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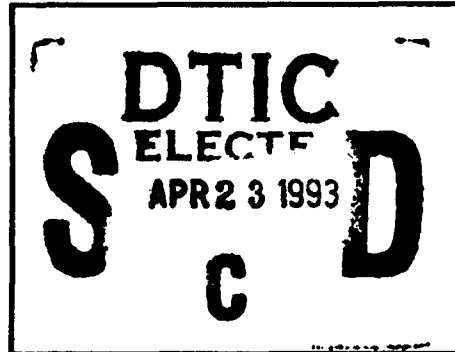
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SET TIME CONTROL STUDIES OF POLYMER CONCRETE

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Robert A. Mosbacher, Secretary
NATIONAL INSTITUTE OF STANDARDS
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Raymond G. Kammer, Acting Director**

NIST

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**U.S. DEPARTMENT OF COMMERCE
Robert A. Mosbacher, Secretary
NATIONAL INSTITUTE OF STANDARDS
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Set time data were obtained for polymer concrete made with a proprietary polyurethane resin for a wide range of aggregate and resin temperatures. Catalyst concentrations were adjusted so that setting occurred within a required time range. The effects of the presence of water and ice on set time were also studied. Set time data were also obtained from pilot tests using another polyurethane and catalyst for various aggregate and resin temperatures and moisture conditions. Considerably more catalyst was required in the pilot tests to obtain comparable set times. The impact of temperature variations on flexural strength was investigated. The flexural strength and failure mechanism at early ages depended on the temperature of aggregate and resin at the time of casting the polymer concrete.

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ABSTRACT

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A model for the prediction of set time of polymer concrete was developed based upon thermodynamic and kinetic principles. The model parameters were determined experimentally from auxiliary laboratory tests conducted separately from the set time tests. Reasonable agreement was found between the model and the data from the set time tests since observed set times and resin temperatures generally agreed with those predicted by the model. Using the model, a series of design charts were prepared which can be used to predict set time when catalyst concentration and initial aggregate and resin temperatures are given, or to

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Key Words: aggregate;flexural strength;heat transfer;model;peak exotherm;polymer concrete;polyurethane;rapid repair;set time;set time prediction model.

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EXECUTIVE SUMMARY

I. BACKGROUND, OBJECTIVES, AND SCOPE

The Air Force Engineering and Services Center (AFESC) has conducted testing of materials for bomb damage repair since 1980. Polyurethane resins have been considered for possible use as a binder with preplaced open-graded aggregate for a rapid setting polymer concrete to form a structural cap to repair areas of bomb-damaged runways. The present study was conducted to characterize the performance of a polymer concrete made using a particular proprietary polyurethane resin.

The objectives of this study were to conduct laboratory tests to (1) obtain set time data for polymer concrete made with a particular proprietary resin under various resin and aggregate temperatures and moisture conditions; (2) to develop a set time prediction model for the polymer concrete based on reaction kinetics and thermodynamics of reaction and heat transfer which predicts set time as a function of system variables; (3) to obtain data from auxiliary tests on the properties of the hardened resins and aggregate and on the rate and heat of reaction of the two-part resin system corresponding to various catalyst levels for input into the set time prediction model; (4) to investigate the effect of temperature variations on the flexural strength of the polymer concrete at an early age, and (5) to obtain set time data from pilot tests of polymer concrete

made using another proprietary polyurethane resin and catalyst, and mineral aggregate cast under various temperature and moisture conditions.

The AFESC provided the proprietary polyurethane resins used in the polymer concrete tests. They also assisted in the development of the experimental design, including selecting aggregates and test temperatures.

II. SET TIME TESTS

The set time tests were conducted in a temperature - controlled environmental chamber. The polymer concrete was cast using equal amounts of a two-component resin, a catalyst, and a round mineral aggregate. The aggregate temperature ranged from -25 to 110°F and the resin temperature ranged from 5 to 110°F. A catalyst was mixed with Resin B (diamine-polyglycol) and then mixed with Resin A (isocyanate). The resulting mixture was quickly poured over aggregate in a plastic bucket. In both air dried and saturated surface dry aggregate tests, the mixed resin percolated through the aggregate and filled the voids. The amount of catalyst was adjusted to provide a set time of about 55 to 75 seconds. The set time was sensitive to the amount of catalyst used, more catalyst gave shorter set time. Set time was determined as the time from the start of mixing of the two resins to the time that set of the mixed resin occurred. The temperature of the polymer

concrete was continuously recorded from thermocouples placed in the aggregate. The set time and temperatures at the time of set and the peak exotherm were reported for 88 tests using dry aggregate, 38 tests using saturated surface dry aggregate, and 40 tests using saturated surface dry aggregate containing ice inclusions.

As expected, the data showed that more catalyst was needed when the resin was cold; it also showed the equally important effect of initial aggregate temperature on set time. There was a consistent trend in the data from the air dried and saturated surface dry aggregate tests which indicated an increase in catalyst amount for a decrease in aggregate and resin temperatures when considering those tests where the set time was in the 55 to 75 second range. A linear relationship between catalyst concentration and resin temperature was suggested for adiabatic mix temperatures above 20°F. This mix temperature is a weighted value of aggregate and resin temperature.

Little difference in set time was observed for polymer concretes cast using air dried aggregate and saturated surface dry aggregate for comparable combinations of aggregate and resin temperatures. The moisture content of the saturated surface dry aggregate ranged from 0.4 to 0.9 percent. The small amount of moisture in the saturated surface dry aggregate did not appreciably affect the set time or the filling of the aggregate voids with resin.

Considerably more catalyst was needed in the set time tests with ice inclusions. The amount of ice ranged from 5 to 15 percent of the mass of aggregate. It was difficult to control set time in these tests. Poor bond between aggregate and resin was observed over the lower part of these test specimens. The results from set time tests with ice inclusions were inconclusive because set time could not generally be accurately determined and in many cases could not be reproduced when comparable amounts of catalyst were used.

III. SET TIME PREDICTION MODEL AND AUXILIARY TESTS FOR MODEL PARAMETERS

The set time prediction model consists of energy balances, one for the resin matrix (continuous phase) and the other for the aggregate particles (dispersed phase), as well as molar balance on the reacting species (resins). It accounts for heat exchange between resin and aggregate and the heat of reaction, as well as heat losses to the surroundings. Model input includes initial temperatures (resin, aggregate, and surroundings), catalyst concentration, moisture and ice content (if present), and mass of aggregate and resin. Model parameters include heat transfer coefficients and time constants, specific heats of the phases, chemical reaction order, reaction activation energies, and parameters measuring the effect catalyst concentration has on the reaction rate constant. Model output predicts set time, resin

conversion, and the temperature of the resin and aggregate as functions of time. For tests with ice inclusions, the model also predicts the fraction of ice which has melted at any time.

In order to independently determine the parameters for the model, separate auxiliary tests were conducted. Resin heat capacities were found in experiments where the resins were allowed to warm in a temperature controlled environment. Heat transfer coefficients and model time constants were determined from tests conducted with water used in place of resin, while reaction parameters were determined from separate tests conducted in insulated containers which did not contain aggregate. These latter tests established a reaction order of 1.5 and a set time which occurred near 60 percent conversion regardless of experimental conditions. The reaction activation energy was found to decrease with increasing catalyst concentration, as would be expected based on kinetic theory. The data collected were fitted to models developed and solved specifically for the auxiliary tests. Because of constraints, the time constant for aggregate heat transfer could not be found independently using this method. Instead its value was determined by matching experimental data of resin temperature for each run directly to the set time model and then using an overall average. Results showed that heat transfer into the aggregate was much faster than into the air.

Reasonable agreement was found between the set time prediction model and the experimental data since observed set time and resin temperatures generally agreed with those predicted by the model. Larger deviations between predicted and experimental results were noted at higher catalyst concentrations and lower initial resin and aggregate temperatures.

IV. SET TIME DESIGN CHARTS

The set time prediction model was used to develop a series of design charts which can be used to predict set time given the catalyst concentration and initial temperatures of the resin and aggregate. The design charts can also be used to determine the catalyst concentration to assure set of the resin within a given time at a specified temperature.

The set time prediction model does not determine catalyst concentration directly, it must be run repeatedly at different catalyst concentrations until one is found that matches the desired set time. Using this method, six design charts were generated from the model. Initial aggregate temperatures selected were -25, 0, 25, 50, 75, and 100°F while initial resin temperatures were varied between 0 and 120°F in increments of 10°F. This gave a total of 308 combinations of set time and initial temperature. The model was run iteratively for each combination in order to find the amount of catalyst to be used to

achieve the desired set time. These data were plotted on the six charts. Each chart is a plot of the catalyst concentration versus the initial resin temperature. The four curves on each chart correspond to set times of 45, 60, 90, and 120 seconds.

In summary, the charts are a graphical representation of the model encoded in the four variables, initial resin temperature, initial aggregate temperature, catalyst concentration, and set time. With any three of the variables known, the fourth can be found using the charts. Use of the charts is illustrated.

V. FLEXURAL STRENGTH

The flexural strength of the polymer concrete was determined using beam specimens tested at an age of 30 minutes. The average value of the flexural strength ranged from 1050 to 425 psi for beam specimens cast at warm temperatures (air and aggregate at 119°F and resin at 91°F) and cold temperatures (air and aggregate at -27°F and resin at 39°F), respectively. Set times for the beam specimens ranged from 30 to 45 seconds. Beams cast with aggregate and resin at the higher temperatures had the highest values of flexural strength. There were eight combinations of aggregate and resin temperatures. The aggregate fractured along the failure surface of beam specimens cast at higher temperatures of aggregate and resin, while for beam specimens cast with lower temperatures, bond failure between aggregate and hardened resin

was discernable. The flexural strength or modulus of rupture data were compared with the adiabatic mix temperature, T_m , which was a weighted value of aggregate and resin temperature at the time of casting a beam specimen. The flexural strength was essentially constant for values of T_m of 70°F or greater. For lower values of T_m , the flexural strength decreased nearly linearly as T_m decreased. It was observed at age 30 minutes that the hardened resin was softer in the five beams cast with lower values of T_m than those cast at the higher temperatures.

VI. PILOT SET TIME TESTS USING ANOTHER POLYURETHANE RESIN

In the 18 pilot tests using equal volumes of another two-component polyurethane resin, considerably more catalyst was needed to obtain comparable set times as compared to the main series of set time tests. There were five combinations of aggregate and resin temperatures in these tests which also included air dry aggregate, saturated surface dry aggregate, and saturated surface dry aggregate with ice inclusions. As the temperature at the time of casting these pilot test specimens decreased, the catalyst concentration needed for equal set time increased considerably. As an example, for specimens cast with an aggregate temperature about -2°F and a resin temperature of 5°F or less, the catalyst volume ratio (volume of catalyst to volume of one polyurethane resin component) was in the range of 0.5 to 1.0 and the set time ranged from 95 to 220 seconds. For comparable specimens in the

main series of set time tests, the catalyst ratio was 0.007 for set time between 67 and 72 seconds. Specimens cast in the pilot tests with resin temperatures of 5°F or lower and those specimens with ice inclusions present exhibited poor bond over their lower half.

1. INTRODUCTION

Polymer concrete made with proprietary polyurethane resins are among several materials being considered by the Air Force Engineering and Services Center (AFESC) for use in rapid repair of runways. In using polymer concrete, a resin may be used as a binder with preplaced open-graded aggregate for a rapid-setting polymer concrete which could be used to form a structural cap to repair areas of bomb-damaged airfield runways. Relatively large bomb craters could be backfilled with pavement debris, rock, or other suitable material. Over this weak backfill, a layer of select aggregate could be placed and leveled even with the surrounding pavement. Polymer resin components mixed with appropriate amounts of catalyst could be applied to the aggregate layer. The mixed resin would flow into the voids in the aggregate and harden to form a polymer concrete structural cap in about a minute. If possible, the structural cap of polymer concrete should support needed aircraft traffic within a half hour after resin application.

The AFESC requested that the National Institute of Standards and Technology (NIST), formerly the National Bureau of Standards (NBS), conduct a study to obtain set time data for polymer concrete made with a particular proprietary polyurethane resin. The polymer concrete was to be made using a wide range of resin and aggregate temperatures. In addition, the impact of the presence of water and ice on set time was to be examined. This

study was required by the AFESC to better characterize the performance of the proprietary resin and the polymer concrete made with it.

1.1 Background

The AFESC has initiated, supported and conducted research on materials for rapid repair of runways for many years [1-13]¹. Many different materials have been investigated for this application, they include polyurethane, methyl methacrylate and other acrylic, polyester, epoxy, and furfuryl alcohol resins and asphalt products, magnesium phosphate cement, high alumina cement, and mono-ammonium phosphate - modified polyphosphate cement composites. Many of the polymer concrete candidate materials investigated involved pouring or applying a mixed two-component polymer, with a catalyst, over open-graded aggregate. Some materials foamed and swelled above the pavement surface [1]. This reaction was attributed to moisture on the surface of the aggregate.

There have been many studies on methyl methacrylate polymer concrete [2,6,9]. In one of the studies, polymer concrete made from a mixture of dry aggregate and methyl methacrylate was reported to be very strong, durable, and to have excellent bond between the polymer and aggregate [2]. In making this type of polymer concrete, polymerization of the monomer in the aggregate is promoted by heat. The resulting composite is a strong,

¹Figures in brackets indicate references listed in Section 8.

durable material which uses the polymer to bond the aggregate together without using water or portland cement. In another study, several resin systems were evaluated for use with microwave curing. Included among these resin systems were polyesters, urea/formaldehyde, phenolics, and epoxies [5]. The urea/formaldehyde, phenolic and epoxy resins were immediately abandoned either because of extreme foaming or incomplete cure.

An unsaturated polyester - styrene formulation was reported to provide for excellent placement and property characteristics above 32°F [4]. At lower temperatures, it was not possible to increase the curing rate enough to meet a one-hour strength criterion while maintaining an acceptable set time [4].

In the early 1980's, a program was conducted to identify and develop potential advanced materials to speed repair of bomb damaged airfield pavements [5]. The program recommended polyurethane resin and modified acrylic resin concretes for structural caps; polyurethane-bonded sand and furan-bonded expanded polystyrene beads for crater fills; and polyurethane resin and modified acrylic resin for soil stabilization. Some apparent deficiencies of polyurethane were reported. They included variations required in catalyst levels and the loss in strength and bond when water was present. The wet flexural strength of the polymer concrete dropped to 500 psi while the bond strength fell to about 70 psi [5]. It was reported that both of these problems could probably

be solved with coupling agents. Moisture can impact the anticipated repair methods and materials in the following three general ways: (1) preventing or degrading the bonding of the polymeric materials to aggregate or pavement, (2) diluting the polymeric material or inhibiting polymerization, and (3) degrading subgrade bearing capacities [5].

In the late 1970's, Rollings [7] reviewed the technical literature and identified seven potential capping materials for expedient repair of small craters in airfield pavements. These materials were tested in the laboratory to develop information on their strengths and curing requirements. Accelerated high alumina cement, magnesium phosphate cement, three commercial asphalt products, and unsurfaced, well-compacted aggregate were recommended for field testing as the most promising small crater repair materials.

Several research programs in the late 1970's investigating the use of organic resin binders reported promising results. Even though there were shortcomings such as limited shelf life, complexity of application, moisture sensitivity, and insufficient adhesion, the most promising candidates included acrylics, polyesters, and epoxy resins [8]. In a study of these candidate materials, the focus was on three technical problems that had to be overcome to develop a satisfactory repair system. These technical problems were adhesion to wet aggregates, cure rate

control for low temperature service, and control of resin viscosity [8].

Silane-modified furfuryl alcohol polymer concrete and mono-ammonium phosphate-modified polyphosphate cement composites were reported to have great potential for use as all-weather rapid repair materials for bomb-damaged runways [10]. It was demonstrated that both of these materials can be mixed and placed on a continuous basis using conventional portland cement concrete equipment and techniques.

Studies were conducted to achieve new materials and equipment required to field an advanced material bomb-damage repair system [11-13]. The two primary types of materials investigated were polyurethanes and acrylics. Screening criteria were based on high early strength in wet and dry environments, with ambient temperatures ranging from -25°F to 125°F and material (aggregates and resin) temperatures varying from 5 to 110°F. The final selected material was polyurethane, modified to improve its wet performance and strength characteristics. The selected placement method was percolation of the polyurethane resin into aggregate, placed in a crater, to form a polymer concrete structural cap [11].

The brief review of literature on rapid runway repair materials presented above is to acquaint the reader with some of the

research conducted over the last 15 years. Some of the concerns about these materials are their cost, early strength development, effect of moisture and temperature on their bond and mechanical strength, variations in the amounts of catalyst needed, complexity of application, changes in viscosity due to environment, and incomplete filling of voids in open graded aggregate by down percolation of a polymer. The overall need is to provide rapid repair materials for bomb-damaged runways which are applicable to a wide range of weather and environmental conditions.

1.2 Objectives

The objectives of this study are:

- (1) to obtain set time data for polymer concrete made with a particular proprietary polyurethane resin and catalyst, and a mineral aggregate under various resin and aggregate temperatures and moisture conditions,
- (2) to develop a set time prediction model for the polymer concrete based on reaction kinetics and the thermodynamics of reaction and heat transfer which predicts set time as a function of system variables,
- (3) to obtain data from auxiliary tests on the properties of the hardened resin and aggregate and on the rate and heat of reaction of the two-part resin system corresponding

to various catalyst levels for input into the set time prediction model,

- (4) to investigate the effect of temperature at the time of casting on the flexural strength of beam specimens of polymer concrete, and
- (5) to obtain set time data from pilot tests of polymer concrete made using another proprietary polyurethane resin and catalyst, and mineral aggregate cast under various temperature and moisture conditions.

1.3 Scope of the Study

Information is needed by the Air Force to better characterize the performance of the polymer concrete material included in this study prior to its use in the field for rapid repair of runways and pavements. The AFESC provided the proprietary polyurethane resins used in the polymer concrete tests.

The AFESC required many specific combinations of aggregate and resin temperatures to be included in the set time tests.

Catalyst concentrations were adjusted so that set time occurred within a required time range. Requirements were also established by AFESC with regard to moisture conditions of the aggregate (air dry or saturated surface dry) at the time of testing, and

specific quantities of ice inclusions to be included in the aggregate prior to adding the resin.

With regard to the effect of temperature on the flexural strength of polymer concrete, the AFESC provided requirements for aggregate and resin temperatures, set time range, size of flexural specimens, and age of specimens at the time of test.

Requirements were also provided by AFESC for conducting the pilot set time tests using another proprietary resin (also a polyurethane). These requirements included temperatures of aggregate and resin and moisture conditions of the aggregate at the time of casting the polymer concrete.

In developing the set time prediction model for the polymer concrete, information on the properties of the hardened resin and the aggregate and on the rate and heat of reaction of the two-part resin system for various amounts of catalyst was needed as input to the model. Auxiliary tests were devised and conducted to provide these data. Most model parameters were determined independently of the polymer concrete set time tests. Model set time predictions were compared with the experimental results. Using the model, design charts were prepared which can be used to predict set time or to select catalyst concentration for a specific set time.

2. LABORATORY TESTS

Laboratory tests were conducted to obtain set time data for polymer concrete made with a proprietary polyurethane resin and catalyst and a mineral aggregate. These tests were carried out over an extensive range of resin and aggregate temperatures. The effects of water and ice inclusions in the aggregate on the set time of the polymer concrete were also investigated.

A model for the prediction of set time of the polymer concrete was developed. The model parameters were determined experimentally from laboratory tests conducted separately from the set time tests. The set time model was developed based on data from the separate or auxiliary small scale tests and was tested using the data from the set time tests.

Laboratory tests were also conducted to determine the flexural strength of the polymer concrete. Beams were cast over an extensive range of resin and aggregate temperatures and were tested at age 30 minutes.

The following Sections (2.1 and 2.2) describe the materials and test procedures used in the set time, auxiliary small scale, and flexural tests.

The AFESC also requested that pilot set time tests of polymer concrete be conducted using another polyurethane resin. The results of these pilot tests are presented in Section 3.4.

2.1 Materials

The materials used in the polymer concrete tests were a two-part polyurethane resin including a catalyst and mineral aggregate.

2.1.1 Polymer

The proprietary two-component resin and catalyst was supplied by AFESC. One component, Component A, was a blend of aromatic isocyanates and hydrocarbons and the other component, Component B, was a blend of diamine, polyglycol, and halogenated hydrocarbons. Information regarding the contents of the catalyst was not available. The AFESC requested that the proprietary resin and catalyst not be analyzed for its composition.

2.1.2 Mineral Aggregate

The smooth surfaced and rounded mineral aggregate, a river run quartz gravel, was from White Marsh, Maryland. It was required to meet the AFESC requirements given in Table 1.

Table 1. AFESC Requirements for Aggregate

<u>Property</u>	<u>Limit</u>	<u>Test Method</u>
Gradation	No. 57 per ASTM D 488 ($< 1\%$ passing No. 8 sieve)	ASTM C 136
Void volume	35 - 40%	ASTM C 29
Abrasion resistance	$< 42\%$	ASTM C 131
Soundness	$< 12\%$ Na_2SO_4 $< 18\%$ MgSO_4	ASTM C 88

Gradation and void volume test results, as determined by NIST, met the AFESC requirements. The void volume ratio ranged from 36 to 38 percent. Data from tests conducted over a period of about 20 years by the National Aggregates Association on aggregate from the same source as that supplied to NIST indicated that the aggregate met the AFESC requirements for abrasion resistance and soundness.

2.2 Test Procedures

Descriptions of the test procedures for the set time, flexural, and auxiliary tests are given in Sections 2.2.1, 2.2.2, and 2.2.3, respectively.

2.2.1 Set Time

Polymer concrete set time tests were conducted in an exhaust hood located in an environmental chamber or room. The hood was 56 in. high, 45-1/2 in. wide, and 32 in. deep. It was fabricated from plywood and painted. The hood had two transparent plastic doors, each about 22-3/4 in. x 56 in. The hood had a high volume of air

flow which exited outside of the building. In addition to providing a safe place to conduct the set time tests, the hood also provided for safe storage of the Part A and Part B resins.

The set time tests were performed over a temperature range of 0°F to 125°F. The AFESC requested that specific combinations of aggregate and resin temperatures be used in the tests. They are given in Table 2. Three conditions of aggregate were included in the tests -- they were air dried (also referred to as dry aggregate), saturated and surface dried (also referred to as wet aggregate), and saturated surface dried with ice inclusions. The saturated surface dry aggregate was kept in water for four or more days at the scheduled set time test temperature, and then prior to testing, towel dried to a saturated surface dry condition. For freezing set time test temperatures, saturated surface dry aggregate was stored at schedule test temperature until testing. For tests where the aggregate temperature was -25°F, the aggregate was kept in a freezer maintained at this temperature. The aggregate was taken from the freezer and the set time tests were conducted as soon as possible in the hood in the environmental chamber at 0°F. For all the other tests, the aggregate was conditioned to test temperature in the environmental chamber which had a temperature range of 0° to 150°F. The test temperature of the aggregate was the same as the environmental chamber, while

Table 2. AFESC Requirements for Combinations of Aggregate and Resin Temperatures Used in Set Time Tests

Set Time Test Conditions - Dry Aggregate								
		Resin Temperature						
°F		110	90	70	55	40	25	5
Aggregate Temperature	125	X	X					
	110	X	X	X				
	90	X	X	X	X			
	70		X	X	X	X		
	55			X	X	X		
	40			X	X	X	X	
	20			X	X	X	X	X
	0			X	X	X	X	X
-25				X	X	X	X	

Set Time Test Conditions - Saturated Surface Dry Aggregate (Wet Aggregate)

Set Time Test Conditions - Saturated Surface Dry Aggregate (Wet Aggregate)								
		Resin Temperature						
°F		110	90	70	55	40	25	5
Aggregate Temperature	125		X					
	110	X		X				
	90		X		X			
	70			X		X		
	55		X		X			
	40			X		X		
	20				X		X	
	0					X		X
	-25							

Set Time Test Conditions - Saturated Surface Dry Aggregate (Wet Aggregate) Containing Ice Inclusions

Set Time Test Conditions - Saturated Surface Dry Aggregate (Wet Aggregate) Containing Ice Inclusions								
		Resin Temperature						
°F		110	90	70	55	40	25	5
Aggregate Temperature	125							
	110							
	90							
	70							
	55							
	40							
	20			X	X	XX	XX	
	0					XX	XXX	XX
	-25						XXX	XXX

Adjust catalyst concentrations so set time falls between 15 and 120 seconds

the resins usually had to be stored in a refrigerator, freezer, or oven, to attain the required test temperatures.

The set time tests were performed by pouring the mixed resin (Components A and B), including catalyst, into a 5-gallon plastic bucket containing 0.44 ft³ of a smooth surface, rounded mineral aggregate (gravel). The weight of the aggregate was 42 lbm (19,230 g) and its depth in the bucket was 8 in. The diameter of the bucket at the bottom was about 10-1/4 in. and at a depth of 8 in. the diameter was about 10-3/4 in. The aggregate was air dried for at least 7 days before placing it in buckets and weighing the test specimens. During air drying, the gravel was spread out to a depth of about 4 in. The moisture content of the air dried gravel was determined to be about 0.08 percent by mass. The void volume ratio of the gravel ranged from 36 to 38 percent.

Equal parts by volume of Part A and Part B resin were used in the set time tests. For each specimen of polymer concrete, 2220 ml (2453 g) of Part A resin and 2220 ml (3048 g) of Part B resin were used. Each of the resins were poured into separate 5 gallon plastic buckets. Immediately prior to casting the polymer concrete, a measured amount of catalyst, at room temperature, was added to the Part B resin and stirred using a wood paddle. The amount of catalyst used for each of the tests with air dried and saturated surface dry aggregate ranged from 0.1 to 17 ml (see Tables 3 and 4). The Part B resin, with catalyst, was poured

Table 3. Set Time Data for Polymer Concrete Specimens with Dry Aggregate

Run Number	Aggregate Temp (°F)	Resin Temp (°F)	Catalyst Ratio By Volume <u>[Catalyst]</u> Part B	Catalyst Volume (ml)	Set Time (s)	Temp at Set Time (°F)	Peak Exotherm Temp (°F)
1	75	75	0.00125	2.775	72	-	177
2	73	72	0.00125	2.775	67	173	173
3	74	40	0.00170	3.774	110	128	129
4	74	40	0.00190	4.218	93	124	132
5	75	40	0.00200	4.440	86	127	129
6	75	90	0.00090	1.998	65	178	178
7	75	90	0.00090	1.998	60	192	196
8	75	55	0.00170	3.774	81	144	144
9	76	55	0.00170	3.774	74	132	137
10	56	70	0.00210	4.662	48	143	144
11	56	70	0.00170	3.774	76	158	162
17	57	70	0.00215	4.780	49	152	153
18	58	71	0.00170	3.774	56	147	149
12	56	57	0.00210	4.662	54	138	141
13	56	57	0.00190	4.218	55	160	168
14	57	56	0.00190	4.218	63	128	131
15	57	42	0.00220	4.884	83	118	118
16	58	40	0.00220	4.884	92	-	-
19	89	88	0.00070	1.554	64	164	168
20	89	89	0.00070	1.554	71	160	160
21	90	71	0.00100	2.220	74	162	164
22	90	71	0.00100	2.220	72	142	148
23	90	54	0.00130	2.886	76	143	145
24	90	54	0.00130	2.886	70	140	144
25	91	109	0.00035	0.777	70	182	182
26	91	110	0.00035	0.777	72	162	175
27	44	41	0.00260	5.772	76	119	120
28	43	41	0.00260	5.772	72	113	113

Table 3. Set Time Data for Polymer Concrete Specimens with Dry Aggregate (Continued)

Run Number	Aggregate Temp (°F)	Resin Temp (°F)	Catalyst Ratio By Volume [Catalyst Part B]	Catalyst Volume (ml)	Set Time (s)	Temp at Set Time (°F)	Peak Exotherm Temp (°F)
29	42	23	0.00290	6.438	94	94	97
30	43	27	0.00310	6.882	66	112	116
31	42	23	0.00310	6.882	71	91	101
32	42	70	0.00200	4.440	41	146	146
33	44	71	0.00180	3.996	47	128	129
34	44	69	0.00150	3.330	76	131	132
35	43	71	0.00150	3.330	66	136	137
36	43	55	0.00205	4.551	67	119	121
37	43	55	0.00205	4.551	73	122	123
38	110	109	0.00010	0.222	70	167	176
39	110	109	0.00010	0.222	106	168	179
40	110	109	0.00010	0.222	92	155	174
41	110	72	0.00600	1.332	72	156	170
42	110	74	0.00060	1.332	80	157	166
43	111	89	0.00038	0.833	81	156	168
44	110	90	0.00038	0.833	89	167	181
45	21	70	0.00195	4.329	68	124	127
46	21	71	0.00195	4.329	66	142	143
47	21	24	0.00335	7.881	74	91	93
48	23	25	0.00355	7.881	73	86	86
49	23	5	0.00425	9.435	96	74	76
50	22	5	0.00450	9.990	126	79	80
55	22	4	0.00540	11.998	104	76	80
56	23	4	0.00630	13.986	79	77	79
57	22	5	0.00630	13.986	71	97	100
51	23	40	0.00300	6.560	67	86	88
52	22	40	0.00300	6.660	67	84	89
53	23	54	0.00245	5.439	53	117	117
54	25	54	0.00230	5.106	61	118	119

Table 3. Set Time Data for Polymer Concrete Specimens with Dry Aggregate (Continued)

Run Number	Aggregate Temp (°F)	Resin Temp (°F)	Catalyst Ratio By Volume [Catalyst Part B]	Catalyst Volume (ml)	Set Time (s)	Temp at Set Time (°F)	Peak Exotherm Temp (°F)
58	123	110	0.00005	0.111	55	182	192
59	123	110	0.00005	0.111	76	178	186
60	123	90	0.00020	0.444	96	171	181
61	123	90	0.00025	0.555	57	185	193
62	122	90	0.00023	0.500	60	177	183
63	1	55	0.00285	6.327	45	125	125
64	2	55	0.00260	5.772	68	94	98
65	3	54	0.00260	5.772	59	98	99
66	3	25	0.00395	8.769	77	67	73
67	4	24	0.00395	8.769	98	73	78
69	4	25	0.00395	8.769	78	90	91
68	5	40	0.00340	7.548	73	103	104
70	6	40	0.00340	7.548	63	117	118
71	7	70	0.00235	5.217	42	140	140
72	4	70	0.00210	4.662	47	125	127
73	4	70	0.00180	3.996	56	159	160
74	5	70	0.00160	3.552	64	106	114
75	7	70	0.00150	3.330	77	102	107
76	2	5	0.00675	14.985	78	65	71
82	0	5	0.00675	14.985	77	65	65
77	-22	5	0.00720	15.984	67	50	57
78	-26	5	0.00720	15.984	72	60	63
79	-24	25	0.00440	9.768	91	49	49
80	-32	25	0.00495	10.989	60	54	57
81	-32	25	0.00480	10.656	67	56	68
83	-26	39	0.00385	8.547	57	79	85
84	-29	41	0.00375	8.325	59	70	90

Table 3. Set Time Data for Polymer Concrete Specimens with Dry Aggregate (Continued)

Run Number	Aggregate Temp (°F)	Resin Temp (°F)	Catalyst Ratio By Volume [<u>Catalyst</u> Part B]	Catalyst Volume (ml)	Set Time (s)	Temp at Set Time (°F)	Peak Exotherm Temp (°F)
85	-33	55	0.00290	6.438	52	75	85
86	-26	54	0.00270	5.994	53	75	109
87	-47	55	0.00240	5.328	60	91	91
88	-25	55	0.00240	5.328	59	54	77

Table 4. Set Time Data for Polymer Concrete Specimens with Saturated Surface Dry Aggregate (Wet Aggregate)

Run Number	Aggregate Temp (°F)	Resin Temp (°F)	Catalyst Ratio By Volume [Catalyst Part B]	Catalyst Volume (ml)	Set Time (s)	Temp at Set Time (°F)	Peak Exotherm Temp (°F)	Moisture Content of Aggregate ^a (%)
89	70	71	0.00125	2.775	68	122	140	0.5
90	71	71	0.00125	2.775	59	145	148	0.5
91	70	40	0.00220	4.884	68	115	122	0.5
92	71	40	0.00220	4.884	72	123	123	0.5
93	55	55	0.00185	4.107	58	110	119	0.9
94	55	55	0.00175	3.885	70	106	121	0.9
95	56	90	0.00120	2.664	50	188	195	0.9
96	56	90	0.00100	2.220	73	146	147	0.9
97	56	90	0.00100	2.220	76	144	148	0.9
99	86	90	0.00070	1.554	58	172	174	0.4
100	86	90	0.00060	1.332	67	141	162	0.4
101	86	55	0.00130	2.886	69	143	147	0.4
102	85	54	0.00130	2.886	67	127	139	0.4
103	44	41	0.00260	5.772	61	102	106	0.6
104	44	42	0.00250	5.550	70	103	108	0.6
105	44	69	0.00150	3.330	64	128	129	0.6
106	44	69	0.00140	3.108	61	129	130	0.6
107	101	106	0.00010	0.222	108	155	171	
108	103	111	0.00015	0.333	58	157	176	0.5
109	103	109	0.00015	0.333	104	162	173	0.5
110	102	108	0.00015	0.333	104	159	177	0.5
111	105	70	0.00070	1.554	68	143	159	0.5
112	101	70	0.00070	1.554	75	146	157	0.5
115	118	70	0.00070	1.554	67	169	184	-
113	131	89	0.00023	0.500	86	186	200	-
114	129	90	0.00025	0.555	77	164	182	-
116	7	5	0.00690	15.318	104	70	73	0.4
117	4	5	0.00770	17.094	59	52	55	0.4
118	9	5	0.00740	16.428	58	74	76	0.4

Table 4. Set Time Data for Polymer Concrete Specimens with Saturated Surface Dry Aggregate (Wet Aggregate) (Continued)

Run Number	Aggregate Temp (°F)	Resin Temp (°F)	Catalyst Ratio By Volume Catalyst Part B	Catalyst Volume (ml)	Set Time (s)	Temp at Set Time (°F)	Peak Exotherm Temp (°F)	Moisture Content of Aggregate ^a (%)
119	5	40	0.00380	8.436	51	72	78	0.4
120	4	40	0.00360	7.992	48	113	124	0.4
121	5	40	0.00330	7.326	54	69	73	0.4
122	19	55	0.00220	4.884	50	89	96	0.8
123	19	54	0.00200	4.440	67	89	95	0.8
124	19	54	0.00200	4.440	66	95	95	0.8
125	20	25	0.00330	7.326	85	64	74	0.8
126	19	25	0.00350	7.770	65	68	78	0.8
127	21	26	0.00345	7.659	76	69	78	0.8

^a Percent by mass

into the Part A resin within 8 to 10 seconds. While pouring, the mixed resins were stirred with a wood paddle. Immediately following this step, the mixed resins were poured into the aggregate within 5 seconds. Photographs of the 5 gallon plastic buckets containing aggregate and polymer concrete are shown in Figure 1. In the set time tests using air dried aggregate and saturated surface dry aggregate, the mixed resins, when poured into the aggregate, filled the voids up to the top surface of aggregate. This was in general the case for all the combinations of aggregate (air dried and saturated surface dried) and resin temperatures included in the 127 set time tests (see Tables 3 and 4). However, this was not the case for tests where ice inclusions were included in the saturated surface dried aggregate. Data from the set time tests using saturated surface dry aggregate containing ice inclusions are listed in Table 5. Information pertaining to the time of set for specimens cast with saturated surface dry aggregate containing ice inclusions is given in Table 6. In this table, the portion of the area of the surface of the test specimen for which the resin appeared to be set or hardened was estimated. Large voids and poor bond of aggregate to hardened resin were observed in these polymer concrete specimens that contained ice inclusions. Some of the hardened polymer concrete specimens were sawed in half to observe the extent to which the resin had filled the voids in the aggregate.



Figure 1. Plastic Buckets Containing Aggregate and Polymer Concrete

Table 5. Set Time Data for Polymer Concrete Specimens with Saturated Surface Dry Aggregate Containing Ice Inclusions

Run Number	Aggregate Temp (°F)	Resin Temp (°F)	Catalyst Ratio By Volume [Catalyst Part B]	Catalyst Volume (ml)	Set Time (s)	Temp at set time (°F)	Peak Exotherm Temp (°F)	Ice Inclusions ^a (%)
128	24	70	0.00180	3.996	(P) ^b 55	86	92	10
129	23	71	0.00540	11.988	—	—	—	10
130	23	70	0.00360	7.992	(P) 31	100	100	10
131	20	70	0.00270	5.994	(P) 35	71	85	10
132	26	68	0.00270	5.994	(P) 30	41	41	20
133	22	70	0.00225	4.995	(P) 660	81	108	5
134	22	69	0.00260	5.772	(P) 35	115	116	5
135	22	41	0.00370	8.214	(P) 225	68	73	5
136	22	40	0.00430	9.546	(P) 80	103	103	5
137	22	40	0.00490	10.878	(P) 38	94	94	5
138	22	55	0.00380	8.436	(P) 50	104	111	5
139	22	56	0.00400	8.880	25	91	92	5
140	25	26	0.00560	12.432	(P) 165	71	87	5
141	25	69	0.00370	8.214	21	87	87	15
142	24	40	0.00530	11.766	(P) 100	80	90	10
143	29	40	0.00590	13.098	(P) 45	69	71	10
144	32	40	0.00620	13.764	(P) 28	88	92	15
145	27	26	0.00680	15.096	(P) 60	78	80	5
146	26	25	0.00720	15.984	(P) 55	72	72	5
147	25	25	0.00770	17.094	(P) 45	79	83	5
148	32	25	0.00870	19.314	(P) 40	96	98	10
149	30	26	0.00910	20.202	(P) 28	96	96	10
150	30	26	0.00910	10.101	(P) 26	51	57	15
151	29	55	0.00500	11.100	(P) 26	109	112	10
152	32	55	0.00500	11.100	(P) 25	134	145	15
153	-1	40	0.00500	11.544	(P) 95	63	77	5
154	-3	40	0.00620	13.764	(P) 30	90	90	5
155	-1	40	0.00730	16.206	22	77	77	10
156	-1	40	0.00720	15.984	(P) 24	37	38	15

Table 5. Set Time Data for Polymer Concrete Specimens with Saturated Surface Dry Aggregate Containing Ice Inclusions (Continued)

Run Number	Aggregate Temp (°F)	Resin Temp (°F)	Catalyst Ratio By Volume [Catalyst Part B]	Catalyst Volume (ml)	Set Time (s)	Temp at set time (°F)	Peak Exotherm Temp (°F)	Ice Inclusions ^a (%)
157	0	25	0.01020	22.644	(P) 27	49	49	5
158	0	25	0.01130	25.086	(P) 26	67	67	10
159	4	26	0.01130	25.086	(P) 23	68	68	15
160	4	5	0.01220	27.084	(P) 80	44	50	5
161	4	6	0.01290	28.638	(P) 45	67	70	5
162	4	5	0.01430	31.745	(P) 30	52	52	10
163	0	6	0.01440	31.968	(P) 25	43	45	15
164	-36	26	0.01250	27.750	(P) 19	51	53	5
165	-34	26	0.01340	29.748	(P) 20	36	59	10
169	-39	25	0.01330	29.526	(P) 22	37	37	15
166	-35	5	0.01530	33.966	(P) 26	100	180	5
167	-44	6	0.01640	36.408	(P) 26	42	42	10
168	-43	5	0.01640	36.408	(P) 29	33	36	15

^a Percent by mass of aggregate

^b Partial set, see Table 6 for information pertaining to time of set

Table 6. Information Pertaining to the Time of Set for Specimens Cast with Saturated Surface Dry Aggregate Containing Ice Inclusions

Test No.

128	Partial set, 55 seconds; total set, 22 minutes.
129	No data, resin set up before it could be poured into gravel.
130	Set time, 31 seconds (about 90% of surface area); steam emitted from between hardened concrete and side of bucket shortly after set.
131	Set time, 35 seconds (about 80% of surface area); polymer concrete was soft or there were voids around the edge of the specimen.
132	Set time, 30 seconds (about 85% of surface area).
133	40% set at 2-1/2 min.; gummy at 3-1/2 min.; about 75% set at 11 min.
134	Set time, 35 seconds (about 90% of surface area).
135	50% set at 3-3/4 min.
136	25% set at 80 sec.; 60% set at 105 sec.; 75% set at 225 sec.; 95% set at 285 sec.
137	Set time, 38 seconds (about 85% of surface area); 90% set at 90 sec.
138	50% set at 50 sec.; 75% set at 75 sec.; 80% set at 95 sec.
139	100% set at 25 sec.
140	50% set at 165 seconds; 90% set at 225 sec.
141	Set time, 21 seconds (100% of area). Note: Small amount of resin (5%) set up before it entered gravel, most of mixed resin (95%) entered gravel; a lot of steam was released from bucket.
142	30% set at 100 sec.; 50% set at 160 sec.; 60% set at 225 sec.; 75% set at 270 sec.; 100% set at 300 sec.

Table 6. Information Pertaining to the Time of Set for Specimens Cast with Saturated Surface Dry Aggregate Containing Ice Inclusions (Continued)

Test No.

143	70% set at 45 sec.; 90% set at 65 sec.
144	Set time, 28 seconds (about 95% of area).
145	20% set at 60 sec.; 40% set at 75 sec.; 60% set at 90 sec.; 80% set at 110 sec.; 90% set at 135 sec.
146	40% set at 55 sec.; 50% set at 80 sec.; 75% set at 90 sec.; 90% set at 110 sec.; 95% set at 135 sec.
147	50% set at 45 sec.; 70% set at 60 sec.; 90% set at 80 sec.; 95% set at 95 sec.
148	40% set at 40 sec.; 50% set at 70 sec.; 75% set at 105 sec.; 90% set at 120 sec.
149	Set time, 28 sec.; (about 95% of area).
150	Set time, 26 sec.; (about 95% of area).
151	Set time, 26 sec.; (about 95% of area).
152	Set time, 25 sec.; (about 95% of area).
153	30% set at 95 sec.; 75% set at 165 sec.; 90% set at 190 sec.
154	Set time, 30 sec.; (about 90% of area).
155	Set time, 22 sec.; (about 100% of area).
156	Set time, 24 sec.; (about 98% of area).
157	Set time, 27 sec.; (about 98% of area).
158	Set time, 26 sec.; (about 98% of area).
159	Set time, 23 sec.; (about 98% of area).
160	50% set at 80 sec.; 90% set at 60 sec.
161	75% set at 45 sec.; 95% set at 60 sec.
162	Set time, 30 seconds (about 95% of area).

**Table 6. Information Pertaining to the Time of Set for
Specimens Cast with Saturated Surface Dry
Aggregate Containing Ice Inclusions (Continued)**

Test No.

163	Set time, 25 seconds (about 95% of area).
164	Set time, 19 sec., (about 98% of area).
165	Set time, 20 sec., (about 98% of area).
166	Set time, 26 sec., (about 95% of area).
167	Set time, 26 sec., (about 98% of area).
168	Set time, 29 sec., (about 98% of area).
169	Set time, 22 sec., (about 95% of area).

Personnel handling the resins were required to wear respirators, protective gloves, and eye protection. Resins were stored in containers in hoods in the laboratories or in containers in a particular building designated as a storage area. The resins were weighed to the amount required in the tests in one gallon metal cans. Prior to testing, the metal cans containing the measured amount of resin were placed in refrigerators, freezers, or ovens to provide the required test temperature of the resin.

Temperature data from the cast polymer concrete were continuously recorded on data-logger tape and on a computer disc. The temperatures were recorded from three thermocouples located at mid-depth in the gravel at the center, at the edge, and half way between the center and edge of the bucket. As previously noted, the depth of gravel in the bucket was 8 in. In this series of tests, the intended set time of the mixed resin in the aggregate was 55-75 seconds. The AFESC requirement for set time was between 15 and 120 seconds. Set time was determined by using a 1/8 in. diameter steel rod to tap the liquid phase of the resin and recording when it became solid. A stopwatch was used to measure, to the nearest second, the time from when the resins were mixed to when set occurred. It was observed at set that the color of the mixed resin in the gravel changed from a dark to light green. In almost all tests where air dried and saturated surface dried aggregate were used, the set of the resin occurred rapidly.

The temperatures of the gravel and resins were measured immediately prior to the set time tests using thermocouples or thermometers. The catalyst was at room temperature when added to the resin, since very small amounts were used.

2.2.2 Flexural Strength

The 4x4x14 in. polymer concrete beams were cast in a temperature controlled environmental chamber. The temperatures of the aggregate and resin used in casting the beam specimens are given in Table 7. The resin temperatures were different from the aggregate temperatures. The aggregate temperature was the same as the air temperature in the environmental chamber except for the aggregate temperature of -25°F. For this case, the air temperature was 0°F. The catalyst ratios were selected in an attempt to produce set time of the resin in the range of 30 to 45 seconds. Catalyst ratios and amounts are given in Table 7 along with set times.

In casting a beam specimen, the gravel was placed in the form and leveled off even with the top surface of the form. The bottom and ends of the forms were 1/2 in.-thick Teflon². The sides of the form were 3/8 in.-thick aluminum, with 1/8 in.-thick Teflon²

²Certain manufacturer names and proprietary materials are included in this report in order to identify and describe some of the materials used in this study. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials identified are necessarily the best available for the purpose used in this study.

Table 7. Flexural Beam Test Data

Run Number	Aggregate Temp	Resin Temp	Catalyst Ratio By Volume Catalyst Part B	Catalyst Volume	Set Time	Max Load	Modulus of Rupture	Avg. Value of Modulus of Rupture
	(°F)	(°F)		(ml)	(s)	(lbf)	(psi)	(psi)
1	72	40	0.00240	2.40	42	4930	924	970
2	72	43	0.00250	2.50	43	5260	986	
3	72	40	0.00260	2.60	40	5340	1001	
4	110	71	0.00800	0.80	47	5840	1095	1049
5	110	72	0.00085	0.85	40	5410	1014	
6	110	73	0.00085	0.85	41	5540	1039	
7	90	55	0.00170	1.70	37	5700	1069	1034
8	90	55	0.00170	1.70	42	5490	1029	
9	90	55	0.00170	1.70	37	5350	1003	
10	119	92	0.00033	0.33	52	5430	1012	1047
11	119	91	0.00037	0.37	53	5740	1076	
12	118	90	0.00420	0.42	54	5610	1052	
13	23	91	0.00100	1.00	27	4970	932	862** 896
14	21	89	0.00060	0.60	59	4920	922	
15	21	90	0.00070	0.70	39	4050	759*	
16	22	90	0.00070	0.70	37	4450	834	
17	22	69	0.00190	1.90	30	4430	831	834
18	20	70	0.00180	1.80	27	4390	823	
19	20	70	0.00160	1.60	36	4530	849	
20	1	56	0.00280	2.80	23	4930	924*	705** 632
21	1	54	0.00250	2.50	37	3840	720	
22	0	55	0.00250	2.50	30	3240	607	
23	0	55	0.00250	2.50	38	3040	570	
24	-25	39	0.00390	3.90	30	3240	608*	470** 424
25	-35	39	0.00380	3.80	32	2160	405	
26	-27	38	0.00370	3.70	68	2130	399	
27	-26	40	0.00380	3.80	28	2500	469	

* Data considered as outlier

** Average value includes outlier

on the inside surfaces of the sides of the form. The forms were assembled with screws which enabled rapid disassembly to remove the beam specimens from the forms about 10 minutes after casting.

About 12.3 lbm (5580 g) of gravel was placed in the forms. Catalyst at room temperature was added to the 1000 ml of Part B resin and mixed using a wood paddle. The Part B resin with catalyst was then quickly poured into the 1000 ml of Part A resin and the mixed resin was stirred during pouring. The mixed resin was immediately poured into the form containing the aggregate. From the time resin mixing started, the resin mixture was poured into the form containing the gravel within 15 seconds.

The beam specimens were tested in flexure at age 30 minutes by third point loading as described by ASTM C 78. They were removed from the forms about 10 minutes after casting and kept in the environmental chamber until age 25 minutes. The beams were then placed in an insulated container and moved from the environmental chamber to the testing machine. The air temperature at the time of flexural test was about 70°F. The beams were removed from the insulated container and positioned in a flexural testing apparatus and the load was applied using a testing machine. An initial load of 2000 to 3000 lbf (about 50 percent of breaking load) was applied to the beams and the rate of loading thereafter was 800 lbf/min. The beams were loaded until failure occurred.

2.2.3 Auxiliary Tests

Small-scale auxiliary tests were conducted to determine parameters for a set time prediction model. As previously noted, most model parameters were determined independently of the polymer concrete set time tests. The auxiliary tests denoted as resin warming, water immersion, and kinetic are described in Appendix A.

3. TEST RESULTS

The results of the set time, flexural strength, and auxiliary tests using the proprietary two-component resin are given in Sections 3.1, 3.2, and 3.3, respectively. The auxiliary small scale tests were conducted to determine the parameters for a set time prediction model. Section 3.4 provides set time data from pilot tests of casting polymer concrete using another proprietary resin and catalyst.

3.1 Set Time

The set time, temperature of mixed resin in the aggregate at set time, and peak exotherm for each of the tests are given in Tables 3, 4, and 5. These tables include data from tests using dry aggregate, saturated surface dry aggregate (wet aggregate), and aggregate with ice inclusions, respectively. Values of initial aggregate and resin temperature, catalyst ratio, and catalyst amount for each test are also given in the tables. It is noted that the ambient temperature and aggregate temperature were essentially the same except for the case where aggregate temperatures were about -25°F. For this case the ambient temperature was about 0°F.

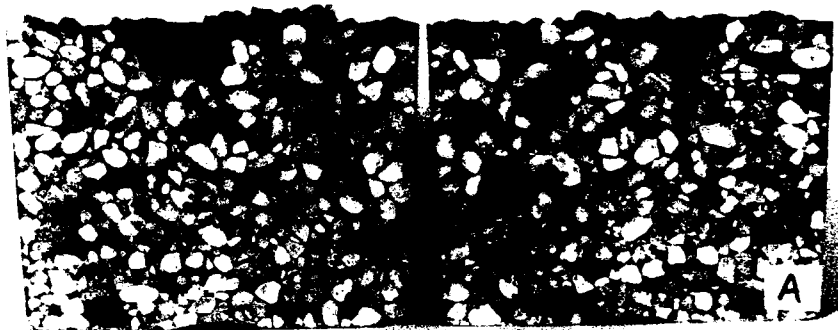
The set time was very sensitive to the amount of catalyst used. Slight changes in the amount of catalyst appreciably affected the

set time. Since very small amounts of catalyst were used, it was at room temperature, 70°F, when added to the Part B resin. In conducting the set time tests, it was intended to narrow the set time to a range of about 55 to 75 seconds. This range was about midway between the AFESC requirement of between 15 to 120 seconds. Therefore, the set time data presented in Tables 3, 4, and 5 are in most cases in the range of 55 to 75 seconds. From the data plotted in Figure 2 for polymer concrete cast with air dry aggregate and with saturated surface dry aggregate, it can be seen that there is a consistent trend in the data when considering those points having set times in the 55 to 75 second range. In Figure 2, the set time(s) are the numbers associated with each data point. The lines drawn in this figure are for different initial aggregate temperatures, T_{ao} . These data are briefly discussed in Section 4.5.1.2. and are compared to data for which a weighted value of aggregate temperature and resin temperature is used instead of the initial resin temperature.

In comparing set times for comparable combinations of aggregate and resin temperatures for polymer concrete cast using air dry aggregate and those cast using saturated surface dry aggregate, little difference was observed. Comparing average temperatures of the polymer concrete at set time and at peak exotherm for specimens cast using air dry aggregate and those cast using saturated surface dry aggregate, the temperature at set time was about 11 percent greater when dry aggregate was used. The peak

exotherm for specimens cast with dry aggregate was about 5 percent greater than for specimens cast with saturated surface dry aggregate. The catalyst ratios were about the same for comparable specimens cast with saturated surface dry aggregate as compared to specimens cast using air dry aggregate. The moisture content of the saturated surface dry aggregate used to cast the polymer concrete ranged from 0.4 to 0.9 percent by weight (see Table 4). As compared to polymer concrete cast using dry aggregate, this small amount of moisture in the aggregate appeared to have relatively little effect on the set time, temperature of concrete at set time, and peak exotherm (see Tables 3 and 4).

Some of the polymer concrete specimens (dry aggregate or saturated surface dry aggregate) were sawed in half to observe the extent to which the resin had filled the voids in the aggregate. From Figures 3 and 4 it can be seen that the resin completely filled the voids in the aggregate. This was the case for the wide range of aggregate and resin temperatures included in the set time tests. Samples denoted as A and B in Figure 3 were from test runs where the aggregate and resin temperatures were about 70°F. In Figure 4, polymer concrete for Test No. 78 and Test No. 118 are shown. In Test No. 78, the room dry aggregate temperature was -26°F and the resin temperature was 5°F. In Test No. 118, the saturated surface dry aggregate temperature was 9°F and the resin temperature was 5°F.



Test No. 1 (Sample A)

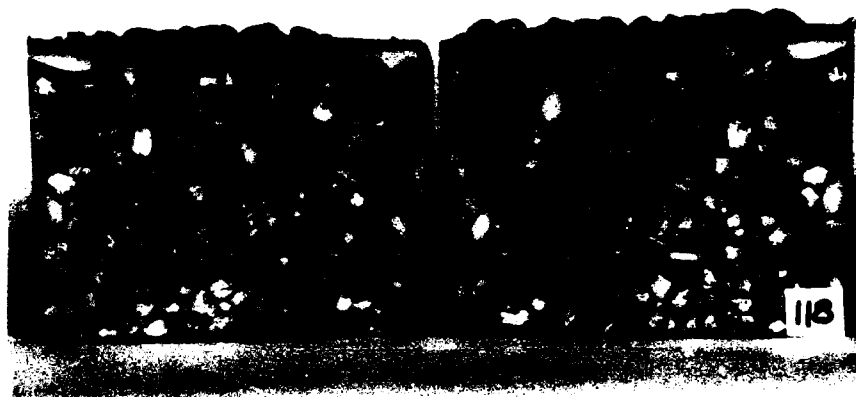


Test No. 2 (Sample B)

Figure 3. Sawed Sections of Polymer Concrete Specimens Cast Using Dry Aggregate at About 70°F.



Test No. 78
Dry Aggregate at -26°F , Resin at 5°F



Test No. 118
Wet Aggregate at 9°F , Resin at 5°F

Figure 4. Sawed Sections of Polymer Concrete Specimens Cast Using Dry Aggregate and Saturated Surface Dry Aggregate at Cold Temperatures.

The results of set time tests using saturated surface dry aggregate containing ice inclusions are reported in Tables 5 and 6. These tables give information about the time of set for this series of tests. In comparing catalyst ratios for set time tests using dry aggregate and saturated surface dry aggregate with aggregate containing ice inclusions, considerably more catalyst was used in the tests with the ice inclusions. It was difficult to control the set time when ice inclusions were in the aggregate. As these tests progressed, apparent short set times (20-30 seconds) were achieved. However, when the polymer concrete samples were examined after the tests, it was observed that only the top portion of the sample, a depth of about 3 to 5 inches, had resin and aggregate bonded together. The bond of the aggregate and resin in the lower parts of the specimens was poor or did not exist. Therefore, since the bond between aggregate and resin in the hardened polymer concrete was poor, the set time data from the specimens cast with saturated surface dry aggregate containing ice inclusions are not applicable for field use. Also, results for test runs with ice inclusions were inconclusive because set times were not reproducible (see Tables 5 and 6).

Photographs of polymer concrete made with ice inclusions are shown in Figures 5 and 6. The poor bond between aggregate and resin is illustrated for Tests No. 144, 149, 150, and 152 in Figure 5 and for Tests No. 154, 157, 160, and 162 in Figure 6.



Test No. 144

Test No. 149



Test No. 150

Test No. 152

Figure 5. Polymer Concrete Specimens Cast with Ice Inclusions (Tests No. 144, 149, 150, and 152).



Test No. 154

Test No. 157



Test No. 160

Test No. 162

**Figure 6. Polymer Concrete Specimens Cast with Ice Inclusions
(Tests No. 154, 157, 160, and 162).**

The aggregate and resin temperatures and the percent ice inclusions for these tests are given in Table 5.

Water is known to affect the rates of many chemical reactions. In this study, only the set time tests using saturated surface dry aggregate with ice inclusions involved appreciable amounts of moisture. As previously noted, considerably more catalyst was required in these tests as compared to tests where air dried or saturated surface dry aggregate was used. Furthermore, the tests which had ice inclusions were inconclusive with regard to set time because set times were not reproducible. Also, for those specimens containing ice-inclusions, the bond between aggregate and hardened resin was poor or did not exist over a large part of the hardened polymer concrete specimens. These differences in test results for polymer concrete specimens containing ice inclusions can also be attributed to the effect of moisture on the chemical reaction during hardening of the polyurethane resins. It is emphasized that very little moisture was present in the saturated surface dry aggregate and that the surface of the aggregate was dry. Since little moisture was present in the saturated surface dry aggregate, it apparently had little effect on the set time compared to tests where air dried aggregate was used.

3.2 Flexural Strength

Data from the flexural tests are presented in Table 7. A photograph of a flexural beam specimen is shown in Figure 7.



Figure 7. Typical Polymer Concrete Flexural Beam Specimen.

The modulus of rupture or flexural strength was determined from beams at age 30 minutes and was calculated as described in ASTM C 78. In this test, flexural strength of the polymer concrete is determined by use of a simple beam with third-point loading. Failure of the beams occurred in the middle third of their span length. The aggregate fractured along the failure line of beams cast at the higher temperatures. Bond failure between the aggregate and resin became more discernible as the casting temperature of the beams decreased. Figure 8 shows the fractured sections of polymer concrete beams from Tests No. 4 and 23. Fractured aggregate can be seen along the failed surfaces of Beam No. 4, whereas pulled out aggregate can be seen along the failed surfaces of Beam No. 23. Beam No. 4 was cast at a high temperature (110°F) and Beam No. 23 was cast at a low temperature (0°F). See Table 7 for aggregate and resin temperatures.

Figure 9 shows the effects of temperature variations of the aggregate and resin on the flexural strength at the time of casting the beams. In this figure, the modulus of rupture is plotted versus T_m . T_m is a weighted value of aggregate temperature and resin temperature at the time of casting a beam specimen. See Section 4.5.1.2 for an explanation of T_m . Temperatures of the aggregate and resin for each flexural test are given in Table 7.



Test No. 4
Aggregate at 110°F, Resin at 71°F



Test No. 23
Aggregate at 0°F, Resin at 55°F

Figure 8. Fractured Sections of Flexural Beam Specimens Cast at High (Test No. 4) and Low (Test No. 23) Temperatures.

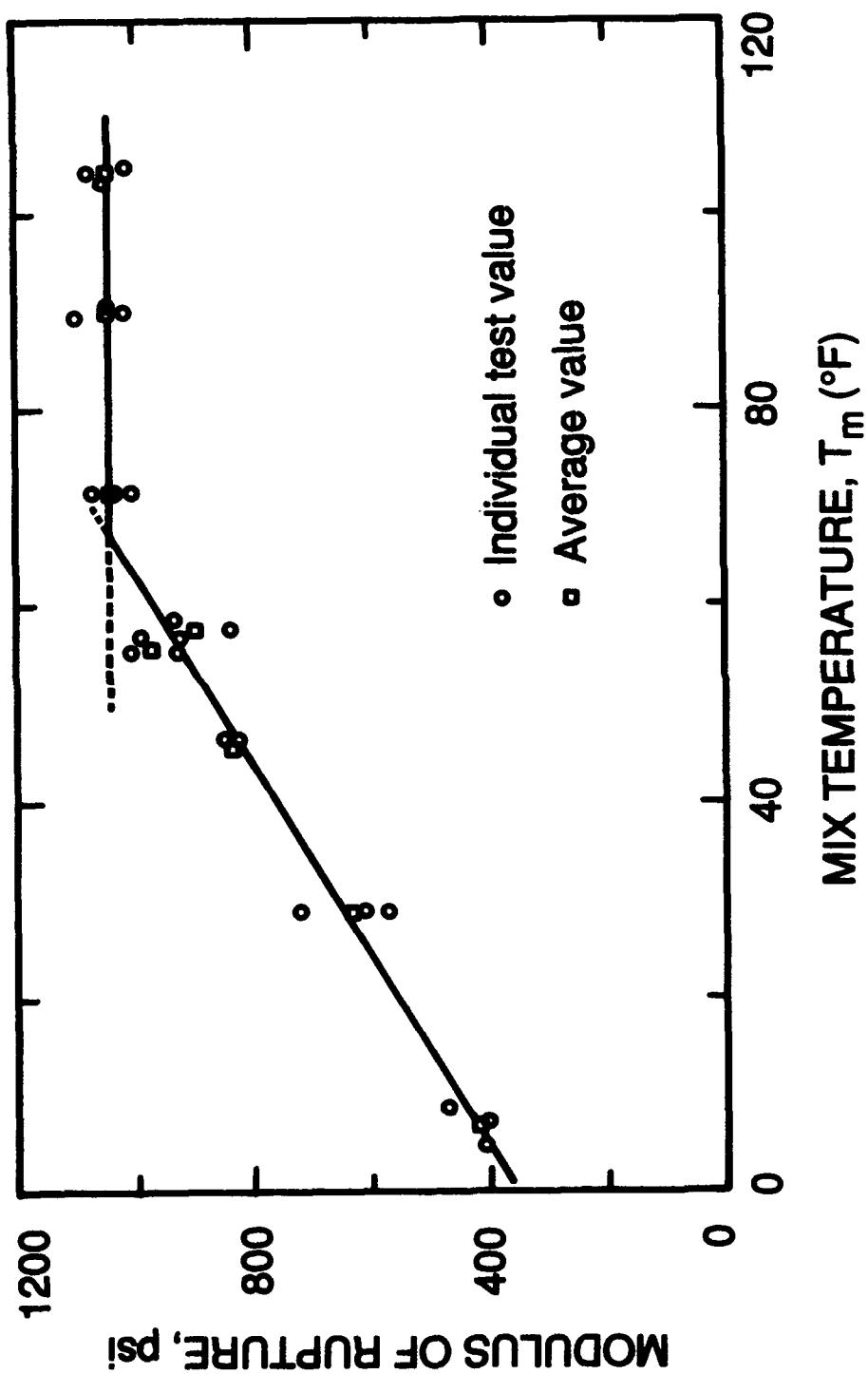


Figure 9. Effects of Temperature Variations of Aggregate and Resin on the Flexural Strength of Polymer Concrete Beam Specimens.

The modulus of rupture was essentially constant for values of T_m above 70°F. For lower values of T_m , the modulus of rupture decreased roughly linearly as T_m decreased. It was observed at a beam age of 30 minutes that the hardened resin in five of the beam specimens was softer than in the other beams. Three of these beams were cast with the aggregate at temperatures between -26 and -33°F, one beam was cast with the aggregate at a temperature of 0°F, and another beam was cast with the aggregate at a temperature of 21°F.

The set times of the resin in casting the 4 x 4 x 14 in. flexural beam specimens were in the range of 30 to 45 seconds. At least three beams were cast for each of the eight different combinations of aggregate and resin temperature as requested by AFESC.

During casting of the beam specimens, the resin flowed through the aggregate and completely filled the voids.

3.3 Auxiliary Tests

Set time prediction model parameters were determined independently in separate tests. Resin heat capacities were found in experiments (denoted as resin warming) where the resins were allowed to warm together with an equivalent amount of water. The heat capacity of the aggregate was taken from the literature. Heat transfer coefficients were determined from tests (denoted as water immersion) conducted with water instead of resin, while reaction

parameters were found from tests (denoted as kinetic) conducted in an insulated container which did not contain aggregate. The results of the auxiliary tests to determine set time model parameters are given in Appendix A.

3.4 Pilot Set Time Tests Using Another Polyurethane Resin

Set time data were obtained from pilot tests by casting a polymer concrete using a different resin (polyurethane) and catalyst than in the main series of tests and using the same mineral aggregate under various temperature and moisture conditions. The pilot set time tests were carried out using the same test procedure as reported in Section 2.2.1. The proprietary resin used in the pilot tests was also a two part polyurethane. The important difference in the pilot tests and the main series of tests, reported in Sections 2.2.1 and 3.1, was that considerably more catalyst was needed in the pilot tests for comparable set times. This was more pronounced for the colder resin and aggregate temperatures. The intent, as in the previous tests, was to have set time between 55 and 75 seconds. Data for the pilot set time tests are reported in Table 8. It is noted that in most of the pilot tests the catalyst was at room temperature (70°F) when added to the Part I resin (phenol formaldehyde). The Part II resin was mostly methylene phenylene isocyanate oligomers. The Part I resin with catalyst was poured into and mixed with the Part II resin. The catalyst was phenylpropylpyridine. Information about

Table 8. Pilot Set Time Tests Using Another Polyurethane Resin

Run Number	Aggregate Temp (°F)	Resin Temp (°F)	Catalyst Ratio by Volume [Catalyst Part 1]	Catalyst ^a Volume (ml)	Set Time (s)	Temp at Set Time (°F)	Peak Exotherm Temp (°F)	Ice Inclusions ^b (%)
170	43	70	0.1410	315	45	91	118	—
171	44	70	0.1320	290	53	103	118	—
172	45	55	0.1344	300	75	102	114	—
173	43	55	0.1500	333	70	133	147	—
174	45 ^c	55	0.1550	344	77	118	130	—
175	44 ^c	55	0.1600	355	66	98	120	—
176	109	107	0.0099	22	104	147	175	—
177	108	108	0.0113	25	98	152	174	—
178	103 ^c	108	0.0135	30	100	153	166	—
179	103 ^c	109	0.0158	35	93	158	180	—
180	23 ^c	55	0.2496	550	140 ^d	120	127	5
181	23 ^c	55	0.2815	625	90 ^e	76	80	5
182	24 ^c	55	0.3041	675	64	101	103	5
183	24 ^c	55	0.3604	800	48	118	125	10
184	-27	5	0.4617	1025	130 ^f	36	52	—
185	-26	5	0.6306	1400	95	15	50	—
186	-27	5	0.7658	1700	220 ^g	17	38	—
188	-22 ^c	1	1.0000	2200	195 ^h	24	53	—

^a Catalyst at room temperature (70°F) was added to resin except for Test No. 186 and 188

^b Percent by mass of aggregate

^c Saturated surface dry aggregate

^d 40% set at 110 s; 80% set at 140 s; 90% set at 195 s

^e 90% set at 90 s

^f 90% set at 130 s; 100% set at 140 s

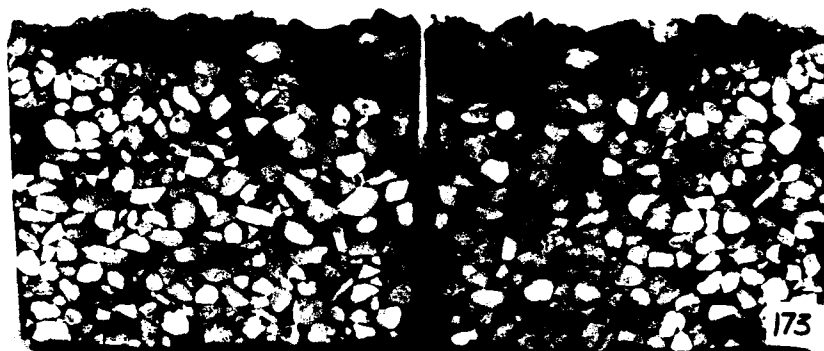
^g 85% set at 220 s

^h 75% set at 195 s

the components of the resins and catalyst were provided by the producer of the material. The AFESC requested that this proprietary resin should not be analyzed for its composition.

The polymer concrete specimens made using air dry aggregate and saturated surface dry aggregate and resin temperatures of 55°F or higher had the voids in the aggregate completely filled with resin. Specimens cast with resin temperatures 5°F or lower and those with ice inclusions present exhibited poor bond over their lower half. Figure 10 shows sawed sections of polymer concrete (Specimens No. 173 and 175) from pilot set time tests. It can be seen that the resin completely filled the voids in the aggregate in these two tests. See Table 8 for aggregate and resin temperatures for these pilot test specimens.

The viscosity of the resin at 5°F was like that of corn syrup. Because of the higher viscosity at this low temperature, the thick resin slowly settled to the bottom of the aggregate. When the low temperature resin set it appeared to be of rubbery consistency.



Test No. 173
Aggregate at 43°F, Resin at 55°F



Test No. 175
Aggregate at 44°F, Resin at 55°F

Figure 10. Sawed Sections of Polymer Concrete Specimens from Pilot Set Time Tests (Tests No. 173 and 175).

4. SET TIME PREDICTION MODEL FOR POLYMER CONCRETE

A mathematical model for the prediction of the set time of polymer concrete was developed based upon thermodynamic and kinetic principles. The model consists of energy balances, one for the resin matrix (continuous phase) and the other for the aggregate particles (dispersed phase), as well as a molar balance on the reacting species (resins). The energy balance is composed of two simultaneous coupled non-linear differential equations, one governing temperatures in the resin and the other temperatures in the aggregate. It accounts for heat exchange between resin and aggregate and the heat of reaction as well as heat losses to the surroundings. The molar balance consists of a single non-linear differential equation governing the conversion of the resins into a polymer product. Because of the heat of reaction, the energy and molar balances are mathematically coupled.

Model input includes initial temperatures (resin, aggregate and surroundings), catalyst concentration, moisture and ice content (if present) and weights of aggregate and resin. Model parameters include heat transfer coefficients and time constants, specific heats of the phases, chemical reaction order, reaction activation energies and parameters measuring the effect catalyst concentration has on the reaction rate constant. Model output predicts set time, resin conversion, and the temperature of the resin and aggregate as functions of time. For runs with ice inclusions the model also predicts the fraction of ice which has melted.

In order to independently determine the parameters of the model, separate auxiliary tests were made. Resin heat capacities were found in experiments where the resins were allowed to warm in a temperature controlled environment. Heat transfer coefficients and model time constants were found from tests conducted with water used in place of resin, while reaction parameters were found from separate runs conducted in insulated containers which contained no aggregate. These latter tests established a reaction order of 1.5 and a set time which occurred near 60 percent conversion of the resin regardless of experimental conditions. These results suggest for the system examined that reaction proceeds by a free radical mechanism which leads to a critical degree of chain branching where set rapidly insues. The reaction activation energy was found to decrease with increasing catalyst concentration, as would be expected based on kinetic theory. The data collected were fitted to models developed and solved specifically for the auxiliary tests. Use of independently determined parameters increased model credibility. Because of constraints, the time constant for aggregate heat transfer could not be independently found in this way. Instead, its value was determined by matching experimental data of resin temperature for each run directly to the set time prediction model and then using an overall average. Results showed that heat transfer into the aggregate was much faster than heat loss to the air.

Values of the parameters obtained were used in the set time prediction model to compare to experimental data of set time and average resin temperature vs. time. Reasonable agreement was found between the model and the data since observed set times and resin temperatures were generally in accord with those predicted by the model. Larger deviations between predicted and experimental results were noted at higher catalyst concentrations and lower initial resin and aggregate temperatures.

The model was run in a simulation mode to produce generic plots which illustrated the effects of model parameters on resin temperature, conversion and predicted set times. Each parameter in turn was varied about its base value with the other parameters fixed at theirs. The relative importance of the governing phenomena was shown to be consistent with expected trends and results from the auxiliary tests.

Methods were also developed to extend this treatment to the simulation of field conditions for rapid runway repair using polymer concrete. By running the model repeatedly a series of design charts was prepared. The design charts can be used to predict set time given the catalyst concentration and initial temperatures of the aggregate and resin, or to determine the catalyst concentration to use to assure set within a given time at specified temperature levels.

4.1 Conceptual Model

The conceptual basis for the mathematical model is discussed in terms of the mechanisms of heat transfer and reaction.

4.1.1 Heat Transfer Mechanisms

In the laboratory set time tests of polymer concrete, both the resins and aggregate were contained in a plastic bucket located in a temperature controlled environmental chamber. The catalyst was first premixed with Resin B (diamine-polyglycol) and then added and mixed with Resin A (isocyanate). The resulting mixture was then rapidly poured over the aggregate. Although the temperature of the chamber remained constant the temperature of the resin rose because the heat of reaction did not have enough time to escape to the surroundings. In the laboratory tests, the temperature of the resin rose rapidly at the start of the tests, sometimes to a maximum or peak exotherm, and then slowly fell to a pseudo-constant value much above ambient. Set generally occurred while the temperature was increasing rapidly but before the peak exotherm. The temperature at set was generally slightly less than the peak exotherm.

Figure 11 depicts the heat flow occurring within the system. The energy of reaction can go into heating the resin and aggregate or be lost to the surroundings through the walls of the bucket. In

runs conducted with moisture or ice inclusions, some of the energy of reaction can be transferred to heat the water and/or melt the ice. In those cases where the aggregate temperature is greater than that of the resin, heat flows the other way, i.e., from aggregate to resin.

It is the relative rate of heat transfer by different mechanisms which determines temperatures within the system, the conversion of the resins and set time. Heat transfer between phases is presumed to be dependent on convection across heat transfer films. Convection occurs between resin and aggregate, between resin and surroundings, and, with moisture or ice inclusions, between resin and water or ice. The less energy consumed in heating the resin, because of losses to the aggregate, moisture, ice or surroundings, the lower will be the temperature of the resin and the longer it will take set to occur. This effect feeds on itself since lowering the resin temperature will result in lower reaction rates leading to longer set times.

4.1.2 Reaction Mechanisms

With polymer reactions, the kinetic equations are normally formulated in terms of reactive groups rather than the actual concentrations of the resins. In this study, the composition and structure of the resins were proprietary and at the request of AFESC were not determined. Thus, it was not possible to determine

the exact amount or nature of reactive groups present in the resin molecules. Reactions can involve chain initiation, propagation, and termination each of which can control reaction during a different period, and one of which may be rate controlling. It is also generally assumed that reaction rates are independent of the degree of polymerization. As molecular weights become larger, at higher degrees of polymerization, this assumption is less likely to be true.

The reaction between the two resins (A and B) is irreversible and is represented by



where a, b and p are the respective stoichiometric coefficients for Resin A, Resin B, and the polymer product P.

From the stoichiometry it follows that:

$$\frac{[A_0] - [A]}{a} = \frac{[B_0] - [B]}{b} = \frac{[P]}{p} \quad (2)$$

Here [A] and [B] are the molar concentrations of the reacting components in the Resins A and B after reaction has started, [P] is the concentration of polymer product P, and [A₀] and [B₀] are the initial concentrations. In the present analysis it is assumed that neither reacting ingredient is present in molar excess. Any other feed ratio would produce a residual amount of

one of the resins whose excess would act as a diluent and contaminant, potentially lowering attainable strengths and increasing set times.

With neither reactant present in molar excess $[B_0] = \frac{b}{a} [A_0]$, so that:

$$[B] = \frac{b}{a} [A] \quad (3)$$

In general, for a power law rate equation, the rate of chemical reaction can be written as:

$$- r_A = k' [A]^r [B]^q \quad (4)$$

where

- r_A is the chemical reaction rate of Resin A (mol A/m³, s)

k' is the reaction rate constant

r is the reaction order for Resin A

q is the reaction order for Resin B

The reaction rate is based on the amount of Resin A reacting per unit volume of solution obtained by mixing both resins together. The minus sign indicates that Resin A is being consumed.

Under condition that neither resin is present in molar excess it follows that:

$$-r_A = k [A]^{r+q} = k [A]^n \quad (5)$$

where $k = \left(\frac{b}{a}\right)^q k'$ is a modified reaction rate constant

Equation (5) results when (3) is substituted into equation (4). The overall reaction order is $n = r+q$. If the reaction was molecular (occurring as written in equation (1)) then the order would in general correspond to the stoichiometry (i.e., $r=a$, and $q=b$) and the overall order would be $(a+b)$, an integer. However, many polymerization reactions are not molecular having non-integral order characteristic of free-radical type reactions [14]. Thus n is unlikely to be an integer.

It is possible to obtain reaction orders and rate constants by analyzing kinetic data in terms of changes of concentrations of reactants (or products) with time. As shown in the next section, thermal data (temperature vs. time) can also be used to obtain information on the kinetics. However, in either case, it is not possible to obtain individual reaction orders, r and q , unless experiments are conducted in which the relative amounts of Resins A and B used are changed from run to run. In the experiments conducted in this study, the amounts of Resins A and B were not varied. Only the amount of catalyst used and the initial

temperature were varied. Thus, only the overall reaction order, n , was obtained.

4.2 Mathematical Model

The mathematical model for set time prediction was developed based on the conceptual model.

4.2.1 Energy Balance: Dry Aggregate

In this section, the aggregate is presumed to be dry so that there is no moisture nor ice inclusions present.

The temperature of the resin (T) and the aggregate (T_a) in the bucket are assumed to vary with time, but not with position within the system. This was observed from data from the three thermocouples in the aggregate in the bucket. The measured temperatures were usually within several degrees from one another after the mixed resins were poured into the aggregate. Accounting for the different modes of heat transfer (refer to Figure 11), a macroscopic energy balance can be written for both the resin and the aggregate. The energy balance has the form:

$$\begin{aligned} \text{Rate of Accumulation} \\ \text{of Energy} \quad = \quad & \sum \text{Rate of Input} \\ & \text{of Energy} \quad - \quad \sum \text{Rate of Output} \\ & \text{of Energy} \\ & + \sum \text{Rate of Appearance of Energy} \\ & \text{by Chemical Reaction} \quad (6) \end{aligned}$$

For the resin the energy balance becomes:

$$\frac{dE_t}{dt} = MC_v \frac{dT}{dt} = -U_o A(T - T_{air}) - h A_a(T - T_a) + (-r_A) (-\Delta H_A)V \quad (7)$$

<u>accumulation</u> <u>of energy</u>	<u>loss of energy</u> <u>to air</u>	<u>loss of energy</u> <u>to aggregate</u>	<u>generation of</u> <u>energy by</u> <u>chemical</u> <u>reaction</u>
---	--	--	--

where

E_t	is the total energy of the resin mixture (J)
U_o	is the overall heat transfer coefficient between the resin and the air ($W/m^2.K$)
h	is the heat transfer coefficient between the resin and the aggregate ($W/m^2.K$)
A	is the surface area of the resin exposed to the air (m^2)
A_a	is the total surface area of the aggregate particles (m^2)
T, T_a, T_{air}	are the temperatures of the resin, aggregate and air respectively (K)
M	is the mass of resin (kg)
C_v	heat capacity of resin ($J/kg.K$)
$-r_A$	is the rate of chemical reaction ($mol A/m^3.s$)
$(-\Delta H_A)$	is the enthalpy of reaction ($J/mol A$)
V	is the volume of resin (m^3)
t	is time(s)

Assuming that potential and kinetic energy changes are negligible, the total energy, E , of the system will be equal to the internal energy U .

$$\frac{dE_t}{dT} = dU = MC_v dT \quad (8)$$

The overall heat transfer coefficient U_o can be found from a knowledge of the dimensions of the bucket, individual inside (resin to bucket) and outside (bucket to air) heat transfer coefficients, and the thermal conductivity of the bucket walls. An expression can be developed for U_o by considering that heat transfer occurs through the bucket walls in series with convection through inside and outside heat transfer films, but in parallel when considering that heat can simultaneously be lost from the sides, top and bottom of the bucket.

An energy balance (equation (7)) can also be written for the aggregate particles. It takes the form:

$$M_a C_{va} \frac{dT_a}{dt} = h A_a (T - T_a) \quad (9)$$

where

M_a is the mass of aggregate (kg)

C_{va} is the heat capacity of the aggregate (J/kg.k)

Equation (9) equates the aggregate's rate of gain of internal energy to the heat flowing into the aggregate particles from the resin. When the aggregate is colder than the resin ($T_a < T$), heat will flow the other way. Under these conditions, equation (9) will still be valid.

4.2.2 Molar Balance

Considering the Resin A contained in the bucket as the system and applying the molar conservation equation:

$$-\frac{dN_A}{dt} = (-r_A) V \quad (10)$$

where N_A is the mols of Resin A contained in the system.

Unlike energy flow, there is no flow of A in or out of the system, so that the depletion of A matches its disappearance by reaction. Since $N_A = [A]V$ and V is constant, it follows from equation (10) that,

$$-\frac{d[A]}{dt} = (-r_A) \quad (11)$$

a result which is true in general for any compound in a batch system. Substituting equation (5), the kinetic rate expression, into equation (11):

$$-\frac{d[A]}{dt} = k [A]^n = k_0 e^{-E/RT} [A]^n \quad (12)$$

In general, as shown by equation (12), the rate constant k will vary with temperature according to the widely used Arrhenius form:

$$k = k_0 e^{-E/RT}$$

where k_0 , the pre-exponential factor, is often presumed constant, but can be a function of temperature or activation energy, E , depending on the theory employed [15].

Equations (7), (9) and (12) comprise a set of three simultaneous non-linear ordinary differential equations governing the temperatures and concentration within the system. Together with their initial conditions, T_0 , T_{a0} and $[A_0]$, they can be solved simultaneously to predict resin and aggregate temperatures as a function of time as well as the concentration of resin remaining at any time.

Knowing the concentration, the conversion of resin (x) can be obtained:

$$x = \frac{[A_0] - [A]}{[A_0]} \quad (13)$$

The conversion will vary from 0 to 1 as reaction proceeds and the resin concentration changes from its initial to final value.

4.2.3 Mathematical Model: Dimensionless Form

The model can also be expressed in dimensionless form in order to facilitate computation. In the dimensionless form, equations (7), (9) and (12) become, respectively, equations (14), (15) and (16):

$$-\frac{dT'}{dt'} = \frac{T' - T'_{\text{air}}}{r} + m (T' - T'_a) - (-\Delta H)' \frac{dx}{dt'}, \quad (14)$$

$$-\frac{dT'_a}{dt'} = (T'_a - T') \quad (15)$$

$$\frac{dx}{dt'} = t_a \beta e^{-E/RT} (1-x)^n \quad (16)$$

where

$$T' = T/T_0, \quad T'_{\text{air}} = T_{\text{air}}/T_0, \quad T'_a = T_a/T_0$$

(dimensionless temperatures)

$$t' = t/t_a, \text{ dimensionless time}$$

$$t_a = \frac{M_a C_{va}}{h A_a}, \text{ aggregate time constant}$$

$$t_{\text{air}} = \frac{M C_v}{U A}, \text{ air time constant}$$

$$m = \frac{M_a C_{va}}{M C_v}, \text{ aggregate-to-resin heat capacity ratio}$$

$$r = \frac{t_{\text{air}}}{t_a}, \text{ time constant ratio}$$

$$(-\Delta H)' = \frac{(-\Delta H_A) V [A_0]}{M C_v T_0}, \text{ dimensionless heat of reaction}$$

$$\beta = [A_0] k_o^n, \text{ modified pre-exponential factor}$$

The primed notation denotes dimensionless quantities. The dimensionless initial conditions are that at time zero,

$T'_0 = 1$, $T'_{a0} = T_{a0}/T_0$ and $x_0 = 0$. In the model the dimensionless time t' is based on the aggregate time constant t_a , i.e., $t' = t/t_a$.

t_{air} and t_a are time constants for the transfer of heat from the resin to the air and aggregate, respectively. They have physical significance because they are a measure of the time taken for the resin to lose a certain amount of energy in the absence of other modes of heat transfer. The ratio of the time constants t_{air}/t_a (denoted by r), which appears in the dimensionless resin energy balance, is the ratio of the rates at which energy produced by the chemical reaction goes into air and the aggregate, respectively. High values of r indicate that heat is transferred much more rapidly to the aggregate than it is to the air. In this situation, the temperatures of the resin and aggregate will rapidly approach each other because heat is only slowly lost to the outside.

Subsequent heat transfer would then occur to the surrounding air with the system cooling as a unit.

Casting the model in dimensionless form has a number of advantages. The number of variables are greatly reduced, the physical significance of model parameters is more apparent and the use of a dimensionless model facilitates comparison with experimental data.

4.3 Modeling Effects of Moisture and Ice

The effects of moisture in aggregate (saturated surface dry) on setting time was also investigated. Between 0.5 and 0.9 percent by mass of moisture was added to the aggregate prior to the tests. In other tests, ice inclusions were added as granulated ice. The model was modified to treat these conditions.

4.3.1 Wet Aggregate (Saturated Surface Dry)

The quartz aggregate was relatively impermeable. Little water was observed on the surface of the saturated surface dry aggregate after towel drying. The aggregate absorbed 0.4 to 0.9 percent water by mass. At temperatures below freezing, small ice crystals were present on the aggregate surfaces. When the reaction began this ice melted. An energy balance on the ice-aggregate system gives an estimate of T_{aio} , the temperature of aggregate reached when ice of mass M_i has melted:

$$T_{aio} = T_{ao} - \frac{M_i \lambda_m}{M_a C_{va}} \quad (17)$$

where λ_m is the latent energy of melting.

For runs made using wet aggregate, T_{aio} is a more representative measure of the initial aggregate temperature than T_{ao} . However, since M_i/M_a is only about 0.003, the value of the second term will be less than a fraction of a degree. Therefore, little

error is introduced in analyzing the wet aggregate runs using the model previously developed for dry aggregate.

4.3.2 Ice Inclusions

In runs made with the addition of granulated ice, the amount of ice employed was sufficiently large (5 to 10 percent by mass of the aggregate) that a significant amount of the reaction energy went into heating the ice to 0°C , melting it, and then warming the water formed above 0°C . In this case, the model had be modified to account for these phenomena. The effect is to split the resin energy balance into three regions or periods, one corresponding to times before the ice begins to melt ($t < t_A$), one while the ice is melting ($t_A < t < t_B$) and the last after all the ice has melted ($t > t_B$). In addition, predictions need to be made of the ice temperature, T_i , the water temperature, T_w , and the fraction, f , of the ice which has melted at any given time. Model development is similar to that for the dry aggregate runs. The dimensionless model is presented below as equations (18) through (23). For ease in interpretation, the equations have been multiplied by T_0 , the initial resin temperature. The time of applicability of each equation is underlined below the equation. Initial conditions are also presented below each equation.

Equations 18, 19 and 20 give the resin energy balance during the three periods.

$$\frac{dT}{dt'} = \frac{T_{\text{air}}}{r} + m (T - T_a) + \frac{m_i}{r_i} (T - T_i) - (-\Delta H)' T_o \frac{dx}{dt'} \quad (18)$$

$$\frac{(T = T_o \text{ at } t = 0)}{\quad} \quad \frac{(t < t_A)}{\quad}$$

$$- \frac{dT}{dt'} = \frac{T - T_{\text{air}}}{r} + m (T - T_a) - (-\Delta H)' T_o \frac{dx}{dt'} + \frac{m_{iw}}{r_{iw}} (T - 273.2) \quad (19)$$

$$\frac{T = T_{AO} \text{ at } t = t_A}{\quad} \quad \frac{(t_A < t < t_B)}{\quad}$$

$$- \frac{dT}{dt'} = \frac{T - T_{\text{air}}}{r} + m (T - T_a) - (-\Delta H)' T_o \frac{dx}{dt'} + \frac{m_w}{r_w} (T - T_w) \quad (20)$$

$$\frac{T = T_{BO} \text{ at } t = t_B}{\quad} \quad \frac{(t > t_B)}{\quad}$$

Equations 21, 22 and 23 give the ice-water energy balance during the three periods.

$$\frac{dT_i}{dt'} = \frac{(T - T_i)}{r_i} \quad \frac{\text{ice only}}{\quad} \quad (21)$$

$$\frac{T_i = T_{i0} \text{ at } t = 0}{\quad} \quad \frac{(t < t_A)}{\quad}$$

$$\frac{df}{dt'} = T_o \frac{(T - 273.2)}{r_{iw}} \quad \frac{\text{ice and water}}{\quad} \quad (22)$$

$$\frac{f = 0 \text{ at } t = t_A}{\quad} \quad \frac{(t_A < t < t_B)}{\quad}$$

$$\frac{dT_w}{dt'} = \frac{(T - T_w)}{r_w} \quad \frac{\text{water only}}{\quad} \quad (23)$$

$$\frac{T_w = T_{w0} = 273.2 \text{ K at } t = t_B}{\quad} \quad \frac{(t > t_B)}{\quad}$$

where

$$r_i = \frac{t_i}{t_a}, \text{ ice time constant ratio}$$

$$\text{with } t_i = \frac{M_i C_{vi}}{h_i A_i}, \text{ ice time constant}$$

and

M_i = mass of ice (kg)

C_{vi} = specific heat of ice (J/kg . K)

h_i = heat transfer coefficient between resin and ice
(W/m² . K)

A_i = surface area of ice (m²)

$$m_i = \frac{M_i C_{vi}}{M C_v}, \text{ ice to resin heat capacity ratio}$$

$$m_{iw} = \frac{M_{iw} C_{viw}}{M C_v}, \text{ ice water to resin heat capacity ratio}$$

$$m_w = \frac{M_w C_{vw}}{M C_v}, \text{ water to resin heat capacity ratio}$$

and

C_{vw} = specific heat of water (J/kg . K)

h_w = heat transfer coefficient between the resin and the water
(W/m² . K)

$$r_{iw} = \frac{t_{iw}}{t_a}, \text{ ice-water time constant ratio}$$

with

$$t_{iw} = \frac{M_i C_{viw}}{h_{iw} A_i}, \text{ ice-water constant}$$

and

C_{viw} = specific heat of ice-water mixture (J/kg · K)

h_{iw} = heat transfer coefficient between the resin and the ice-water (W/m² · K)

$$r_w = \frac{t_w}{t_a}, \text{ water time constant ratio}$$

with

$$t_w = \frac{M_i C_{vw}}{h_w A_i}, \text{ water time constant}$$

The differential equations for the aggregate energy balance, equation (15), and the reaction kinetics, equation (16), are the same as when the aggregate is dry. T_{A0} is the resin temperature when the ice first melts ($t = t_A$), while T_{B0} is the resin temperature when all the ice has melted ($t = t_B$). T_{i0} is the initial ice temperature. All the ice will have melted (at $t = t_B$) when $f = 1$. Considering that water and ice have similar specific heats and heat transfer coefficients, it is reasonable to assume that $m_i = m_{iw} = m_w$. The differential equations governing the model for the system with ice inclusions [equations (15), (16), and (18) through (23)] can be programmed and solved to predict

resin, aggregate, ice and water temperatures as well as the conversion and fraction of ice melted at any time.

4.4 Model Parameters

In developing the set time prediction model for polymer concrete, information on the properties of the resins and aggregate, on the rate of internal and external heat transfer, and on the rate and heat of reaction of the two-part resin system using various amounts of catalyst was needed as input to the set time prediction model. This section summarizes model parameters, the methods used to find them and discusses their significance.

4.4.1 Determination of Model Parameters

Table 9 presents a summary of the values of the model parameters. These were determined from auxiliary tests, from accepted literature values, from model equations and from the simulation tests themselves. The mathematical model contains geometric parameters like mass and density, thermal parameters like specific heats and heat transfer coefficients, and kinetic parameters like activation energy and reaction order. Although geometric parameters can be measured directly and others like specific heat can be obtained from the literature, the other model parameters are unknown. Separate auxiliary tests were devised and conducted to provide these data so that most model

Table 9. Set Time Model Parameters

<u>Parameter</u>	<u>Value</u>	<u>Test Method or Citation</u>
C_{vA}	1.846 kJ/kg.K	auxiliary - resin warming
C_{vB}	1.788 kJ/kg.K	auxiliary - resin warming
C_v	1.748 kJ/kg.K	calculated - weighted average
C_{va}	1.088 kJ/kg.K	literature [16]
m	2.176	equation (14)
U_o	9.56×10^{-2} kJ/kg $m^2 \cdot s$	equation (A1)
r	> 100	auxiliary - water immersion
t_{air}	2.38×10^4 s	auxiliary - water immersion
t_a	95.2 s	simulation fit, weighted average
$\Delta H'$	0.3626	auxiliary - kinetic, equation (A12)
n	1.5	auxiliary - kinetic
E_o	6800 cal/g mol	auxiliary - kinetic
E_m	9230 cal/g mol	auxiliary - kinetic
m_o	1540 g mol/cal	auxiliary - kinetic
β_o	4.09×10^2 s ⁻¹	auxiliary - kinetic
α	5.6×10^{-4} g mol/cal	auxiliary - kinetic

parameters were determined independently of the polymer concrete set time experiments. The experimental procedure for the auxiliary tests is explained in Appendix A. Along with the best values obtained for the model parameters, Table 9 also provides the test method used in the auxiliary tests to determine the parameters. Appendix A provides the model development that was used to obtain these parameters.

In its dimensionless form the overall mathematical model contains eight unknown model constants, the air and aggregate time constants, t_{air} and t_a ; the heat capacity ratio, m , the time constant ratio r ; the dimensionless heat of reaction, $\Delta H'$; the reaction order, n ; and the kinetic factor, β . Additional kinetic parameters are involved in finding the temperature dependence of β . The three auxiliary test methods used to find model parameters have been designated as resin warming tests (used to determine heat capacity parameters and thermal parameters, m and U_0 , C_{vA} , C_{vB} , C_v and m), water immersion tests (used to determine, or attempt to determine, time constant and thermal parameters, r , t_{air} , t_a , and U_0), and kinetic tests (used to determine kinetic parameters $\Delta H'$, n , E_0 , E_m , m'_0 , β_0 and α). In Appendix A, theory and procedures for determining these parameters are presented for each test method. The parameter, t_a , was an average value, found by fitting test data for individual simulation runs directly to the mathematical model. The determination of t_a is discussed in Section 4.4.2.

4.4.2 Discussion of Results

The heat capacities found from the resin warming tests and overall heat transfer coefficients are consistent with generally accepted literature values [17]. The parameter m , defined as $M_a C_{va} / M C_v$, is a measure of the thermal inertia of the aggregate as compared to that of the mixed resin. A value of $m \approx 2$ (Table 9) indicates that the aggregate has about twice the ability to absorb thermal energy. The values of the time constants give a measure of how fast energy goes from the resin to the air (t_{air}) or to the aggregate (t_a). Since it was found that $t_{air} \gg t_a$, the energy of reaction is predicted to go rapidly into the aggregate and only slowly into the air. This is confirmed by the parameter, r , the ratio of t_{air} to t_a . In the auxiliary resin warming tests, this parameter was established to be large. The value calculated from t_{air}/t_a is 250, which indicates that energy goes into the aggregate 250 times faster than it is lost to the air. These results are consistent with the fact that the resin and aggregate are in direct physical contact while the air is external to the buckets used in the experiments. Since air also has a relatively low thermal conductivity, reaction energy is channeled into heating the resin and aggregate rather than being lost to the surroundings. In addition, the total surface area of the aggregate (A_a) is much greater than that of the bucket exposed to air (A), so that the energy of reaction more easily flows into the aggregate.

The kinetic parameters listed in Table 9 were all obtained in separate auxiliary tests. The procedures used to find the kinetic parameters are summarized in Appendix A (Section A.3.2.2). The reaction order of 1.5 is non-integral. Its value suggests that the polymerization process proceeds by a non-elementary reaction mechanism, perhaps involving chain branching [18]. The activation energies, E_o and E_m , are also in the range typical of many polymerization reactions [19]. The fact that the activation energy for polymerization (E) decreases with catalyst concentration is also consistent with kinetic theory [19]. It would be expected that an increased concentration of catalyst would provide more sites for reaction, thereby lowering the energy barrier for reaction. This is also consistent with the concept that more catalyst lowers set time since, with a lower activation energy, the critical degree of chain branching for setting would occur sooner.

4.5 Model Validation

To validate the mathematical model, its predictions were compared with experimental data, and the consistency of its predictions was investigated when model parameters were varied around base or average values. In this section, the model predictions are compared to experimental set times and to data of resin temperature vs. time. Model predictions are illustrated and discussed and methods are reported for determining the best value of the

aggregate time constant, t_a . Also, model implementation and predictions are presented.

4.5.1 Comparison of Model Predictions with Experimental Data

4.5.1.1 Comparison with Set Times

Set time data were collected for both the auxiliary kinetic tests and the set time simulation experiments. In this section these tests and experiments are discussed and the results compared to one another.

To predict the set time of polymer concrete, it is necessary to establish the conditions which influence set. The experiments conducted both with and without the addition of aggregate show that set occurs most rapidly when initial resin temperature, initial aggregate temperature and catalyst concentration are all high. Conversely, when the resin and aggregate are cold and the catalyst concentration is low, set is retarded. Since temperature is a measure of the degree of reaction, these facts are consistent with the expectation that set is correlated with the amount of reaction which has occurred.

4.5.1.2 Empirical Modeling of Set Time

Preliminary modeling of set time predictions was empirical. It was based on the concept that, since both temperature and catalyst influence set time, there might be a correlation between them. Two approaches were taken. In the first, catalyst concentration was plotted against initial resin temperature (Figure 2). As expected, the data showed that more catalyst was needed when the resin was cold; it also showed the equally important effect of initial aggregate temperature on set time. In the second approach, which did account for aggregate temperature, the catalyst concentration was plotted against the adiabatic mix temperature, T_m (Figure 12). T_m is defined as:

$$T_m = \frac{M C_v T_o + M_a C_{va} T_{ao}}{M C_v + M_a C_{va}} \quad (24)$$

T_m is the temperature which would be achieved if the aggregate and resin were mixed in the absence of reaction and heat transfer to the surroundings. A similar mixture temperature has been recommended by ACI for use in calculations involving cold weather concreting systems [20].

Although there are a number of outlying points in Figure 12, especially for the runs made with ice inclusions, where set was ill-defined, a single curve could be drawn through the data.

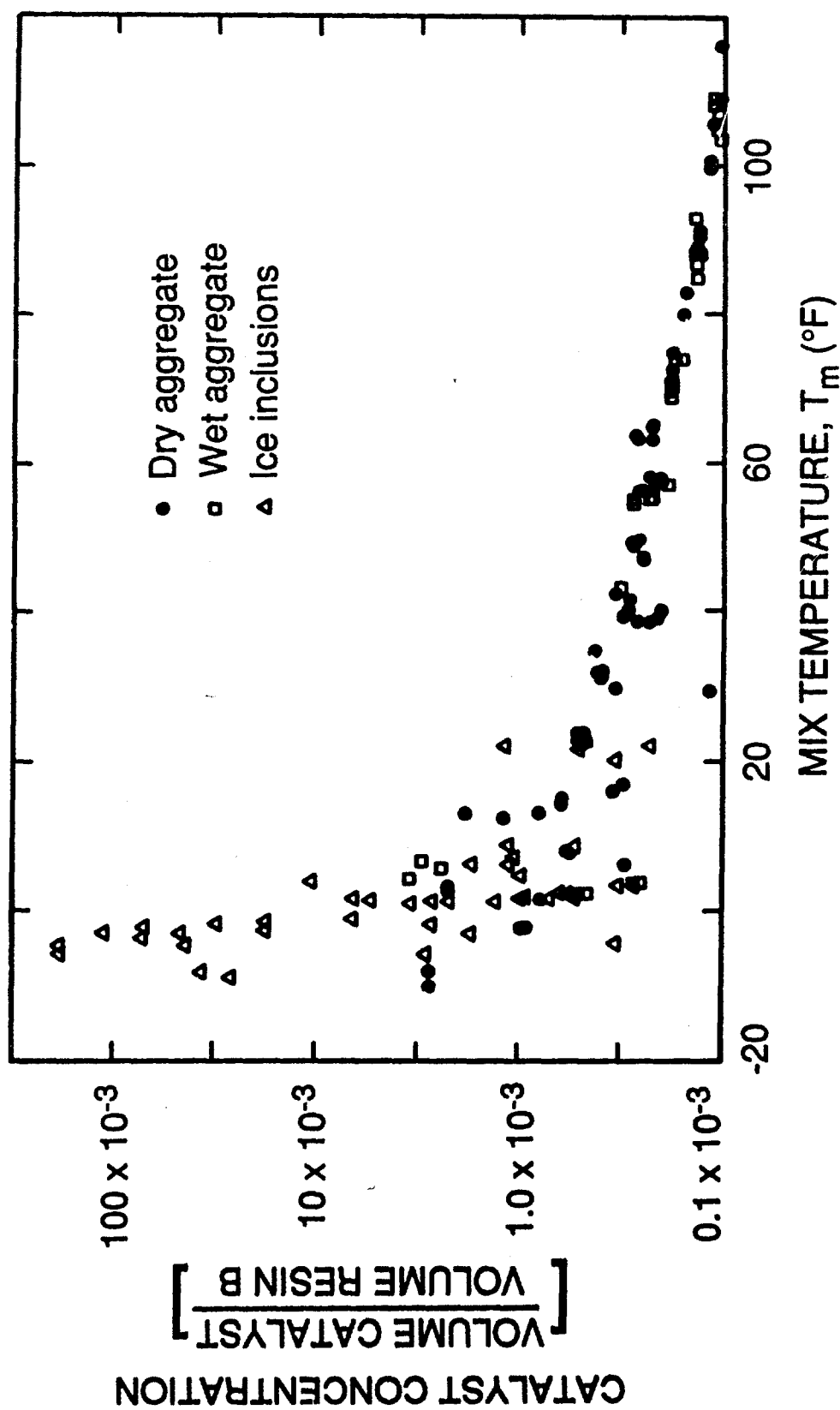


Figure 12. Plot of Catalyst Concentration Versus Adiabatic Mix Temperature, T_m , for Set Times of 40 to 120 seconds.

This is unlike the first approach (Figure 2) where the correlation between catalyst concentration and resin temperature levels was not as discernible. A linear relationship is suggested for adiabatic mix temperatures, T_m above 20°F. Figure 12 can not be used to predict set sufficiently precisely because experimental set times varied over a fairly wide range (40-120 s).

This wide range of experimental set times explains some of the scatter in Figure 12. Although the correlation shown in Figure 12 is not based on first principles, it is nevertheless useful since it shows that as temperatures increase much less catalyst is required for approximately equal set times.

4.5.1.3 Mathematical Modeling of Set Time Prediction

Mathematical modeling of the prediction of set time is based on the mathematical model developed to predict temperatures and resin conversions, and the concept, previously discussed, that set occurs at or near a specific value of resin conversion. Although plausible, this hypothesis is rather sweeping in scope and needs experimental verification.

For the experiments conducted in small insulated beakers with no aggregate (auxiliary kinetic tests), set time was accurately recorded for each test. At each resin temperature and catalyst level employed, Table 10 lists the observed set time (t_s) and

conversion at set (x_s). The three replicate runs gave reproducible values of resin conversion but not of set time, which for two of these runs differed by a factor of two. In general, the results show that higher catalyst concentrations and initial resin temperatures do indeed lower set time. This is consistent with an interpretation based on the principles of chemical reaction and heat transfer. The higher the catalyst concentration (C) and initial resin temperature (T_0), the faster the reaction and the more heat is liberated at any given time. This effect is autothermal since as the temperature rises the reaction accelerates. Results from the auxiliary kinetic tests show that resin temperature only approaches a constant value when most of the energy of reaction has been expended, well beyond set.

The critical value of resin conversion where set occurs (x_s) could depend on both C and T_0 . However, Table 10 shows no clear correlation with either variable. At 40°, 71° and 90°F the average values of conversion at set are 0.59, 0.61, and 0.53, respectively. As catalyst concentration increases at a given initial resin temperature, Table 10 shows that the set time conversion also remains relatively constant, with slightly larger values at $C = 3$. It appears, then, that within experimental error, x_s is independent of C and T_0 . The average value of x_s for all of the 21 tests is $x_s = 0.589 \pm 0.152$. With

Table 10. Observed Set Time (t_s) and calculated Resin Conversion at Set (x_s) Determined from Auxiliary Kinetic Tests

<u>Catalyst Concentration (C)</u> 1000 x $\frac{\text{vol catalyst}}{\text{volume Resin B}}$	<u>Initial Resin Temperature (°F)</u>		
	<u>40</u>	<u>71</u>	<u>90</u>
0	0.656 (291) ⁺	0.735 (255)	0.573 (88)
0.3	0.669 (194) 0.643 (205)	0.619 (105)	0.571 (57)
0.4	0.620 (172)	0.607 (78)	0.540 (45)
0.7	0.622 (108)	0.573 (55) 0.472 (13)	0.475 (27)
1.3	0.528 (60) 0.692 (64)*	0.487 (32)	0.563 (21)
2.6	0.544 (44)	--	--
5.0	--	0.586 (17)	--
7.8	0.429 (15)	--	--

⁺ numbers in parenthesis are the observed set times, t_s , in s.

* $C = 1.25 \times 10^{-3}$ for this test.

the runs at $C = 0$ omitted, this becomes $x_s = 0.576 \pm 0.152$. Accordingly, the criterion that set occurs when $x_s = 0.58$ was adopted.

For the main simulation experiments, the experimental set times were also measured. These can be compared to the predictions of the model by running the mathematical model until the conversion reaches 58 percent. This criterion is applied to all of the runs made with dry and saturated surface dry aggregate. The time when this occurs is the predicted set time. A bias plot can then be prepared of predicted vs. experimental set times. Figure 13 presents such a plot with $x_s = 0.58$ for the dry and saturated surface dry aggregate runs. Dry aggregate runs are marked by closed circles and saturated surface dry aggregate by open circles. The bias line shown represents perfect correlation (no error). Although there is a good deal of scatter, the data are essentially evenly distributed about the bias line which indicates a fair correlation between theory and experiment. When the analysis was redone, postulating that set occurred at conversions of 50 and 65 percent, the correlations exhibited more scatter than when $x_s = 0.58$. In addition, most of the data points lay below the bias line when a 50 percent conversion measure of set was used, and above the bias line when a 65 percent measure was adopted. Further, points on the 58 percent bias plot matching simulation experiments with similar catalyst and temperature levels did not always lie on one side of the bias line as opposed

to the other; but were scattered around the line in a random way irrespective of experimental conditions. In conclusion, the hypothesis that set occurred near 60 percent conversion regardless of conditions was confirmed by results from both the auxiliary kinetic tests and the polymer concrete set time tests.

In summary, results from both the auxiliary kinetic tests and the set time tests were consistent with the concept that set occurs when the polyurethane product has achieved a critical amount of cross-linking or chain branching and is no longer able to maintain a liquid state. In this interpretation, set is delayed at low temperatures because the resin molecules are not sufficiently activated to have reached the critical degree of cross-linking where solidification (polymerization) occurs.

4.5.1.4 Comparison of Model Predictions with Resin Temperature - Time Data

In this section, resin temperatures for a typical experimental run are compared to the predictions of the model. Figure 14 shows such a prediction for a typical experimental run, with $T_0 = 70^\circ\text{F}$, $T_{a0} = 56^\circ\text{F}$ and $C = 2.1 \times 10^{-3}$. The data points shown are the average of the three thermocouple readings at the corresponding times. The predictions of the model, shown as the solid curve, are in good agreement with the data. Agreement is even better before set occurs ($t_s = 48$ s for this run).

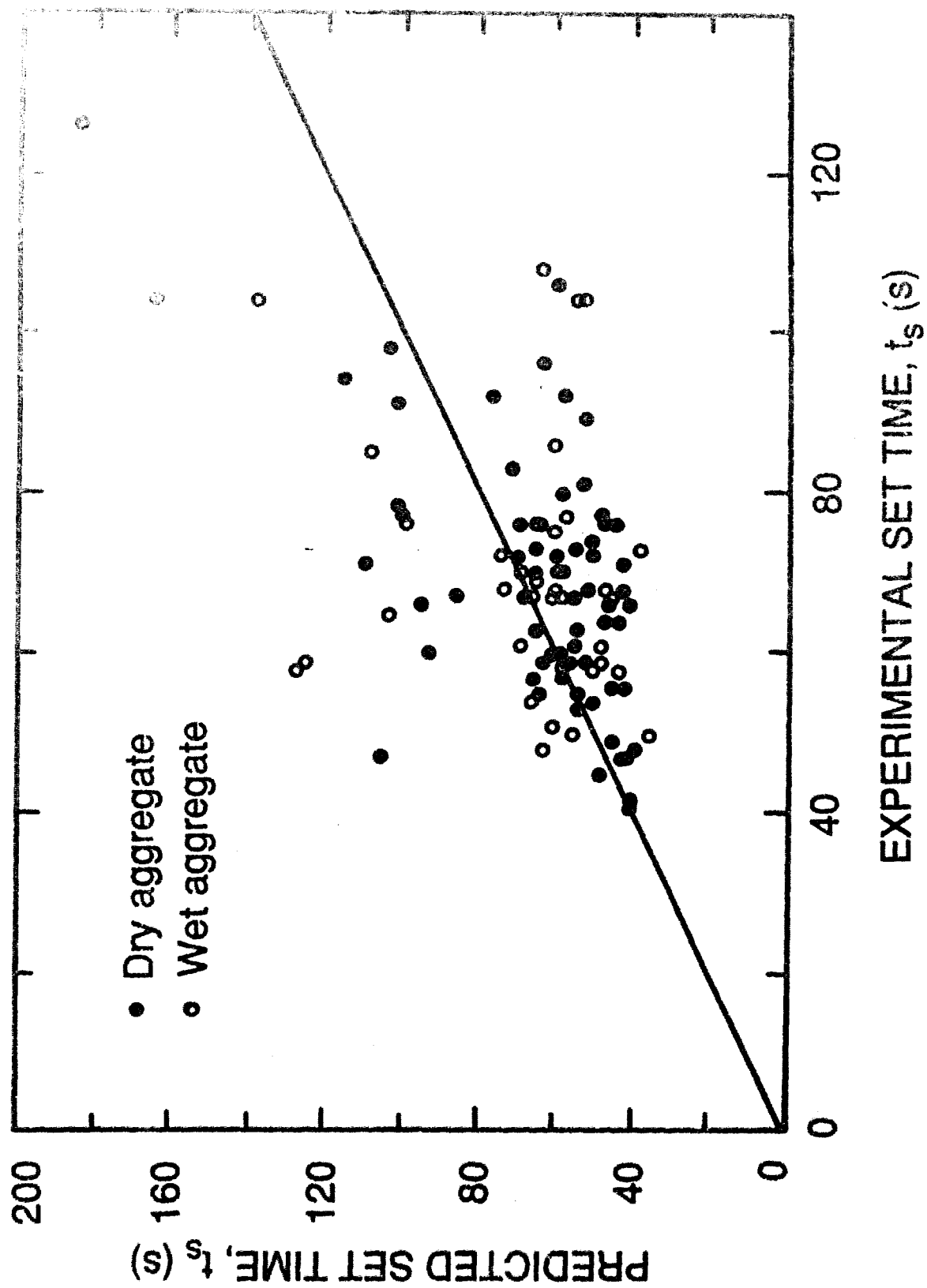


Figure 13. Predicted Versus Experimental Set Times Corresponding to $\gamma_g = 0.56$.

In general, the mathematical model predicted resin temperature vs. time traces which gave reasonable agreement with experimental data. This was further confirmed by the relatively low standard deviations between experimental and predicted values found for most runs. However, some runs at low temperature had high standard deviations and showed data which deviated considerably from the predicted curve. Better agreement could be reached if model parameters were further adjusted. For the test shown, an almost exact match between theory and data results if $t_a = 86$ s and $m = 2.0$ (not shown). However such parameter adjustment sacrifices model credibility for fittability. In this study all the parameter of the model except t_a were kept at the values determined independently (Table 9) when assessing model validity.

For all of the runs, the value of the parameter m was fixed at its value of 2.176, as determined from auxiliary tests. It is also possible to determine m from the simulation experiments. Using the model at steady state, with the parameter r large (e.g., $r > 100$), the aggregate and resin can be shown to reach a common final temperature (T_f) given by:

$$T_f = \frac{m T_{ao} + T_o [1 + \Delta H']}{1 + m} \quad (25)$$

This was confirmed by examining the resin temperature-time traces for each run, almost all of which approach a horizontal asymptote at long times. Using values of T_f , equation (25) can be solved

for m for each run. The average m for the dry aggregate runs was 2.167 which agrees quite well with the value of 2.176 determined independently in the auxiliary resin warming tests (refer to Appendix A, Section A.1). This prediction provides further confirmation of the model.

4.5.1.5 Determination of Aggregate Time Constant, t_a

In this study, the time constant for heat transfer into the aggregate, t_a , could not be established independently because sufficient auxiliary test data (water immersion) were not available during the short time period when most of the heat was going into the aggregate. In effect, this makes t_a an adjustable constant which can only be found by fitting test data from the simulation runs themselves.

With the other parameters fixed at the values independently established (Table 9), t_a was found for each run by finding the value which minimized the variance or error sum of squares between the model and the data points. For example, the value of t_a found for the run illustrated in Figure 14 is 102 s. In general, values of the aggregate time constant found by this method did not vary with experimental conditions, although greater variances were noted at high levels of catalyst concentration and temperature. To determine an average value of t_a for all runs, the individual time constants were summed using

the reciprocal of the variance as a weighting factor. For the dry aggregate runs, the average value was 66.4 s, while for the wet aggregate runs it was 122.2 s, to yield a composite average of $t_a = 95.2$ s. This average value is the one used in subsequent analyses and it is the one reported in Table 9. Because of the variability in the data, no such analysis was performed on data for the experimental runs made with ice inclusions.

4.5.2 Model Application

Model validation can be provided not only by comparing observed set times and resin temperatures to theory but by the predictions it makes in untested regions. In this section the implementation of the model and the predictions that it makes are discussed and illustrated.

4.5.2.1 Model Implementation

In implementation, the differential equations of the model were solved on the computer in their dimensionless form. A standard differential equations solver was used which employed a variable step size and a choice of several generally accepted integration routines. Solutions were checked for numerical accuracy by running the computer program with smaller and smaller step sizes until no change in output was detected and by comparing model output to analytical solutions, where available. From a knowledge

of model parameters and experimental conditions, the dimensionless output was translated to predictions of actual temperatures and conversion as a function of time.

In implementation, the program was modified to account for the mixing and pouring process. In the experiments, during the first ten seconds, the resins and catalyst were being mixed, after which it took about five additional seconds to fill the buckets containing the aggregate with the mixed resins. In the model, the term corresponding to heat loss of the aggregate was not added until 12.5 seconds into the computer program. In effect this split the model into two submodels, one before this time and one after. At this time, the values of the dependent variables (T' , T_a' and x) were set equal to one another so that the final conditions for the first submodel became the initial conditions for the second. The models ran sequentially on the computer.

4.5.2.2 Discussion and Illustration of Model Predictions

In this section, the results of model calculations simulating the setting performance of polymer concrete for anticipated ranges of experimental conditions, are presented. For the calculations, the parameters of the model were fixed at the base values given in Table 9. With the other parameters fixed, the parameter of interest was then varied about its base value in order to assess its effect on model performance. Results are most conveniently

shown graphically. Unless otherwise noted, the illustrations shown in this section are based on the model parameters given in Table 9 and with experimental conditions: $T_0 = 70^\circ\text{F}$, $T_{a0} = 56^\circ\text{F}$ and $C = 2.1 \times 10^{-3}$.

Figure 15 shows the effect of the parameter m on predicted resin temperature. The temperature first rises rapidly towards a maximum (peak exotherm) and then falls slowly to a horizontal asymptote. At early times, there is little effect of m on predicted resin temperatures. At later times, for higher values of m , corresponding to a higher loading of cold aggregate, the temperature drops more rapidly and sooner from its maximum. With less aggregate, the temperature continues to rise longer and then drops slowly from its maximum value. All these results are consistent with expectations. The more aggregate, the more energy will be removed from the resin and the lower will be the final temperature. Thermal lag prevents this effect from being important for this system until about 30 seconds have elapsed.

For the conditions investigated, Figure 16 shows that the parameter m has only a small effect on resin conversion, smaller values of m producing only marginally higher conversions at a given time. As shown in the figure, the predicted set times (t_s at $x_s = 0.58$) are almost identical; quadrupling the relative amount of aggregate only delays set for a few seconds. For the conditions examined, it can be concluded that the reaction is

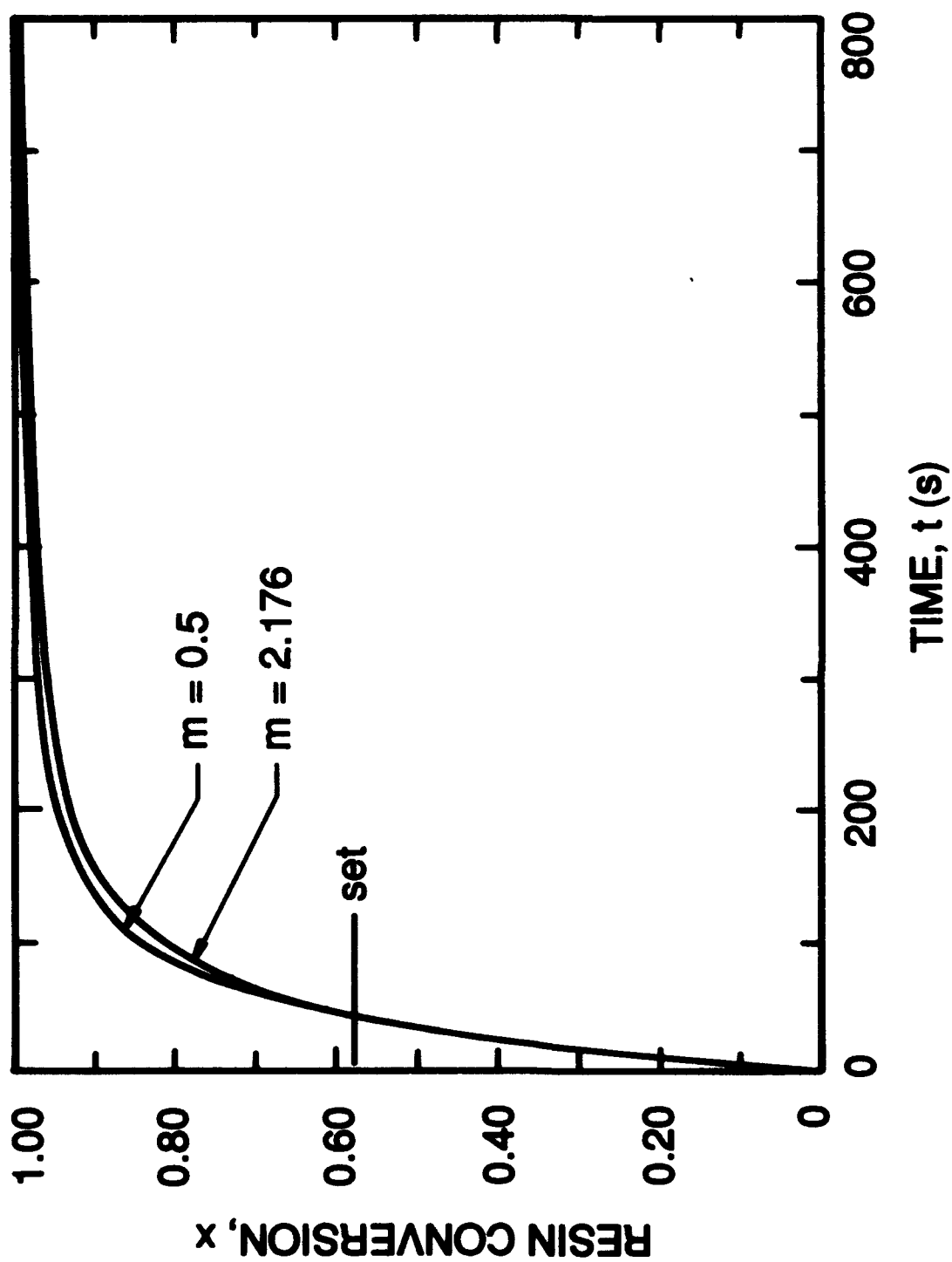


Figure 16. Effect of Parameter m on Resin Conversion.

sufficiently exothermic so that most of the energy of reaction goes into heating the resin, rather than the aggregate, a conclusion which is also confirmed by Figure 15. When the aggregate is considerably colder than the resin, this is less likely to be true.

Figure 17 predicts how the resin conversion varies with time with the initial temperature of the resin shown as a parameter. For each curve, the catalyst concentration was 0.0021 (volume catalyst/volume Resin B). As expected, lowering the initial temperature of the resin lowers conversion at a given time, especially at the colder temperature (4°F), where set is predicted to occur in 240s. Set this late would probably be unacceptable under field conditions. These model predictions show that more catalyst needs to be added to the resin in order to accelerate set.

Figure 18 predicts the way resin conversion varies with time at different levels of catalyst concentration. Raising the catalyst concentration is shown to raise the resin conversion at a given time and to accelerate set. The lower curve gives the prediction when no catalyst is added. This confirms the experimental results found in the auxiliary tests that reaction and set, although much delayed, do occur in the absence of catalyst.

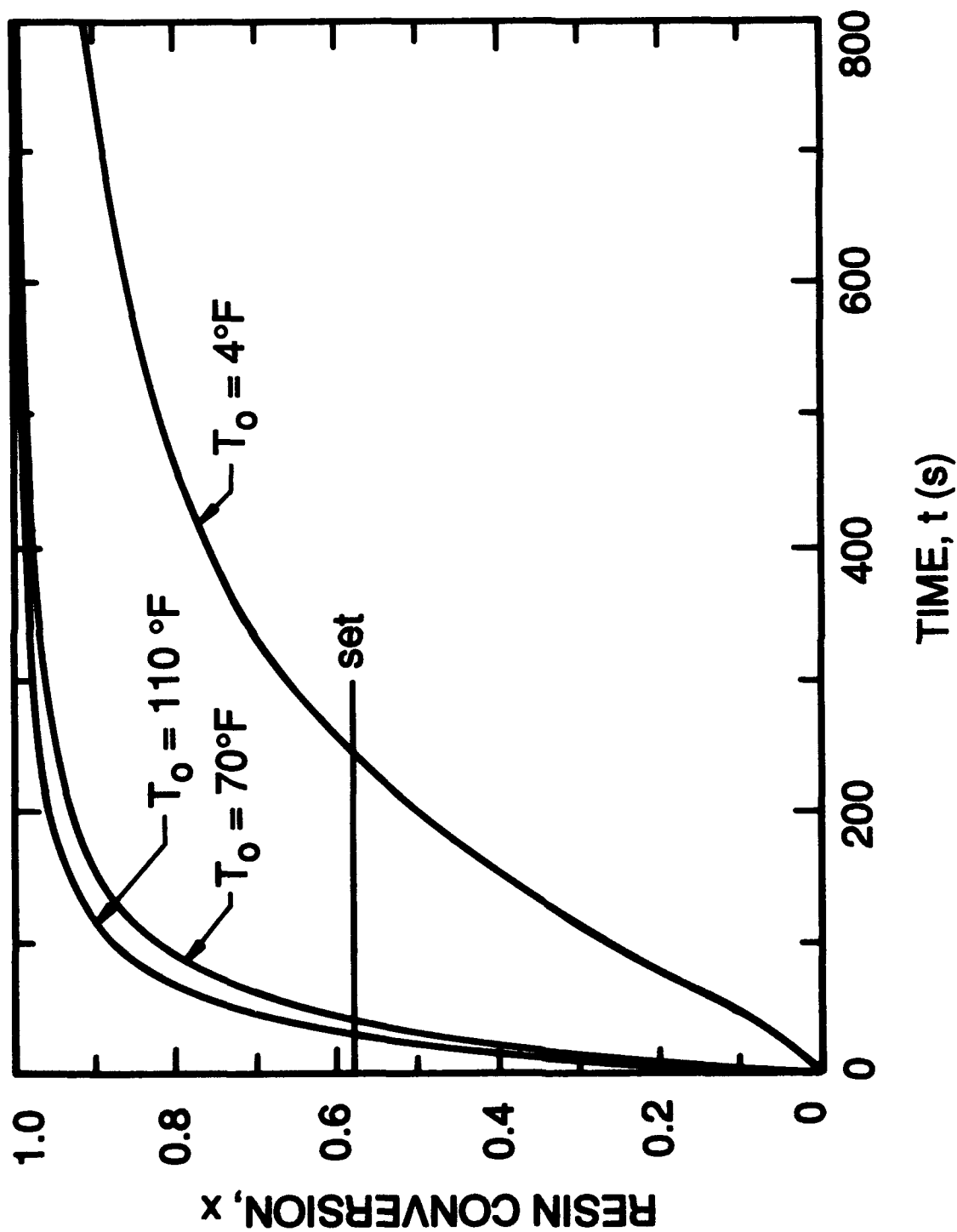


Figure 17. Effect of Initial Resin Temperature on Resin Conversion.

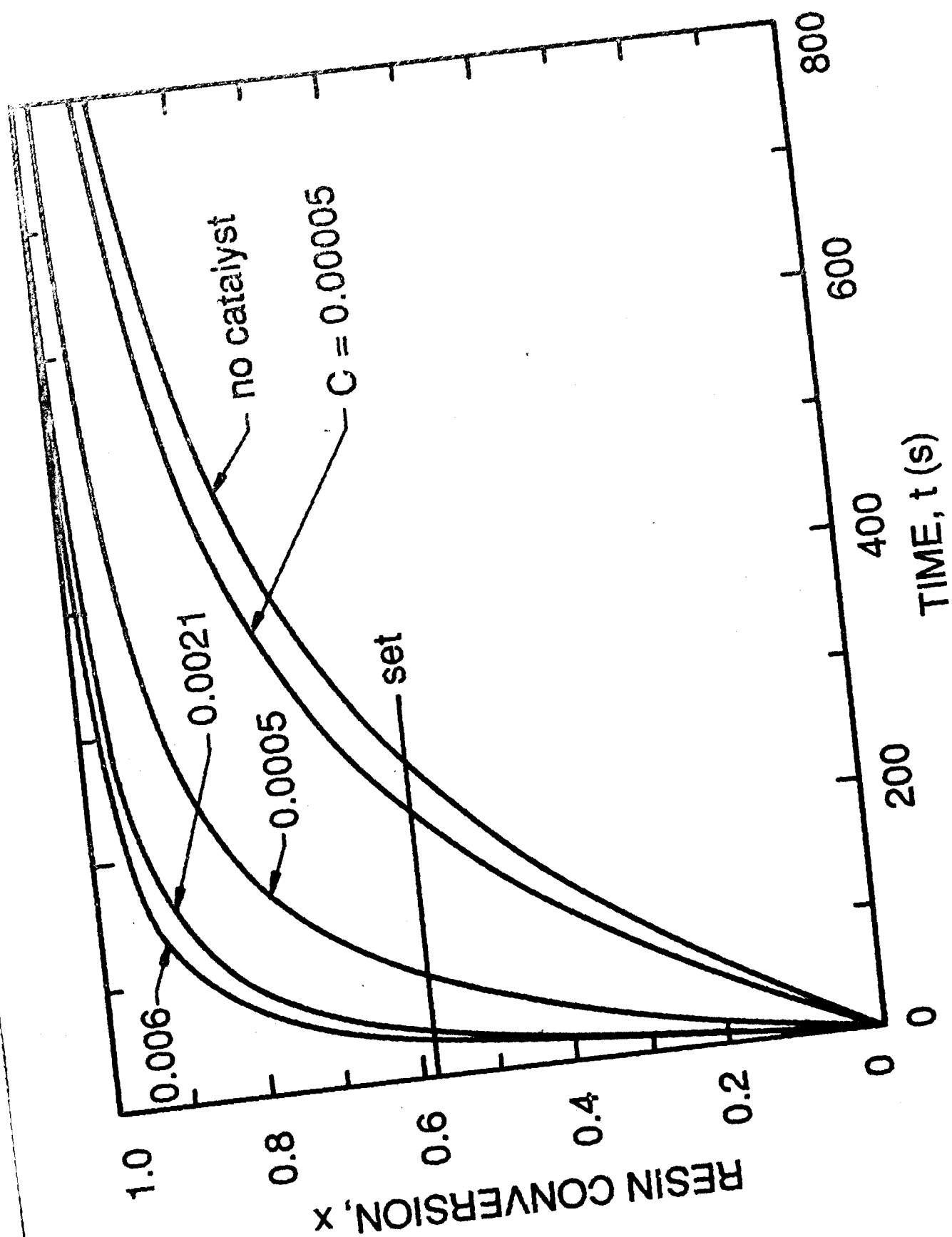


Figure 18. Effect of catalyst concentration on Resin Conversion.

5. SET TIME DESIGN CHARTS

With the validity of the model established and its parameters estimated, the model can be used to predict set time under a wide range of conditions. Given the initial temperatures of the resin and aggregate and the temperature of the surroundings, the model will predict the catalyst concentration to use to achieve a desired set time. By running the model under a variety of conditions, design charts can be prepared which enable set time to be predicted under field conditions.

It is important to mention that since all experiments were made using the same concentration of the two resins (those corresponding to equal volumes), it is not possible to make predictions for resin concentrations different from those used in the set time tests nor for other resins. However, if the catalyst employed in the tests is diluted or strengthened in the amount of its unknown active ingredient, predictions can still be made by adjusting, in proportion, the catalyst concentrations used in the model. Additional experimental tests would need to be conducted over a range of concentrations in order to ascertain more fully the effect of resin concentration on the kinetics and heat transfer of the setting reaction.

5.1 Development of Design Charts

The model predicts the set time directly. Thus, for given values of initial resin and aggregate temperature, fixing the catalyst concentration will predict the set time. The model calculations are carried forward in time until the critical conversion is reached and set occurs. A more practical problem is determining what catalyst concentration to use to achieve a prescribed set time under specific conditions. Since the model does not determine catalyst concentration directly it must be run repeatedly at different concentrations until one is found which matches the desired set time. This is inconvenient in practice.

To eliminate this problem the model was used to generate design charts. Set times of 45, 60, 90 and 120 s were used. Initial aggregate temperatures, T_{ao} , chosen were -25, 0, 25, 50, 75 and 100°F, while initial resin temperature was varied between 0 and 120°F in increments of 10°F. This gave a total of 308 combinations of set time and initial temperature. The model was run iteratively for each combination in order to find the amount of catalyst to be used to achieve the desired set time. Convergence was taken when the set time was matched to within ± 2 s. The points shown in the charts are the result. A smooth curve was drawn through these points. As in the experimental tests, the temperature of the air used in the calculations was considered equal to the initial temperature of the aggregate. Other air temperatures

should not affect the prediction appreciably, since the calculations show that set usually occurs before much energy has had a chance to be transferred to the environment.

5.2 Use of Design Charts

There are six design charts designated C-1 through C-6 (Figures 19-24), one for each initial aggregate temperature: $T_{a0} = -25, 0, 25, 50, 75$ and 100°F . Each chart is a plot of the catalyst concentration, C , vs. the initial resin temperature, T_0 , in $^\circ\text{F}$. With the ordinate plotted on a log scale, the curves on the charts are quasi-linear. Each curve corresponds to a different set time ($t_s = 45, 60, 90$ or 120s). The charts are a graphical representation of the model encoded in four variables (T_0 , T_{a0} , C and t_s). With any three of the variables specified, the fourth can be found using the charts.

As an example, their use is shown in Chart C-1 (Figure 19), with $T_{a0} = -25^\circ\text{F}$. As illustrated, to find the amount of catalyst to use if the desired set time is 45s and the aggregate is at -25°F with the resin supplied at 60°F , enter the $T_{a0} = -25^\circ\text{F}$ chart on the abscissa at 60°F , draw a vertical line to the ordinate and read off the catalyst concentration, $C = 3.0 \times 10^{-3}$. This translates into using 0.3 percent by volume of catalyst per volume of Resin B employed.

SET TIME DESIGN CHART C-1

Aggregate Temperature: $T_{a0} = -25^{\circ}\text{F}$

Parameter: t_s , set time, seconds

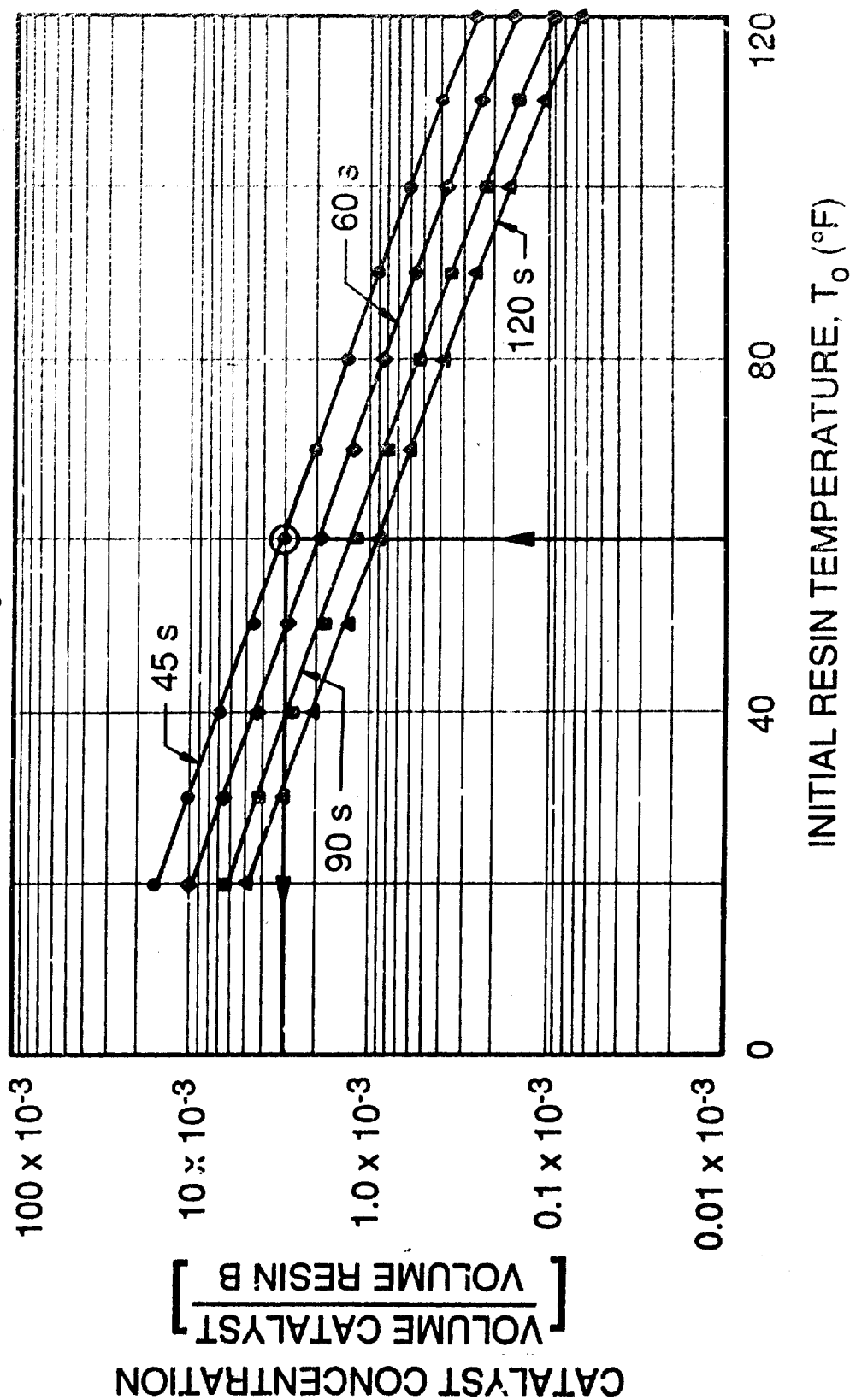


Figure 19. Set Time Design Chart for Aggregate Temperature (T_{a0}) = -25°F .

SET TIME DESIGN CHART C-2

Aggregate Temperature: $T_{a0} = 0^{\circ}\text{F}$

Parameter: t_s , set time, seconds

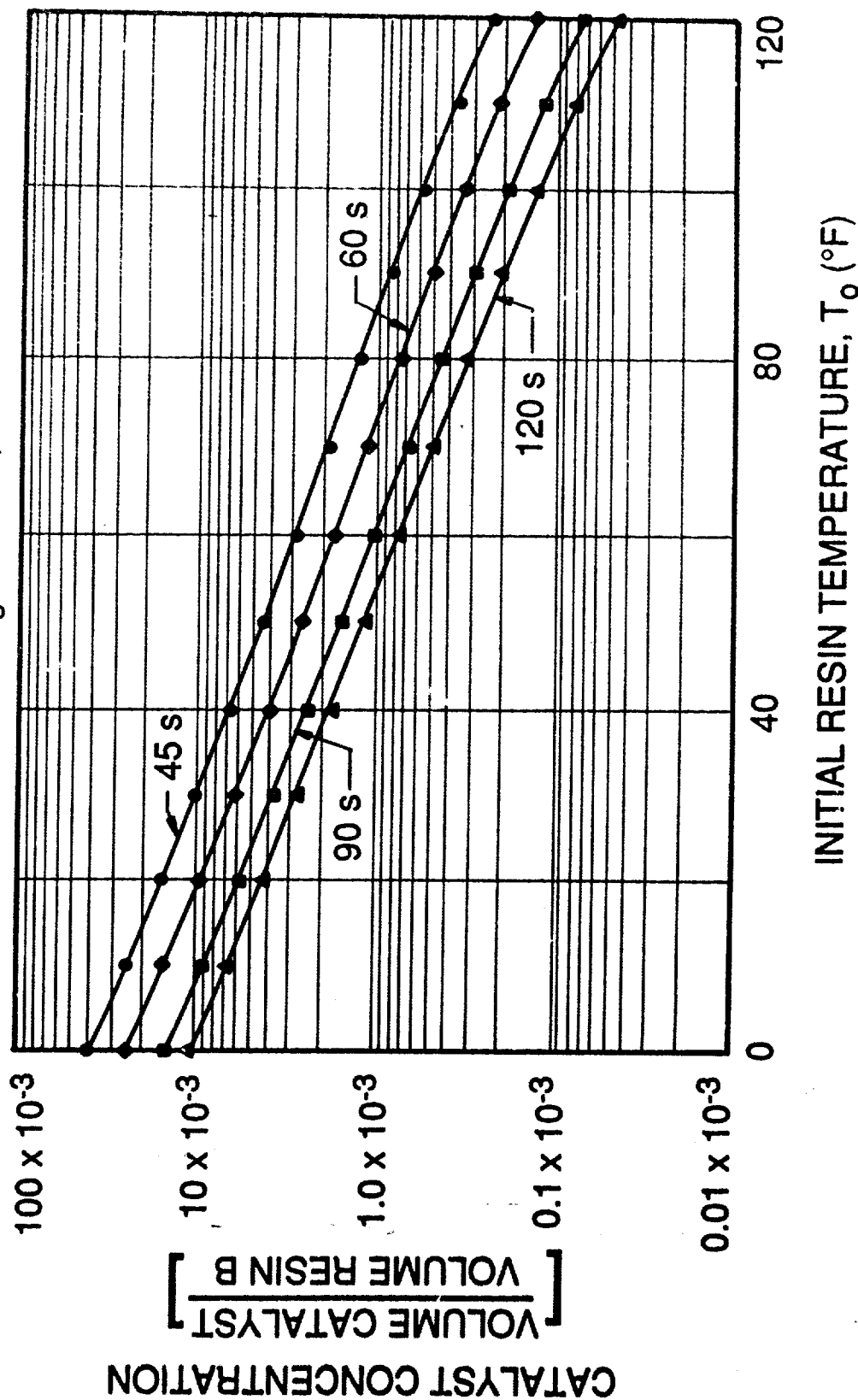


Figure 20. Set Time Design Chart for Aggregate Temperature (T_{a0}) = 0°F .

SET TIME DESIGN CHART C-3
 Aggregate Temperature: $T_{a0} = 25^{\circ}\text{F}$
 Parameter: t_s , set time, seconds

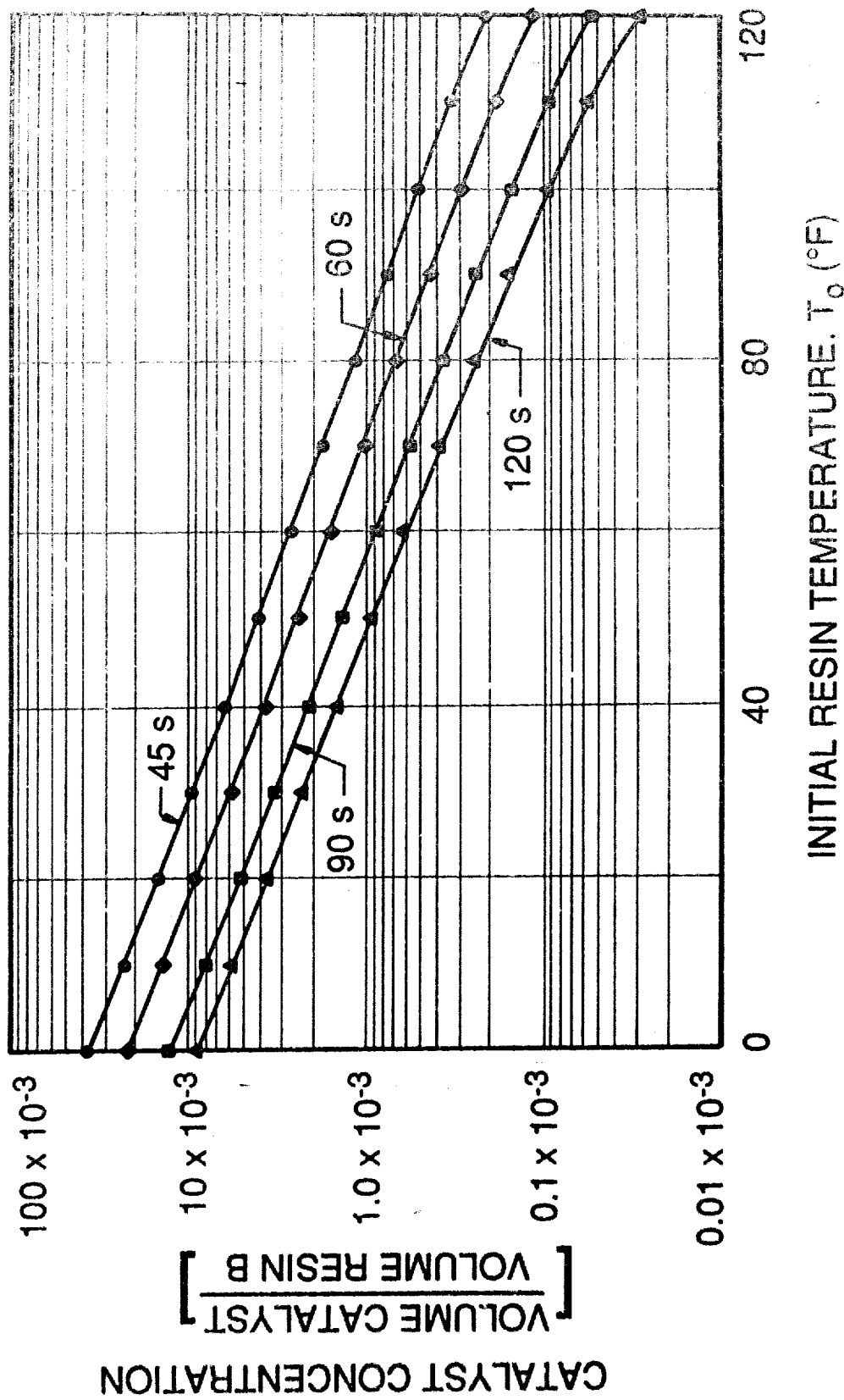


Figure 21. Set Time Design Chart for Aggregate Temperature (T_{a0}) = 25°F .

SET TIME DESIGN CHART C-4

Aggregate Temperature: $T_{ac} = 50^{\circ}\text{F}$

Parameter: t_s , set time, seconds

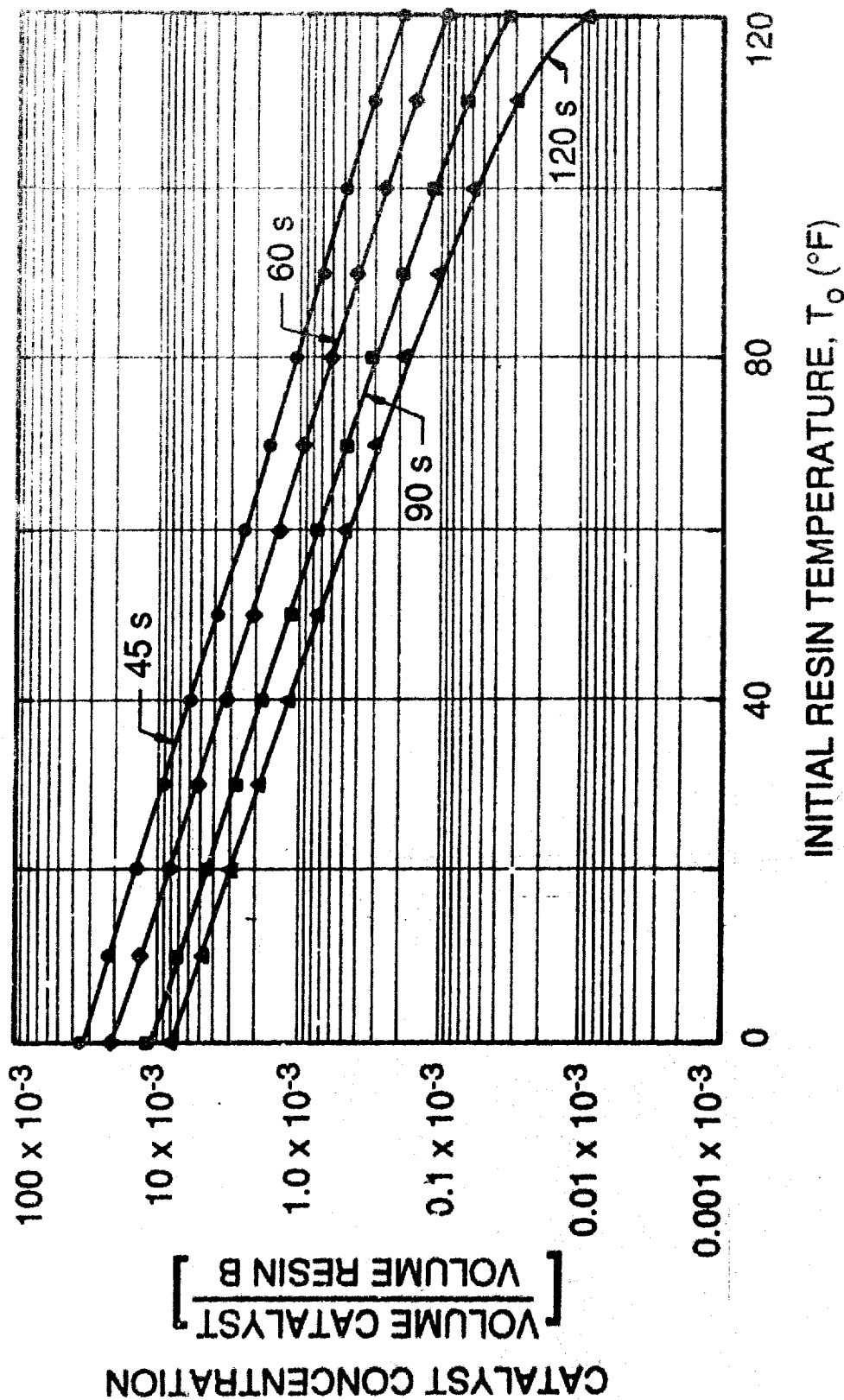


Figure 22. Set Time Design Chart for Aggregate Temperature (T_{ao}) = 50°F .

SET TIME DESIGN CHART C-5

Aggregate Temperature: $T_{ao} = 75^{\circ}\text{F}$

Parameter: t_s , set time, seconds

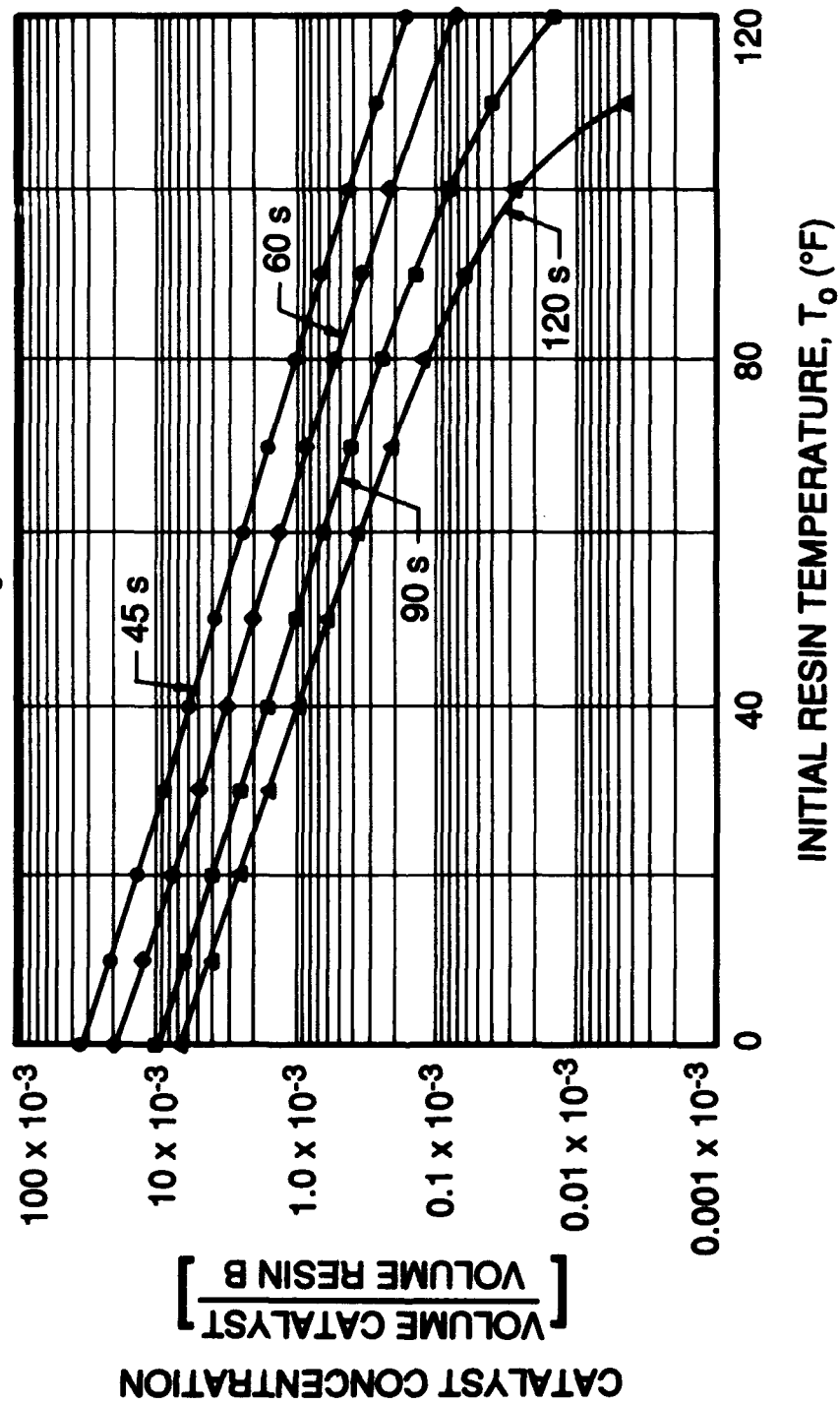


Figure 23. Set Time Design Chart for Aggregate Temperature (T_{ao}) = 75°F .

SET TIME DESIGN CHART C-6

Aggregate Temperature: $T_{a0} = 100^{\circ}\text{F}$

Parameter: t_s , set time, seconds

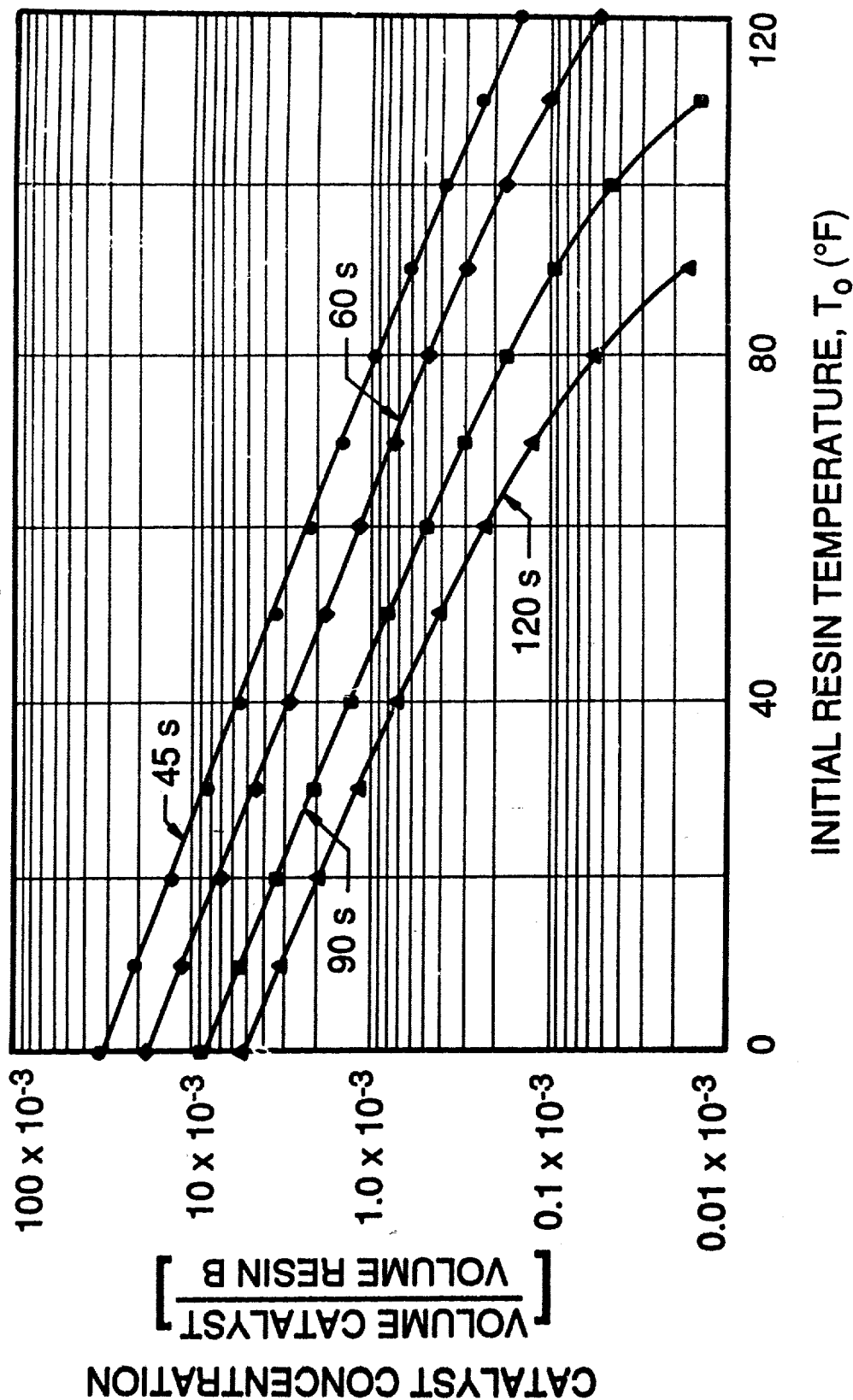


Figure 24. Set Time Design Chart for Aggregate Temperature (T_{a0}) = 100°F .

The problem of determining what set time will be achieved for a given catalyst concentration is worked similarly. The appropriate chart at the aggregate temperature T_{a0} is first selected. On this chart a horizontal line is drawn from the given C and a vertical line from the resin temperature T_0 . The intersection of these lines will determine the predicted set time t_s , which can be read from the curves on the figure. In cases where the intersection point lies between two set time curves, linear interpolation can provide an estimate of t_s . Other problems of interest include finding how hot the resin must be to insure, for a given catalyst concentration and aggregate temperature, that set will occur within a specified period. This is the inverse of the first problem. A horizontal line is drawn from the given catalyst concentration to the set time curve. At the intersection, a vertical line is drawn to the abscissa and the resin temperature is found. Temperatures lower than this will not cause set within the desired time unless more catalyst is used. Interpolation can also be used for set times other than those provided on the charts.

6. SUMMARY

Proprietary polyurethane resins are among several materials considered by the Air Force Engineering and Services Center (AFESC) for use in rapid repair of runways. In this application, the resin is used as a binder with preplaced open-graded aggregate for a rapid setting polymer concrete. The AFESC requested that the National Institute of Standards and Technology (NIST) conduct a study to obtain set time data for polymer concrete made with a particular two-component proprietary polyurethane resin and catalyst. The polymer concrete was to be made using a wide range of aggregate and resin temperatures. In addition, the impact of the presence of water and ice on set time was to be examined. This study was required by AFESC to better characterize the performance of the proprietary resin and the polymer concrete made using the resin.

The major portion of this study was devoted to obtaining set time data for the polymer concrete for a wide range of aggregate and resin temperatures and in developing and solving a set time prediction model. The effect of the presence of water and ice inclusions on set time was also included in the study. The model parameters were determined experimentally from auxiliary tests conducted separately from the set time tests. The effect of temperature variations of aggregate and resin on the flexural strength of polymer concrete at early ages was also investigated.

Finally, some pilot tests were conducted to obtain set time data for polymer concrete cast using another proprietary polyurethane resin and catalyst. Various aggregate and resin temperatures and moisture conditions were also used in casting the polymer concrete in the pilot tests.

The set time tests were carried out in a temperature-controlled environmental chamber. The polymer concrete was cast using equal amounts of a two-component resin, a catalyst, and 0.44 ft³ of a smooth surface, rounded mineral aggregate (quartz). The aggregate temperature ranged from -25 to 110°F. A catalyst was mixed with Resin B (diamine - polyglycol) and then mixed with Resin A (isocyanate). The resulting mixture was quickly poured over aggregate in a plastic bucket. The mixed resin percolated through the air dried and the saturated surface dry aggregate and filled the voids. The amount of catalyst was adjusted to provide for a set time of about 55 to 75 seconds. Set time was determined as the time from the start of mixing of the two resins to the time that set of the mixed resin occurred. The set time was very sensitive to the amount of catalyst used. The temperature of the polymer concrete was continuously recorded from thermocouples placed in the aggregate. The temperatures at the time of set of the resin and the peak exotherm were reported. Set was observed by a rapid change of color of the mixed resin in the gravel and by tapping the top surface of the polymer concrete with a steel rod and noting when the resin became solid.

Little difference in set time was observed for polymer concretes cast using air dry aggregate and saturated surface dry aggregate (wet aggregate) for comparable combinations of aggregate and resin temperatures. The moisture content of the saturated surface dry aggregate ranged from 0.4 to 0.9 percent by mass. In Section 1 of this report, some concerns involved with rapid runway materials were noted, including the effect of moisture on the properties of the polymer concrete. It appears that the small amount of moisture in the saturated surface dry aggregate did not appreciably affect the set time or the filling of the aggregate voids with resin.

Considerably more catalyst was used in the set time tests with ice inclusions. It was difficult to control set time in these tests. In examining the polymer concrete specimens which contained ice inclusions, the bond between aggregate and hardened resin over the lower half of the specimens was poor or did not exist. This was particularly obvious for specimens with short set times because the resin set before it could completely percolate through the aggregate. Since the bond between aggregate and hardened resin was poor, it was recommended that data from the set time tests which included ice should not be used for field application. In addition, results from set time tests with ice inclusions were inconclusive because set times could not in general be accurately determined and in many cases could not be reproduced when comparable amounts of catalyst were used.

The set time prediction model consists of energy balances, one for the resin matrix (continuous phase) and the other for the aggregate particles (dispersed phase), as well as a molar balance on the reacting species (resins). It accounts for heat exchange between resin and aggregate and the heat of reaction as well as heat losses to the surroundings. Model input includes initial temperatures (resin, aggregate, and surroundings), catalyst concentration, moisture and ice content (if present), and mass of aggregate and resin. Model parameters include heat transfer coefficients and time constants, specific heats of the phases, chemical reaction order, reaction activation energies, and parameters measuring the effect catalyst concentration has on the reaction rate constant. Model output predicts set time, resin conversion, and the temperature of the resin and aggregate as functions of time. For tests with ice inclusions, the model also predicts the fraction of ice which has melted.

In order to independently determine the parameters for the model, separate auxiliary tests were conducted. Resin heat capacities were found in experiments where the resins were allowed to warm in a temperature controlled environment. Heat transfer coefficients and model time constants were determined from tests conducted with water used in place of resin, while reaction parameters were determined from separate tests conducted in insulated containers which did not contain aggregate. These latter tests established a reaction order of 1.5 and a set time which occurred near 60

percent conversion regardless of experimental conditions. The reaction activation energy was found to decrease with increasing catalyst concentration, as would be expected based on kinetic theory. The data collected were fitted to models developed and solved specifically for the auxiliary tests. Because of constraints, the time constant for aggregate heat transfer could not be found independently using this method. Instead its value was determined by matching experimental data of resin temperature for each run directly to the set time model and then using an overall average. Results showed that heat transfer into the aggregate was much faster than into the air.

Reasonable agreement was found between the set time prediction model and the experimental data since observed set time and resin temperatures were generally in accord with those predicted by the model. Larger deviations between predicted and experimental results were noted at higher catalyst concentrations and lower initial resin and aggregate temperatures.

The set time prediction model was used to develop a series of design charts which can be used to predict set time given the catalyst concentration and initial temperatures of the aggregate and resin. The design charts can also be used to determine the catalyst concentration to use to assure set of the resin within a given time and at specified temperature.

The flexural strength of the polymer concrete was determined using beam specimens tested at an age of 30 minutes. Set times for the beam specimens were in the range of 30 to 45 seconds. Beams cast with aggregate and resin at the higher temperatures had the highest values of flexural strength. Along the failure surface of these beam specimens, the aggregate fractured while, for beam specimens cast with lower temperatures of aggregate and resin, bond failure between aggregate and hardened resin was discernable. The flexural strength or modulus of rupture data were compared with the adiabatic mix temperature, T_m , which was a weighted value of aggregate and resin temperature at the time of casting a beam specimen. The flexural strength was essentially constant for values of T_m of 70°F or greater. For lower values of T_m , the flexural strength decreased nearly linearly as T_m decreased. It was observed at age 30 minutes that the hardened resin was softer in the five beams cast with lower values of T_m than those cast at the higher temperatures.

In pilot tests using another polyurethane resin, considerably more catalyst was needed to obtain comparable set times as compared to the other set time tests. As the temperature at the time of casting these pilot test specimens decreased, the catalyst concentration needed for equal set time increased considerably. As an example, for specimens cast with an aggregate temperature about -2°F and a resin temperature of 5°F or less, the catalyst volume ratio was in the range of 0.5 to 1.0 and the

set time ranged from 95 to 220 seconds. For comparable specimens in the main series of set time tests, the catalyst ratio was 0.007 for set time between 67 and 72 seconds. Specimens cast in the pilot tests with resin temperatures of 5°F or lower and those with ice inclusions present exhibited poor bond over their lower half.

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APPENDIX A - DETERMINATION OF MODEL PARAMETERS FROM AUXILIARY TEST RESULTS

Table 9, in the main body of this report, presents a summary of the model parameters used in the set time prediction model. Most of these parameters were determined in one of the three types of auxiliary tests: resin warming (parameters C_{VA} , C_{VB} , and C_V), water immersion tests (parameters r , t_{air} , t_a , and U_0), and kinetic tests (parameters $\Delta H'$, n , E_0 , E_n , m_0 , ω_0 , and α). In this appendix, theory and procedures for determining these parameters are presented for each test method. A brief summary of the auxiliary experiments is also provided.

A.1 Resin Warming Auxiliary Test Results

A.1.1 Experiments

Resin specific heats can be found by comparing temperature-time data for warming resins to that of warming water under the same experimental conditions. Since the specific heat of water is known it acts as an experimental control. In the tests, three separate 1000 ml polyethylene bottles with screw tops were individually filled with water, Resin A, and Resin B to the shoulder of the bottles. Each bottle was fitted with two thermocouples, whose lead wires passed through a thin hollow reinforced plastic tube into the center of the liquid. The tube was centered and supported by a stopper fitted into the neck of the bottle. The three bottles were initially sealed and stored

at 35°F overnight. At the beginning of the experiment, they were placed in an environmental chamber at 90°F. Data from the six thermocouples were taken every 4 s for the first 240 s and every 60 s thereafter. The duration of the run was 9000 s. The data for the test are given in Table A1 (end of Appendix). For each bottle, the average of the two adjacent thermocouple readings is reported.

A.1.2 Theory

An energy balance for this system yeilds:

$$-MC_v \frac{dT}{dt} = U_o A_o [T - T_{air}] \quad (A1)$$

whose solution is:

$$Y = \frac{T_{air} - T}{T_{air} - T_o} = \exp \left[- \frac{U_o A_o}{MC_v} t \right] \quad (A2)$$

In equations (A1) and (A2), T is the temperature of the liquid, T_o is its initial value and T_{air} is the temperature of the air outside the bottle. U_o is the overall heat transfer coefficient based on the outside area A_o. Y is a dimensionless temperature which is computed at each time. Equation (A2) can be linearized to give:

$$\ln Y = - v t \quad (A3)$$

where

$$v = \frac{U_o A_o}{MC_v}$$

A.1.3 Results

Equation (A3) predicts that a plot of $\ln Y$ vs. t should be linear with a slope of v . Figure A1 shows such a plot for the three data sets. Because the bottles are exposed to air which, together with polyethylene, is a good insulator, the temperature of the resin is presumed to be independent of position after an initial period during which initial temperature gradients become flat. For the data collected this occurred at about 2000 s. Accordingly, the data was analyzed with $t_o = 2044$ s, with this time subtracted away from all subsequent data. The value of T_o was taken as the temperature at t_o and the three lines were statistically forced through the point $Y = 1$, $t = t_o$. The value of T_{air} in equation (A2) was taken equal to the average recorded temperature of the environmental chamber (92.7°F) during the time span used in the data analysis.

For the three lines shown in Figure A1, the values of v were found to be $1.150 \times 10^{-4} \text{ s}^{-1}$, $2.342 \times 10^{-4} \text{ s}^{-1}$ and $2.085 \times 10^{-4} \text{ s}^{-1}$, for the water, Resin A and Resin B, respectively.

In the analysis, $U_o A_o$, the product of the heat transfer coefficient and exposed surface area, is presumed constant. This is likely because of the experimental design: all three liquids

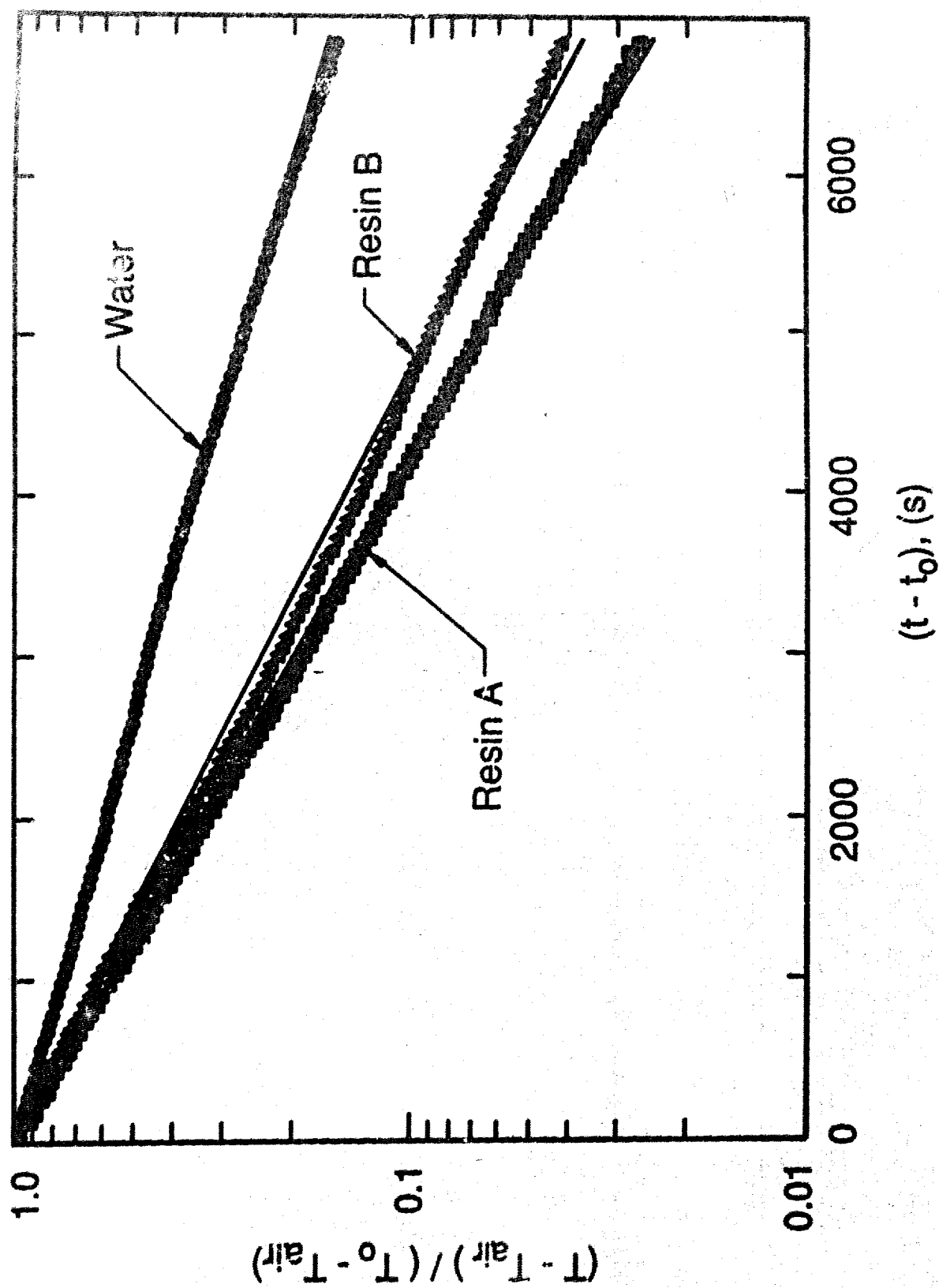


Figure A1. Determination of Resin Heat Capacities ($\ln Y$ versus t); from Resin Warming Auxiliary Tests.

were exposed to the same environment at the same time. From the value of v for water, the mass of the water (0.9566 kg) and its specific heat at the average temperature (4.181 kJ/kg.K), the value of U_oA_o was found to be 4.60×10^{-4} kJ/K.s. For an exposed surface area of 4.81×10^{-2} m², this resulted in an overall heat transfer coefficient of 9.56×10^{-2} kJ/kg m².s. This result is consistent with the magnitude of heat transfer coefficients reported for free convection from cooling and heating cylinders [17]. With U_oA_o constant, the slopes of the lines for the two resins can be used to find their specific heats. This procedure predicted that $C_{vA} = 1.846$ kJ/kg.K and $C_{vB} = 1.669$ kJ/kg.K. For the mass of Resin A and Resin B used in the set time tests (Table 9), the weighted composite specific heat for the mixed resin was of $C_v = 1.748$ kJ/kg.K. Using this value and the masses of aggregate and resin used in the regular tests, the value of m was calculated as 2.176.

A.2 Water Immersion Auxiliary Test Results

A.2.1 Experiment

A test was conducted in the same bucket employed in the set time tests using the same grade and weight of aggregate. However, no resin was used. Instead, cold water was employed in a volume equal to the total volume of resin. The water was poured over the hot aggregate (within 10s) and temperatures were recorded as before, at mid-depth in the center, halfway between the center

and the bucket wall, and at the bucket wall. Data for this test of water temperature versus time for the average of the three thermocouples are presented in Table A2. A plot of the data for the thermocouple halfway between the center and bucket wall is shown in Figure A2. This temperature was within a degree of the average value for times beyond 600 s.

A.2.2 Theory

For this experiment, the energy balances for the water and the aggregate are given by equations (A3) and (A4), respectively:

$$-\frac{dT_w}{dt'} = \frac{T_w - T_{air}}{r} + m(T_w - T_a) \quad \text{water} \quad (A3)$$

$$-\frac{dT_a}{dt'} = (T_a - T) \quad \text{aggregate} \quad (A4)$$

The initial temperatures of the water and aggregate are T_{w0} and T_{a0} , respectively.

Equation (A3) can easily be obtained by setting the reaction term equal to zero in Equation 14, the energy balance for the resin, and letting $T = T_w$. In effect, the energy balance for the water is equal to that for the resin with the reaction term deleted. The aggregate energy balance (Equation A4) remains the same as Equation 15. An analytical solution of these equations is

Table A2. Data for Water Immersion Auxiliary Tests ^{1/}

<u>t(min)</u>	<u>T_w(°F)</u>	<u>t(min)</u>	<u>T_w(°F)</u>	<u>t(min)</u>	<u>T_w(°F)</u>
0.167	47	230	96.0	580	111.7
0.233	48.5	240	97.0	600	112.2
0.283	50	250	98.0	620	112.7
0.35	52.7	260	98.5	640	113.2
0.40	53.5	270	99.0	660	113.6
0.45	53.5	280	99.5	680	114.0
15	74.8	290	100.0	700	114.5
25	76.0	300	100.7	720	114.7
35	77.2	310	101.2	740	115.0
45	78.5	320	102.0	760	115.3
55	79.5	330	102.5	780	115.5
80	82.5	340	103.0	800	116.0
95	84.0	350	103.5	820	116.2
105	85.3	360	104.0	840	116.5
115	86.3	370	104.5	860	116.7
125	87.2	380	105.0	900	117.0
135	88.0	400	105.8	930	117.2
145	89.0	420	106.5	960	117.5
155	90.0	440	107.5	1020	118.0
165	90.7	460	108.0	1050	118.3
180	92.0	480	108.8	1110	118.5
190	93.0	500	109.7	1140	118.7
200	93.7	520	110.3	1200	119.0
210	94.5	540	110.6	1230	119.0
220	95.3	560	111.2	1320	119.5
				1340	119.5

^{1/} Initial water temperature (T_{wo}) = 36°F
Initial aggregate temperature (T_{ao}) = 115°F
Air temperature (T_{air}) = 125°F

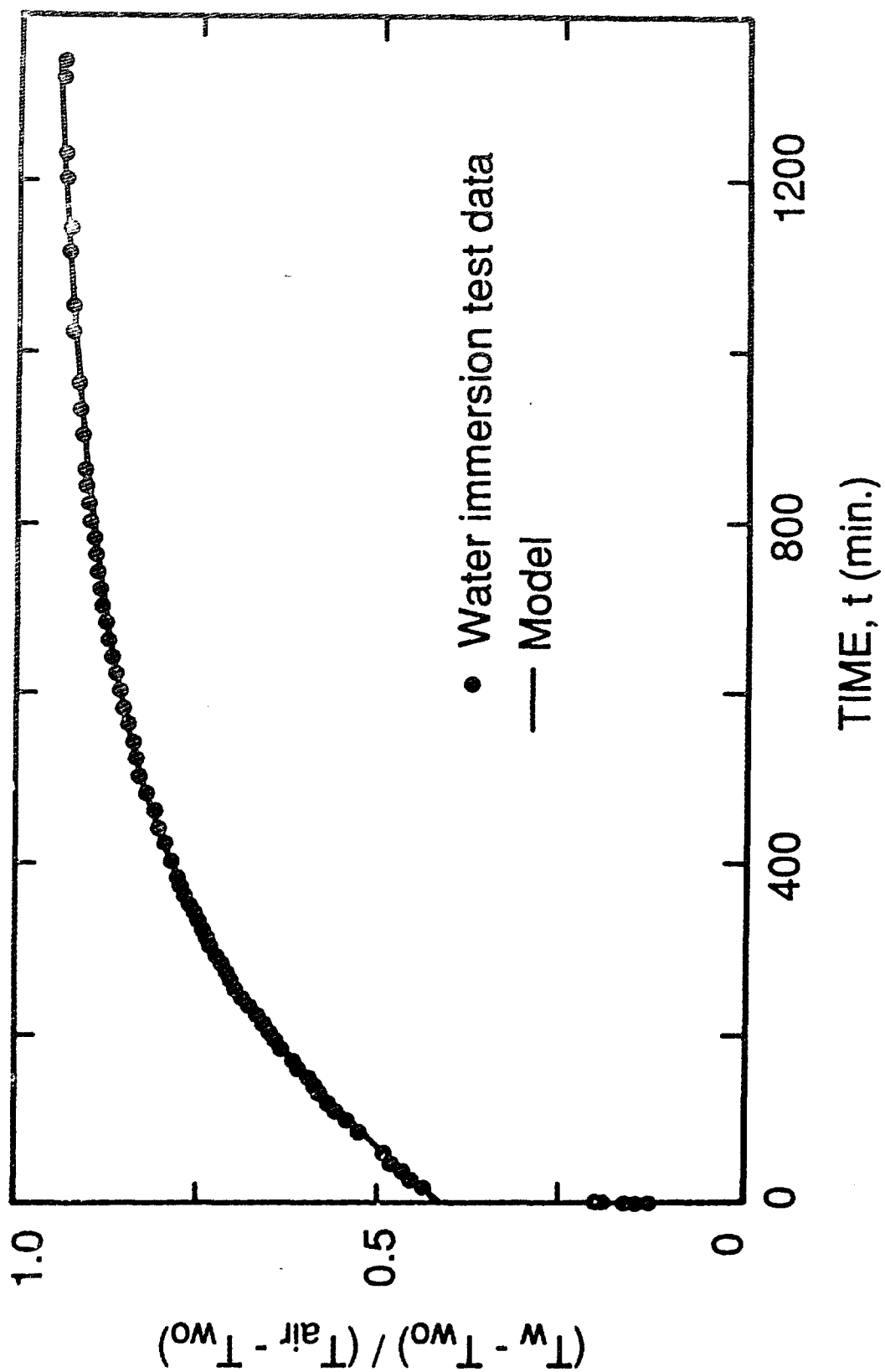


Figure A2. Determination of Model Heat Transfer and Time Constants from Water Immersion Auxiliary Tests.

possible using the method of Laplace transforms. The solution is:

$$\frac{T_w - T_{air}}{T_{wo} - T_{air}} = \frac{X}{2b(1-\omega_o)} \quad (A5)$$

where

$$X = \begin{cases} [r + \omega_o (1-a-b) - (a-b)] e^{-(a-b)t/t_{air}} \\ -[r + \omega_o (1-a+b) - (a+b)] e^{-(a+b)t/t_{air}} \end{cases} \quad (A6)$$

with

$$\omega_o = \frac{T_{air} - T_{ao}}{T_{wo} - T_{ao}} \quad (A7)$$

$$2a = (m+1)r + 1, \quad b = \sqrt{\left(\frac{m+1}{2}\right)^2 + r^2} \left(\frac{m-1}{2}\right) r + \frac{1}{4} \quad (A8)$$

$$\text{and} \quad \frac{T_w - T_a}{T_{wo} - T_{ao}} = \frac{Z}{2b} \quad (A9)$$

where

$$Z = (-a + b + \omega_o) e^{-(a-b)t/t_{air}} - (a - b - \omega_o) e^{-(a+b)t/t_{air}} \quad (A10)$$

At any time, t , the water temperature, T_w , can be found from equation (A5), while the aggregate temperature, T_a , can then be found from equation (A9).

A.2.3 Results

Under the experimental conditions employed in the tests, the dimensionless temperature parameter ω_0 was -0.1266 . To determine the values of r and t_{air} , a two-dimensional search was first made. A value of t_{air} was assumed and, for each data point a reduced time, t/t_{air} , was calculated. r was then varied until the sum of squares of the deviations was minimized. A new t_{air} was then assumed and the procedure repeated to search for an (r, t_{air}) pair which was a global minimum. However, no such minimum was found. It was not possible to find a finite value of r which gave a realistic fit to the data. The problem stemmed from the fact that no data was collected between 30 and 200s when most of the temperature change occurred. Also, during the first 30s, the three thermocouple gave widely different values so this data could not be analyzed by itself. It was noted, however, that all of the thermocouple readings collected at longer times (beyond 600s) were within two degrees of each other, indicating that temperature gradients within the system had equilibrated by then. At later times, it appeared the system was cooling as a whole, losing heat to the air. These facts indicated that r should be large. Accordingly, the data was reanalyzed with the assumption that r took on very large values. In effect, this reduced the analysis to a one-parameter search, finding the best value of t_{air} . The fit is indicated by the solid curve in Figure A2, which gave $t_{air} = 2.38 \times 10^4 \text{s}$ (396 min). This analysis still leaves the value of the aggregate time constant, t_a , undetermined,

although it does indicate that it should be relatively small compared to t_{air} .

A.3 Kinetic Auxiliary Test Results

The thermodynamic and kinetic parameters are those associated with the polymerization reaction. These include the modified heat of reaction, $\Delta H'$, reaction order, n , activation energy, E , and the modified pre-exponential factor, β . All of these parameters are unknown and must be determined experimentally.

A.3.1 Experiments

Parameters were evaluated in independent experiments in which no aggregate was used and in which the reactor was insulated. For this purpose, experiments were conducted using beakers placed in insulated plastic buckets. A two-inch-thick foam polyurethane lid was fitted into the top of the bucket over the top of the beaker. Thermocouples which passed through the foam polyurethane and into the beaker measured three mid-depth temperatures: at the center of the beaker, halfway out, and near the wall. This matched the thermocouple arrangement in the set time tests conducted with aggregate. As in those tests, runs were conducted by first mixing catalyst with Resin B and then mixing it with Resin A for 4 or 5 seconds. The mixture (500 ml) which consisted of equal parts of Part A and Part B resins was then quickly poured into the beaker. The concentration of catalyst used was

in the range employed in the set time tests. Resin temperatures were measured every 1 or 2 seconds. Because the beaker was insulated, measured temperatures were usually within a degree of one another. The average of the three temperatures was used in model calculations.

Table A3 summarizes the experimental conditions employed to determine the kinetics of reaction. Included are the catalyst concentration, C (expressed as a volume percent of Resin B x 1000) and the initial resin temperature. As in the set time tests, equal volumes of the two resins were mixed, so that the relative proportions of the two resins were the same. Three temperatures were used: 40°, 70° and 90°F. At each temperature, there were either five or seven catalyst levels, including runs made with no catalyst. Several replicate tests were made. The resin temperature-time data for all of the 21 runs made are given in Table A4 (end of Appendix) along with the experimental conditions and observed set times.

Table A3. Experimental Design for Determination of Kinetic Parameters

<u>Initial Resin Temperature °K(°F)</u>	<u>Catalyst Concentration x 1000 C x 10³</u>	<u>Number of Experiments</u>
278 (40)	0, 0.3, 0.4, 0.7 1.3, 2.6, 7.8	7
295 (71)	0, 0.3, 0.4, 0.7 1.25, 1.3, 5.0	8
305 (90)	0, 0.3, 0.4 0.7, 1.3	6

A.3.2 Results

A.3.2.1 Thermodynamic Parameter $(\Delta H)'$

Because the system was well insulated in the auxiliary kinetic tests, the parameter r can be set arbitrarily large in the resin energy balance. In addition, there is no term corresponding to heat loss into the aggregate. With these simplifications, the resin energy balance can be solved to give:

$$T - T_0 = T_0 (\Delta H)' \quad (A11)$$

This equation states mathematically that the adiabatic temperature rise in the insulated beaker will be directly proportional to resin conversion. In fact, the unknown dimensionless heat of reaction can be found from the final temperature, T_f , which is reached when $x = 1$:

$$(\Delta H)' = \frac{T_f - T_0}{T_0} \quad (A12)$$

For each run the value of $(\Delta H)'$ was calculated from equation (A12). Values of the set time, t_s , for each run are presented in Table A4. It was found that $(\Delta H)'$ was independent of the initial temperature so that an average value of $(\Delta H)' = 0.3626$ could be used in the analysis. The average of $(\Delta H)' = 0.3626$ is the value

reported in Table 9 and used in model predictions of set time performance.

The conversion, x , at any time, t , can conveniently be found as the fraction of the accomplished temperature change:

$$x = \frac{T - T_o}{T_f - T_o} \quad (\text{A13})$$

This is illustrated in Figure A3, where the conversion at any time is depicted as the ratio of the distances denoted by a and b .

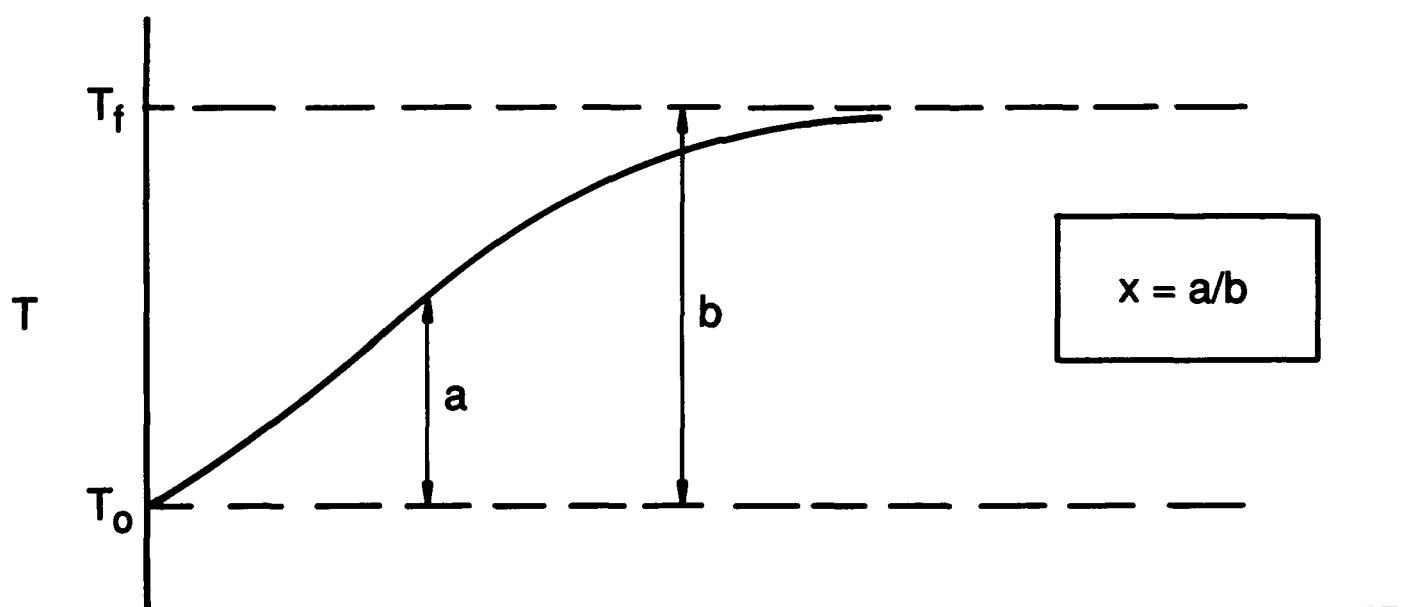


Figure A3. Determination of Conversion from Adiabatic Temperature-Time Profiles.

A.3.2.2 Kinetic Parameters - Analysis of Results

Using equation (A13), the kinetic rate equation can be rearranged to give:

$$\text{INT}(x) = \int_0^x \exp \left[\frac{E}{R T_0 (1 + (\Delta H)'x)} \right] \frac{dx}{(1-x)^n} = \beta t$$

INT(x) is the value of the defined intergral at any conversion x. In equation (A14) there are three unknowns, n the reaction order, E the activation energy, and β the modified pre-exponential factor. Because of the integral it is not possible to solve directly for these parameters, and an iterative procedure must be used.

In the analysis¹ E was varied in increments of 200 from 1000 to 10,000 cal/g mol and n in increments of 0.5 from 0.5 to 3. The (x,t) data of Table A4 was analyzed for each possible pair of (E,n) values. With E and n fixed, the value of INT(x) is determined by the integral in equation (A14). The value of β was then found from the least squares slope of INT(x) vs. time. Since INT(x) vs t is forced through the origin (INT(0) = 0 at t = 0) the statistics of zero force was used. Using this procedure, (E,n) pairs at each of the possible combinations were chosen. For each pair, the sum

¹This method is only possible for adiabatic systems where the temperatures can be written explicitly as a function of conversion. When there is heat exchange to the surroundings or another phase present, the system is non-adiabatic, and solution by this method is not possible.

of squares of the deviations (s^2) between the theoretical and experimental temperature predictions was made. For almost all runs, one of these (E,n) pairs had the lowest value of s^2 . The pair then determined the best values of E and n.

Figure A4 shows the fit obtained by this method for a run with $T_0 = 71^\circ\text{F}$ and $C = 1.25 \times 10^{-3}$. The solid curve is the prediction of the model with $E = 2000 \text{ cal/g mol}$ and $n = 1.5$. The analysis for all the runs showed that $n = 1.5$ was by far the most common best value of reaction order. The best values of the activation energy, however, were not constant from run to run. They appeared to depend on both the initial resin temperature and the catalyst concentration. Accordingly, n was fixed at 1.5 for all runs and the analysis was redone to adjust the best value of the activation energy E. In general, this changed the value of E only slightly.

Table A5 presents the best values of E (cal/g mol) at each catalyst level C and initial temperature T_0 . The three replicate runs gave good reproducibility. The run at $C = 5 \times 10^{-3}$ gave an inordinately low value of E and was not used in subsequent data analysis. The table shows, in general, that E decreases as C and t_0 increase. Lower activation energies at higher catalyst concentrations and higher initial temperatures are consistent with the function of the catalyst, which provides more sites where reaction can occur. Also lower activation energies raise reaction rates, accelerating set.

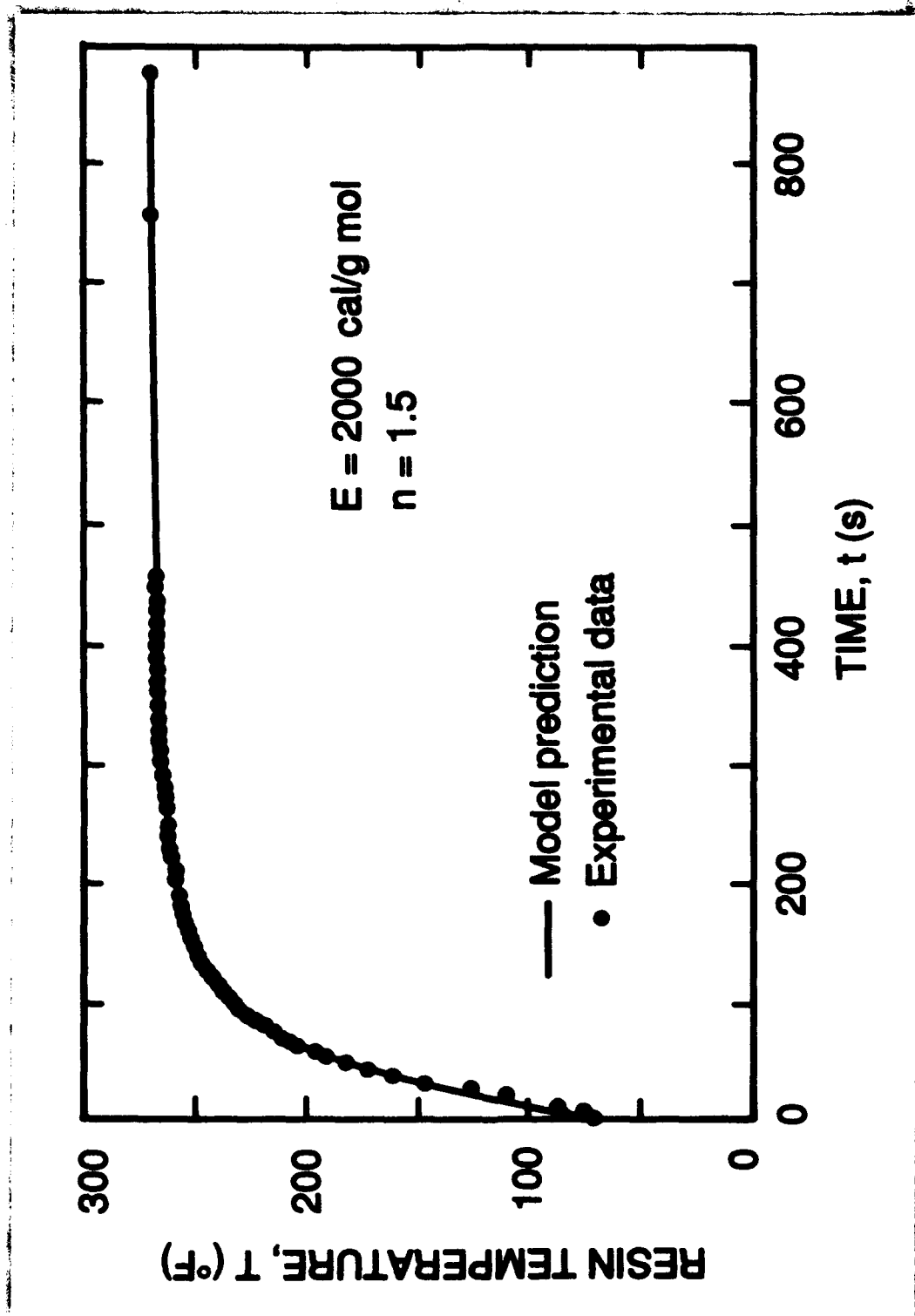


Figure A4. Kinetic Submodel Fit (T versus t) for $C = 1.25 \times 10^{-3}$ and $T = 71^\circ\text{F}$.

Table A5. Calculated Activation Energies E (cal/g mol)

Catalyst Concentration x 1000 (C x 10 ³) -----	Activation Energy for Indicated Initial Resin Temperature, T ₀ (°F) -----		
	<u>40</u>	<u>71</u>	<u>90</u>
0	6600	7200	6600
0.3	5800 5600	4300	4600
0.4	5400 4600	4900	2700
0.7	5500	3050	1600
1.3	3200 2100	2300 [†]	1800
2.6	2800	--	--
5.0	--	400	--
7.8	2500	--	--

[†] obtained for C = 1.25 x 10⁻³

It was found that a linear fit was obtained when the data of Table A5 was correlated with an equation of the form:

$$\frac{1}{E} - \frac{1}{E_0} = m'C \quad (A15)$$

E_0 is the zero concentration activation energy (at $C=0$) and m is the slope of a plot of $(1/E - 1/E_0)$ vs. C . The slope, m' , varies with the initial resin temperature. The best values obtained were $m = 8.30 \times 10^{-5}$, 2.25×10^{-4} and 3.79×10^{-4} g mol/cal at 40° , 71° and 90°F , respectively. The lines were all forced through $E_0 = 6800$, the average of the $C = 0$ values in Table A5.

The value of m' itself was found to correlate well with T_0 when an Arrhenius type plot of $\log m'$ vs $1/T_0$ was made. The correlating equation is:

$$\log \frac{m'}{m'_0} = \frac{-E_m}{2.3 R T_0} \quad (A16)$$

The best values of the intercept and activation energy were found to be:

$$m'_0 = 1.54 \times 10^3 \frac{\text{g mol}}{\text{cal}} \text{ and } E_m = 9230 \frac{\text{cal}}{\text{g mol}} .$$

The sub-model corresponding to equations (A15) and (A16) can be shown to follow second order kinetics of the form:

$$\frac{dE}{dC} = m' C^2 \quad (A17)$$

where

$$m' = m_0' C^{-E_m/RT_0} \quad (A18)$$

Table A6 presents the best values of the modified pre-exponential factor β (s^{-1}) found at each catalyst level C and initial temperature T_0 . The reported values are associated with the activation energies reported in Table A5. β was found to correlate well with the activation energy, regardless of the value of the activation energy or initial resin temperature. β can be found directly from the correlating equation:

$$\log \beta/\beta_0 = \alpha E \quad (A19)$$

To summarize, the overall submodel which predicts the activation energy, E , and modified pre-exponential factor, β , is given by equations (A15), (A16) and (A17). The values of n and $(\Delta H)'$ were fixed at 1.5 and 0.3626, respectively. These equations and values were incorporated into the model in the kinetic rate law [Equation (16)] and reported in Table 9. Because of the additional uncertainty which use of these correlating equations introduces into the predictions of the model, backplots were made of temperature vs. time to see how well the submodel itself agreed

Table A6. Calculated Modified Pre-Exponential Factors, β (s^{-1})

Catalyst Concentration x 1000 ($C \times 10^3$)	Modified Pre-Exponential Factor for Indicated Initial Resin Temperature T_0 ($^{\circ}F$)		
	<u>40</u>	<u>71</u>	<u>90</u>
0	197	347	231
0.3	69.6 53.9	7.6	17.7
0.4	40.9	17.9	1.13
0.7	82.8	1.82	0.26
1.3	2.45	0.69 [†] 0.62	0.65
2.6	1.88	--	--
7.8	2.27	--	--

[†]obtained for $C = 1.25$

with the experimental data. Reasonable predictions resulted at 40°F and 71°F with the poorest fit between the data and submodel predictions found at 90°F and the highest catalyst concentrations.

Table A1. Data for Resin Warming Auxiliary Tests

<u>Time</u> <u>s</u>	<u>Water Temp.</u> <u>(°F)</u>	<u>Resin A Temp.</u> <u>(°F)</u>	<u>Resin B Temp.</u> <u>(°F)</u>	<u>Air Temp.</u> <u>(°F)</u>
0	35.00	35.60	35.35	88.0
4	35.35	35.70	35.40	88.1
8	35.40	35.80	35.40	88.3
12	35.40	35.80	35.40	88.4
16	35.45	35.80	35.40	88.5
20	35.50	35.80	35.40	88.6
24	35.45	35.80	35.40	88.8
28	35.50	35.80	35.40	88.9
32	35.50	35.80	35.40	88.9
36	35.50	35.90	35.40	89.1
40	35.50	35.90	35.45	89.4
44	35.55	36.00	35.40	89.5
48	35.60	36.00	35.40	89.6
52	35.60	36.00	35.40	89.7
57	35.60	36.00	35.45	89.7
61	35.65	36.10	35.45	89.9
65	35.70	36.15	35.45	89.9
69	35.65	36.15	35.45	90.0
73	35.65	36.20	35.45	90.1
77	35.70	36.20	35.45	90.1
81	35.75	36.25	35.45	90.2
85	35.75	36.30	35.45	90.3
89	35.80	36.35	35.50	90.4
93	35.80	36.40	35.45	90.4
97	35.80	36.40	35.55	90.5
101	35.85	36.40	35.55	90.5
105	35.85	36.50	35.55	90.5
109	35.90	36.55	35.55	90.6
114	35.90	36.60	35.55	90.6
118	35.90	36.60	35.55	90.6
122	35.95	36.65	35.55	90.6
126	36.00	36.70	35.55	90.6
130	36.00	36.75	35.55	90.7
134	36.00	36.80	35.55	90.7
138	36.05	36.80	35.60	90.7
142	36.10	36.90	35.60	90.7
146	36.10	36.90	35.55	90.7
150	36.10	36.95	35.60	90.7
154	36.10	37.05	35.65	90.8
158	36.15	37.05	35.60	90.8
162	36.20	37.10	35.65	90.8
166	36.20	37.15	35.65	90.8
171	36.25	37.15	35.60	90.8
175	36.25	37.25	35.65	90.8
179	36.30	37.25	35.65	90.8

Table A1. Data for Resin Warming Auxiliary Tests (Continued)

<u>Time s</u>	<u>Water Temp. (°F)</u>	<u>Resin A Temp. (°F)</u>	<u>Resin B Temp. (°F)</u>	<u>Air Temp. (°F)</u>
183	36.30	37.20	35.60	90.8
187	36.30	37.25	35.60	90.8
191	36.25	37.35	35.60	90.9
195	36.40	37.45	35.65	90.8
199	36.15	37.55	35.65	90.9
203	36.40	37.55	35.65	90.0
207	36.45	37.60	35.70	90.9
211	36.45	37.65	35.65	91.0
215	36.45	37.75	35.65	91.0
219	36.50	37.75	35.70	91.0
224	36.50	37.80	35.70	91.0
228	36.55	37.90	35.70	91.0
232	26.55	37.95	35.75	91.0
236	36.55	38.00	35.70	90.9
240	36.55	38.00	35.70	91.0
304	36.75	38.90	35.75	91.0
364	36.95	39.80	35.90	91.0
424	37.20	40.65	36.00	91.1
484	37.30	41.55	36.10	91.1
544	37.40	42.45	36.25	91.2
604	37.80	43.25	36.40	91.2
664	38.95	44.05	36.60	91.3
724	40.75	44.75	36.75	91.2
784	41.60	45.65	37.05	91.4
844	42.15	46.40	37.30	91.3
904	42.60	47.05	37.60	91.4
964	42.05	47.90	37.85	91.3
1024	43.30	48.50	37.90	91.2
1084	43.85	49.35	38.50	91.5
1144	44.30	50.05	38.90	91.6
1204	44.65	50.70	39.20	91.6
1264	45.05	51.30	39.60	91.6
1324	45.40	51.95	40.05	91.6
1384	45.80	52.55	40.45	91.5
1444	46.20	53.15	40.90	91.5
1504	46.60	53.70	41.30	91.5
1564	46.95	54.25	41.80	91.5
1624	47.30	54.85	42.25	91.6
1684	47.70	55.35	42.70	91.7
1744	48.00	55.85	43.15	91.7
1804	48.40	56.30	53.65	91.8
1864	49.10	57.30	44.60	91.9
1924	49.45	57.80	45.15	91.9
1984	49.75	58.20	45.65	91.9
2044	50.10	58.65	46.20	91.9
2104	50.40	59.15	46.75	91.9
2164	50.75	59.65	47.25	92.0
2224	51.10	60.15	47.75	92.0

Table A1. Data for Resin Warming Auxiliary Tests (Continued)

<u>Time</u> <u>s</u>	<u>Water Temp.</u> <u>(°F)</u>	<u>Resin A Temp.</u> <u>(°F)</u>	<u>Resin B Temp.</u> <u>(°F)</u>	<u>Air Temp.</u> <u>(°F)</u>
2284	51.40	60.65	48.20	92.1
2344	51.65	61.05	48.75	92.1
2404	52.00	61.55	49.30	92.1
2464	52.30	62.00	49.85	92.2
2524	52.60	62.45	50.40	92.2
2584	52.90	62.90	50.95	92.2
2644	53.15	63.35	51.55	92.1
2704	53.40	63.70	52.00	92.2
2764	53.70	64.15	52.55	92.1
2824	54.00	64.55	53.05	92.1
2884	54.20	64.95	53.55	92.2
2944	54.60	65.45	54.15	92.2
3004	54.80	65.85	54.60	92.3
3064	55.10	66.25	55.10	92.3
3124	55.40	66.60	55.60	92.4
3184	55.60	67.05	56.10	92.3
3244	55.90	67.45	56.65	92.2
3304	56.15	67.80	57.05	92.2
3364	56.35	68.15	57.65	92.1
3424	56.60	68.50	58.05	92.2
3484	56.80	68.80	58.45	92.3
3544	57.00	69.20	58.95	92.2
3604	57.20	69.45	59.45	92.3
3664	57.55	69.80	59.95	92.3
3724	57.80	70.15	60.35	92.2
3784	58.05	70.50	60.80	92.4
3844	58.20	70.80	61.25	92.4
3904	58.50	71.10	61.60	92.4
3964	58.65	71.40	62.00	92.5
4024	58.85	71.70	62.45	92.5
4084	59.05	71.95	62.85	92.5
4144	59.30	72.30	63.25	92.6
4204	59.50	72.60	63.70	92.5
4264	59.70	72.95	64.05	92.4
4324	59.60	73.20	64.50	92.4
4384	60.10	73.50	64.85	92.4
4444	60.30	73.75	65.25	92.5
4504	60.50	73.95	65.60	92.5
4564	60.70	74.20	65.95	92.5
4624	61.00	74.55	66.40	92.5
4684	61.10	74.80	66.70	92.7
4744	61.30	75.00	67.05	92.6
4804	61.50	75.25	67.35	92.7
4864	61.60	75.50	67.65	92.7
4924	61.85	75.80	68.05	92.7
4984	62.00	75.95	68.30	92.6
5044	62.20	76.25	68.65	92.8
5104	62.40	76.45	68.90	92.7

Table A1. Data for Resin Warming Auxiliary Tests (Continued)

<u>Time</u> <u>s</u>	<u>Water Temp.</u> <u>(°F)</u>	<u>Resin A Temp.</u> <u>(°F)</u>	<u>Resin B Temp.</u> <u>(°F)</u>	<u>Air Temp.</u> <u>(°F)</u>
5164	62.55	76.65	69.20	92.7
5224	62.75	76.85	69.45	92.8
5284	62.95	77.05	69.70	92.7
5344	63.15	77.30	70.00	92.8
5404	63.30	77.50	70.30	92.8
5464	63.50	77.75	70.60	92.9
5524	63.75	77.95	70.85	92.8
5584	63.85	78.15	71.10	92.9
5644	64.05	78.30	71.40	92.8
5704	64.25	78.50	71.70	92.9
5764	64.45	78.65	71.90	92.9
5824	64.70	78.85	72.20	92.8
5884	64.85	79.05	72.45	92.8
5944	65.10	79.20	72.70	92.9
6004	65.25	79.35	72.90	92.8
6064	65.45	79.55	73.15	92.9
6124	65.65	79.70	73.35	92.8
6184	65.90	79.95	73.55	92.8
6244	66.05	80.05	73.80	92.8
6304	66.30	80.25	74.00	92.8
6364	66.50	80.45	74.25	92.9
6424	66.75	80.65	74.45	92.9
6484	66.90	80.75	74.65	92.9
6544	67.05	80.90	74.80	92.9
6604	67.25	81.05	75.00	93.0
6664	67.45	81.20	75.20	92.9
6724	67.65	81.35	75.40	92.9
6784	67.85	81.50	75.55	92.9
6844	68.05	81.65	75.75	93.0
6904	68.25	81.85	76.00	93.0
6964	68.40	81.95	76.10	92.9
7024	68.60	82.10	76.30	93.0
7084	68.75	82.15	76.45	92.9
7144	68.95	82.35	76.60	92.9
7204	69.05	82.45	76.80	93.1
7264	69.30	82.55	77.00	92.9
7324	69.45	82.75	77.10	92.9
7384	69.65	82.85	77.30	93.1
7444	69.85	83.00	77.45	93.0
7504	69.96	83.05	77.60	93.1
7564	70.15	83.25	77.80	93.1
7624	70.25	83.35	78.00	93.1
7684	70.45	83.50	78.20	93.1
7744	70.65	83.65	78.30	93.1
7804	70.85	83.70	78.50	93.1
7864	71.05	83.90	78.65	93.1
7924	71.10	84.00	78.75	93.1
7984	71.25	84.05	78.90	93.2

Table A1. Data for Resin Warming Auxiliary Tests (Continued)

<u>Time</u> <u>s</u>	<u>Water Temp.</u> <u>(°F)</u>	<u>Resin A Temp.</u> <u>(°F)</u>	<u>Resin B Temp.</u> <u>(°F)</u>	<u>Air Temp.</u> <u>(°F)</u>
8044	71.45	84.15	79.05	93.2
8104	71.65	84.30	79.20	93.1
8164	71.80	84.50	79.40	93.2
8224	72.00	84.60	79.50	93.2
8284	72.15	84.65	79.65	93.2
8344	72.30	84.70	79.75	93.2
8404	72.45	84.85	79.95	93.3
8464	72.60	85.00	80.10	93.3
8524	72.75	85.10	80.20	93.3
8584	72.95	85.15	80.35	93.1
8644	73.10	85.25	80.45	93.2
8704	73.30	85.35	80.60	93.3
8764	73.35	85.45	80.75	93.3
8824	73.55	85.50	80.85	93.2
8884	73.70	85.65	80.95	93.3

Table A4. Resin Temperature Versus Time Data for Kinetic Auxiliary Tests

Run No. 1 Beaker Test

$T_o = 71^\circ\text{F}$

$T_{air} = 71^\circ\text{F}$

$T_{max} = 272^\circ\text{F}$

$C = 1.25 \times 10^{-3}$

Set Time = 64 s

<u>Time (s)</u>	<u>T ($^\circ\text{F}$)</u>	<u>Time (s)</u>	<u>T ($^\circ\text{F}$)</u>
2.0	70.1	172.4	254.9
6.0	74.4	176.7	255.9
10.7	86.3	182.2	256.2
20.1	109.6	186.4	256.7
25.6	124.6	197.4	257.6
30.8	146.5	206.6	258.7
35.5	161.0	216.8	259.6
41.3	172.0	225.2	260.5
47.2	181.6	235.2	261.3
51.7	190.2	243.2	261.7
57.3	196.2	257.3	262.4
61.7	203.8	267.9	263.2
64.2	207.1	275.1	263.5
66.7	209.5	287.2	264.0
71.3	213.3	296.9	264.5
77.3	217.4	306.2	264.9
81.8	221.4	315.3	265.4
86.2	225.6	324.0	265.9
91.3	230.0	334.3	266.0
97.8	232.3	345.0	266.4
101.7	234.7	356.9	266.5
106.7	236.5	366.3	266.6
111.3	238.4	376.1	266.7
116.1	240.9	385.5	267.1
120.6	243.1	396.5	267.1
126.7	245.3	405.3	267.1
130.6	247.1	415.1	267.3
137.2	248.5	426.0	267.2
142.9	249.9	434.1	267.5
147.1	251.3	434.1	267.5
153.2	252.2	455.7	268.2
158.6	253.1	753.0	268.2
163.4	254.0	874.5	270.2
167.2	254.7		

Table A4. Resin Temperature Versus Time Data for
Kinetic Auxiliary Tests (Continued)

Run No. 2

Beaker Test

$T_o = 70^\circ\text{F}$

$T_{air} = 71^\circ\text{F}$

$T_{max} = 261^\circ\text{F}$

$C = 0.4 \times 10^{-3}$

Set Time = --- s

<u>Time (s)</u>	<u>T ($^\circ\text{F}$)</u>	<u>Time (s)</u>	<u>T ($^\circ\text{F}$)</u>
0.4	70.2	171.7	244.7
11.2	78.5	175.8	245.6
16.0	85.2	180.3	246.6
20.8	91.1	184.8	247.4
25.6	99.0	189.9	248.4
29.6	110.7	195.4	249.2
33.9	118.2	201.8	250.3
38.0	127.0	206.3	250.5
43.0	138.1	211.2	250.8
47.8	149.4	217.0	251.6
53.9	157.8	223.9	252.1
62.0	169.1	226.6	252.7
67.0	176.3	232.1	252.9
70.9	183.9	237.0	253.3
76.0	192.2	240.9	254.2
82.1	199.5	245.7	255.0
86.3	203.0	257.6	255.4
90.2	207.5	266.7	256.0
95.9	212.4	275.8	256.4
101.7	216.2	285.8	256.8
106.4	218.9	295.6	256.9
112.4	222.4	305.6	257.3
116.9	225.7	315.9	257.5
122.8	228.4	325.5	257.7
126.7	230.9	332.0	258.7
131.2	233.9	390.4	259.7
136.8	235.4	442.3	260.2
142.0	236.9	460.9	260.3
146.7	238.4	521.3	260.3
151.8	240.4	580.9	260.6
157.4	241.0	642.4	260.8
162.0	242.2	772.0	260.9
167.5	243.4		

Table A4. Resin Temperature Versus Time Data for Kinetic Auxiliary Tests (Continued)

Run No. 3 Beaker Test

$T_o = 71^\circ\text{F}$

$T_{\text{air}} = 71^\circ\text{F}$

$T_{\text{max}} = 268^\circ\text{F}$

$C = 0.3 \times 10^{-3}$

Set Time = 105 s

<u>Time (s)</u>	<u>T ($^\circ\text{F}$)</u>	<u>Time (s)</u>	<u>T ($^\circ\text{F}$)</u>
2.0	70.0	182.7	235.8
13.2	77.2	187.6	237.7
17.4	81.1	192.6	238.9
21.1	85.7	198.4	240.6
26.1	89.6	203.5	242.4
31.8	94.2	205.8	243.0
37.2	101.9	212.0	245.2
42.0	108.2	215.8	246.0
47.0	113.4	222.1	247.3
52.7	120.5	226.3	248.0
58.8	127.2	235.1	249.8
61.8	133.4	240.0	250.5
67.0	141.7	246.6	251.2
71.0	149.5	252.0	251.9
75.9	156.6	259.0	252.7
80.8	165.2	265.5	253.2
88.1	173.5	273.4	253.9
96.4	182.3	280.2	254.3
100.4	187.5	286.0	254.9
105.5	192.2	313.1	256.0
111.0	197.1	340.3	257.4
114.5	200.8	400.5	259.3
120.3	205.0	461.6	261.5
125.1	209.0	520.7	262.4
130.6	211.9	582.1	263.7
136.4	214.1	625.0	263.7
141.8	217.0	645.2	264.1
147.4	220.3	705.5	264.7
152.6	223.2	742.7	264.7
157.1	225.9	822.8	265.5
163.4	228.2	885.0	265.6
168.1	230.6	942.7	265.7
173.2	232.8	1003.2	266.0
178.1	234.5	1060.7	265.8

Table A4. Resin Temperature Versus Time Data for
Kinetic Auxiliary Tests (Continued)

Run No. 4

Beaker Test

$T_O = 71^\circ\text{F}$

$T_{\text{air}} = 71^\circ\text{F}$

$T_{\text{max}} = 269^\circ\text{F}$

$C = 5.0 \times 10^{-3}$

Set Time = 17 s

<u>Time (s)</u>	<u>T ($^\circ\text{F}$)</u>
1.4	69.5
6.8	98.0
11.0	149.4
16.1	173.4
21.9	193.9
31.9	220.2
37.8	227.7
42.2	233.1
48.3	236.7
54.3	239.9
57.9	243.0
63.4	245.7
68.1	247.2
72.5	248.5
76.9	249.8
82.5	251.5
87.3	252.4
92.7	253.6
98.4	254.2
102.5	254.6
107.5	255.3
111.3	255.9
121.0	256.9
132.5	257.5
140.9	258.6
153.7	258.8
162.4	259.8
172.1	260.2
182.3	260.8
193.2	261.0
203.5	261.8
267.3	263.9
285.4	263.9
323.7	264.9
386.3	265.6
445.0	266.0
505.4	266.7
565.3	267.0
625.4	267.4
686.0	267.5

Table A4. Resin Temperature Versus Time Data for
Kinetic Auxiliary Tests (Continued)

Run No. 2A Beaker Test

$T_o = 90^\circ\text{F}$

$T_{\text{air}} = 90^\circ\text{F}$

$T_{\text{max}} = 282^\circ\text{F}$

$C = 0.0$ Set Time = 88 s

<u>Time (s)</u>	<u>T ($^\circ\text{F}$)</u>	<u>Time (s)</u>	<u>T ($^\circ\text{F}$)</u>
0.9	90.4	127.0	244.0
6.9	91.0	132.4	247.4
10.7	94.6	139.1	251.2
14.6	97.9	143.9	253.2
19.1	103.2	147.6	255.6
24.6	110.7	153.5	258.0
29.6	115.8	157.4	259.2
35.3	121.6	163.3	261.1
39.8	127.8	167.5	263.1
44.6	133.2	171.9	264.4
51.4	139.1	179.3	266.1
54.1	148.2	182.3	266.7
58.7	155.3	188.0	268.1
62.9	161.7	192.8	269.3
67.5	169.6	197.0	270.3
72.5	177.8	201.2	271.3
76.9	184.9	207.4	272.5
82.8	193.5	211.0	272.6
86.2	199.7	215.3	273.7
91.0	207.9	219.6	274.6
94.4	214.2	225.2	275.1
99.5	219.5	231.2	276.0
103.7	224.4	236.8	276.5
108.5	230.0	385.8	281.0
112.3	234.5	445.4	281.4
117.2	237.8	504.2	281.5
112.1	240.9		

Table A4. Resin Temperature Versus Time Data for
Kinetic Auxiliary Tests (Continued)

Run No. 3A Beaker Test

$T_0 = 90^\circ\text{F}$

$T_{\text{air}} = 90^\circ\text{F}$

$T_{\text{max}} = 285^\circ\text{F}$

$C = 0.7 \times 10^{-3}$

Set Time = 13 s

<u>T ($^\circ\text{F}$)</u>	<u>Time (s)</u>
1.9	90.5
3.9	121.4
6.0	172.7
10.6	194.9
13.7	209.7
18.2	220.7
23.1	230.8
29.2	238.0
33.9	245.0
37.4	250.3
43.6	254.4
49.6	257.7
53.0	259.6
58.1	262.3
63.6	263.6
68.1	266.5
79.4	269.7
82.3	270.3
87.0	271.4
93.2	272.6
96.8	273.1
101.8	274.0
106.8	274.7
110.8	275.3
116.1	275.9
121.1	275.8
125.5	276.6
130.8	277.0
135.6	277.5
143.2	277.8
148.6	278.2
158.2	278.8
166.8	279.2
178.1	279.5
187.5	280.0
195.8	280.1
255.7	281.7
319.8	282.1
381.1	282.8
438.7	283.0
504.4	283.4
564.1	283.8

Table A4. Resin Temperature Versus Time Data for
Kinetic Auxiliary Tests (Continued)

Run No. 4A Beaker Test

$T_0 = 90^\circ\text{F}$

$T_{\text{air}} = 90^\circ\text{F}$

$T_{\text{max}} = 272^\circ\text{F}$

$C = 0.3 \times 10^{-3}$

Set Time = 57 s

<u>Time (s)</u>	<u>T ($^\circ\text{F}$)</u>	<u>Time (s)</u>	<u>T ($^\circ\text{F}$)</u>
1.2	90.4	116.5	247.5
9.9	100.5	120.8	249.3
13.8	109.4	128.2	251.2
18.1	116.8	131.1	253.3
23.8	128.6	137.0	255.0
28.4	137.5	142.0	256.1
33.2	149.1	146.8	257.0
38.0	158.5	152.7	257.9
40.9	170.0	159.0	258.9
48.2	179.3	164.7	259.8
52.5	188.0	166.6	260.2
57.4	195.6	171.5	261.1
62.1	201.7	177.1	261.9
65.5	207.9	182.4	262.6
70.6	213.6	187.4	263.1
74.6	218.0	193.1	263.6
80.2	221.8	198.0	264.3
82.8	226.2	201.2	264.8
88.8	229.7	211.0	265.0
92.9	234.4	220.6	265.0
99.0	237.8	280.7	270.0
102.4	240.2	339.7	271.4
108.2	243.1	460.2	271.7
112.5	244.6	519.6	271.7

Table A4. Resin Temperature Versus Time Data for
Kinetic Auxiliary Tests (Continued)

Run No. 1B Beaker Test

$T_o = 40^\circ\text{F}$

$T_{air} = 38^\circ\text{F}$

$T_{max} = 231^\circ\text{F}$

$C = 2.6 \times 10^{-3}$

Set Time = 44 s

<u>Time (s)</u>	<u>T ($^\circ\text{F}$)</u>	<u>Time (s)</u>	<u>T ($^\circ\text{F}$)</u>
0.7	40.4	137.0	211.5
6.7	49.0	142.0	212.0
11.0	55.6	149.9	213.1
16.8	69.4	153.6	213.2
22.4	80.9	159.7	214.2
26.5	93.4	164.6	215.5
31.2	109.4	170.8	215.4
37.1	123.7	176.1	215.7
41.9	135.2	179.5	216.4
47.7	147.0	185.6	217.2
54.1	155.5	188.7	217.5
59.9	163.8	193.7	218.0
65.1	170.7	198.4	218.3
69.5	175.8	205.5	219.4
75.2	180.8	215.6	219.7
80.2	185.5	221.5	220.3
83.9	189.3	232.7	221.0
89.3	191.9	252.3	222.0
94.7	194.8	260.0	222.3
99.6	196.8	318.9	224.8
104.6	198.8	376.7	226.4
108.7	201.0	437.0	227.4
114.1	203.0	497.4	227.5
119.0	205.0	554.1	227.9
123.6	206.7	617.1	228.1
129.2	208.3	737.3	228.3

Table A4. Resin Temperature Versus Time Data for
Kinetic Auxiliary Tests (Continued)

Run No. 2B Beaker Test

$T_O = 40^\circ\text{F}$

$T_{\text{air}} = 37^\circ\text{F}$

$T_{\text{max}} = 289^\circ\text{F}$

$C = 0.0$

Set Time = 291 s

<u>Time (s)</u>	<u>T ($^\circ\text{F}$)</u>	<u>Time (s)</u>	<u>T ($^\circ\text{F}$)</u>
-0.3	40.5	292.1	162.4
9.5	42.1	302.0	167.3
19.1	44.6	312.5	171.9
28.6	46.5	323.4	176.0
40.5	48.7	331.3	180.2
50.1	51.0	339.8	183.3
61.6	53.7	349.9	187.3
71.0	57.2	360.3	190.3
80.2	60.9	371.2	193.4
90.4	65.0	382.0	195.0
99.7	67.6	391.2	197.3
118.9	73.4	401.5	199.2
129.6	77.7	411.6	201.4
138.8	82.0	422.6	203.4
150.8	86.5	432.4	204.9
161.3	90.6	442.1	207.2
170.7	95.0	448.4	207.6
181.6	101.3	512.3	214.4
190.4	106.9	570.8	217.6
200.1	111.8	632.5	220.1
210.6	118.0	692.2	222.0
220.5	123.6	751.3	223.6
230.3	129.7	812.1	224.3
238.5	133.9	869.5	224.6
250.0	140.4	930.2	225.3
261.0	146.1	990.0	225.7
272.4	152.1	1051.7	225.8
282.0	156.4		

Table A4. Resin Temperature Versus Time Data for
Kinetic Auxiliary Tests (Continued)

Run No. 3B

Beaker Test

$T_o = 40^\circ\text{F}$

$T_{\text{air}} = 37^\circ\text{F}$

$T_{\text{max}} = 238^\circ\text{F}$

$C = 7.8 \times 10^{-3}$

Set Time = 15 s

<u>Time (s)</u>	<u>T ($^\circ\text{F}$)</u>
-1.5	40.4
3.9	47.2
12.7	78.7
18.0	125.0
22.5	149.2
28.6	167.8
32.9	181.6
39.4	194.9
43.5	201.8
49.3	207.2
55.9	211.1
61.1	214.0
65.0	215.6
71.7	218.7
74.9	219.8
80.3	221.2
84.7	222.1
89.9	224.1
96.6	224.8
99.3	225.8
106.0	225.9
109.0	227.1
113.9	227.5
120.2	228.1
128.3	229.3
138.7	229.7
147.8	230.0
161.0	231.2
170.4	231.5
181.4	232.0
189.8	232.0
200.0	232.2
211.8	232.8
217.8	232.5
229.9	233.3
239.8	233.1
242.9	234.3
304.3	234.6
424.0	235.1
483.3	235.1
602.5	235.3

Table A4. Resin Temperature Versus Time Data for
Kinetic Auxiliary Tests (Continued)

Run No. 4B Beaker Test

$T_o = 40^\circ\text{F}$

$T_{air} = 38^\circ\text{F}$

$T_{max} = 235^\circ\text{F}$

$C = 1.3 \times 10^{-3}$

Set Time = 60 s

<u>Time (s)</u>	<u>T ($^\circ\text{F}$)</u>	<u>Time (s)</u>	<u>T ($^\circ\text{F}$)</u>
-0.4	40.2	153.7	206.2
5.3	41.7	159.8	207.4
12.3	48.5	166.3	209.1
15.5	53.7	169.5	209.9
20.9	62.7	174.7	211.2
26.5	69.7	181.1	212.2
29.8	79.4	184.7	212.9
36.3	88.0	190.1	213.6
41.0	98.5	195.6	214.4
47.9	111.2	200.4	215.3
52.2	122.4	206.5	215.7
58.0	132.4	210.9	216.7
64.4	141.4	214.5	217.2
69.1	149.8	225.0	217.8
75.1	156.4	232.5	218.7
78.8	162.2	242.3	220.1
84.2	169.2	254.9	221.0
90.2	173.3	259.3	221.5
94.3	176.3	267.0	222.3
98.5	181.5	276.8	223.6
105.6	185.8	283.2	224.3
110.1	189.0	293.5	225.0
114.2	191.7	354.1	227.8
118.6	193.2	412.9	229.5
124.4	195.9	472.0	230.9
129.2	197.8	532.0	231.4
132.3	199.0	593.1	232.0
138.4	201.3	713.0	232.5
143.1	203.1	771.2	232.5
148.2	204.8	831.4	233.0

Table A4. Resin Temperature Versus Time Data for Kinetic Auxiliary Tests (Continued)

Run No. 1C Beaker Test

$T_0 = 71^\circ\text{F}$

$T_{\text{air}} = 71^\circ\text{F}$

$T_{\text{max}} = 255^\circ\text{F}$

$C = 0.4 \times 10^{-3}$

Set Time = 78 s

<u>Time (s)</u>	<u>T (F)</u>	<u>Time (s)</u>	<u>T (F)</u>	<u>Time (s)</u>	<u>T (F)</u>
0	72.7	71	172.0	141	225.9
2	72.6	72	173.9	143	226.5
4	72.5	74	175.9	144	227.2
5	72.6	75	177.8	146	227.8
7	74.3	77	179.7	147	228.4
8	76.3	79	181.5	149	229.0
10	78.3	80	183.3	151	229.6
12	80.0	82	185.0	152	230.2
13	82.2	84	186.6	154	230.8
15	84.2	85	188.3	155	231.3
16	86.4	87	189.8	157	231.9
18	88.3	88	191.4	159	232.4
20	90.4	90	192.9	160	232.9
21	92.7	91	194.4	162	233.4
23	94.9	93	195.8	163	233.9
24	96.9	95	197.2	165	234.4
26	99.2	96	198.5	167	234.9
28	101.5	98	199.9	168	235.3
29	104.0	99	201.2	170	235.8
31	106.9	101	202.4	171	236.2
32	108.9	103	203.7	173	236.7
34	111.4	104	204.8	174	237.1
36	113.9	106	206.0	176	237.5
37	116.3	107	207.1	178	237.9
39	119.0	109	208.2	179	238.3
40	121.7	111	209.4	181	238.6
42	124.5	112	210.4	183	239.0
44	127.2	114	211.4	184	239.4
45	130.0	115	212.4	186	239.8
47	132.8	117	213.4	187	240.1
48	135.7	119	214.4	189	240.4
50	138.6	120	215.4	190	240.8
52	141.4	122	216.3	192	241.1
53	144.2	123	217.2	194	241.5
55	147.0	125	218.0	195	241.8
56	149.7	127	218.9	197	242.0
58	152.4	128	219.8	198	242.4
59	155.0	130	220.6	200	242.7
61	157.7	131	221.4	202	242.9
63	160.2	133	222.2	203	243.2
64	162.7	135	222.9	205	243.5
66	165.1	136	223.7	206	243.7
68	167.4	138	224.5	208	244.0
69	170.2	139	225.2	210	244.2

Table A4. Resin Temperature Versus Time Data for
Kinetic Auxiliary Tests (Continued)

Run No. 1C Beaker Test

$T_o = 71^\circ\text{F}$

$T_{\text{air}} = 71^\circ\text{F}$

$T_{\text{max}} = 255^\circ\text{F}$

$C = 0.4 \times 10^{-3}$

Set Time = 78 s

<u>Time (s)</u>	<u>T (F)</u>	<u>Time (s)</u>	<u>T (F)</u>	<u>Time (s)</u>	<u>T (F)</u>
211	244.5	224	246.2	237	247.7
213	244.7	226	246.4	238	247.9
214	245.0	227	246.6	240	248.1
216	245.2	229	246.8	242	248.2
218	245.4	230	247.0	243	252.5
219	245.6	232	247.2	303	254.3
221	245.8	234	247.4	363	255.0
222	246.0	235	247.5		

Table A4. Resin Temperature Versus Time Data for Kinetic Auxiliary Tests (Continued)

Run No. 2C Beaker Test

$T_0 = 71^\circ\text{F}$

$T_{\text{air}} = 71^\circ\text{F}$

$T_{\text{max}} = 264^\circ\text{F}$

$C = 0.7 \times 10^{-3}$

Set Time = 55 s

<u>Time (s)</u>	<u>T (F)</u>	<u>Time (s)</u>	<u>T (F)</u>	<u>Time (s)</u>	<u>T (F)</u>
0	76.4	74	203.0	144	240.8
5	77.5	75	204.4	145	241.3
7	80.5	77	205.8	147	241.7
8	83.0	78	207.1	149	242.2
10	86.1	80	208.4	150	242.6
11	89.1	82	209.8	152	243.0
13	92.2	83	211.1	154	243.3
15	94.7	85	212.3	155	243.7
16	98.5	86	213.5	157	244.1
18	102.0	88	214.6	158	244.5
20	105.0	90	215.8	160	244.8
21	108.4	91	216.9	161	245.1
23	112.1	93	218.0	163	245.5
24	116.2	94	219.0	165	245.8
26	120.5	96	220.1	166	246.1
27	124.5	98	221.1	168	246.4
29	128.4	99	222.1	169	246.7
31	132.5	101	223.0	171	247.0
32	136.8	102	224.0	173	247.3
34	141.1	104	224.9	174	247.6
35	145.4	106	225.7	176	247.9
37	149.6	107	226.5	177	248.1
39	153.5	109	227.4	179	248.4
40	157.2	110	228.1	181	248.6
42	160.8	112	228.9	182	248.9
43	163.9	114	229.6	184	249.1
45	167.0	115	230.4	185	249.4
47	169.9	117	231.1	187	249.6
48	172.5	118	231.8	189	249.8
50	175.0	120	232.5	190	250.0
51	177.3	122	233.1	192	250.2
53	179.6	123	233.8	193	250.5
55	181.8	125	234.4	195	250.7
56	183.9	126	235.1	197	250.9
58	186.0	128	235.6	198	251.1
59	187.9	130	236.2	200	251.2
61	189.8	131	236.8	201	251.4
63	191.6	133	237.4	203	251.6
64	193.4	134	237.9	205	251.8
66	195.1	136	238.4	206	252.1
67	196.8	138	238.9	208	252.2
69	198.4	139	239.4	209	252.4
71	199.9	141	239.9	211	252.5
72	201.5	142	240.3	213	252.7

Table A4. Resin Temperature Versus Time Data for Kinetic Auxiliary Tests (Continued)

Run No. 2C Beaker Test

$T_O = 71^\circ\text{F}$

$T_{air} = 71^\circ\text{F}$

$T_{max} = 264^\circ\text{F}$

$C = 0.7 \times 10^{-3}$

Set Time = 55 s

<u>Time (s)</u>	<u>T (F)</u>	<u>Time (s)</u>	<u>T (F)</u>	<u>Time (s)</u>	<u>T (F)</u>
214	252.9	228	254.2	243	258.6
216	253.0	230	254.3	303	260.6
217	253.2	232	254.5	363	261.9
219	253.3	233	254.6	423	262.8
221	253.5	235	254.7	483	263.4
222	253.7	237	254.8	543	263.9
224	253.8	238	255.0	603	264.1
225	253.9	240	255.1	663	264.3
227	254.0	241	255.2		

Table A4. Resin Temperature Versus Time Data for Kinetic
Auxiliary Tests (Continued)

Run No. 3C Beaker Test

$T_o = 72^\circ\text{F}$ $T_{\text{air}} = 73^\circ\text{F}$ $T_{\text{max}} = 268^\circ\text{F}$

$C = 1.3 \times 10^{-3}$ Set Time = 32s

<u>Time(s)</u>	<u>T (°F)</u>	<u>Time(s)</u>	<u>T (°F)</u>	<u>Time(s)</u>	<u>T (°F)</u>
0	74.6	70	222.0	141	251.3
1	74.4	71	223.2	142	251.7
3	75.3	73	224.5	144	251.9
4	79.0	75	225.6	145	252.3
6	83.4	76	226.6	247	252.6
8	87.6	78	227.7	149	252.9
9	92.7	79	228.7	150	253.2
11	97.6	81	229.7	152	253.4
12	103.3	83	230.7	154	253.7
14	108.5	84	231.6	155	253.9
16	114.7	86	232.5	157	254.1
17	121.7	87	233.4	158	254.4
19	128.2	89	234.2	160	254.6
20	135.1	91	235.1	162	254.9
22	142.0	92	235.9	163	255.1
24	148.7	94	236.7	165	255.3
25	254.9	95	237.4	166	255.5
27	160.0	97	238.1	168	255.7
28	164.4	99	238.8	169	255.9
30	168.6	100	239.6	170	256.1
32	172.3	102	240.2	172	256.3
33	175.7	103	240.8	173	256.4
35	178.9	105	241.5	175	256.7
36	181.9	107	242.1	177	256.8
38	184.7	108	242.7	178	257.0
39	187.5	110	243.3	180	257.2
41	190.0	112	243.8	182	257.3
43	192.5	113	244.3	183	257.5
44	194.8	115	244.9	185	257.7
46	197.0	116	245.4	186	257.8
47	199.1	118	245.9	188	257.9
49	201.1	120	246.3	189	258.1
51	203.1	121	246.8	191	258.3
52	205.0	123	247.2	193	258.4
54	206.8	124	247.7	194	258.6
55	208.6	126	248.1	196	258.6
57	210.3	128	248.5	198	258.8
59	211.9	129	248.8	199	258.9
60	213.5	131	249.3	201	259.0
62	215.0	132	249.6	202	259.2
63	216.5	134	250.0	204	259.3
65	218.0	136	250.4	206	259.4
67	219.3	137	250.7	207	259.6
68	220.6	139	251.0	209	259.7

Table A4. Resin Temperature Versus Time Data for Kinetic
Auxiliary Tests (Continued)

Run No. 3C Beaker Test

$T_o = 72^{\circ}\text{F}$ $T_{\text{air}} = 73^{\circ}\text{F}$ $T_{\text{max}} = 268^{\circ}\text{F}$

$C = 1.3 \times 10^{-3}$ Set Time = 32s

<u>Time(s)</u>	<u>T (°F)</u>	<u>Time(s)</u>	<u>T (°F)</u>	<u>Time(s)</u>	<u>T (°F)</u>
210	259.8	228	260.9	363	266.2
212	259.9	230	261.0	423	266.8
214	260.0	231	261.1	483	267.2
215	260.1	233	261.2	543	267.5
217	260.2	234	261.2	603	267.6
218	260.3	236	261.3	663	267.6
220	260.4	238	261.4	723	267.6
222	260.5	239	261.5	783	267.5
223	260.6	241	261.6	843	267.3
225	260.7	243	263.9	903	266.9
227	260.8	303	265.3	963	266.7

Table A4. Resin Temperature Versus Time Data for Kinetic Auxiliary Tests (Continued)

Run No. 1D Beaker Test

$T_o = 41^\circ\text{F}$ $T_{air} = 40^\circ\text{F}$ $T_{max} = 234^\circ\text{F}$

$C = 0.3 \times 10^{-3}$ Set Time = 205s

<u>Time(s)</u>	<u>T (°F)</u>	<u>Time(s)</u>	<u>T (°F)</u>	<u>Time(s)</u>	<u>T (°F)</u>
5	41.5	75	73.5	146	123.1
6	41.8	77	74.4	148	124.4
8	42.5	79	75.2	150	125.7
9	43.0	80	76.1	151	127.0
11	43.7	82	77.0	153	128.2
13	44.3	83	77.8	154	129.6
14	44.9	85	78.7	156	130.9
16	45.6	87	79.7	158	132.1
18	46.1	88	80.6	159	133.4
19	46.9	90	81.6	161	134.7
21	47.6	92	82.5	162	136.0
22	48.3	93	83.5	164	137.2
24	49.1	95	84.4	166	138.5
26	49.8	96	85.5	167	139.7
27	50.4	98	86.5	169	140.9
29	51.1	100	87.5	170	142.1
30	51.9	101	88.5	172	143.3
32	52.6	103	89.6	174	144.4
34	53.2	104	90.6	175	145.6
35	53.9	106	91.7	177	146.6
37	54.6	108	92.8	179	147.8
38	55.3	109	93.9	180	148.9
40	56.0	111	95.0	182	150.0
42	56.8	112	96.1	183	151.1
43	57.5	114	97.3	185	152.2
45	58.3	116	98.5	187	153.3
47	59.0	117	99.7	188	154.3
48	59.7	119	100.9	190	155.4
50	60.5	121	102.1	191	156.5
51	61.3	122	103.3	193	157.5
53	62.0	124	104.5	195	158.6
55	62.8	125	105.8	196	159.6
56	63.5	127	107.1	198	160.6
58	64.3	129	108.4	199	161.6
59	65.1	130	109.7	201	162.5
61	65.9	132	111.1	203	163.5
63	66.7	133	112.4	204	164.5
64	67.5	135	113.7	206	165.4
66	68.3	137	115.1	208	166.3
67	69.2	138	116.5	209	167.2
69	70.0	140	117.8	211	168.1
71	70.9	141	119.2	212	169.1
72	71.7	143	120.5	214	169.9
74	72.6	145	121.8	216	170.7

Table A4. Resin Temperature Versus Time Data for Kinetic
Auxiliary Tests (Continued)

Run No. 1D Beaker Test

$T_o = 41^\circ\text{F}$ $T_{air} = 40^\circ\text{F}$ $T_{max} = 234^\circ\text{F}$

$C = 0.3 \times 10^{-3}$ Set Time = 205s

<u>Time(s)</u>	<u>T (°F)</u>	<u>Time(s)</u>	<u>T (°F)</u>	<u>Time(s)</u>	<u>T (°F)</u>
217	171.5	241	182.3	266	191.1
219	172.4	243	183.0	326	207.0
221	173.1	245	183.6	386	216.7
222	173.9	246	184.2	446	222.7
224	174.6	248	184.9	506	226.4
225	175.4	250	185.4	566	228.8
227	176.1	251	186.0	626	230.5
229	176.8	253	186.7	686	231.6
230	177.5	254	187.2	746	232.4
232	178.3	256	187.8	806	233.1
233	179.0	258	188.4	866	233.4
235	179.7	259	189.0	826	233.7
237	180.3	261	189.5	866	233.9
240	181.7	264	190.6		

Table A4. Resin Temperature Versus Time Data for Kinetic
Auxiliary Tests (Continued)

Run No. 2D Beaker Test

$T_o = 41^\circ\text{F}$ $T_{air} = 40^\circ\text{F}$ $T_{max} = 235^\circ\text{F}$

$C = 0.4 \times 10^{-3}$ Set Time = 172s

<u>Time(s)</u>	<u>T (°F)</u>	<u>Time(s)</u>	<u>T (°F)</u>	<u>Time(s)</u>	<u>T (°F)</u>
0	42.5	71	79.1	142	139.8
2	42.5	73	80.1	144	141.2
4	41.5	75	81.2	145	142.5
5	41.9	76	82.3	147	143.8
7	42.5	78	83.4	149	145.2
8	43.2	79	84.6	150	146.5
10	44.1	81	85.8	152	147.7
12	44.9	83	87.0	153	148.9
13	45.7	84	88.2	155	150.1
15	46.5	86	89.4	157	151.4
16	47.7	87	90.6	158	152.5
18	48.6	89	92.0	160	153.8
20	49.2	91	93.3	161	154.9
21	49.9	92	94.6	163	156.1
23	50.8	94	95.9	165	157.3
25	51.6	96	97.1	166	158.3
26	52.6	97	98.4	168	159.5
28	53.5	99	99.7	170	160.5
29	54.3	100	101.1	171	161.7
31	55.2	102	102.5	173	162.7
33	56.0	104	103.9	174	163.7
34	56.8	105	105.4	176	164.8
36	57.8	107	106.9	178	165.8
37	58.6	108	108.4	179	166.7
39	59.5	110	109.9	181	167.8
41	60.3	112	111.5	182	168.7
42	61.2	113	113.0	184	169.7
44	62.1	115	114.6	186	170.6
45	63.1	116	116.1	187	171.4
47	64.0	118	117.7	189	172.3
49	64.9	120	119.3	190	173.1
50	65.8	121	120.9	192	173.9
52	66.8	123	122.4	194	174.8
54	67.7	125	123.9	195	175.5
55	68.7	126	125.4	197	176.3
57	69.7	128	126.9	199	177.1
58	70.7	129	128.4	200	177.8
60	71.7	131	129.9	202	178.6
62	72.7	133	131.4	203	179.3
63	73.8	134	132.8	205	180.0
65	74.7	136	134.3	207	180.7
67	75.7	137	135.7	208	181.4
68	76.8	139	137.1	210	182.1
70	77.9	141	138.5	211	182.8

Table A4. Resin Temperature Versus Time Data for Kinetic
Auxiliary Tests (Continued)

Run No. 2D Beaker Test

$T_O = 41^\circ\text{F}$ $T_{air} = 40^\circ\text{F}$ $T_{max} = 235^\circ\text{F}$

$C = 0.4 \times 10^{-3}$ Set Time = 172s

<u>Time(s)</u>	<u>T (°F)</u>	<u>Time(s)</u>	<u>T (°F)</u>	<u>Time(s)</u>	<u>T (°F)</u>
213	183.4	231	190.3	366	219.4
215	184.1	232	190.8	426	224.9
216	184.8	234	191.4	486	228.2
218	185.4	236	191.9	546	230.4
219	186.0	237	192.5	606	231.9
221	186.7	239	193.0	666	232.9
223	187.3	240	193.5	726	233.6
224	187.9	242	194.1	786	234.1
226	188.5	244	194.6	846	234.4
228	189.1	245	195.1	906	234.6
229	189.7	306	210.3		

Table A4. Resin Temperature Versus Time Data for Kinetic
Auxiliary Tests (Continued)

Run No. 3D Beaker Test

$T_o = 41^\circ\text{F}$ $T_{\text{air}} = 40^\circ\text{F}$ $T_{\text{max}} = 214^\circ\text{F}$

$C = 0.7 \times 10^{-3}$ Set Time = 108s

<u>Time(s)</u>	<u>T (°F)</u>	<u>Time(s)</u>	<u>T (°F)</u>	<u>Time(s)</u>	<u>T (°F)</u>
5	43.4	77	114.1	148	177.8
6	44.2	79	116.5	150	178.6
9	46.2	80	118.9	151	179.3
11	47.3	82	121.2	153	180.0
13	48.5	84	123.5	155	180.7
14	49.7	85	125.8	156	181.4
16	50.9	87	128.0	158	182.1
18	52.2	88	130.3	159	182.7
19	53.5	90	132.4	161	183.3
21	54.8	92	134.6	163	183.9
22	56.1	93	136.7	164	184.4
24	57.5	95	138.7	166	185.0
26	58.8	96	140.4	167	185.6
27	60.1	98	142.0	169	186.2
29	61.4	100	143.6	171	186.6
30	68.9	101	145.1	172	187.2
32	64.3	103	146.7	174	187.7
34	65.7	105	148.2	176	188.2
35	67.0	106	149.7	177	188.7
37	68.4	108	151.2	179	189.2
38	69.9	109	152.7	180	189.7
40	71.3	111	154.1	182	190.3
42	72.9	113	155.4	184	190.8
43	74.4	114	156.7	185	191.2
45	75.9	116	158.0	187	191.7
47	77.4	117	159.3	189	192.1
48	78.9	119	160.5	190	192.6
50	80.5	121	161.8	192	193.0
51	82.1	122	162.9	193	193.5
53	83.7	124	164.1	195	194.0
55	85.3	126	165.2	197	194.3
56	87.1	127	166.3	198	194.9
58	88.9	129	167.4	200	195.2
59	90.9	130	168.4	201	195.6
61	92.8	132	169.4	203	196.1
63	94.7	134	170.4	205	196.4
64	96.7	135	171.2	206	196.8
66	98.8	137	172.1	208	197.2
67	100.9	138	173.0	209	197.6
69	102.9	140	173.9	211	197.9
71	105.1	142	174.7	213	198.3
72	107.3	143	175.5	214	198.6
74	109.6	145	176.3	216	199.0
76	111.8	147	177.1	218	199.2

Table A4. Resin Temperature Versus Time Data for Kinetic
Auxiliary Tests (Continued)

Run No. 3D Beaker Test

$T_o = 41^\circ\text{F}$ $T_{\text{air}} = 40^\circ\text{F}$ $T_{\text{max}} = 214^\circ\text{F}$

$C = 0.7 \times 10^{-3}$ Set Time = 108s

<u>Time(s)</u>	<u>T (°F)</u>	<u>Time(s)</u>	<u>T (°F)</u>	<u>Time(s)</u>	<u>T (°F)</u>
219	199.6	231	201.8	242	203.7
221	199.9	232	202.0	243	203.9
222	200.2	234	202.3	245	204.2
224	200.6	235	202.5	305	210.4
226	200.9	237	202.9	365	213.0
227	201.2	239	203.1	425	213.7
229	201.5	240	203.4		

Table A4. Resin Temperature Versus Time Data for Kinetic Auxiliary Tests (Continued)

Run No. 4D Beaker Test

$T_o = 41^\circ\text{F}$ $T_{air} = 40^\circ\text{F}$ $T_{max} = 236^\circ\text{F}$

$C = 0.3 \times 10^{-3}$ Set Time = 194s

<u>Time(s)</u>	<u>T (°F)</u>	<u>Time(s)</u>	<u>T (°F)</u>	<u>Time(s)</u>	<u>T (°F)</u>
3	43.2	79	82.9	150	140.4
5	43.4	81	83.9	152	141.8
7	44.0	82	85.0	153	143.1
13	46.8	84	86.1	155	144.4
15	47.6	86	87.2	157	145.6
16	48.4	87	88.3	158	147.0
18	49.1	89	89.5	160	142.2
19	49.8	90	90.6	162	149.4
21	50.5	92	91.7	163	150.8
23	51.3	94	92.9	165	151.9
24	52.1	95	94.2	166	153.1
26	52.9	97	95.4	168	154.3
27	53.7	98	96.6	170	155.5
29	54.6	100	97.8	171	156.7
31	55.3	102	99.1	173	157.9
32	56.2	103	100.4	174	159.0
34	57.0	105	101.7	176	160.1
36	57.8	107	103.0	178	161.2
37	58.7	108	104.3	179	162.3
39	59.5	110	105.7	181	163.4
40	60.3	111	107.1	183	164.4
42	61.2	113	108.4	184	165.5
44	62.0	115	109.9	186	166.5
45	62.9	116	111.2	187	167.5
47	63.8	118	112.6	189	168.5
48	64.6	120	114.1	191	169.5
50	65.6	121	115.5	192	170.4
52	66.4	123	117.0	194	171.3
53	67.3	124	118.4	195	172.2
55	68.2	126	119.9	197	173.1
57	69.1	128	121.3	199	173.9
58	70.1	129	122.7	200	174.8
60	71.0	131	124.0	202	175.6
61	72.0	132	125.4	204	176.4
63	72.9	134	126.8	205	177.2
65	73.9	136	128.2	207	178.0
66	74.9	137	129.6	208	178.7
68	75.8	139	131.0	210	179.5
69	76.8	140	132.4	212	180.3
71	77.7	142	133.7	213	181.1
73	78.7	144	135.1	215	181.8
74	79.7	145	136.4	217	182.4
76	80.8	147	137.7	218	183.2
78	81.8	149	139.1	220	183.8

Table A4. Resin Temperature Versus Time Data for Kinetic
Auxiliary Tests (Continued)

Run No. 4D Beaker Test

$T_0 = 41^\circ\text{F}$ $T_{\text{air}} = 40^\circ\text{F}$ $T_{\text{max}} = 236^\circ\text{F}$

$C = 0.3 \times 10^{-3}$ Set Time = 194s

<u>Time(s)</u>	<u>T (°F)</u>	<u>Time(s)</u>	<u>T (°F)</u>	<u>Time(s)</u>	<u>T (°F)</u>
221	184.6	236	190.2	426	225.3
223	185.2	238	190.8	486	228.7
225	185.9	239	191.4	546	231.0
226	186.5	241	192.0	606	232.5
228	187.2	242	192.5	666	233.5
229	187.8	244	193.1	726	234.2
231	188.4	246	193.7	786	234.7
233	189.0	306	209.8	846	235.0
234	189.6	366	219.4	906	235.2

Table A4. Resin Temperature Versus Time Data for Kinetic Auxiliary Tests (Continued)

Run No. 1E Beaker Test

$T_o = 91^\circ\text{F}$ $T_{\text{air}} = 90^\circ\text{F}$ $T_{\text{max}} = 286^\circ\text{F}$

$C = 0.4 \times 10^{-3}$ Set Time = 45s

<u>Time(s)</u>	<u>T (°F)</u>	<u>Time(s)</u>	<u>T (°F)</u>	<u>Time(s)</u>	<u>T (°F)</u>
0	91.7	61	221.8	121	260.7
1	91.8	63	223.5	122	261.1
2	91.9	64	224.9	124	261.5
4	94.5	66	226.6	125	261.9
5	97.4	67	227.9	126	262.3
6	101.1	69	229.5	128	262.6
8	103.8	70	230.9	129	263.0
9	106.4	72	232.4	130	263.5
10	109.5	73	233.7	132	263.8
12	112.4	75	235.1	133	264.1
13	116.2	77	236.4	134	264.4
15	119.7	78	237.7	135	264.7
16	123.8	80	238.9	136	265.0
17	127.0	81	240.1	137	265.3
19	130.4	83	241.3	139	265.6
20	134.9	85	242.4	140	265.9
22	138.2	86	243.2	141	266.2
23	142.8	87	244.1	143	266.5
24	146.5	89	245.1	144	266.7
26	150.5	90	245.9	145	267.0
27	155.2	91	246.7	146	267.3
29	159.1	93	247.7	147	267.5
30	164.1	94	248.4	148	267.7
31	168.1	95	249.1	150	268.0
33	172.8	96	249.8	151	268.2
34	176.5	98	250.6	152	268.5
36	180.5	99	251.3	154	268.7
37	183.4	100	251.9	155	268.9
38	186.2	101	252.5	156	269.1
39	189.2	103	253.1	157	269.3
40	191.6	104	253.7	158	269.5
41	193.8	105	254.4	160	269.7
43	196.5	107	255.0	161	269.9
45	199.2	108	255.5	162	270.2
46	201.7	109	256.1	164	270.3
48	203.7	110	256.6	165	270.5
49	205.6	112	257.2	166	270.8
50	207.9	113	257.6	168	271.0
52	210.1	114	258.2	169	271.1
54	212.3	115	258.6	170	271.3
55	214.4	117	259.1	171	271.4
57	216.4	118	259.5	172	271.6
58	218.0	119	259.9	173	271.8
60	220.0	120	260.3	175	271.9

Table A4. Resin Temperature Versus Time Data for Kinetic
Auxiliary Tests (Continued)

Run No. 1E Beaker Test

$T_o = 91^{\circ}\text{F}$ $T_{\text{air}} = 90^{\circ}\text{F}$ $T_{\text{max}} = 286^{\circ}\text{F}$

$C = 0.4 \times 10^{-3}$ Set Time = 45s

<u>Time(s)</u>	<u>T (°F)</u>	<u>Time(s)</u>	<u>T (°F)</u>	<u>Time(s)</u>	<u>T (°F)</u>
176	272.1	201	274.8	227	276.9
177	272.2	202	274.9	228	277.0
178	272.4	204	275.1	230	277.1
179	272.5	205	275.1	231	277.2
180	272.7	206	275.3	232	277.2
182	272.8	207	275.4	233	277.3
183	273.0	209	275.5	234	277.4
184	273.1	210	275.6	236	277.5
186	273.3	211	275.7	237	277.6
187	273.4	212	275.8	238	277.7
188	273.5	214	276.0	240	277.8
190	273.7	215	276.0	301	280.5
191	273.8	216	276.1	361	282.2
192	273.9	218	276.2	421	283.4
193	274.1	219	276.3	481	284.2
194	274.2	220	276.4	541	284.8
195	274.3	222	276.5	601	285.2
197	274.4	223	276.6	661	285.4
198	274.6	224	276.7	721	285.6
200	274.7	226	276.8		

Table A4. Resin Temperature Versus Time Data for Kinetic Auxiliary Tests (Continued)

Run No. 2E Beaker Test

$T_o = 91^\circ\text{F}$ $T_{air} = 90^\circ\text{F}$ $T_{max} = 292^\circ\text{F}$

$C = 0.7 \times 10^{-3}$ Set Time = 27s

<u>Time(s)</u>	<u>T (°F)</u>	<u>Time(s)</u>	<u>T (°F)</u>	<u>Time(s)</u>	<u>T (°F)</u>
0	92.6	51	222.2	102	261.0
1	92.3	52	223.6	103	261.5
2	94.1	53	225.1	104	262.0
4	97.4	54	226.4	106	262.5
5	100.5	56	227.7	107	263.0
6	104.9	57	229.0	108	263.4
7	107.7	58	230.2	109	263.9
8	111.0	59	231.5	110	264.3
9	114.4	60	232.6	111	264.7
10	118.7	61	233.8	112	265.1
12	122.3	63	234.9	114	265.5
13	125.5	64	236.0	115	265.8
14	129.2	65	237.1	116	266.2
15	133.8	66	238.1	117	266.6
16	138.0	67	239.2	118	266.9
17	143.4	68	240.2	119	267.3
19	148.5	70	241.2	121	267.6
20	153.8	71	242.1	122	268.0
21	158.6	72	243.1	123	268.3
22	163.4	73	244.0	124	268.6
23	168.0	74	244.9	125	268.9
24	172.0	75	245.7	126	269.2
26	175.7	77	246.6	128	269.5
27	179.0	78	247.5	129	269.8
28	182.0	79	248.2	130	270.1
29	184.9	80	249.1	131	270.4
30	187.5	81	249.8	132	270.6
31	190.1	82	250.6	133	270.9
32	192.5	83	251.3	135	271.2
34	194.9	85	252.1	136	271.4
35	197.1	86	252.8	137	271.7
36	199.3	87	253.5	138	271.9
37	201.4	88	254.2	139	272.2
38	203.4	89	254.8	140	272.4
39	205.3	90	255.5	141	272.6
41	207.2	92	256.1	143	272.9
42	209.0	93	256.7	144	273.1
43	210.8	94	257.3	145	273.3
44	212.6	95	257.8	146	273.5
45	214.2	96	258.4	147	273.8
46	215.9	97	259.0	148	274.0
48	217.6	99	259.5	150	274.2
49	219.1	100	260.0	151	274.4
50	220.7	101	260.5	152	274.6

Table A4. Resin Temperature Versus Time Data for Kinetic Auxiliary Tests (Continued)

Run No. 2E Beaker Test

$T_0 = 91^\circ\text{F}$ $T_{\text{air}} = 90^\circ\text{F}$ $T_{\text{max}} = 292^\circ\text{F}$

$C = 0.7 \times 10^{-3}$ Set Time = 27s

<u>Time(s)</u>	<u>T (°F)</u>	<u>Time(s)</u>	<u>T (°F)</u>	<u>Time(s)</u>	<u>T (°F)</u>
153	274.8	167	276.9	181	278.6
154	275.0	168	277.0	182	278.7
155	275.1	169	277.2	183	283.6
157	275.3	170	277.3	243	286.5
158	275.5	172	277.5	303	288.4
159	275.7	173	277.6	363	289.8
160	275.9	174	277.7	423	290.7
161	276.1	175	277.9	483	291.4
162	276.2	176	278.0	543	291.9
164	276.3	177	278.2	603	292.3
165	276.5	179	278.3	663	292.4
166	276.7	180	278.5	723	292.5

Table A4. Resin Temperature Versus Time Data for Kinetic
Auxiliary Tests (Continued)

Run No. 3E Beaker Test

$T_o = 91^\circ\text{F}$

$T_{air} = 90^\circ\text{F}$

$T_{max} = 271^\circ\text{F}$

$C = 1.3 \times 10^{-3}$

Set Time = 21 s

<u>Time (s)</u>	<u>T ($^\circ\text{F}$)</u>	<u>Time (s)</u>	<u>T ($^\circ\text{F}$)</u>	<u>Time (s)</u>	<u>T ($^\circ\text{F}$)</u>
0	91.7	43	225.0	85	255.4
1	94.6	44	226.2	86	255.9
2	99.6	45	227.5	87	256.3
3	105.7	46	228.7	88	256.7
4	111.6	47	229.9	89	257.1
6	118.5	48	230.9	90	257.6
7	124.8	50	232.2	91	258.0
8	131.2	51	233.2	93	258.3
9	138.8	52	234.3	94	258.7
10	144.9	53	235.3	95	259.1
11	151.6	54	236.3	96	259.4
12	159.3	55	237.3	97	259.8
14	166.6	56	238.3	98	260.1
15	173.6	57	239.2	100	260.4
16	177.9	58	240.1	101	260.7
17	182.5	59	241.0	102	261.0
18	186.3	60	241.9	103	261.3
19	189.1	61	242.7	104	261.6
21	191.4	62	243.6	105	261.9
22	193.7	64	244.3	107	262.1
23	195.9	65	245.1	108	262.4
24	198.0	66	245.9	109	262.6
25	200.1	67	246.6	110	262.9
26	202.1	68	247.3	111	263.1
28	204.0	69	248.0	112	263.3
29	205.9	71	248.7	114	263.6
30	207.7	72	249.3	115	263.8
31	209.5	73	249.9	116	264.0
32	211.3	74	205.6	117	264.2
33	212.9	75	251.2	118	264.4
35	214.6	76	251.8	119	264.6
36	216.1	78	252.4	120	264.8
37	217.7	79	252.9	182	269.9
38	219.2	80	253.5	242	271.0
39	220.7	81	253.9	302	271.0
40	222.2	82	254.5	362	271.6
41	223.6	83	255.0		