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Fire Resistant Resilient Foams
Final Report

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DIVISION OF INTERNATIONAL HARVESTER

FOREWORD

This Final Technical Report documents work performed by the Research Department, Solar Division International Harvester, San Diego, California, under NASA-LBJohnson Space Center Contract NAS9-14718 for the period of 1 July 1975 through 31 December 1975 with extension to 16 February 1976.

The program is being administered by the R&T Procurement Branch, NASA-LBJohnson Space Center, Houston, Texas, under the technical direction of Mr. D. E. Supkis, technical monitor.

Dr. John Gagliani is the Principal Investigator (Solar Research Department) under the general direction of Mr. W. A. Compton, Director of Research. Also contributing to the work reported here are Mr. Usman Sorathia, Research Engineer, and Mr. A. N. Hammer, Research Engineer.

ABSTRACT

This work, primarily concerns the formulation, screening, optimization and characterization of open-cell fire resistant, low-smoke emitting, thermally stable resilient polyimide foams suitable for seat cushions in commercial aircraft and spacecraft.

Secondary program objectives are to obtain maximum improvement of tension, elongation and tear characteristics of the foams, while maintaining resiliency, thermal stability, low smoke emission and other properties of the polyimide foams known to be presently desirable attributes of these materials.

CONTENTS

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CONTENTS (Contd)

ILLUSTRATIONS

TABLES

1

PROGRAM SCOPE AND OBJECTIVES

The primary program objective was the development, optimization and characterization of resilient and flexible open-cell foams for use as seat cushions in commercial aircraft, spacecraft or other confined or artificially supported environments. Unlike existing foam materials, the new foams must combine three important attributes:

1. Inherent nonburning characteristics and resistance to high intensity ignition sources without loss of foam integrity.
2. No discernible smoke formation upon combustion.
3. No detectable toxic by-product of combustion.

To meet these requirements, new foam compositions were developed, evaluated and screened to select an optimum composition for the proposed application.

Solar has built upon the background of open-cell polyimide foam technology previously established at the Solar Research Laboratories. These polyimide resins are characterized by a totally organic molecular structure which is thermally stable and fire resistant. These resins undergo intumescent behavior during burning without producing detectable quantities of smoke or toxic by-products. This behavior prevents catastrophic spread of the fire over entire compartments or structures.

The program work plan included the synthesis of 33 copolyimide and terpolyimide foam precursors followed by processing the precursors to open-cell foams for evaluation and screening purposes.

The thirty-three polyimide foams were narrowed to three best formulations through mechanical property tests. Mechanical tests included tear, tension, and elongation. Advanced foam modifications followed with attempts to optimize the mechanical properties, while maintaining resiliency, fire retardancy, thermal stability, low smoke emission and other properties of the foams known to be desirable attributes of these materials. The two most responsive and promising foam compositions were selected finally for more thorough mechanical, physical, thermal, and environmental testing.

This program consisted of five tasks leading to the selection of an open-cell polyimide foam submitted to NASA-LBJ Space Center. The work plan constituting the various tasks of the Program Schedule is shown in Figure 1.

In Task I, Synthesis of Polyimide Foam Precursors, a total of 33 copolyimide and terpolyimide resins were synthesized and included studies of esterification agents, concentration of surface active agents and polymer structures.

Task II, Preparation of Foams and Preliminary Testings, followed with foaming the precursors and evaluation of the foams for tear resistance, tension and elongation characteristics. The 33 polyimide compositions were narrowed to three best formulations for advanced foam modifications.

Task III, Polyimide Foam Modification, followed with attempts to optimize the mechanical properties through synthesis modification and addition of short fibers or fillers. These included Kevlar, Nomex, Kynol, graphite, hydrated alumina, fumed silica, and others.

The one or two most responsive polyimide foam compositions were selected for complete characterization in accordance with the recommended procedures. This work constituted Task IV, Characterization of Candidate Polyimide Foams. At the completion of this phase all mechanical, physical, environmental, and flammability characteristics were ranked to select and recommend two specific compositions for seat cushion applications.

The preparation of samples of the optimized foams constituted the final Task V, Fabrication and Submittal of Final Specimens to NASA-LBJ. The overall technical content of the program covered a period of six months plus one and one half months extension.

REPORTING TASK	1975						1976	
	J	A	S	O	N	D	J	F
Work Plan Preparation	▼							
I. Synthesis of Polyimide Foam Precursors (20-30)								
Order Raw Materials	▼							
Ester Evaluation	▼							
Surface Active Agent Evaluation		▼						
Randomness of Polymer Structure		▼						
II. Preparation of Foams and Preliminary Testing			▼					
Tear Resistance			▼					
Tension and Elongation			▼					
Selection of 2-4 Candidates			▼					
III. Polyimide Foams Modification								
Fiber Addition				▼				
Filler Addition				▼				
Selection of 2 Candidates				▼				
IV. Characterization of Candidate (2) Polyimide Foams								
Physical Properties					▼			
Environmental and Chemical Properties					▼			
Flammability Properties						▼		
Selection of Optimum Foam Composition						▼		
V. Fabrication and Submittal of Final Specimens To NASA-LBJ							▼	
VI. Monthly Technical Progress Reports		▼		▼	▼	▼		
Review Mid Term Report			▼					
Final Report								▼

FIGURE 1. PROGRAM SCHEDULE

2

BACKGROUND AND PROGRAM APPROACH

The technology for conventional foamed plastics has been available for many years and a large number of highly flexible and resilient foams have been developed to satisfy increased market applications. Unfortunately conventional foams are highly combustible materials and undergo various physical and chemical changes when exposed to high temperature ignition sources. Many melt before starting to burn and burn just like liquids; others are flammable and burn with formation of gaseous products and smoke. Modifications of these polymers have been carried out to produce flame retardant materials possessing self-extinguishing characteristics. Generally this is achieved through the use of flame retardant additives or by modification of the polymer structure with reactive additions.

Many efforts to make conventional foams fire retardant have perversely increased the hazard to personnel in the vicinity of fires. Once ignited in an intensively hot fire, these modified foams undergo thermal decomposition and release toxic gases and smoke. Smoke and toxic gases are critical factors in fires occurring in confined or small compartments and are often the major cause of death due to smoke inhalation and asphyxiation.

New approaches to the flammability problem of plastic materials have been devised at Solar Research Laboratories. This consisted in synthesizing a whole new polymer system rather than modifying existing polymers. This new polymer is based on polyimide technology previously developed by Solar. Foams prepared from polyimide resins are thermally stable, fire resistant andproduce virtually no smoke when exposed to open fires. These are open-cell foams that can be produced in density range of from 16 to 640 Kg/m^3 (1 to 40 lb/ft^3) and can be modified with reinforcing fibers or fillers to produce cellular materials for specific applications. In addition to the modification with fibers or fillers, the selection of reactants and their molecular ratio permits modification of the basic polymer structure which can result in foam properties ranging from high resiliency and flexibility to brittleness and high rigidity.

Previously developed foaming conditions and procedures also have been shown to have considerable effect on the cellular structure and mechanical properties of the foams and optimum conditions have been found to vary for each foam precursor composition. Foaming procedures were evaluated and selected to arrive at an optimum

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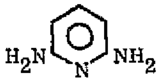
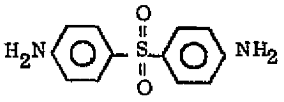
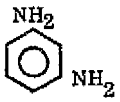
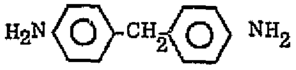
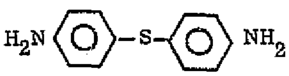
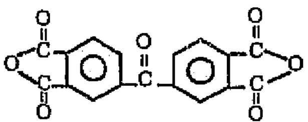
procedure for use in screening the final polyimide foam candidates before submittal of the final specimens to NASA-LBJohnson Space Center.

Prior Solar Research Laboratory polyimide foam technology is based upon the use and reaction of at least one heterocyclic diamine and at least one aromatic diamine possessing low basicity constant with an aromatic tetraacid possessing low acidity constant, as has been stated in more than one patent assigned to Solar. These reactants have proven to yield the most resilient and flexible foams and to maintain these properties to cryogenic temperature.

The addition of more reactive diamines and tetraacids produces foams which are brittle and rigid. These last reactants, however, were utilized to modify the present foams to obtain specific foam properties. The diamines and dianhydrides utilized in this program and their relevant physical properties are given in Table I. These reactants have been selected on the basis of their availability, cost and on their ability to yield foams possessing a wide range of properties from which to select candidates for advanced modification.

TABLE I

DIAMINES AND DIANHYDRIDES AND THEIR PROPERTIES

Diamines/Dianhydride	Structure	Melting Point
2,6 Diaminopyridine		393-395°K (248-252°F)
4,4' Diaminodiphenysulfone		449-450°K (349-351°F)
meta Phenylenediamine		335-336°K (144-145°F)
Methylenedianiline		366-367°K (199-201°F)
Thiodianiline		381-382°K (226-228°F)
Benzophenone 3,3',4,4' Tetra-carboxylic acid dianhydride		497-499°K (435-439°F)

3

EXPERIMENTAL PROCEDURES

The candidate polyimide foam precursors are prepared in a 2 liter 3-neck flask equipped with thermometer, mechanical stirrer and reflux condenser. Benzophenone 3,3',4,4'tetracarboxylic acid dianhydride (BTDA) and the esterifying alcohol or alcohols are charged in the flask and the mixture refluxed until solution of the BTDA occurs. The mixture is then refluxed for an additional 30 minutes to insure complete esterification of the BTDA to its half ester.

The mixture of diamines is added to the diester solution at 343°K (158°F) and reacted at 343-348°K (158-167°F) for 30 minutes, followed by addition of the surfactant (if any). The heavy syrup is allowed to cool to 313-323°K (104-122°F) with agitation and is then transferred into aluminum dishes for the subsequent drying step. This is carried out by heating the syrup in a circulating air oven at 355°K (180°F) for 12 hours (or overnight) followed by drying in a vacuum oven at 353-363°K (176-194°F) for 60-90 minutes. Thereafter the polyimide foam precursor is pulverized into a powder having a maximum particle size of 297 microns (100% through 50 mesh screen). The free flowing powder is then analyzed for percent volatile, melting point, and for foaming behavior and a portion saved for evaluation of stability in storage over a period of at least one month.

The percent volatile is obtained by measuring the weight loss of a sample heated at 589°K (600°F) for one hour; and the melting point by capillary method in a Thomas Hoover Capillary Melting Point Apparatus. Foaming behavior is studied by first spreading the powder at 2.5 mm (0.1 inch) thickness over an aluminum foil layed on an aluminum plate and heating at 589°K (600°F) in an oven for 30 minutes. The foam rise, cellular structure, skin formation, resiliency and other properties are observed for preliminary screening. This foaming procedure was utilized without exception for all precursors under study in Task I and Task II.

Figure 2 shows two 15 x 30 x 5 cm thick (6 x 12 x 2 in.) polyimide foam sheets foamed by this method, together with the sample of the liquid resins and powder foam precursors (Foam Resin No. 1 at left and Foam Resin No. 27 at right, Table II). These two precursors show normal foaming behavior and produce resilient foams with good cellular structure. Figures 3, 4, and 5 show abnormal foaming behavior of Foam Resins No. 17, 20, and 22. Foam Resin No. 17 (Fig. 3) is characterized by low rise

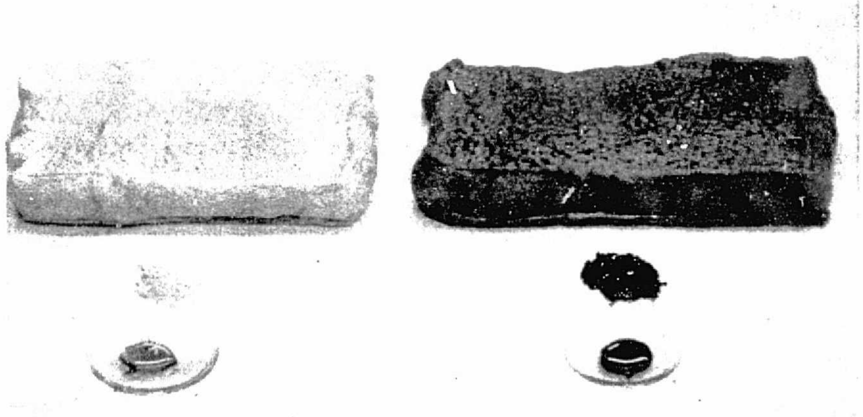


FIGURE 2. LIQUID AND POWDER POLYIMIDE FOAM PRECURSORS AND RESILIENT POLYIMIDE FOAMS - NORMAL RISE

and rigidity; Foam Resin No. 20 (Fig. 4) produces a very brittle foam easy to crush manually; and Foam Resin No. 22 (Fig. 5) is characterized by heterogeneous foaming and low rise.

These polyimide foam sheets were used to prepare test specimens for preliminary screening of the foams by determination of tension, elongation and tear characteristics. Tension and elongation test specimens were die cut from sheet material as shown in Figure 6. The die is seen in Figure 7.

The cellular structure of the polyimide foam varies with reactant composition as clearly shown in Figure 6. Resins No. 15, 25, and 27 show good cellular structure and foam rise, while Resins No. 2 and 21 are brittle and were damaged during the die cutting operation. Tear test specimens (Fig. 8) were cut and slit with a bandsaw. The tension test specimen configuration and dimensions are as described in ASTM Designation D-1564 covering standard methods of testing slab flexible urethane foams; the standard tear specimen however, has been altered slightly by lengthening the specified 3.81 cm (1.5 in.) cut to 6.35 cm (2.5 in.). This permitted easier clamping of many marginally flexible foam specimens in the test device.

All tests were made in accordance with the procedures described in ASTM Designation D-1564, Suffix T (tension and elongation) and Suffic G (tear) using an Instron Tester Model TTD. The ultimate elongation of the test specimen was obtained by an optical method which permits more accurate measurement at high [51 cm (20 in.) per minute] strain rate.

TABLE II

POLYIMIDE FOAM PRECURSORS AND POLYIMIDE FOAM CHARACTERISTICS

Polyimide Foam Precursors							Polyimide Foams			
Foam Resin No.	Composition	Molecular Ratio	BTDA Half Ester	L5420 (%)	MP (°K)	Volatile (%)	Density (Kg/m^3)	Tension (N/m^2)	Elongation (%)	Tear (N/m)
1	BTDA:2,6DAP:4,4'DADPS	1:0.5:0.5	Ethyl	0	402-411	17.7	29.52	86.17 x 10^3	36.62	108.5 (1)
2	BTDA:2,6DAP:4,4'DADPS	1:0.5:0.5	Ethyl	2.5	413-417	17.2	35.5	55.6 x 10^3	27.6	56.0 (2)
3	BTDA:2,6DAP:4,4'DADPS	1:0.5:0.5	Ethyl	5.0	407-415	17.7	32.0	24.8 x 10^3	15.0	105.0 (3)
4	BTDA:2,6DAP:4,4'DADPS	1:0.5:0.5	Ethyl	7.5	423-428	18.0	21.0	20.33 x 10^3	2.5	45.5 (4)
5	BTDA:2,6DAP:4,4'DADPS	1:0.5:0.5	Methyl	2.5	408-413	15.1	32.48	45.5 x 10^3	21.0	73.5 (2)
6	BTDA:2,6DAP:4,4'DADPS	1:0.5:0.5	Propyl	2.5	395-409	20.9	--	22.47 x 10^3	14.3	46.9 (4)
7 & 8	BTDA:2,6DAP:4,4'DADPS	1:0.5:0.5	Methyl	0	405-412	15.6	--	55.15 x 10^3	15.33	108.5 (3)
9	BTDA:2,6DAP:4,4'DADPS	1:0.5:0.5	Ethyl	0.8	405-413	17.7	29.8	42.7 x 10^3	17.0	56.0 (2)
10	BTDA:2,6DAP:4,4'DADPS	1:0.5:0.5	Methyl	5	417-424	16.2	49.64	38.14 x 10^3	11.3	73.5 (3)
11	BTDA:2,6DAP:4,4'DADPS	1:0.5:0.5	Methyl/Ethyl	0.8	428-433	15.8	39.2	57.33 x 10^3	20.6	91.0 (2)
12	BTDA:2,6DAP:4,4'DADPS	1:0.5:0.5	Methyl/Ethyl Propyl	0.8	401-408	18.0	21.4	38.6 x 10^3	27.0	52.5 (2)
13 & 14	Repeat of No. 1 and 2	--	--	--	--	--	--	--	--	--
15	BTDA:2,6DAP:4,4'DADPS	1:0.75:0.25	Ethyl	0	408-413	18.7	28.48	57.8 x 10^3	32.4	157.6 (1)
16	BTDA:2,6DAP:4,4'DADPS	1:0.25:0.75	Ethyl	0	403-409	16.0	39.08	71.97 x 10^3	24.0	166.3 (1)
17	BTDA:2,6DAP:MDA	1:0.5:0.5	Ethyl	0	429-439	14.6	--	27.5 x 10^3	8.0	-- (5)
18	BTDA:2,6DAP:MDA	1:0.75:0.25	Ethyl	0	414-419	17.[illegible]	--	10.11 x 10^3	8.6	-- (5)
19	BTDA:2,6DAPmPDA	1:0.5:0.5	Ethyl	0	463-483	17.9	--	25.5 x 10^3	11.5	-- (5)
20	BTDA:2,6DAPmPDA	1:0.75:0.25	Ethyl	0	433-448	19.1	--	-- (5)	-- (5)	-- (5)
21	BTDA:2,6DAP:mPDA:4,4'DADPS	1:0.5:0.25:0.25	Ethyl	0	411-418	18.0	43.2	31.2 x 10^3	4.66	-- (5)
22	BTDA:2,6DAP:mPDA:MDA	1:0.5:0.25:0.25	Ethyl	0	433-438	16.4	29.5	--	--	-- (5)
23	BTDA:2,6DAP,mPDA,TDA	1:0.5:0.25:0.25	Ethyl	0	412-418	17.7	42.4	56.99 x 10^3	24.6	-- (5)
24	BTDA:0.26DAP,TDA,MDA	1:0.5:0.25:0.25	Ethyl	0	447-456	15.5	--	--	--	-- (5)
25	BTDA:2,6DAP:4,4'DADPS	1:0.85:0.15	Ethyl	0	411-418	18.6	32.5	91.0 x 10^3	38.6	192.6 (1)
26	BTDA:2,6DAP:TDA	1:0.5:0.5	Ethyl	0	445-453	16.0	41.36	46.0 x 10^3	17.6	-- (5)
27	BTDA:2,6DAP:TDA,mPDA	1:0.75:0.15:0.1	Ethyl	0	413-418	18.9	31.68	94.2 x 10^3	19.0	145.3 (1)
28	BTDA:2,6DAP:TDA:mPDA	1:0.6:0.3:0.1	Ethyl	0	418-423	17.1	36.16	73.07 x 10^3	28.0	110.3 (2)
29	BTDA:2,6DAP:TDA	1:0.85:0.15	Ethyl	0	414-417	19.4	43.7	113.7 x 10^3	30.5	288.9 (1)
30	BTDA:2,6DAP,4,4'DADPS	1:0.5:0.5	Methyl/Ethyl/ Propyl	0	417-419	17.8	38.27	47.7 x 10^3	23.8	133.0 (2)
31	BTDA:2,6DAP:4,4'DADPS	1:0.95:0.05	Ethyl	0	397-409	21.6	15.2	69.9 x 10^3	37.5	127.8 (2)
32	BTDA:2,6DAP:TDA	1:0.95:0.05	Ethyl	0	399-401	23.2	13.2	61.8 x 10^3	16.3	110.8 (2)
33	BTDA:2,6DAP:TDA	1:0.75:0.25	Ethyl	0	414-419	18.7	17.9	62.0 x 10^3	14.0	87.6 (4)

(1) Resilient, good cellular structure.

(2) Marginally resilient.

(3) Brittle, poor structure.

(4) Brittle, easy to crush manually.

(5) Very brittle, broke on clamping in tear and/or tension testing.

Abbreviation	Name
BTDA	Benzophenone - 3,3',4,4' tetracarboxylic acid dianhydride
2,6DAP	2,6 - Diaminopyridine
4,4'DADPS	4,4' - Diaminodiphenyl sulfone
mPDA	meta Phenylenediamine
MDA	Methylene Dianiline
TDA	Thiodianiline

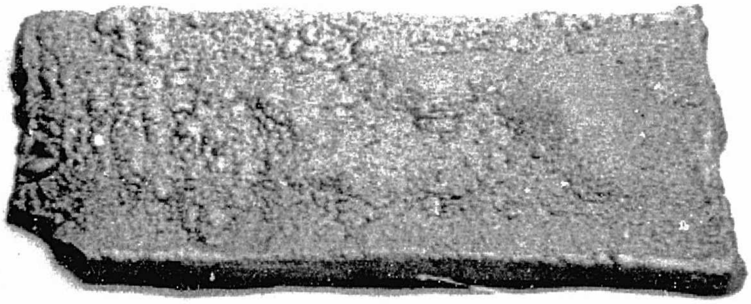


FIGURE 3. RIGID POLYIMIDE FOAM - LOW RISE

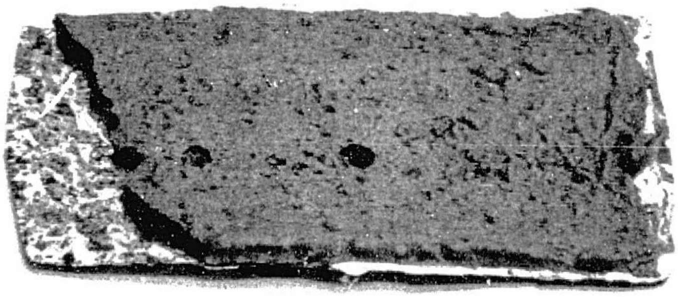


FIGURE 4. BRITTLE POLYIMIDE FOAM - LOW RISE

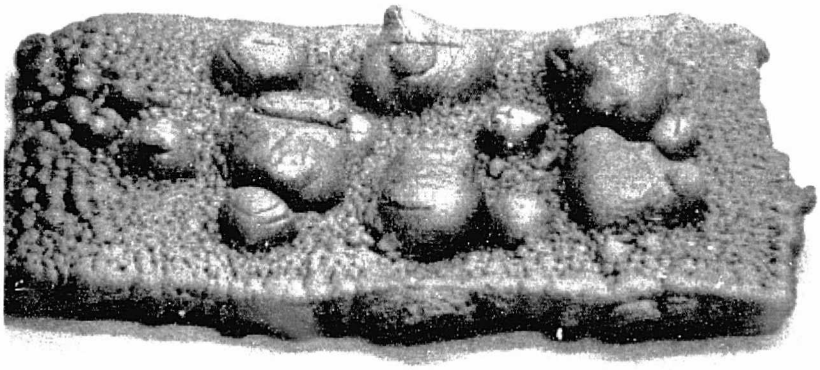
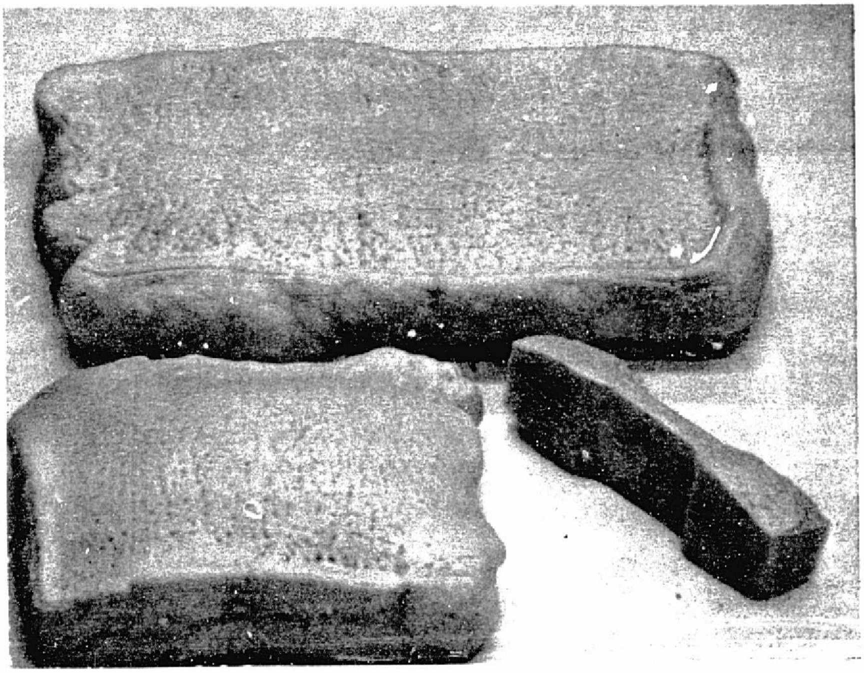


FIGURE 5. POLYIMIDE FOAM - HETEROGENEOUS RISE

Foam Resin No. 15 -

Homogeneous cellular structure, resilient foam



Foam Resin No. 25 -

Homogeneous cellular structure, resilient foam

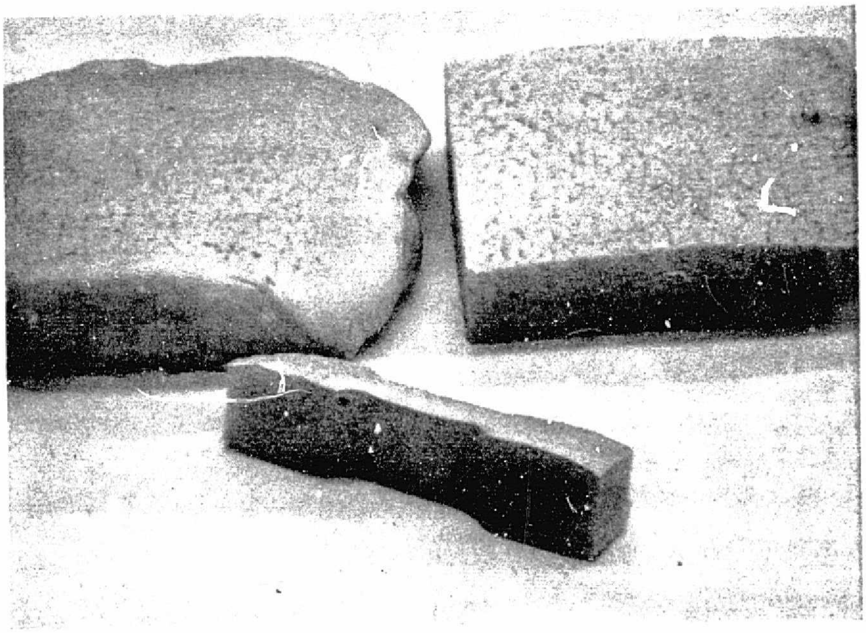
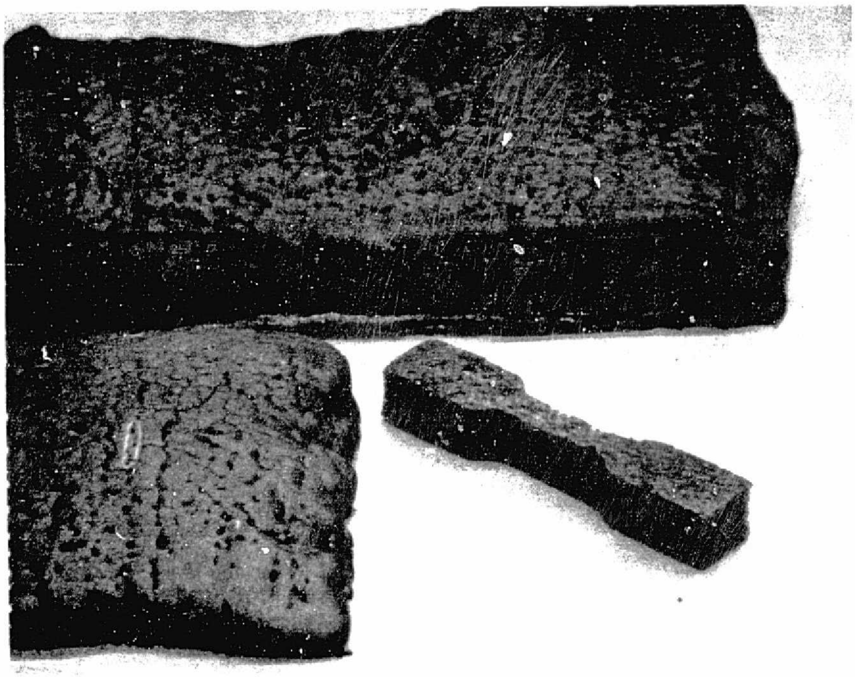


FIGURE 6. DIE CUT TENSION AND ELONGATION SPECIMENS FROM FLAT SHEET MATERIAL (Sheet 1 of 3)

Foam Resin No. 27 -

Homogeneous cellular structure, resilient foam



Foam Resin No. 2 -

Marginally brittle foam

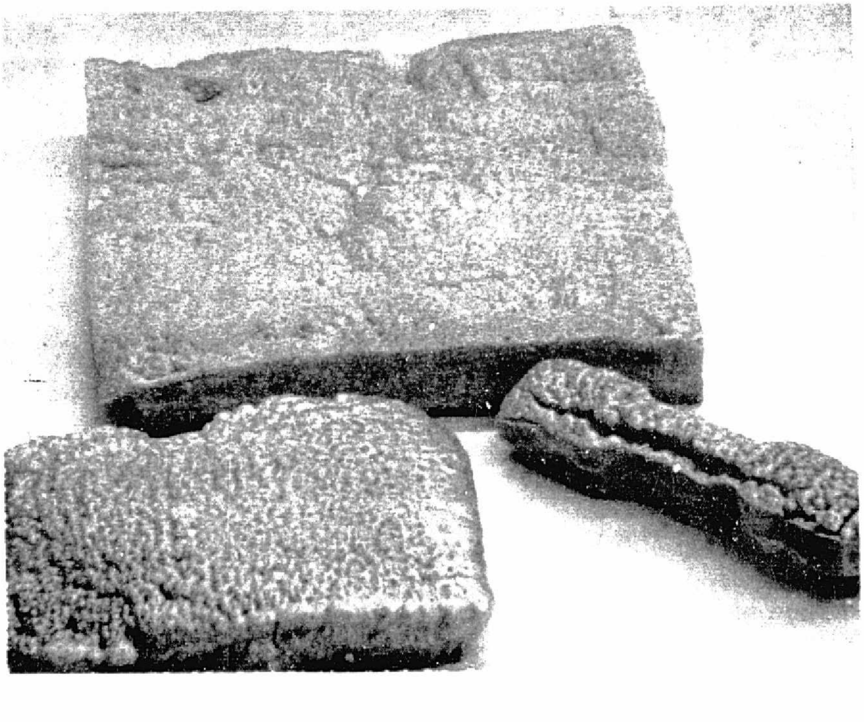
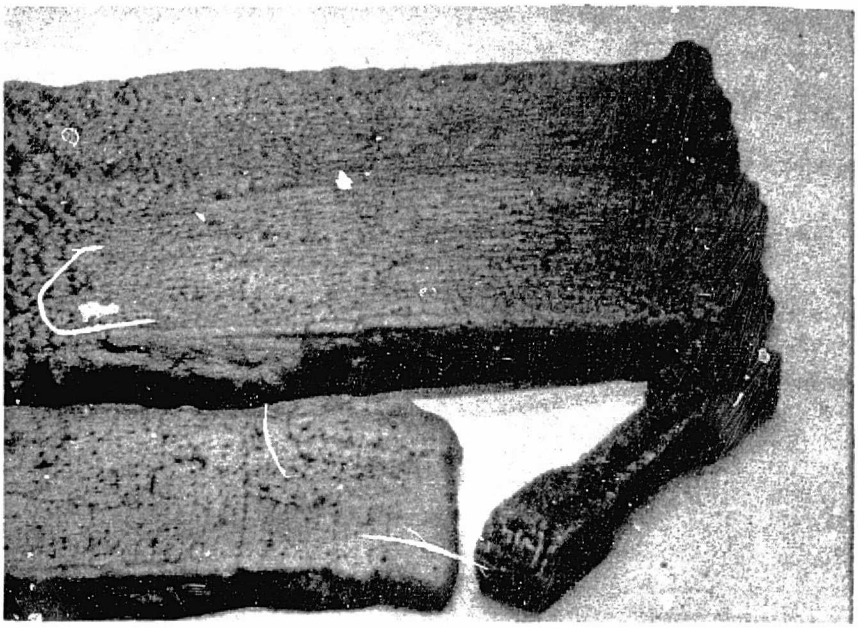


FIGURE 6. DIE CUT TENSION AND ELONGATION SPECIMENS FROM FLAT SHEET MATERIAL (Sheet 2 of 3)



Foam Resin No. 21 -

Brittle foam

FIGURE 6. DIE CUT TENSION AND ELONGATION SPECIMENS FROM FLAT SHEET MATERIAL (Sheet 3 of 3)

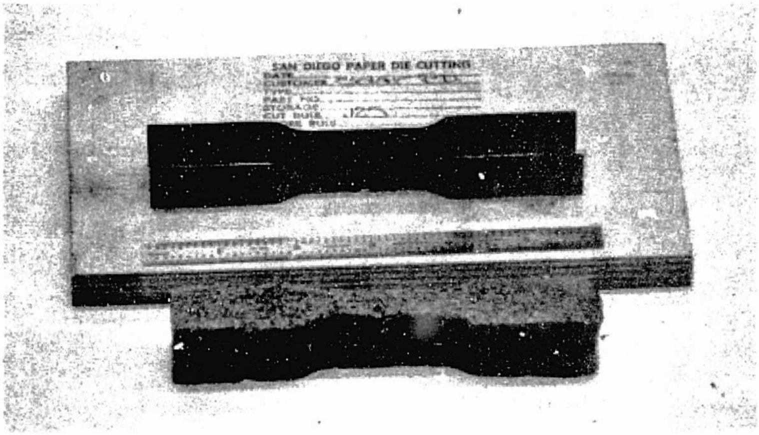


FIGURE 7. DIE FOR STAMPING OUT SPECIMENS FOR TENSION AND ELONGATION TESTS

3.1 SELECTION OF RAW MATERIALS

The availability of a wide range of aromatic diamines and dianhydrides enables the mechanical and thermal properties of polyimide materials to be varied within wide limits. However, it has been previously established under one or more of Solar's existing patents that the diamines employed in preparation of polyimide foams must be selected from those that have primary amine base dissociation constants lower than

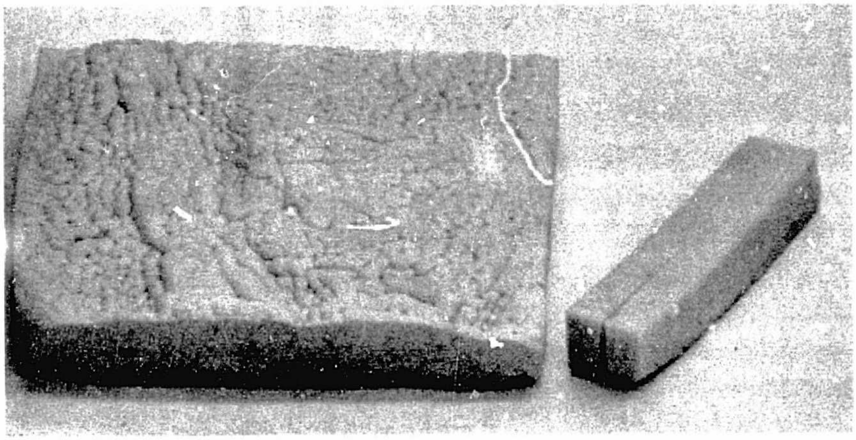


FIGURE 8. TEAR TEST SPECIMEN CUT FROM FLAT SHEET MATERIAL

10^{-10} and that at least one of the diamines be an heterocyclic diamine. Previously it has been also established that a low acidity constant dianhydride, one not exceeding a K_a of 10^{-5}, is just as essential to produce flexible, and resilient polyimide foams. As a result of these previous studies, the most promising diamines and dianhydrides and their relevant physical properties taken from the open literature are given in Table I.

3.2 PURIFICATION OF RAW MATERIALS

- 2, 6 Diamino pyridine. This highly purified diamine (M. P. 393-395°K, 248-252°F) was obtained from Koppers & Co. and used without purification.

- 4, 4'Diaminodiphenyl sulfone. This highly purified diamine was obtained from Roussel Corp. and used without purification (M. P. 449-450°K, 349-351°F).

- Thiodianiline. This purified diamine (M. P. 378-380°K, 221-224°F) was obtained from Research Organic/Inorganic Chemical Corp. and used without purification.

- Methylene-dianiline. This commercial grade diamine (M. P. 360-363°K, 189-194°F) was obtained from Aldrich Chemical Corp. and used without purification.

- m-Phenylendiamine. This commercial grade diamine was obtained from Aldrich Chemical Corp. and purified by vacuum distillation. The fraction melting at 335.5-336.0°K (144.2-145.1°F) was collected and used.

- Benzophenone 3,3',4,4' tetracarboxylic acid dianhydride. This material was obtained from Gulf Oil Company Chemical Department. The off-white powder (M. P. 493-496°K, 428-433°F) was washed with acetone and dried at 393°K (248°F) to yield a material (M. P. 497-499°K, 435-439°F) suitable for synthesis of polyimide foam precursors.

- L-5420. A silicon surfactant was used as received from Union Carbide Corp.

- Ethyl alcohol. Mallinkrodt catalog No. 7019 reagent alcohol.

- Methyl alcohol. Mallinkrodt catalog No. 3016.

- n-Propyl alcohol. Mallinkrodt catalog No. 7169.

Infra-red spectra of the polymerization components were obtained and formed the basis for standardization of future lots.

4

EXPERIMENTAL RESULTS

A summary of important experimental data derived from Task I and II is given in Table II. The 33 polyimide foam precursor compositions, ratio of reactants, melting point, volatile content, and mechanical and physical properties of the respective foams are detailed. During Task II the best 22 polyimide foam compositions selected in preliminary screening tests were further narrowed to three through comparison of foam properties and mechanical testing.

The three candidates are foam Resin No. 29, No. 25, and No. 15. Foams produced from these resins met tension and, with the exception of No. 15, which was slightly low, tear goals, but were deficient in elongation. Mechanical property goals for the foams are listed in Table III. The polyimide foam precursors and final foams are discussed below and categorized into compositional systems. Most foams met the density goal of 40 Kg/m^3 (2.5 lbs/ft^3).

4.1 THE SYSTEM BTDA:2,6DAP:4,4'DADPS

The initial work of Tasks I and II covered the evaluation and screening of this system since it is known from the earlier work in polyimide technology carried out at Solar to be a most likely candidate. All candidates in the subject system consist of copolyimide foam precursors and copolyimide foams at various reactant ratios prepared

TABLE III

PROGRAM GOALS - MECHANICAL PROPERTIES

Ultimate Tensile Strength, Minimum	82.74 x 10^3 N/m^2	12.0 psi
Tear Strength, Minimum	175.1 N/m	1.0 lbs/inch
Elongation Under Load Minimum	80% in 2.54 cm	80% in 1 inch
Density, Maximum	40 Kg/m^3	2.5 lbs/ft^3

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with different esterifying agents and various concentrations of the L-5420 silicone surfactant.

Room temperature tension strength and elongation of foams prepared from precursors made with various esters for this system, at reactants ratio of 1:0.5:0.5, are reported in Figure 9. The half ethyl ester of benzophenone, 3, 3', 4, 4'tetracarboxylic acid shows best tension and elongation characteristics in addition to best foam structure and resiliency. The half methyl ester produces marginally resilient foams. The half n-propyl ester produces highly brittle and rigid foams which possess poor cellular structure. It may be interesting to note however that these last foams show outstanding fire-containing properties based on preliminary tests only. Figure 10 shows photographs of polyimide foams obtained with specific esters. The change of cellular structure is clearly visible with increasing molecular weight of the esterification agent. The effect of mixed esters is shown in Figure 11. Foams produced by this technique are resilient and possess a good cellular structure compared to foams

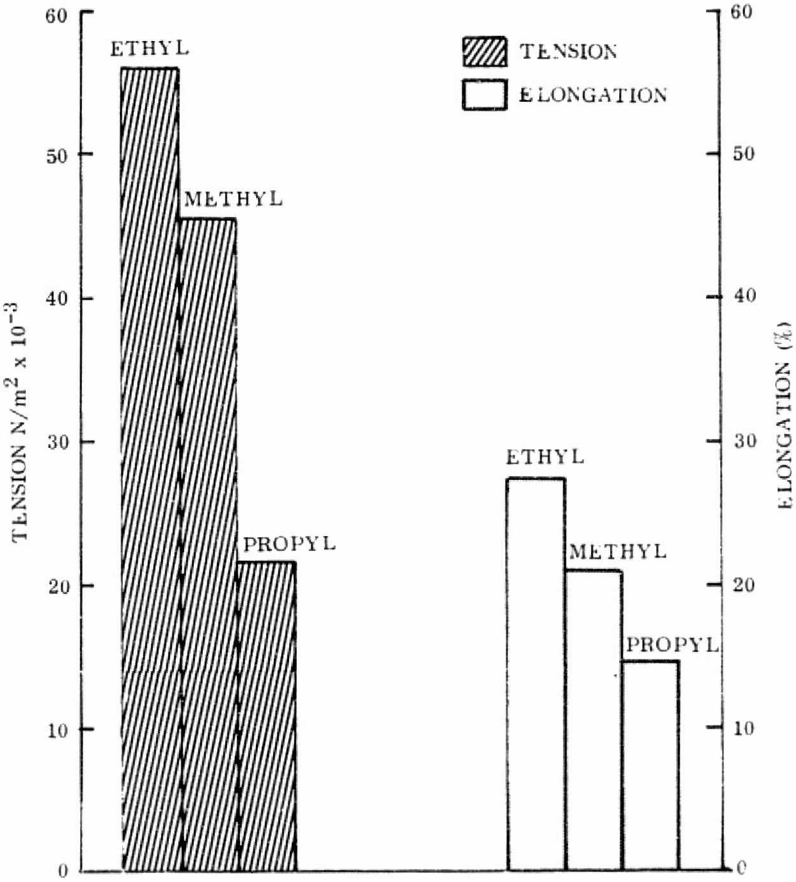
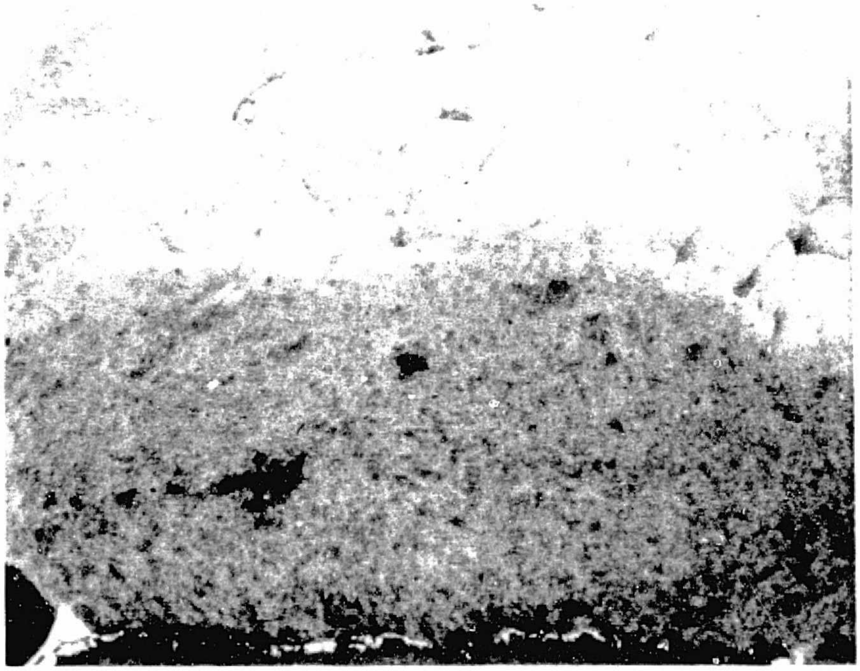


FIGURE 9. EFFECT OF HALF ESTER ON MECHANICAL PROPERTIES OF POLYIMIDE FOAMS; BTDA:2, 6DAP:4, 4'DADPS SYSTEM

a) Methyl ester



b) Ethyl ester

FIGURE 10. EFFECT OF HALF ESTERS OF BENZOPHENONE 3,3',4,4' TETRACARBOXYLIC ACID ON POLYIMIDE FOAM PROPERTIES (2.5% L-5420) (Sheet 1 of 2)

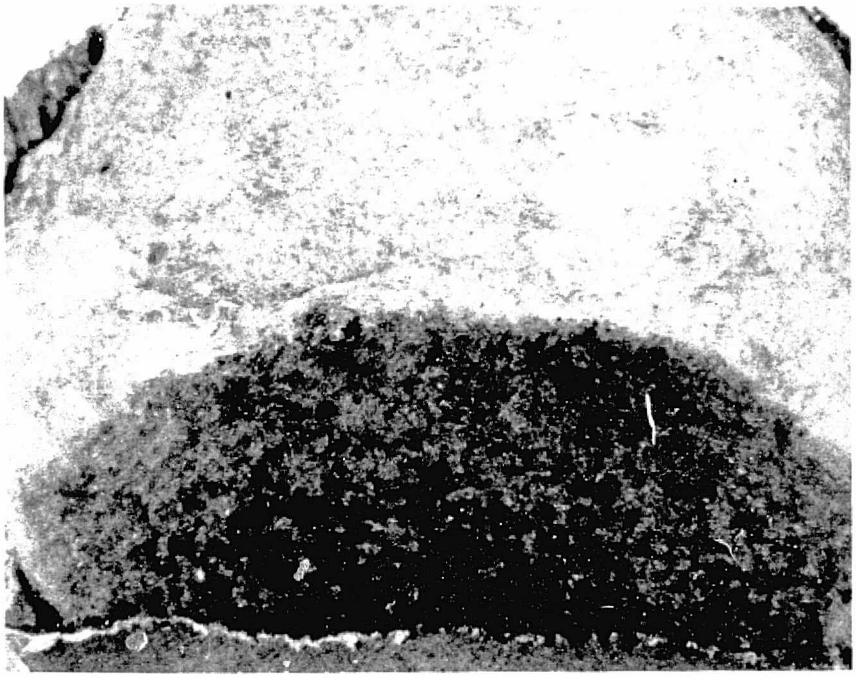
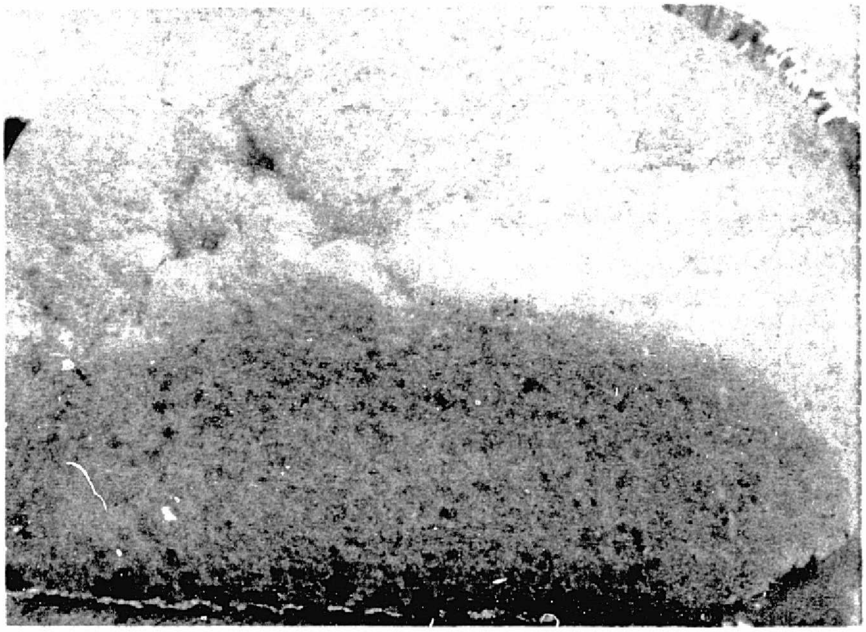


FIGURE 10. EFFECT OF HALF ESTERS OF BENZOPHENONE 3,3',4,4' TETRACARBOXYLIC ACID ON POLYIMIDE FOAM PROPERTIES (2.5% L-5420) (Sheet 2 of 2)

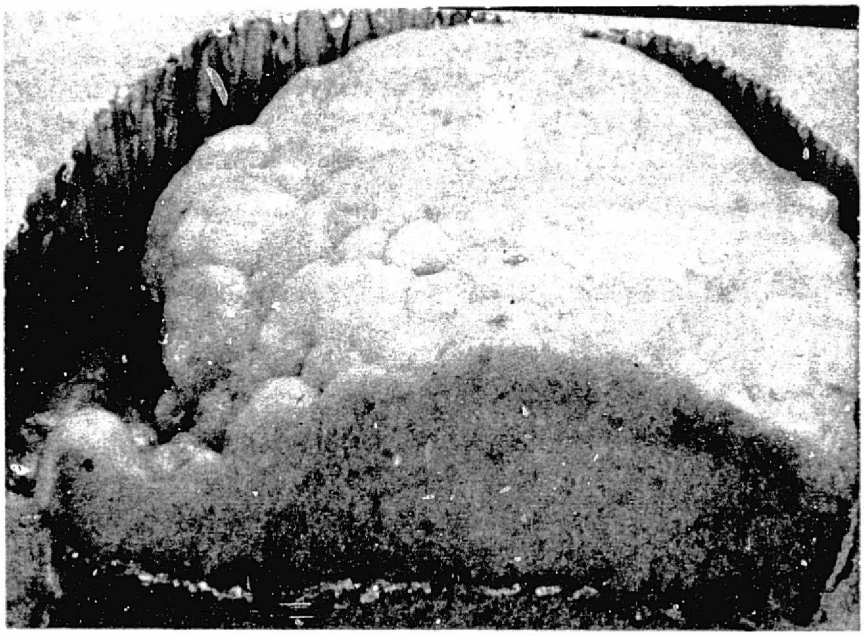
prepared with propyl or methyl esters only. This may be the result of a more controlled release of vapor (alcohol and water) during the polymerization reaction. On the basis of these results, the half ethyl esters of BTDA were chosen for synthesis of the polyimide foam precursors made in Task I and evaluated in Task II of the program.

In foaming technology, the use of a surface active agent, such as L-5240, is known to yield more homogeneous foam structures and better foaming behavior. Part of the work carried out in Task I was primarily designed to assess foam properties at various surfactant concentrations. Room temperature tension strength determination for the copolymer system 1:0.5:0.5 using the ethyl ester at increasing concentration of L-5420 surfactant is shown in Figure 12. It is evident that high levels of L-5420 affect the tensile properties of the polyimide foams quite drastically in addition to producing increasingly brittle foams.

While there may be a beneficial effect at low surfactant concentration (0.1-0.5%) these results suggest that appreciable crosslinking may occur when a silicon surface active agent of the type of L-5420 is used. Similar trends are noticed with methyl esters (Foam Resins No. 5, 7, 8, and 10). Figure 13 shows the effect of high concentration of L-5420 on the cellular structure and on foaming behavior. On the basis of



a) Methyl-ethyl esters



b) Methyl-ethyl-propyl esters

FIGURE 11. EFFECT OF MIXED ESTERS OF BENZOPHENONE 3,3',4,4' TETRACARBOXYLIC ACID ON POLYIMIDE FOAM PROPERTIES (0.8% L-5420)

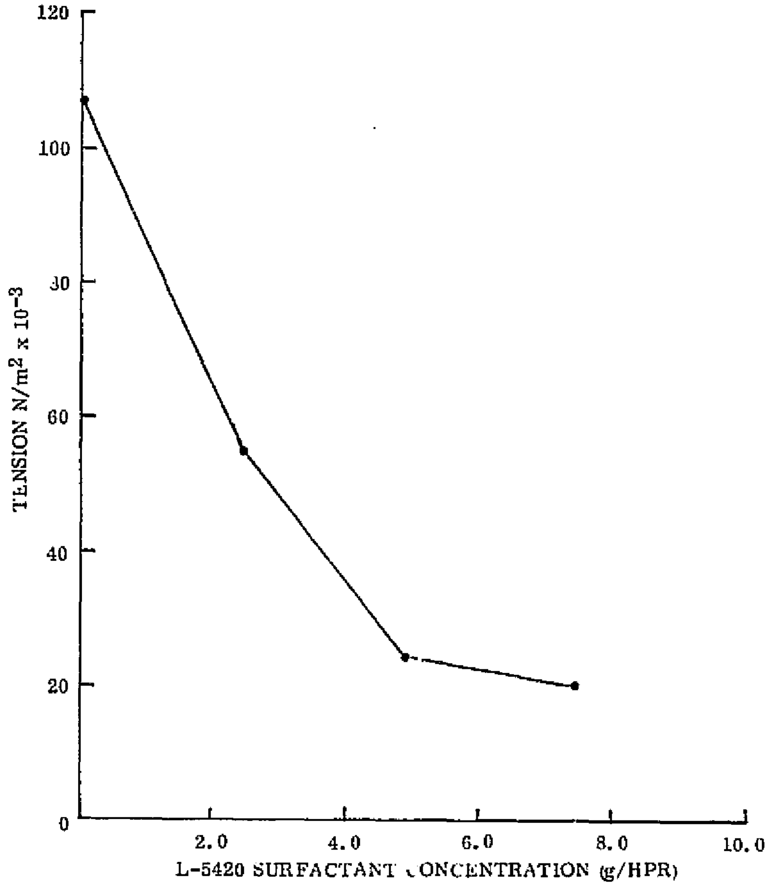


FIGURE 12. SILICONE SURFACTANT EFFECT ON MECHANICAL PROPERTIES OF POLYIMIDE FOAMS; BTDA:2,6DAP: 4,4'DAPS SYSTEM

these results the use of surfactants was discontinued pending more complete analysis in Task III.

These experiments were also designed to offer an assessment of the relative strength of copolyimide resins prepared at different reactants ratio. This is shown in Figure 14. Foam produced at high 2,6DAP ratio appears to possess higher tension and elongation characteristics. Additionally the tear resistance at higher 2,6DAP ratio appears to improve, however, at the limit of the homopolymer system, all properties decline again.

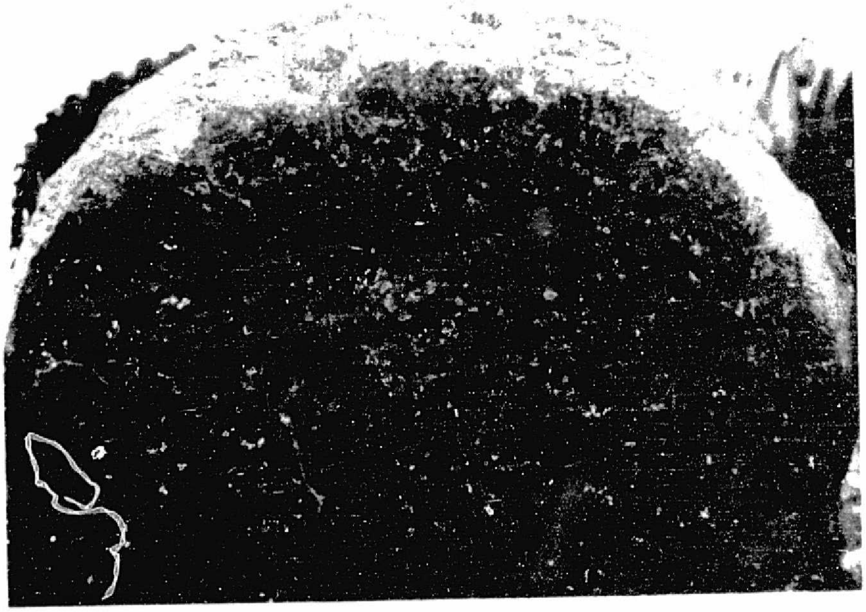
As a point of interest the ratio of reactants is found to influence the foam structure. The low ratio of 2,6DAP yields the most homogeneous foam structures, but marginal flexibility and resiliency, while at increasing ratio of 2,6DAP, the foam structure is comparatively marginal but the foams are more resilient and flexible. Finally, at the limit of the homopolymer system (0.95:0.05) the foam structure is drastically affected. This difference in cellular structure (density is also

a) 0% L-5420

b) 0.8% L-5420

FIGURE 13. EFFECT OF CONCENTRATION OF L-5420 SURFACTANT ON CELLULAR STRUCTURE OF POLYIMIDE FOAM (ETHYL ESTERS) (Sheet 1 of 2)

c) 5% L-5420



d) 7.5% L-5420

FIGURE 13. EFFECT OF CONCENTRATION OF L-5420 SURFACTANT ON CELLULAR STRUCTURE OF POLYIMIDE FOAM (ETHYL ESTERS) (Sheet 2 of 2)

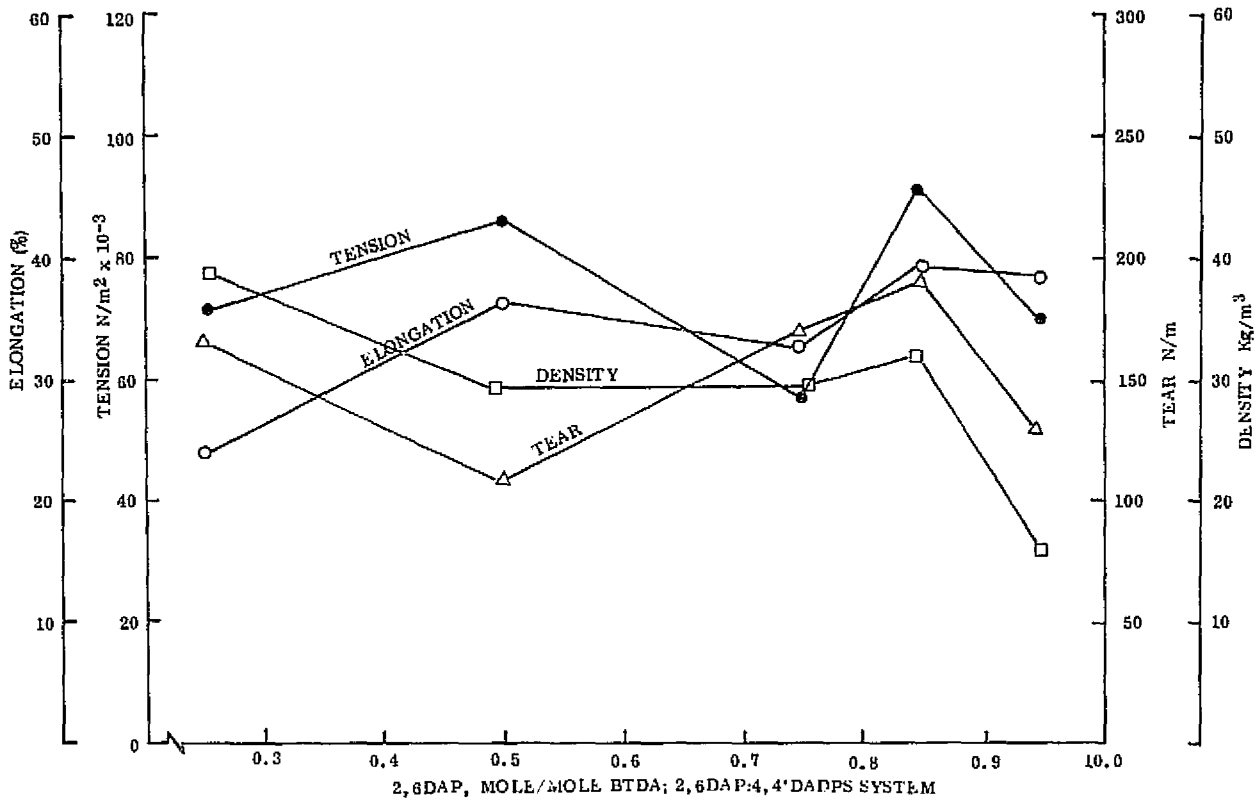


FIGURE 14. REACTANTS RATIO: EFFECT ON POLYIMIDE FOAM PROPERTIES

affected) can be attributed only to a difference in foaming behavior of the precursors made at various reactants ratio, since synthesis of the precursors and foaming procedures were kept constant throughout Task I and Task II.

4.2 THE SYSTEMS: BTDA:2,6DAP:TDA
BTDA:2,6DAP:MDA
BTDA:2,6DAP:mPDA

The BTDA:2,6DAP:MDA and BTDA:2,6DAP:mPDA systems produce polyimide foams which are rigid and in a few cases (Foam Resin No. 20) easy to crush manually. However, many of these foams have been found to possess good fire containing properties and superior hydrolytic stability. These two systems were eliminated from further studies, but may be potentially useful in other applications requiring the use of more rigid fire containing light weight structures.

The BTDA:2,6DAP:TDA system offers exceptional mechanical properties at high 2,6DAP ratio but is still deficient in elongation characteristics. This is shown in Figure 15. Polyimide foams produced from this copolymer system appear to be more dependent on the reactant ratio than those of the system discussed in the previous paragraph. This effect is evident from the data of Figure 15 which shows no foaming

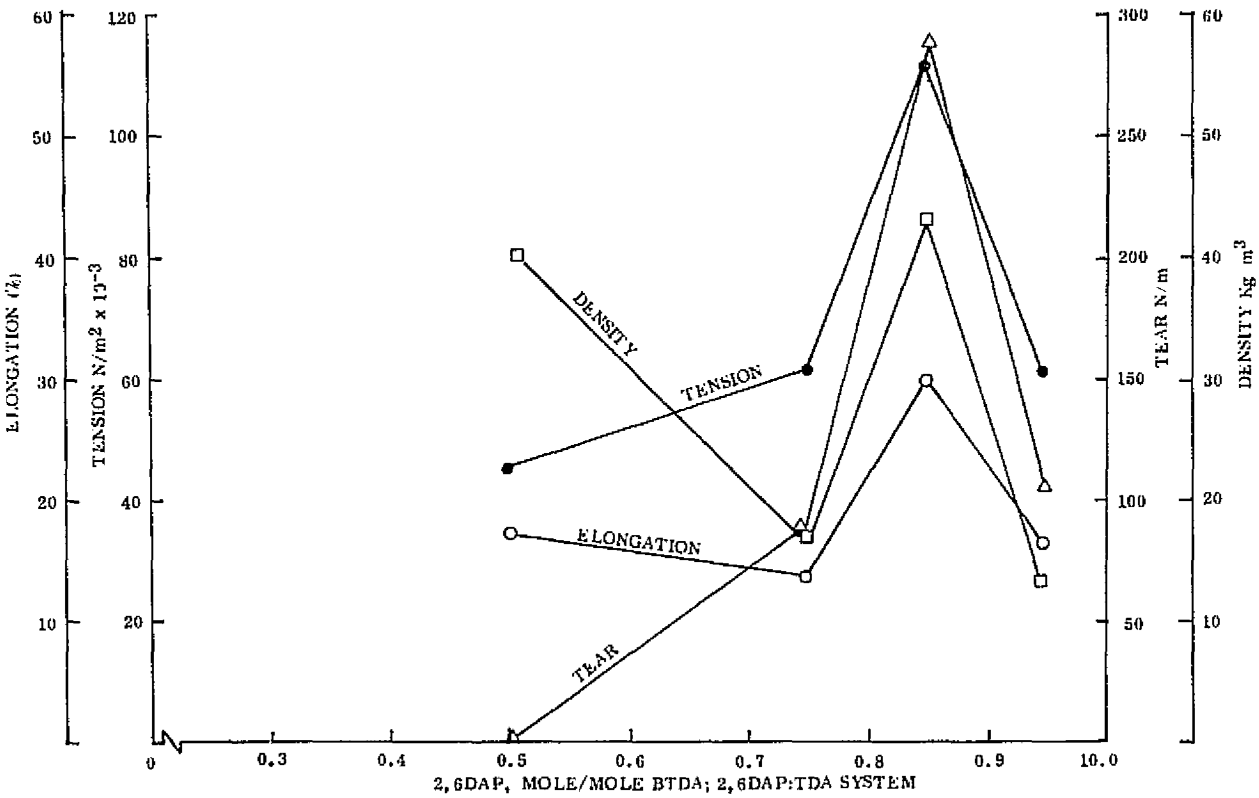


FIGURE 15. REACTANTS RATIO: EFFECT ON POLYIMIDE FOAM PROPERTIES

properties at 2,6DAP ratio below 0.5 and the highest tension and tear properties for a 2,6DAP ratio of 0.85 with high resiliency, flexibility and good cellular structure of the foams. As for the previous system, the beneficial effect on the high 2,6DAP ratio is lost when the homopolymer conditions are approached (Foam Resin No. 32) as shown by lower mechanical properties. The copolymer of Foam Resin No. 29 at a reactant ratio of 1:0.85:0.15 was one of the resins selected as a candidate for advanced modification in Task III, however, as with the previous system, this foams is still deficient in elongation characteristics.

4.3 THE TERPOLYMER SYSTEMS: BTDA:2,6DAP:mPDA:TDA
BTDA:2,6DAP:MDA:TDA

These systems were included in the study to evaluate the effect of randomness of the distribution of the mesomers in the polymer chain upon the flexibility and mechanical properties of the foams. Terpolymer produced with high ratio of mPDA and MDA (Foam Resin No. 23 and 24) produced brittle and rigid foams. This was expected in view of similar effects in the respective copolymer systems.

At lower ratio of mPDA (Foam Resin No. 27 and 28) resiliency and cellular structure were drastically improved and mechanical properties (Resin No. 27) restored to considerably higher levels. These two terpolymer systems possess excellent foaming characteristics and good fire-containing properties, but suffer in flexibility and resiliency due to the presence of more reactive aromatic diamines (mPDA and MDA) in the polymer structure.

4.4 POLYIMIDE FOAMS MODIFICATION - TASK III

Experimental work in Task III, Polyimide Foam Modification, included evaluation of fibers and fillers combined with foam synthesis and foaming process studies by the use of surface active agents. The work was organized in accordance with the general approach of attempting the improvement of tension, elongation and tear characteristics through:

1. Upgrading the synthesis with controlled addition of surfactants and improving the foaming methods using the system BTDA:2,6DAP:TDA of Resin No. 29.
2. Controlled addition of short fibers using the system BTDA:2,6DAP: 4,4'DADPS of Resin No. 15.
3. Controlled addition of fillers using the system BTDA:2,6DAP:4,4'DADPS of Resin No. 25.
4. Combination of the above parameters.

A total of 19 copolyimides, prepared in Task III of the program and reported in Table IV, were evaluated.

In general, the addition of fillers or fibers was shown to have an adverse effect on mechanical properties of polyimide foams. The fillers were compatible with the polyimide foams (except aluminum which exhibited segregation during foaming) and were blended with the polyimide precursor during the synthesis process.

The fibers were easily dispersed in the liquid polyimide resins; however, separation occurred during the grinding process, except for carbon and graphite fibers which became pulverized. Low concentration of a surface active agent, L-5420, produced the most homogeneous foam structures, but the mechanical properties of the foams were adversely effected. Table V shows the effect of various additives, fillers and fibers to tension and elongation of the polyimide foam systems of Resins No. 29, 25 and 15.

TABLE IV

POLYIMIDE FOAM PRECURSORS

Resin No.	Polyimide Precursor	Molecular Ratio	Ester	Additive	% Volatile	Type of Foam
29-7	BTDA:2,6DAP:TDA	1:0.85:0.15	Ethyl	0.1% L-5420	--	Resilient - fine cellular structure
29-8	BTDA:2,6DAP:TDA	1:0.85:0.15	Ethyl	0.2% L-5420	--	Resilient - fine cellular structure
29-9	BTDA:2,6DAP:TDA	1:0.85:0.15	Ethyl	0.3% L-5420	19.3	Moderately resilient
29-10	BTDA:2,6DAP:TDA	1:0.85:0.15	Ethyl	0.5% L-5420	19.05	Moderately resilient
29-11	BTDA:2,6DAP:TDA	1:0.85:0.15	Methyl/ethyl/propyl	0.2% L-5420	18.54	Moderately resilient
29-12	BTDA:2,6DAP:TDA	1:0.85:0.15	Methyl/ethyl	0.2% L-5420	18.15	Moderately resilient
29-13	BTDA:2,6DAP:TDA	1:0.85:0.15	Ethyl	0.15% L-5420	19.27	Resilient - fine cellular structure
25-2	BTDA:2,6DAP:4,4'DADPS	1:0.85:0.15	Ethyl	15% Al powder	18.57	Resilient - fine cellular structure
25-3	BRDA:2,6DAP:4,4'DADPS	1:0.85:0.15	Ethyl	15% TiO_2	18.21	Brittle foam
25-4	BTDA:2,6DAP:4,4'DADPS	1:0.85:0.15	Ethyl	2% Vulcan XC-72	19.58	Resilient - fine cellular structure
25-5	BTDA:2,6DAP:4,4'DADPS	1:0.85:0.15	Ethyl	5% Graphite powder	--	Resilient - fine cellular structure
25-6	BTDA:2,6DAP:4,4'DADPS	1:0.85:0.15	Ethyl	1% Cab-0-Sil	20.5	Moderately brittle foam
25-7	BTDA:2,6DAP:4,4'DADPS	1:0.85:0.15	Ethyl	5% $Al(OH)_3$	21.7	Brittle foam
15-2	BTDA:2,6DAP:4,4'DADPS	1:0.75:0.25	Ethyl	3% Kevlar Fibers	--	
15-3	BTDA:2,6DAP:4,4'DADPS	1:0.75:0.25	Ethyl	3% Nomex Fibers	--	
15-4	BTDA:2,6DAP:4,4'DADPS	1:0.75:0.25	Ethyl	3% Kynol Fibers	--	
15-5	BTDA:2,6DAP:4,4'DADPS	1:0.75:0.25	Ethyl	3% Graphite Fibers	17.3	Resilient - fine cellular structure
15-6	BTDA:2,6DAP:4,4'DADPS	1:0.75:0.25	Ethyl	3% Carbon Fibers	19.18	Resilient - fine cellular structure
15-7	BTDA:2,6DAP:4,4'DADPS	1:0.75:0.25	Ethyl	3% Fiberfrax	19.19	Resilient - fine cellular structure

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TABLE V

EFFECT OF FILLERS IN TENSILE PROPERTIES

Resin No.	Filler and %		Tension $N/m^2 \times 10^{-3}$	Elongation
25	None		91.0	38.6
25	Graphite	5%	96.5	25.3
25	Carbon	1%	41.3	23.7
25	Carbon	2%	24.0	23.6
25	Alum. powder	15%	22.0	21.4
25	Cab-o-syl	1%	33.0	20.0
25	$Al(OH)_3$	5%	35.8	16.0
25	TiO_2	15%	27.5	5.7
15	None		57.8	32.4
15	Fiberfrax	3%	54.4	14.7
15	Carbon Fiber	3%	52.4	12.5
15	Graphite Fiber	3%	82.7	10.0
15	Nomex Fiber	3%	22.7	13.3
15	Kynol Fiber	3%	Broke upon stamping	
29	None		113.7	30.5
29	0.3% L-5420		59.2	14.3
29	0.20% L-5420		67.0	8.6
29	0.15% L-5420		71.6	16.9
29	0.5% L-5420		Broke upon stamping	

4.5 FOAMING OF POLYIMIDE FOAMS - THEORETICAL DISCUSSION

Most thermoplastics and thermosetting resins can be processed into foamed plastic with density characteristics dictated by the end use of the finished foams and determined by formulation and foaming processes.

Methods of foaming fall within the boundaries of three basic procedures (Ref. 1):

1. Mechanical frothing.
2. Dissolving a gas or low boiling point liquid in the resin.
3. Release of by-products during the course of a reaction.

In our specific case, the procedure belongs to the third category whereby an increase in temperature is accompanied by dehydration and dealcoholation, resulting in the rise of bubbles, beyond super saturation limit, and causing the molten phase to expand in the form of foam.

It is theoretically possible to obtain a wide spectrum of rigidity (or flexibility) in the final foam by varying the functionality or reactivity of the reactants. The reason for this is that change in the functionality of reactants varies the number of branch points and the distance between the branch chains. In general, the greater the functionality, the larger the number of branching sites, and hence the mobility of polymer chains is lowered. Thus the rigidity is increased. By the same token, increase in reactivity of the monomers yields less flexible structure since the polymerization rate does not allow proper expansion of the cells.

As previously stated in the Experimental Procedures of Section 3, the monomeric polyimide precursor is subject to deliberate process control depending on the end use of the finished foam. To prepare a resin which can be foamed to a flexible and resilient structure, it is imperative that volatile concentrations be decreased below 20 percent. This is done by heating the resin in a circulating air oven at 377°K (220°F) and results in an increase of the melting point. At this stage, the resin has no true softening point since dehydration and dealcoholation occur with heat and cause foaming and cyclization to form a polyimide. Extensive cyclization does not begin until the temperature of 533°K (500°F) is attained but the cellular structure will form at temperatures as low as 422°K (300°F). Thus the preparation of foamable resin can be monitored by the increase in softening point range with heating. From the viewpoint of good foaming procedures, it is advisable to keep the softening range of resin below the temperature where extensive polyimide formation will occur [533°K (500°F)]. In this way the volatiles will come out of the molten phase facilitating the rise of bubbles beyond super saturation limit. Thereafter imidization will occur by heating to cause the removal of H_2O and alcohol.

4.5.1 Mechanism of Foam Formation

Several stages are involved in the formation of foam. In the preliminary stage, the foam precursor melts around 408-418°K (275-293°F). Extensive amidization takes place around 425°K (306°F) accompanied by dehydration and dealcoholation generating gas in solution in liquid phase. The gas becomes dispersed in the liquid phase until its saturation limit in solution is reached, then becomes super saturated and finally comes out of solution in the form of bubbles. Although it may not fit the scientific description for nucleation, the formation of bubbles in an example of nucleation, the process of generating a new phase. When the bubble is first formed, it is spherical in shape surrounded by a viscous liquid phase since extensive imidization has not begun. As dehydration and dealcoholation progress, bubbles rise if concentration exceeds super saturation limit, or the bubbles may diffuse from the liquid phase into existing bubbles causing them to become larger. The bubbles may also diffuse to external surfaces. The three processes are competitive depending on the number of bubbles formed, amount of volatiles available, the rate at which gas becomes available, and the volume to surface relationships. As more bubbles form, and the bubbles grow, the foam volume increases - thus the liquid phase becomes progressively thinner and distance between the bubbles decrease. As the liquid-viscous phase becomes less than 25 percent of the volume of the foam, bubbles eventually lose their spherical shape and assume a structure bounded by several membranes (Ref. 2). When no additional gas is available, bubbles can grow only by diffusion of gas from small bubbles into large bubbles, by coalescence, or because of exothermic expansion of gas in bubbles. The rates of these processes depend on a number of variables, the most important being the temperature and viscosity of the viscous-phase. The completion of dehydration brings about the final change from the liquid-to-viscous to a plastic gel of high viscosity and finally to a linear polymer of viscoelastic nature. At this time the foam is cured.

4.5.2 Particle Size and Foam Resin Thickness

As previously stated, the polyimide precursor has a softening temperature range of 408-418°K (275-293°F). Since the initial foaming temperature adopted in the process is in the range of 561°K (550°F), it is apparent that the precursor undergoes melting before the amidization and imidization stages. It is assumed from this thermal consideration that particle size of the monomeric precursor would have no effect on the final cell structure of the foam. However, non-uniformity with large deviation in particle size will cause different concentration gradient of volatiles at different coordinates of the foam, resulting in large deviations in the dimensions and number of bubbles. This gives rise to non-homogeneous distribution of density in the foam. It has been found that uniformity of coating is very important in making large specimens.

Samples were made with 1.5, 2.5, 3.0, 4.0 mm (50, 100, 120 150 mil) thickness of coating. Three mm coating (120 mil) gave the best results in terms of the rise and cell structure of foam. Theoretically, the thinner the coating thickness, the better is the foam, since the rising bubbles have least resistance to growth.

4.5.3 Volatiles

The most important factor involved in producing foams with good cellular structure is the control of the percent volatiles. Below the critical percent volatile content (this critical limit varies from system to system) no foaming will take place regardless of the temperature at which the system is heated, but excess of volatiles results in poor foam structure with poor mechanical properties. It appears that volatile contents in excess of 20 percent give foam samples with brittle structure and dark spots. The volatiles in the present system are due to the esterification agent (ethanol) and to the water evolved during the condensation polymerization. The lack of foam formation below a critical volatile content is attributed to the fact that polymer formation takes place with a low gas evolution which is insufficient to foam the mass. On the other end, an excess of volatiles in the polyimide precursor tends to produce rupture of a great number of bubbles in which the gas becomes trapped and results in high foam rise, large cellular structure and low foam density.

4.5.4 Surfactants

The resistance to volatile flow greatly affects cell structure of the foam. Dealcoholation and dehydration takes place during amidization and imidization. This results in the formation of a large number of gas bubbles. The bubbles grow and stabilize as the liquid matrix increases in viscosity and finally solidify as a continuous phase. Hence the colloidal aspects of bubbles is controlled by factors such as surface tension, viscosity, and dispersion of bubbles.

To disperse a given volume of gas in a unit volume of liquid, the amount of energy required is

$$\Delta F = \gamma A$$

where

γ = surface tension

A = interfacial area.

This relation suggests that greater increase in the free energy of the system is required to produce fine cullular structures and lowering the surface tension of the liquid, e.g., by the addition of surfactant, will reduce the free energy requirements for fine cell structure.

The progress in diffusion of gas from the liquid phase into the cell changes the cell size of the foam. At equilibrium, the difference between the gas pressure in a spherical bubble and gas pressure in a surrounding liquid, is given by

$$\Delta P = \frac{2\gamma}{R}$$

where

R = radius of bubble.

It is obvious from the above relation that the larger is the radius of the bubble, the lower the pressure difference. Thus, pressure in liquid phase being constant, it is also evident that smaller bubbles have larger gas pressure than a larger bubble. The difference in gas pressure between a large bubble and a small bubble is given by

$$\Delta P = 2\gamma \left[\frac{1}{R_1} - \frac{1}{R_2}\right]$$

where

$R_1 < R_2$

It is evident from the above theoretical consideration that gas will diffuse from smaller bubbles into the large bubble, and that while the small bubbles tend to disappear with time, the large bubbles grow with time. Thus, in a polydisperse system, while the average bubble size increases with time, the number of bubbles decreases and this process gives rise to large cell size. It will be noted that low value of surface tension gives lower difference in pressure between bubbles of different sizes, thus surfactants will improve the bubble stability giving larger number of cells and lower average size of cells. The cellular structure obtained in this latter case is the finest and best, but the foams produced lack resiliency, elasticity and resistance to mechanical breakdown.

4.5.5 Cell Structure and Major Properties Relationships

Foam is a mass of bubbles or cells formed by the polymer which is distributed between the walls of the bubbles and the lines where bubbles intersect. In an open cell flexible foam, at least two walls in each cell must be ruptured for gases to pass freely through the foam during the foaming process to form the most ordered structure.

4.5.6 Tensile, Elongation and Tear Strength

In general, the finer the cell size and the higher the density, the greater is the tensile strength. The reason for the effect of cell size on tensile strength is found in the strength of individual line of intersection between the cells or strands. The foam tensile strength can be calculated from the strength of a single strand and the number of strands per square inch.

$$\text{Tensile Strength} = \frac{\text{Force}}{\text{Area}} = \frac{\text{Force}}{\text{Strand}} \times \frac{\text{Strands}}{\text{Inch}^2}$$

In determination of tensile strengths, actual values are lower than the value determined by above considerations. It is believed that such a large discrepancy, normally found, is due to unequal distribution of forces among the strands, causing some of the strands to break before maximum load is applied to the rest.

A further consequence of the properties of the walls is that, at low elongation characteristics, all walls break, propagating failure through the structure.

Tear strength is related to pore size and depends on tensile stress and elongation. High tensile strength foams have higher tear strength characteristics.

4.6 EXPERIMENTAL FOAMING STUDIES

A series of controlled heating rate tests were conducted to establish the parameters which affect the foaming of selected polyimide precursors. In all tests a 0.25 cm (0.1 in.) layer of powder was spread on an instrumented (Type K thermocouple) aluminum plate and melted at various temperatures and various rates of heating. Heating power was provided by a 10 kW Tocco induction motor generator set, acting through a steel susceptor plate on which the aluminum sample plate rests. Upon melting of the resin at the selected heating rate and temperature the aluminum plate was immediately transferred to a pre-heated forced air oven for foaming and, in some cases a second oven, for curing. Table VI gives particulars of the various cycles investigated and observations as to the character of the foams.

The most significant observation is the general superiority of the No. 29-4 precursor, containing no surfactant, to the 29-8, containing 0.2 percent. Even the best of the foams made from surfactant-containing precursors exhibited crumbling in repeated squeezing cycles, and were judged less suitable for the intended application. Stiffness of the foam was seen to be an inverse function of the cell size. The source of blow holes in the foam is seen to be bubbling of the melted precursor due to too rapid temperature rise and/or too high a temperature. Maximum limits established were approximately 503°K (446°F) at a heating rate of 35°K (63°F) per minute or 533°K (500°F) at 18°K (32°F) per minute. Lower melting and curing temperatures tend to produce a smaller cell foam which is tougher but less resilient.

TABLE VI

FOAMING TESTS

Run No.	Precursor	Melting Cycle			Foaming Cycle			Observations
		Time (min.)	Temperature		Time (min.)	Temperature		
			°K	°F		°K	°F	
1	29-8 0.2%-L-5420	6.8	533	500		561	550	Easily torn. High, heterogeneous rise. Large cells. Brittle. Melted resin bubbled at 505°K (450°F).
2	29-8 0.2% L-5420	6.0	500	441	15	561	550	Even, high rise. Small cells. Homogeneous but 1 cm thick hard skin on upper side. Easily torn.
3	29-8 0.2% L-5420	6.0	500	441	15	589	600	Similar to #2 but with less skin on upper side. Larger cell size.
4	29-8 0.2% L-5420	3.8	500	441	15	589	600	Melted resin bubbled at 450°K (350°F). Foam similar to #2 but tougher. Medium cell size. Large blow holes at bottom.
5	29-8 0.2% L-5420	3.4	450	350	15	589	600	Similar to #4 but without blow holes. Tougher but less resilient.
6	29-8 0.2% L-5420	13.8	533	500	15	589	600	Melted resin did not bubble. No blow holes. Large cell size. Easily torn. Good resilience.
7	29-8 0.2% L-5420	6.5	477	400	3 +15	533 589	500 600	Small pore size. Tougher but less resilient.
8	29-8 0.2% L-5420	6.2	450	350	3 +15	533 589	500 600	Small pore size. Similar to #5.
9	29-8 0.2% L-5420	4.5	436	325	3 +15	547 589	525 600	Small cell size. Toughest foam of this compositiom but only moderately resilient.
10	29-8 0.2% L-5420	4.5	436	325	3 +15	505 589	450 600	Small cell size. Similar to #9.
11	29-8 0.2% L-5420	4.5	436	325	3 +3 +15	455 455 589	360 360 600	Foam fell after first 3 minutes at 455°K (360°F). Small cell size. Moderately resilient and tough.
12	29-4 0.0% L-5420	4.0	436	325	6 +15	455 589	360 600	Very stiff, but not brittle foam. Low rise. Small cell size.
13	29-4 0.0% L-5420	4.0	436	325	15	589	600	Less stiff than #12. Good rise. Small cell size.
14	29-4 0.0% L-5420	10.0	505	450	3 +15	477 589	400 600	Very small cell size. Low rise. Stiffness between #12 and #13. Poor resilience.
15	29-4 0.0% L-5420	4.0	436	325	10 +15	450 589	350 600	Small cell size. Low rise. Brittle.
16	29-4 0.0% L-5420	6.0	477	400	5 +15	533 589	500 600	Medium rise. Small cell size. Marginally brittle.
17	29-4 0.0% L-5420	6.0	477	400	15	589	600	High rise. Medium small cell size. Resilient, tough foam. Best of all samples.

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Oven heating tests were also conducted to establish the process parameters for fabrication of larger size foam samples. In all tests, a 0.25 cm (0.1 in.) layer of the powder was spread over an area of 15 by 30 cm (6 by 12 in.) on an aluminum foil placed over a 0.15 cm (0.063 in.) aluminum plate and foamed at various temperatures in a circulating air oven. In the last stages of this work, this technique was modified by using open-weave glass cloth for easier release of volatiles.

Foam made from surfactant-containing precursors exhibited the best foam rise and best cellular structure and seemed to be less sensitive to process and foaming conditions. However, these foams possessed low resiliency characteristics and exhibited crumbling in repeated squeezing cycles.

Foam produced from precursors containing no surfactant were found to be more sensitive to process conditions, foaming temperature and heating rates. Lower foaming temperatures [477-505°K (400-450°F)] with curing at 589°K (600°F), produced foams with small but homogeneous cell size, which exhibited good resiliency and high stiffness. At higher foaming temperature, 533-561°K (500-550°F) with curing at 589°K (600°F), the cellular structure became more irregular, but the foam exhibited high resiliency and high flexibility. Foam properties were found to be markedly affected by B-staging processes. If the B-staging is conducted at too high a temperature, the resulting foam tends to be more brittle and has an irregular cell structure. This has been found to be particularly true for the system of Resin No. 29 and less for that of Resin No. 25.

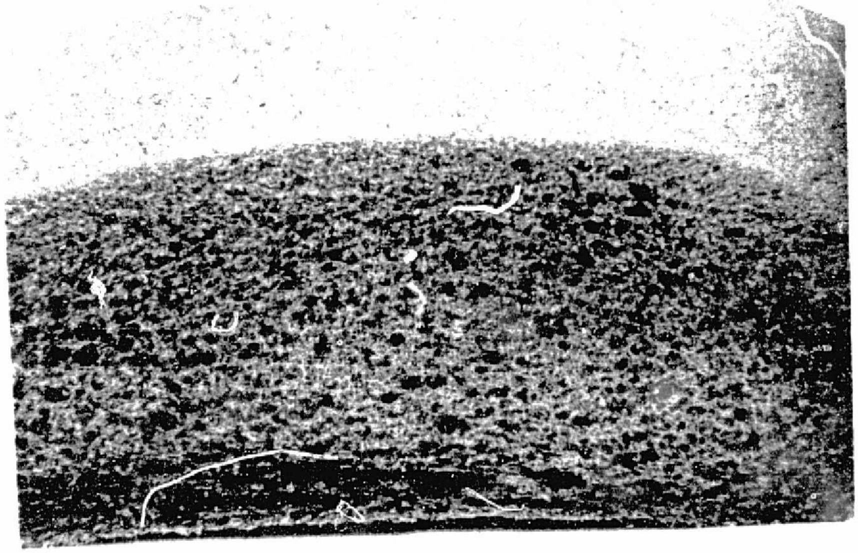
Figure 16 is a series of photographs of foams produced at temperatures incrementally increased from 477°K (400°F) to 561°K (550°F). The same precursor, Resin No. 29, was used for all samples. Table VII shows the effect on properties of cell size changes, as a function of temperature. The relationship is also presented graphically in Figure 17, second or third order polynominal curve fits of the data, all having correlation coefficients of 0.98 or higher.

4.7 CHARACTERIZATION OF FINAL TWO CANDIDATES

The characterization of the final two candidates, Foams No. 25 and 29, was conducted using large foam specimens only, prepared as described in Section 5, Fabrication of Large Specimens.

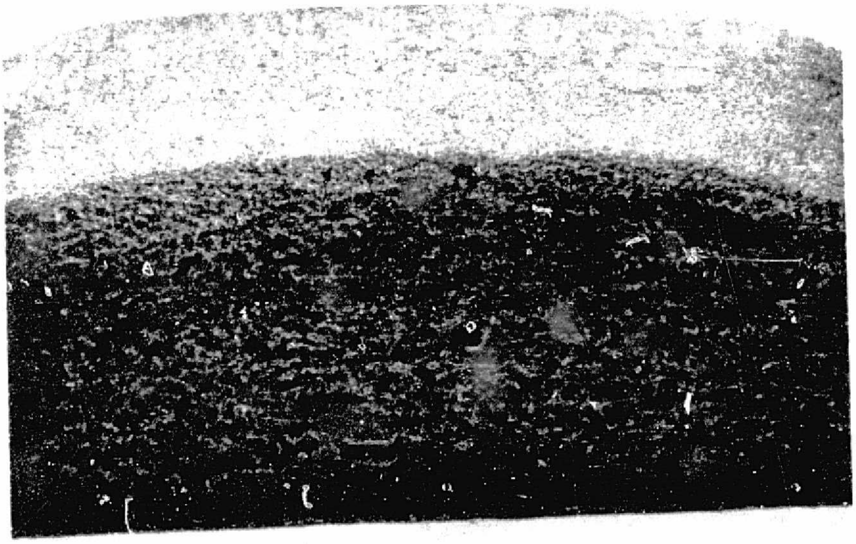
4.7.1 Fatigue Testing

One sample each of Foams 25 and 29 was subjected to fatigue testing. Preliminary indentation deflection loads, measured on an Instron Universal tester were as follows:



477°K (400°F),
15 minutes

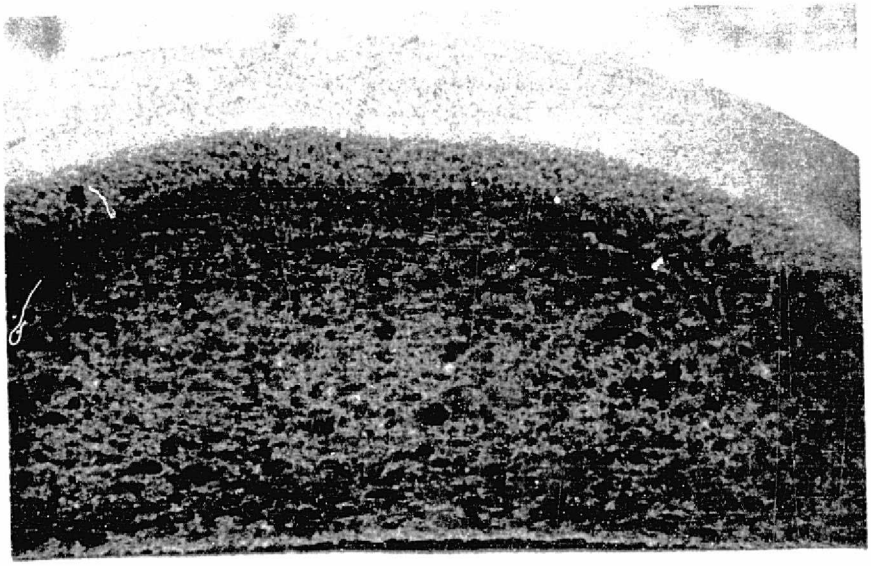
589°K (600°F),
15 minutes



491°K (425°F),
15 minutes

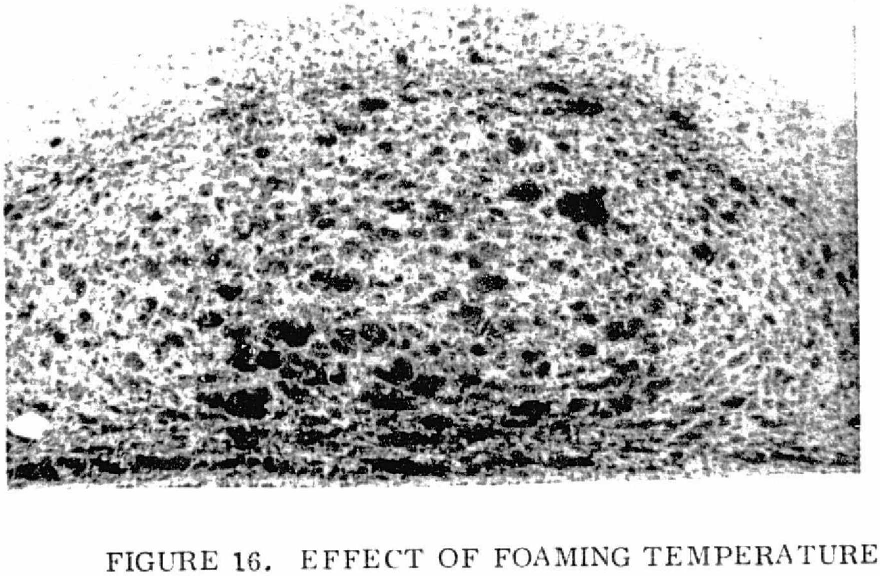
589°K (600°F),
15 minutes

FIGURE 16. EFFECT OF FOAMING TEMPERATURES ON CELLULAR STRUCTURE OF RESIN NO. 29 (Sheet 1 of 3)



505°K (450°F),
15 minutes

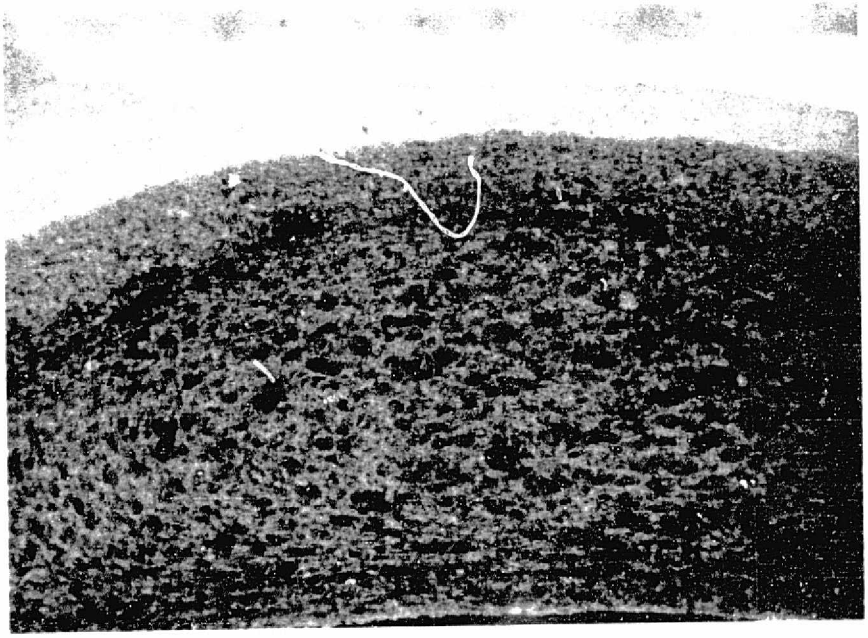
589°K (600°F),
15 minutes



533°K (500°F),
15 minutes

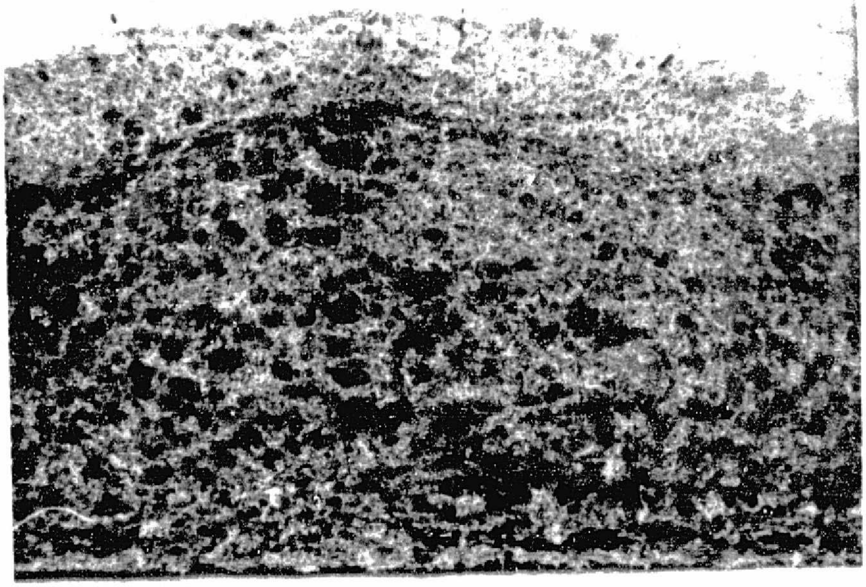
589°K (600°F),
15 minutes

FIGURE 16. EFFECT OF FOAMING TEMPERATURES ON CELLULAR STRUCTURE OF RESIN NO. 29 (Sheet 2 of 3)



547°K (525°F), 15 minutes

589°K (600°F), 15 minutes



561°K (550°F), 15 minutes

589°K (600°F), 15 minutes

FIGURE 16. EFFECT OF FOAMING TEMPERATURES ON CELLULAR STRUCTURE OF RESIN NO. 29 (Sheet 3 of 3)

TABLE VII

INFLUENCE OF FOAMING TEMPERATURE ON PROPERTIES

Foaming Temperature		Density		ILD 5.08 cm (2 in.) Diameter Circle*				Resilience
				Lbf		N		
°K	°F	Kg/M^3	lbs/ft^3	25%	65%	25%	65%	%
477	400	28.16	1.76	6.6	35	29.4	155.7	75
491	425	23.20	1.45	4.1	18	18.2	80.1	74
505	450	18.88	1.18	4.0	21	17.8	93.4	69
533	500	16.80	1.05	1.5	5.5	6.7	24.5	67
547	525	17.60	1.10	1.9	5.9	8.5	26.2	66
561	550	16.32	1.02	2.2	7.5	9.8	33.4	66

* Smaller area used to accommodate sub-size samples

Sample	Original Thickness		Indentation Load Deflection			
			N		Lbf	
	cm	in.	25%	65%	25%	65%
F-399	4.45	1.75	137.8	1174.2	31	264
F-406	3.80	1.50	164.5	731.7	31	192

Fatigue cycling was conducted at the laboratory of General Tire and Rubber Co., Orange, California, on their machines. The apparatus and procedure was identical to that prescribed by ASTM D-1564, Suffix H, Procedure B, except that flexing was conducted at the rate of 40 cycles per minute, slightly faster than the specified 28 ± 2.

Both samples suffered significant deterioration in less than the required 20,000 cycles and the test was discontinued at about 6700 cycles for Resin No. 25 and about 2000 cycles for Resin No. 29. The extent of the structural breakdown, seen in Figure 18 was such that post-test ILD measurements could not be made.

4.7.2 Density Tests

This method covers determination of the density of the polyimide foams by calculation from weight and volume of regularly shaped large specimens.

Three specimens of Resin No. 25 and three specimens of Resin No. 29 were tested. Tests were made in accordance with ASTM Designation D-1564, Suffix W. The results are summarized in Table VIII.

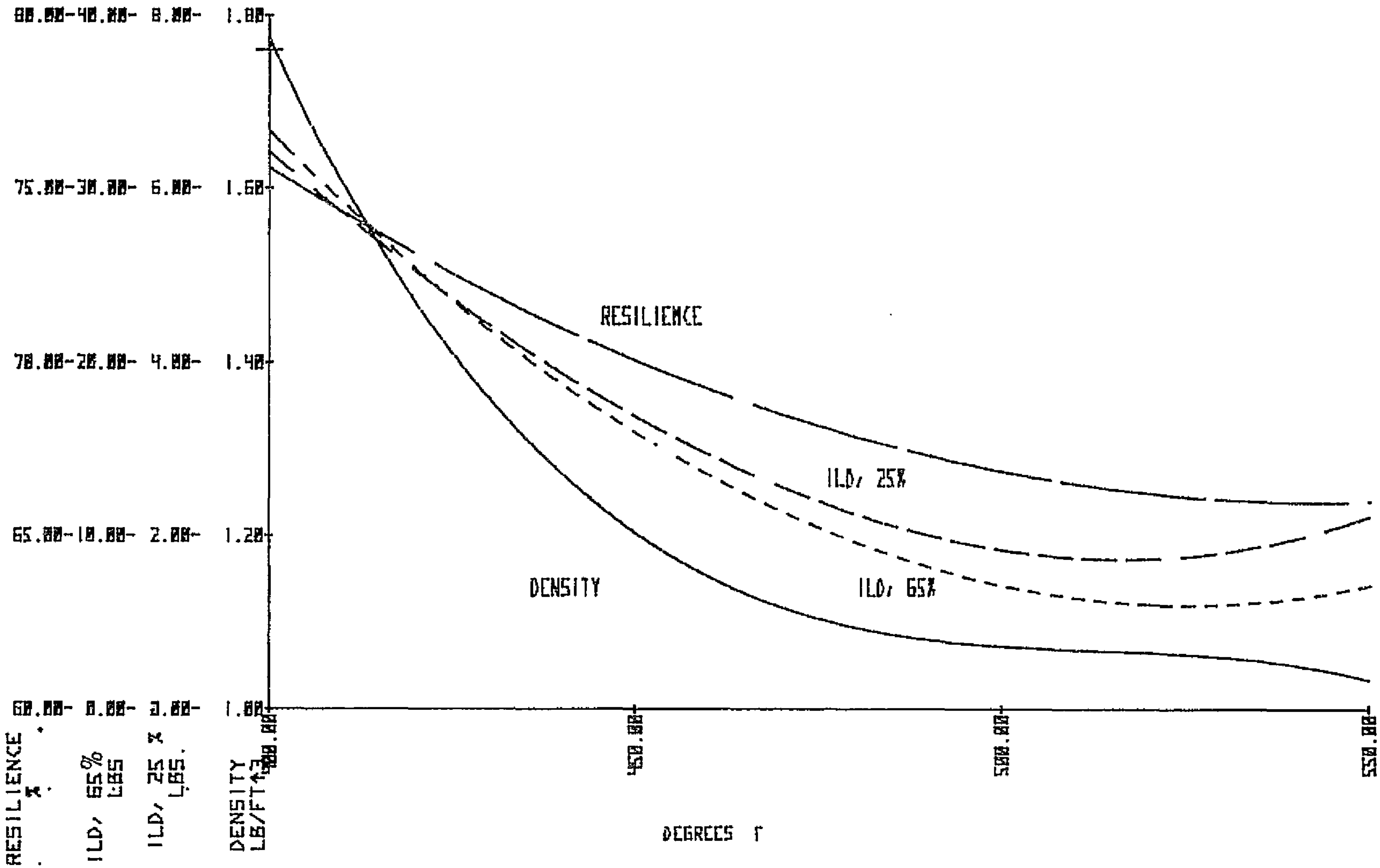
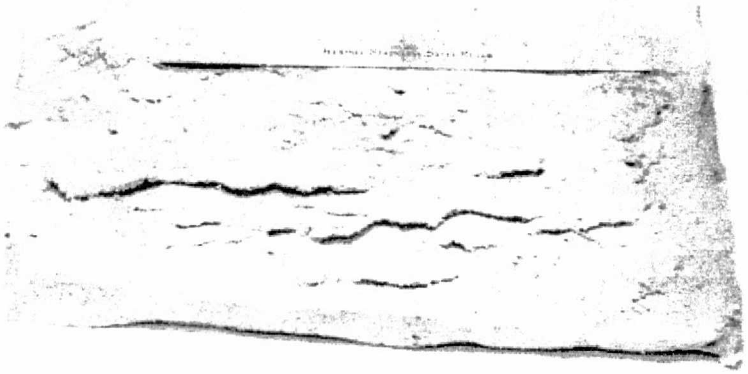
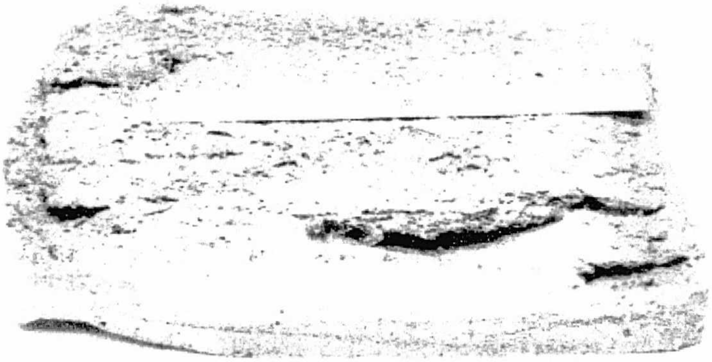


FIGURE 17. INFLUENCE OF FOAMING TEMPERATURE ON PROPERTIES



A. Foam No. 25 after 6700 cycles



B. Foam No. 29 after 2000 cycles

FIGURE 18. DELAMINATION OF FOAM SAMPLES IN FATIGUE TESTS

TABLE VIII

FOAM DENSITY

	lb/ft^3	Kg/m^3
Resin No. 25		
F-415	1.13	18.08
F-400	1.27	20.32
F-400	1.40	22.40
Average	1.27	20.27
Resin No. 29		
F-432	1.40	22.40
F-430	1.52	24.32
F-426	1.32	21.12
Average	1.41	22.61
Goal	2.5 max.	40.0 max.

4.7.3 Constant Deflection Compression Set Test

Three samples each of foams prepared from Resin No. 25 and Resin No. 29 were cut on a bandsaw to the configuration and dimensions described in ASTM D-1564, Method B. Tests were made according to the same procedure by deflecting the foam specimens at 50 and 90 percent of their thickness and reporting the compression set expressed as a percentage of the original thickness. The results are summarized in Table IX.

4.7.4 Tensile Strength and Elongation

Three specimens each of Foam No. 25 and No. 29 were prepared by stamping out large sheet material (30 x 45 x 2.5 cm [12 x 18 x 2 in.]) using the die shown in Figure 7. The tensile test specimens and configuration are as described in ASTM Designation D-1564, Suffix T, covering standard methods of testing flexible urethane foams and tests made in accordance with the same procedures using an Instron Tester Model TTD.

The ultimate elongation of the specimens was obtained by a double exposure photographic technique by measuring the travel of two steel pins inserted in the

TABLE IX

FOAM COMPRESSION, PERCENT PERMANENT SET

	50 Percent	90 Percent
Resin No. 25		
F-394	19.8	37.0
F-394	17.0	37.0
F-395	10.0	37.0
Average	15.6	37.0
Resin No. 29		
F-379	9.5	40.0
F-396	5.0	30.5
F-379	5.0	38.4
Average	6.5	36.3
Goal	7.0 max.	12.0 max.

specimens at 2.5 cm (1.0 in.) distance. The distance of the pins at the start of the test, the travel produced by the application of the load and their final position at break was measured to obtain the elongation of the specimens. The results are summarized in Table X.

4.7.5 Tear Strength

Tear specimens were cut from foam sheets 30 x 45 x 2.5 cm (12 x 18 x 1 in.) and slit with a bandsaw to the configuration and dimensions described in ASTM Designation D-1564, Suffix G. Tests were made in accordance with the same procedures. The results are summarized in Table XI.

4.7.6 Indentation Load Deflection Tests

Three test specimens each of Foam No. 25 and No. 29 were cut to the configuration and dimensions described in ASTM Designation D-1564, Method A. Tests were made in accordance with the same procedure and results reported as pounds-force per 50 in.^{2} or newtons per 3.2 dm^2 required for 25 and 65 percent indentation. The results are reported in Table XII.

TABLE X

TENSILE STRENGTH AND ELONGATION

	psi	N/m^2	%
Resin #25			
F-401	11.2	77.20×10^3	24.5
F-444	9.8	67.56×10^3	18.5
F-395	8.4	57.90×10^3	16.5
Average	9.8	67.56×10^3	19.8
Resin #29			
F-423	12.2	84.1×10^3	23.7
F-424	15.8	108.9×10^3	29.2
F-423	11.4	77.2×10^3	21.8
Average	13.1	90.1×10^3	24.9
Goal	12 Min.	82.7×10^3 Min.	80.0 Min.

TABLE XI

TEAR STRENGTH

	Lbs. - Inch	N/m
Resin #25		
F-394	0.94	165
F-98	1.05	184
F-376	0.93	163
Average	0.97	171
Resin #29		
F-371	1.03	180
F-377	1.06	186
F-404	1.00	175
Average	1.03	180
Goal	1.0 Min.	175 Min.

TABLE XII

INDENTATION LOAD DEFLECTION

	Pound-Force/50 in.^{2}		N/3.2 dm^2	
	25%	65%	25%	65%
Resin #25				
F-452	32.0	342.0	142.3	1521.2
F-401	35.0	149.0	155.6	662.7
F-399	31.0	264.0	137.8	1174.2
Average	32.7	252.0	145.3	1119.4
Resin #29				
F-380	20.0	95.0	88.9	422.5
F-406	37.0	192.0	164.5	731.7
F-408	32.0	237.0	142.3	632.9
Average	29.7	175.0	131.9	595.7
Goal	25-35	65-90	111-155	289-400

4.7.7 Steam Autoclave

This test consists of treating the foam specimens in an autoclave, to evaluate the effects of high pressure steam on physical properties of the foam.

Three specimens each of Resin No. 25 and No. 29 were cut to 50 x 50 x 25 mm (2 x 2 x 1 in.), and tested in steam autoclave in accordance with the precedure described in ASTM D-1564, Condition "B". After 5 hours of exposure period, the specimens in the autoclave were found to be distintegrated, and no further testing was possible.

4.7.8 Corrosion Test

This test determines the corrosive nature of foam specimens on aluminum components. The test was conducted in accordance with ASTM Designation B-117 which replaces Federal Test Method Standard No. 151, Method 811.

Four aluminum panels 75 x 50 x 1.6 mm (3 x 2 x 0.064 in.) were cleaned, sand blasted and coated with P-527-66 epoxy polyimide primer (Andrew Brown Co., Los Angeles, CA) followed by a white acrylic lacquer. The panels were then over-coated with a clear acrylic lacquer and dried for 72 hours before testing.

Three specimens each of polyimide foam prepared from Resin No. 25 and No. 29 were used and each specimen supported between two coated aluminum panels in the form of sandwich and held tight by stainless steel fastners. The specimens were mounted in the salt spray chamber approximately 30 degrees from the vertical and nearly parallel to the direction of flow of the fog at an average temperature of 368 ± 5°K (203 ± 9°F). The exposure period was 14 days. A careful and immediate examination for the extent of corrosion of the aluminum panels in contact with the foam specimens was made after this exposure period. The examination showed no sign of corrosion, spotting or discoloration.

4.7.9 Dry Heat

This test consists of exposing foam tensile specimens in an air-circulating oven at 413°K (284°F) and observing the effect on tensile properties of the foam.

The test was carried out as described in ASTM D-1564, Suffix A, and the test specimens prepared to the dimensions and configuration described in the same procedure. Three specimens each of Resin No. 25 and No. 29 were tested by exposing them to the above reported temperature conditions for a period of 22 hours and the change of mean tensile strength of unexposed and exposed specimens recorded. The results are summarized in Table XIII.

4.7.10 Resilience Test - Ball Rebound

This test determined the resilience of foams by measuring the capacity of the material to absorb energy in the elastic range, and to return this energy during the recovery from the deformation. The ball rebound test was carried out according to the procedure described in ASTM Designation D-1564, Suffix B, using a tester fabricated and calibrated in accordance with the same procedure. Three specimens each of foams derived from Resin No. 25 and No. 29 were tested and the results summarized in Table XIV.

4.7.11 Oxygen Index

This method determines the relative flammability of the foams by measuring the minimum concentration of O_2 in a flowing mixture of O_2 and N_2 that will just support combustion.

The test apparatus for this evaluation was prepared (75 ID x 450 mm H) as described in ASTM Designation D-2863. Five specimens each of Resin No. 25 and No. 29 were tested. No unusual behavior during burning was noticed. Dripping, bending, and smoking were found to be absent. The results are summarized in Table XV.

TABLE XIII

DRY HEAT TEST

	Tensile Strength			
	Exposed		Unexposed	
	psi	$N/m^2 \times 10^3$	psi	$N/m^2 \times 10^3$
<u>Resin #25</u>				
F-450	10.72	73.88	11.2	77.19
F-444	12.80	88.21	9.8	67.54
F-395	7.15	49.28	8.4	57.89
Average	10.2	70.30	9.8	67.54
Percent Change	4.0% (Increase)			
<u>Resin #29</u>				
F-423	12.92	89.04	12.2	84.08
F-429	12.0	82.70	15.8	108.89
F-423	12.2	84.08	11.4	78.57
Average	12.37	85.25	13.1	90.28
Percent Change	7.3% (Decrease)			
Goal	10.0% Decrease, Max.			

4.7.12 Smoke Density Test

This test measures smoke generating characteristics of solid materials by the attenuation of a light beam by suspended particulate matter generated from materials under both pyrolitic decomposition (smoldering) and flaming combustion within a closed chamber.

The test was carried out in accordance with NBS procedure utilizing NBS Smoke Density Chamber (Ref. American Instrument Co., Aminco Catalog No. 4-5800, Instruction No. 941). Results are obtained in terms of specific optical density.

Six specimens each of Resin No. 25 and No. 29 were used for testing purpose, three for test under flaming exposure and three for test under non-flaming (smoldering) exposure. The specimens were cut to size (76.2 x 76.2 x 13 mm) (3 x 3 x 1/2 in.) and preconditioned in accordance with NBS procedure. Furnace output irradiance was calibrated prior to each set of tests. The tests were conducted for an exposure period

TABLE XIV

RESILIENCE TEST - BALL REBOUND

	Rebound Value %
<u>Resin #25</u>	
F-415	57
F-400	52
F-412	53
Ball Rebound Resilience Value	54
<u>Resin #29</u>	
F-381	60
F-372	57
F-426	57
Ball Rebound Resilience Value	58
Goal	55 Minimum

of 20 minutes. Uncorrected specific optical density was calculated according to the formula

$$Ds = G[\log_{10} (100/T)],$$

where

Ds = specific optical density

T = % transmittance

G = geometrical factor (132)

The results are summarized in Table XVI.

4.7.13 Odor Test

Foams prepared from Resins No. 25 and No. 29 are free from any odor when inspected at room temperature and after conditioning the specimens for one hour at 344°K (160°F).

TABLE XV

OXYGEN INDEX

	Lowest Oxygen Index
Resin #25	
F-445	44
F-394	43
F-314	42
F-399	44
F-412	46
Average	43.8
Resin #29	
F-372	44
F-403	45
F-424	42
F-396	46
F-386	45
Average	44.4
Goal	40.0 Minimum

4.7.14 Toxic By-Products of Combustion

Foam produced from Resins No. 25 and No. 29 are free from chemically bound chlorine, fluorine and bromine. Furthermore the combustion products are not contaminated with these toxic products or derivitives of them. Both Resins No. 25 and No. 29 contain bound sulfur. During combustion most of the sulfur remains chemically bound in the char and is released as sulfur dioxide after prolonged exposure to intensive heat sources. The content of hydrogen cyanide in the combustion products has been found to be in the range of 1 ppm.

4.7.15 Thermal Stability

Stability was evaluated by thermogravimetric analysis (TGA) conducted by West Coast Technical Service, Cerritos, California. One sample each of Resin Foams 25 and 29 were analyzed at a heating rate of 10K° (18F°) per minute in air atmosphere. Both were stable to 673°K (752°F).

TABLE XVI

SMOKE DENSITY TEST RESULTS

	D_S Condition	
	Smoldering	Flaming
<u>Foam No. 25</u>		
F-394	0	0
F-395	0	0
F-395	0	0
Average	0	0
<u>Foam No. 29</u>		
F-416	1.1	0.5
F-416	1.0	0.7
F-416	0.8	0.4
Average	1.0	0.5
Goal	70 max.	70 max.

4.7.16 Summary of Results

Table XVII is a summary of results of all tests.

TABLE XVII

SUMMARY OF RESULTS

Property	Goal	Resin #29	Resin #25
Density			
Kg/m^3	40.0 max.	22.56	20.32
lbs/ft^3	2.5 max.	1.41	1.27
Tensile Strength			
N/m^2	82.7 x 10^3 min.	90.3 x 10^3	67.56 x 10^3
psi	12.0 min.	13.1	9.8
Elongation			
Percent	80.0 min.	23.9	19.5
Tear Resistance			
N/m	175.0 min.	181.0	171.0
lbs/inch	1.0 min.	1.03	0.976
Fatigue			
Loss I.L.D.-Percent after 20,000 cycles	20.0 max	Failure by delamination at 2000 cycles	Failure by delamination at 00 cycles
Indentation Load Deflection I.L.D.			
25%-N/3.2 dm^2	111-155	132.1	145.4
lb-force/50 in^2	25-35	29.7	32.7
65%-N/3.2 dm^2	289-400	587.5	1116.4
lb-force/50 in^2	65-90	175.0	251.0
Compression Set			
50 percent	7 max.	6.5	15.6
90 percent	12 max.	36.3	37.0
Steam Autoclave			
Loss I.D.L.-percent	20 max.	Failure by degradation	Failure by degradation
Corrosion (Aluminum)	None	No evidence	No evidence
Odor			
Room Temperature	None	Not detectable	Not detectable
344°K - 160 F	None	Not detectable	Not detectable
Dry Heat			
Loss Tensile Strength-Percent	20 max.	7.3	4.0 (increase)
Resilience			
Rebound Value	55 min.	58.0	54.0
Oxygen Index	40 min.	44.4	43.8
Smoke Density			
DMS Uncorrected			
Non-Flaming-Percent	50-70	1.0	0.0
Flaming - Percent	50-70	0.5	0.0
Toxic Products of Combustions (Tentative)			
HCl - ppm	10	None present	None present
HF - ppm	10	None present	None present
H_2S - ppm	10	None present	None present
HCN - ppm	10	1.0*	1.0*
Thermostability			
Loss at 477°K (400°F)	No loss	No Loss	No Loss

*NASA LBJ Data

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5

FABRICATION OF LARGE SPECIMENS

The following final procedures are typical of those used to prepare the copolyimide foam Resins No. 25 and 29 and the respective resilient foams.

5.1 MONOMERIC LIQUID PRECURSOR - RESIN NO. 25

Benzophenone tetracarboxylic acid dianhydride (BTDA) (322.23 g, 1.0 mole) was added to 240 ml of 2-B ethyl alcohol and 12 ml of water in a 1-liter, 3-neck flask, equipped with thermometer, mechanical stirrer and reflux condenser. After addition, the mixture was heated to reflux and refluxed until clear. The mixture was then refluxed for an additional 30 minutes to assure complete esterification of the BTDA to its half ester, and then was cooled to 343°K (158°F).

2,6 Diamino pyridine (92.84 g, 0.85 moles) and 4,4'diaminodiphenylsulfone (37.24 g, 0.15 moles) were added to the half ester solution and the mixture refluxed at 358-360°K (185-188°F) for 30 minutes. The highly viscous solution was allowed to cool to 313-323°K (104-122°F) with agitation and transferred into three 30 x 30 x 1 cm (12 x 12 x 0.4 in.) aluminum dishes for further processing.

5.2 COPOLYIMIDE FOAM RESIN NO. 25

The monomeric liquid precursor was dried to remove the excess solvent. This was accomplished by heating the syrup in a circulating air oven at 361-365°K (190-195°F) for 12-15 hours (or overnight), followed by drying in a vacuum oven at 366-377°K (200-220°F) for 60-90 minutes. Thereafter, the solid prepolymer having a melting point of 378-383°K (221-230°F) was crushed and ground. The powder resin was B-staged in a circulating air oven at 377°K (220°F) for 2 hours or until a melting point of 403-418°K (265-293°F) was obtained. The foam resin was pulverized into a powder having a maximum particle size of 297 microns (100% through 50 mesh screen) and was used to prepare foam sheets.

5.3 MONOMERIC LIQUID PRECURSOR - RESIN NO. 29

Benzophenone tetracarboxylic acid dianhydride (BTDA) (322.23 g, 1.0 mole) was added to 240 ml of 2-B ethyl alcohol and 12 ml of water in a 1-liter, 3-neck flask, equipped with thermometer, mechanical stirrer and reflux condenser. After addition, the mixture was heated to reflux and refluxed until clear. The mixture was then refluxed for an additional 30 minutes to assure complete esterification of the BTDA to its half ester, and then was cooled to 343°K (158°F).

2,6 Diaminopyridine (92.84 g, 0.85 moles) and thiodianiline (32.44 g, 0.15 moles) were added to the half ester solution and the mixture refluxed at 358-360°K (185-188°F) for 30 minutes. The highly viscous solution was allowed to cool to 313-323°K (104-122°F) with agitation and transferred into three 30 x 30 x 1 cm (12 x 12 x 0.4 in.) aluminum dishes for further processing.

5.4 COPOLYIMIDE FOAM RESIN NO. 29

The monomeric liquid precursor was dried to remove the excess solvent. This was accomplished by heating the syrup in a circulating air oven at 361-365°K (190-195°F) for 12-15 hours (or overnight) followed by drying in a vacuum oven at 350-355°K (170-180°F) for 60-90 minutes. Thereafter the solid prepolymer having a melting point of 378-383°K (221-230°F) was crushed and ground. The powder resin was B-staged in a circulating air oven at 377°K (220°F) for 2 hours or until a melting point of 403-418°K (265-293°F) was obtained. The foam resin was pulverized into a powder having a maximum particle size of 297 microns (100% through 50 mesh screen) and used to prepare foam sheets.

5.5 FABRICATION OF POLYIMIDE FOAM SHEETS - RESIN NO. 25 AND NO. 29

A typical foam specimen was made by spreading a 0.25-0.375 cm (0.1-0.15 in.) thick layer of the powder foam resin over an area of 32 x 45 cm (13 x 18 in.) on an open weave glass fabric and by foaming it in a circulating air oven at 561°K (550°F) for 15 minutes, followed by final curing at 589°K (600°F) for an additional 15 minutes. The open weave glass fabric was pealed off and the foam cut on a medium-speed friction saw to have essentially parallel top and bottom surfaces and vertical sides.

5.6 PROBLEMS IN SCALING-UP TO LARGE SPECIMENS

The polyimides studied in this program have presented considerable problems in scaling-up to large specimens largely due to low diffusion characteristics of the volatiles evolving during the condensation polymerization reaction. Problem areas during scaling-up can be broadly classified into five categories:

1. Mass and thickness effect
2. Gas evolution
3. Thermal conductivity of foams

4. Thermal gradients
5. Embrittlement of foam.

5.6.1 Mass and Thickness Effect

In polyimide foaming processes the smaller the coating thickness, the better will be the foam structure and properties. As described earlier, in the final stages of the foaming process bubbles lose their spherical shape and assume a structure bounded by several membranes. This results in irregular flow paths of volatiles which leads to increased volumes of volatiles trapped within the foam matrices. The poor diffusional characteristics of the volatiles, mainly water and alcohol, increase the chances of hydrolytic reactions, as it will be discussed later, and inhibits the final imidization of the resin. This behavior tends to produce brittle foams.

In an attempt to eliminate, or at least minimize this effect, studies were carried out to reduce the volatile content of the foam resin and to increase the degree of freedom of escape of volatiles from the bottom surface by foaming on open weave fabrics. Both approaches yielded better results.

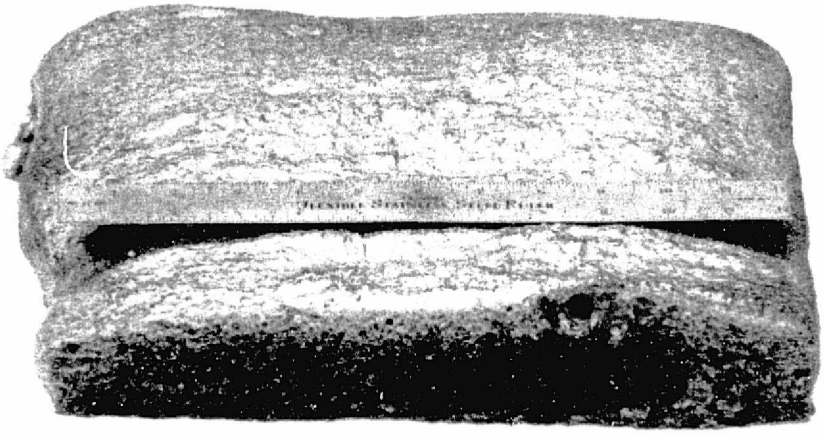
5.6.2 Gas Evolution

The volatiles initially present in the monomeric precursor range from 17 to 20 percent. Critical volatile content necessary to make polyimide foams is approximately 14 percent. Volatiles play an important part not only as they are responsible for the foaming process by producing bubbles which then stabilize to cell structure, but also in increasing the free macroscopic volume which affects the mechanical properties of the foam.

Escape of volatiles during the processing of the foams is a competitive process between diffusion of bubbles, rupture of bubbles, and growth of bubbles. In the fabrication of large specimens, devolatilization has been found to occur in an abnormal manner since bubbles rupture or stabilize before they reach the external surfaces for release. This results in brittle foam structure with poor mechanical properties, and large voids in the body of the foams. Figure 19 presents an example of the type of defect experienced in the larger samples, together with samples of Resins No. 25 and 29 which were satisfactorily foamed.

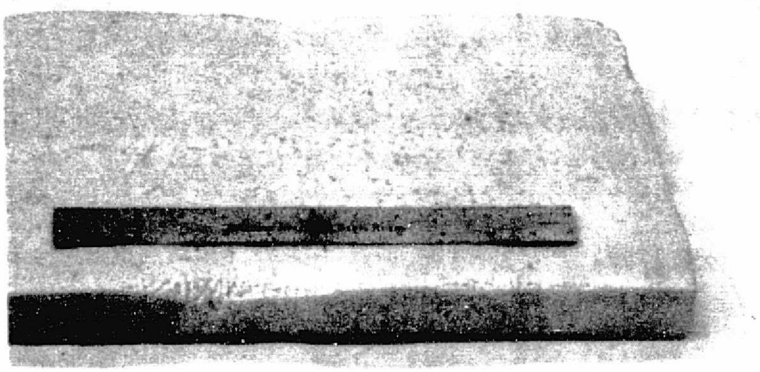
5.6.3 Thermal Conductivity of Foams

Fully cured open cell foams in general have poor thermal conductivities. The lower thermal transmission can be disastrous especially if imidization reactions are inhibited for it can cause localized heating of the reactive monomers and provide regions for degradative reactions which are chain terminating. Indeed, the thermal



a) Typical void formation in large sample of Foam No. 29

b) Satisfactorily foamed sample of Foam No. 25



c) Satisfactorily foamed sample of Foam No. 29

FIGURE 19. LARGE FOAM PANELS

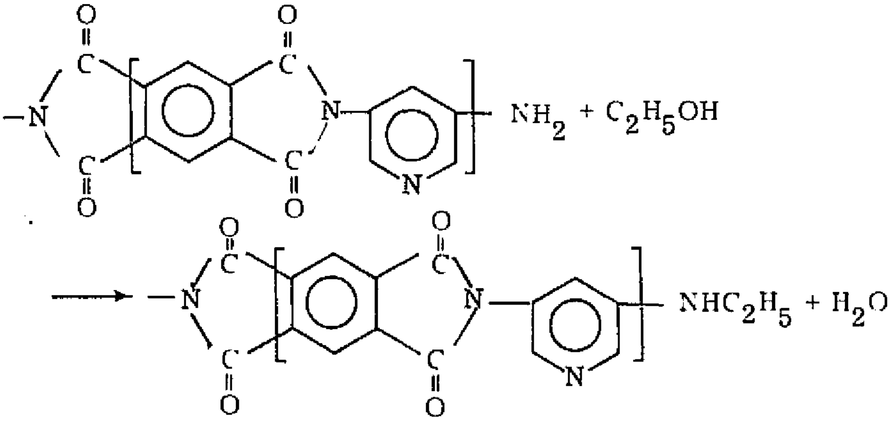
gradients formed with poor thermally conductive foam materials can only increase the volume of trapped gases because stabilization of the cells located at higher temperature regions is taking place, thus blocking the flow path of volatiles. One way to minimize this problem is to use perforated plates associated with highly porous fabric to support the coating.

5.6.4 Embrittlement of Foams

It is recognized that the unique properties of polymers - e.g., the elasticity, the strength the toughness, the flexibility, are attributable to the long chain structure of polymers. It is believed that in the fabrication of large polyimide, open cell foam specimens, the realization of high enough molecular weight may be hampered by chain-terminating reactions. These chain-terminating reactions are mainly responsible for embrittlement of the foams. Hypothetical discussions of the reactions which may be occurring is presented below.

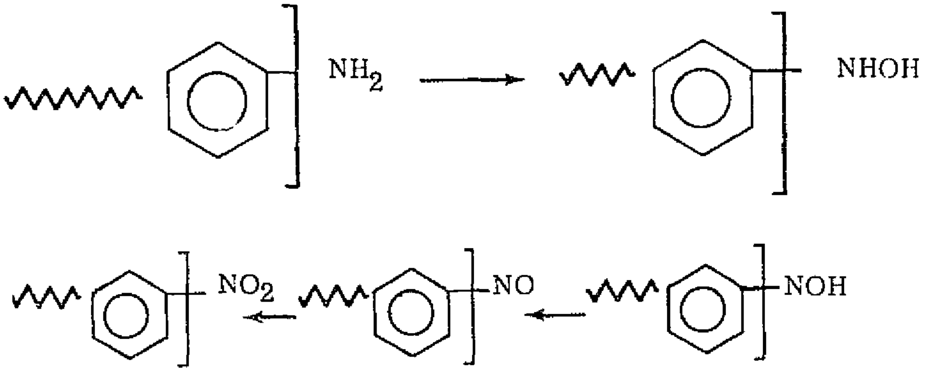
1. Secondary amines may be produced when the aromatic diamine reacts with the esterifying alcohol during abnormal foaming behavior, as shown below.

   Such a side reaction will terminate the condensation polymerization reaction with a decrease in molecular weight. The water released during the reaction of formation of the secondary amine will add to the problem by increasing the chances of hydrolytic cleavage as it will be shown later.

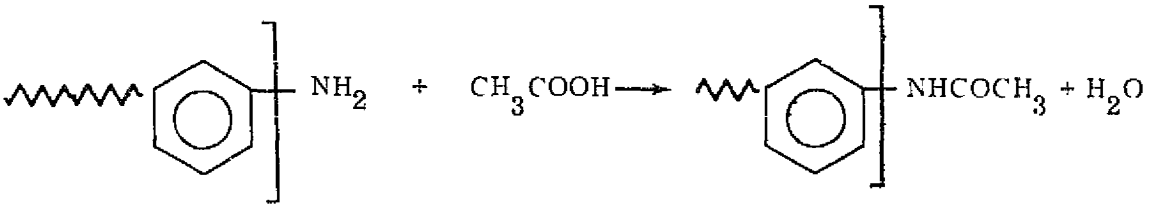


   This product cannot further enter into condensation polymerization to form a polyimide linkage.

2. Aromatic amines can be oxidized, during the abnormal foaming behavior, to produce a series of products which possess chain terminating characteristics.

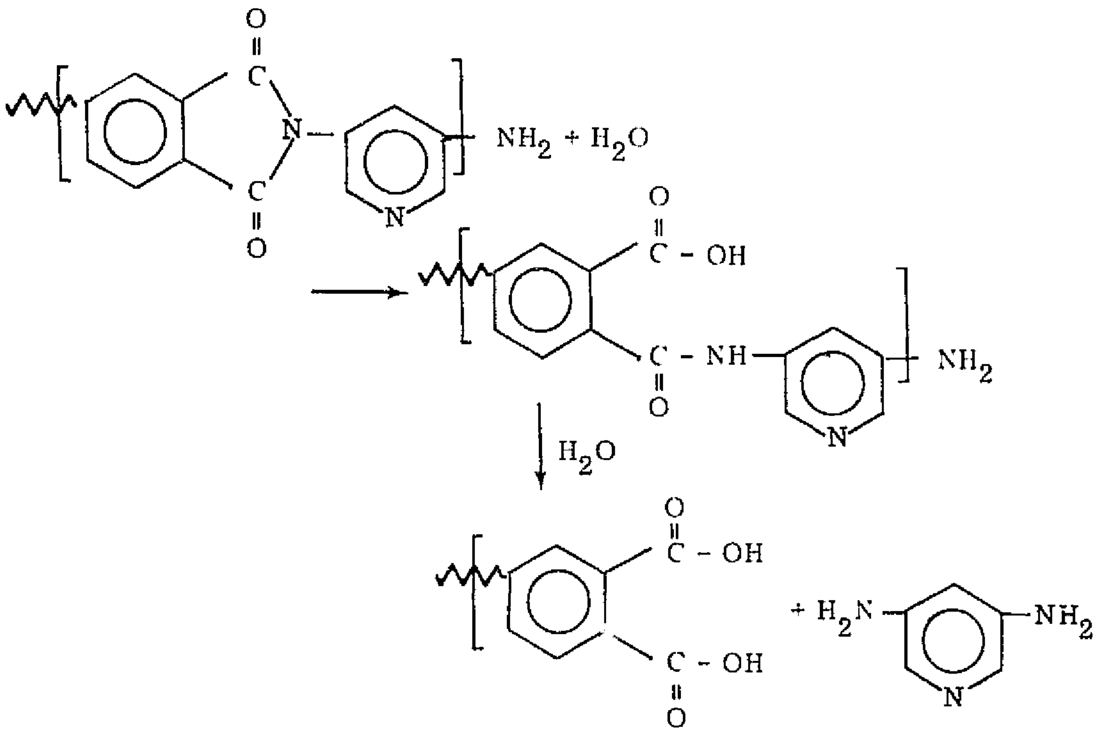


3. Ethanol is present during the polyimidization reaction. This alcohol can be oxidized to acetic acid during the abnormal foaming behavior and can react with the primary amide group to form an unreactive monomer, thus terminating the polycondensation.



4. The volatiles formed during the foaming process consist of water and ethanol. De-alcoholation and dehydration lead to the formation of the polyimide linkage. However, during the abnormal foaming behavior these molecules can attack the growing polyimide chain and terminate the polymerization reaction. Alcohol can enter back into reaction by the mechanism discussed in Section 5.6.4 (1) (but only if temperature exceeds 561°K (550°F), and if free diamines are available). The water can enter back into reaction by hydrolytic cleavage of the imide group. This reaction is known to occur during exposure of the foams to high or low pressure steam.

Thus a brittle polyimide structure and low molecular weight polymers are formed in addition to cleavage back to the monomers when extreme hydrolytic conditions are used.



It should be emphasized that the possible degradative reactions reported here have not been studied in detail as they were beyond the scope of our program. Some of these reactions actually do take place during the abnormal foaming process, i.e., acetic acid formation while others have shown evidence to occur by the characteristics of the resulting foams, i.e., dark color, pungent odor, brittleness and hydrolytic instability of the foams to water at higher temperatures.

Brittle foams formed at these abnormal conditions are in most cases irreversible inasmuch as thermal heating does not reconstitute the imide linkages since the reactive groups responsible for the imidization reaction are no longer present in the stoichiometric ratio.

6

DISCUSSION OF TEST RESULTS

In this section are discussed the more significant deviations in foam properties to the technical development goals covered in ASTM Designation D-1564. Attempts are made here to correlate the deviations, under the condition of testing, with the physical and chemical properties of the material under test.

6.1 FATIGUE PROPERTIES OF POLYIMIDE FOAMS

When subjected to cyclic mechanical stresses, the candidate polyimide foams No. 25 and No. 29 failed at 6700 and 2000 cycles respectively, and the extent of the failure was such that ILD measurements could not be made subsequent to cycling. The duration of the test was considerably lower than the required 20,000 cycles.

During cyclic compression of open cell foams (as in fatigue testing) the pumping of air through the structure acts as a damping mechanism abetting the life of the structure. The existence of large voids within the foam introduces a condition which reduces the available damping, in localized areas, allowing more of the dynamic stresses of the fatigue loading to be transmitted to the foam cell structure. Local deformation of the cells is greater, exceeding the fatigue or proportional limit of the material, and recovery is less complete. Further, the irregularity of the cells in these areas constitutes a stress raiser condition, also detracting from fatigue life.

The fatigue testing of Foams No. 25 and No. 29 was conducted on samples produced during the initial stages of scaling-up the foaming process. These specimens were seen to have large voids with delaminated surfaces in the horizontal plane of the foam, resulting from excess volatiles trapped during the foaming process.

The testing frequency of 40 cpm, slightly higher than the 28 cpm specified by ASTM D-1564, may also have contributed to a more rapid deterioration of the structure in not allowing sufficient time for full elastic recovery (Ref. 3).

Efforts in the last phase of this program were dedicated to improving the process of fabrication of large foam specimens with considerable success. However, more work will have to be carried out to produce polyimide foams with more homogeneous cellular structure. Improvement of the cellular structure of polyimide foams will also result in improved mechanical properties, in particular elongation, which is also a property in which these foams are deficient.

6.2 STEAM AUTOCLAVE TESTING

This test involved heating foam specimens in a steam autoclave at a temperature of 393°K (250°F) for a period of 5 hours. During this test significant chemical breakdown occurred.

Polyimide molding resins are known to have good hydrolytic stability and to be little or not affected by boiling water tests over extended periods of time. Those resins, however, are produced by reacting tetraacid dianhydrides possessing high acidity constant ($K_a 10^{-2}$) with diamines possessing high primary amine dissociation constants ($K_b 10^{-8}$).

The polyimide component of the foams studied under this program are produced by reaction of low acidity tetraacid dianhydrides with low basicity diamines. The resultant imide group appears to possess drastically lower hydrolytic stability. Hydrolysis of this type of polyimide resins occurs by conversion of the polyimide group to a polyamic acid with destruction of the resilience of the foam structure. The polyamic structure so formed reacts at the test conditions with steam and is further degraded.

Tests were also carried out to evaluate the effects of boiling water on samples of Foam No. 25 and No. 29.

Boiling water for a period of three hours did not appear to degrade the chemical structure of polyimide foams; however, extended exposures at the same conditions for 5 hours produced hydrolysis of the imide groups.

Further studies were conducted to evaluate the hydrolytic resistance of other copolyimide resins synthesized within the scope of this program. In preliminary experiments it was found that polyimide foams produced with strong diamines (Resin No. 28 and No. 19) were resistant to boiling water conditions for extended periods of up to 20 hours without visible degradation, however, these foams are more rigid and brittle than is desirable for seating. These studies indicate that resistance of polyimide foams to steam autoclave may be improved if such a requirement is imposed on the material.

For the present time it is recommended that the steam autoclave test be replaced by a humidity test which more closely represents the actual environments in which these foams are used. The maximum level of humidity, temperature and duration of the test must be established in order to arrive at a criteria of acceptance.

7

RECOMMENDATIONS FOR FUTURE WORK

To overcome the problems associated with abnormal foaming behavior experienced in the fabrication of large foam specimens and to develop pilot plant capabilities; the following suggestions are recommended.

The use of new, improved surface active agents associated with foam resins possessing higher melting points and lower volatile content may resolve the problem associated with escape of the volatiles to the external surfaces and improve foam structure and properties by reducing the chances for abnormal chain terminating reactions caused by the [illegible] volatiles.

As part of this study a re-evaluation of the most promising resins developed during this program and of the alcohols is recommended. New heating methods which afford a more homogeneous heat transfer through the foam such as dielectric, induction and microwave heating will be considered.

Finally, new improved thermal cycles with multi-stage foaming techniques are recommended. These will utilize various modes of heating the growing foam matrix to facilitate the escape of volatiles before stabilization of the cell strucutre occurs. These techniques may include vacuum heating, absorbant support materials for foaming and perforated molds.

8

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