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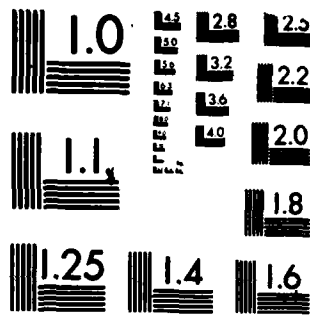
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HEAT - INITIATED FURAN RESIN FOR RAPID RUNWAY REPAIR

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AUGUST 1983

FINAL REPORT
MARCH - SEPTEMBER 1982

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| 20. ABSTRACT (Continue on reverse side if necessary and identify by block number) This project established the feasibility of a furan polymer concrete composition utilizing an inorganic latent catalyst which (2) achieves a longer working time; (2) has reduced mixing complexity, and (2) possesses less sensitivity to variations in material temperature than previous compositions. This composition can be heat initiated to begin polymerization at any time (cont) → | | |

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up to the end of the working time and attains a minimum average flexural strength of greater than 500 psi 1 hour after placement.

Several promising concepts were briefly explored in addition to the inorganic latent catalyst approach-(which eventually was found to offer the fastest, though not necessarily the best, route to a heat-initiated furan resin-based concrete). The inorganic latent catalyst approach was unable to achieve cure through exotherm propagation at the lower temperatures using a flame-point initiation. Flame-point initiation consists of heating a portion of the repair surface with an open flame and allowing the exotherm to carry the polymerization (cure) throughout the polymer concrete. Due to the failure of this approach, a more conventional active acid blend with a freezing point below 5°F was used as a catalyst at the lower temperatures.

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PREFACE

This report was prepared by the Columbus Laboratories of the Battelle Memorial Institute, Columbus, Ohio, under Contract No. F08635-82-C-0187, for the Air Force Engineering and Services Center, Engineering and Services Laboratory, (AFESC/RD), Tyndall AFB Florida 32403.

This report summarizes work done between 10 March 1982 and 30 September 1982. Captain Richard M. Gibbs, AFESC/RDCR, was the Project Officer.

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

This technical report has been reviewed and is approved for publication.

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SECTION I INTRODUCTION

1. BACKGROUND

In previous work on the ongoing bomb damage repair (BDR) program at Battelle, furan (furfuryl alcohol-based) prepolymers had shown excellent potential for use as structural cap materials for rapid runway repair (RRR) (Reference 1). These resin systems had demonstrated acceptable cure rates and high flexural strength development within 1 hour over a wide range of required environmental conditions (-5°F to 125°F, wet and dry). In addition, these resins are relatively inexpensive (\$0.75 to \$0.95 per pound) and, owing to their agricultural origin, the price of furan systems is not directly dependent on fossil fuel prices. Moreover, availability is assured, based on a renewable resource originating within the continental United States. The furan resins are currently mass produced in commercial quantities, assuring future availability.

A possible drawback to the use of these resin systems is that the catalyst level must be varied considerably to obtain an adequate cure rate over the required environmental temperature range of -25° to +125°F, wet and dry. As the environmental temperature decreases, the catalyst concentration must be increased over that required at 125°F. For example, at 105°F, 3 percent catalyst is required and at -20°F, 27 percent catalyst is required. At low temperatures, more catalyst is required to initiate sufficient reaction to produce enough heat (exotherm) to increase the temperature of the resin/aggregate mixture to a point where the reaction rate is acceptable (reaction rate increases with temperature). However, at these high catalyst concentrations, the working time with the resin is very short (4 minutes). Therefore, the problem is twofold. First, the large range of catalyst concentrations introduces complexity into the mixing process. Second, at high catalyst concentrations, the highly reactive furan systems are difficult to control and provide little "in-crater" working time.

2. OBJECTIVE

This program sought to reduce the mix complexity (catalyst variation over material temperature range) and fast-set characteristics of the furan candidates by developing a furan-based BDR material system with less sensitivity to environmental conditions and increased "in-crater" working time. In practice, once this system is placed in the crater, the runway repair team can initiate cure of the repair surface at will (by flame or some other heat source), and the high exotherm of the curing system (>200°F) will, in turn, initiate the cure of adjacent areas. Ideally, the above system would be of the same composition at all test temperatures, provide a minimum 30-minute working time at the highest material temperature, and achieve a minimum of 500 psi flexural strength 1 hour after the components are mixed.

3. CONCEPT

It was observed in the previous BDR work carried out at Battelle that curing of furan resins normally begins at one point (the area of greatest heat buildup, near the center of the resin mass) and moves outward. Therefore, the basis of this program is the artificial establishment of a center of heat buildup by initiating (through the use of a heat source such as a flame) a specially formulated furan/catalyst system at a point in the repair mass. Once the temperature in the area of the heat buildup rises to a certain temperature, polymerization occurs. The heat given off by this polymerization then initiates the cure of adjacent areas in the same manner in which the flame initially induced polymerization.

4. RESEARCH APPROACH

Both the large material temperature range (from 5° to 110°F based on review of material temperatures in storage), and the relatively long working time requirement placed demands on the active acid catalyst systems

which made a simple reformulation of the previous BDR furan system unfeasible for the heat initiation approach. This was mainly due to the freezing point (-20°F) of most commercially available benzene sulfonic acid solutions (active catalyst) making application at lower material temperatures impossible. It was also felt that a faster reacting resin would be required to obtain the maximum propagation rate in a heat-induced system, and that this faster reacting resin would require a concentration of active catalyst so low that uniform distribution in the resin or on the sand would be extremely difficult to obtain in the field.

Due to the multiple screening requirements (catalysts and resins) and the definable transition requirements between the identification and screening stages, the research program was divided into three separate tasks. This task approach expedited progress toward a final heat-initiated composition. A flow diagram of the research approach is given in Figure 1.

In Task 1, a brief literature and commercial survey was conducted to identify active and latent catalysts for use in combination with an external heat source. In addition, furan resins from various suppliers were obtained to determine the best resin for use in conjunction with the chosen catalyst. The greatest emphasis was placed on commercially available materials.

In Task 2, the interaction between the catalyst and resin candidates was investigated using small (5 1/2-inch by 2-inch by 1-inch) flame-initiated polymer mortar* bars. Curing tests were run at 110°F material and environmental temperatures in order to determine working time under these conditions. The same compositions that gave adequate working time at the higher temperatures were then tested under room temperature and 5°F conditions to determine if they could be flame initiated. Screening of various coupling agents for the application was also performed. Also, glass fibers were investigated with respect to flexural strength enhancement.

In Task 3, properties such as cure rate and flexural strength development at -25°F (5°F materials), 70°F , and 125°F (110°F materials) were evaluated for the catalyst/furan combinations which provided adequate "in-crater" working time and were the least sensitive to environmental conditions. These properties were determined on 4- by 4- by 14-inch beams of heat-initiated mortar mixes.

* Polymer mortar = furan resin/latent catalyst and sand.

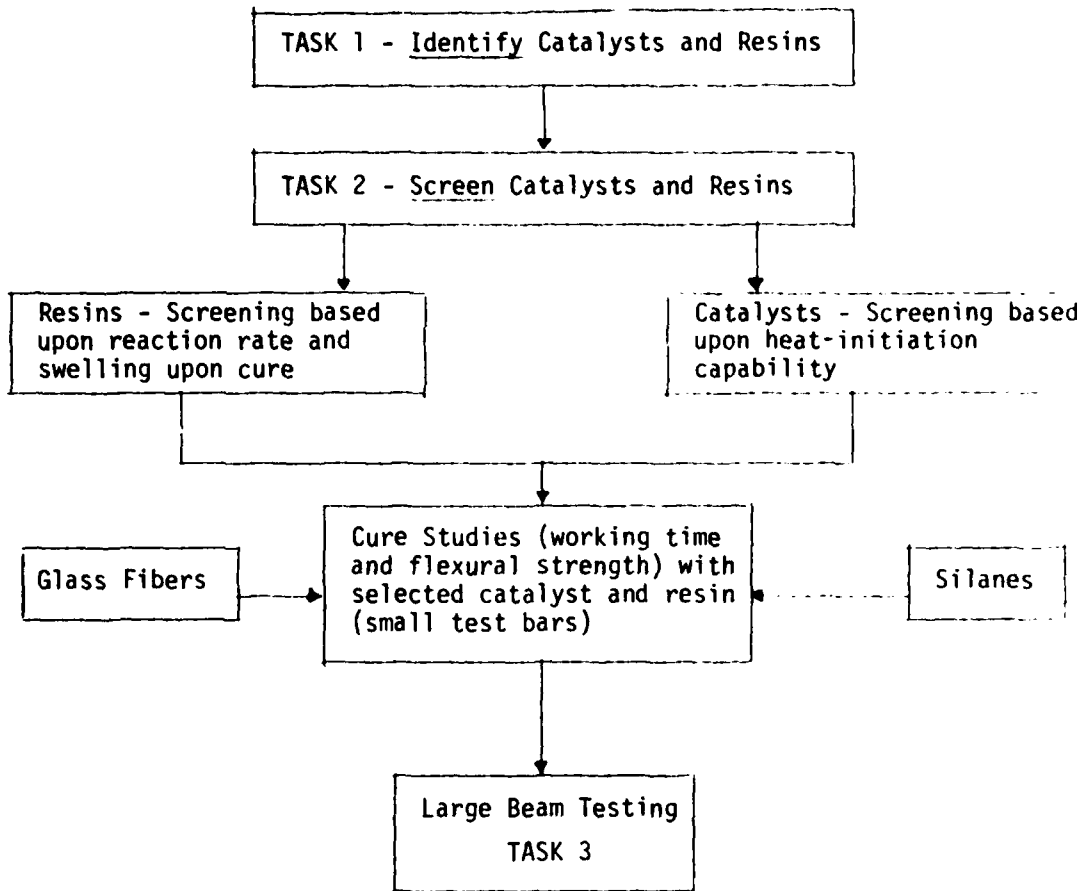


Figure 1. Flow Diagram of Research Approach

SECTION II RESEARCH RESULTS

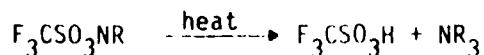
1. TASK 1 - CATALYST AND RESIN IDENTIFICATION

a. Catalysts

The heat-initiated approach to the curing of furan polymer concrete or mortar requires material reactivity properties approaching dormancy until initiated. Due to the uniqueness of this approach and the unknown availability of catalysts which would be useful for this concept, a brief commercial survey was performed and in-house catalysis experts were consulted. Results of these efforts indicated that commercial inorganic latent catalysts, alone or in conjunction with active catalysts, showed the best overall potential for obtaining a heat-initiated polymer concrete or mortar. Other types of latent catalysts including amine-blocked acids (amine triflates) and acid esters (acids reacted with an alcohol) were also identified as being potentially useful for this heat-initiated application. The above catalyst candidates are described in the following sections and summarized in Table 1. Due to time constraints, as well as the exploratory study nature of this program, evaluation of the catalyst candidates (concepts) in the screening task was limited to only those catalysts which showed the greatest potential for producing a heat-initiated composition.

(1) Amine-Blocked Acid Catalysts

This approach involves the use of amine-blocked acids which, when heated, liberate an active acid and an amine. This "true" unblocking upon heating is possible only with compounds whose components do not covalently bond when combined (Reference 2). Illustrated below is the unblocking of an amine triflate (3M Products).



where R = carbon chain.

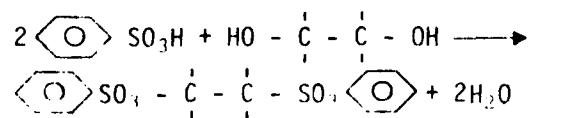
TABLE 1. CATALYST CANDIDATES

| Designation | Description | Example |
|------------------------------------|----------------------------------------------------------------------|----------------------------------------------|
| Amine-Blocked Acid Catalysts | Organic Acid Reacted With Various Amines | Ammonium Triflate |
| Acid Esters | Acids Reacted With Various Low Molecular Weight Alcohols | Alkyl Acid Phosphates |
| Active Acid | Commercial Active Acids | Benzene Sulfonic Acid Phosphoric Acid |
| Latent Inorganic Catalysts | Active Acid Salts | Zinc Chloride, Cupric Chloride |
| Active/Latent Catalyst Combination | Active - Active Acids Latent - Esters, Latent Inorganic Catalysts | Benzene Sulfonic Acid and Cupric Chloride |

These types of catalysts are possibly the truest forms of latent catalysts in that only heat is required for release of the active acid catalyst. This unblocking mechanism closely parallels the catalyst properties desired for the heat initiated approach.

(2) Ester Hydrolysis

This concept was developed due to the observation in previous BDR materials work at Battelle that an ethylene glycol-diluted benzene sulfonic acid solution used for furan catalysis became weaker (increased cure times) over a period of time. At that time, it was postulated that the ethylene glycol and the benzene sulfonic acid reacted to form an ester (no catalytic activity) as illustrated below:



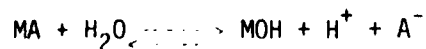
Since the above reaction is reversible, it was felt that heat-accelerated ester decomposition (through hydrolysis) could serve as a latent catalyst approach.

(3) Active Acid

This approach involves the use of an active acid, benzene sulfonic acid, at a level which would self-initiate but provide the required working time at the 110°F material temperature and which would initiate cure upon localized heating at 5°F and 70°F material temperatures. This is the approach most commonly used with furan resins in foundry applications. A variety of acids, including modified or unmodified organic and inorganic acids are presently commercially available.

(4) Latent Inorganic Catalyst

This approach is based on the reaction (hydrolysis) of a metal halide salt with available water to produce an active acid (References 3,4).



where M = metal

A = halogen

Furan laminates are commercially produced using metal halides as catalysts. An acid salt of this type ultimately proved to be the latent catalyst used successfully for the heat-initiated furan concrete cure at 70° and 110° F material temperatures.

Metal halide salts suitable for this application should exhibit ease of hydrolysis and acceptable water solubility. Salts which are very hydrophilic (zinc and tin chlorides) are difficult to use in the dry state due to their tendency to clump and/or form solutions unless completely protected from atmospheric moisture. Salts which have low water solubilities will have low acid production and, therefore, were not considered.

(5) Active/Latent Catalyst Combination

This approach involves the use of an active acid to increase the rate of acid production by the acid salts discussed in the previous section. Hydrolysis of the acid salts can be increased in two ways:

(a) Creation of an acidic environment by addition of a weak active acid which can increase the hydrolysis of the salt.

(b) Forcing production of the acid component of the acid salt by precipitating the metal ion from solution.

Potential benefits of this dual catalyst approach include reduced handling hazards due to the use of less corrosive catalysts and possibly better control of curing of the furan mortar mix. If required, this approach also makes possible a faster curing system for low material temperatures.

b. Resins

Concurrent with the catalyst search, nine different furan resin systems were identified (see Table 2). All but one of these (Delta Airkure[®] 06-00, a proprietary blend of furfuryl alcohol monomer) are of the urea-formaldehyde (urfuryl alcohol type used in foundry sand as a binder. These foundry resins were chosen because of their characteristics of high reactivity, low viscosity, known good adhesion to silaceous materials, and current high production/low cost advantages. Based on presumed resin cure rate requirements for the heat-initiated approach, the candidate furan resins from previous BDR materials work at Battelle (Ashland Chem-Res[®] 200 and 280) were not considered the best for this application. However, these resins were also evaluated. Table 2 lists the resin candidates considered for the heat-initiated approach.

TABLE 2. RESIN CANDIDATES

| Designation | Type | Manufacturer |
|-----------------------------|---------------------------------------------------------------|----------------------------|
| Airkure [®] 06-00 | Furfuryl alcohol monomer with proprietary cross-linking agent | Delta Resin & Refractories |
| Airkure [®] 06-22 | Urea-formaldehyde furfuryl alcohol prepolymer | Delta Resin & Refractories |
| Airkure [®] 06-612 | Urea-formaldehyde furfuryl alcohol prepolymer | Delta Resin & Refractories |
| Chem Rez [®] 200 | Urea-formaldehyde furfuryl alcohol prepolymer | Ashland Chemical |
| Chem Rez [®] 201 | Urea-formaldehyde furfuryl alcohol prepolymer | Ashland Chemical |
| Chem Rez [®] 280 | Urea-formaldehyde furfuryl alcohol prepolymer | Ashland Chemical |
| CLI-100 | Urea-formaldehyde furfuryl alcohol prepolymer | Core Lube Santech |
| Furathane [®] | Urea-formaldehyde furfuryl alcohol prepolymer | Atlas Mineral & Chemical |
| 931 | Urea-formaldehyde furfuryl alcohol prepolymer | Acme Resins |

2. TASK 2 - CATALYST AND RESIN SCREENING

a. Catalysts

The screening of catalyst concepts was largely accomplished through investigating the 110°F (material temperature) working time of polymer mortars consisting of the identified catalyst systems mixed with Chem-Rez[®] 280^{*} and sand. In this working time test, 2- by 1- by 5 1/2-inch mortar bars (with mortar ingredients at 110°F) were placed in a 110°F oven to identify any problems inherent to a given catalyst approach. A mortar composition which did not give an acceptable working time at this material temperature was reformulated and tested again. If the composition exhibited an acceptable working time, the same mortar mix was then tested for working time and cure propagation at 70°F material temperature. If the composition was unacceptable due to a short working time or no cure, the catalyst was rejected. The following sections summarize the results obtained with the different catalyst concepts.

(1) Amine-Blocked Acid Catalysts

Amine-blocked triflic acid (trifluoromethane sulfonic acid) salts were identified as the most applicable due to the high catalyzing strength of the released acid. Unfortunately, the amine triflate catalysts of interest for this program release an amine gas^{**} when dissociating. In thin films, for which this technology was developed, release of the amine gas does not pose a problem. In a polymer concrete matrix, however, gas release would probably cause swelling which would render the surface unusable and/or have a deleterious effect on strength.

Despite this potential disadvantage, the ability of amine triflates to initiate the cure of a furan resin mortar mix (a 5 1/2- by 2- by 1-inch bar) was tested at room temperature. Even though a very reactive furan resin (Airkure[®] 06-612) was used, cure did not propagate outside the area of heat application. It is postulated that the exotherm of

* This material was used as a reference resin due to the time lapse in delivery of the other resins.

** The most reactive amine triflates in terms of low temperature unblocking contain amines which are gaseous.

the furan cure reaction is insufficient to cause the unblocking of triflate catalyst outside the area of heat application. As a result, amine triflate catalysts appear to be unsuitable for heat-initiated cure of furan mortar mixes.

(2) Ester Hydrolysis

Limited testing of this concept was performed. A toluene sulfonic acid ester of ethylene glycol was synthesized in the laboratory and tested for acid release upon heating. This dispersion was heated to 160°F and cooled to the original temperature. The pH readings taken before and after the heating revealed a change from 3 to 2.3, indicating release of an acid.

Despite advantages such as storage stability and ease of handling, the use of ester hydrolysis as a latent, heat-initiated catalyst approach was dropped in favor of a more promising approach (latent inorganic catalyst, discussed below) which required less exploratory development.

(3) Active Acid

The benzene sulfonic acid was eliminated as an active catalyst from consideration for the heat-initiated cure concept. The benzene sulfonic acid solution freezes at approximately 20°F which would make mixing and placement of the mix at lower temperatures a difficult operation. However, two active acid materials were found which did not freeze at the required 5°F material temperature. These proprietary catalysts (CLI6850 and CLI6850F from Core Lube Santec®) were highly concentrated (96-percent) mixes of xylene and benzene sulfonic acids. However, such a low level of these highly concentrated catalysts would be required at the 110°F material temperature that uniform dispersion of the catalysts in the resin or on the sand and curing control would likely be a problem. These mixing difficulties are anticipated based on experience gained during previous RRR laboratory work at Battelle. In this work, a very short working time, 13 minutes, was obtained at 110°F material temperature even though only 3 percent of a 65-percent by weight benzene sulfonic acid solution was used.

(4) Latent Inorganic Catalyst (Metal Halide)

This approach, using cupric chloride dihydrate as the metal halide, ultimately proved to be the simplest method of producing a mix with the desired working time and the ability to be heat-initiated. However, problems were encountered at lower material temperatures when mortar

compositions containing cupric chloride dihydrate, initiated in the area of (flame application), did not propagate. This nonpropagation may be due to the short length of time the samples were exposed to the initiating flame, resulting in insufficient heat buildup for the propagation to take place. A longer initial heating period to insure start of propagation may solve this problem.

(5) Active/Latent Combination

Small bar tests using combinations of the active and latent acid catalysts showed that, while catalyst combinations had potential for producing fast cure rates, small variations in levels of either catalyst could produce large variations in cure rate properties. This property made these systems difficult to control and the active/latent concept was dropped.

b. Resins

In this evaluation, a combination of high reactivity (to ensure cure propagation at low material temperatures) and low gel size upon curing (to minimize swelling in the polymer concrete repair) was sought to determine these properties.

The nine furan resins were cured with an active acid catalyst (a 65-percent toluene sulfonic acid solution) in order to determine their relative gel times and extent of swelling (foaming) (Table 3). Gel times were given a relative ranking (1 = fastest, 9 = slowest) based on time to initial reaction, and gel size formation (relative swelling) was given the same type of relative ranking (1 = smallest, 9 = largest volume increase over unreacted neat resin volume). The resin having the lowest numerical value upon summing the two relative rankings would represent the best combination of properties. Delta Airkure® 06-612 exhibited the lowest summation and was chosen for final formulation testing in combination with cupric chloride dihydrate as the latent catalyst.

c. Cure Studies with Selected Catalyst and Resin

The laboratory screening in Task 2 identified cupric chloride dihydrate and Airkure® 06-612 as the materials of choice for use in the heat-initiated approach. The final mix ratios of these materials were determined by using a commercial grade of cupric chloride dihydrate (Spec 101 available from Harshaw Chemical Company) as the catalyst in

TABLE 3. RESIN TEST RESULTS

| Resin | Supplier | Time to Reaction(a) minutes:seconds | Relative Swelling(b) | Relative Gel Time(c) | b+c |
|-----------------|-------------------------------|----------------------------------------|----------------------|----------------------|-----|
| 931 | Acme Resins | 1:37 | 7 | 4 | 11 |
| Furathane® | Atlas Mineral and Chemical | 22:00 | 3 | 8 | 11 |
| Airkure® 06-00 | Delta Resins and Refractories | 1:26 | 9 | 3 | 12 |
| Airkure® 06-612 | Delta Resins and Refractories | 0:40 | 4 | 2 | 6 |
| Airkure® 06-22 | Delta Resins and Refractories | 0:30 | 8 | 1 | 9 |
| Chem Rez® 200 | Ashland Chemical | 2:54 | 2 | 7 | 9 |
| Chem Rez® 201 | Ashland Chemical | 2:18 | 5 | 6 | 11 |
| Chem Rez® 280 | Ashland Chemical | 2:03 | 6 | 5 | 11 |
| CLI-100 | Core Lube Santech | >60:00 | 1 | 9 | 10 |

(a) Resin plus 0.25 percent by weight of A1100 silane mixed with 5 percent of a 65 percent solution of p-toluene sulfonic acid.

(b) 1 = smallest swelling volume. In order to better picture the swelling range, CLI-100 showed no swelling, whereas the Airkure 06-00 increased in volume by a factor of 800-900 percent upon curing.

(c) 1 = shortest time to gel.

small beam tests at 110°F material temperature. These tests were run in an oven to simulate 125°F environmental temperatures. The goal was to find a level of catalyst which would give a mix working time of 30 minutes at these temperatures (with no initiation). This mix would then be retested at room temperature for its ability to be flame-initiated and for its propagation properties. The following composition gave a 20-minute working time at the 110°F material temperature.

78.4 g Airkure^(R) 06-612
 1.6 g Ethylene glycol
 0.2 g A-1102 silane
 4.4 g Cupric chloride dihydrate
 310.0 g Washed silica sand.

d. Silane Additions

During the course of the lab screening (Task 2) phase, a brief study was conducted with silane coupling agents.

The goal of the silane studies was to find the best silane coupling agent for promoting adhesion of the selected furan resin to the silica. To this end A-189 (a mercaptosilane), and A-1160 (a ureidosilane), silanes from Union Carbide, were evaluated against the A-1102 (aminosilane). The results are shown below.

| Name, Type | Flexural Strength ⁽¹⁾ | Strength Increase Compared to No Silane |
|---------------------------------|----------------------------------|-----------------------------------------|
| No Silane | 730 | |
| A-189 ⁽²⁾ , mercapto | 885 | 121 percent |
| A-1102 ⁽²⁾ , amino | 1062 | 145 percent |
| A-1160 ⁽²⁾ , ureido | 1233 | 169 percent |

(1) Measurements taken 1 hour after mixing, 1/2 hour after initiation.

(2) Union Carbide product.

These tests were run on small beams using the same composition as the final room temperature composition. While these results indicated that the A-1160 silane could improve the strength of the final composition, both the A-1160 and the A-189 also reduced the working time of the composition, leading to their elimination.

e. Fiberglass Additions

Glass fiber additions were briefly attempted to improve the engineering properties in large (4- by 4- by 14-inch) beam tests utilizing on-hand glass fibers (PPG type M 1/8-inch fiber, Table 4). It was found that these fibers were not well suited to this application due to their tendency to clump and resulted in no discernible change in flexural strength and a somewhat larger range of deviation. An interesting unanticipated result was that the composition seemed to propagate faster than an identical composition without the glass fiber addition. This may be due to the fiberglass clumps acting as pipelines to the heated, polymerizing resins and hence, allowing for faster propagation in the heat-initiated composition.

3. TASK 3 - ENGINEERING PROPERTIES

Compositions utilizing the latent catalyst approach were scaled up to 4- by 4- by 14-inch beam size to determine their flexural strength and cure times at 5°F, 77°F, and 107°F material temperatures and cured at -25°F, 77°F, and 125°F environments, respectively. These results are summarized in Table 4 and Table 5. As shown in these tables, the cupric chloride dihydrate system which performed well at 77°F and 107°F material temperatures did not propagate at 5°F.

Due to the failure of the cupric chloride dihydrate system to propagate at the lower temperature, attempts were made with higher levels of the cupric chloride. These too failed in the same manner (Table 5). Finally, an active catalyst, CLI6850F (Cure Lube Santec[®]), was tried in lieu of the cupric chloride dihydrate for low-temperature curing. The concentration used proved to be too high for a 30-minute work time but demonstrated that furan polymers have the ability to cure in a -25°F environment at 5°F material temperatures (Table 5).

TABLE 4. COMPOSITION AND PROPERTIES OF HEAT-INITIATED CURING SYSTEM AT ROOM TEMPERATURE AND ABOVE

| Material Temperature | 77°F | 77°F | 77°F | 107°F |
|-----------------------------------|-------------|------------|------------|------------|
| Curing Temperature | 77°F | 77°F | 77°F | 125°F |
| Formulation Components | | | | |
| Sand, grams | 5850 | 6000 | 5820 | 6000 |
| Glass fiber(a), grams | -- | -- | 180 | -- |
| Airkure 06-612, grams | 1424 | 1440 | 1440 | 1440 |
| Ethylene glycol, grams | 85 | 29 | 29 | 29 |
| A-1100 silane, grams | 3.6 | 3.7 | 3.7 | 3.7 |
| Cupric chloride dihydrate, grams | 78.1 | 77.1 | 77.1 | 77.1 |
| Average Flexural Strength, psi(b) | 370 | 510 | 500 | 520 |
| Working Time(c) | >90 minutes | 99 minutes | 99 minutes | 18 minutes |

(a) PPG type "M" glass fiber, 1/8 inch.

(b) Measured after 1 hour on 4- by 4- by 14-inch beams; average of three specimens.

(c) Determined on identical uninitiated beams.

TABLE 5. COMPOSITION AND PROPERTIES OF HEAT-INITIATED CURING SYSTEMS AT COLD TEMPERATURES

| Material Temperature | 5°F | 5°F | 5°F | 5°F |
|-----------------------------------|------------|----------------------|-------|-------|
| Curing Temperature | -25°F | -25°F | -25°F | -25°F |
| Formulation Components | | | | |
| Sand, grams | 6000 | 6000 | 6000 | 6000 |
| Airkure® 06-6i2, grams | 1440 | 1440 | 1440 | 1440 |
| Ethylene glycol, grams | 29 | 29 | 29 | 29 |
| A-1100 silane, grams | 3.7 | 3.7 | 3.7 | 3.7 |
| Cupric chloride dihydrate, grams | --- | 77.1 | 172.8 | 345.6 |
| CLI6850F, grams | 367 | -- | -- | -- |
| Average Flexural Strength, psi(a) | 520 | Curing initiated but | | |
| Working Time | 10 minutes | did not propagate | | |

(a) Measured after 1 hour on 4- by 4- by 14-inch beams; average of the specimens.

Attempts to overcome the lack of cure propagation of the cupric chloride system at low temperature by flame initiation over the full surface were not successful. Although the surface was completely cured, the cure did not propagate downward.

SECTION III CONCLUSIONS

The feasibility of lengthening the working time of furan resin concretes while permitting rapid strength development through a heat-initiated curing process was demonstrated. The successful development involved the combination of a selected latent catalyst with a selected reactive furan resin. Curing of bars or beams molded from this slowly reacting system was initiated by heating a small area with a flame. The exotherm generated at this spot, in turn, initiated curing of adjacent areas, and curing them propagated throughout the bar or beam.

Using cupric chloride as the catalyst and a commercial furan resin (Delta Airkure[®] 06-612) as the binder, flexural strength values above 500 psi were attained within 1 hour after heat initiation of curing at temperatures of 77° or 125°F. The sand mortar used in these experiments had a working time of greater than 90 minutes at 77°F and of 18 minutes at 125°F.

At material temperatures of 5°F and with a curing temperature of -25°F, curing could be initiated but did not propagate with the cupric chloride-catalyzed Airkure[®] 06-612 combination. The use of an active catalyst (a mixture of xylene and benzene sulfonic acids) in place of the cupric chloride resulted in rapid propagation of heat-initiated curing at the low temperature condition. The particular composition used had a relatively short working time of 10 minutes and had begun to cure when heat was applied.

Although feasibility has been demonstrated and encouraging results have been achieved in this exploratory program, considerably more data and information must be obtained before the merits of this approach can be fully evaluated in comparison with other systems now under development in the Rapid Runway Repair Program.

The major deficiency of the system at this early stage of development is the necessity to use a different catalyst at low temperatures. Potential methods of overcoming this limitation include:

a. Initiation of curing over the full surface of a structural cap, for example, through the use of a burnable liquid or gel spread over the surface and ignited. This would give a longer and broader initiation than the flame application in a small area used in lab work.

b. Use of a different catalyst or a combination of an active and latent catalyst at the lower material temperature to promote curing as well as control.

c. Incorporation of metal (steel) fibers which will improve transfer of heat throughout the resin so as to enhance propagation of the heat-initiated cure and possibly through a redox reaction with the cupric chloride will generate hydrogen ions to promote polymerization of the furan as well as an improvement in engineering properties.

SECTION IV RECOMMENDATIONS

In view of the promising results achieved in this exploratory program and the potential advantages of furan resin concretes (low cost, high strength, independence from fossil fuel supplies), it is recommended that the work be continued at a modest level of effort.

It is recommended that the following approaches be explored with the objective of achieving, over the full environmental range, a working time of at least 30 minutes and a 1-hour flexural strength of at least 500 psi.

- a. Modification of the heat-initiated curing procedure to enhance propagation at low temperatures through application of heat to the full surface rather than just one portion of the surface.
- b. Organic latent catalysts in place of the cupric chloride catalyst to promote higher cross-linking and higher flexural strength.
- c. Combinations of an active and a latent catalyst based on the benzene/xylene/sulfonic acid mixture as the active catalyst and cupric chloride as the latent catalyst.
- d. Addition of steel fibers.
- e. Identification and use of other furan resin types to identify any potential advantages that may exist in their use.

REFERENCES

- (1) Boyer, J. P., et al., Advanced Materials Development for Repair of Bomb Damaged Runways, F08635-80-C-0206, 1982.
- (2) Alm, Roger R., "Formulation Techniques Using Triflic Acid Salts," Modern Paints and Coatings, October 1980.
- (3) Masterton, W. L., and Slevinski, E. J., Chemical Principles, p 545, 1969.
- (4) Cotton, A. F., and Wilkinson, G., Advanced Inorganic Chemistry, p 576, 1966.

APPENDIX A

Storage, Handling and Safety Information of Formulation Components

All resins and additives used in the heat-initiated furan polymer concrete are commercially available. Following are the safety and handling information provided by the manufacturers of the products used in this study.

1. Airkure[®] 06-612
(urea-formaldehyde furfuryl alcohol resin)
Delta Resins and Refractories Inc.
17350 Ryan Road
Detroit, Michigan 48212

Specific gravity 1.16
Flash point (tag open cup) 193°F

Storage: Airkure[®] 06-612 is considered stable but containers should be protected from physical damage. Store in a cool, dry, well-ventilated location away from sources of ignition, oxidizing materials, and strong acids.

Safety and Handling: Use adequate ventilation. Safety glasses (goggles) and gloves should be used when working with this material.

Skin Contact: Wash with soap and water.

Eye Contact: Flush with water, consult physician.

2. Cupric Chloride Spec 101
(cupric chloride dihydrate crystal)
The Harshaw Chemical Company
1945 East 97th Street
Cleveland, Ohio 44106

Bulk Density = 10 lbs/gal
Flash point >300°F

Storage: Cupric chloride dihydrate should be kept in sealed, corrosion-proof containers and protected from mixing with acid-reactive materials.

Safety and Handling: Use adequate ventilation. Safety glasses (goggles) and gloves should be used when working with this material.

Skin Contact: Wash with soap and water.

Eye Contact: Flush with water, consult physician.

3. CLI-6850F
(benzene/hylene sulfonic acid concentrated mix)
Core-Lube Sontec
P.O. Box 811
Danville, Illinois 61832

Specific gravity 1.28
Flash point (seta flash-closed cup) 120+°F

Storage: Store in corrosion-proof drums away from acid-reactive materials.

Safety and Handling: Use adequate ventilation: Safety goggles (chemical splash type) and neoprene gloves should be used when working with this material.

Skin Contact: Flush with soap and water.

Eye Contact: Wash repeatedly with soap and water. Call physician.

4. Silane A-1102
(silane ester)
Union Carbide Corporation
Silicones and Urethane Intermediates
Old Ridgebury Road
Danbury, Connecticut 06817

Specific gravity = 0.95
Flash point (Pensky-Martin Closed
cup) ASTM 093 160°F

Storage: Store in sealed containers away from heat, open flames, and water vapor.

Safety and Handling: Use with adequate ventilation. Safety goggles, apron, and plastic or rubber gloves should be used when working with this material.

Skin Contact: Flush with water and wash thoroughly.

Eye Contact: Immediately flush eye contact with water for 15 minutes. Obtain medical advice.

