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PREPARATION, TESTING AND DELIVERY OF LOW DENSITY POLYIMIDE FOAM PANELS

By George L. Ball III, Larry K. Post,
and Ival O. Salyer

April 1975

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Prepared under Contract No. NAS2-8440 by
MONSANTO RESEARCH CORPORATION
DAYTON LABORATORY
Dayton, Ohio 45407

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FOREWORD

This report summarizes the results of a study for the "Preparation, Testing, and Delivery of Low-Density Polyimide Foam Panels" and was performed under National Aeronautics and Space Admininistration Contract No. NAS 2-8440. The work was conducted between 28 June 1974 and 17 February 1975. Mr. Paul M. Sawko was the NASA Technical Monitor.

The Principal Investigator for Monsanto Research Corporation was George L. Ball III. Professional assistance was provided by Larry K. Post and Ival O. Salyer.

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1. SUMMARY

The objective of this effort was to prepare 225, 76 cm x 76 cm x 5.1 cm (30 in. x 30 in. x 2 in.) polyimide foam panels with a minimum average density of 48 kg/m^3 (3 lb/ft^3). The panels were to be postcured in stages to 300°C (570°F) to maximize their thermal and fire resistance performance.

Two hundred ten (210) low-density polyimide foam panels were cast and postcured. Of the 210 panels, 175 met the density requirements, while the other 35 ranged between 32 kg/m^3 (2 lb/ft^3) and 48 kg/m^3 (3 lb/ft^3). Importantly, even the lower density panels were tough enough to handle with ease, indicating that fragility or friability was not a problem with this system. All of the panels (some shown in Figure 1) were delivered to the U. S. Bureau of Mines Experimental Station at Bruceton, Pa.

As a starting point, a formulation for the preparation of 32 kg/m^3 (2 lb/ft^3) polyimide foam panels was supplied by the Ames Laboratory of NASA. Four major differences in the foam to be produced had to be considered however. These included:

(1) That foams having higher densities [48 kg/m^3 (3 lb/ft^3)] were to be produced;

(2) That fire retardant was not to be included;

(3) That the panels were to be approximately 0.028 cubic meters (1 cubic foot) in volume (much larger than ever before fabricated); and

(4) That the foam panels were to be postcured.

The NASA-Ames formulation was advantageous in that the raw materials are mixed as liquids, then cast into a mold to produce the final desired shape. In the process, it is necessary that the mold be preheated to 230°C (445°F), but this was not anticipated to be a significant problem.

Optimizing the formulation and the process for the production of consistent high density, polyimide foam panels proved most difficult. A number of factors negatively affected control of the foam structure and density. A major unanticipated factor was the excessive pressure generated by the high temperature foaming reaction (imidization). This pressure caused rupturing of the aluminum molds and spilling of the foam. A series of significant changes in the mold design were required to accomodate the situation.

Figure 1. Postcured Molded Polyimide Foam Panels

It was necessary to adjust the formula (silicone content) daily to achieve reasonable control of cell structure and size. The reason for this adjustment could not be associated with humidity, atmospheric pressure, temperature or time, even though control of humidity and moisture was known to be important. None of these difficulties were encountered in previous laboratory experiments involving fractional (0.005) cubic foot moldings.

2. INTRODUCTION

Plastic foams based on polyimide resins have been shown to be stable at relatively high temperatures and to possess very low flame spread and smoke generation characteristics. Accordingly, they could be highly effective in minimizing fire propogation.

A system and process had been developed by NASA-Ames to prepare low-density [32 kg/m^3; 2 lb/ft^3] polyimide foam from a liquid formulation [Ref. 1]. The system is based on the reaction of micropulverized grade (325 mesh) pyromellitic dianhydride (PMDA) [Ref. 2] with a polymeric diisocyanate (PAPI 901) [Ref. 3]. Carbon dioxide is produced from the alkanolamine (Amine 220) [Ref. 4] catalyzed reaction of water with the isocyanate. The CO_2 acts as a blowing agent which generates an initial foam structure. Additional foaming then occurs upon heating to 200°C (390°F) wherein imidization is progressing and the resultant condensation products evolve rapidly. Typical of most foams, a silicone surfactant (DC193) [Ref. 5] is incorporated to improve the foam cell size and uniformity.

The work reported herein includes the tasks required to fabricate 225 48 kg/m^3 (3 lb/ft^3) polyimide foam panels with dimensions of 76 cm x 76 cm x 5.1 cm (30 in. x 30 in. x 2 in.) using the NASA-Ames polyimide formula as a guideline.

The panels were to be postcured at elevated temperatures to achieve maximum thermal and fire resistance. Incorporation of a fire retardant into the formulation was considered at the outset. Thus, the effects of a flame retardant (Flameout 5600B1) [Ref. 6] were investigated, but eliminated in preference to the postcuring approach. The high cost and poor availability of the Flameout was a factor in this decision.

3. EXPERIMENTAL DISCUSSION

The experimental discussion is designed to show specifically how the polyimide foam panels were prepared, to provide background into the chemistry of the system and to elicit some of the problem areas (which proved to be numerous).

3.1 CHEMISTRY OF THE SYSTEM (Background)

The reaction of a dianhydride with diisocyanate at high temperatures yields a polyimide with the liberation of carbon dioxide [Ref. 7-12]. However, this reaction is not compatible with foam formation because the carbon dioxide is generated at the higher temperatures after the gelling process. It has been demonstrated that polyimide foams can be obtained if the reaction of the diisocyanate with the dianhydride is conducted in dimethyl sulfoxide in the presence of catalytic amounts of an active hydrogen containing compound [Ref. 13].

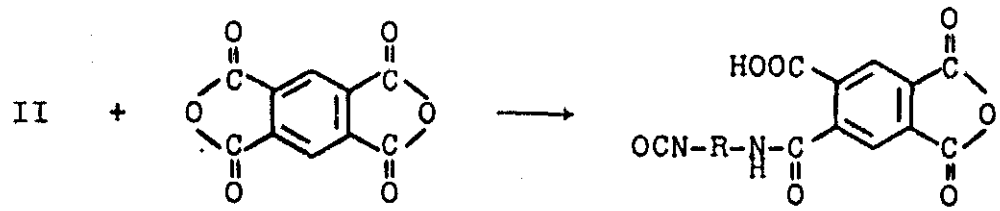
In a process developed by NASA-Ames, this chemical route was used to generate carbon dioxide at room temperature and provide nucleation early in the reaction sequence. This was accomplished through the room temperature, base catalyzed reaction of water and isocyanate to produce the unstable carbamic acid (I) [Ref. 14].

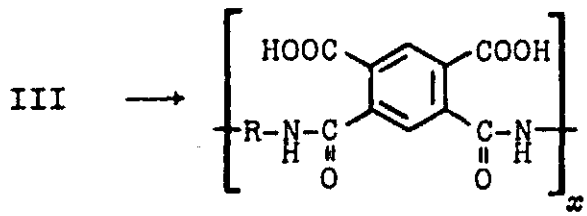
$$\text{OCN-R-NCO} \xrightarrow[\text{cat.(amine)}]{H_2O} \underset{\text{I}}{\text{OCN-R-NHCOOH}}$$

Carbon dioxide is liberated in the spontaneous decomposition of this carbamic acid to the isocyanate-amine (II). The reaction

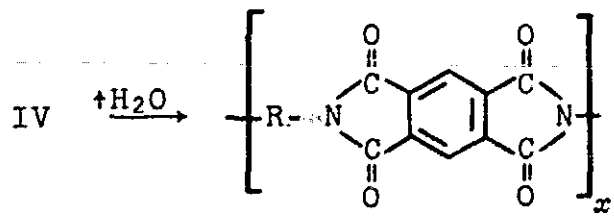
$$\text{I} \xrightarrow{\uparrow CO_2} \underset{\text{II}}{\text{OCN-R-NH}_2}$$

of pyromellitic dianhydride and this primary amine yields an amic-acid (III) which builds rapidly to the polyamic acid (IV).





Cyclization to the polyimide (V) then occurs at elevated temperatures with the evolution of water.



This water acts as a blowing agent (especially at the 200°C temperature), further expanding the foam and rupturing cell walls.

3.2 THE FOAM FORMULATION

The foam formulation supplied by NASA-Ames was to be used as a guideline. Therefore, experimental work was initiated to obtain a reproducible formula for the preparation of higher density polyimide panels. After considerable effort, a polyimide foam formulation was generated which is illustrated in Table 1. This formulation was used to make all the panels except that it was necessary to adjust the amount of silicone surfactant (DC-193) daily, based on how well the mold was filled following the first casting of the day. The reason for this variation could never be completely explained or associated directly with variations in humidity, atmospheric pressure, temperature or time. The effect of adjusting the DC-193 was to control the initial foam rise time.

Table 1. Polyimide Foam Formulation

Weight	%	Ingredient	
1211.1 g (2.67 lb)	60.89	PAPI 901[a]	Part A
605.6 g (1.34 lb)	30.45	PMDA[b]	Part A
90.7 g (0.20 lb)	4.56	DC-193[c]	Part B
45.4 g (0.10 lb)	2.28	H_2O	Part B
36.3 g (0.08 lb)	1.82	Amine 220[d]	Part C

(a) Trademark of the Upjohn Company.
(b) Available in a micropulverized grade (325 mesh) from Princeton Chemical Research Inc., P.O. Box 652, Princeton, New Jersey 08540 on a custom synthesis basis.
(c) Trademark of Dow Corning Company.
(d) Trademark of Union Carbide Company. No longer commercially available.

It was later found that the majority of our problems in defining the best formulation first in the laboratory and then in the larger molds was due to wide variations in the starting materials. This was especially true of the pyromellitic dianhydride (PMDA) which exhibited variations in moisture content. The PMDA, finally delivered in a large quantity for the project, was quite dry (which is preferred), and in this respect did not meet the original specification indicated by the NASA-Ames publication.

In this formulation, excess isocyanate is incorporated to reduce the viscosity of the mix, provide adequate source for the blowing agent and form an isocyanurate ring which helps to preserve the thermal stability of the system.

A method to generate a foam having a density of 48 kg/m^3 (3 lb/ft^3) or greater using free rise was not found. Free rise, in essence, produced those previously reported foams in the 32 kg/m^3 (2 lb/ft^3) range. Accordingly, increases in density had to be achieved through confining ingredients within a mold.

Because the initial NASA-Ames formulation [Ref. 1] indicated that a flame retardant (Flameout 5600B-1) [Ref. 6] was desirable, some initial studies were conducted with it in the system. Interestingly, it was found that the flame retardant acted as a nucleator and stabilizer, providing improved uniformity of molded parts. It also seemed to reduce the problem of adhesion to molds. NASA-Ames, however, decided that it was best to introduce fire resistance characteristics through the postcure, therefore the flame retardant was not included in any of the scale-up work.

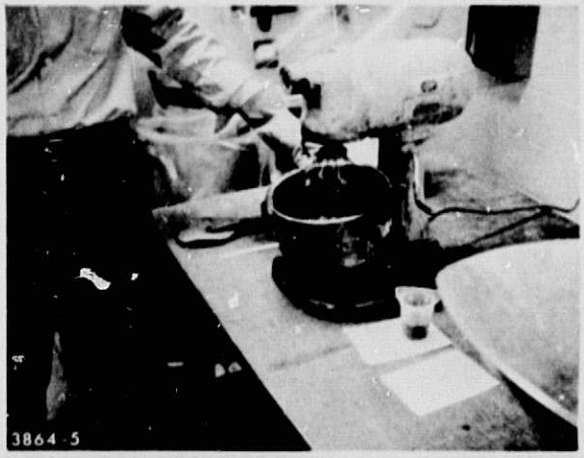
3.3 THE MOLDING PROCESS

The molding process consisted of simply mixing the three components illustrated in Table 1 together, charging these to a hot mold, enclosing the mold and letting it cure in the oven for 45 minutes at 200°C (390°F).

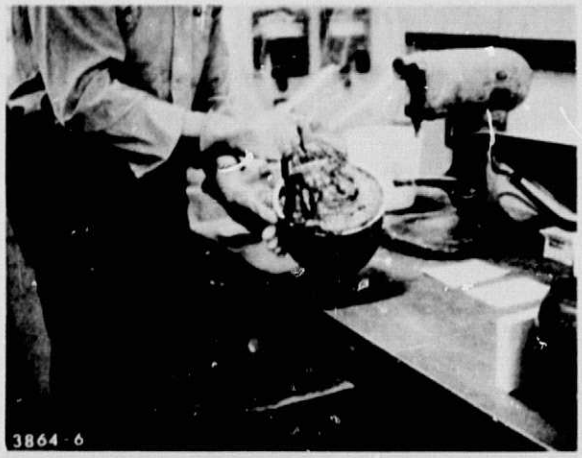
Some variations of this technique, however, were investigated The mixing procedure, illustrated in Figure 2, shows a planetary type Hobart mixer being used for the blending. The actual procedure involved adding the two components of Part A to the mixing bowl and stirring at high speed until homogeneous. This generally took approximately 2 minutes.

(a) Weighing raw materials

(b) After mixing Part A



(c) After mixing Part A and Part B



(d) After mixing all three parts together

Figure 2. Preparation of Molding Formulation.

The components of Part B were then mixed together separately, added to the Part A and mixed for an additional 2 minutes. Finally, Part C was added and mixed for an additional minute.

Following the mixing of all three parts, the ingredients were left to rise in the mixing bowl and to bubble for at least 1 minute before charging to the mold. This was found to be advantageous in minimizing initial mold pressure, improving the uniformity of the foam and permitting more time for closing of the mold.

Prior to the mixing of the ingredients, the mold (described in Section 3.6) was preheated to 230°C (445°F). It was expected that heating to this temperature would provide sufficient storage of heat to keep the mold at at least 200°C (390°F) during its filling and closure.

The casting procedure consisted of charging the aluminum mold with the blended ingredients. This is illustrated in Figure 3, where the materials appear to be very thixotropic. The mold is then closed and immediately inserted back into the 200°C (390°F) oven for a period of 45 minutes. Clamping the lid on the mold proved to be a very difficult problem, for a variety of reasons, discussed in Section 3.6. Finally, C-clamps were used all around the mold which required additional time for closure as well as slowing the initial foaming process. After the cure the mold is immediately removed from the hot oven, opened and the part taken out while still hot. Some cleaning is usually required to eliminate residual pieces of foam, especially foam extruded out through various small openings in the mold. The mold is then placed back into the radiant oven for preheating and the start of the next cycle.

3.4 POSTCURING OF THE FOAM PANELS

The guideline postcuring procedure for the polyimide foam panels called for a staged postcure of 15 minutes at 200°C (390°F), 15 minutes at 250°C (480°F) and 15 minutes at 300°C (570°F).

The ovens used for initial preparation of the foams and postcuring were the same, and consisted of electric radiant panels (specifically pizza ovens). Radiant heaters are on both the top and bottom of the ovens, spaced approximately 20 cm (8 inches) apart.

Initial attempts at poscuring the foams using the 15 minute cycles showed that this was not sufficient time to heat the foams throughout, thus introducing only a surface postcure. Accordingly, the procedure was modified to consist of 20 minute postcure periods. However, to minimize scorching (especially at 300°C) and maximize penetration of the heat, two panels were postcured at once but with each surface being exposed to the direct radiant heat for only a 10 minute period. This was done by placing the two panels into the oven, allowing them to postcure for 10 minutes, then reversing the position of the two foam panels to expose the inside surfaces to the direct radiant heat. In such a manner, a good uniform postcure was effected which was directly reflected by an even dark brown color introduced at 300°C (570°F) in contrast to the golden brown color of the as-molded pieces.

3.5 THE POLYIMIDE FOAM PANELS

The polyimide foam panels were outstanding from the viewpoint of strength, toughness and resiliency. Such toughness was really not anticipated, based on some earlier examination of small laboratory samples.

Some variation in density within panels was encountered, due primarily to skinning effects, where the hot foaming ingredients forced their way through the already formed foam to the surface. Here the foaming material was densified to a relatively thick skin. This, however, did not seem to have any significant effect on the overall properties of the foam panels.

Although no actual mechanical properties were measured for the foam panels, it is expected that the compressive strengths would be those expected of foams having a density of 48 kg/m^3 (3 lb/ft^3), up exponentially from the 32 kg/m^3 (2 lb/ft^3) density foams.

The foams were strong enough to simply be surrounded by cardboard and banded for shipment, thus providing their own free standing container. This packaging technique is illustrated in Figure 1.

3.6 THE MOLDS

A number of design criteria were initially set down for the molds to be used in preparation of the polyimide foams. These included:

- inside dimensions of 76 cm x 76 cm x 5.1 cm (30 in. x 30 in. x 2 in.);
- mold material to be at least 1 cm (3/8 inch) thick aluminum;
- lid of mold was to be provided with quick clamping devices for easy and fast closure;
- a means for supporting two wires going thru the foam was to be provided;
- total height of the mold was to be restricted to 10.2 cm (4 inches) so that two molds could be accommodated in one oven simultaneously;
- inside mold surfaces were to be coated with Teflon to provide release; and
- weight of the mold was to be minimized to facilitate its handling.

The mold can be seen partly in Figure 3. It consisted of basically square 1.25 cm (1/2 inch) thick aluminum plates separated by a frame to provide the necessary inside depth dimension. The lid was hinged at one end to facilitate closure and easy access for charging and removing of the finished part.

The side plates actually consisted of two 2.5 cm (1 inch) square bars stacked on top of each other with dowel pins for alignment and screws to hold them secure. This arrangement allowed for supporting of the two wires within the foam and disassembly so that the foam could be retrieved with the wires intact. This requirement complicated the design of the mold. It was eventually found to be unnecessary since the foam was tough enough such that the wires could be inserted after the moldings were cast.

Figure 3. Charging of the Aluminum Mold with the Molding Formulation.

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The only appropriate devices finally found to clamp the mold and hold it closed during the foaming process were C-clamps (12) around all the edges. Obviously, this type of clamping required considerable time for closing and opening, but a variety of quick action type clamping devices (all designed to take the temperatures and pressures expected) proved unsatisfactory in earlier experiments.

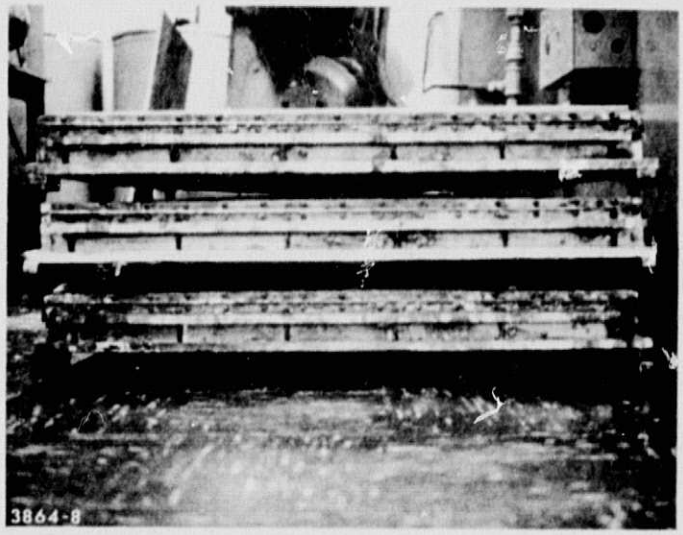
Whereas the clamps did hold the mold closed, this resulted in some secondary damage to the molds, specifically warpage of the aluminum plates, which is illustrated in Figure 4. This was due to the internally generated pressure during the foaming of the panels. This pressure was maximum about 10 minutes after placing the mold into the oven. When the clamps did not hold the mold together the result was expansion of the foam from within the mold outward until it filled the entire oven. This resulted in cleaning problems of both the mold and oven, and produced an unusable part.

Having determined that the aluminum could not withstand the pressure without deflection, it was decided to build a steel mold using 1.25 cm (1/2 inch) thick steel and to bolt it together. To reduce the time required to close the mold, the lid was split two thirds and one third, allowing two thirds of the mold to be bolted shut prior to the adding of the foam ingredients. Once the foam ingredients were added only about a dozen bolts needed to be inserted. Such a mold was fabricated and the first attempt at molding a part resulted in blowing the hinges off the end of the mold. Replacing the hinges and doubling up on the bolts with the hinges on, a second molding was made which actually caused a deflection of the 1.25 cm (1/2 inch) thick steel. The results indicated that a different mold design will be required for preparation of the higher density foams, and that much higher pressures will have to be accommodated for processing the foams.

4. CONCLUSIONS

The polyimide foam formulations supplied by NASA-Ames can be used to prepare 48 kg/m^3 (3 lb/ft^3) polyimide foams having a high degree of toughness and resiliency, and reasonable uniformity, in terms of density, cell size and structure.

This formulation allows for the relatively simple production of polyimide foam panels which should possess the desirable characteristics of low flame spread and smoke generation.



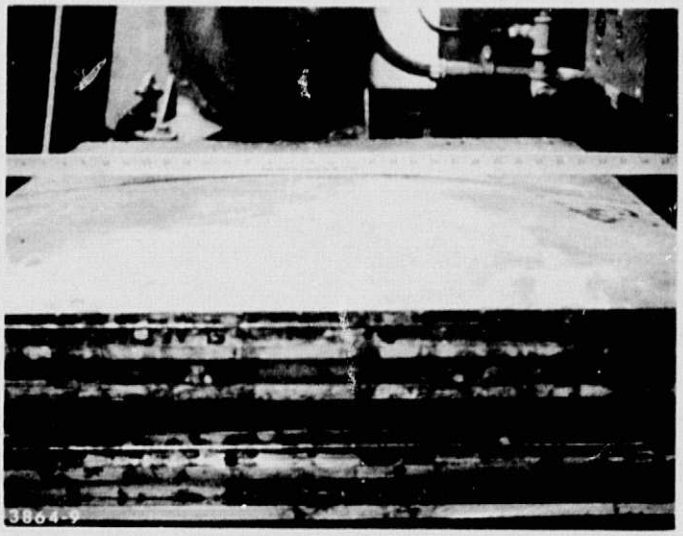


Figure 4. Illustration of Warpage in the Aluminum Molds Encountered Due to Excessive Internal Pressure Generated During Molding of the Polyimide Foam.

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In spite of the materials' excellent mechanical properties, and our ability to finally prepare some foam panels, processing problems remained to be solved. These are largely related to the excessively high pressure generated in the imidization of the polyimide during the foaming cycle. This excessive pressure results from the need to make a higher density foam, over that achieved through free rise of the system, and the attendant necessity to contain the high pressures in a closed mold.

In the preparation of the 76 cm x 76 cm x 5 cm (30 in. x 30 in. x 2 in.) panels, it was found that 1 cm (3/8 in.) thick aluminum was not adequate. It was anticipated that even 1.25 cm (1/2 in.) thick steel would be marginal for such a mold. One problem is that the pressure could not be vented using any normal technique and thus had to be confined by the mold.

The foam formulation is very sensitive to minor amounts of moisture, including that in the various raw material ingredients and the relative humidity. Variations in moisture content were found in the pyromellitic dianhydride, as an example.

The pyromellitic dianhydride obtained from a sole source for this project did not meet the specifications supplied by NASA-Ames. This required adjustments in the formulation, based on the differences in water content.

Control of mold temperature was most important and needed to be maintained within ±5C° (±10°F) to provide consistency in the molding procedure. Radiant type ovens were found to be acceptable for the molding (and the postcuring), but some forced air circulation would probably be more desirable.

Day-to-day variation in the foaming of the ingredients occurred which could not be attributed to any specific factors. This was reflected in the degree of fill in the mold. This was corrected daily by adjustment in the amount of silicone surfactant. The only remaining variable that could not be studied very well was release of pressure from the mold. This was because the molds could not be reproducibly closed, and may have been a factor in the variability.

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