

AD-A059 698

DOW CHEMICAL U S A WALNUT CREEK CALIF  
FABRICATION OF FIBERGLASS REINFORCED PLASTIC SURFACING UNDER WE--ETC(U)  
SEP 78 T J WEST

F/G 11/2

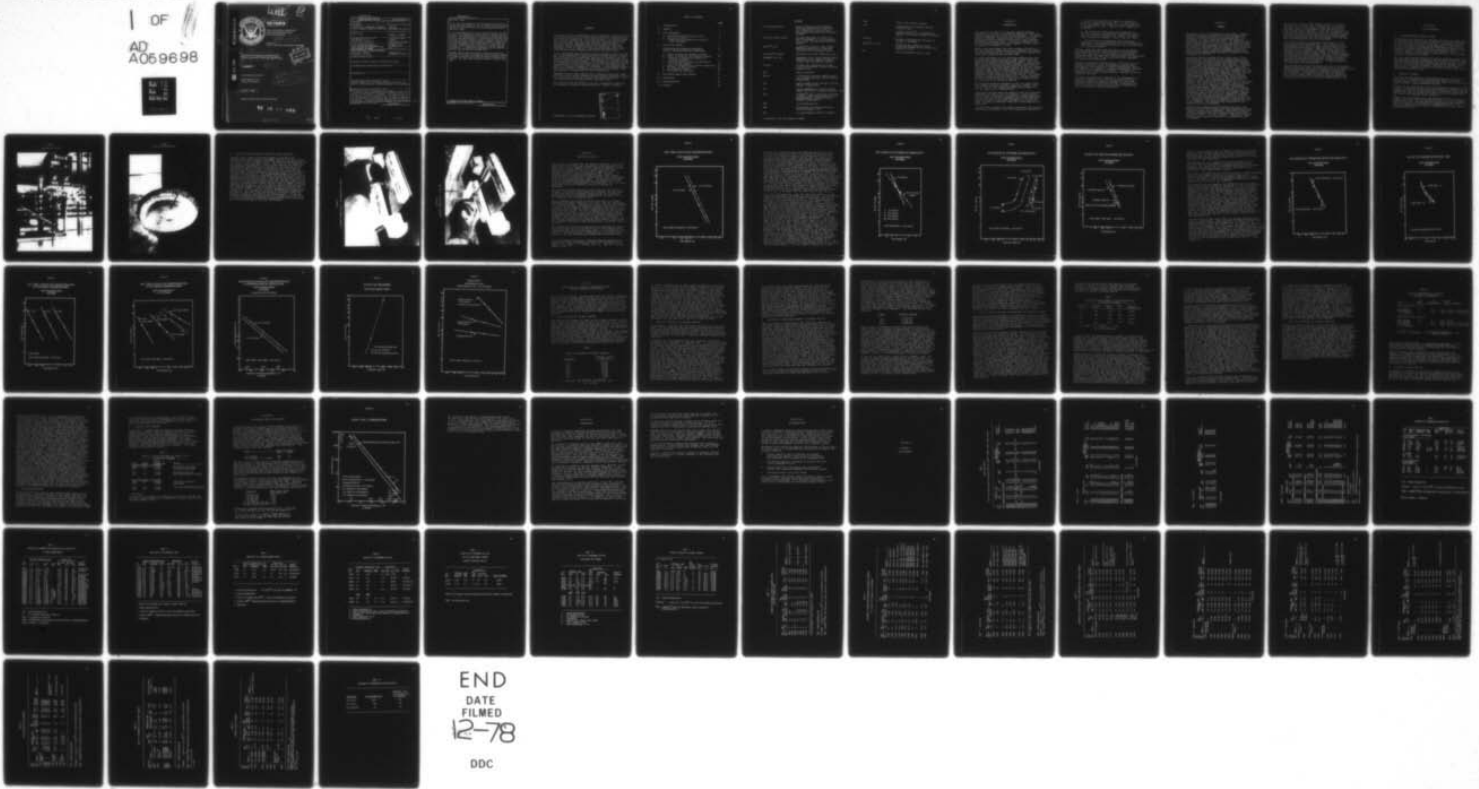
N68305-77-C-0005

UNCLASSIFIED

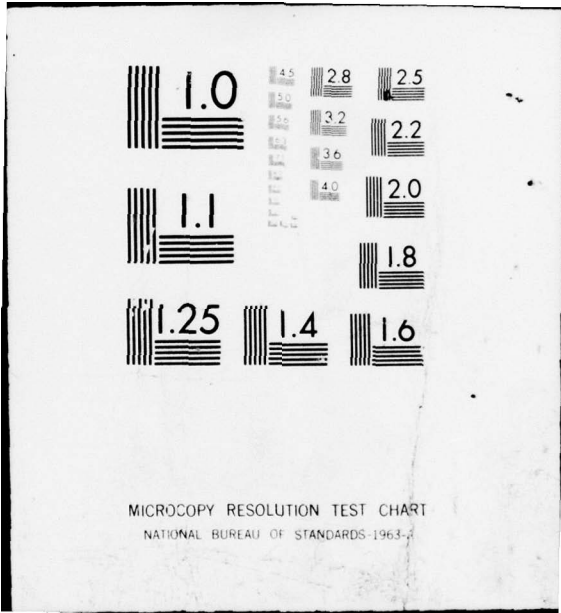
CEL-CR-78.018

NL

1 OF 11  
AD  
A069898



END  
DATE  
FILMED  
12-78  
DDC



MICROCOPY RESOLUTION TEST CHART  
NATIONAL BUREAU OF STANDARDS-1963-A

AD A059698



LEVEL

18 CELL

12

19  
CR-78.018

CIVIL ENGINEERING LABORATORY  
Naval Construction Battalion Center  
Port Hueneme, California

20 Theo J. West

Sponsored by  
NAVAL FACILITIES ENGINEERING COMMAND

DDC FILE COPY

6  
9 Final rept.  
FABRICATION OF FIBERGLASS REINFORCED  
PLASTIC SURFACING UNDER WET CONDITIONS.

DDC  
OCT 10 1978  
RECEIVED  
F

11  
September 1978

12 72p.

An Investigation Conducted by  
DOW CHEMICAL U.S.A.  
Walnut Creek, California

16 F53536

17 YF5353609L

15 N68305-77-C-0005

Approved for public release; distribution unlimited.

78 10 06 099

408749

JOB

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER CR 78.018 <sup>✓</sup>	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) FABRICATION OF FIBERGLASS REINFORCED PLASTIC SURFACING UNDER WET CONDITIONS		5. TYPE OF REPORT & PERIOD COVERED Final May 1978
7. AUTHOR(s) Theo J. West		6. PERFORMING ORG. REPORT NUMBER
9. PERFORMING ORGANIZATION NAME AND ADDRESS Dow Chemical U.S.A. Walnut Creek, California		8. CONTRACT OR GRANT NUMBER(s) N68305-77-C-0005 <sup>new</sup>
11. CONTROLLING OFFICE NAME AND ADDRESS Civil Engineering Laboratory Naval Construction Battalion Center Port Hueneme, CA 93043		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS 62760N; YF53.536.091.01.003D
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office) Naval Facilities Engineering Command 200 Stovall Street Alexandria, VA 22332		12. REPORT DATE September 1978
		13. NUMBER OF PAGES 69
		15. SECURITY CLASS. (of this report) Unclassified
16. DISTRIBUTION STATEMENT (of this Report)  Approved for public release; distribution unlimited.		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Chemical composition, fiberglass reinforced plastic(s), FRP, glass reinforced plastics, reinforced plastics, soil surfacings		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The purpose of this investigation was to develop a system to be used in the construction of fiberglass-reinforced plastic sur- facings for soil under wet conditions. The effect of water in the substrate and in the fiberglass mat, on laminate properties, has been defined and solutions have been developed for some of the problems. A system of chemical components has been develop-		

DD FORM 1473 1 JAN 73 EDITION OF 1 NOV 65 IS OBSOLETE

UNCLASSIFIED  
SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

78 10 08 099

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

Block 20. Cont'd

ed for the field placement of the reinforced plastic soil surfacings under wet conditions, that is superior to that presently used and is usable with the basic spray equipment now used by the Marine Corps.

It was established that the resin viscosity should be less than 100 cps at the temperature of application for optimum flexural strength. The incorporation of a surfactant into the wet fiberglass mat was found to result in improved resin penetration into the woven roving and increased flexural strength. The addition of 15 percent styrene to the presently used Port Hueneme resin (Selection RS50338) and the incorporation of Triton X100 into the water in the fiberglass mat results in flexural strengths of 25,000 psi - a considerable improvement over the 4,000 psi obtained with undiluted Port Hueneme resin.

DERAKANE\* 510-A-40 when diluted with 15 percent styrene and, used with Triton X100, gives laminates having flexural strengths of 30,000 psi, meeting the 28,000 psi flexural strength specification. This resin does not have the desired five year shelf life.

\*Trademark of The Dow Chemical Company

DD FORM 1473 1 JAN 73 EDITION OF 1 NOV 65 IS OBSOLETE

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

## ABSTRACT

The purpose of this investigation was to develop a system to be used in the construction of fiberglass-reinforced plastic surfacings for soil under wet conditions. The effect of water on laminate properties, in the substrate and in the fiberglass mat has been defined and solutions have been developed for some of the problems. A system of chemical components has been developed for the field placement of the reinforced plastic soil surfacings under wet conditions, that is superior to that presently used and is usable with the basic spray equipment now used by the Marine Corps.

It was established that the resin viscosity should be less than 100 cps at the temperature of application for optimum flexural strength. The incorporation of a surfactant into the wet fiberglass mat was found to result in improved resin penetration into the woven roving and increased flexural strength. The addition of 15 percent styrene to the presently used Port Hueneme resin (Selectron RS50338) and the incorporation of Triton X100 into the water in the fiberglass mat results in flexural strengths of 25,000 psi - a considerable improvement over the 4000 psi obtained with undiluted Port Hueneme resin. The influence of temperature was also investigated.

DERAKANE\* 510-A-40 when diluted with 15 percent styrene and, used with Triton X100, gives laminates having flexural strengths of 30,000 psi, meeting the 28,000 psi flexural strength specification. This resin does not have the desired five year shelf life.

This investigation was funded by the Civil Engineering Laboratory, Port Hueneme, California; under Contract No. N68305-77-C-0005.

ACCESSION for	
NTIS	Wing Section <input checked="" type="checkbox"/>
DDC	Bull Section <input type="checkbox"/>
UNANNOUNCED	<input type="checkbox"/>
JUSTIFICATION	
BY	
DISTRIBUTION/AVAILABILITY STATEMENT	
CLASSIFICATION	
A	

\*Trademark of The Dow Chemical Company

## TABLE OF CONTENTS

	<u>Page</u>
I. INTRODUCTION	1
II. SUMMARY	3
III. TEST PROCEDURES	5
A. Accelerated Shelf Stability Tests	5
B. Reactivity Studies	5
C. Preparation and Mechanical Testing of Glass Laminates	8
IV. REACTIVITY STUDIES	11
V. PREPARATION OF FIBERGLASS REINFORCED PLASTIC LAMINATES UNDER WET CONDITIONS	25
A. Effect of Water on Flexural Strength	25
B. Effect of Substrate on Flexural Strength	26
C. Influence of Fabrication Methods on Flexural Strength	27
D. Effect of Resin Viscosity & Surfactants on Flexural Strength	29
E. Effect of Temperature on Laminate Properties	32
F. Influence of Resin Density	33
G. Miscellaneous Resins	34
H. Fiberglass Mat Treatment	35
VI. ACCELERATED SHELF LIFE STUDIES	37
VII. CONCLUSIONS	41
VIII. RECOMMENDATIONS	43
IX. APPENDIX	45

## GLOSSARY

Port Hueneme Resin	Resin received from Port Hueneme, Selectron RS50338 (PPG Industries, Inc.) Resin SR3704 plus 400 ppm dinitrophenol and 200 ppm p-toluhydroquinone.
Kirtland Primary Resin	Kirtland AFB resin 73% ALTEK B-25 and 24% DERAKANE* 510, a brominated vinyl ester, 300 ppm added toluhydroquinone.
ALTEC <sup>(R)</sup> 8-52	Isophthalic polyester resin (Alpha Chemical Corporation); formulated from ALTEC 8-60 by adding styrene.
SELECTRON <sup>(R)</sup> SR3704	Polyester resin (PPG Industries, Inc.)
DERAKANE 510-A-40	Brominated vinyl ester formulated from DERAKANE 510-A by adding 40 percent styrene (The Dow Chemical Company).
Styrene	Styrene, 99%, inhibited 10-15 ppm p-tert-butylcatechol (Aldrich Chemical Company, Inc.)
BPO	Benzoyl Peroxide
BZQ-40	A 40% benzoyl peroxide pourable paste (US Peroxygen Division, Witco Chemical Corporation).
CHP	Cumene hydroperoxide (Lucidol Division, Pennwalt Corporation)
CoN	Cobalt naphthenate, 6 percent cobalt (Nuodex Division of Tenneco Chemicals, Inc.)
DDM	LUPERSOL <sup>(R)</sup> DDM, a 60 percent solution of methyl ethyl ketone peroxide in dimethylphthalate (Lucidol Division, Pennwalt Corporation).
DMA	N,N-Dimethylaniline.
DMT	N,N-Dimethyl-p-toluidine (Aldrich Chemical Company, Inc.)
DNP	2,4-dinitrophenol (Pfaltz & Baurer).

\*Trademark of The Dow Chemical Company

MEKP	Methyl ethyl ketone peroxide
THQ	Tolhydroquinone (Eastman Chemical Products, Inc.)
V	Vanadium TEN CEM <sup>(R)</sup> , 4% Vanadium as vanadium neodecanoate (Mooney Chemicals, Inc.).
Promoter	Mixture of Vanadium TEN CEM and N,N-Dimethyl-p-toluidine
FABMAT <sup>(R)</sup> C-4020	Fiberglass mat composed of woven roving and chopped strand (Fiber Glass Industries, Inc.).
phr	Parts per hundred parts of resin.

SECTION I  
INTRODUCTION

The object of the work is to develop improved chemical components to be used in constructing fiberglass-reinforced plastic surfacings for soil in wet environments. The improved chemical components shall have shelf lives of five years minimum and shall be usable with the basic spray equipment now used by the Marine Corps. The work was funded by the Civil Engineering Laboratory, Port Hueneme, CA under Phase I of Contract No. N68305-77-C-0005.

Marine Corps requirements for rapid response and mobility call for methods by which Marine Corps engineers can upgrade the load-carrying capacity of native soils for temporary but often heavy vehicular and aircraft loads.

A recent development in soil surfacing techniques has been the fiberglass reinforced plastic (FRP) system called the Advanced Multipurpose Surfacing System (AMSS). The system pumps resin, catalyst and promoter through a hand-held spray gun, from which the materials are directed onto and into a fiberglass mat previously placed directly on the soil surface. Two resin hoses, one with added catalyst and one with added promoter, supply resin to two nozzles on the spray gun, combining the materials in two V-shaped fan sprays which intersect a short distance outside the nozzles. This system provides a promoted and activated resin. Further blending of these liquids occurs as a result of over-lapping passes of the spray on the fiberglass matting.

The fiberglass material presently in use is a woven roving with random fiberglass backing, supplied as FABMAT C-4020. This is a 40 oz. per square yard woven roving backed by 2 oz. per square foot of random fiber.

Application consumes about one pound of resin and associated components per square foot of fiberglass. Resin gelation time of about 10 minutes is obtained at working temperatures of over 40°F. One or two laminated layers of this FRP have been successfully utilized for expedient soil surfacings under a variety of vehicular loads over a wide range of soil conditions.

As constituted, however, the present system has the following deficiencies according to the Civil Engineering Laboratory:

- a. The FRP can be placed only under dry conditions at ambient temperatures above 40° F. Present Marine Corps requirements show a need for soil surfacings down to temperatures of -65° F and up to 140° F under wet conditions.
- b. The system now relies upon close tolerances in metering the flow of promoter and catalyst to provide a rapid (10 minutes) gelation time. Other, less sensitive techniques are needed to assure short gel times.
- c. The materials will propagate flames under some conditions. Fire retardancy and/or a self extinguishing capability are necessary features for use of the material in a combat environment.

Chemical components have been developed by the Government for formulating FRP soil surfacings that (1) have minimum shelf lives of 5 years, (2) are usable in constructing surfacings under dry conditions between ambient air temperatures of 40°F to 120°F, and (3) are usable with spray equipment now used by the Marine Corps.

In order to obtain the working life at 75°F of five years, a stabilized polyester resin, designated as RS50338, was developed. The new catalyst is cumene hydroperoxide (CHP); the promoter is a solution of vanadium neodecanoate (Vanadium Ten Cem) and N,N-dimethyl-p-toluidine. A retarder was developed, methyl ethyl ketone peroxide, that can be used to extend the gel time.

This work is specifically addressed to the development of a system of components to be used in the construction of fiberglass-reinforced plastic surfacings for soil under conditions where the fiberglass matting is completely wet with water (such as from a rainstorm) and the underlying soil is completely saturated with water.

## SECTION II

## SUMMARY

The purpose of this investigation is to develop a chemical component system to be used for the field placement of a fiberglass-reinforced plastic soil surfacing under wet conditions, as from a rainstorm, where the ambient air temperature is between 32°F and 125°F. The components shall have a minimum shelf life of five years and shall be usable with the basic spray equipment now used by the Marine Corps. The contract requirement that the chemicals have a five year shelf life has, for all practical purposes, limited this work to resin systems previously developed for the Civil Engineering Laboratory under Contract No. N68305-76-C-0003, see Report No. CR77.017.

Reactivity studies were made of the resins used in this investigation. The control of the polymerization is more critical in the presence of water than when the fiberglass soil surfacing is prepared under dry conditions. The water acts as a heat sink and therefore more catalyst is required if a properly cured resin is to be achieved. The resin should not cure instantaneously as time is needed to allow the resin to displace the water from the fiberglass mat. The requirement of large amounts of catalyst to satisfy the heat capacity of the system and yet retard the gel time was accomplished by the use of methyl ethyl ketone peroxide, Lupersol<sup>(R)</sup> DDM. The resin used in most of this work was obtained from the Civil Engineering Laboratory and is a polyester resin produced by PPG Industries, Inc. as Selectron RS50338. This resin can only be properly cured by the use of a catalyst system composed of cumene hydroperoxide, vanadium neodecanoate (Vanadium Ten Cem), N,N-dimethyl-p-toluidine using methyl ethyl ketone peroxide as a retarder. The gel time can be varied from 10 to 30 minutes over the temperature range of 32°F and 125°F. The promoter composed of the Vanadium Ten Cem and the N,N-dimethyl-p-toluidine does have some limitations because variability of the Ten Cem from batch to batch and also because of age effects when it is formulated with the N,N-dimethyl-p-toluidine for use as the promoter. This requires that each batch of the Vanadium Ten Cem be calibrated.

Laminates were prepared using fiberglass mats and a hand lay-up technique that simulated the field preparation of the fiberglass plastic soil surfacings. The plastic reinforced laminates prepared under wet conditions were cured under 1 mm to 3 mm (0.039" - 0.118") of water. Flexural and tensile strengths were measured according to the appropriate ASTM test method.

The presence of only a small amount of water, 5% based on the dry mat) can result in a 70 percent loss in flexural strength. This is the amount of water that would result from the exposure of the FABMAT C-4020 for one hour to a 0.01 inch per hour rainstorm. A soil that is saturated with water has an equally deleterious effect on flexural strength. The effect of water in the substrate and in the fiberglass mat, on laminate properties, has been defined and solutions have been developed to some of the problems.

A low resin viscosity is necessary if the water is to be displaced from the fiberglass mats. The dilution of the Port Hueneme resin with 15 percent styrene results in much improved flexural strengths. When using this resin the incorporation of a nonionic surfactant, Triton X100, into the water in the fiberglass mat results in improved resin penetration and flexural strengths that are within 10 percent of specification. The brominated vinyl ester resin DERAKANE 510-A-40 when diluted with 15 percent styrene and used in conjunction with Triton X100 does give flexural strengths that meet the contract specification. It does not meet the contract shelf life specification.

The incorporation of the Triton X100 into the wet fiberglass FABMAT C-4020 will require an additional step in the constructing of fiberglassreinforced plastic surfacings of soils under wet conditions. A concentrated (10 percent) solution of Triton X100 in water would be sprayed onto the fiberglass mat. The mat would then be rolled to insure mixing of the surfactant with water in the mat before applying the resin.

SECTION III  
TEST PROCEDURES

A. ACCELERATED SHELF STABILITY TESTS

A three-dram vial filled to the shoulder with resin and capped with an aluminum-lined cap was used for testing. The resin volume and air space in the vial were held constant. Approximately 10 grams of resin were used, the exact weight depending on resin density. Care was exercised in testing the gel times because the gel first formed at the bottom of the vessel and a completely static test was avoided. However, oxygen in the air space can also reactivate the inhibitor to give falsely long stabilities, and therefore extensive agitation was avoided.

The vials were carefully inverted to minimize both the mixing of air into the sample and the formation of gel at the bottom of the vial. The samples were checked periodically from hourly at 120°C to daily at 80°C. The end point can be anticipated by the decrease rate of bubble rise as viscosity increases. The point at which the air bubble would no longer rise to the top of the vial was taken as the gel point or end of the test.

B. REACTIVITY STUDIES

Reactivity testing consisted of determining the gel time, time to peak exotherm, temperature at peak exotherm, degree of cure by hardness (Barcol #934). Determinations were made with a Sunshine gel tester and with a time/temperature recorder.

Samples for the Sunshine gel tests were prepared by thoroughly mixing 10 grams of properly catalyzed resin and pouring the mixture into the Sunshine gel tube to the specified level. The switch controlling the spindle and timer was turned on and the gel time was recorded from the timer on the Sunshine tester (Figure 1).

Samples for the exothermic test were prepared by mixing 20 grams of properly catalyzed resin and pouring the resin in a 2-inch diameter aluminum foil dish. An iron-constantan thermocouple was imbedded in the resin (Figure 2) and attached to a temperature recorder. The changes in temperature were used to determine time to peak exotherm and temperature rise.

FIGURE 1  
SUNSHINE GEL TESTER

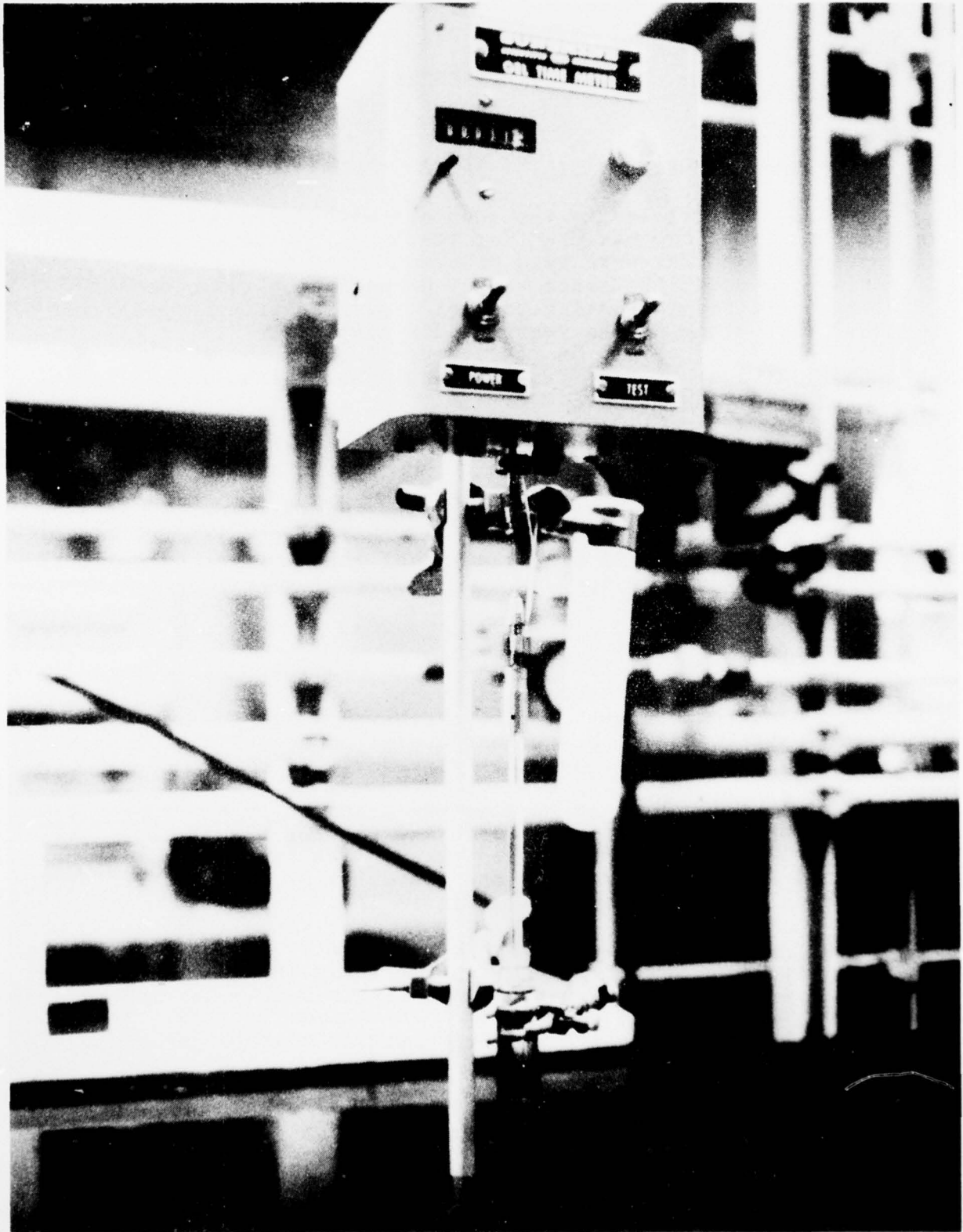


FIGURE 2  
EXOTHERM DETERMINATION



### C. PREPARATION AND MECHANICAL TESTING OF GLASS LAMINATES

Laminates were prepared using three types of fiberglass mat - chopped strand, woven roving, and FABMAT C-4020 at a resin to glass ratio of 60 to 40 by weight. Most of the work was done using two plies of 6 inch by 9 inch of FABMAT C-4020. The first ply of fiberglass was placed on the substrate, either a Mylar sheet or wet sand, into an adjustable frame made of 0.5 inch thick x 2 inches wide of the appropriate lengths of TEFLON to contain the mat. The frame was held in place by lead weights (see Figure 3). This frame was used to insure that when the laminates were prepared under wet conditions, the water did not run off. The predetermined amount of resin and catalyst at the appropriate temperature was then distributed over the fiberglass mat by pouring (Figure 3), and then rolled with a parallel groved roller until the resin was forced into the mat (Figure 4). In the case of the laminates prepared under wet conditions, the resin was allowed to exotherm before adding the next layer of FABMAT C-4020 and repeating the procedure. This was done to simulate field fabrication. The laminates prepared under wet conditions were cured under from 1 mm to 3 mm (0.039" - 0.118") of water, depending on the saturation of the mats. The laminate was cured at the appropriate temperature and then cut into test strips and tested on an Instron tester for flexural strength as specified in the ASTM procedure. In the case of tensile strengths the appropriate size specimens were milled from 0.75 inch strips using a Tensilcut milling machine and tested using the Instron following the specified ASTM method.

FIGURE 3  
LAMINATE FABRICATION - DISTRIBUTION OF RESIN



FIGURE 4  
LAMINATE FABRICATION - ROLLING



SECTION IV  
REACTIVITY STUDIES

The contract requirement that the chemical components "shall have shelf lives of (a) five years minimum for those components to be used in the wet environment" for all intents and purposes limited this work, to the use of the resin system developed under Contract No. N68305-76-C-0003, see report number CR77.017<sup>1</sup>. The catalysts used were cumene hydroperoxide (CHP) vanadium neodecanoate (V), methyl ethyl ketone peroxide (DDM), benzoyl peroxide (BPO), N,N-dimethyl-p-toluidine (DMT), cobalt naphthenate (CoN) and N,N-dimethylaniline (DMA). The polyester resin used by the Civil Engineering Laboratory at Port Hueneme and by the previous workers is manufactured by PPG Industries, Inc. All tests were made using resin supplied by the Civil Engineering Laboratory.

The gel time, a direct measure of reactivity, was obtained using 10 grams of catalyzed resin mixture in a Sunshine Gel Time Meter. At the same time the exothermic polymerization was followed by measuring the time and temperature behavior of 20 grams (0.25" x 2.0" diameter) of the catalyzed resin.

The 5% Vanadium Ten Cem used in the previous work is no longer manufactured by Mooney Chemicals, Inc. and is now only supplied as a 4% vanadium product. Although the product contains less vanadium, it is more active than the previous 5% product (see Figure 5). At a promoter (3p V:2p DMT) to cumene hydroperoxide ratio of 1 to 0.25 only 86 percent as much catalyst is required as with the previous 5% Ten Cem see Figure 5. In view of the extensive study made by Drake<sup>1</sup> showing that the optimum cure was obtained using a promoter composed of 3 parts of V Ten Cem to 2 parts of N,N-dimethyl-p-toluidine (DMT), most of this work was done using this ratio. The gel time was controlled by varying the total catalyst again using the previously determined cumene hydroperoxide to promoter ratio of 1 to 0.25.

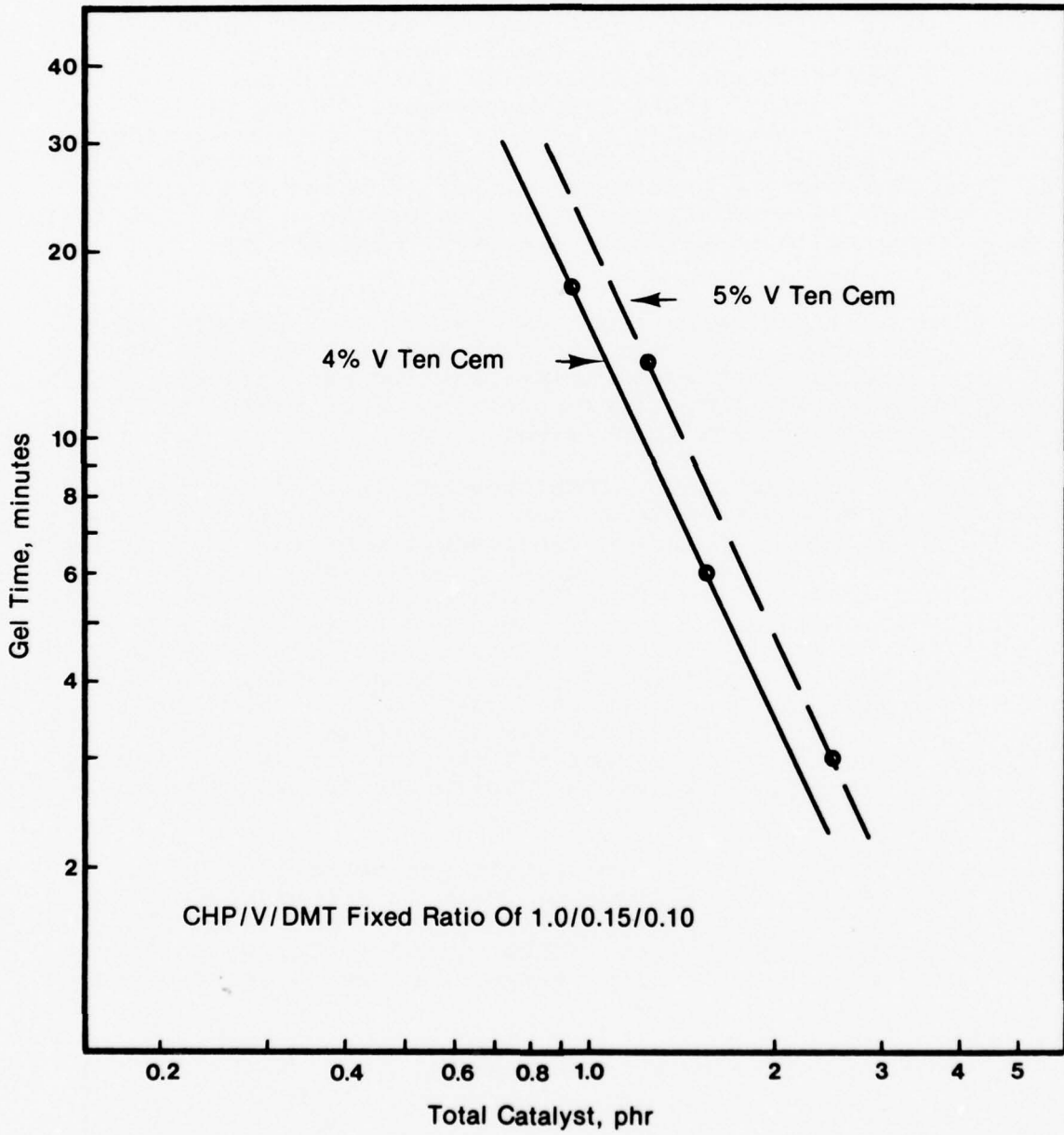
The influence of water on the reactivity was determined by adding 20 grams of water to the 20 grams of resin in the aluminum dish and allowing the resin to cure under water. It was found that this results in an increased time to exotherm, due to increased heat capacity, and also decreased peak temperature and lowered barcol

<sup>1</sup>Civil Engineering Laboratory, "Improved Chemical Components For Formulating Fiberglass-Reinforced Plastic Soil Surfacing," by S. S. Drake, H. E. Filter, D. L. Stevens, CR77.017, (May 1977, The Dow Chemical Company).

Figure 5

### GEL TIME vs CATALYST CONCENTRATION

PORT HUENEME RESIN  
(RS 50338)



hardness but a good cure was still obtained (see Table 1). The fact that the presence of water increases the time required for the resin to exotherm, because of the moderating effect of the increased heat capacity, made it obvious that the preparation of composites under wet conditions would require increased amounts of catalyst if the desired polymerization was to be attained. The use of increased amounts of catalyst results in rapid gelation and in the laboratory gives problems in composite fabrication that would not necessarily be encountered in the field. In the laboratory, the resin and catalyst are mixed in a cup and then poured onto the fiberglass. Several minutes are required for this operation, while in field applications instantaneous mixing is obtained. Therefore, to prevent large increases in resin viscosity, before incorporating the resin into the fiberglass the retarder, methyl ethyl ketone peroxide, Lupersol<sup>(R)</sup> DDM (DDM), was used. Reactivity studies were made using the polyester resin RS50338 as manufactured and with added styrene. The purpose of adding the styrene was to reduce the resin viscosity (see Section VD). It was found that the addition of styrene resulted in a change in reactivity (see Table 1 and Figure 6). Resin RS50338 containing an additional 10%, 15% or 20% styrene was found to have equal reactivity (see Figure 6). However, when the Lupersol DDM retarder is used, this is no longer the case (see Figure 7 and Table 1).

All of this investigation, except for the final stages, was made using the same batch of 4% V Ten Cem, Control S5335. The reactivity studies at 32°F (0°C) and 120°F (48.9°C) were made using another batch of 4% V Ten Cem Control LB-267-43. The composites made at 33°C and 120°F were also prepared using this sample. There is a variation in activity between these batches. Promoter made with the new batch of V Ten Cem has only slightly different activity than that obtained with the previous sample when used without Lupersol DDM. However, it is more sensitive to the inhibitor Lupersol DDM. In the case of Port Hueneme resin only 0.38 phr of DDM is required to obtain a gel time of 10 minutes using the new Ten Cem while 0.54 phr of DDM had been required previously. In both cases, the catalyst was composed of 2.5 phr cumene hydroperoxide, 0.375 phr 4% V Ten Cem and 0.25 phr N,N dimethyl-p-toluidine. The promoter made with this batch also showed a rapid change in activity with time (see Figure 8). When freshly made it was less active than after it had aged for two days. The gel time decreased from 11.3 minutes to 8.9 minutes after three days. No further change in activity was observed on an additional four days of aging. The reason for this behavior is not known but a similar effect of age had been observed by Drake<sup>1</sup>. It is possible that the V Ten Cem and N,N dimethyl-p-toluidine are not readily soluble in one another and that they slowly dissolve and increase in activity. To test this hypothesis the V Ten Cem and N,N dimethyl-p-toluidine were added separately and a gel time of 7.9 minutes was obtained as compared to 8.9 minutes obtained with the promoter that had aged seven days. This indicates that slow solubility or deflocculation might be the reason for the aging behavior. It is not known if Control Lot S-5335

Figure 6

## INFLUENCE OF STYRENE ON REACTIVITY

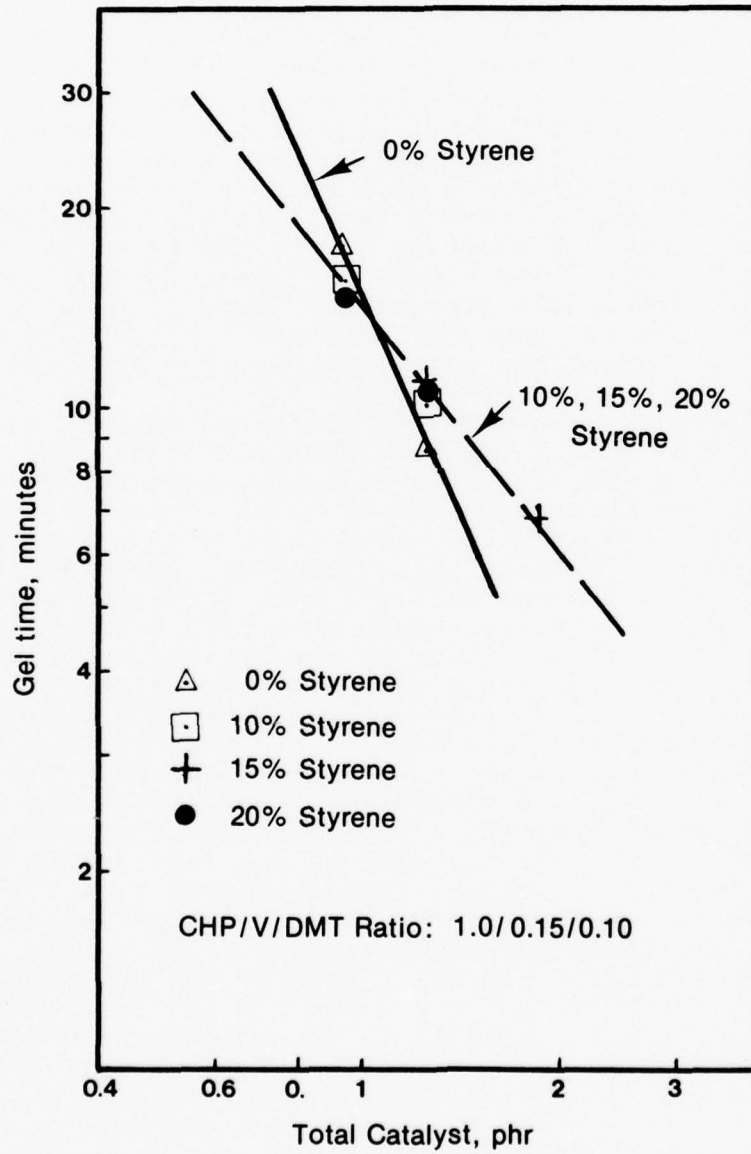
PORT HUENEME RESIN  
(RS 50338)

Figure 7

## INFLUENCE OF STYRENE ON REACTIVITY

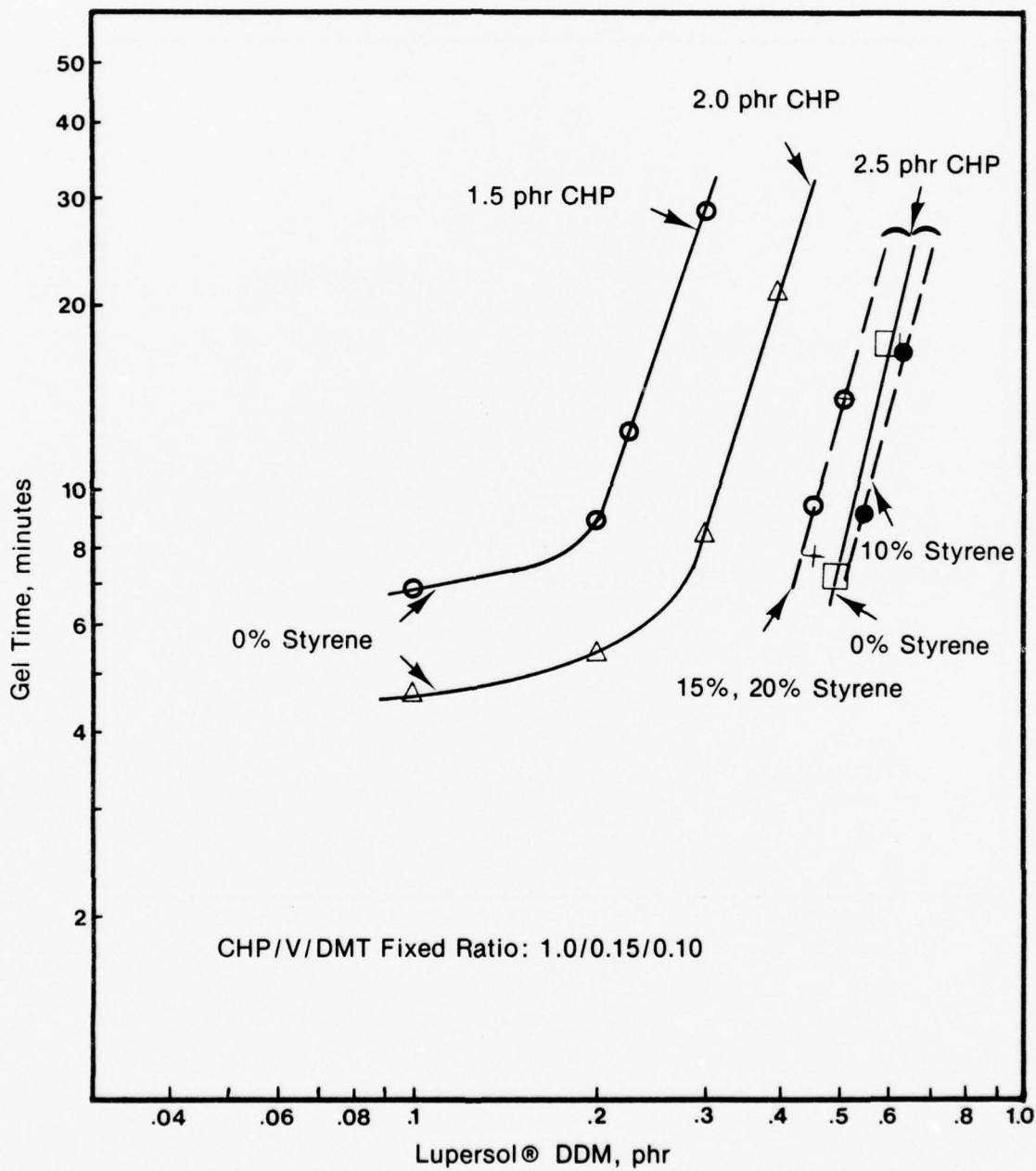
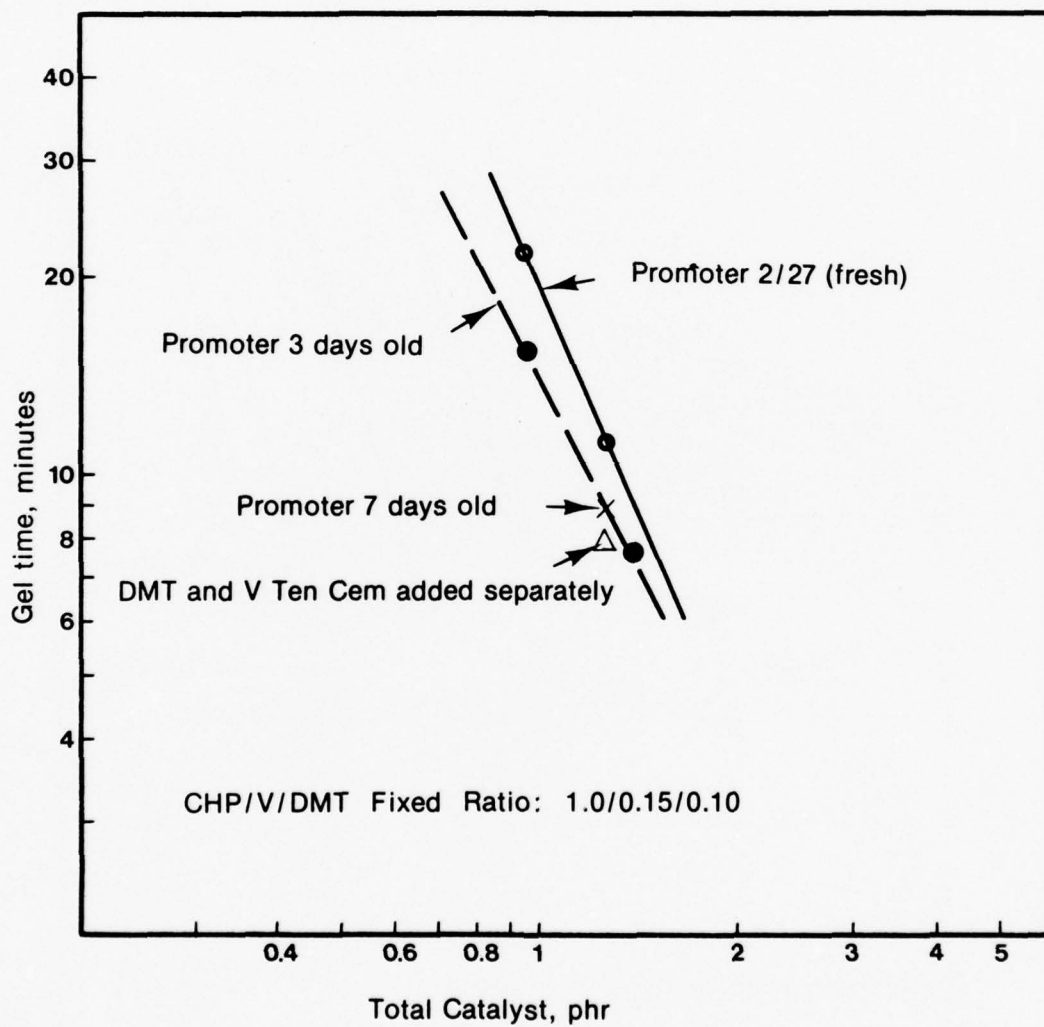
PORT HUENEME RESIN  
(RS 50338)

Figure 8

## EFFECT OF AGE ON PROMOTER ACTIVITY

PORT HUENEME RESIN  
(RS 50338)

showed a similar behavior but no change in activity was observed during its use. In any event the V Ten Cem LB-267-43 after two days aging has the same activity as S-5335. All activity tests that were made using a promoter prepared from LB-267-43 V Ten Cem were aged two days before use.

Mooney Chemicals, Inc., manufacturer of the Vanadium Ten Cem, was contacted, but could offer no explanation for the aging behavior. They stated that the vanadium neodecanoate is difficult to manufacture and that the activity does vary from batch to batch and is only manufactured to order.

The effect of changing the ratio of the promoter to cumene hydroperoxide as well as the promoter ratio on gel time is presented in Table 3, and Figures 9 and 10 for a promoter composed of 3 parts of 4% V Ten Cem to 2 parts of N, N-dimethyl-p-toluidine and for a promoter composed of equal parts of the components.

The reactivity of Port Hueneme resin (RS50338) and Port Hueneme resin with 15% added styrene was determined at 32°F (0°C) and 120°F (48.9°C) (see Table 2 and Figures 11 and 12). As can be observed from Figure 12, the gel time obtained is a function of the heat transfer. AT 32°F, using the Port Hueneme resin with 15 percent added styrene, a gel time of 18.5 minutes was obtained when a liquid cooled jacket was used. The gel time decreased to 12.6 minutes when an air jacket was used. This is a result of less heat being removed with the air jacket giving decreased gel time. In the case of field application, under cold conditions it would be expected that the reactivity should approach the gel times obtained using a liquid jacket. At elevated temperatures, i.e., 120°F air temperature, the field application is more complicated in that the ground temperature through most of the day will be greater than the ambient air temperature resulting in shorter gel time. A plot for the selection of catalyst concentration over the temperature range from 32° F (0°C) to 120° F (48.9° C) is shown in Figure 13.

The reactivity of other resins than Port Hueneme polyester resin were also investigated. Tests were made of Selectron SR3703 (Port Hueneme RS50338 without added stabilizer) (see Table 4). The Kirtland Primary resin (76% Altek<sup>(R)</sup> 8-52, an isophthalic polyester resin, and 24% DERAKANE 510, a brominated polyester) were also investigated (see Table 5 and Figure 14). In order to study the effect of resin density as well as viscosity on the preparation of wet composites the reactivity of DERAKANE 510-A-40 was investigated using various catalysts (see Tables 6 and 7 and Figure 15). The DERAKANE 510-A-40 is not as active as the Port Hueneme resin and becomes less active on the addition of 15% styrene (see Tables 3, 8 and Figure 15).

Figure 9

## INFLUENCE OF PROMOTER RATIO ON REACTIVITY

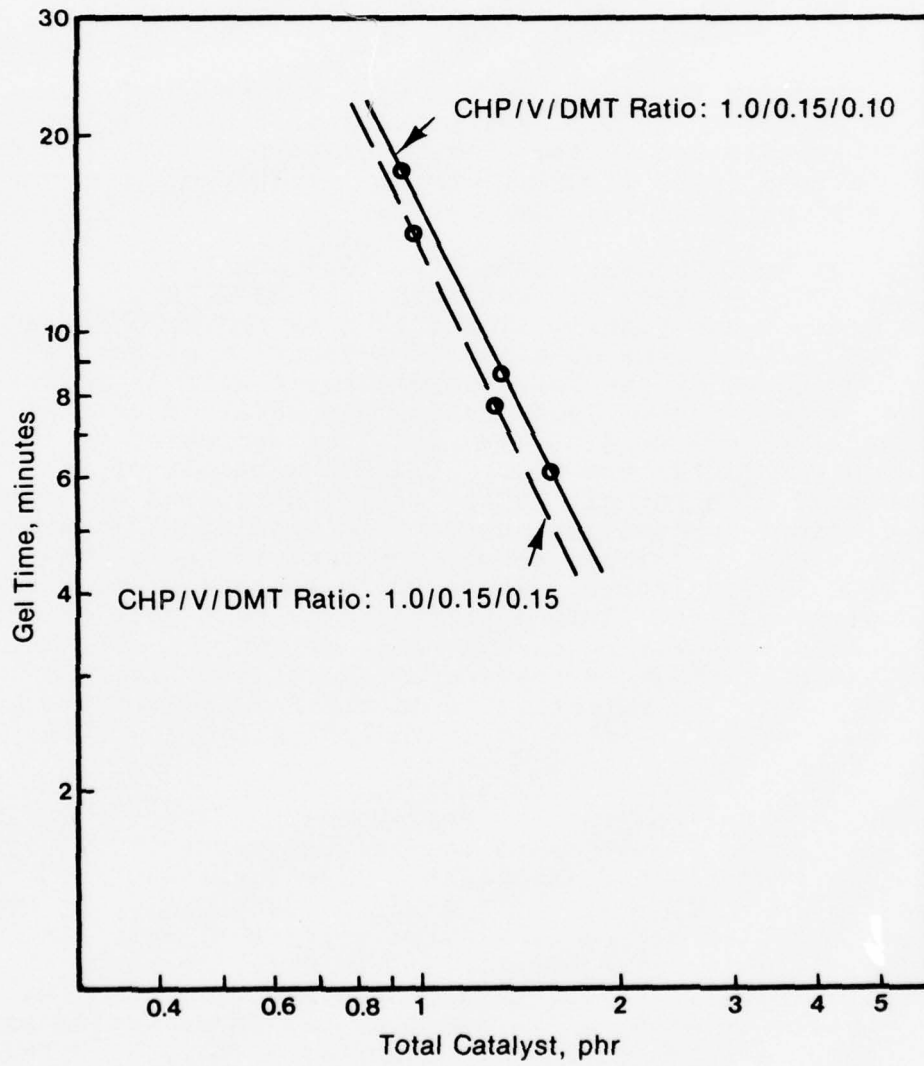
PORT HUENEME RESIN  
(RS 50338)

Figure 10

## EFFECT OF PROMOTER ON GEL TIME

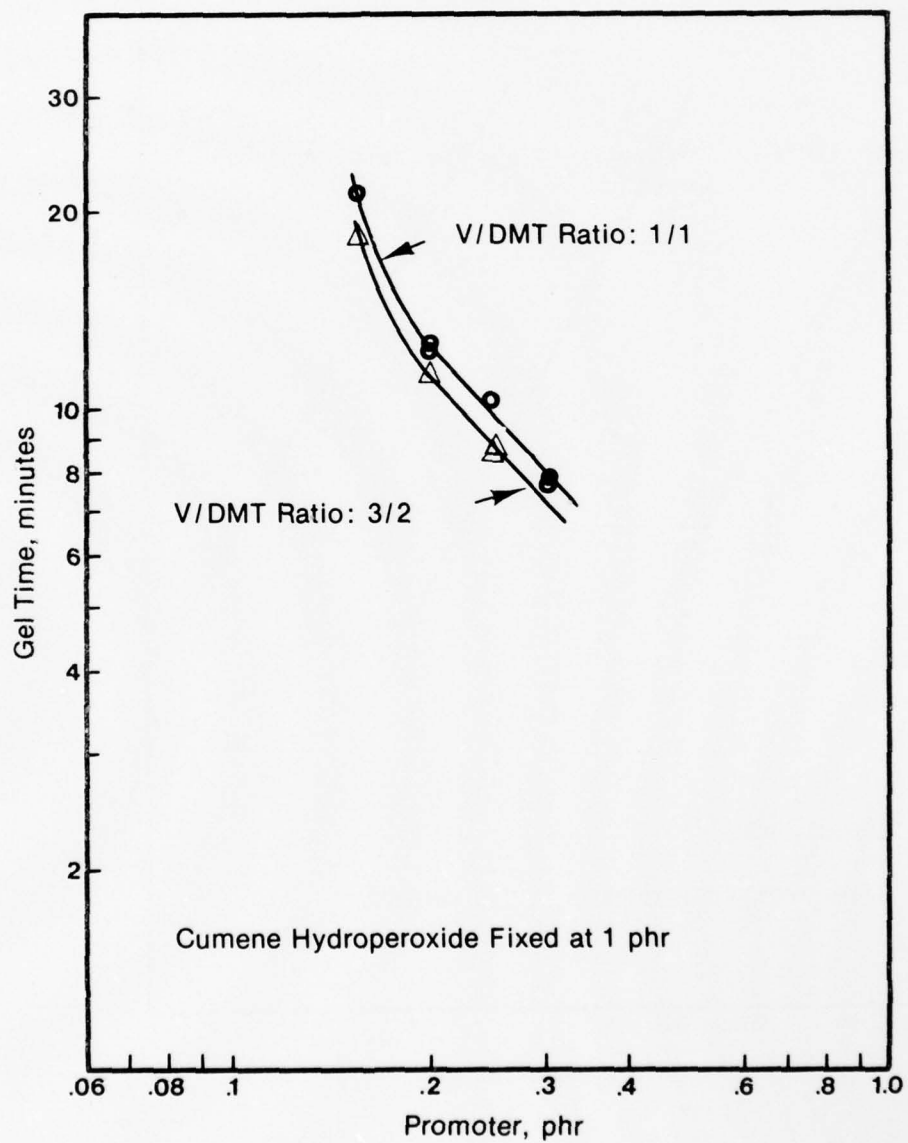
PORT HUENEME RESIN  
(RS 50338)

Figure 11

### GEL TIME vs CATALYST CONCENTRATION AT DIFFERENT TEMPERATURES

PORT HUENEME RESIN  
(RS 50338)

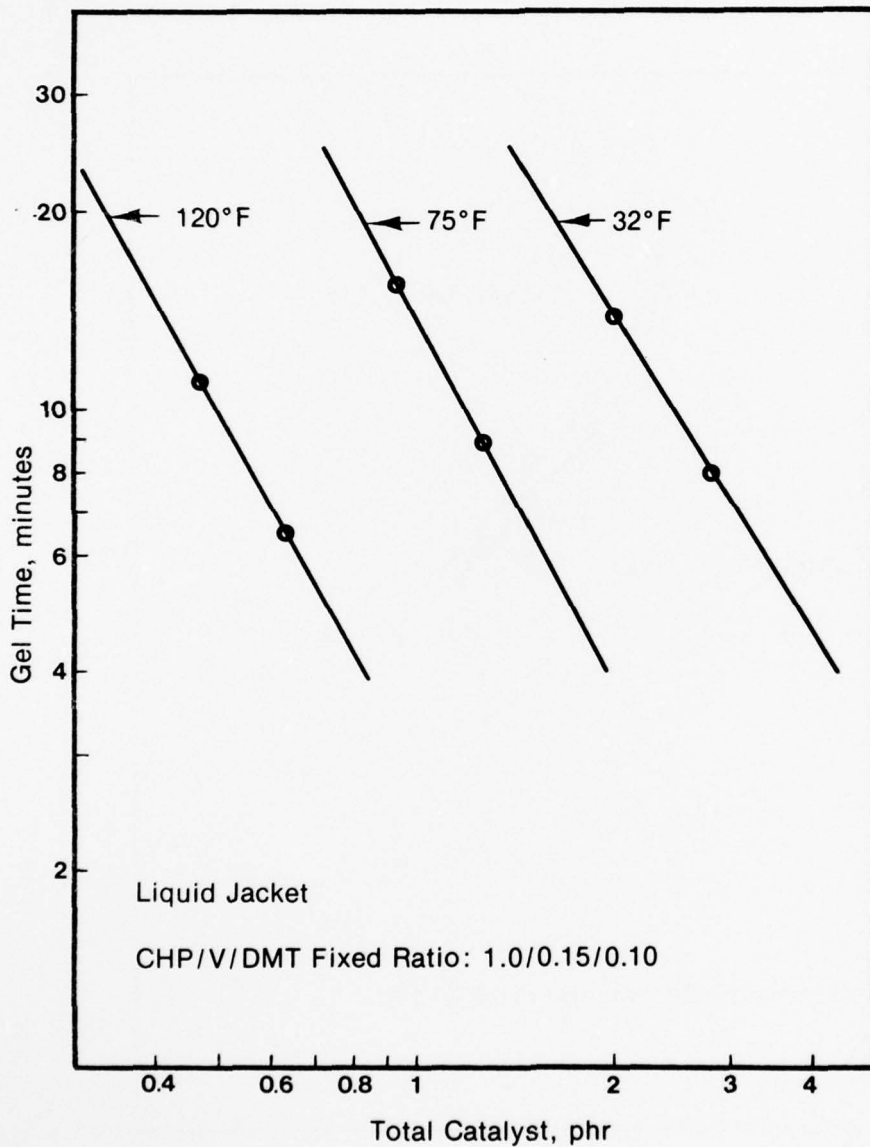


Figure 12

### GEL TIME vs CATALYST CONCENTRATION AT DIFFERENT TEMPERATURES

PORT HUENEME RESIN  
+ 15% STYRENE

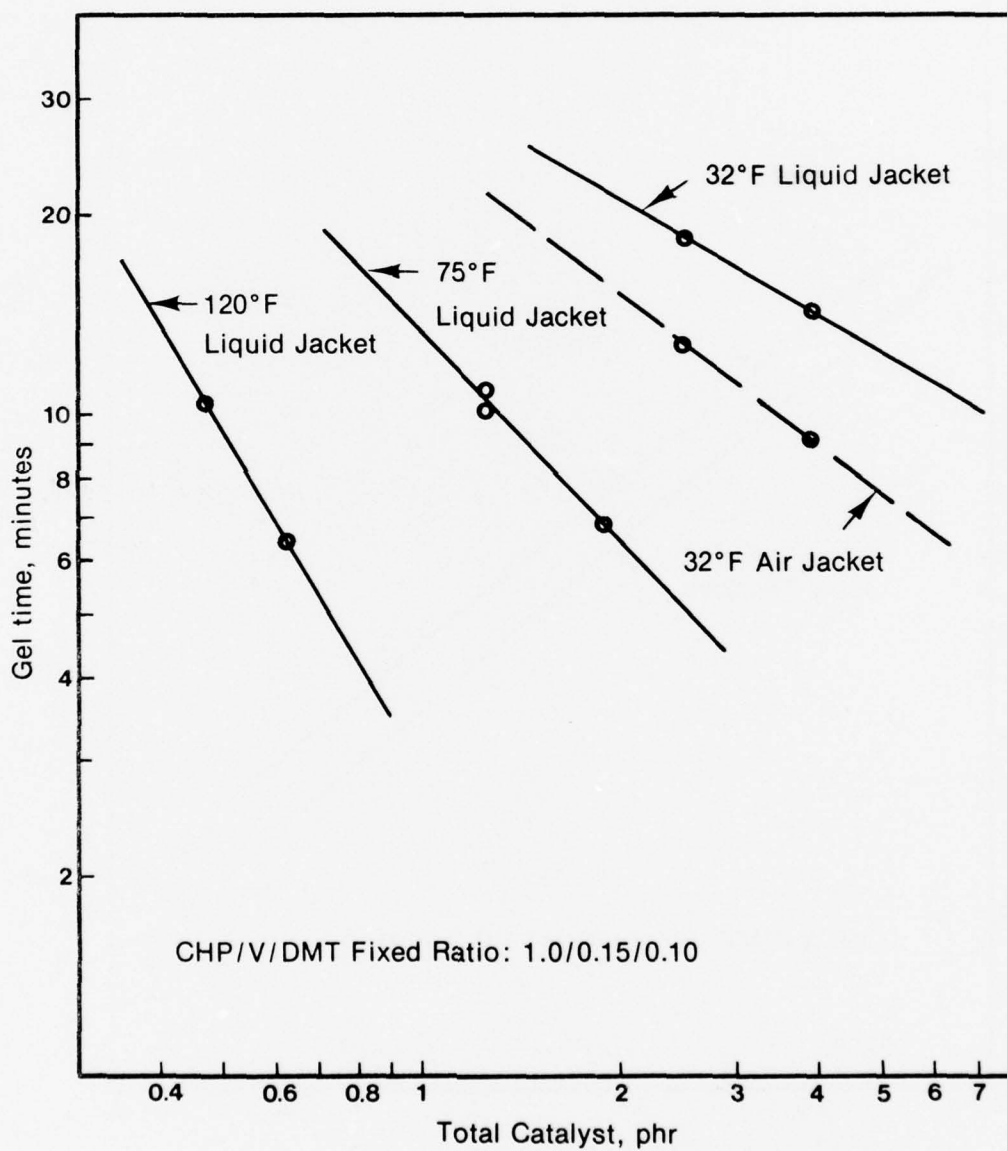


Figure 13  
SELECTION OF CATALYST CONCENTRATION  
vs TEMPERATURE OF APPLICATION

PORT HUENEME RESIN  
(RS 50338)

(Constant Gel Time, 10 minutes)

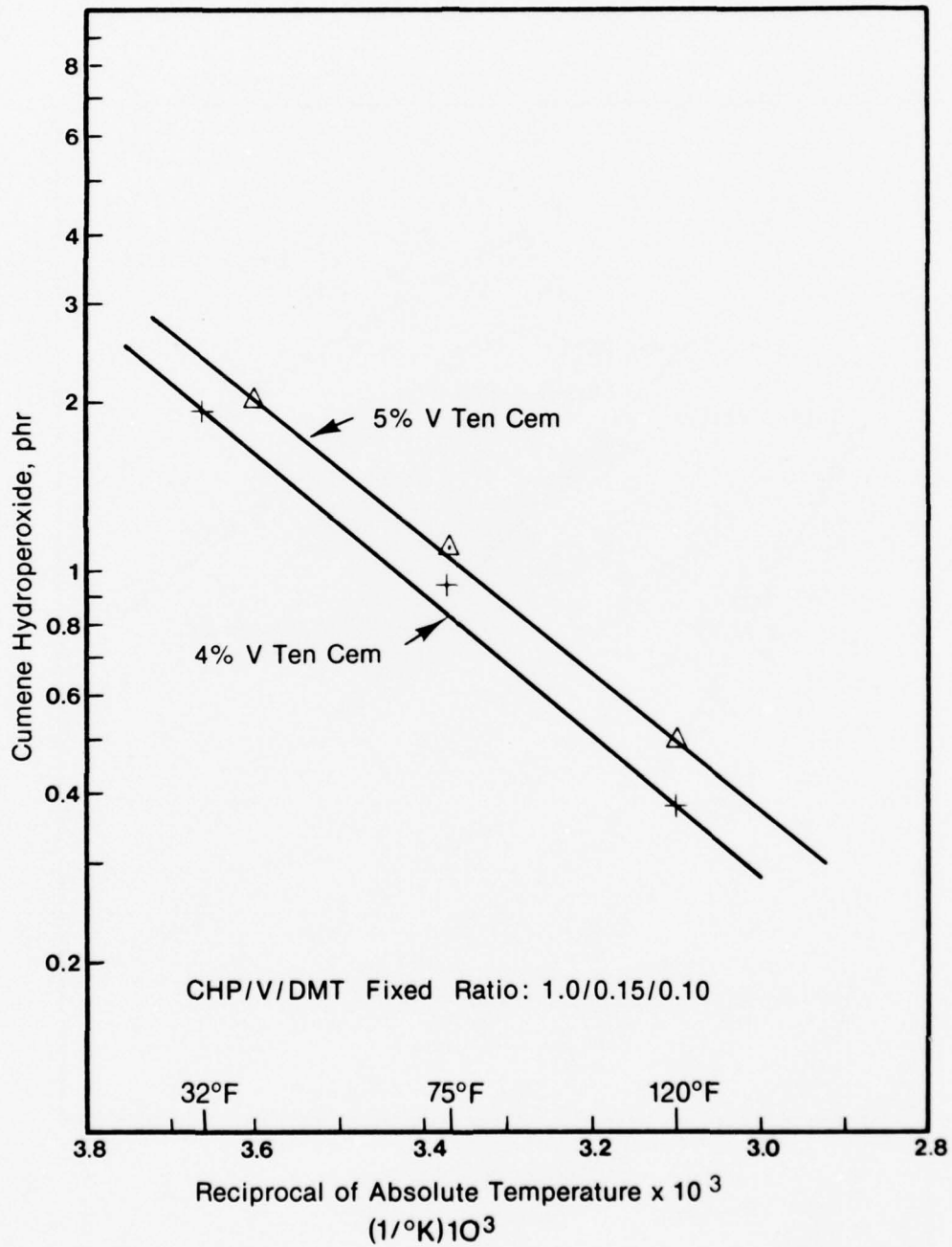


Figure 14

## EFFECT OF RETARDER

## KIRTLAND PRIMARY RESIN

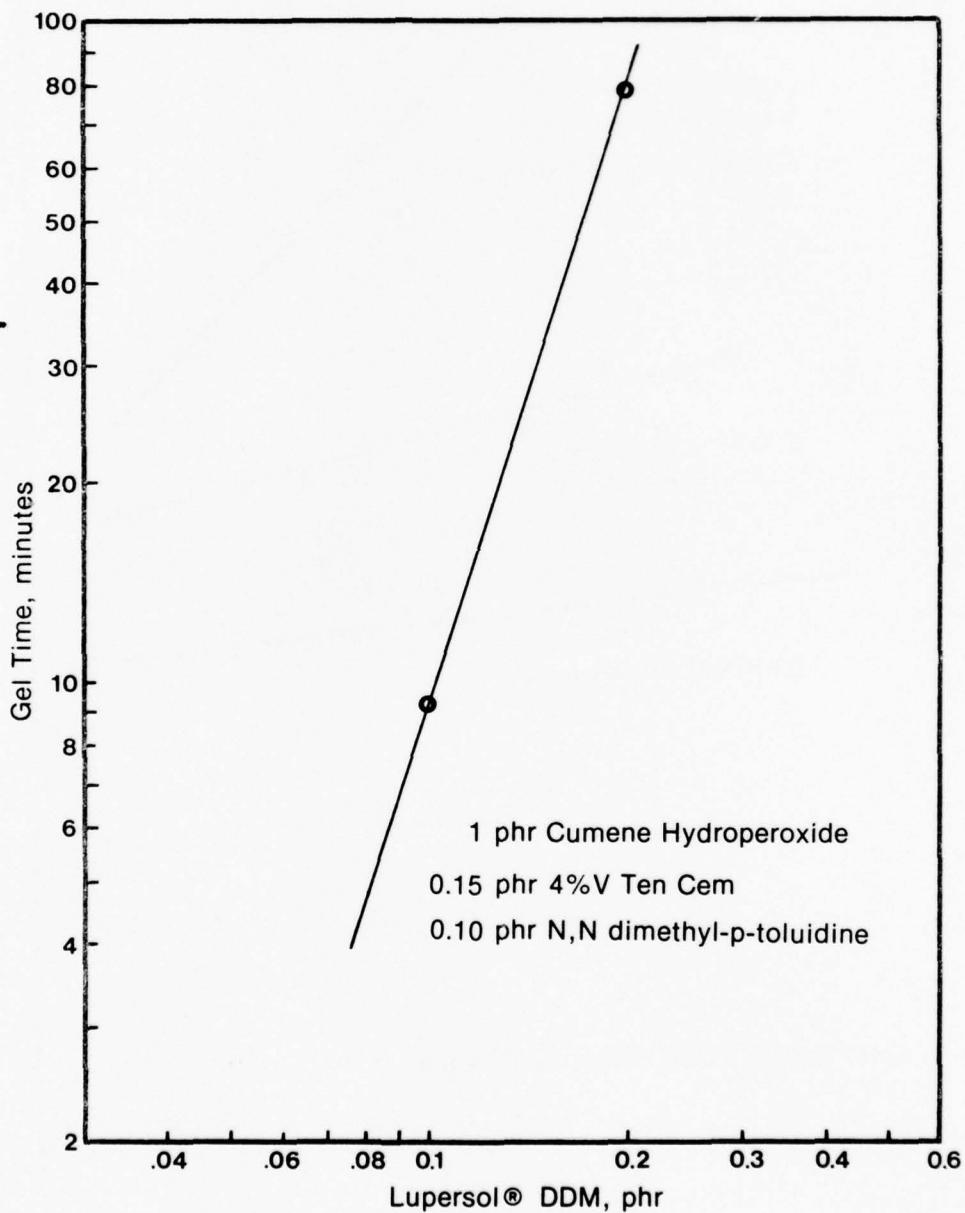
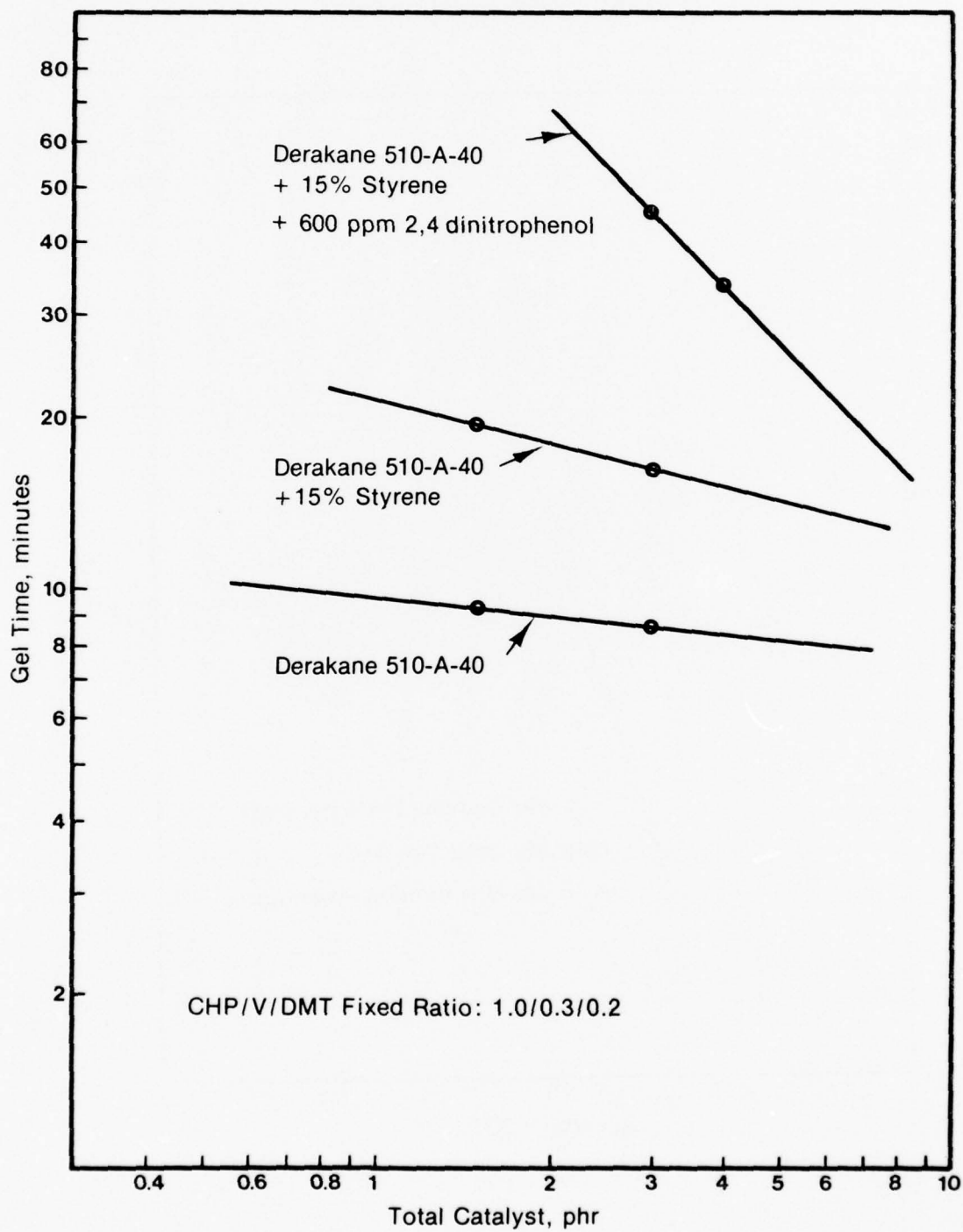


Figure 15

REACTIVITY  
DERAKANE 510-A-40  
DERAKANE 510-A-40 + 15% STYRENE



## SECTION V

PREPARATION OF FIBERGLASS REINFORCED PLASTIC  
LAMINATES UNDER WET CONDITIONS

As discussed previously, the requirement that the chemical components have a five year minimum shelf life restricted most of the work to an effort to modify the previously developed resin system to wet conditions. Most of the fiberglass laminates were made using the fiberglass material presently used by the Civil Engineering Laboratory at Port Hueneme. This is a woven roving with a random fiberglass backing manufactured by Fiberglass Industries, Amsterdam, New York. This is a 40 oz. per square yard woven roving backed by 2 oz. per square foot of random fiber and is designated as FABMAT C-4020 by the manufacturer.

## A. EFFECT OF WATER ON FLEXURAL STRENGTH

The study of the influence of water on the flexural strength of fiberglass laminates was made using two plies of 6 inch by 9 inch FABMAT C-4020. These fiberglass laminates were prepared using the hand lay-up technique used in the previous work done for the Civil Engineering Laboratory and is described in detail in the test section. The fiberglass mats were wet using two different methods. The low moisture mats (10% moisture based on the dry mat weight) were prepared by carefully misting the alternate sides of the mat until the desired water content was attained. The higher water content fiberglass mats were prepared by covering with distilled water and then draining, if necessary, on paper towels. The catalyst, promoter and inhibitor were varied with the moisture content to insure adequate polymerization. The results obtained are presented in Table A (see Table 9).

TABLE A

## EFFECT OF MOISTURE ON FLEXURAL STRENGTH

<u>% Moisture*</u>	<u>Flexural Strength</u> <u>Lbs/sq in.</u>
0	39,600
4.8	10,800
10.2	12,000
25.8	13,000
25.8	11,700
27.4	13,460
50.4	6,100
71.4	3,600
71.7	3,900

$$* \% \text{ Moisture} = \frac{\text{wt. wet mat} - \text{wt. dry mat}}{\text{wt. dry mat}} \times 100$$

As might be expected, even a small amount of moisture, 4.8 percent has a most harmful effect on the flexural strength of the laminate resulting in a 70 percent loss in strength. This is the moisture content that would result from a one hour exposure of the FABMAT C-4020 to a 0.01 inch per hour rainfall. Increasing the moisture content to 27.4 percent has no significant effect on the flexural strength but higher moisture levels do result in a further loss in flexural strength (see Table A). The results indicate that the major reason for the loss of flexural strength of laminates made under wet conditions is due, for the most part, to the inability of the resin to bond to the wet fiberglass mat, not to poor resin cure. The maximum amount of water that the FABMAT C-4020 will hold is 70 percent by weight of mat and this amounts to about 0.45 cc of water per cc of resin. To put it another way, at a 70 percent water content the fiberglass mat would be holding the maximum amount of water that it could contain. In all cases, placement of the resin resulted in free water covering the resin surface so that, in effect, all of the tests made at 70 percent water in the fiberglass mat were made under 3 mm (0.11 inches) of water.

#### B. EFFECT OF SUBSTRATE ON FLEXURAL STRENGTH

The influence of water in the soil under the fiberglass was investigated. It was found that when fiberglass laminates were made using 100 percent water-saturated sand as a substrate this had a most deleterious effect on the flexural strength. The flexural strength decreased from 36,000 psi obtained with dry fiberglass laminates and a Mylar substrate to 4,600 psi - 8,600 psi with the saturated sand substrate.

A laminate was also prepared on the water saturated sand using fiberglass mats containing 70.4 percent water. A flexural strength of 4,450 psi was obtained (see Table 10). This compares to the 3,700 psi obtained with mats containing 71 percent water and a Mylar substrate. This shows that when a laminate is prepared from wet fiberglass mats on saturated sand that further loss in flexural strength does not result. Using dry sand as a substrate flexural strengths of 36,700 psi were obtained. The loss in strength that results when the laminate is prepared on the wet substrate is as great as when the fiberglass is wetted. Therefore, the loss in strength must be due to the wicking of the water into the fiberglass mat. Until this time the fiberglass laminates had been prepared by placing the fiberglass mat on the substrate, pouring the appropriate amount of resin onto the fiberglass mat and then rolling; followed by the immediate placement of the second mat, etc. This technique is satisfactory under dry conditions. It does not, however, simulate field practice. Under wet conditions, the fabrication technique might have an influence on the fiberglass laminate properties as a result of different dispersion of the water in the resin, water migration may be different dependent on the mat placement, i.e., woven roving up or down, wicking from the soil, etc. In order to more nearly simulate the field application of fiberglass laminates,

the following laboratory fabrication method was used, hereafter referred to as the sequential method. In this technique after applying the resin to the first fiberglass mat the resin was allowed to exotherm before applying the second fiberglass mat and resin since this is the way it is done in the field. This change in the method of fabrication (allowing the resin to exotherm between layers) resulted in the flexural strength increasing to approximately 15,000 psi. No doubt due to the fact that moisture only entered into the first fiberglass mat. It was thought that placing the cut strand side of the FABMAT C-4020 in contact with the wet sand rather than the woven roving side would result in less wicking and improved flexural strength but no improvement resulted (see Table 10). In a further effort to decrease the wicking of water into the mat the FABMAT C-4020 was treated with dichlorodimethylsilane to increase the hydrophobicity. This treatment did not result in any improvement in the flexural strength of the laminate prepared on the wet substrate.

#### C. INFLUENCE OF FABRICATION METHODS ON FLEXURAL STRENGTH

Since the method of fabrication of the fiberglass laminates on 100 percent water saturated sand did have an effect on the flexural strength a study was made to more completely insure that the proper laboratory technique was used. In the field preparation of fiberglass laminates the FABMAT C-4020 is placed on the soil with the woven roving side down and the resin and catalyst are sprayed onto the mat and rolled. After the resin has exothermed the second layer of mat is spread, again with the woven roving side down, and the resin applied and rolled. The same method of preparation was followed in the laboratory. Tests were made to determine if this sequential method of allowing the resin to exotherm between layers and if the direction of placement of the woven roving would have any influence on the flexural strength of laminates. As would be expected when dry fiberglass mats were used the method of fabrication, sequential or non-sequential, nor the placement of the woven roving, either up or down, had any effect on the flexural strengths (see Table 11). All of the flexural strengths were determined with the specimens placed in the test machine so that the woven roving was on the side of maximum stress. Tests were also made where two layers of wet fiberglass mat were used. Again, the placement of the woven roving side, either up or down, was not found to have any significant influence on the flexural strength using mats containing 25 percent water. Nor did allowing the resin to exotherm before applying the second mat have any influence on strength.

In the work reported in a previous section, it had been observed that the laminates prepared using Port Hueneme resin and FABMAT C-4020 under wet conditions had shown what appeared to be very poor

penetration of the resin into the fibers of the woven roving. The inability of the resin to displace the water trapped in the strands of the continuous fiber is no doubt the reason for the marked loss in flexural strength in the presence of relatively small amounts of water (5-10%). In an effort to confirm that the lack of resin penetration into the woven roving is the major reason for the loss in strength, laminates were prepared using only chopped strand mats. The use of the chopped strand mats should insure good resin penetration. Fiberglass laminates were prepared by placing 3 layers of 2 oz/ft<sup>2</sup> chopped strand (either wet or dry) on the Mylar sheet. Then the desired amount of resin and catalyst was added and the layer rolled. After the resin had exothermed, a second layer was placed on top of the cured resin. The reason for using three of the chopped strand mats in each layer was to have about the same amount of glass in the finished laminate as in the case of the FABMAT C-4020 laminates. The following results were obtained:

<u>% Water</u>	<u>Flexural Strength</u>
0	21,750 psi
25.5	18,360 psi
26.0	19,530 psi
69.8	14,440 psi

These results are markedly different from those obtained with FABMAT C-4020. The presence of approximately 26 percent water in the chopped strand laminates resulted in only a 13 percent loss in flexural strength as compared to up to a 60 percent loss in flexural strength with the laminates prepared with the FABMAT containing the woven roving. Increasing the water content of the chopped strand mats to 69.8 percent resulted in only a 34 percent loss in flexural strength as compared to the 90 percent loss in flexural strength obtained when the FABMAT C-4020 was used. As further confirmation laminates were prepared using two layers where each layer was composed of two layers of 18.5 oz/yd<sup>2</sup> of woven roving and one layer of 2 oz/ft<sup>2</sup> of chopped strand. In the case of the laminates the no water flexural strength was 41,000 psi (see Table 11) and when 24.5 percent water was in the fiberglass a strength of 9,830 psi was obtained. This is a 76 percent decrease in flexural strength.

A test was also made using a single layer of FABMAT C-4020. The no water average flexural strength was 22,910 psi and when 70.6 percent water was in the mat, the strength was 1,860 psi, a decrease of 92 percent. These results seem to confirm the conclusion that the major effect of water is to prevent the penetration of resin into the woven roving and not resin cure or resin adhesion. If it were poor cure at the fiber surface resulting in poor adhesion, the chopped strand laminates should have shown greater decreases in flexural strength than the 13 percent obtained at 26 percent water content and the 34 percent at 69.8 percent water.

In view of the relatively small loss in strength obtained with laminates from the wet chopped strand fiberglass mats an effort was made to obtain a spun strand woven roving. In the presently used FABMAT C-4020 the woven mat is manufactured from continuous strand roving - parallel glass strands. The spun strand roving is also made from continuous filament strands in which the continuous strands are looped back and forth upon themselves and held in roving form by a slight twist and by the use of a resinous size. This is a more bulky roving and would no doubt result in lower dry strength laminates. The converse should be true for laminates prepared under wet conditions. The more open nature of the spun woven roving should result in better resin penetration and increased strength. Efforts were made to obtain such a fiberglass mat but at this time no supplier has been located.

#### D. EFFECT OF RESIN VISCOSITY AND SURFACTANTS ON FLEXURAL STRENGTH

The previous work has shown that if satisfactory flexural strengths are to be obtained using FABMAT C-4020 mats that better resin penetration into the woven roving must be obtained. One way to accomplish this is to decrease the viscosity of the Port Hueneme resin by dilution with styrene. In doing this not only is the viscosity reduced but at the same time the resin density is decreased. The lowered resin density will result in poor water displacement as the resin density approaches the water density.

In the first test that was made, the Port Hueneme resin was diluted with an additional 10 percent of styrene. This resulted in the viscosity decreasing from 218 cps to 109 cps and at the same time the density decreased from 1.093 g/cc to 1.07 g/cc. As would be expected, the addition of the styrene resulted in changed reactivity (see reactivity section of this report). Laminates were made using the FABMAT C-4020 fiberglass mats containing 25 percent water. Flexural strengths ranging from 20,850 psi to 23,450 psi (average 22,150 psi) were obtained (see Table 12). This is a significant improvement over the 13,000-16,000 psi flexural strengths obtained with laminates prepared from mats containing 25% water and with Port Hueneme resin without additional styrene. A laminate was also fabricated from fiberglass mats containing 70.8 percent water. A flexural strength of 12,440 psi, with the Port Hueneme resin with added 10 percent styrene, was obtained as compared to 4000 psi with Port Hueneme resin. It is felt these improvements in flexural strength are due, for the most part, to improved resin penetration into the woven roving as a result of the lower resin viscosity. These laminates were prepared using two different types of rollers to determine if the resin could be mechanically forced into the woven roving to displace the water. A paddle roller was used in the hope that its kneading action would result in better water displacement than the normally used vertical disk roller. No significant difference in flexural strength resulted from the use of these different type rollers in the preparation of the laminates.

In view of these results where the addition of 10 percent styrene (by weight) to the Port Hueneme resin (RS50338) resulted in increased flexural strength under wet conditions; the effect of further dilution with styrene was investigated (see Table 12, and the following Table B).

TABLE B

Effect of Styrene Added to Port Hueneme Resin  
on Flexural Strength

Styrene* %	Viscosity cps	Density g/cc	Water %	Flexural Strength-psi
0	218	1.093	70	4,000
10	109	1.07	70.8	12,440
15	80	1.06	70.9	18,770
20	55	1.05	70.3	12,340

$$*\% \text{ styrene} = \frac{\text{wt. styrene}}{\text{wt. of RS50338 resin}} \times 100$$

As can be seen, the optimum flexural strength is obtained on the addition of 15 percent styrene to the Port Hueneme resin. This results in a flexural strength of 18,770 psi for a laminate prepared from mats containing 70 percent water; further dilution results in decreased strength. The dilution of the resin with styrene had no effect on the flexural strength of laminates prepared from dry mats being 42,000 + 2,000 psi. Although the addition of styrene has resulted in a 470 percent increase in flexural strength to 18,700 psi, it is still 10,000 psi short of the desired flexural strength of 28,000 psi.

Another approach to obtaining increased flexural strengths is to treat the water so that it is more easily displaced by the resin. This could be done by adding an appropriate surfactant. This would result in not only a decrease in the interfacial tension, but also in the surface tension of the water. The first tests were made using Triton X100, a water-soluble isooctyl phenoxy polyethoxy ethanol. This surfactant was chosen because it is non-ionic and should have no influence on the reactivity and did not. It also has the property of being biodegradable. The first tests were made by wetting the mat to 25 percent water and then spraying the mat with a one percent solution of Triton X100 until the mat contained 5 to 8 percent (by weight) of the 1 percent solution (final surfactant concentration being 0.17 - 0.24 Triton X100). Flexural strengths of 17,000 psi were obtained, only a slight improvement over water alone but enough to indicate that this approach had promise. A laminate was then made on which the FABMAT was wet with the one percent Triton X100

in water and gave a flexural strength of 25,280 psi (see Table 12) at 25 percent fluid as compared to 13,000 psi with water. On increasing the moisture content to 69.6 percent using the surfactant solution a flexural strength of 17,670 psi was obtained as compared to 4000 psi with water alone. This significant increase in strength shows that the addition of a surfactant, to change the surface tension and interfacial tension, does result in better displacement of the water from the fiberglass mat.

Laminates were prepared using Port Hueneme resin containing 10 percent styrene. Flexural strengths of 23,080 psi were obtained at 24.1 percent saturation and 24,610 psi at 68.1 percent saturation with Triton X100 solution. At 15 percent styrene and 70 percent surfactant saturation the flexural strength averaged 25,080 psi. These flexural strengths approach the desired 28,000 psi. Indications are that 1% Triton X100 is more than is required since reducing the concentration to 0.5% did not result in a significant change in flexural strength, 17,670 psi to 16,820 psi, in the case of Port Hueneme resin with 70% mat saturations.

If surfactants are to be used in the field the method of application would be to spray a concentrated solution of the surfactant, in water, onto the wet mat and then allow the surfactant to mix with the water in the mat either by diffusion alone or by mixing with a roller or some other mechanical method. The effectiveness of diffusion was determined using Port Hueneme resin diluted with 15 percent styrene (Table 12). The mat containing 69.7 percent water was sprayed with a 10 percent Triton X100 solution (12.5 percent added based on dry mat) onto the wet mats and allowed to stand thirty minutes before adding the resin. In this case a flexural strength of 19,660 psi was obtained as compared to 23,320 psi when the mats contained 70 percent of one percent Triton X100. Although the total fluid in the mats was greater in the diffusion test, 82.2 percent as compared to 70.4 percent, the sixteen percent loss in flexural strength indicates that some mechanical mixing would be desirable. This was done in a similar way except that after spraying the 10 percent water solution of Triton X100 onto the wet mat, the mat was then rolled with the same roller that is used to distribute the resin. Again, the fiberglass mats contained about 70 percent water and from 5.1 to 11.1 percent (by weight of dry mat) of the Triton X100 solution was sprayed onto the mats. The flexural strengths obtained averaged  $15,610 \pm 1,050$  psi in this case as compared to  $17,200 \pm 400$  obtained with a 1 percent Triton X100 solution in the mats (see Table 12). These tests were made using Port Hueneme resin. The results show that the beneficial effect of a surfactant can be obtained by spraying a concentrated solution onto the water saturated FABMAT C-4020 followed by rolling.

It was not possible because of the contract time limitations to undertake a surfactant optimization investigation. Some tests were made using other surfactants. Triton CF-76, a nonionic detergent, appeared to be more effective than the Triton X100 in the case of

Port Hueneme resin giving a flexural strength of 22,860 psi as compared to the 17,200 psi obtained with Triton X100. Both tests were made using mats containing 70 percent of a one percent surfactant solution (Table 12). However, the Triton CF-76 does not offer any advantage over Triton X100 when used in conjunction with the less viscous Port Hueneme resin containing 15 percent styrene; 25,800 psi flexural strength compared to 25,080 psi with Triton X100. Pyronate 50, a water-soluble petroleum sulfonate, was tested using fiberglass mats containing 72.4 percent of a one percent solution. It was found that under these conditions the Port Hueneme resin did not cure. In view of this the use of ionic surfactants does not appear to be promising. At low water saturations (24%) spraying the mat with ethyl alcohol (2B formulation) was found to have a beneficial effect on flexural strength, but at 70 percent water the converse is true. A laminate prepared using mats containing 70.3 percent water and then spraying with alcohol (13.2% by weight of dry mat) had a flexural strength of 10,360 psi using Port Hueneme resin containing 15 percent styrene. Under these conditions alcohol is not effective.

#### E. EFFECT OF TEMPERATURE ON LAMINATE PROPERTIES

Studies were made at 33°F (0.6°C) and 120°F (48.9°C) of the effect of temperature on the flexural strength of laminates prepared using Port Hueneme resin and Port Hueneme resin containing 15 percent styrene (see Table 14). At the same time the influence of temperature on the viscosity of these resins was also obtained (see Table 16). All materials used in preparation of the laminates were pre-heated or cooled to temperature and the laminates were held at this temperature overnight. Samples were cut and the flexural strengths determined within two hours after cutting so that the low temperature laminates would not give false results (see Table C). As might be expected, the laminates prepared with wet mats at 33°F had low flexural strengths; 4,290 psi with Port Hueneme resin and 9,240 psi with Port Hueneme resin containing 15% styrene. This is a result of two factors: one of increased resin viscosity (see Table 2) that results in poor penetration into the woven roving and second, poor resin cure. Conversely, increasing the temperature to 120° F resulted in good resin penetration, cure and flexural strengths of 33,410 psi to 35,470 psi for these resins with mats containing 70 percent water (see Table C).

TABLE C  
Effect of Temperature on Flexural  
Strength of Laminates

Resin	%* Water	%* Surfactant	Strength psi	Remarks
Temperature 33°F (0.6°C).				
Port Hueneme	0	74.1	Flex. 4,290	1% Triton X100
Port Hueneme +15% Styrene	0	72.3	Flex. 9,240	1% Triton X100
Temperature 120°F (48.9°C)				
Port Hueneme	73.4	0	Flex. 33,990	
Port Hueneme	0	70.2	Flex. 33,410	1% Triton X100
Port Hueneme +15% Styrene	0	71.0	Flex. 35,470	1% Triton X100

$$*\% \text{ Water or surfactant} = \frac{\text{wt of water or surfactant}}{\text{dry wt of mat}} \times 100$$

These results indicate that at a high ambient temperature (120°F), Port Hueneme resin will give satisfactory strengths when used under wet conditions and the use of surfactants will not result in any increase in flexural strength.

Tensile strengths were determined for Port Hueneme resin, Port Hueneme resin containing 15 percent styrene and DERAKANE 510-A-40 containing 15 percent styrene under wet conditions, 70 percent water with and without Triton X100 and at 75°F (23.9°C). The lowest tensile strength obtained was 16,630 psi to a high of 26,300 (see Table 15). In all cases, the tensile strength was greater than the 13,000 psi specified in the contract.

#### F. INFLUENCE OF RESIN DENSITY

As discussed previously, if satisfactory flexural strengths are to be obtained it is necessary that the resin penetrate the woven roving and displace the water. In order to accomplish this, the resin must be fluid with low viscosity, and also it should be dense since gravity acting on the density difference between the resin and the water

supplies the driving force. This is supplemented by mechanical work supplied by the roller on the fluid filled fiberglass mat. One of the most dense resins available is a brominated vinyl ester resin DERAKANE 510-A-40 manufactured by The Dow Chemical Company. This resin has a density of 1.22 as compared to 1.093 for Port Hueneme resin. The first tests were made using the recommended methyl ethyl ketone peroxide catalyst but the laminates would not cure properly under wet conditions. The catalyst was changed to cumene hydroperoxide and the Port Hueneme resin promoter with which satisfactory cures were obtained. Laminates prepared at 25 and 70 percent water had flexural strengths of 15,240 psi and 14,310 psi, respectively. This resin did not show the desired result of high flexural strength due to density. Surprisingly, little change in strength resulted with increased water saturation. The DERAKANE 510-A-40 was then diluted with 15 percent styrene to reduce the viscosity from 335 cps to 85 cps and the density from 1.22 to 1.17. Laminates made with DERAKANE 510-A-40 + 15% styrene had a flexural strength of 30,000 psi at 25 percent water (Table 12). and 24,160 psi at 71.4 percent water. Laminates prepared from mats containing 28.6 and 68.8 percent of a one percent solution of Triton X100 gave flexural strengths of 26,570 psi and 30,300 psi, respectively. The influence of further dilution of the DERAKANE 510-A-40 with styrene was continued using DERAKANE with an additional 20 percent styrene. Flexural strengths of 25,390 psi were obtained with laminates prepared from fiberglass mats containing 70 percent water and 29,130 psi from mats containing 70.2 percent of one percent Triton X100; no improvement over the DERAKANE 510-A-40 plus 15 percent styrene. The results obtained with the DERAKANE 510-A-40 indicate that low resin viscosity is more important in obtaining good resin penetration into the woven roving than resin density. The DERAKANE 510-A-40 plus 15 percent of styrene gives flexural strengths that are at the low end of the flexural strength specification without the use of a surfactant. When used in conjunction with Triton X100 it produces laminates that meet specifications for flexural strength. It does not meet the five year shelf life specification and when diluted with styrene shows poor reactivity, see previous section on reactivity. It is the best resin tested for use under wet conditions and it and the other vinyl ester resins should be investigated further for use under wet conditions.

#### G. MISCELLANEOUS RESINS

Selectron SR3703 (Port Hueneme resin without added stabilizer) was investigated to determine if a more reactive resin would give improved strengths under wet conditions. The SR3703 when used with fiberglass mats containing 5 percent water gave laminates with flexural strengths of 20,000 to 26,000 psi an increase of about 50 percent over the Port Hueneme resin (Table 13). When the water content in the mats was increased to 25 percent the flexural strength obtained with the SR3703 laminates were equal to, but no better than,

that obtained with Port Hueneme resin. The Kirtland Primary resin (76% Altek 8-52 and 24% DERAKANE 510) was also evaluated and showed no advantage over Port Hueneme resin when used under wet conditions (see Table 13).

#### H. FIBERGLASS MAT TREATMENT

In an effort to obtain improved flexural strengths under wet conditions the FABMAT C-4020 was treated with various organic silane compounds to increase the hydrophobicity of the fiberglass. If the glass fibers could be made more hydrophobic, this should result in better resin penetration into the woven roving and improved flexural strengths. The FABMAT C-4020 was treated with dichlorodimethylsilane, octadecyltrichlorosilane and diphenyldichlorosilane. The fiberglass mats were silaned by both vapor and liquid phase treatment. The results obtained are presented in Table D.

TABLE D  
Effect of Silane Treatment of FABMAT C-4020  
on Flexural Strength

Run No.	% Water	Flexural Strength, psi	Remarks
<u>Port Hueneme Resin + 10% Styrene</u>			
0105B	25.3	24,420)	Mat treated, vapor phase octadecyltrichlorosilane
0206A	70.8	16,880)	
0111C	0	17,330)	Mat treated with octadecyltrichlorosilane in toluene
0112A	24.9	21,080)	
<u>Port Hueneme Resin + 15% Styrene</u>			
0109B	24.5	17,400)	Vapor phase octadecyltrichlorosilane
0109C	0	18,060)	
0126A	25.8	27,500)	Vapor phase diphenyldichlorosilane
0206A	70.8	16,880)	

In no case did an increase in flexural strength result from the use of silane treated fiberglass as compared to laminates prepared from untreated FABMAT C-4020.

SECTION VI  
ACCELERATED SHELF LIFE STUDIES

Accelerated shelf life studies of Port Hueneme resin and Port Hueneme resin with 15 percent added styrene have been made. This was done to determine if the addition of styrene to the Port Hueneme resin would have an adverse<sup>2</sup> effect on the shelf life at 75° F. According to the work of Filter<sup>2</sup> and Lard<sup>3</sup>, the shelf life at 75° F for any given resin system can be predicted from the elevated temperature studies. A straight line is obtained when the shelf life is plotted against the reciprocal of the absolute temperature and the point at which this line intercepts the 75° F line is the 75° F shelf life. Shelf lives predicted from accelerated aging studies based on field experience are conservative. The following shelf lives were obtained:

Resin	Shelf Life Hours	
	80°C	120°C
Port Hueneme	269	10
Port Hueneme + 15% styrene	262	9

The shelf life vs reciprocal of the absolute temperature plot is given in Figure 16. The addition of the 15 percent styrene has a negligible effect on the shelf life of this polyester resin since both resins have estimated shelf lives of over 11 years. The fact that the Port Hueneme resin had an estimated shelf life this long was rather surprising since at the time of the initiation of the test the resin had been in outside storage at Port Hueneme for over a year.

The DERAKANE 510-A-40 vinyl ester resin and DERAKANE 510-A-40 containing 15 percent styrene were also investigated and were found to have shelf lives of less than one hour at 120°C. Toluhydroquinone (THQ) and 2,4 dinitrophenol (DNP) were then tested as stabilizers for the DERAKANE 510-A-40 containing 15 percent styrene at 120°C. The following shelf lives were obtained (see Figure 16):

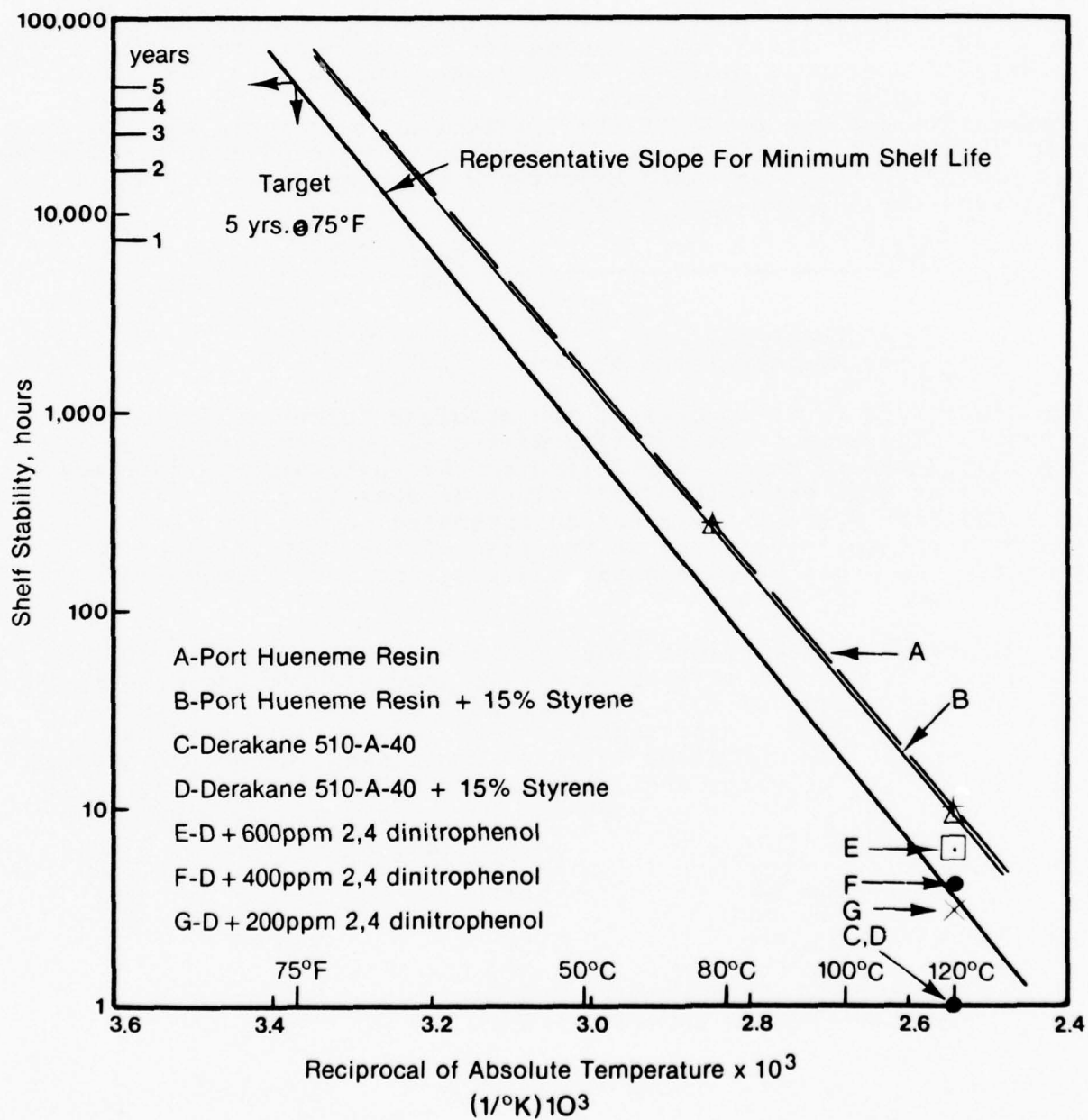
Stabilizer	Shelf Life, 120°C
0	Less than 1 hr
600 ppm THQ	2 hrs
600 ppm DNP	6 hrs
400 ppm DNP	4 hrs
200 ppm DNP	2 hrs
400 ppm THQ+200 ppm DNP	5 hrs
300 ppm THQ+200 ppm THQ	5 hrs

<sup>2</sup>Kirtland AFB, "Expedient Surfacing Materials", by H. E. Filter and S. S. Drake, AFWL-TR-73-70, (Oct. 1973, The Dow Chemical Co.).

<sup>3</sup>E. W. Lard, R. G. Rice, E. E. Stahly, "Storage Stability of Unsaturated Polyesters", Ind. Eng. Chem. Prod. Res. Develop., Vol. 10, No. 4, P. 391 (1971).

Figure 16

## SHELF LIFE vs TEMPERATURE



The addition of 600 ppm of 2,4 dinitrophenol does result in significant stabilization increasing the 75°F shelf life to 5 years. Unfortunately, this also results in decreased reactivity and a satisfactory cure can no longer be obtained with benzoyl peroxide or cumene hydroperoxide with the resin containing 400 ppm or 600 ppm of 2,4 dinitrophenol. The toluhydroquinone and 2,4 dinitrophenol did not show any synergistic stabilization with the DERA-KANE 510-A-40 plus 15 percent styrene as was observed by Drake, et al<sup>1</sup>, for the Port Hueneme resin.

## SECTION VII

## CONCLUSIONS

A system of chemical components has been developed for the field placement of fiberglass reinforced plastic soil surfacings under wet conditions that is superior to that presently used and is usable with the basic spray equipment now used by the Marine Corps. It does require an additional spray and rolling step before application of the resin.

The presence of 70 percent water in the FABMAT C-4020 and in the soil results in laminates that have flexural strengths of about 4,000 psi when fabricated from the presently used Selectron RS 50338 resin. The same flexural strength is obtained whether the wet fiberglass mat is used on a dry or wet substrate. The presence of as little as five percent moisture in the mats results in a 75 percent loss in flexural strength. This loss in strength is due to the lack of resin penetration into the woven roving layer of the FABMAT C-4020. Laminates prepared from chopped strand fiberglass mats containing 25 percent water that permit easy resin penetration, have a negligible loss in flexural strength as compared to a dry mat prepared laminate.

The addition of styrene to the Port Hueneme resin (RS50338) results in decreased viscosity and improved flexural strengths. It was found that the optimum results were obtained on the addition of 15 percent of styrene. At this styrene concentration the lowered resin viscosity, 80 cps, resulted in a flexural strength of 18,770 psi for a laminate prepared from water saturated FABMAT C-4020, which is a considerable improvement over the 4,000 psi obtained with undiluted Port Hueneme resin.

The incorporation of a nonionic surfactant, Triton X100, into the water in the fiberglass mat results in better resin penetration, or better water displacement, and increased flexural strength. The use of 1 percent solution of Triton X100 in the FABMAT C-4020 results in a flexural strength of 17,000 psi using laminates prepared from Port Hueneme resin and saturated mats. Under the same conditions, saturated mats, but using Port Hueneme resin plus 15 percent styrene, flexural strengths of 25,000 psi were obtained. This is within 10 percent of the desired 28,000 psi. The addition of the styrene does not change the shelf life of the resin as measured by gelation.

In field operations under wet conditions the real shelf life will be greatly reduced since these flexural strengths can not be obtained with high resin viscosity.

At 120°F the desired flexural strength can be obtained under wet conditions without surfactant or resin dilution. At 33°F flexural strengths greater than 10,000 psi were not obtained with either the use of a surfactant or diluted Port Hueneme resin.

DERAKANE 510-A-40, a brominated vinyl ester resin, when diluted with 15 percent styrene gives a flexural strength of 24,000 psi under wet conditions. When the saturated FABMAT C-4020 contains 1 percent Triton X100, laminates can be produced having flexural strengths of 30,000 psi; meets specification. This resin does not have the desired shelf life or reactivity.

All of the laminates prepared from saturated mats using Port Hueneme resin, styrene diluted Port Hueneme resin and DERAKANE give tensile strengths greater than 16,000 psi, well over the specified 13,000 psi.

Efforts to improve the flexural strength of laminates prepared under wet conditions by silane treatment of the fiberglass mat was not effective.

SECTION VIII  
RECOMMENDATIONS

A chemical component system has been developed that can be used to construct fiberglass reinforced plastic surfacing for soils under wet conditions. It is recommended that a field trial be made. This should be done to determine if field fabrication will result in the development of deficiencies in the incorporation of the surfactant and resin into the wet fiberglass mats. These tests should be made using both Port Hueneme resin (RS50338) plus 15 percent styrene and DERAKANE 510-A-40 with 15 percent styrene.

Development costs prohibited complete investigation in several areas. In view of this it is recommended that further work be done on the following subjects:

1. Studies should be made to determine the optimum surfactant and method of application to incorporate the surfactant into the water in the fiberglass mats.
2. A stabilizer should be developed to increase the shelf life of DERAKANE 510-A-40.
3. A need exists for a more active and controllable catalyst for stabilized DERAKANE 510-A-40 plus styrene.
4. Investigate other vinyl ester resins.

It is recommended that further efforts be made to obtain a woven fiberglass fabric mat made from spun strand roving with a chromium size to determine if the improved resin penetration into such a fabric would permit the use of more viscous resins.

SECTION IX  
APPENDIX  
TEST RESULTS

TABLE 1  
RESIN REACTIVITY  
(All tests made using 4% Vanadium Ten Cem, Control S5335, except where noted)

Test No.	Catalyst - phr		DMT <sup>3</sup>	DDM <sup>4</sup>	Gel Time Min	Reactivity		Barcol <sup>5</sup> Hardness
	CHP <sup>1</sup>	V <sup>2</sup>				Exotherm ΔT°C	Min	
Port Hueneme Resin RS 50338								
0824A	0.75	0.15	0.10	0	11.8	152	20	47/48
0824B	0.75	0.15	0.10	0	10.7	152	20	45/43
0824C	1.25	0.186	0.124	0	6.1	176	9	47/46
0824E	1.0	0.15	0.10	0	8.6	152	15	48/49
0825A	0.75	0.114	0.076	0	17.6	133	36	Cured
20 grams of water added to the 20 grams of resin in dish for next two runs.								
0824D	1.25	0.186	0.124	0	6.1	106	15	30/47
0824F	1.0	0.15	0.10	0	9.0	70	26	30/42
No Water in following runs.								
0116A	1.0	0.1	0.15	0	7.9	145	15	45/44
0116B	1.0	0.1	0.10	0	12.0	133	24	44/46
0116C	1.0	0.1	0.12	0	10.6	153	20	45/45
0116D	1.0	0.15	0.15	0	7.1	148	12	48/44
0116E	1.0	0.15	0.10	0	11.0	153	20	48/44
1013A	1.5	0.225	0.15	0	5.6	176	8	43/40
1013B	1.5	0.225	0.15	0.1	6.9	163	11	45/38
1013D	1.5	0.225	0.15	0.2	8.8	149	15	37-43/42

(Continued)

TABLE 1 (Continued)

Test No.	Catalyst - phr		DMT <sup>3</sup>	DDM <sup>4</sup>	Reactivity		Barcol <sup>5</sup> Hardness
	CHP <sup>1</sup>	V <sup>2</sup>			Gel Time Min	Exotherm $\Delta T^{\circ}C$ Min	
1012	1.5	0.225	0.15	0.225	12.4	140	47/47
1013E	1.5	0.225	0.15	0.3	28.3	146	46/42
1017A	1.5	0.27	0.18	0.2	7.2	146	47/41-46
1014A	1.5	0.27	0.18	0.3	11.3	148	Cured
1017B	1.5	0.27	0.18	0.4	29.3	135	33-45/44
1017C	1.5	0.27	0.18	0.5	61.4	122	43-46/44
0913B	2.0	0.3	0.2	0	3.8	185	45-48/42
0913A	2.0	0.3	0.2	0.1	4.6	186	38-45/43
0913C	2.0	0.3	0.2	0.2	5.3	202	43/43
0914B	2.0	0.3	0.2	0.3	8.4	182	44/43
0914C	2.0	0.3	0.2	0.4	20.1	168	46/45
0914A	2.0	0.3	0.2	0.78	183	165	46/42-47
1215A	2.5*	0.375	0.25	0.5	7.2	159	43/43
1215B	2.5	0.375	0.25	0.6	17.2	138	45/43-46
1215C	2.5	0.45	0.3	0.6	7.2	167	40-45/42
1215D	2.5	0.45	0.3	0.64	10.2	153	42-45/43
<b>Port Hueneme Resin + 10% Styrene</b>							
1209A	1.0	0.15	0.10	0	8.2	149	45-48/40-45
0323A	1.0	0.15	0.10	0	10.0	140	43-47/39-43
0323B	0.75	0.1125	0.075	0	15.8	143	46/41
1209B	0.56	0.105	0.07	0	15.2	109	42/33-38
1209C	1.5	0.225	0.15	0.2	8.1	165	45/35-38

(Continued)

TABLE 1 (Continued)

Test No.	Catalyst - phr		DMT <sup>3</sup>	DDM <sup>4</sup>	Reactivity		Barcol <sup>5</sup> Hardness
	CHP <sup>1</sup>	V <sup>2</sup>			Gel Time Min	Exotherm $\Delta T^{\circ}C$ Min	
1212A	1.5	0.225	0.15	0.3	9.3	151	42/38
1212B	1.5	0.225	0.15	0.4	19.6	146	45/44
1212D	2.0	0.3	0.2	0.4	7.9	148	40/37
1213B	2.5	0.375	0.25	0.5	6.5	160	41/36
1213C	2.5	0.375	0.25	0.55	9.0	164	43/39
1213A	2.5	0.375	0.25	0.625	17.3	160	43/38

(Continued)

TABLE 1 (Continued)

Test No.	Catalyst - phr			DDM <sup>4</sup>	Reactivity		Barcol <sup>5</sup> Hardness
	CHP <sup>1</sup>	V <sup>2</sup>	DMT <sup>3</sup>		Gel Time Min	Exotherm $\Delta T^{\circ}C$	
<u>Port Hueneme Resin + 15% Styrene</u>							
0127A	1.0	0.15	0.10	0	10.9	162	41/36
0127B	1.5	0.225	0.15	0	6.8	167	46/39
0127D	2.5	0.375	0.25	0.45	7.7	182	43/37
0127C	2.5	0.375	0.25	0.5	14.0	146	46/39
<u>Port Hueneme Resin + 20% Styrene</u>							
0215A	1.0	0.15	0.10	0	10.5	177	46/37
0215B	0.75	0.1125	0.075	0	14.5	146	45/40
0215D	2.5	0.375	0.25	0.45	9.4	202	Shattered
0215C	2.5	0.375	0.25	0.5	14.5	199	Shattered
<u>Port Hueneme Resin V-Control LB-267-43</u>							
0227A	1.0	0.15	0.10	0	11.3	127	47/44
0227B	0.75	0.1125	0.075	0	21.5	--	37/23
Fresh batch promoter							
0227D	1.0	0.15	0.10	0	10.5	135	45/40
0227E	0.75	0.1125	0.075	0	20.2	92	43/33-38
0301D	1.0	0.15	0.10	0	8.9	144	Cured
0301E	0.75	0.1125	0.075	0	15.2	105	Cured
0306C	1.0	0.15	0.10	0	8.9	139	Cured
0228F	2.5	0.375	0.25	0.34	7.0	179	Shattered
0228D	2.5	0.375	0.25	0.406	11.2	161	Shattered
0228B	2.5	0.375	0.25	0.438	13.2	164	Shattered
0228C	2.5	0.375	0.25	0.438	14.3	163	Shattered
0228E	2.5	0.375	0.25	0.5	31	157	Shattered
Vand DMT added separately							
0303A	1.0	0.15	0.10	0	7.9	137	Cured

<sup>1</sup>CHP - Cumene hydroperoxide<sup>2</sup>V - 4% V TEN CEM<sup>3</sup>DMT - N, N dimethyl-p-toluidine<sup>4</sup>DDM - LUPERSOL-DDM, 60% methyl ethyl ketone peroxide in dimethylphthalate<sup>5</sup>Barcol Hardness - Top/Bottom

TABLE 2  
INFLUENCE OF TEMPERATURE ON REACTIVITY

Temp °F	Catalyst CHP <sup>1</sup>	Composition- Promoter <sup>2</sup>	-phr <sub>3</sub> DDM <sup>3</sup>	Reactivity			Barcol Hardness
				Gel Time Min.	Exotherm Min. ΔT-°C		
Port Hueneme Resin + 15% Styrene Liquid Jacket							
32	2.0	0.5	-	18.5	46.2	92	35-40/33
32	3.125	0.78	-	14.2	37	63	39-40/0
120	0.375	0.094	-	10.3	-	-	21/0
120	0.5	0.125	-	6.4	-	-	42/34-38
120	1.0	0.25	0.3125	8.4	10.5	127	Shattered
120	1.0	0.25	0.375	13.3	17	136	Shattered
Air Jacket							
32	2.0	0.5	-	12.6	67	30	39-40/36-38
32	3.125	0.78	-	9.1	47	73	39-42/0?
Port Hueneme Resin Liquid Jacket							
32	1.6	0.4	-	13.8	45.5	97	42/15
32	2.24	0.56	-	8.0	22.	124	42/17
120	0.5	0.125	-	6.0	-	-	38-42/42
120	0.375	0.094	-	11.0	-	-	35/38-42

<sup>1</sup>CHP - Cumene Hydroperoxide

<sup>2</sup>Promoter - 3 parts 4% V Ten Cem<sup>(R)</sup> to 2 part N,N dimethyl-p-toluidine

<sup>3</sup>\*DDM - LUPERSOL<sup>(R)</sup> DDM, 60% methylethyl ketone peroxide in dimethylphthalate

<sup>4</sup>Barcol Hardness - Top/Bottom

TABLE 3  
 INFLUENCE OF PROMOTER AND INHIBITOR ON THE REACTIVITY  
 OF PORT HUENEME RESIN

Test No.	Catalyst Composition-phr				Reactivity			Barcol <sup>5</sup> Hardness
	CHP <sup>1</sup>	V <sup>2</sup>	DMT <sup>3</sup>	DDM <sup>4</sup>	Gel Time Min.	Exotherm $\Delta T^{\circ}C$	Min.	
0221E	1.0	0.15	0.15	-	7.6	147	14	44-46/43-44
0221F	0.75	0.1125	0.1125	-	14.0	131	30.7	45-46/40
0222B	1.0	0.15	0.15	-	7.8	145	15.5	-
0330A	1.0	0.125	0.125	-	10.3	158	19	45-47/41-42
0330B	1.0	0.1	0.1	-	12.4	124	30	49/44-45
0330D	1.0	0.18	0.12	-	7.9	139	14.8	47-48/37
0330G	1.0	0.18	0.12	-	7.8	139	14.0	43-45/37-38
0330E	1.0	0.15	0.10	-	8.7	154	16.0	46-48/42
0330F	1.0	0.15	0.10	-	8.6	152	17.5	45-47/38-41
0330C	1.0	0.12	0.08	-	12.2	115	29	45-48/41-42
0330H	1.0	0.12	0.08	-	11.3	135	24.3	42-43/40-42
0221H	2.5	0.375	0.375	0.5	28	173	29.7	Shattered
0329C	2.5	0.375	0.375	0.45	25.7	173	29	Shattered
0329B	2.5	0.375	0.375	0.406	17.8	177	21	Shattered
0222D	2.5	0.375	0.375	0.406	16.3	178	16.8	Shattered
0222F	2.5	0.375	0.375	0.375	7.9	176	9.5	Shattered
0222E	2.5	0.375	0.375	0.33	4.9	188	6.0	Shattered
0222C	2.5	0.375	0.375	0.2	3.0	186	40	Shattered
0330I	2.5	0.0936	0.0624	0	18.5	-	-	Poor Cure
0330J	2.5	0.078	0.078	0	21.5	92	55	Poor Cure

<sup>1</sup>CHP - Cumene hydroperoxide

<sup>2</sup>V - 4% V TEN CEM (new batch) LB-267-43

<sup>3</sup>DMT - N,N dimethyl-p-toluidine

<sup>4</sup>DDM - LUPERSOL-DDM, 60% methylethyl ketone peroxide in dimethylphthalate

<sup>5</sup>Barcol hardness - Top/Bottom

TABLE 4  
 REACTIVITY OF SELECTRON SR 3703\*

No.	Catalyst Composition-phr			Reactivity			Barcol <sup>4</sup> Hardness
	CHP <sup>1</sup>	Promoter <sup>2</sup>	DDM <sup>3</sup>	Gel Time	$\Delta T^{\circ}C$ ,	Min.	
1111A	1.0	0.25	0	<1.3 min	175	- 2.5	48-49/42-43
1111B	0.5	0.125	0	2.9	177	- 4.8	46-49/43-46
1111C	0.5	0.0625	0	8.4	113	- 16.25	43-46/38-39
1111D	0.5	0.25	0.4	>32	163	- 78	46-48/42-48
1111E	0.5	0.25	0.2	5.2	153	- 9.5	46-49/41-42
1111F	0.5	0.25	0.3	26.5	159	- 30	44/39-41
1111G	0.5	0.125	0.2	-	184	- 61	45-48/45-48
1111H	0.5	0.125	0.1	10	Lost	- 15	45-58/43-45
1114D	0.5	0.25	0.25	15.9	155	- 24	47/46-48
1115A	0.5	0.25	0.25	17.5	163	- 29	--
1115B	0.5	0.25	0.25	16.9	154	- 25.5	--
1115D	0.5	0.25	0.25	17.1	171	- 23	--
1116C	1.5	0.375	0.21	8.7	169	- 13.5	Cracked
1121A	1.0	0.25	0.2	5.1	174	- 8	45-47/42-43
1121B	1.0	0.25	0.3	29.6	168	- 35	46-47/43-44
1121C	1.0	0.5	0.3	2.4	180	- 4.25	45-47/42-43
1121D	1.0	0.5	0.5	7.7	151	- 11.3	43-44/42-43

\* Same as Port Hueneme resin except no added inhibitor.

1. Cumene hydroperoxide.

2. 3 parts 4% Vanadium TEN CEM, 2 parts N,N dimethyl-p-toluidine.

3. Lupersol DDM<sup>(R)</sup> - Methyleneethylketone peroxide in dimethyl phthalate.

4. Top/Bottom

TABLE 5  
 REACTIVITY OF KIRTLAND PRIMARY RESIN\*

No.	Catalyst Composition, phr			Reactivity		Barcol <sup>4</sup> Hardness
	CHP <sup>1</sup>	Promoter <sup>2</sup>	DDM <sup>3</sup>	Gel Time	$\Delta T^{\circ}C$ , Min	
1116B	1.0	0.25	0.2	78 min	155 - 100	42/45/36-38
1116D	1.0	0.25	0	4.1	175 - 8.5	43-46/44-45
1116E	1.0	0.25	0.1	9.2	106 - 11	42-43/42

\* Kirtland Primary Resin - 76% ALTEK<sup>(R)</sup> 8-52 and 24% DERAKANE 510

1. Cumene hydroperoxide.

2. 3 parts 4% Vanadium TEN CEM<sup>(R)</sup>, 2 parts N,N dimethyl-p-toluidine.

3. Lupersol DDM<sup>(R)</sup>- Methyleneethylketone peroxide in dimethylphthalate.

4. Top/Bottom

TABLE 6  
 REACTIVITY OF DERAKANE 510-A-40

Test No.	Catalyst Composition - phr			Reactivity		Barcol <sup>4</sup> Hardness
	CHP <sup>1</sup>	Promoter <sup>2</sup>	DDM <sup>3</sup>	Gel Time	$\Delta T^{\circ}C$ Min	
1207B	1.0	0.25	-	12.1 min	13-36	0
1207C	1.0	0.5	-	9.2	85-22.5	36-38/27
1208A	1.5	0.75	-	9.6	88-20	35-36/30-32
1207D	2.0	0.5	-	-	56-22.5	32-34/16-17
1208B	2.0	1.0	-	8.6	82-15.2	33-35/28
	<u>CoN<sup>5</sup></u>	<u>DMA<sup>6</sup></u>				
1208C	0.2	0.1	1.5	15.7	56-37.2	33-36/22
1208D	0.2	0.2	1.5	11.2	82-21.8	37-38/27-29

1 - Cumene hydroperoxide.

2 - 3 part 4% Vanadium Ten Cem, 2 parts N,N dimethyl-p-toluidine

3 - Lupersol DDM - Methyleneethylketone peroxide in dimethylphthalate.

4 - Top/Bottom

5 - Cobalt napthenate, 6% Co

6 - N,N-dimethylaniline

TABLE 7  
 REACTIVITY OF DERAKANE 510-A-40  
 WITH 15% ADDITIONAL STYRENE  
 Benzoyl Peroxide Catalyst

Test No.	Catalyst - phr		Reactivity			Barcol Hardness
	BZQ-40 <sup>1</sup>	DMA <sup>2</sup>	Gel Time Min.	Exotherm $\Delta T^{\circ}C$	Min.	
0126D	2.66	0.21	15	83	29	33/25
0126E	3.75	0.3	9.2	92	20	30/22

<sup>1</sup>BZQ-40; 40% Benzoyl peroxide pourable paste (Witco Chemical Corporation)

<sup>2</sup>DMA - N,N Dimethylaniline

TABLE 8  
 REACTIVITY OF DERAKANE 510-A-40  
 CONTAINING 15% STYRENE

Test No.	Catalyst - phr			Reactivity			Barcol <sup>4</sup> Hardness
	CHP <sup>1</sup>	V <sup>2</sup>	DMT <sup>3</sup>	Gel Time Min.	Exotherm $\Delta T^{\circ}C$	Min.	
1221A	1.0	0.3	0.2	19.3	45	59	21/6
1221C	1.0	0.6	0.4	23.5	-	>60	-
1221B	2.0	0.6	0.4	16.2	66	36	33/22
0123C	2.5	0.45	0.3	20.7	-	>55	-
Resin + 600 ppm 2,4 dinitrophenol							
0310A	2.0	0.6	0.4	45	-	-	0
0310B	3.0	0.9	0.6	33.3	4	~65	0
	DDM <sup>5</sup>	DMA <sup>6</sup>	CoN <sup>7</sup>				
1215E	1.0	0.15	0.15	24.5	<10	>62	0
1215F	2.0	0.3	0.3	17.6	42	42	28/2
1227A	1.0	0.15	0.3	15.7	35	51	18/0
1227B	1.5	0.225	0.45	11.3	63	32	30/21
1227C	1.0	0.2	0.4	13.0	60	36	32/15
1227D	1.5	0.3	0.6	10.0	78	21	35/20

- 1 - Cumene hydroperoxide
- 2 - 4% Vanadium Ten Cem
- 3 - N,N dimethyl-p-toluidine
- 4 - Top/Bottom
- 5 - Lupersol DDM - methyl ethyl ketone
- 6 - N,N - dimethylaniline
- 7 - Cobalt naphthenate, 6% Co

TABLE 9  
EFFECT OF WATER ON FLEXURAL STRENGTH

---

Port Hueneme Resin

Com- posite No.	Water %	Catalyst - phr			Gel Time Minutes Surplus	Exo- therm Min.	Resin %	Flexural Strength psi
		CHP <sup>1</sup>	Pro- moter <sup>2</sup>	DDM <sup>3</sup>				
0912	0	0.96	0.24	0	-	29	-	39,600
1025A	4.8	1.0	0.25	0	11	20	58.9	10,830
1024A	10.2	1.0	0.25	0	8	16	59.0	12,030
0928A	25.8	2.0	0.5	0.4	-	20	58.7	12,960
0928B	25.8	2.0	0.5	0.4	-	28	50.2	11,700
1012A	27.4	1.5	0.375	0.225	13	27	61.9	13,460
1011B	27.8	2.0	0.5	0.31	8	14	63.0	7,280
1007W	28.4	2.0	0.5	0.31	-	28	59.9	17,210
1027A	50.4	2.0	0.5	0.32	11	34	61.9	6,140
1018B	71.4	1.5	0.45	0.3	11	34	63.0	3,620
1018C	71.7	2.0	0.5	0.31	8	23	60.4	3,860

---

<sup>1</sup>CHP - Cumene Hydroperoxide

<sup>2</sup>Promoter - 3 parts 4% V Ten Cem<sup>(R)</sup> to 2 part N,N dimethyl-p-toluidine

<sup>3</sup>DDM - LUPERSOL<sup>(R)</sup> DDM, 60% methylethyl ketone peroxide in dimethylphthalate

TABLE 10  
COMPOSITES PREPARED ON WATER SATURATED SAND  
WITH PORT HUENEME RESIN

Com- posite No.	Mat Water %	Catalyst - phr		Ge1 Time Minutes Surplus	Exo- therm Minutes	Resin %	Flexural Strength psi	Remarks	
		CHP <sup>1</sup>	Promoter <sup>2</sup>						
1027B	0	1.0	0.25	-	10	18	59.3	4,630	Woven up, not sequential
1028A	0	2.0	0.5	0.31	8	16	62.4	8,600	" " "
1028B	70.4	2.0	0.5	0.31	10	31	63.1	4,450	" " "
1101A	0	1.5	0.375	0.225	11	32	55.3	9,760	Woven up, sequential
1103A	0	1.5	0.375	0.225	13	28	59.1	14,680	" " "
1103B	0	1.5	0.375	0.225	14	28	61.5	16,600	** " " "
1110A	0	1.5	0.375	0.225	12	22	63.1	14,400	Woven down, sequential

\*\*Dichlorodimethyl silane treated mat - washed

- <sup>1</sup>CHP - Cumene Hydroperoxide
- <sup>2</sup>Promoter - 3 parts 4% V Ten Cem<sup>(R)</sup> to 2 part N,N dimethyl-p-toluidine
- <sup>3</sup>DDM - LUPERSOL<sup>(R)</sup> DDM, 60% methyl ethyl ketone peroxide in dimethylphthalate

TABLE 11

## INFLUENCE OF FABRICATION METHODS ON FLEXURAL STRENGTH\*

All tests Port Hueneme resin RS50338

Com- posite No.	Mat Water %	Catalyst - phr		Gel Time Minutes Surplus	Exotherm Minutes	Resin %	Flexural Strength psi	Remarks
		CHP	Promoter <sup>2</sup> DDM <sup>3</sup>					
1104B	25	1.5	0.375	11	27	61.3	11,050	Woven up, sequential
1023B	27	1.5	0.375	9	--	60.4	16,300	Woven up, sequential
1012A	27.4	1.5	0.375	13	27	61.9	13,460	Woven up, not sequential
1107B	26.4	1.5	0.375	12	28	60.8	19,260	Woven down, not sequential
1107C	25.8	1.75	0.5	8	12	63.4	17,600	Woven down, not sequential
1109A	25.7	1.5	0.375	12	21	66.2	14,110	Woven down, sequential, resin poured not rolled
1109B	27.0	1.5	0.375	13	22	66.1	13,060	Woven down, sequential, resin poured not rolled
1108A	0	1.0	0.25	10	19	65.4	35,990	Woven down, sequential
0912	0	0.96	0.24	--	29	--	39,600	Woven down, not sequential
1019A	70.6	1.5	0.45	11		61.4	1,860	One layer Fabmat C-4020
1109E	5.2	1.5	0.375	12	23	64.9	13,660	One layer Fabmat C-4020

(Continued)

TABLE 11 (Continued)

Com- posite No.	Mat Water %	Catalyst - phr		Gel Time Minutes Surplus	Exotherm Minutes	Resin %	Flexural Strength psi	Remarks
		CHP <sup>1</sup>	Promoter <sup>2</sup> DDM <sup>3</sup>					
1020A	0	1.0	0.25	0	36	60.3	23,500	One layer Fabmat C-4020
1020C	0	1.5	0.375	0.21	34	58.4	22,320	One layer Fabmat C-4020
1206A	0	1.0	0.25	0	26	61.8	21,750	Six layers of 2 oz./ft <sup>2</sup> chopped strand mat
1206B	25.5	1.5	0.375	0.21	32	63.2	18,360	Six layers of 2 oz./ft <sup>2</sup> chopped strand mat
1207A	26.0	2.0	0.5	0.32	20	62.4	19,530	Six layers of 2 oz./ft <sup>2</sup> chopped strand mat
0109A	69.8	2.5	0.625	0.55	51	63.2	14,440	Six layers of 2 oz./ft <sup>2</sup> chopped strand mat
1214C	0	1.0	0.25	0	28	58.0	41,000	Four layers of 18.5 oz. 1 yd <sup>2</sup> woven roving, two layers 2 oz./ft <sup>2</sup> of chopped strand
1214D	24.5	2.0	0.5	0.31	27	56.4	9,830	

\* All composites 2 layers of FABMAT C-4020 except where noted.

<sup>1</sup>CHP - Cumene Hydroperoxide

<sup>2</sup>Promoter - 3 parts 4% V Ten Cem<sup>(R)</sup> to 2 part N,N dimethyl-p-toluidine

<sup>3</sup>DDM - LUPERSOL<sup>(R)</sup> DDM, 60% methylethyl ketone peroxide in dimethylphthalate

TABLE 12

## INFLUENCE OF RESIN VISCOSITY AND SURFACTANTS ON FLEXURAL STRENGTH

Com- pos- ite No.	Resin	Mat Fluid %	Catalyst - phr		Gel Time Minutes	Exo- therm Min.	Resin %	Flexural Strength psi	Remarks	
			CHP <sup>1</sup>	Promo- ter <sup>2</sup>						DDM <sup>3</sup>
0118A	Port Hueneme	25.5TX1	2.5	0.625	0.55	7	26	59.9	25,280	TX1-1% solution Triton X100
0123A	"	69.6TX1	2.5	0.625	0.55	12	37	58.4	17,670	
0313C	"	72.9TX.5	2.5	0.625	0.46	8	25	57.5	16,820	TX.5-0.5% solution Triton X100
0214C	"	69.1CF	2.5	0.625	0.55	13	41	57.9	22,860	CF-1% solution Triton CF-76
0117A	"	25.1W 5.1TX1	2.5	0.625	0.55	10	33	55.5	16,590	W-% Water in Mat then sprayed with 1% sol'n of Triton X100
0117B	"	24.8W 8.6TX1	2.5	0.625	0.55	12	--	56.8	14,520	
0223A	"	71.4W	2.5	0.625	0.45	8	27	56.6	14,610	
0223B	"	11.1TX1 69.0W 7.4TX1	2.5	0.625	0.45	10	32	60.3	16,740	
0309A	"	72.4P	2.5	0.625	0.47	Did not cure				P-0.5% sol'n of Pyronate 50
0118B	"	24.7W 6.3A/c	2.5	0.625	0.55	7	26	58.0	21,490	A/c - 2 B alcohol (ethyl alcohol)
0119A	"	24.4 16.1A/c	2.5	0.625	0.55	8	37	59.7	20,770	

(Continued)

TABLE 12 (Continued)

Com- pos- ite No.	Resin	Mat Fluid %	Catalyst - phr		Gel Time Minutes Surplus	Exo- therm Min.	Resin Strength psi	Flexural Strength psi	Remarks	
			CHP <sup>1</sup> ter <sup>2</sup>	DDM <sup>3</sup>						
1219A	Port Hueneme + 10% Styrene	0	1.5	0.375	0.3	15	17	60.7	45,160	
1219B	"	24.9W	2.5	0.625	0.55	10	21	65.0	23,430	
1219C	"	25.5W	2.5	0.625	0.55	8	23	61.0	20,850	
0124B	"	24.1TX1	2.5	0.625	0.55	9	26	59.7	23,080	
1220A	"	70.8W	2.5	0.625	0.55	12	44	60.6	12,440	
0124A	"	68.1TX1	2.5	0.625	0.55	--	--	55.7	24,610	
0214B	"	24.9W	2.5	0.625	0.55	7	18	61.7	23,450	Paddle rolled
0201B	P.H. + 15% Styrene	0	1.0	0.25	0	11	19	58.0	42,260	
0201A	"	70.9W	2.5	0.625	0.47	9	38	61.0	18,770	
0213A	"	70.4TX1	2.5	0.625	0.48	10	34	57.2	23,320	
0301A	"	70.2TX1	2.5	0.625	0.4	7	23	57.6	26,850	
0301F	"	73.4CF	2.5	0.625	0.46	11	30	56.6	25,800	

(Continued)

TABLE 12 (Continued)

Com- pos- ite No.	Resin	Mat Fluid %	Catalyst - phr		Gel Time Minutes Surplus	Exo- therm Min.	Flexural Strength psi	Remarks	
			CHP <sup>1</sup>	Promo- ter <sup>2</sup>					
0213B	P.H. + 15% Styrene	69.0W 12.5TX10	2.5	0.625	0.5	9	--	19,660	Wet mat sprayed with 10% sol'n of Triton X100
0302F	"	70.3W 13.2A/c	2.5	0.625	0.47	12	--	10,360	Wet mat sprayed with 2B alcohol
0216B	P.H. + 20% Styrene	0	1.0	0.25	0	12	25	44,420	
0216A	"	26.0	2.5	0.625	0.47	10	31	21,750	
0215B	"	70.3	2.5	0.625	0.47	14	32	12,340	
0111B	Derakane 510-A-40	0	2.0	1.0	0	7	17	40,520	
0110B	"	24.6W	2.0	1.0	0	9	15	15,240	
0119B	"	70.9W	2.0	1.0	0	7	18	14,310	
0111A	"	0	--	--	--	12	26	42,100	1.5 phr DDM, 0.2 phr DMA, 0.2 phr CoN
0110A	"	24.7W	--	--	--	12	--	3,620	1.5 phr DDM, 0.2 phr DMA, 0.2 phr CoN

(Continued)

TABLE 12 (Continued)

Com- pos- ite No.	Resin	Mat Fluid %	Catalyst - phr		Gel Time Minutes Surplus	Exo- therm Min.	Resin %	Flexural Strength psi	Remarks
			CHP <sup>1</sup>	Promo- ter <sup>2</sup>					
0105A	Derakane 510-A-40 + 15% Styrene	0	--	--	12	29	57.9	42,960	1.5 phr DDM, 0.3 phr DMA, 0.6 phr Con
0104A	"	24.8W	--	--	12	--	62.1	14,190	"
0123C	"	25.5W	2.5	1.25	0	18	62.2	30,000	"
0124C	"	28.6TX1	2.5	1.25	0	17	62.7	26,570	"
0125B	"	26.1W	2.5	1.25	0	18	63.1	30,690	"
0125A	"	71.4W	2.5	1.25	0	16	65.9	24,160	"
0125C	"	68.8TX1	2.5	1.25	0	17	57.8	30,300	"
0209A	"	69.6W	--	--	9	24	59.4	26,040	1.4 phr B2Q-40, 0.28 phr DMA
0307B	Derakane 510-A-40 + 20% Styrene	0	2.0	1.0	0	19	56.4	43,010	
0307A	"	70.0W	2.5	1.25	0	19	55.7	25,390	
0308A	"	70.2TX1	2.5	1.25	0	19	59.9	29,130	

<sup>1</sup>CHP - Cumene Hydroperoxide

<sup>2</sup>Promoter - 3 parts 4% V Ten Cem (R) to 2 part N,N dimethyl-p-toluidine

<sup>3</sup>DDM - LUPERSOL(R) DDM, 60% methylethyl ketone peroxide in dimethylphthalate

TABLE 13

## MISCELLANEOUS RESIN LAMINATES

Com- pos- ite No.	Resin	Mat Fluid %	Catalyst - phr			Gel Time Minutes Surplus	Exo- therm Min.	Resin %	Flexural Strength	Remarks
			CHP <sup>1</sup>	ter <sup>2</sup>	DDM <sup>3</sup>					
1115E	Selectron									
	SR3703	0	0.5	0.25	0.25	14	60.3	30,740		
1114A	"	5.2W	0.5	0.25	0.25	11	58.3	20,190		
1115C	"	5.1W	0.5	0.25	0.25	10	61.8	26,080		
1121F	"	25.3W	1.0	0.5	0.5	6	64.2	13,870		
1128B	"	24.7W	1.0	0.5	0.55	10	64.9	10,600	dichlorodimethyl silane treated mat	
1122A	Kirtland									
	Primary	29.6W	1.0	0.25	0.11	9	60.7	17,850		
1122B	"	0	1.0	0.25	0.11	10	61.7	25,590	On 100% Saturated Sand	
1123A	Port									
	Hueneme	0	1.27	0.318	0	5	61.0	36,770	On Dry Sand	
1123B	"	0	1.27	0.318	0	6	61.9	36,710		

<sup>1</sup>CHP - Cumene Hydroperoxide<sup>2</sup>Promoter - 3 parts 4% V Ten Cem<sup>(R)</sup> to 2 part N,N dimethyl-p-toluidine<sup>3</sup>DDM - LUPERSOL<sup>(R)</sup> DDM, 60% methylethyl ketone peroxide in dimethylphthalate

TABLE 14  
EFFECT OF TEMPERATURE ON FLEXURAL STRENGTH

Composite No.	Resin	Temp °F	Mat Fluid %	Catalyst - phr			Resin %	Flexural Strength psi
				CHP <sup>1</sup>	Promoter <sup>2</sup>	DDM <sup>3</sup>		
0321A	Port Hueneme	33	74.1TX1	2.0	0.5	0	58.5	4,290
--	"	40	0	2.0	0.5	0	--	35,400
0320A	P.H. + 15% Styrene	33	72.3TX1	3.0	0.75	0	56.3	9,240
--	Port Hueneme	120	0	0.5	0.125	0	--	42,800
0327A	Port Hueneme	120	73.4W	1.0	0.25	0.3	61.8	33,990
0322A	Port Hueneme	120	70.2TX1	1.0	0.25	0.3	60.1	33,410
0322F	P.H. + 15% Styrene	120	71.0TX1	1.0	0.25	0.33	59.1	35,470

<sup>1</sup> CHP - Cumene Hydroperoxide

<sup>2</sup> Promoter - 3 parts 4% V Ten Cem<sup>(R)</sup> to 2 part N,N dimethyl-p-toluidine

<sup>3</sup> DDM - LUPERSOL<sup>(R)</sup> DDM, 60% methylethyl ketone peroxide in dimethylphthalate

TXI - 1% Triton X100

W - Water

TABLE 15  
LAMINATE TENSILE STRENGTH

Com- pos- ite No.	Resin	Mat Fluid %	Catalyst - phr		Gel Time Minutes	Surplus	Exo- therm Min.	Resin %	Tensile Strength psi	Remarks
			CHP <sup>1</sup>	Promo- ter <sup>2</sup>						
0314A	Port Hueneme	71.4	2.5	0.625	0.47	10	34	61.3	17,240	75°F Ambient Temperature
0314B	Port Hueneme	70.6TX1	2.5	0.625	0.47	10	33	62.4	18,050	
--	Port Hueneme	0	1.0	0.25	0	--	--	--	20,500	
0314C	Port Hueneme + 15% Styrene	70TX1	2.5	0.625	0.5	11	43	57.7	18,800	
0315A	"	72.2W	2.5	0.625	0.5	10	--	61.2	16,630	
0315B	"	0	1.0	0.25	0	12	19	61.6	23,350	
0316A	Derakane 510- A-40 + 15% Styrene	70.5TX1	2.5	1.25	0	19	44	62.0	22,700	
0316B	"	0	2.5	1.25	0	16	23	61.6	26,300	

<sup>1</sup> CHP - Cumene Hydroperoxide

<sup>2</sup> Promoter - 3 parts 4% V Ten Cem (R) to 2 part N,N dimethyl-p-toluidine

<sup>3</sup> DDM - LUPERSOL(R) DDM, 60% methylethyl ketone peroxide in dimethylphthalate

W - Water

TX1 - 1% Triton X100

TABLE 16  
INFLUENCE OF TEMPERATURE ON RESIN VISCOSITY

---

<u>Temperature</u>	<u>Port Hueneme Resin</u>	<u>Viscosity - cps</u> <u>Port Hueneme Resin</u> <u>+ 15% Styrene</u>
32°F (0°C)	1050	260
77°F (25°C)	218	80
120°F (48.9°C)	63	28

---