Sources of sparking must be eliminated. Careful coordination must be maintained with the equipment manufacturer to insure that safety requirements are satisfied.

4.3 Repair of Cracks

Cracks in concrete can be repaired with PC but widening or sawing may be required. Special machines such as the McDonald Scabbler® can be used to widen cracks (Fig. 4.10). The recommended size is 3/4 to 1 in. in width and 1 to 2 in. in depth (Fig. 4.11). The cracks should be clean and dry prior to applying monomer.

To seal the cracks below the widened area a monomer system as used for the preplaced aggregate system can be poured into the cracks.

Fig. 4.7 Adding Liquid Component to Mixer.

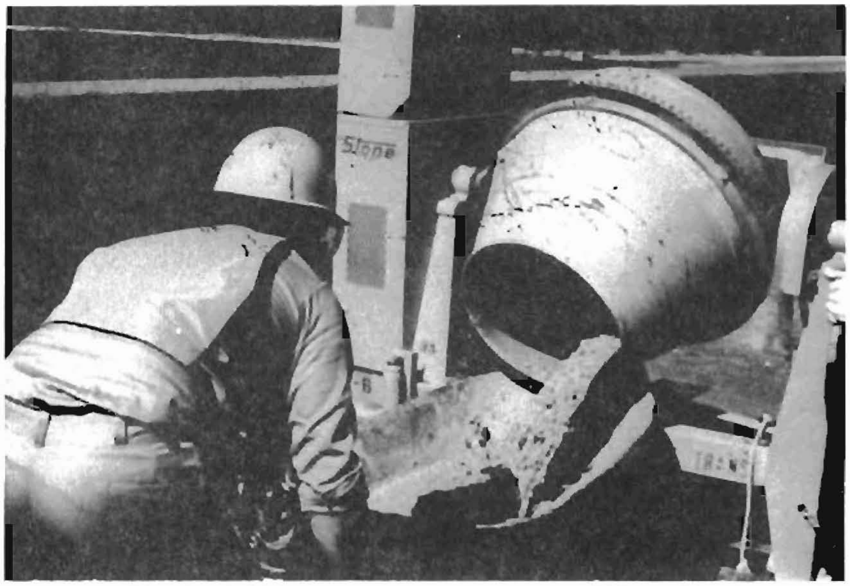


Fig. 4.8 Discharging PC from Mixer. Workability is Similar to Normal Concrete.

Fig. 4.9 PC Being Discharged from Concrete Mobile®.

Fig. 4.10 Opening (Chasing) Cracks.

Fig. 4.11 Opened Crack.

Sand should be poured in to fill the cracks (Fig. 4.12). PMMA can be added to the sand in the amount of 3 percent PMMA by weight of the sand to help hold the monomer in place. Monomer is added to completely saturate the sand.

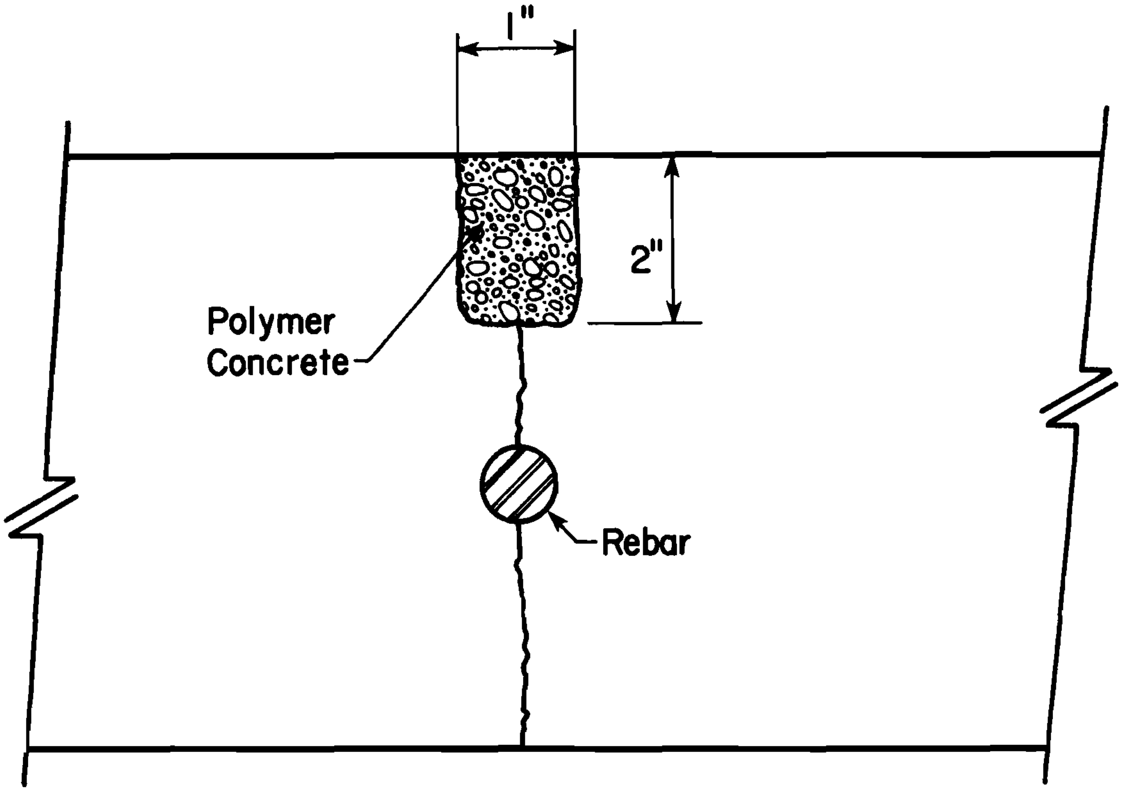
To prevent the loss of monomer, the bottom of the widened cracks can be sealed with silicone or latex caulking compound, polyester putty, or modeling clay prior to application of the monomer.

4.4 Cleanup

Cleanup can be accomplished using MMA as a solvent. However, nonvolatile solvents such as methylene chloride (MeCl) are preferable and should be used to clean moving parts, such as mixing augers.

4.5 Sample Specifications

Two sample specifications for polymer concrete repair are contained in Appendix C. One describes the user formulated PC which is applicable to the preplaced aggregate method (or mixed in concrete mixer). The other describes the premixed, two component system which has a color and workability similar to concrete.



Crack Repair

Fig. 4.12 Section Through Repaired Crack.

CHAPTER 5

SAFETY AND HANDLING

5.1 Introduction

The chemicals used in making polymer concrete require careful attention to safety and handling. Most of the chemicals are at least mildly toxic and flammable, but, with proper safety and handling precautions these materials can be used safely.

Education of personnel using or handling the chemicals should be an integral part of the training program. All personnel who are engaged in either handling or applying the chemicals should be thoroughly and regularly briefed on the handling of the chemicals, the use of safety equipment, fire prevention, fire control and first aid procedures. Only essential personnel should handle the chemicals, and safety equipment should be readily available and in proper condition. Reference 4 provides additional information on safety relating to concrete polymer materials.

5.2 Physiological Effects and Safety

Table 5.1 summarizes the symptoms and first aid requirements for the chemicals used in producing PC. Medical personnel should become familiar with the chemicals used so that, in the event of an emergency, no time is lost in treating injured workers.

Safety equipment should include protective clothing, such as splashproof safety goggles, impervious and flame-resistant aprons, gloves and boots. Where ventilation is poor and/or where monomer

Table 5.1 PHYSIOLOGICAL EFFECTS AND PROTECTIVE MEASURES.

MMA	Skin Contact	Eye Contact	Inhalation	Ingestion
Symptom	Mild irritation or rash, is a possible sensitizer.	Burning sensation; extreme cases can cause corneal damage.	Irritating smell at very low levels becoming painful to eyes, ears, nose, and throat at higher levels. Headache may result from long exposure. OSHA specifies exposure limit of 100 ppm for 8-hour time-weighted average.	Dermatitis and narcosis may develop.
First Aid	Wash thoroughly with soap and water.	Flush eyes immediately with water for 15 minutes. Seek medical assistance.	Remove person to fresh air; apply artificial respiration in extreme cases.	Induce vomiting; obtain medical attention.
Protective Measures	Wear impervious gloves, boots, aprons.	Wear splash-proof goggles; have eyewash nearby.	Provide adequate ventilation in closed spaces. Wear organic respirators.	

Table 5.1 PHYSIOLOGICAL EFFECTS AND PROTECTIVE MEASURES. (continued)

TMPTMA	Skin Contact	Eye Contact	Inhalation	Ingestion
Symptom	Not as irritating as MMA, but similar precautions should be taken	Less irritating than MMA, but similar precautions should be taken.	Low volatility; no special ventilation or respirators required.	Similar to MMA.
DMT				
Symptom	Very toxic, easily absorbed through skin. Symptoms include nausea, dizziness, weakness and cyanosis.	Same as for skin.	Vapors toxic; cyanosis symptoms.	Very toxic.
First Aid	Immediately wash affected area with soap and water; remove contaminated clothing.		Remove to fresh air. Use artificial respiration for troubled breathing.	Induce vomiting.
Protective Measures	Wear impervious gloves, boots, and apron.	Wear splash-proof goggles.		
BzP				
Symptom	Mild irritant	Mild irritant	No problem with liquid dispersion	Not particularly toxic.
First Aid	Wash well with soap and water.	Flush eyes with water for 15 minutes. Seek medical attention.		Induce vomiting.

vapor concentrations are high, an organic vapor respirator should be used.

Any skin contact with the chemicals, especially DMPT, should be avoided. If a splash or spill should result in some chemicals making contact with the skin, the area should be washed immediately for 15 minutes with clean water, after which medical assistance should be obtained. A portable eyewash station is recommended at all storage and application sites.

Excessive MMA and DMT vapor concentrations should be avoided. The Occupational Safety and Health Administration (OSHA) has specified a limit, based on an 8-hour time-weighted average of 100 parts per million (ppm) although few workers could probably comfortably endure such a high concentration for very long since less than one ppm can be detected by many people.

Headaches sometimes result from lengthy exposure. If overexposure occurs, the person should be removed to fresh air. Artificial respiration may be required in severe cases.

Should any of the chemicals be accidentally swallowed, vomiting should be induced and medical attention provided immediately.

5.3 Flammability and Fire Protection

Table 5.2 summarizes fire protection and flammability. All of the chemicals, especially MMA and BzP, are flammable, similar to gasoline. Therefore, all open flame, sparks, or other sources of ignition, including cigarettes, should be kept at least 50 feet from any of the chemicals in open areas and not allowed in enclosed areas.

Contamination should be avoided, especially direct contamination of BzP with concentrated DMT, which could easily generate enough heat and flammable gases to start a fire; hence, they must be stored or handled separately. When mixing the monomer for polymerization,

TABLE 5.2 FLAMMABILITY AND PRECAUTIONS.

MMA

1. Very flammable; similar to gasoline.
2. Avoid heat, flame, and sparks.
3. Extinguish fire with CO_2, dry chemicals, or foam.
4. Cool heated drums with cold water spray.
5. Avoid contamination with BzP until ready for field application.
6. Wear breathing apparatus when fighting MMA fire.

TMPTMA

1. Flammable.
2. Avoid heat, flame, and sparks.
3. Extinguish fire with CO_2, dry chemicals, or foam.
4. Cool heated drums with cold water spray.
5. Avoid contamination with peroxides, oxidizing agents, iron.
6. Carbon monoxide and carbon dioxide are products of decomposition

BzP

1. Flammable; burns vigorously, difficult to extinguish.
2. Avoid heat, flame, and sparks.
3. Extinguish fire from a distance with water, CO_2, dry chemicals, or foam.
4. Cool heated drums with cold water spray.
5. Avoid contamination with acids, DMT, and other reducing agents, most metals and other oxidizing agents.
6. Diphenyl (white smoke) is a by-product of no-flame decomposition from chemical contamination. Diphenyl is toxic and extremely flammable gas.
7. Evacuate personnel from immediate area of fire.

DMT

1. Flammable.
2. Avoid heat, flame, or sparks.
3. Extinguish fire from a distance with water, CO_2, dry chemicals or foam.
4. Cool heated drums with cold water spray.
5. Avoid contamination with oxidizing agents, especially BzP in bulk.
6. Wear self-contained breathing apparatus when fighting DMT fire.

the DMT should be mixed into the MMA/TMPTMA solution thoroughly before any BzP is mixed in.

Other fire prevention measures include grounding all metal storage and mixing containers and posting No-Smoking signs at storage and preparation sites. Fire extinguishers should be dry chemical, foam or carbon dioxide types and should be on hand wherever the chemicals are stored or used.

5.4 Storage and Handling

Although safety in handling has been emphasized, careful storage practices are also necessary. Because of the flammability of the chemicals, several precautions should be apparent. Table 5.3 summarizes flammability and fire protection requirements.

All chemicals should be stored in tightly-closed containers, preferably the original shipping containers. These containers should be kept clean and dry and clearly labeled to avoid any contamination with other chemicals. Storage of all chemicals should be at temperatures of not less than 60°F to insure fast setting times in cold weather.

It is extremely important to store and handle the BzP separately from the DMPT. Otherwise, any accidental leakage or spillage could cause a fire.

Monomers also must have special considerations regarding storage. Because of their natural tendency to polymerize, inhibitors must be added by the manufacturers prior to shipping to insure longer predictable shelf life. During storage of the MMA or TMPTMA, the inhibitor is slowly used up and will then auto polymerize with the accompanying temperature and vapor pressure build up in the closed container. Eventually, this could cause the drum to burst. As long as MMA has 10 parts of MEHQ per million added to it and is stored at or below 75°F (25°C), it should remain in good condtion for 2 or 3 years. TMPTMA needs 100 parts MEHQ per million at the 75°F storage

Table 5.3 STORAGE REQUIREMENTS.

MMA	1. Keep away from sources of heat, sparks, and direct sunlight. 2. Ground all handling equipment. 3. Store between 60° and 80°F. 4. Check inhibitor level once each year to maintain minimum of 10 ppm MEHQ. 5. Prevent storage drums or containers from corroding. 6. Ventilate storage area.
TMPTMA	Same as MMA except: maintain minimum of 100 ppm of MEHQ.
BzP	Same as MMA except: 1. Never store in metal or glass containers. 2. For best results, use in 12 months or less. 3. Never store near DMT since contact in bulk can cause fire or explosion. 4. Store at 70°F or below.
DMT	Same as MMA. Do not permit contact with BzP in bulk.

temperature to remain stable. At least once each 6 months, the inhibitor levels should be checked.

When initiator is added to monomer, it speeds up the neutralization of the inhibitor and actually accelerates the natural polymerization process. For this reason, initiated monomer (monomer containing BzP) should never be stored.

Copper or copper alloys should not be used in any of the vessels or plumbing that comes into contact with the monomer because of the possibility of chemical reactions which may cause accidental bulk polymerization.

When chemicals have been spilled or have leaked, proper disposal methods must be followed. The first step is to absorb the chemical into a large quantity of sand or clay or any other nonflammable absorbant. The contaminated absorbant is then placed into a large strong plastic bag (in the case of very large spills, the contaminated material should be placed into an open pit). Then wet the contaminated absorbant with water and bury it in an acceptable dump or land fill area.

Excess initiated monomer should be promoted with DMT and made into polymer concrete by adding sand and allowing the mixture to cure before disposing of it in a land fill. Full or partial drums of MMA can be disposed of by adding initiator and promoter according to Table 3.1 and pouring the mixture into aggregate-filled drums or other containers.

Empty chemical containers must not be reused. Empty containers are likely to become contaminated and filled with potentially explosive mixtures of air and heavy chemical vapors. Under no circumstances should the tops be cut off the drums since sparks or heat from any cutting process could ignite the vapors in the drum causing an explosion.

APPENDIX A

APPENDIX A

DETERMINATION OF INHIBITOR CONCENTRATION IN MONOMERS BY THE PEAK EXOTHERM METHOD (Ref 5)

A. Introduction

This method is applicable to most inhibitor-monomer systems; however, a calibration curve must be made for each system. The only time when an actual inhibitor concentration determination cannot be made is with a mixed monomer system. In this case, since there are two inhibitors, the peak exotherm method cannot distinguish between the two and therefore only a comparison to the original peak exotherm time can be made. An increase of time indicates that the monomer system is more stable than it was originally and a decrease in time means that the system is less stable.

A detailed description will be given for the measurement of hydroquinone (HQ) in methyl methacrylate (MMA) and this procedure can be applied to other inhibitor-monomer systems, such as methyl ester of hydroquinone (MEHQ).

B. Equipment and Reagents

The following equipment is required for the determination of inhibitor concentrations:

1. Temperature bath: e.g., Lauda K 2/R with 0° to 100°C regulator or equivalent.
2. Recorder using J thermocouple to measure 0° to 250°C ± 0.1°C.
3. Test tubes (16 mm x 150 mm).
4. Thermocouple wells (3 mm x 150 mm).
5. Purified hydroquinone with melting point of 171° to 173°C.
6. Hydroquinone-free methyl methacrylate (Section 6).

C. Procedure for Preparation of HQ-Free Material

Using a 500 ml separatory funnel, extract the required amount of water insoluble inhibited MMA with successive amounts of 15 wt percent sodium hydroxide solution containing 10 wt percent sodium chloride. Use a ratio of 5 parts by volume of monomer to 1 part of caustic solution. Continue the extraction until the caustic layer (lower portion of separatory funnel) is practically colorless; then wash with distilled water until the final water wash, when tested with phenolphthalein paper, is neutral. The extracted material is then dried over anhydrous sodium sulfate or silica gel until clear and finally it is filtered. The uninhibited monomer is stored in a brown bottle having a screw top with an aluminum foil liner, under refrigeration, until it is ready to be used. The monomer can generally be stored under refrigeration for 90 days. However, before it is used in this procedure, a few drops should be added to 100 cc of methyl alcohol. If any precipitate is seen, the monomer should be discarded and a fresh batch should be made.

D. Procedure

1. Using HQ-free monomer, make solutions containing 15, 30, 45, 60, and 75 ppm by weight of hydroquinone (or MEHQ).

   Example:

   100.0 gm of HQ-free methyl methacrylate
   0.003 gm of hydroquinone

   $$\frac{0.003}{100.3} = \frac{30}{10^6} = 30 \text{ ppm hydroquinone}$$

2. Transfer 10 gm of monomer with a known quantity of inhibitor to a 16 x 150 mm test tube and add 1% by weight (0.10 gm) of benzoyl peroxide. Shake vigorously until the peroxide is completely in solution.
3. Place the "J" thermocouple from the temperature recorder in

the glass thermocouple well. Push the glass thermocouple well through a rubber stopper that will fit the top of the test tube containing the MMA. Let the thermocouple well submerge into the liquid halfway.

4. Start the recorder and then place the test tube containing the monomer and thermocouple in the temperature bath which has been set at 70°C.
5. On the temperature recorder chart paper, mark the point of test tube insertion into the temperature bath. Allow the run to continue past the point that the peak exotherm occurs. This is the point where monomer polymerization takes place.
6. Measure the time in minutes from the initial insertion into the temperature bath to the point of the peak exotherm as shown in Fig. A.1.
7. Measure the peak exotherms for all the concentrations of hydroquinone previously mentioned.
8. Plot the inhibitor concentration in ppm on the abscissa vs the time of peak exotherm in minutes as the ordinate. The resulting curve should be a straight line through the plotted points. This is the calibration curve for hydroquinone in methyl methacrylate. Figure A.2 is a calibration curve for the determination of hydroquinone in methyl methacrylate.
9. A sample containing an unknown quantity of hydroquinone can be checked by adding the benzoyl peroxide and then measuring its peak exotherm time. Read the inhibitor concentration from the intersection of the peak exotherm time of the unknown with the calibration curve.

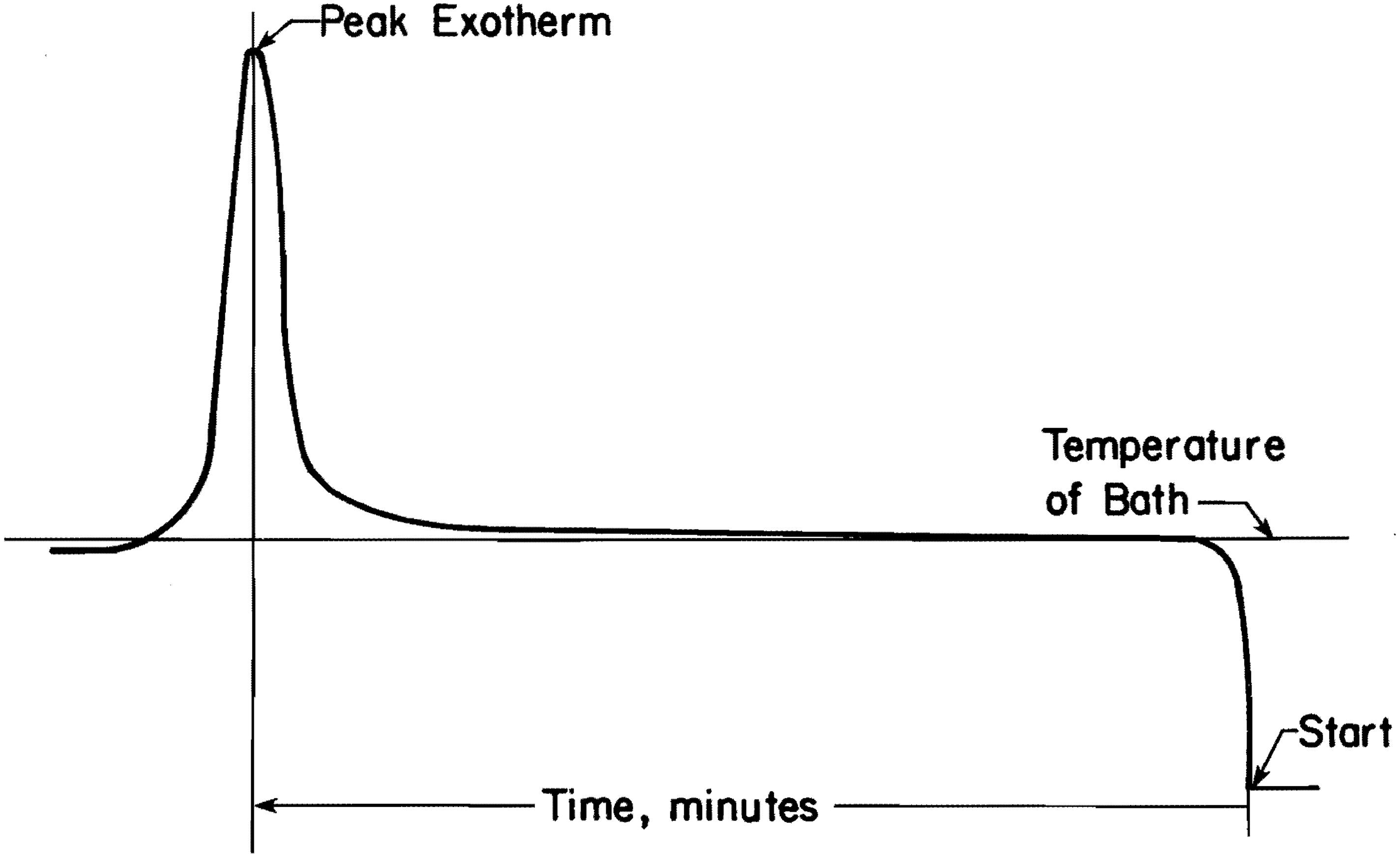


Fig. A.1 Exotherm Versus Time for MMA with 1 percent Bzp at 70°C.

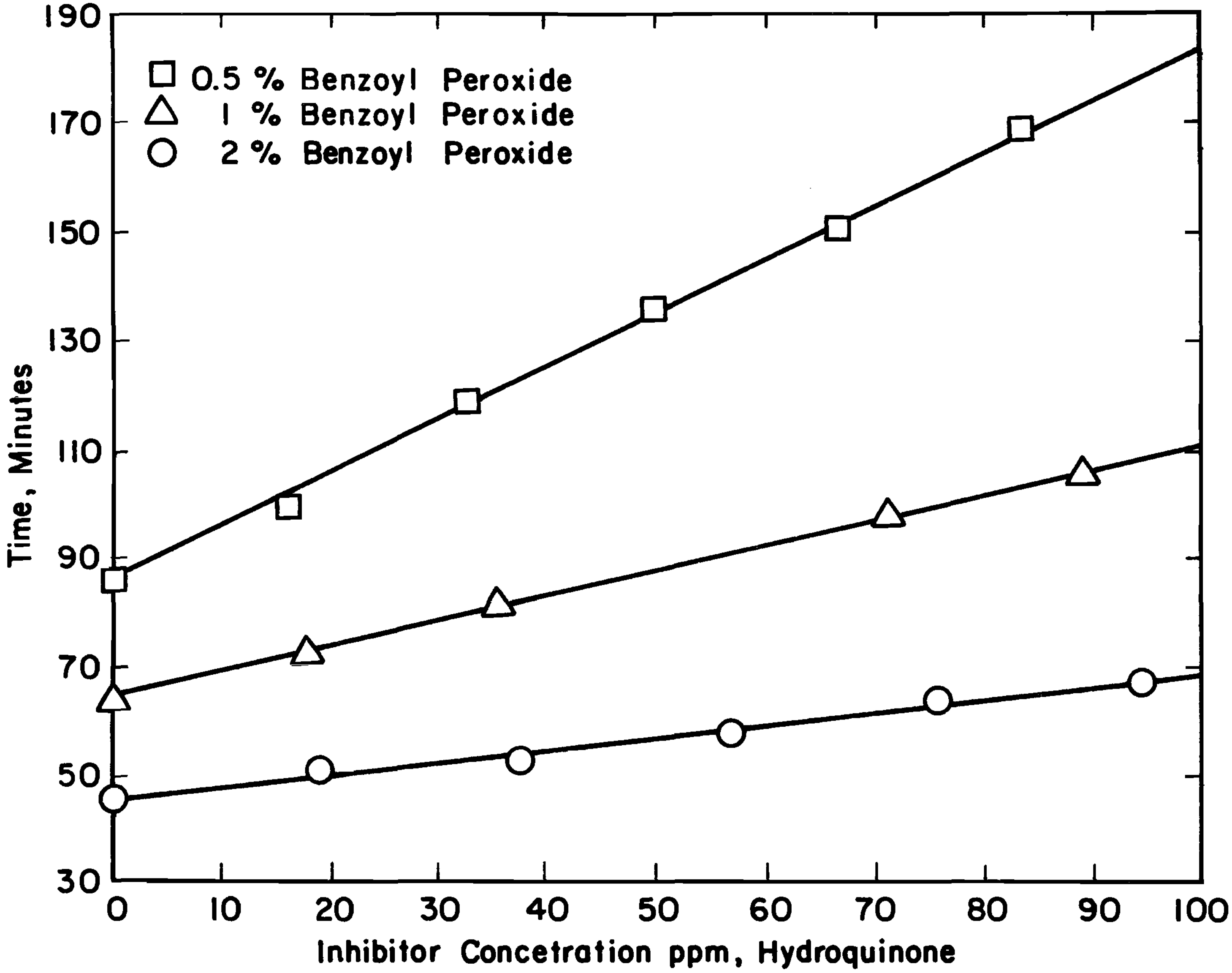


Fig. A.2 Time to Peak Exotherm Versus Inhibitor Concentration for 70°C.

APPENDIX B

APPENDIX B
ALPHABETICAL LISTING OF CHEMICAL SUPPLIERS

AMERICAN CYANAMID COMPANY
Organic Chemical Division
Bound Brook NJ 08805

Mike Taleho, Sales
Jim Dusbacky, Technical Representative
201/356-2000

CELANESE CHEMICAL CO., INC.
1250 W. Mockingbird Lane
Dallas TX 75247

Dwight D. Edman
214/689-8018

E.I. DUPONT DE NEMOURS AND COMPANY,INC.
Polymer Products Division
Chestnut Run
Wilmington DE 19898

Bob Feild, Representative
302/744-9888

LUCIDOL, DIVISION OF PENNWALT CORPORATION
1740 Military Road
Buffalo NY 14240

Doug Bolton or Judy Midreal
716/877-1740

NORAC COMPANY
405 South Motor Avenue
Azusa CA 91702
213/334-2908

NOURY CHEMICAL CORPORATION
Burt NY 14028

Dotty Kendrick or Bob Markevich
716/778-8554

REICHHOLD CHEMICALS, INC.
2601 Reichhold Road
P.O. Box 9405
Austin TX 78766

Kathryn Gann
512/836-1426

ROHM AND HAAS COMPANY
Independence Mall West
Philadelphia PA 19105

Dorothy Dondici
215/592-3236

ROHM AND HAAS COMPANY (REGIONAL OFFICE - SOUTHWEST)
4585 Simonton Road
Dallas TX 75240

Margaret Pursel or Tom Purcell or Ron Young (Tech. Rep.)

SARTOMER COMPANY
Bolmar and Nields Street
Westchester PA 19380

Charles Demos
215/692-8400

SILIKAL OF NORTH AMERICA, INC.
305 Orange Street
Bridge CT 06607

203/333-1013

U.S. PEROXYGEN, DIVISION OF WITCO CHEMICAL CORPORATION
850 Morton Avenue
Richmond CA 94804

Nancy Bentson
415/233-5911

R.S.A. CORPORATION
690 Saw Mill River Road
Ardsley NY 10502

P.O. Box 262
Stratford CT 06497

Kate Stewart
203/377-5550

Bob Anthony
914/693-1818
914/693-2493

WARE CHEMICAL COMPANY
1525 Stratford Avenue

APPENDIX C

SUGGESTED SPECIFICATION
CONCRETE STRUCTURE PATCHING WITH POLYMER CONCRETE

TEXAS STATE DEPARTMENT OF HIGHWAYS AND PUBLIC TRANSPORTATION

SUGGESTED SPECIFICATION
CONCRETE STRUCTURE PATCHING WITH POLYMER CONCRETE
(7-1-83)

1. Description: This Specification covers the materials and method of placement for patching concrete structures with polymer concrete, where the aggregate is first placed in the void to be patched followed by saturation with the liquid monomer mixture.

2. Materials: The patching material will consist of a monomeric or a pre-polymeric liquid mixture and aggregate with a gradation appropriate for the desired density. The polymer shall be made by combining monomers and/or polymer catalysts and an accelerator.

   A. The monomers will be methyl methacrylate (MMA) and trimethylolpropane trimethacrylate (TMPTMA). The MMA will be polymerization grade, 99.8 percent minimum purity, containing not less than 9 ppm nor more than 100 ppm of methyl ester of hydroquinone inhibitor (MEHQ). The TMPTMA will be polymerization grade, 98.5 percent minimum purity, containing not less than 90 ppm nor more than 125 ppm of MEHQ.

   B. The catalyst will be benzoyl peroxide (BzP). The BzP will be of liquid form, 40 percent purity.

   C. The accelerator will be N-N-dimethyl para-toluidine (DMPT) undistilled, 93 percent minimum purity.

   D. The thickener will be poly methyl methacrylate (PMMA) powder.

   E. Coarse aggregate will consist of clean, hard, durable and dry, particles of gravel, or crushed stone or a combination thereof containing max. 0.5 percent moisture.

   F. Fine aggregate will consist of clean, hard, durable and dry particles of natural or manufactured sand, with or without mineral filler. If included, mineral filler will consist of stone dust, crushed sand, blow sand or other such material as may be approved. The fine aggregates will contain no more than 0.5 percent moisture.

   G. Storage of Polymer Materials. Polymer materials should be stored in accordance with manufacturer's recommendations. All materials should be kept in a cool ventilated area out of direct sunlight in white containers. The catalyst (BzP) should be kept in a cool, dark place to prevent decomposition. Under no circumstances should the catalyst (BzP) and accelerator (DMPT) be allowed to come into direct contact, and should be stored in separate areas. Open flame

2. G. (continued)

or other fire hazards should not be permitted in the storage areas. The cautions of gasoline flammability should apply as well to polymer materials in their unpolymerized state.

3. Construction Methods.

A. Mix Design.

(1) Liquid Monomer. For the active liquid monomer mixture, the following proportion by weight should be used.

a. MMA: 95%

b. TMPTMA: 5%

c. BzP: from 1% pure BzP (2.5% of 40% BzP liquid dispersion) at 110°F to 3% pure BzP (7.5% of 40% BzP liquid dispersion) at 30°F.

d. DMPT: from .2% at 110°F to 1.5% at 30°F (see accompanying graph in appendix)

For estimating purposes, the unit weight of this mixture may be assumed to be 8 pounds per gallon (.96 gram per cubic centimeter).

(2) Aggregate. For small volumes of patch material, fine aggregate by itself may be used. For larger volumes, a combination of fine and coarse aggregates should be used. A typical aggregate proportion is as follows:

a. Coarse Aggregate (1/4"-3/4" crushed limestone or river gravel): 50%

b. Sand (Regular Concrete Sand): 50%

c. Mineral Filler: If desired, an addition of up to 20% more filler

For estimating purposes, the unit weight of aggregate may be taken as 120 pounds per cubic foot.

The aggregate should be dry prior to use. In order to save time at the job site, dried properly proportioned aggregate can be prepackaged.

(3) Quantity Worksheet. Required quantities of the active liquid monomer components may be determined using a worksheet along the lines of that shown in Appendix 1 of this Specification.

3. B. Preparation.

(1) In order to achieve good bond between the repair material and the existing concrete all unsound material should be removed and the patch surfaces swept or blown clean. The sides of the patch should be approximately vertical but need not be saw cut. Exposed reinforcing steel should be completely cleaned of corrosion or any foreign material.

(2) All surfaces to be bonded within the patch must be dry in order to allow penetration of monomer liquid to allow bonding and reinforcement on the bottom and/or around the perimeter of patch. If the surfaces are wet or damp, drying may be accomplished using open-flame burners, infrared heaters, warm forced air, heat lamps, or other such devices. Care must be taken to prevent damage to the surface of the concrete resulting from excessive heat. After the surface is dried, it should be allowed to cool down to approximately 90°F.

(3) When patching surfaces topped with asphaltic materials, the asphaltic material should be removed from around the perimeter of the patch for a distance of at least 6".

(4) Holes and cracks should be sealed to prevent leakage of monomer. This may be accomplished by one or more of the following materials.

a. Silicone Adhesive, caulking, or acrylic latex caulking (requires a minimum of 8 hours to cure)

b. Polyester Putty (requires 15 minutes for curing)

c. Thin layer of concrete or mortar on bottom of repair area (cure for 24 hours)

C. Aggregate Placement. The dried premixed aggregate is placed in the prepared patch area. The aggregate should be tamped into place for compaction to reduce the void volume.

D. Mixing of Liquid Monomer. The liquid monomer should not be initiated until just prior to application. The liquid monomer solution should be stirred with wooden paddles until the components are thoroughly mixed. Metal stirring rods should not be used in metal containers. All mixing should be done in a shaded area. Only amounts of liquid monomer that can be used in a short time should be mixed. The steps for mixing the liquid monomer solution are as follows:

(1) Mix the MMA and TMPTMA together.

(2) Add the DMPT and stir until it is all dissolved. Do Not mix the BzP and DMPT together directly.

3. D. (continued)

(3) Just prior to application, mix in the BzP.

E. Application of Liquid Monomer. The liquid monomer mixture should be poured over the in-place aggregate until all voids are filled. The aggregate should be rodded or vibrated to minimize entrapped air in repairs with depths greater than 3".

F. For improved workability and retention of monomer in the aggregate, thickener may be premixed in the aggregate prior to adding monomer. Up to 3% thickener by weight of aggregate is usually added.

G. Finishing and Curing. After the liquid is in place, the surface should be troweled smooth as quickly as possible. In areas where there is standing liquid present, sand should be spread and troweled in place. Sand should also be spread over any exposed aggregate.

Since some liquid will be absorbed into the concrete around the patch, extra liquid should be poured over the patch to prevent drying out and assure saturation until polymerization begins to take place.

The patch should be covered with a sheet of plastic film to minimize evaporation. At the discretion of the engineer, a 90% sand: 10% PMMA powder mixture may be sprinkled over the repair surface in lieu of the sheet film.

H. Personnel Protection. In handling the polymer materials, workmen should wear protective goggles and gloves. Rubber or plastic aprons are also suggested. Saturated clothing should be removed and the affected skin washed with soap and water.

The cautions of gasoline flammability should apply as well to polymer materials in their unpolymerized state. Smoking or any open flames in the area where polymer materials are being handled should be prohibited.

I. Cleanup and Disposal of Excess Monomer. Tools and containers may be cleaned with Acetone. Excess monomer which has been mixed with the catalyst and accelerator should be disposed by permitting it to polymerize in an open container and discarded. The mixed monomer solution should never be tightly sealed.

DETERMINATION OF POLYMER CONCRETE MATERIALS QUANTITIES

General:

MMA + TMPTMA + DMPT Weight = 8 lbs per gal. or 3785 g/gal.

Density of Materials

MMA, TMPTMA, 40% BzP Dispersion, DMPT = 96 g/cc

Monomer Formulation (by weight)

MMA = 95%, TMPTMA = 5%, 40% BzP Dispersion = 3%, DMPT = 0.6% (see *)

Aggregate Blend

Unit Weight of Aggregate Blend = UWA lbs per cu ft
Void Ratio of Aggregate Blend = VA

Calculation of Quantities:

VR = Volume of Repair = _____ x _____ x _____ = _____ cu in. = _____ cu ft

WA = Weight of Aggregate for Repair = VR cu ft x UWA lb per cu ft = _____ lbs.

WM = Weight of Monomer to Fill Voids = WA lbs x VA = _____ lbs

VM = Amount of Monomer for Repair = $\frac{\text{WM lbs}}{\text{8 lbs/gal}}$ (3785cc/gal) x 1.3 = _____ cc

NOTE: The 1.3 allows for evaporation and absorption.

Amounts of: MMA = VM cc x 0.95 = __________cc

TMPTMA = VM cc x 0.05 = __________cc

40% BzP Disp = VM cc x 0.025 = __________ gm (see *)

DMPT = VM cc x 0.005 = __________cc (see *)

*The quantities of BzP and DMPT should each be adjusted according to temperature chart for BzP and DMPT addition.

SUGGESTED SPECIFICATIONS
CONCRETE STRUCTURES PATCHING WITH 2 COMPONENT PREPACKAGED P.C.

SUGGESTED SPECIFICATIONS
CONCRETE STRUCTURES PATCHING WITH 2 COMPONENT PREPACKAGED P.C.

1. Description: This specification covers the materials and methods of placement for patching concrete structures with prepackaged two-component polymethyl methacrylate concrete.

2. Materials: The patching material will consist of a monomeric or prepolymeric liquid mixture as the first packaged component.

   A. The monomers will be methyl methacrylate (MMA) and trimethylolpropane trimethacrylate (TMPTMA). The MMA will be polymerization grade, 99.8 percent minimum purity, containing not less than 9 ppm nor more than 100 ppm of methyl ester of hydroquinone inhibitor (MEHQ). The TMPTMA will be polymerization grade, 98.5 percent minimum purity, containing not less than 90 ppm nor more than 125 ppm of MEHQ.

   B. The catalyst will be benzoyl peroxide (BzP). The BzP will be of liquid form, 40 percent purity in an inert waterless plasticizer.

   C. The accelerator will be N-N-dimethyl para-toluidine (DMPT) undistilled, 93 percent minimum purity.

   D. The thickener will be poly methyl methacrylate (PMMA) powder.

   E. Coarse aggregate will consist of clear, hard, durable and dry particles of gravel, or crushed stone or a combination thereof containing max. 0.5 percent moisture.

   F. Fine aggregate will consist of clean, hard, durable and dry particles of natural or manufactured sand, with or without mineral filler. If included, mineral filler will consist of stone dust, crushed sand, blow sand or other such material as may be approved. The fine aggregates will contain no more than 0.5 percent moisture.

   G. Storage of Polymer Materials. Polymer materials should be stored in accordance with manufacturer's recommendations. All materials should be kept in a cool ventilated area out of direct sunlight in white containers. The catalyst (BzP) should be kept in a cool, dark place to prevent decomposition. Under no circumstances should the catalyst (BzP) and accelerator (DMPT) be allowed to come into direct contact, and should be stored in separate areas. Open flame or other fire hazards should not be permitted in the storage areas. The cautions of gasoline flammability should apply as well to polymer materials in the unpolymerized state.

3. Pre-job Site Mixing:

   A. Mix design. Typical usage would be 9 to 11 percent liquid component by total weight of aggregate and monomer systems.

(1) Liquid monomer component. For this reactive mixture, the following proportions by weight should be used.

  a. MMA: 97 percent
  b. TMPTMA: 3 percent
  c. DMPT: according to attached temperature curves (Appendix II)

(2) Dry aggregate package. All aggregates must be oven-dried. Types and relative volumes of repairs may dictate that the project engineer make changes in the gradation of the coarse aggregates (C.A.). Typical aggregate and additive proportions are as follows:

  a. Coarse Aggregates. (1/4 to 3/4" crushed limestone or river gravel); Depending upon the application: 0 to 50 percent
  b. Sand (over-dried concrete sand): 50 to 100 percent
  c. Colorants:
     Titanium dioxide (rutile form): 1.0 percent wt of aggregate
     Carbon black: 0.003 percent wt of aggregate
  d. Thickener (DMMA powder). (This helps to retain the monomer and improves the workability of the PC): 3 percent wt of aggregate
  e. BzP (temperature and chemical sensitive initiator): approx. 0.15 percent of wt of aggregate depending upon ambient temperature. Monomer is approx. 9 percent of whole system which is approx. 10 percent of the weight of aggregates. From Appendix II: at temperatures from 40°F to 100°F, BzP (pure) is 1 to 2 percent of monomer so we picked 1.5 percent to approximate. Then BzP is 1.5 percent x 10 percent = 0.15 percent of the weight of aggregates)

B. Quantities: 120 lbs dry aggregate mix and 12 lb liquid mix will fill a cubic foot repair (Quantity Worksheet, Appendix I).

4. Construction Methods

A. Preparation

(1) In order to achieve good bond between the repair material and the existing concrete, all unsound material should be removed and the repair surfaces swept or blown clean. The sides of the repair should be approximately vertical but need not be saw cut. Exposed reinforcing steel should be completely cleaned of corrosion or any foreign material.

(2) All surfaces to be bonded within the repair must be dry in order to allow penetration of monomer liquid to allow bonding and reinforcement on the bottom and/or around the perimeter of repair. If the surfaces are wet or damp, drying may be accomplished using open-flame burners,

infrared heaters, warm forced air, heat lamps, or other such devices. Care must be taken to prevent damage to the surface of the concrete resulting from excessive heat. After the surface is dried, it should be allowed to cool down to approximately 90°F.

(3) When repairing surfaces topped with asphaltic materials, the asphaltic material should be removed from around the perimeter of the repair for a distance of at least 6 in.

B. Mixing. Because of typically short working times, the liquid component should not be mixed with the dry component until such time as the entire crew is ready for immediate placement. Mixing times should be at least 1 minute and no longer than 2 minutes. Typical working times are from 10 minutes to 25 minutes depending upon the temperature of components, the mixer, and the pavement as well as upon the initiator-accelerator levels. Mixing can be done in a wheelbarrow or even a large heavy-weight plastic bag for small patches.

For larger patches a conventional concrete mixer may be used but under no circumstances should a ready-mix truck be used. On large projects mobile batching facilities have been successfully used.

C. Placement. The well-mixed matrix can be placed, rodded or vibrated, and trowel-finished similarly as for portland cement concrete. A little extra monomer may be sprinkled on the top to increase workability during finishing and to minimize polymer concrete surface adhesion to the trowel.

Because of the fast setting times, finishing should be done as quickly as possible and then left alone till cure, or an unsightly surface finish will result.

D. Personnel Protection. In handling the polymer materials, workmen should wear protective goggles and gloves. Rubber or plastic aprons are also suggested. Saturated clothing should be removed and the affected skin washed with soap and water.

The cautions of gasoline flammability should apply as well to polymer materials in their unpolymerized state. Smoking or any open flames in the area where polymer materials are being handled should be prohibited.

E. Cleanup and Disposal of Excess Monomer. Tools and containers may be cleaned with methylene chloride. Excess monomer which have been mixed with the catalyst and accelerator should be disposed by permitting it to polymerize in an <u>open</u> container and discarded. The mixed monomer solution should never be tightly sealed.

APPENDIX I
DETERMINATION OF POLYMER CONCRETE MATERIALS QUANTITIES

General:

MMA & TMPTMA & DMPT Weight = 8 lbs per gal or 3785 g/gal

Density of Materials

MMA, TMPTMA, 40% BzP Dispersion, DMPT = 96/cc

Monomer Formulation (by weight)

MMA = 97%, TMPTMA = 3% (0.6% see *)

Aggregate Blend

48% sand, 48% C.A., PMMA 3%, Titanium Dioxide 1%, Carbon black .003%, 40% BzP Disp. = 0.15% wt of aggregate (see *)

Unit Weight of Aggregate Blend = UWA lbs per cu ft

Void Ratio of Aggregate Blend = VA

Calculation of Quantities:

VR = Volume of Repair = _____ x _____ x _____ = _____ cu in. = _____ cu ft

WA = Weight of Aggregate for Repair = VR cu ft x UWA lb per cu ft = _____ lbs

WM = Weight of Monomer to Fill Voids = WA lbs x VA = _____ lbs

VM = Amount of Monomer for Repair = $\frac{\text{WM lbs}}{\text{8 lbs/gal}}$ (3785 cc/gal) = _____ cc

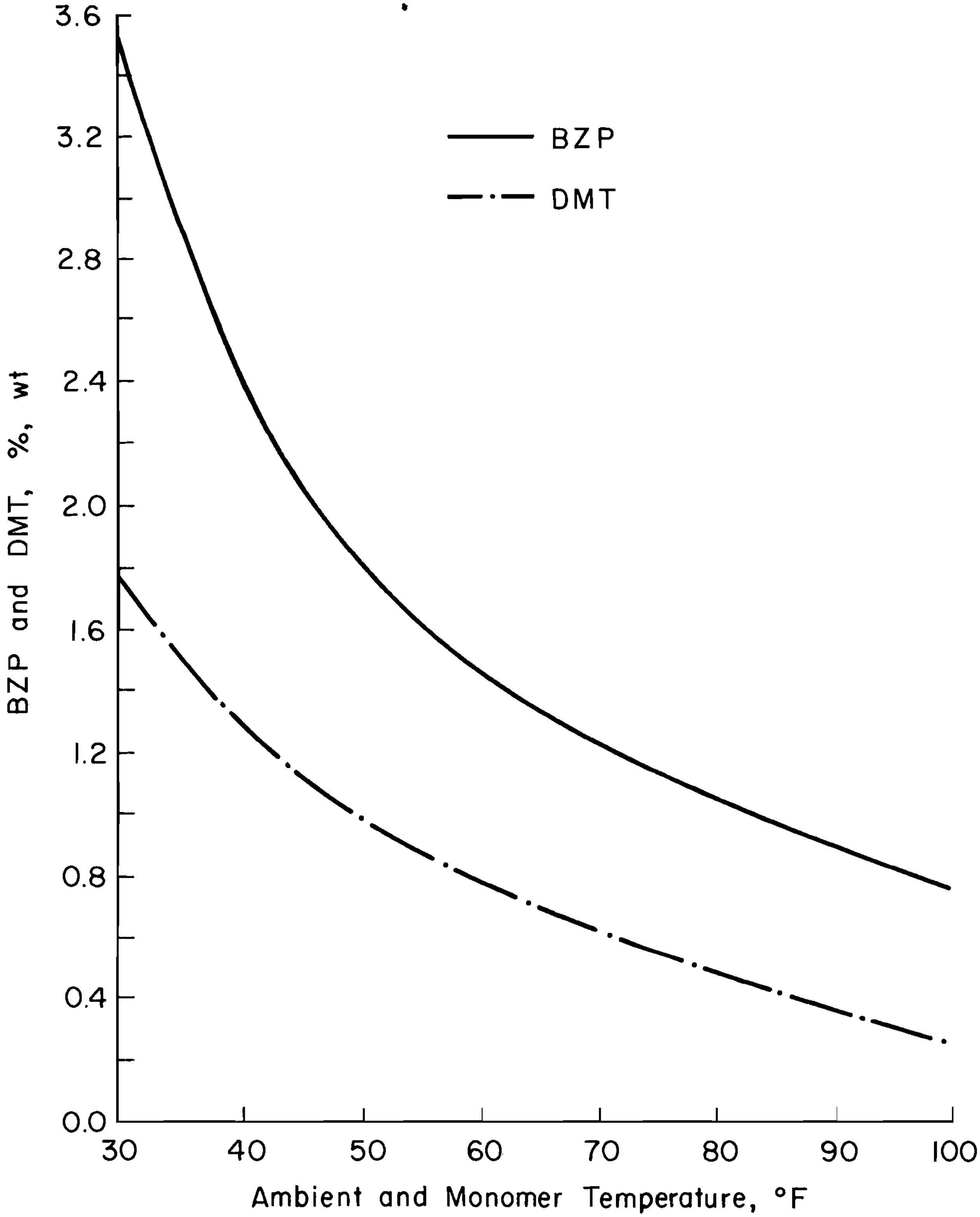
Amounts of: MMA = VM cc x 0.97 = __________ cc

TMPTMA = VM cc x 0.03 = __________ cc

40% BzP Disp = VM cc x 0.025 = __________ gm (see *)

DMPT = VM cc x 0.005 = __________ cc (see *)

*The quantities of BzP and DMPT should each be adjusted according to temperature chart to BzP and DMPT addition.



Appendix II. Tentative Recommended Percentages of BzP and DMPT (8).

REFERENCES

1. Fowler, David W. and Paul, Donald R., "Polymer Concrete Repair of Bridge Decks," Research Report 114-8, Project 3-9-71-114, Center for Highway Research, The University of Texas at Austin, March 1979.

2. Fontana, Jack J. and Bartholomew, John, "Polymer Concrete Patching Manual," Report No. FHWA-IP-82-10, U.S. Department of Transportation, June 1982.

3. Meyer, Alvin H., McCullough, B. Frank, and Fowler, David W., "Polymer Concrete for Precast Repair of Continuously Reinforced Concrete Pavement on IH 30, Near Mt. Pleasant," Research Report 246-1, Project 3-18-79-246, Center for Transportation Research, Bureau of Engineering Research, The University of Texas at Austin, August 1981.

4. Fowler, David W., Kukacka, Lawrence E., Paul, Donald R., Schrader, Ernest K. and Smoak, W. Glenn, "Safety Aspects of Concrete-Polymer Materials," Polymers in Concrete International Symposium, Publication SP-58, American Concrete Institute, pp. 123-137.

5. Fontana, J. and Columbo, P., "Determination of Inhibitor Concentration in Monomers by the Peak Exotherm Method," Brookhaven National Laboratories, Upton N.Y.