NASA CONTRACTOR REPORT

NASA CR-2222

NASA CR-2222

DEVELOPMENT OF PYRRONE STRUCTURAL FOAMS FOR HONEYCOMB FILLER

by B. G. Kimmel

Prepared by
HUGHES AIRCRAFT COMPANY
Culver City, Calif. 90230
for Langley Research Center

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION • WASHINGTON, D. C. • MARCH 1973

1. Report No. NASA CR-2222

2. Government Accession No.

3. Recipient's Catalog No.

4. Title and Subtitle

DEVELOPMENT OF PYRRONE STRUCTURAL FOAMS FOR HONEYCOMB FILLER

5. Report Date March 1973

6. Performing Organization Code

7. Author(s) B. G. Kimmel

8. Performing Organization Report No. P72-294

9. Performing Organization Name and Address

Hughes Aircraft Company
Culver City, Calif. 90230

10. Work Unit No. 501-21-23-02

11. Contract or Grant No. NAS1-10869

12. Sponsoring Agency Name and Address

National Aeronautics and Space Administration
Washington, DC 20546

13. Type of Report and Period Covered Contractor Report

14. Sponsoring Agency Code

15. Supplementary Notes

16. Abstract

The development of techniques for the preparation of pyrrone structural foams for use as honeycomb filler is described. The feasibility of preparing foams from polymers formed by the condensation of 3,3'-diaminobenzidine (DAB), or 3,3',4,4'-tetraaminobenzophenone (TABP), with 3,3',4,4'-benzophenone tetracarboxylic dianhydride (BTDA) was investigated. Initially, most of the effort was devoted to preparing pyrrone prepolymers with improved and more reproducible foaming properties for making chemically blown foams. When it became apparent that very high curing shrinkages would not allow the use of unfilled pyrrone prepolymers in a "foam-in-place" process, emphasis was shifted from chemically blown foams to syntactic foams. Syntactic foam formulations containing hollow carbon microspheres were developed. Syntactic foams made from selected formulations were found to have very low coefficients of thermal expansion. A technique was developed for the emplacement of pyrrone syntactic foam formulations in honeycomb core structures.

17. Key Words (Suggested by Author(s))

Pyrrone
Carbon microsphere
Syntactic foam
Honeycomb filler

18. Distribution Statement

Unclassified - Unlimited

19. Security Classif. (of this report) Unclassified

20. Security Classif. (of this page) Unclassified

21. No. of Pages 47

22. Price* $3.00

*For sale by the National Technical Information Service, Springfield, Virginia 22151

FOREWORD

This report was prepared by Hughes Aircraft Company to cover work performed under Contract NAS 1-10869 "Development of Pyrrone Structural Foams and Adhesives", administered by Langley Research Center, National Aeronautics and Space Administration.

The program at Hughes was performed under the direction of Mr. Boyce G. Kimmel, Head, Composite Materials Development Group, Materials Technology Department, Equipment Engineering Divisions. Dr. Leroy J. Miller directed the synthesis and chemical characterization of the polymer systems, while Mr. Kimmel was responsible for the development and characterization of the syntactic foam systems.

The assistance of Mr. Ray E. Lawrence in chemical synthesis and Mr. Arturo A. Castillo in foam fabrication and Mr. James R. Shackleton in preparing the scanning electron micrographs is gratefully acknowledged.

CONTENTS

ILLUSTRATIONS

TABLES

DEVELOPMENT OF PYRRONE STRUCTURAL FOAMS FOR HONEYCOMB FILLER

by B. G. Kimmel*

1.0 SUMMARY

This report describes the development of techniques for the preparation of structural foams from the Pyrrone polymers for use as honeycomb filler. The Pyrrones are formed by the condensation reaction of aromatic dianhydride with aromatic tetramines.

The feasibility of preparing structural foams from polymers formed by the condensation of 3,3'-diaminobenzidine (DAB) and 3,3',4,4'-tetraaminobenzophenone (TABP) with 3,3',4,4'-benzophenone tetracarboxylic dianhydride (BTDA) was investigated. Initially, most of the effort was devoted to preparing Pyrrone prepolymers with improved and more reproducible foaming properties for making chemically blown foams. When it became apparent that very high curing shrinkages would not allow the use of unfilled Pyrrone prepolymers in a "foam-in-place" process, emphasis was shifted from chemically blown foams to syntactic foams. Syntactic foam formulations containing hollow carbon microspheres were developed. Syntactic foams made from selected formulations were found to have very low curing shrinkages and extremely low coefficients of thermal expansion. A technique was developed for the emplacement of Pyrrone syntactic foam formulations in honeycomb core structures.

---

*Member of the Technical Staff, Materials Technology Department, Equipment Engineering Divisions, Hughes Aircraft Company, Culver City, California.

2.0 INTRODUCTION

The Pyrrones (polyimidazopyrrolones), a new class of polymer developed at the NASA Langley Research Center, offer promise in present and future aerospace applications.

Pyrrones may be synthesized by the reaction of cyclic diahydrides and tetraamines under comparatively simple reaction conditions (Reference 1). Depending on the starting materials, two basic structures can be obtained: the "stepladder" and "ladder" polymers. In the stepladder form, the polyaromatic moieties are linked by single bonds. The ladder polymer is linked by double bonds at each end of the basic Pyrrone unit to form a continuous double strand polymer.

Previous work (Reference 2) on the chemistry and processing of Pyrrone foams showed that these polymers offer much promise in thermal structural applications. The main objective of this program was the development of Pyrrone foam formulations which could be readily emplaced into cellular or honeycomb structures. The program included the development and characterization of BTDA-DAB and BTDA-TABP foams, initially in the form of chemically blown systems. Later work was performed on BTDA-DAB syntactic foams with minimum curing shrinkage.

3.0 CHEMICALLY BLOWN FOAMS

3.1 BTDA-DAB FOAMS

3.1.1 Resin Synthesis — General Procedure

The synthesis of the BTDA-DAB resins consisted of two main steps, the preparation of an ester of BTDA with ethanol and reaction of this ester with an equivalent amount of DAB.

The BTDA was dissolved in excess absolute ethanol. After adding the required quantity of concentrated H_2SO_4 (which acts catalytically and shortens the time required to reach equilibrium), the mixture was maintained at reflux temperature for 24 hours or longer. After completion of the esterification, the excess ethanol was removed by distillation and the crude product was dissolved in benzene. This solution was washed several times with aqueous sodium bicarbonate solution. The solution was then treated with a desiccant to remove any residual water and the solvent removed to yield an ester of relatively low carboxyl content. An ester fraction of relatively high carboxyl content was recovered by acidification and purification of the first bicarbonate wash fraction.

The low carboxyl ester (or a combination of low and high carboxyl esters) was then placed in a resin reaction kettle and heated under argon to the reaction temperature (Figure 1 shows the apparatus). An equivalent molar quantity of solid DAB was added to the ester while stirring. The resulting melt was stirred at the desired reaction temperature (usually $453^{o}K$) for a time usually somewhat in excess of that required for the evolution of ethanol to subside. The reaction was terminated by cooling the melt in an ice bath to obtain a hard glassy product. The addition of liquid nitrogen shattered

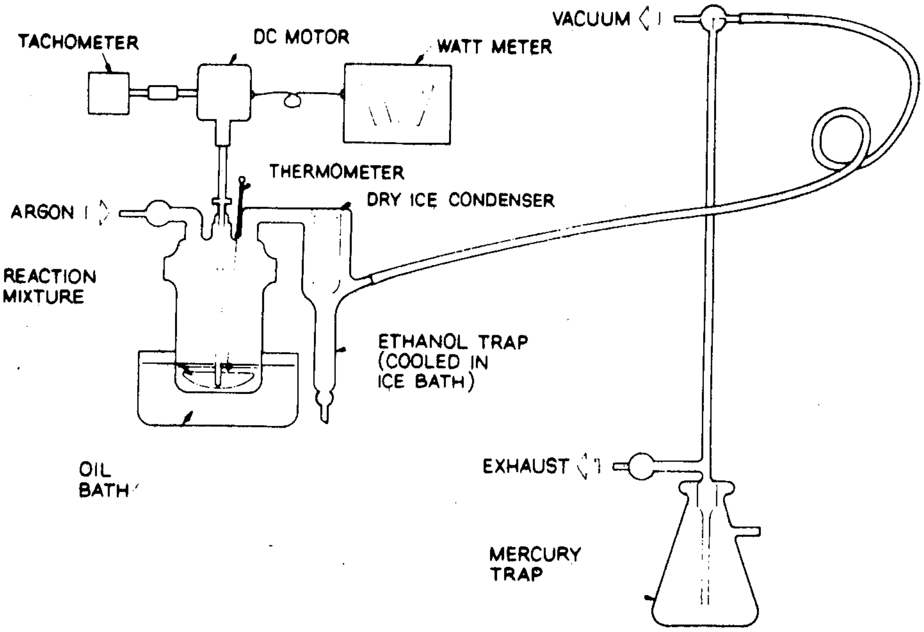


Figure 1. Apparatus for BTDA-EtOH-DAB Pyrrone preparation.

the product into fine particles and allowed convenient removal from the reaction vessel. Finally, the resin was ground to pass an 80-mesh sieve and dried under vacuum for 16 hours at 323°K.

3.1.2 Problems Related to Resin Synthesis

Previous work (Reference 2) has shown batch-to-batch variations in the resins which affect markedly the foaming characteristics. Attempts to define and measure those resin properties having the greatest influence on the foaming characteristics were partially successful. Resins prepared from BTDA esters of controlled carboxyl content and reacted to give an inherent viscosity of 0.050 to 0.060 usually, though not always, yield chemically blown foams of good quality.

Monitoring the progress of the BTDA-DAB polymerization is relatively difficult, since these resins are synthesized by a melt polymerization process. Several methods have been tried, with partial success, to monitor the progress of the reaction. These include viscosity measurements, collection and measurement of the ethanol of reaction and measurement of the power consumption of the stirring motor used to mix the contents of the reaction kettle. The latter method was partially successful but was also deemed unsatisfactory, since the power consumption was greatly affected by the degree to which the resin adhered to the stirring paddle.

The most reliable method appears to be to react each resin batch for a length of time at a temperature known by experience to yield a resin with good foaming characteristics. This method works reasonably well for successive batches made from a single master batch of ester. However, different batches of ester have been found to require different reaction times.

3.1.3 Monitoring of Resin Synthesis by Dielectrometry

The feasibility of monitoring the synthesis of BTDA-DAB resin by means of an automatic dielectrometer was investigated. This device continuously monitors the dissipation factor of a resin system either with increasing temperature or over a period of time at a single temperature.

Several curing tests were performed by the manufacturer of the dielectrometer in which the dissipation factor of several samples of BTDA-DAB resin was monitored during cure. Unfortunately, the temperature was not maintained at one level and it could not be determined whether the dissipation factor could be used as a response in indicating the degree of advancement of a Pyrrone prepolymer. However, the shape of the dissipation factor curves indicated this method of monitoring to be promising.

Tests were performed later by Hughes in which a BTDA-DAB resin was monitored continuously while being maintained within a narrow temperature range. The test setup consisted of a small piece (approximately 5 cm square) of 108 style glass fabric coated with BTDA-DAB resin sandwiched between two aluminum foil electrodes. This assembly was insulated top and bottom with two mil polyimide film and placed in a small laboratory press with platens controlled at a nominal temperature of 453^{o}K.

The dissipation factor decreased as expected with resin advancement. However, the decrease was very gradual over the entire range of advancement corresponding to an increase in melting point from 383^{o} to 431^{o}K. In particular, the slope of the curve in the region corresponding to a melting point of 398^{o}K (resins with this melting point have been found by experience to yield foams of high quality) was very low, indicating that dissipation factor would not be a good response for monitoring the synthesis of a Pyrrone prepolymer. The distinctive curves obtained by the manufacturer apparently corresponded to a much higher degree of polymerization than that occurring during resin synthesis and suggest the possibility of using dielectrometry to monitor the cure of Pyrrones.

3.1.4 Effect of Synthesis Conditions on Foaming Characteristics

Shortly after the start of the program, it was found necessary to purchase DAB from a second supplier since DAB was no longer available from the first supplier.

The behavior of the resin made from the second DAB during the course of the reaction in the resin kettle was substantially different. Previously, the only way to monitor the course of the reaction was to observe the increase in viscosity of the melt. The reaction was then stopped at the point at which stirring was no longer possible. With the second DAB, the melt became very viscous about 30 minutes earlier than had ever been observed in preparing a resin from the standard mixed ester. However, even though it was viscous, the melt remained stirrable throughout the course of the reaction. Therefore, the reaction was terminated after the time at which the melt ordinarily would have become non-stirrable. The viscosity apparently reached a plateau and remained there for an unknown amount of reaction time.

This difference in behavior may be due to the fact that the second DAB was more finely divided than the first DAB. The second DAB appeared to coalesce into lumps before it melted, and consequently dispersed more slowly into the reaction mixture. In any event, this anomalous behavior made it almost impossible to monitor the progress of the reaction of BTDA and the second DAB.

These difficulties, as well as previous difficulties in preparing resins with desirable and reproducible foaming characteristics, prompted the re-examination of the purity of each of the intermediates.

1. DAB

   Elemental analyses were run on the second DAB and the first DAB with the following results.

Element	Second DAB	First DAB	Theoretical
C	67.25	67.28	67.26
H	6.60	6.56	6.59
N	25.98	25.93	26.15
O	0.10	0.13	---
Cl	NONE	NONE	---
(ash)	0.10	0.07	---

It can be seen from the preceding results that the DAB from the two sources was fairly pure with no significant difference in composition. Any impurities in the DAB would have to exert their effects when present in only trace quantities.

2. Low Carboxyl Ester

A typical batch was examined for contaminants and found to contain only traces of metals (0.0047% Na, 0.0018% Mg, and others in lesser amounts) with conversion to the sulfate ash yielding only 0.025 percent of weight of the sample. Ethanol and a higher boiling material were detected in the low carboxyl ester by gas chromatography although these compounds were not measured quantitatively.

3. High Carboxyl Ester

The high carboxyl ester used in recent preparations was found by analysis to contain 18.8 equivalent-percent free carboxylic acid. Theoretically, if the acid-containing ester were separated cleanly from the tetraethyl ester, the acid-containing ester would contain at least 25 equivalent-percent free carboxylic acid. This is true because at least one of the carboxyl groups out of the four per molecule must remain unesterified in order for the molecule to be soluble in the aqueous sodium bicarbonate solution. A small quantity of diethyl ester may also be present and therefore one would expect the free carboxylic acid to be slightly higher than 25 equivalent-percent. Since only 18.8 percent was found, it was rationalized that the tetraethyl ester was not separated cleanly from the aqueous extracts. This is a reasonable rationalization since, in practice, an emulsion formed during the extraction of the acid, and it was extremely difficult to separate the benzene solution clear from the aqueous phase. Thus, in order to keep the benzene phase free of salt, the emulsion layer was taken off with the aqueous extracts. The aqueous extracts, including any suspended tetraester, were acidified to precipitate the high carboxyl content ester. The product was analyzed to determine the free carboxylic acid content, and the remainder was assumed to be completely esterified BTDA. A possible flaw in this procedure was the error introduced if some sodium salt of the carboxylic acid remained trapped in the product when it was precipitated from the aqueous extracts with acid. Emission spectroscopic analyses were run on a typical batch of high carboxyl ester which had been used in preparing BTDA-DAB resins with poor foaming characteristics. This high carboxyl ester was found to contain 0.75 percent magnesium and 0.20 percent sodium as well as traces of other metals (<0.004 percent). An ash weight equal to 4.33 percent of the sample weight was obtained on conversion to a sulfate ash. If the sodium and magnesium were present as salts of the carboxylic acids, this could account for the low acid content of the sample. It seems likely that the low acid content was observed because some of the carboxyl groups were neutralized and were present in the form of their magnesium and sodium salts. The percentages of these metals correspond to a reduction in the acid content from a theoretical 25 equivalent-percent to 20.4 equivalent-percent. Such salts could conceivably change the viscosity and surface tension of the resin melt and alter its foaming characteristics.

The preceding analyses indicated strongly that the principal reason for the difficulties experienced in making resins with good foaming characteristics was impurities in the high carboxyl fraction used in making the mixed esters required for the resin synthesis. Accordingly, a quantity of impure, high carboxyl ester (18.8 equivalent-percent carboxylic acid) was dissolved in benzene and rewashed with dilute hydrochloric acid. The benzene solution was separated and evaporated in a flash evaporator without drying over anhydrous magnesium sulfate. The resulting product had a carboxylic acid content of 25.0 equivalent-percent. This purified, high carboxyl ester was combined with low carboxyl ester to yield a mixed ester containing 3.5 equivalent-percent carboxylic acid. A portion of the mixed ester was molecularly distilled at a temperature of 423°K and a pressure of 47 N/m^2. Approximately 10 percent of the ester distilled and approximately one percent condensed in the liquid nitrogen trap. The remainder passed through the still without distilling.

Five 0.34-kg test batches of BTDA-DAB resin were prepared from the combined esters reworked as described above. Resins were made with DAB from the first and from the second supplier. In one case, the DAB was reacted with the purified mixed esters with a carboxyl content of 3.5 equivalent-percent and an equivalent weight of 121.3, and in the other case with a molecularly distilled mixed ester with a carboxyl content of 3.9 equivalent-percent and an equivalent weight of 119.9. In making all of these resins, the amount of BTDA mixed ester reacted with the DAB was based on the theoretical equivalent weight of 117.6. An additional resin was made from the second DAB and the purified ester (not molecularly distilled) in which the weight of the ester was based on the experimentally determined value of 121.3. The reaction time was 110 minutes at 453°K in all cases.

The foaming behavior of these resins was determined by preparing small moldings with a nominal 480 kg/m^3 density in a 28.6 mm diameter steel mold. Moldings were prepared after various degrees of advancement obtained by heating the resins under vacuum at 450°K. The standard procedure was used in which the vacuum-advanced material was wet-ground with trifluorotrichloroethane in a ball mill jar, dried and mixed with 0.1 PHR of Celogen OT in a high speed blender. After vacuum drying the resin-Celogen OT mixture at 339°K, it was cured in a closed mold for 5 hours at 408°K and from 408°K to 533°K for 5 hours. After determination of the density, the cured moldings were sectioned and examined for cell size and uniformity of cell structure. Several conclusions can be drawn from the test results which are summarized in Table I.

TABLE I. EFFECT OF SYNTHESIS CONDITIONS ON FOAMING CHARACTERISTICS OF BTDA-DAB RESINS

Resin Number G1325-09-	Stoichiometry	DAB	Ester	Melting Point, $^{\circ}$K	Inherent Viscosity	Foaming Characteristics
1	Theor. Eq. Wt. of Ester	Second	Molecularly Distilled	368-373	0.053	• Advanced 1 hr (MP, 378-383°K) - Strong, but scattered, large cells • Advanced 2 hrs (MP, 388°K) - Uniform, fine cells, few large cells • Advanced 3 hrs (MP, 393°K) - Uniform, fine cells
5	Theor. Eq. Wt. of Ester	Second	Not Molecularly Distilled	373-378	0.057	• Advanced 1 hr (MP, 378°K) - Small, uniform cells except few large cells • Advanced 2 hrs (MP, 383-388°K) - Small, uniform cells except few large cells • Advanced 3 hrs (MP, 393-398°K) - Small, uniform cells
2	Theor. Eq. Wt. of Ester	First	Molecularly Distilled	368-373	0.054	• Advanced 1 hr (MP, 388°K) - Medium cells, few large cells • Advanced 2 hrs (MP, 403-408°K) - Fine cell structure but several fine cracks • Advanced 3 hrs (MP, 413-418°K) - Poor cell structure, extensive cracking
3	Theor. Eq. Wt. of Ester	First	Not Molecularly Distilled	378-383	0.052	• Advanced 1 hr (MP, 378-383°K) - Fine cell structure • Advanced 2 hrs (MP, 403-408°K) - Fine cells but extensive cracking • Advanced 3 hrs (MP, 413-418°K) - Fine cells, but appears friable
4	Exper. Det'd. Eq. Wt. of Ester	Second	Not Molecularly Distilled	373	0.054	• Advanced 1 hr (MP, 383-388°K) - Medium cells, few large cells • Advanced 2 hrs (MP, 393°K) - Medium cells, few large cells • Advanced 3 hrs (MP, 408-413°K) - Poor cell structure, cracking

- molecular distillation of the ester to remove the last traces of volatiles does not affect the foaming characteristics
- the resins made from the second DAB seem to give foams of somewhat higher quality and, interestingly, appear to advance less rapidly by heating under vacuum than the resins made from the first DAB (compare resin No. 1 and 2 in Table).
- The resin made from the second DAB and the relative amount of BTDA ester based on the experimentally determined equivalent weight was somewhat inferior in its foaming characteristics to the resin made from the relative amount of BTDA ester based on the theoretical equivalent weight.
- in general, the resins prepared from the purified esters have better foaming characteristics than those prepared from relatively impure esters.

3.1.5 Curing Shrinkage

Curing shrinkage was determined in the course of preparing a number of chemically blown foams from BTDA-DAB resins. Shrinkages compared closely with those reported previously: approximately 6 linear-percent molding shrinkage and 6 linear-percent additional postcuring shrinkage for a total of 12 linear-percent.

3.1.6 Foam from Commerical Resin

A BTDA-DAB resin from a commercial plastics company was evaluated for foaming characteristics. The following properties were determined for this material:

Melting point	358^{o}-363^{o}K
Inherent viscosity	0.046

- Analysis (Galbraith)
  C - 67.30 percent
  H - 5.62 percent
  N - 7.32 percent
  O - 20.03 percent (direct)
- Weight loss after drying 16 hours at 338^{o}-343^{o}K at pressure less than 133 N/m^2 - 0.55 percent

Foam moldings 57 mm in diameter were prepared from the commercial resin by the standard compounding and molding techniques used in evaluating the Hughes resins. The resin as received gave foams of poor quality as expected. Vacuum oven advancement for one hour at 450°K increased the melting point to 388-393°K and resulted in a strong, tough foam with a cell size in the range of 0.50 to 1.00 mm. Vacuum advancement for 1-1/2 hours at 450°K increased the melting point to 393°K and yielded a foam of excellent quality with relatively uniform cells in the range of 0.25-0.38 mm. One interesting property of this resin was the relatively short time required for advancement to the desired melting point of approximately 393°K. By comparison, Hughes resin No. G1325-09-5 had a melting point of 393-398°K after vacuum oven advancement for 3 hours.

The first attempt to mold a relatively large block (38 mm x 114 mm x 165 mm) with a fine cell structure was unsuccessful. A considerable amount of resin flowed from the mold giving a molded block with a density of 447 kg/m^3 instead of the predicted 480 kg/m^3. The resulting foam appeared to be very strong, but the cell structure was very coarse with an average cell size of approximately 3 mm. The cause of the problem was felt to be too much clearance between the cavity and punch of the mold. Another molding was prepared from the same material using a slightly larger punch (Clearance on each side 0.08-0.10 mm). The resulting foam was of excellent quality with a uniform, fine cell structure almost identical to that obtained with the same resin in the 57 mm mold.

Based on the above results, it was concluded that mold clearance is very critical in the preparation of high quality, chemically blown Pyrrone foams.

3.2 BTDA-TABP FOAMS

3.2.1 Resin Synthesis

Three 0.34-kg batches of BTDA-TABP prepolymer were prepared from TABP and BTDA-ethanol ester No. E1706-97R (carboxyl content = 0.60 equivalent-percent). The reactions were run under argon at a bath temperature of 488°K. The system was periodically evacuated to remove alcohol of reaction. The following formulation was used for all three runs:

BTDA-ethanol ester No. E1706-97R:	194.4 gm
TABP :	100.0 gm

The solid TABP was added under argon at a bath temperature of 488°K and the reactions continued under argon as per the following schedules:

- Run No. 1: (E1706-100-1): The reaction mixture was blended for 5 minutes and then evacuated for 5 minutes. However, alcohol evolution was not observed for 13 minutes after TABP addition. Therefore the system was re-evacuated for a period of 5 minutes. Significant thickening of the reaction mixture was observed 30 minutes after TABP addition, and the system was re-evacuated another 5 minutes. The reaction was quenched in an ice bath after a total reaction time of 50 minutes. The product had an inherent viscosity of 0.093 (at 2.5 gm/100cc DMF concentration) and a melting point of 418°K.
- Run No. 2: (E1706-100-2): The reaction mixture was again blended for 5 minutes after addition of solid TABP. It was stirred for 15 minutes before evacuating the system for a period of 5 minutes. The reaction was quenched in an ice bath after a total reaction time of 30 minutes. The product had an inherent viscosity of .044 (at 2.5 gm/100 cc DMF concentration) and a melting point of 378°K.
- Run No. 3: (E1706-100-3): The reaction mixture was again blended for 5 minutes after addition of solid TABP and stirred for 15 minutes before evacuation for a period of 5 minutes. It was evacuated again after 8 minutes, and quenched in an ice bath after a total reaction time of 40 minutes. The product had an inherent viscosity of 0.046 (at 2.5 gm/100 cc DMF concentration) and a melting point of 383°K.

3.2.2 Preparation of Foams

Pyrrone foams were prepared from the BTDA-TABP prepolymers as follows: The prepolymer was ground to pass a 125 μm sieve and compounded with 0.1 percent of blowing agent by wet blending with a low boiling liquid (trichlorotrifluoroethane) in a high speed blender. After the liquid was removed by filtration, the prepolymer-blowing agent mixture was dried in a vacuum oven for 2 hours at 327°K. Finally the foam was prepared by curing the proper charge weight of the compounded material in a Teflon-coated steel mold. The specific molding procedure involved preforming the mixture cold under 34.5 MN/m^2 pressure, raising and shimming the punch to obtain the desired mold volume and the required foam density, clamping the mold, and curing over the range from 408° to 533°K. The cure consisted of placing the mold assembly in a cold oven, heating the oven to 408°K (about 20 minutes), maintaining the oven temperature at 408°K for 5 hours and heating from 408° to 533°K over a period of 5 hours. Table II summarizes the results of the evaluation of the three BTDA-TABP prepolymers from moldings with a nominal density of 480 kg/m^3 made in a 28.6 mm diameter cylindrical mold.

TABLE II. PREPARATION OF FOAMS WITH BTDA-TABP PREPOLYMERS

Prepolymer Number	Melting Point °K	Blowing Agent	Foam Density kg/m^3	Linear Shrinkage, Percent	Appearance
E1706-100-1	418	Celogen AZ*	466	2.0	Uniform, fine cells (0.25-0.76 mm dia.)
E1706-100-2	378	No blowing agent	463	3.8	Extremely coarse, non-uniform cells (3.2-6.4 mm dia.)
E1706-100-3	383	Celogen OT**	466	4.8	Relatively coarse, non-uniform cells (0.8-3.2 mm dia.)

Decomposition temperature, 450°K
Decomposition temperature, 403°K

The preliminary results indicated that chemically blown foams could be prepared from BTDA-TABP prepolymers. It should be noted that the curing shrinkage of the E1706-100-1 prepolymer was considerably less than those values previously obtained for chemically blown BTDA-DAB (5.8 percent linear shrinkage).

The influence of oven advancement on the foaming characteristics of Resin No. E1706-100-2 was briefly studied. Small quantities of resin were heated at 450°K in a vacuum oven for periods ranging from 40 minutes to 6 hours. After determination of the melting point, each material was compounded with 0.1 weight-percent of either Celogen OT or Celogen AZ and molded to obtain foams with a nominal density of 480 kg/m^3. Table III summarizes the results.

It appears that the BTDA-TABP resin should be advanced to a melting point of 408-413°K and compounded with Celogen OT blowing agent to obtain uniform, fine-celled foams.

TABLE III. EFFECT OF OVEN ADVANCEMENT AND BLOWING AGENT ON BTDA-TABP FOAMING CHARACTERISTICS

Time at 450°K, minutes	Melting Point, °K	Blowing Agent	Cell Structure of Resulting Foam
0 (as prepared)	378	Celogen OT	Extremely coarse
40	378	Celogen OT	(Not Determined)
90	378	Celogen OT	Very coarse; 1.6-3.2 mm cells
135	383-388	Celogen OT	Very coarse; 1.6-3.2 mm cells
165	388-393	Celogen OT	Coarse; most cells 1.6 mm, few large cells
180	393-398	Celogen OT	Coarse; most cells 1.6 mm, few large cells
240	408-413	None	Coarse, few cells 3.2 mm
240	408-413	Celogen OT	Extremely uniform, cells 0.13-0.25 mm
240	408-413	Celogen AZ	Fairly uniform; indication of incomplete foaming
300	413-418	Celogen OT Celogen AZ	Specimens extremely poor for both blowing agents
360	433-438	-	(No specimens prepared)

3.2.3 Characterization

A foam block measuring 38 mm x 114 mm x 165 mm was molded from BTDA-TABP resin containing 0.1 weight-percent of Celogen OT. The resin, which had a melting point of 383°K as synthesized, was advanced in a vacuum oven for 5 hours at 450°K to give a product with a melting point of 408°K. The advanced resin was ground to pass 80 mesh prior to being compounded with the blowing agent.

The molding shrinkage of the large block was found to be 4.8-5.0 linear-percent, substantially higher than that previously found (approximately 2.0 linear-percent) for the initial small moldings made from resin advanced to a melting point of 408-413°K.

Postcuring in argon to a maximum temperature of 644°K resulted in an additional shrinkage of 5.6 linear-percent (based on original mold dimension) for a total molding-postcuring shrinkage of 10.0 linear-percent.

Compressive strength tests per ASTM D695 were run at room temperature and 644°K on the postcured foam. Cylindrical specimens 13 mm in diameter by 25 mm long were machined both parallel and perpendicular to the pressing direction. The following compressive strength values were obtained:

- room temperature, pressing direction - 17.79 MN/m^2 (2580 psi)
- room temperature, perpendicular to pressing direction - 15.44 MN/m^2 (2240 psi)
- 644°K (30 min at 644°K), perpendicular to pressing direction - 5.10 MN/m^2 (740 psi).

3.3 CONCLUSIONS

Chemically blown foams may be prepared readily from BTDA-TABP resins by the same general procedures used for preparing chemically blown foams from the BTDA-DAB resins. The only apparent difference is the requirement for a melting point of the resin of 408-413°K to obtain uniform, fine-celled foams compared with the optimum melting point of 393-398°K for the BTDA-DAB system. The compressive strength of the BTDA-TABP chemically blown foam (18 MN/m^2) is comparable to that of chemically blown foams made from BTDA-DAB resin (21 MN/m^2) for densities of 480 kg/m^3.

4.0 BTDA-DAB SYNTACTIC FOAMS

4.1 INTRODUCTION

The investigation of syntactic Pyrrones was prompted by the need for a foam-in-place system with far less curing and postcuring shrinkage than observed for the systems previously investigated. This low shrinkage requirement probably excludes chemically blown systems completely. Emphasis was placed on developing syntactic foam systems with minimum curing shrinkage which could be emplaced readily in honeycomb structures. Carbon microspheres with nominal diameter of 200 μm (Reference 3) were used as the syntactic filler.

4.2 PREPARATION

Each syntactic foam formulation was calculated from the required density for the foam, the true density of the hollow microspheres and the volume fraction of the microspheres desired in the cured foam. For example, the formulation for a 320 kg/m^3 syntactic foam containing 74 volume-percent microspheres was calculated as follows:

- True density of microspheres = 237 kg/m^3 (determined pycnometrically)
- Desired volume fraction of microspheres = 0.74
- Weight microspheres per cubic meter of foam = 0.74 x 237 = 175 kg
- Desired density = 320 kg/m^3
- Weight-percentage microspheres = $\frac{175}{320} \times 100 = 55$

The formulations were mixed thoroughly in a high speed blender using trichlorotrifluoroethane as a suspension medium. Following removal of the medium by drying, a weighed quantity of the mixture was molded in a mold landed to give the required mold volume and density.

The postcuring procedure was similar to that used for postcuring chemically blown Pyrrone foams. Molded foams were postcured in either argon or air with the oven temperature being programmed at a controlled rate to the maximum postcure temperature.

4.3 PRELIMINARY EVALUATION

Syntactic foams with a nominal density of 480 kg/m^3 were prepared containing, respectively, 50 and 60 volume-percent (25 and 30 weight-percent) carbon microspheres. The formulations were molded in a 57 mm-diameter steel mold which had been preheated to 450°K, cured for one hour at 450°K and one hour at 533°K.

The resulting moldings were uniform in cross-section and fine-celled as expected. The molding shrinkage was substantially less than those shrinkages observed for typical chemically blown foams. The formulation containing 50 volume-percent microspheres shrank 1.33 linear-percent upon molding while the other formulation containing 60 volume-percent microspheres shrank only 0.67 linear-percent. By comparison, most chemically blown foams underwent molding shrinkages in the range of 6 to 7 linear-percent.

Portions of the above moldings were postcured in argon to a maximum temperature of 644°K. This postcure resulted in an additional shrinkage of 1.8 to 2.0 linear-percent for a total linear shrinkage of slightly over 3 linear-percent for the 50 volume-percent formulation and approximately 2.5 linear-percent for the 60 volume-percent formulation. Cylindrical compressive test specimens, 13 mm in diameter by 25 mm long were machined from portions of the syntactic foam moldings, both as molded and postcured. Compressive tests were run per ASTM D695 at room temperature to assess the effect of postcuring on the strength properties. Table IV summarizes the test results.

The compressive strength values were relatively low for a 480 kg/m^3 syntactic foam, both before and after postcure. By comparison, typical 480 kg/m^3 syntactic foams made from glass bubbles and BTDA-EG-DAB tetraester type resin had a compressive strength of approximately 20.7 MN/m^2

TABLE IV. EFFECT OF POSTCURE (ARGON, 644°K) ON COMPRESSIVE STRENGTH OF PYRRONE SYNTACTIC FOAMS

Molding Number	Volume-Percent Microspheres	Average Compressive Strength, MN/m^2	
		Before Postcure	After Postcure
3	50	7.6	7.9
5	50	9.0	7.0
6	60	9.2	10.9
7	60	12.4	10.3
8	60	13.8	12.0

(Reference 2). The data indicate that postcuring may degrade the compressive strength, although one molding was apparently unchanged and another appeared to increase in compressive strength as a result of postcure.

Further work on the development of syntactic foams principally involved curing of various formulations of BTDA-DAB resin and hollow carbon microspheres. For the sake of comparison, formulations of BTDA-EG-DAB (tetraester) with carbon microspheres and BTDA-DAB with B35D glass bubbles were also evaluated. Various formulations were prepared for moldings with a controlled volume-percentage of microspheres and density. These formulations were cured either in a 57 mm-diameter closed mold to a controlled density or in a 60 mm-diameter open cylindrical cup. In the latter case, the formulation was packed dry in the cup prior to cure. All of the foams were cured one hour at 450°K and one hour at 533°K and postcured in argon to 644°K.

Table V summarizes the results obtained for the various formulations. It is immediately evident that the curing shrinkage of the dry, pack-in-place formulations is markedly higher than that of the corresponding molded foams. These results are to be expected since the curing shrinkage is highly dependent on the degree of packing of the carbon microspheres. The relatively high shrinkage of the pack-in-place foams prompted attempts to prepare formulations containing a sufficient quantity of solvent (in this case, p-dioxane) to

TABLE V. EVALUATION OF PYRRONE SYNTACTIC FOAMS (BTDA-DAB/CARBON MICROSPHERES)

Formulation Number	Weight Percent Pyrrone	Calculated Volume Fraction Microspheres At Density of ( )	Type of Foam	Molded Density, kg/m^3	Postcured[1] Density, kg/m^3	Curing[2] Shrinkage, linear percent	Postcuring[3] Shrinkage, linear percent
11	70	0.60 (480 kg/m^3)	Molded	479	420	1.33	0.99
			Open Cup	458	426	10.1	1.17
12	65	0.60 (400 kg/m^3)	Molded	421	388	2.44	1.42
			Open Cup	400	383	9.47	0.59
13	56	0.60 (320 kg/m^3)	Molded	373	354	4.76	0.19
14	40	0.60 (240 kg/m^3)	Molded	268	256	2.22	0.27
			Open Cup	261	249	5.68	0.18
15	12	0.60 (160 kg/m^3)	Molded	200	207	1.33	0.36
			Open Cup	208	210	0.72	0.64
16	45	0.74 (320 kg/m^3)	Molded	340	324	0.53	0.14
17	75	0.50 (480 kg/m^3)	Molded	479	442	0.98	0.32
18	70	0.60 (480 kg/m^3)	Molded	469	428	1.33	0.63

(1) Density determined from weight and dimensions of 12.70 mm x 25.40 mm rod machined from postcured foam.

(2) Based on diameter of cold mold.

(3) Based on diameter of cured foam.

allow more efficient packing. The use of dioxane resulted in much lower curing shrinkage with values less than 1.0 linear-percent being obtained. However, difficulty was experienced in volatilizing the dioxane prior to cure, which resulted in excessive foaming and foams with large irregular cells. In one case, slow careful drying at 380°K and curing under pressure gave a 320 kg/m^3 foam of excellent appearance with a curing shrinkage of approximately 0.25 linear-percent. A substantial amount of resin flowed from the mold during cure. However, the low shrinkage indicated that the microspheres were very closely packed.

Compressive strength tests per ASTM D695 were run on cylindrical specimens cut from each of the foams and moldings. The results, summarized in Table VI, show only small differences in density and compressive strength. The compressive strength values for the BTDA-EG-DAB/carbon microspheres foam and the BTDA-DAB/glass bubble foam indicate strongly that moldings containing carbon microspheres are inherently weaker than those containing the glass bubbles. The compressive strength is seen to be highly dependent on density. For example, the molded 208 kg/m^3 foam had only 6 percent of the compressive strength of the molded 480 kg/m^3 foam.

Based on the results of the preliminary evaluation, it was concluded that curing and postcuring shrinkage could be markedly reduced by the use of hollow carbon microspheres as a syntactic filler. Two formulations, No. 16 (74 volume-percent microspheres, 320 kg/m^3) and No. 11 (60 volume-percent microspheres, 480 kg/m^3) were chosen for further evaluation. The former was chosen for its particularly low curing shrinkage and the latter for its combination of relatively high strength properties and moderately low curing shrinkage. Open cup foaming, as expected, resulted in substantially larger shrinkages than those observed for the corresponding molded formulations. Softening of the BTDA-DAB resin by the admixture of a small quantity of solvent resulted in low curing chrinkages. However, this method was not practical for the filling of honeycomb structures due to the difficulty in removing the solvent prior to cure. A more practical approach was heating the dry formulation to obtain a soft paste and forcing the heated formulation into the honeycomb cells under pressure. This latter method will be described in detail in the section which describes the emplacement techniques.

TABLE VI. COMPRESSIVE STRENGTH OF PYRRONE SYNTACTIC FOAMS (BTDA-DAB/CARBON MICROSPHERES, EXCEPT AS INDICATED)

Formulation Number	Weight Percent Pyrrone	Calculated Volume Fraction Microspheres At Density of ( )	Type of Foam	Postcured	Density, kg/m^3	Average Compressive Strength, MN/m^2
11	70	0.60 (480 kg/m^3)	Molded	No	479	11.4
			Molded	Yes	420	10.6
			Open Cup	No	458	11.9
			Open Cup	Yes	426	11.8
12	65	0.60 (400 kg/m^3)	Molded	No	421	4.9
			Molded	Yes	388	5.0
			Open Cup	No	400	6.5
			Open Cup	Yes	383	5.6
13	56	0.60 (320 kg/m^3)	Molded	No	373	6.3
			Molded	Yes	354	5.8
14	40	0.60 (240 kg/m^3)	Molded	No	268	2.9
			Molded	Yes	256	2.5
			Open Cup	No	261	3.0
			Open Cup	Yes	450	3.0
15	12	0.60 (160 kg/m^3)	Molded	No	200	0.7
			Molded	Yes	207	0.7
			Open Cup	No	208	1.0
			Open Cup	Yes	210	0.9
16	45	0.74 (320 kg/m^3)	Molded	No	340	4.6
			Molded	Yes	324	4.4
17	75	0.50 (480 kg/m^3)	Molded	No	479	6.1
			Molded	Yes	442	5.9
18	70	0.60 (480 kg/m^3)	Molded	No	469	10.1
			Molded	Yes	428	10.8
19*	47.5	--	Molded	No	452	8.5
			Molded	Yes	429	9.9
21**	60	0.63 (480 kg/m^3)	Molded	No	493	26.2
			Molded	Yes	437	28.4

*BTDA-EG-DAB/Carbon Microspheres
**BTDA-DAB/Glass Bubbles

4.4 POSTCURE STUDIES

In accordance with the Statement of Work requirement specifying a maximum processing temperature of 550°F (561°K), the effect of postcuring to a maximum temperature of 561°K was investigated. Two blocks of syntactic foam (45 weight-percent Pyrrone, nominal density 320 kg/m^3 cut from the same molding were postcured in air and argon, respectively, to a maximum temperature of 561°K. The foam postcured in argon lost 6.8 weight-percent and shrank approximately 0.3 linear-percent, while the foam postcured in air lost 13.7 weight-percent and shrank approximately 1.65 linear-percent. Compressive strength measurements per ASTM D695 were made at room temperature, 533° and 589°K. The specimens consisted of cylinders 12.7 mm in diameter by 25.4 mm long with the specimen axis parallel to the pressing direction. Table VII summarizes the test data.

TABLE VII. EFFECT OF POSTCURE ATMOSPHERE ON COMPRESSIVE STRENGTH OF PYRRONE FOAM (561°K POSTCURE)

Test Temperature, °K	Compressive Strength, MN/m^2			
	Argon Postcure		Air Postcure	
	Average*	Std. Dev.	Average*	Std. Dev.
292	5.21	0.06	3.28	0.26
533	4.17	0.14	2.25	0.13
589	4.43	0.22	2.30	0.20

*Average of four determinations

The results show conclusively that postcuring in argon results in improved compressive strength at all test temperatures. Additionally, the retention of compressive strength at elevated temperatures for the foam postcured in argon is very good: 80 percent at 533°K and 85 percent at 589°K. The results indicate very strongly that postcuring in an inert atmosphere is essential to obtain maximum compressive strength

4.5 EMPLACEMENT TECHNIQUES

Based on the preliminary evaluation, the most practical approach for emplacing syntactic Pyrrone foams in honeycomb structures was deemed to be heating the dry formulation anf forcing the heated mixture into the honeycomb cells.

Two formulations, No. 11 (480 kg/m^3, 60 volume percent microspheres) and No. 16 (320 kg/m^3, 74 volume-percent microspheres) were successfully emplaced in stainless steel and titanium honeycomb core by this method. The resin-microsphere mixture, contained in a small cylinder, was placed in an oven at 477°K for 10 minutes. The preheated mixture, which had a dough-like consistency, was then forced into the honeycomb cells by applying moderate pressure to a small piston in the cylindrical container. Initially, this process was accomplished manually. Later, a controlled pressure of 1.03 MN/m^2 was applied by means of a small laboratory press. The honeycomb section with the emplaced foam formulation was placed between aluminum plates (coated with mold release) and cured in a laboratory press for one hour at 477°K and one hour at 533°K.

Very little shrinkage away from the honeycomb cell walls was observed for formulation No. 11 while no visual evidence of shrinkage was detected with formulation No. 16. Initially, almost no adhesion was obtained between the titanium and the cured syntactic foam, even though the honeycomb was thoroughly cleaned for 10 minutes at 366°K in Prebond 700. The degree of adhesion was markedly improved by priming the titanium honeycomb with a 30 percent solution of BTDA-DAB resin in p-dioxane and oven-drying for 30 minutes at 450°K. Syntactic foams cured in the primed titanium honeycomb adhered extremely well to the cell walls. Attempts to push the cured foam from the cells indicated that the shear strength of the bond exceeded the compressive strength of the foam.

A honeycomb specimen was made from titanium honeycomb and formulation No. 16 in which the central portion of the honeycomb was removed and replaced with a tubular aluminum insert. This procedure allowed the accurate determination of the density, curing shrinkage and postcuring shrinkage of the emplaced foam. The resultant foam had a density of 400 kg/m^3 and had a "cold die-cold part" curing shrinkage of approximately

0.2 linear-percent. When the differential expansion of the aluminum tube and the foam was taken into consideration, the actual curing shrinkage of the foam at the curing temperature was calculated to be approximately 0.6 linear-percent. Postcuring in argon to 644°K resulted in an additional shrinkage of 0.9 linear-percent, giving a total shrinkage of 1.5 linear-percent.

Most of the honeycomb specimens with filled cells were oven-cured while sandwiched between two aluminum plates coated with mold release. However, some specimens were oven-cured successfully with no containment whatever. The syntactic foam formulation did not run out as a result of such a cure procedure. It appears that large honeycomb sections could readily be filled with a syntactic foam formulation and oven-cured without any need for special fixtures or tooling to confine the foam formulation during cure.

4.6 CHARACTERIZATION

4.6.1 Thermal Expansion

Initial measurements were made in a quartz tube dilatometer over the range of 191 to 450°K on syntactic foams prepared from four different formulations of Pyrrone prepolymer and carbon microspheres and one formulation containing glass bubbles as the filler. The values were fairly low, lying in the range of 5.6×10^{-6} to $12.2 \times 10^{-6}/^{\circ}C$ as shown in Table VIII.

TABLE VIII. THERMAL EXPANSION OF PYRRONE SYNTACTIC FOAMS (TEMPERATURE RANGE, 191° to 450°K)

Formulation Number	Weight Percent Pyrrone	Type of Pyrrone	Type of Filler	Density, kg/m^3	Thermal Expansion, $(C^{o})^{-1}$
16	45	BTDA-DAB	Carbon	320	5.6×10^{-6}
17	75	BTDA-DAB	Carbon	448	12.2×10^{-6}
18	70	BTDA-DAB	Carbon	432	10.8×10^{-6}
19	47.5	BTDA-EG-DAB	Carbon	432	6.5×10^{-6}
21	60	BTDA-DAB	Glass	432	11.7×10^{-6}

The extremely low coefficient of thermal expansion ($5.6 \times 10^{-6}/C^{o}$) of the foam molded from formulation No. 16 prompted further thermal expansion measurements using a highly accurate Tuckerman optical strain gauge. Eight separate runs were made on one specimen, four from 300^{o} to $450^{o}K$ and the remainder from 300^{o} to $183^{o}K$. The average value from 300^{o} to $450^{o}K$ was $3.062 \times 10^{-6}/C^{o}$ with a standard deviation of $0.013 \times 10^{-6}/C^{o}$. The average value from 300^{o} to $185^{o}K$ was $3.452 \times 10^{-6}/C^{o}$ with a standard deviation of $0.013 \times 10^{-6}/C^{o}$.

4.6.2 Embedment Strength

Embedment strength test specimens having the configuration described in Boeing Material Specification 8-126 were prepared from foam formulation number 16 with a nominal density of 320 kg/m^3. Each specimen consisted of a 25.4-mm wide titanium alloy strip embedded in a small section of polyimide-fiberglass honeycomb, the cells of which were filled with the syntactic foam (see Figure 2). The test consisted of measuring the load required to pull the strip from the foam-filled honeycomb section. Surprisingly, somewhat higher embedment strength values were obtained at $533^{o}K$ than at room temperature. Some extremely low individual test values were attributed to misalignment of the specimen in the test fixture. Table IX lists the complete test results.

4.6.3 Shear Strength

The shear strength measurements per FTMS 406, method 1041, were made a room temperature on the 320 kg/m^3 syntactic foam (Formulation No. 16). The test specimens were rectangular with nominal dimensions of 6 mm by 19 mm by 76 mm. The spread in the test results for a total of ten individual determinations was relatively large with an average value of 1.80 MN/m^2 and a standard deviation of 0.64 MN/m^2 (coefficient of variation = 34 percent).

4.6.4 Compressive Strength of Pyrrone Foam/Polyimide Honeycomb

The compressive strength was determined per ASTM D695 for a combined structure consisting of the 320 kg/m^3 syntactic foam (Formulation No. 16) emplaced in polyimide honeycomb. Tests were run at room temperature, 533^{o} and $589^{o}K$ with all tests being made in the cell direction. Each

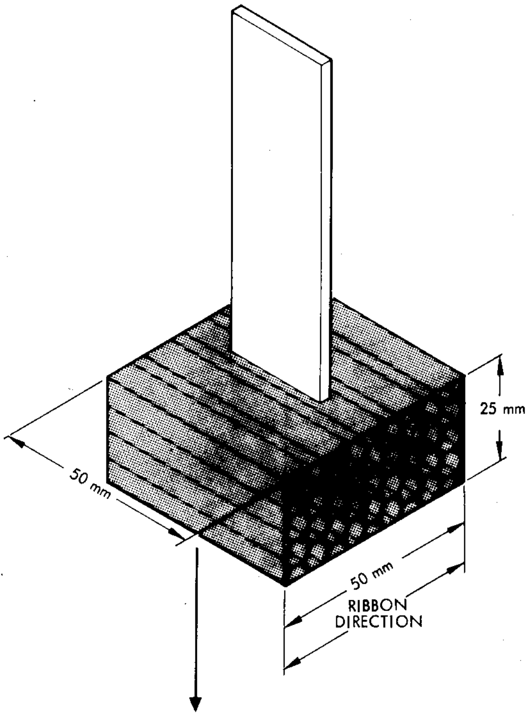


Figure 2. Embedment test specimen.

TABLE IX. EMBEDMENT STRENGTH OF PYRRONE SYNTACTIC FOAM

Embedment Strength, newtons	
Room Temperature	533°K
200	534
356	556
578	133
356	667
311	111
178	
Average 330	Average 400

test specimen consisted of a block 20 mm x 20 mm x 41 mm thick. The conpressive modulus was determined from crosshead movement. Table X summarizes the test results.

TABLE X. COMPRESSIVE STRENGTH OF PYRRONE FOAM COMBINED WITH POLYIMIDE HONEYCOMB

Test Temperature	Compressive Strength, MN/m^2		Modulus, MN/m^2	
	Average*	Std. Dev.	Average	Std. Dev.
Room Temperature	5.52 (6)	0.34	230	16
533°K	4.39 (5)	0.09	160	20
589°K	3.66 (4)	0.15	160	6.6

*Number in parentheses indicates number of individual tests.

4.6.5 Effect of High Temperature Conditioning on the Weight, Dimensions and Compressive Strength of Pyrrone Foam

Syntactic foams (postcured in argon to 644°K) were conditioned in air at temperatures of 533° and 589°K for periods of 500 and 1000 hours. Two types of foam were evaluated: a 320 kg/m^3 foam containing 45 weight-percent Pyrrone (Formulation 16) and a 480 kg/m^3 foam containing 70 weight-percent Pyrrone (Formulation 11).

Table XI summarizes the effect of this conditioning on the dimensions, weight and density. The results shown both density grades of foam to be reasonably stable after 500 hours at 533°K, but far less stable for the other exposure conditions.

The compressive strength properties were determined per ASTM D695 on cylindrical specimens nominally 13 mm in diameter by 25 mm long. The modulus in compression was calculated from crosshead motion. Three measurements were made for each combination of foam density, conditioning procedure and test temperature. The individual values and averages are given in Table XII. The data indicate both syntactic foam formulations to be fairly stable after 500 hours at 533°K, but far less stable for the other exposure conditions. The 480 kg/m^3 foam, in particular, was so extensively

TABLE XI. EFFECT OF HIGH TEMPERATURE CONDITIONING ON WEIGHT AND DIMENSIONS OF PYRRONE SYNTACTIC FOAMS
(644°K Argon Postcure)

Nominal Foam Density, kg/m^3	Weight Percent Pyrrone	Property	Initial	533°K Conditioning		589°K Conditioning	
				500 Hours	1000 Hours	500 Hours	1000 Hours
320	45	Weight, grams	40.358	38.258			
			34.752		24.414		
			37.458			32.362	
			37.331				15.969
		Loss of Weight, percent	--	5.20	29.7	13.6	57.2
		Change in Length, percent	--	1.33	5.51	2.83	4.96
		Change in Width, percent	--	1.25	4.74	2.83	5.34
		Change in Thickness, percent	--	1.31	4.55	2.89	6.30
		Density, kg/m^3	320	317			
			295		242		
			317			300	
			322				189
480	70	Weight, grams	45.586	41.559			
			59.760		49.115		
			51.903			40.950	
			59.835				22.264
		Loss of Weight, percent	--	8.83	17.8	21.1	62.8
		Change in Length, percent	--	2.49	3.76	10.74	*
		Change in Width, percent	--	2.62	3.53	9.29	*
		Change in Thickness, percent	--	1.68	3.27	6.30	*
		Density, kg/m^3	432	421			
			447		408		
			384			394	
			450				*

*Could not be determined; specimen cracked and broken into many pieces.

TABLE XII. EFFECT OF HIGH TEMPERATURE CONDITIONING ON THE COMPRESSIVE STRENGTH PROPERTIES OF PYRRONE SYNTACTIC FOAMS

Nominal Density, kg/m^3	Weight Percent Pyrrone	Conditioning Procedure, (Type)	Test Temperature					
			Room Temperature		533°K		589°K	
			Compressive Strength, MN/m^2	Modulus, MN/m^2	Compressive Strength, MN/m^2	Modulus, MN/m^2	Compressive Strength, MN/m^2	Modulus, MN/m^2
320	45	None (Type A)*	6.73 5.98 5.86	330 320 370	4.92 5.49 5.01	230 220 210	5.10 5.59 5.23	230 220 230
		Average	6.19	340	5.14	220	5.31	230
		None (Type B)**	8.00 5.99 7.24	290 460 570	5.61 5.27 5.74	230 220 250	4.88 6.09 5.32	190 230 210
		Average	7.08	440	5.54	230	5.43	210
		500 Hrs. at 533°K (Type A)	3.33 3.20 3.12	180 210 160	2.74 2.97 2.10	120 150 90	2.85 2.54 2.66	110 110 120
		Average	3.22	180	2.60	120	2.68	110
		1000 Hrs. at 533°K (Type A)	1.88 1.72 1.78	100 90 90	1.39 1.28 1.38	80 70 110	1.41 1.31 1.34	58 55 53
		Average	1.79	90	1.35	90	1.35	55
		500 Hrs. at 589°K (Type A)	1.06 0.92 1.09	40 50 83	0.64 0.57 0.81	38 25 26	0.46 0.94 0.63	27 39 28
		Average	1.02	58	0.67	30	0.68	31
		1000 Hrs. at 589°K (Type A)	0.39 0.38 0.37	23 17 19	0.26 0.26 0.22	19 14 5	0.26 0.25	14 12
		Average	0.38	20	0.25	13	0.26	13

*Type A specimens machined with axis parallel to molding direction.
**Type B specimens machined with axis perpendicular to molding direction.

(Continued next page)

(Table XII, concluded)

Nominal Density, kg/m^3	Weight Percent Pyrrone	Conditioning Procedure (Type)	Test Temperature					
			Room Temperature		533°K		589°K	
			Compressive Strength, MN/m^2	Modulus, MN/m^2	Compressive Strength, MN/m^2	Modulus, MN/m^2	Compressive Strength, MN/m^2	Modulus, MN/m^2
480	70	None (Type A)*	14.2	830	14.5	560	11.8	480
			12.8	830	8.5	430	12.3	430
			10.5	830	9.3	280	9.0	320
		Average	12.5	830	10.8	420	11.0	410
		None (Type B)**	14.7	600	9.0	370	13.3	390
			16.7	590	15.5	480	17.8	500
			11.6	480	11.2	380	10.1	330
		Average	14.3	560	11.9	410	13.7	410
		500 Hrs. at 533°K (Type A)	9.79	870	5.79	240	6.06	230
			8.69	390	5.62	300	6.65	270
			6.34	280	5.72	280		
		Average	8.27	510	5.71	270	6.36	250
		1000 Hrs. at 533°K (Type A)	6.10	240	5.72	210	5.92	240
			5.72	230	5.82	220	3.71	220
			6.58	240	5.40	200	6.20	230
		Average	6.13	240	5.65	210	5.28	230
		500 Hrs. at 589°K (Type A)	7.10	270	(Not Determined)		(Not Determined)	
			4.56	180				
			5.20	210				
		Average	5.62	220				
		1000 Hrs. at 589°K (Type A)	(Not Determined)		(Not Determined)		(Not Determined)	

*Type A specimens machined with axis parallel to molding direction.
**Type B specimens machined with axis perpendicular to molding direction.

cracked after 500 hours at 589°K that test specimens could only be machined for room temperature tests. No specimens could be machined from the 480 kg/m^3 foam postcured 1000 hours at 589°K.

4.6.6 Effect of Conditioning at 533°K on the Compressive Strength of Foam Postcured to 561°K

Two foam blocks measuring 38 mm by 165 mm by 229 mm were molded to a density of nominally 320 kg/m^3 from a formulation containing 45 weight-percent Pyrrone and 55 weight-percent carbon microspheres (Formulation 16). After postcuring in argon to 561°K, each molding was cut into three sections. One section from each block was set aside while the other two sections were conditioned for 500 and 1000 hours, respectively, at 533°K.

Cylindrical specimens measuring 13 mm in diameter by 25 mm long were machined from each section. Originally, it was planned to prepare forty specimens from each section, twenty each with the axis parallel and perpendicular, respectively, to the molding direction. However, the number of specimens was limited by machining difficulties to as low as five specimens for some combinations of specimen orientation, conditioning procedure and test temperature.

The compressive strength properties were determined per ASTM D695 at room temperature and 533°K. The modulus in compression was determined from crosshead motion. The test results, summarized in Table XIII, indicate approximately 50-60 percent retention of original compressive strength after 500 hours and approximately 30-35 percent after 1000 hours. The foam appears to be slightly stronger perpendicular to the pressing direction than parallel to the pressing direction.

4.6.7 Volume Fraction of Continuous Voids

Impregnation with an epoxy resin under moderate pressure was used to estimate the fraction of continuous voids in small sections cut from representative moldings of 320 kg/m^3 (Formulation No. 16) and 480-kg/m^3 (Formulation No. 11) foam. The method consists of vacuum-pressure impregnation of preweighed slabs of foam (maximum thickness, 3 mm) with a mixture of epoxy resin and hardener. The specimens are covered with the resin-hardener mixture while under vacuum and subjected to a pressure of

TABLE XIII. EFFECT OF CONDITIONING AT 533°K ON COMPRESSIVE STRENGTH OF PYRRONE SYNTACTIC FOAM (Postcured to 561°K in Argon)

Block No.	Specimen Type*	Conditioning Procedure, Hours at 533°K	Test Temperature							
			Room Temperature				533°K			
			Compressive Strength, MN/m^2**		Modulus, MN/m^2		Compressive Strength, MN/m^2**		Modulus, MN/m^2	
			Average	Std Dev	Average	Std Dev	Average	Std Dev	Average	Std Dev
2	A	None	4.88(10)	1.90	240	12	3.56(9)	0.73	190	40
		500	2.40(7)	0.09	190	10	1.83(7)	0.10	80	4
		1000	1.59(6)	0.11	90	5	1.20(5)	0.48	58	8
	B	None	5.07(10)	0.37	390	25	3.92(9)	0.50	210	37
		500	2.68(7)	0.36	220	34	2.24(7)	0.21	100	14
		1000	1.73(6)	0.10	100	14	1.28(6)	0.12	64	21
3	A	None	5.64(10)	0.54	540	39	5.41(9)	0.44	250	41
		500	3.12(7)	0.17	170	7	2.76(8)	0.26	130	28
		1000	1.98(5)	0.61	110	27	1.56(5)	0.21	80	12
	B	None	6.38(10)	1.31	430	150	5.63(10)	0.72	260	30
		500	3.13(8)	0.16	180	18	2.81(8)	0.25	150	18
		1000	2.25(5)	0.12	120	25	1.82(5)	0.11	120	39

*A = parallel to pressing direction; B = perpendicular to pressing direction

**Number in parentheses refer to number of individual determinations

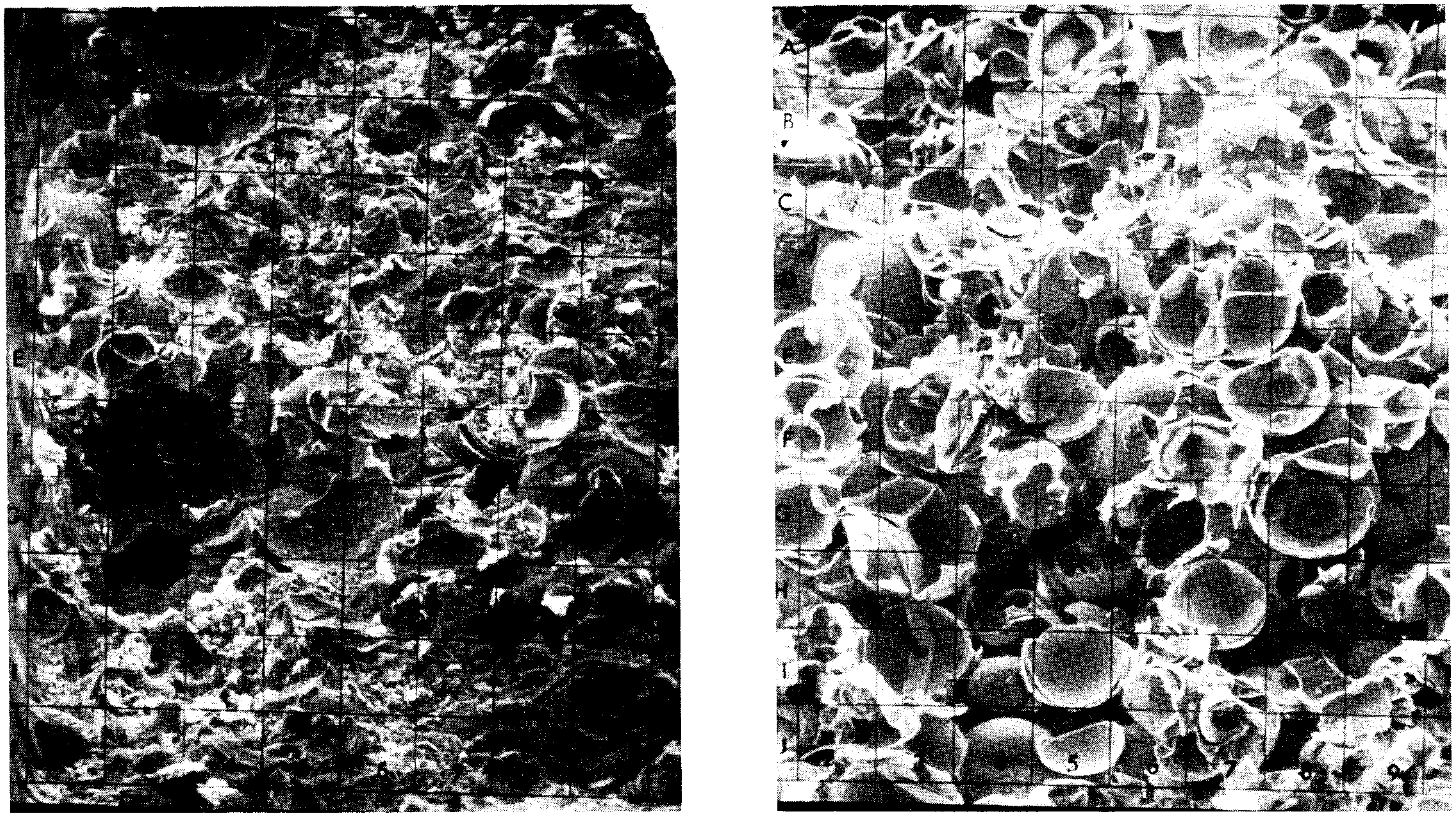
0.45 MN/m^2 (absolute) for one hour. After wiping the excess resin from the impregnated foam blocks with acetone-moistened tissues, the slabs are reweighed. The volume fraction pregnable voids (assumed to be the same as the volume fraction continuous voids) is calculated from the unimpregnated foam density, the weight increase as a result of impregnation and the density of the uncured impregnating resin. The volume fraction of continuous voids for the two foams was very close: 0.590 for formulation No. 16 and 0.555 for formulation No. 11.

4.6.8 Microscopic Examination of Foams

Portions of a 320 kg/m^3 syntactic foam molded from Formulation No. 16 were examined by means of a scanning electron microscope. Figure 3 shows typical SEM photographs of both machined and fractured surfaces. The fractured surfaces show far more detail, as expected, than the machined surfaces. The photographs show very clearly the very close packing of the carbon microspheres and also very interesting features such as double walls and septums in some microspheres. It is difficult to judge by the photographs what fraction of the microspheres would be broken in the interior of a typical foam since only a fractured surface is shown.

4.7 CONCLUSIONS

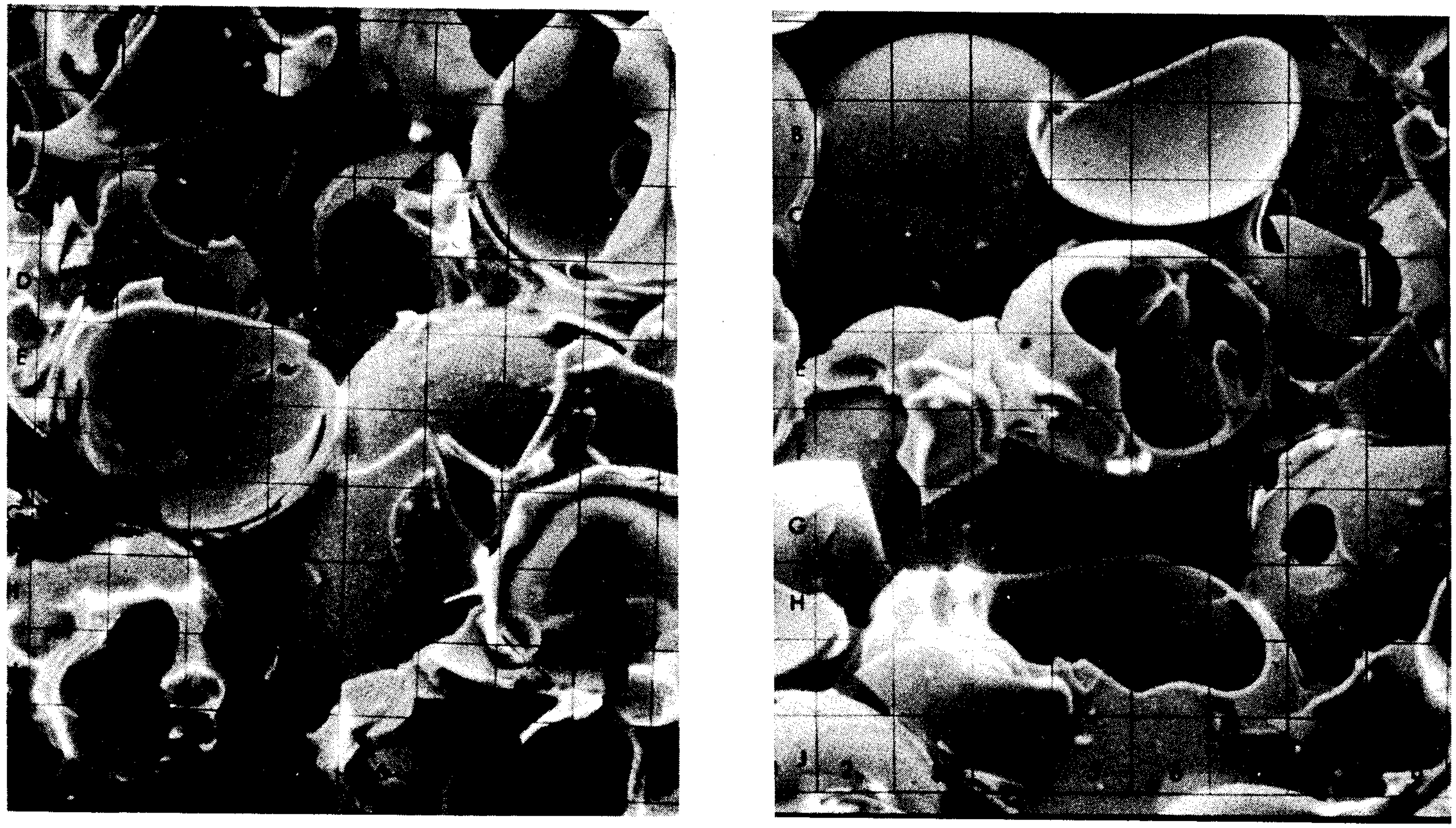
Syntactic foams may be prepared readily from mixtures of BTDA-DAB resins and hollow carbon microspheres. The resulting foams have low curing shrinkages and very low coefficients of thermal expansion. These foam formulations may be readily emplaced in honeycomb structures by heating the dry formulation to a soft, dough-like consistency and forcing the heated mixture into the honeycomb cells. Final cure of the emplaced foam can be accomplished by a simple oven cure with no need for containment during cure.



a. Machined surface — 100X

b. Fractured surface — 100X

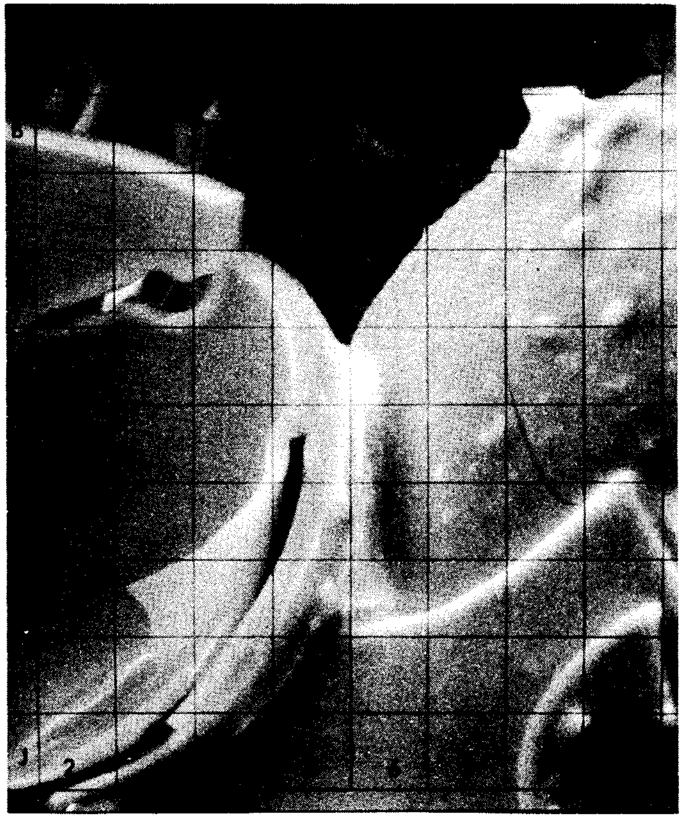
Figure 3. Scanning electron micrographs of typical syntactic foam.



c. Fractured surface — 300X

d. Fractured surface — 300X

Figure 3. Scanning electron micrographs of typical syntactic foam (Continued).



e. Fractured surface — 1000X

Figure 3. Scanning electron micrographs of typical syntactic foam (Concluded).

5.0 REFERENCES

1. Bell, Vernon L., Polyimidazopyrrolones, Encyclopedia of Polymer Science and Technology, Vol. 11, pp 240-246, John Wiley & Sons, Inc., 1969.

2. Kimmel, B. G., and Karre, L. E., "Preparation and Characterization of the Pyrrones as Thermal Structural Materials", NASA CR-1791, September 1971.

3. Amagi, Y., Nishimura, Y., and Gomi, S.: Hollow Carbon Microspheres from Pitch Material and Their Applications, Soc. Aerospace Mat. Process Engr., Tech. Papers Vol. 16, 1971. pp 315-324.

NASA-Langley, 1973 —— 18 CR-2222

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
WASHINGTON, D.C. 20546

OFFICIAL BUSINESS
PENALTY FOR PRIVATE USE $300

SPECIAL FOURTH-CLASS RATE
BOOK

POSTAGE AND FEES PAID
NATIONAL AERONAUTICS AND
SPACE ADMINISTRATION
451

U.S.MAIL

018 001 C1 U 18 730216 S00942DS
DEPT OF THE ARMY
PICATINNY ARSENAL
PLASTICS TECHNICAL EVALUATION CENTER
ATTN: SMUPA-VP3
DOVER NJ 07801

POSTMASTER : If Undeliverable (Section 158 Postal Manual) Do Not Return

> *"The aeronautical and space activities of the United States shall be conducted so as to contribute . . . to the expansion of human knowledge of phenomena in the atmosphere and space. The Administration shall provide for the widest practicable and appropriate dissemination of information concerning its activities and the results thereof."*
>
> —NATIONAL AERONAUTICS AND SPACE ACT OF 1958

NASA SCIENTIFIC AND TECHNICAL PUBLICATIONS

TECHNICAL REPORTS: Scientific and technical information considered important, complete, and a lasting contribution to existing knowledge.

TECHNICAL NOTES: Information less broad in scope but nevertheless of importance as a contribution to existing knowledge.

TECHNICAL MEMORANDUMS: Information receiving limited distribution because of preliminary data, security classification, or other reasons. Also includes conference proceedings with either limited or unlimited distribution.

CONTRACTOR REPORTS: Scientific and technical information generated under a NASA contract or grant and considered an important contribution to existing knowledge.

TECHNICAL TRANSLATIONS: Information published in a foreign language considered to merit NASA distribution in English.

SPECIAL PUBLICATIONS: Information derived from or of value to NASA activities. Publications include final reports of major projects, monographs, data compilations, handbooks, sourcebooks, and special bibliographies.

TECHNOLOGY UTILIZATION PUBLICATIONS: Information on technology used by NASA that may be of particular interest in commercial and other non-aerospace applications. Publications include Tech Briefs, Technology Utilization Reports and Technology Surveys.

Details on the availability of these publications may be obtained from:

SCIENTIFIC AND TECHNICAL INFORMATION OFFICE
NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
Washington, D.C. 20546