BDX-613-69

CONF-650902-1

THERMAL CHARACTERISTICS OF SOME RIGID URETHANE FOAMS

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INTRODUCTION

The use of rigid urethane foams as insulative materials and structural members is rapidly increasing as their unusually low thermal conductivities and good strength-to-weight ratio become better established. Service temperatures for these applications, as well as others, range from cryogenic to somewhat above normal room conditions.

The utility of rigid urethane foams in higher temperature applications has been limited, to a certain degree, by the lack of significant information concerning the thermal stability of these materials. However, thermal characteristics of urethanes themselves have long been known, for Hofmann in 1870 showed that an aromatic urethane dissociates into an isocyanate and an alcohol between 170° to 180°C (5). Another investigator has also made an extensive quantitative study of the kinetics of the urethane dissociation and is in good agreement with this early work (10). Additional kinetic studies of this decomposition in several solvents indicate that the reaction proceeds at an appreciable rate even at 150°C (6) (8).

Some data on the thermal stability properties of urethane elastomers and low density fluorocarbon blown foams have been published (1) (4) (9). Compressive strength data at elevated temperatures has also been determined on a rigid urethane foam system at various densities (3). Still there exists a considerable absence of detailed information concerning the thermal service limitations for rigid urethane foams.

The work reported in this paper is directed toward both a theoretical and practical aspect for the determination of some of the thermal characteristics for rigid urethane foams. The methods used to measure the parameters include: compressive strength properties at elevated temperatures, thermogravimetric analysis, differential thermal analysis, heat aging (somewhat of a static thermal stability test), and elemental chemical analysis. A possible correlation between physical and thermal properties is suggested as a guide for determining the elevated service temperatures for these materials.

EXPERIMENTAL

Materials. The three rigid urethane foam formulations chosen for this study show a wide range of molecular structure. A brief description of each is listed below.

Foam 1 - An aromatic dibasic acid-based polyester/toluene diisocyanate (TDI) prepolymer foam.

Foam 2 - An E-caprolactone - pentaerythritol polyester/toluene diisocyanate (TDI) prepolymer (20%) - polymethylene polyphenylisocyanate (PAPI) (80%) material.

Foam 3 - A commercial high temperature rigid urethane foam based on a polyester and polymethylene polyphenylisocyanate (PAPI).

Formulations from which foam samples were prepared are summarized in Table I. The molded foam test specimens prepared for this work were made from hand (high-speed air stirrer) mixed material. The foam blocks were cured for 10 hours at 325°F and had a core density of 20 pcf.

Ultimate Compressive Strength.

This test was conducted in accordance with ASTM D-695 over a temperature range of -73°C to +232°C. The test specimens used were one-inch cubes machined from the cores of the molded foam blocks. The specimens were conditioned for at least two hours at the test temperature before testing, and compressed parallel to foam rise. A loading rate of 0.050 inch/minute was used, with five determinations being made at each test temperature.

Thermogravimetric Analysis (TGA).

All thermogravimetric analyses were made with an Aminco Therm-Grav No 4-4430. The material samples used in the analyses were from foam sections taken from five or six different locations on the core of each foam block. The foam sections were then ground into a fine powder with a ball mill. The following parameters were employed on each sample.

Sample Weight - 100 mg
Temperature Range - 25 - 500°C
Heating Rate - 6°C/minute
Sample Atmosphere - Air

Differential Thermal Analysis (DTA).

All differential thermal analyses were made with an Aminco Thermoanalyzer No 4-4442. Powdered foam samples, prepared by the same method used for the TGA samples, were used in the analyses. The following parameters were employed for each sample.

Sample Weight - 9-12 mg
Temperature Range - 25 - 600°C
Heating Rate - 4°C/min
Reference: Empty cup of similar weight to sample cup.

Heat Aging.

Small cylinders of foam (approximately 1/4 inch in diameter and 1/4 inch high) were placed in aluminum pans and then weighed to the nearest 0.1 mg. The initial weights of the samples were between 1.03-1.11 grams. The pans were then placed into a forced air oven maintained at 175 ± 2°C. The weight loss was determined daily for four days and then at longer time intervals, by cooling the samples to room temperature and weighing to the nearest 0.1 mg.

Nitrogen Analysis.

Nitrogen Analyses (in duplicate) were made on foam powder, with a Coleman Nitrogen Analyzer.

TABLE I

FORMULATIONS FOR RIGID URETHANE FOAMS

Raw Materials	Formulation (Parts by weight) Foam 1 Aromatic Dibasic Acid Polyester-TDI(1) Prepolymer Urethane Foam	Foam 2 E-Caprolactone Polyester-TDI(1) Prepolymer/PAPI(2) Urethane Foam	Foam 3 Polyester-PAPI(2) Urethane Foam
Aromatic Dibasic Acid Polyester, Hydroxyl No. 575	100	---	---
E-Caprolactone Polyester, Hydroxyl No. 605	---	100	---
Commercial Polyester, Hydroxyl No. 600	---	---	100
Toluene Diisocyanate (TDI) Prepolymer			
A. Foam 1, Amine Equivalent 129	162		---
B. Foam 2, Amine Equivalent 135		38	
Polymethylene Polyphenyl isocyanate (PAPI), Amine Equivalent 134	---	139	170
Distilled Water	1.95	1.50	1.70
Additives (Cell Stabilizers, Amine Catalyst, etc.)	3.0	6.0	5.0

(1) 80/20 Toluene Diisocyanate - Mobay Chemical Company

(2) Polymethylene Polyphenylisocyanate - The Upjohn Company

RESULTS AND DISCUSSION

From Figure 1, we note that the compressive strength of the toluene diisocyanate (TDI) based Foam 1 drops off at a considerable rate after 120°C (250°F), while both Foams 2 and 3, which contain polymethylene polyphenylisocyanate, retain reasonable compressive properties up to 175°C (350°F). The loss in compressive properties occurs at temperatures somewhat below those reported for the thermal decomposition (150-200°C) of the chemical linkages usually found in rigid urethane foams (11). Therefore, it can be surmised that retention of compressive strength of rigid urethane foams at elevated temperatures is not solely dependent upon the various chemical linkages involved in foam formation, and that other parameters must also be considered. These parameters should include: hydrogen bonding, bulkiness of the molecules involved, and stability of the chemical constituents themselves. However, because of the complex nature of the chemical makeup of rigid urethane foams, these additional and important factors do not readily lend themselves to analysis, so one must be content to measure other more tangible parameters.

As a continuation of this practical approach to the determination of thermal characteristics of urethane foams, a TGA was made on each of three foam systems. The TGA thermograms, Figures 2, 3 and 4, all have the same general shape. An initial weight loss is noted between 150 to 265°C (depending upon the material), and continues at a similar rate to a temperature of approximately 324 - 350°C. In this temperature range weight loss continues, but at a slower rate. The change of weight loss rate would indicate a change in the decomposition mechanism.

The two temperature ranges show that different types of decomposition can occur. The initial weight loss is thought to be due to oxidation of the urethane linkages and loss of CO_2 and volatile products. The latter decomposition mechanism is suspected of being a complete depolymerization of the existing polymer fragment (12). The temperature of initial weight loss and the approximately temperature of change of weight loss rate from the TGA analyses are shown in Table II. The corresponding percent weight loss for the initial decomposition and the total weight loss is also given. The foams are listed in order of increasing stability according to temperature of initial weight loss.

These two decomposition temperatures are in general agreement with other TGA analysis of rigid urethane foams (1). The actual chemical products liberated at these temperatures have not, as yet, been clearly defined. Some studies of the thermal decomposition of substituted urethanes have shown that three general reactions may take place, in the temperature range of the first weight loss found for the TGA analysis (2) (7). These reactions are given in Table III.

The actual degradation of rigid urethane foams at elevated temperatures is not as simple as the mechanisms proposed in Table III indicate. Several additional factors are present that tend to obscure the over-all details of total decomposition.

1. Various chemical linkages, other than the urethane, are present in foam.
2. No allowance is made for complete oxidative breakdown of the polymer.
3. The degradation products may further react to form new chemicals, which in turn break down.

This complicated picture is just for the initial weight loss temperature range; countless possibilities exist for the second temperature range.

COMPRESSIVE STRENGTH CURVES
FOR RIGID URETHANE FOAMS

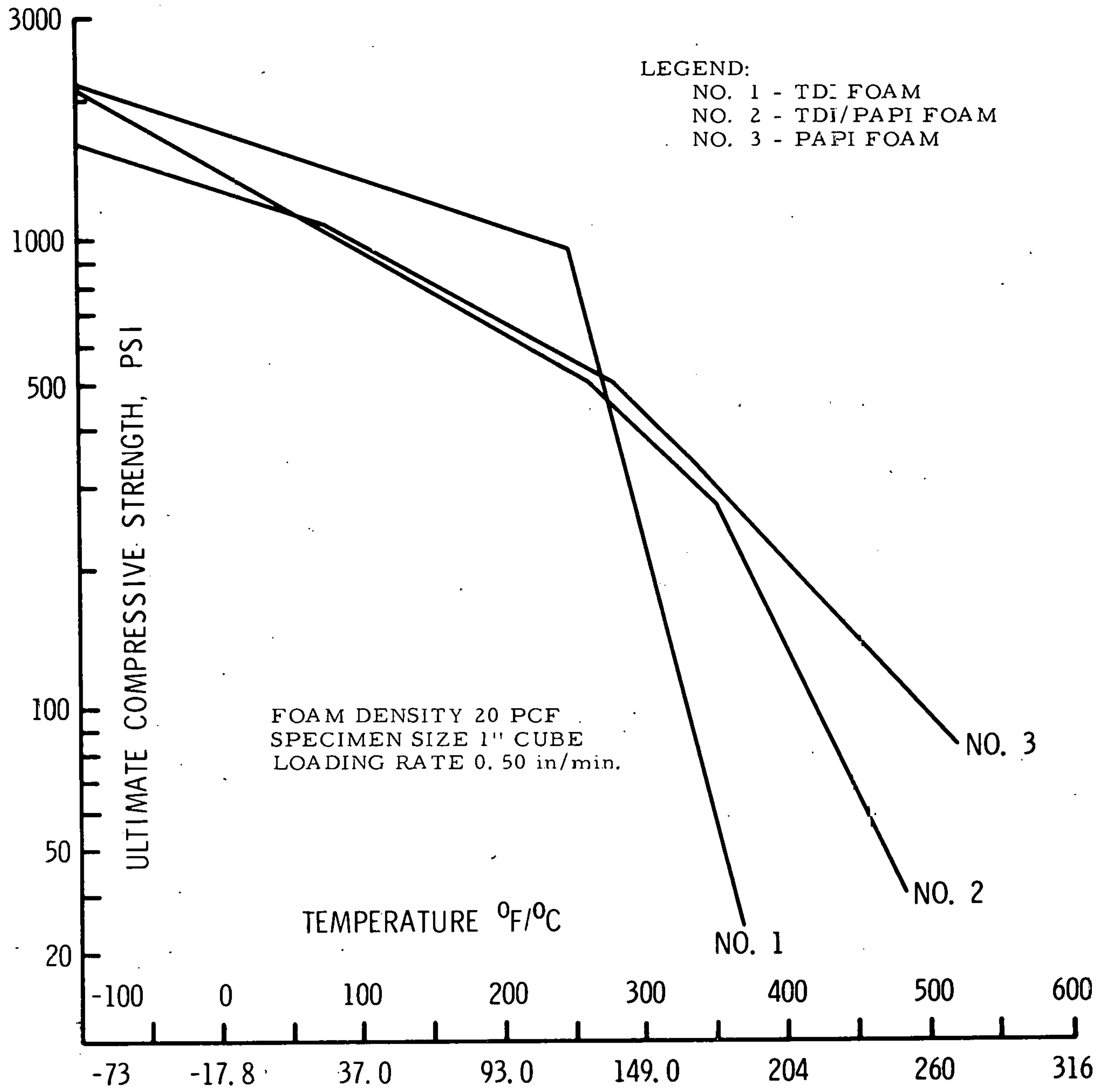

FIGURE 1

TABLE II

TGA DATA FOR RIGID URETHANE FOAMS

Foam No.	Initial Wt Loss Temp °C	Initial Wt Loss, %	Second Wt Loss Temp °C	Total Wt Loss, %
1. (TDI)	240 - 250	52	335	81
2. (TDI/PAPI)	250	50	350	74
3. (PAPI)	265	32	345	80

TGA CURVE FOR TDI FOAM (FOAM 1)

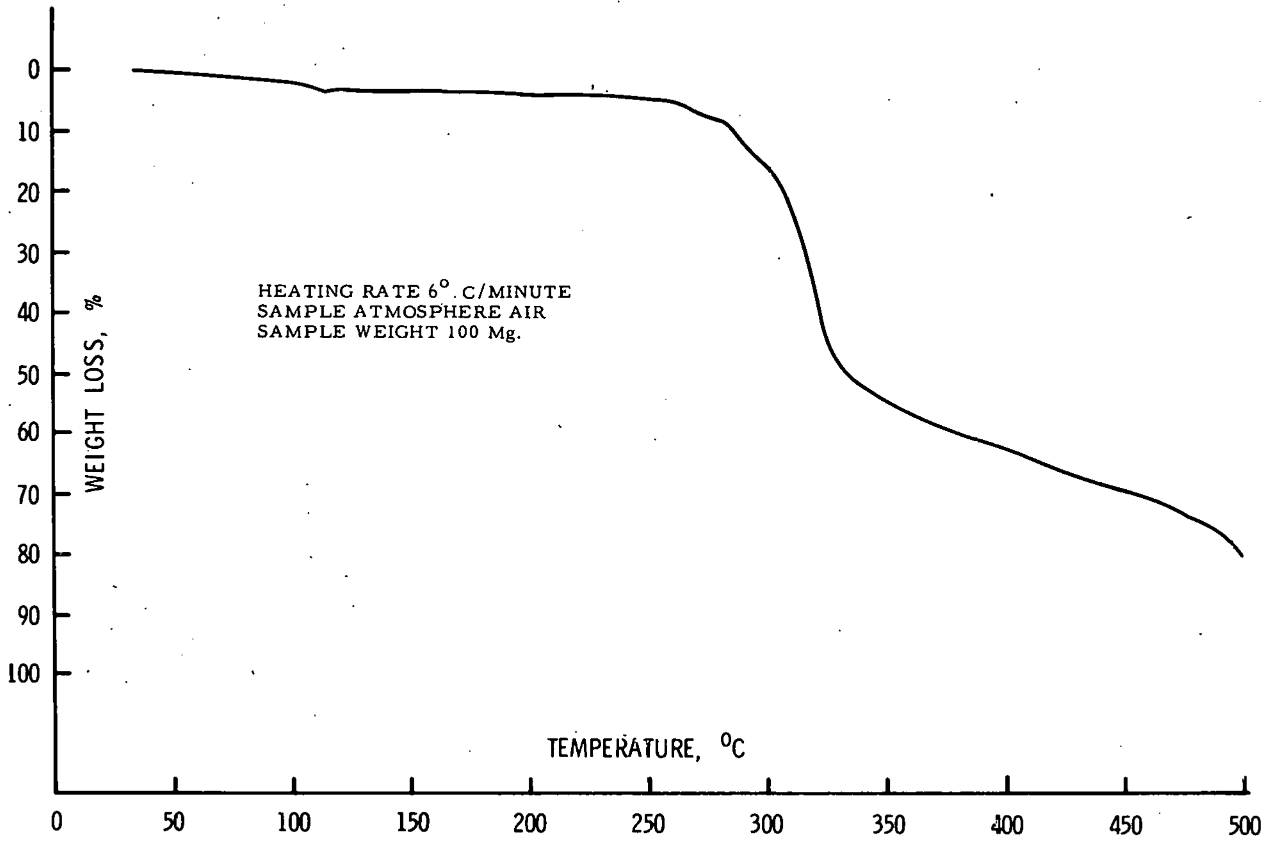

FIGURE 2

TGA CURVE FOR TDI/PAPI FOAM (FOAM 2)

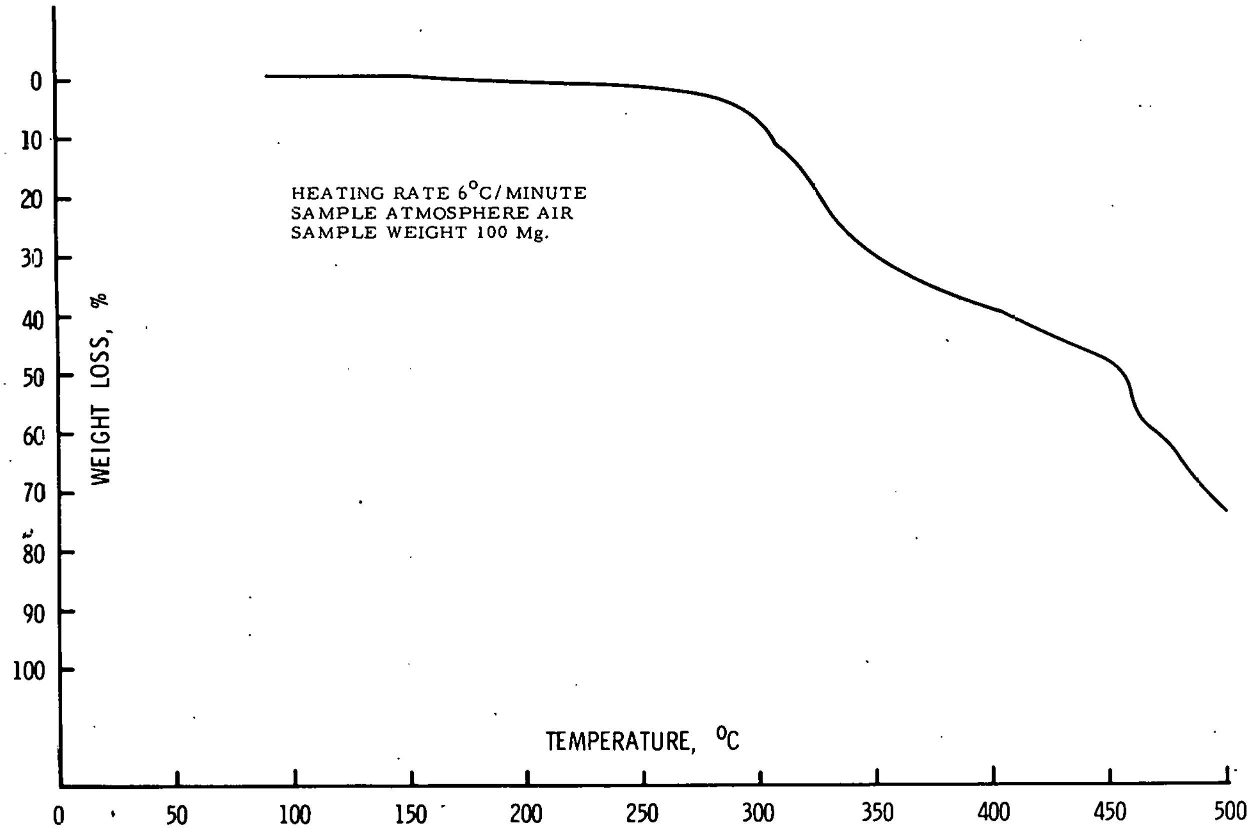

FIGURE 3

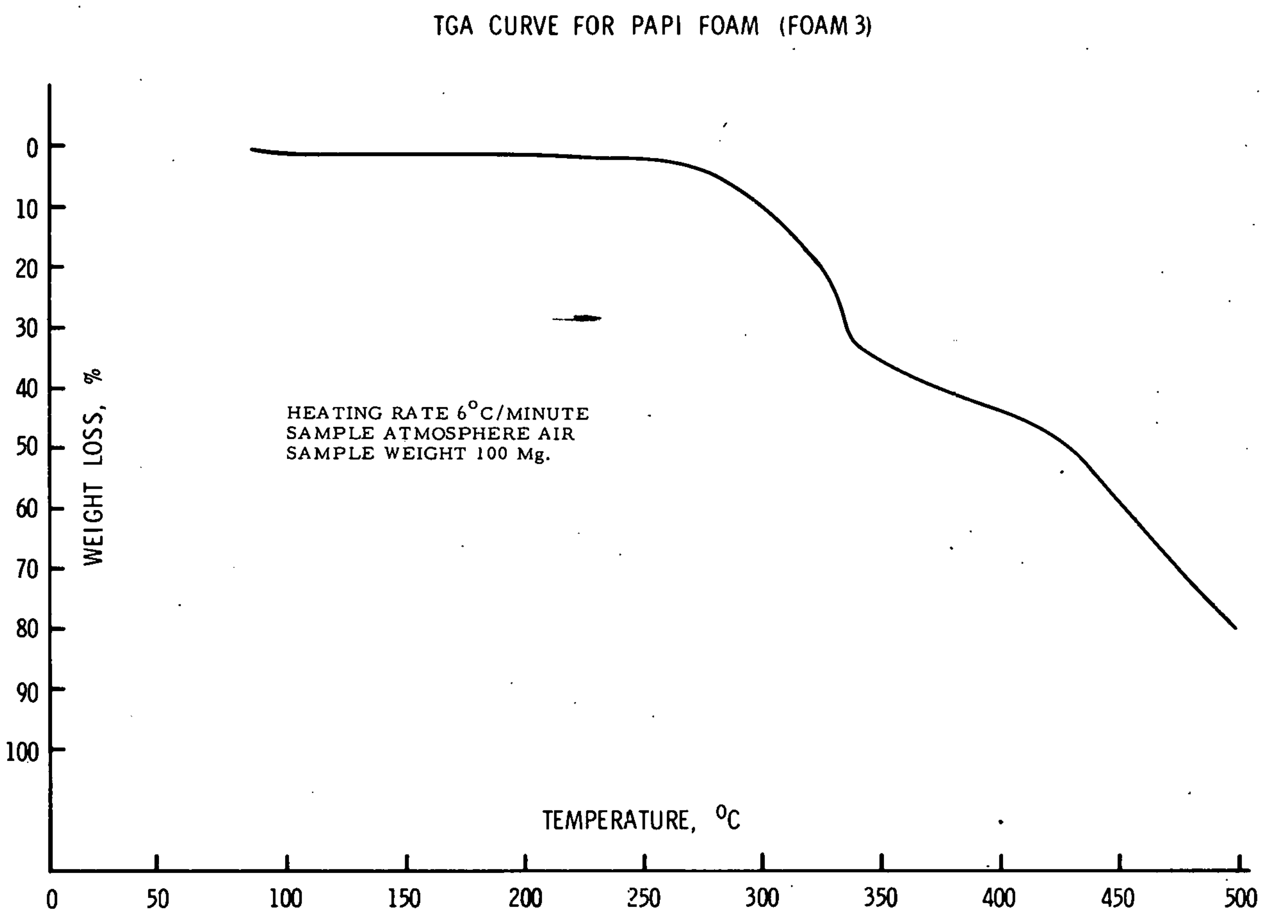

FIGURE 4

TABLE III

POSSIBLE DEGRADATION PRODUCTS FOR URETHANES AT 200-300°C

A. Dissociation to Isocyanate and Alcohol

$$RNHCOOR^1 \qquad RNCO + R^1OH$$

B. Formation of Primary Amine and Olefin

$$RNHCOOCH_2CHR^1 \qquad RNH_2 + CO_2 + R^1CH = CH_2$$

C. Formation of Secondary Amine

$$RNHCOOR^1 \qquad RN_HR^1 + CO_2$$

As still another measurement of their thermal stability, a DTA was made for each of the three foams. These DTA thermograms are given in Figure 5. A comparison of the DTA and TGA thermograms of each foam shows that in all cases the first DTA exotherm began at approximately the same temperature that initial weight loss started during TGA. The temperature at which the initial weight loss was observed by TGA is marked "A" on each corresponding DTA curve. Further comparison shows that the termination of the first decomposition mechanism during TGA occurred at temperatures near a maximum of an exothermic reaction by DTA. These points are marked "B" on the corresponding DTA curves.

The other characteristics of the DTA curves, such as the shoulder observed between points A and B, and other maxima after point B, are yet to be identified. The shoulders between A and B may well represent a change in decomposition mechanism. Such a case was not observed by TGA; however, a change in decomposition mechanism which had no change in rate of weight loss associated with it would not be observed by TGA. Foams 2 and 3, both containing PAPI, showed shoulders between A and B occurring at higher temperatures than Foam 1, which was based solely on TDI. It is certainly possible that the diisocyanate component may be responsible for such shoulders. However, complete identification would require extensive additional investigation.

It was also observed that Foam 1 gave a very sharp DTA maximum near 330°C, which neither of the other foams exhibited. Both Foams 2 and 3 did show maxima, but not nearly of the same intensity and at a considerably higher temperature. This would indicate that the foams containing PAPI had higher thermal stability. That is, the exothermic reaction associated with initial decomposition of the PAPI foams reached a maximum at higher temperatures than did the TDI foam.

The last broad exotherm, shown on the DTA curves in Figure 5, occurred at nearly the same temperature (+525°C) for all three foams. This exotherm is believed to be due to the final decomposition of the foam. These decomposition products are considered to consist mainly of H_2O, CO_2, and N_2.

Heat aging results are graphically represented in Figure 6 as a plot of percent weight loss against time at 175°C. Foam 3, containing only PAPI, was the most stable to heat aging, while Foam 1, containing only TDI, was the least stable, as indicated by weight loss. Foam 2, containing both TDI and PAPI, was intermediate.

Infrared analysis of the foams, before heat aging, showed that all three foams contained unreacted free isocyanate as determined by the presence of an adsorbance at 4.4 microns. The order of increasing amounts of unreacted isocyanate is Foam 2 $<$ Foam 3 $<$ Foam 1. No excess free isocyanate was detectable by infrared analysis after heat aging.

The percent nitrogen determined for each foam is shown in Table IV. The results listed in Table IV tend to correlate with the other findings presented throughout this report. The TDI-based Foam 1 contained the most nitrogen, yet it was found to be the least thermally stable in the various tests performed. The high nitrogen content found for Foam 1 could indicate a high degree of cross-link density. If this is true, the work presented here would show that thermal stability is more dependent upon the type of cross-link present than on the amount. The nitrogen content for PAPI containing Foams 2 and 3 is in line with the other thermal properties found for these materials. Foam 2 (TDI/PAPI) has intermediate heat resistance and nitrogen content, while Foam 3 (PAPI) has the least nitrogen content, and the greatest thermal stability.

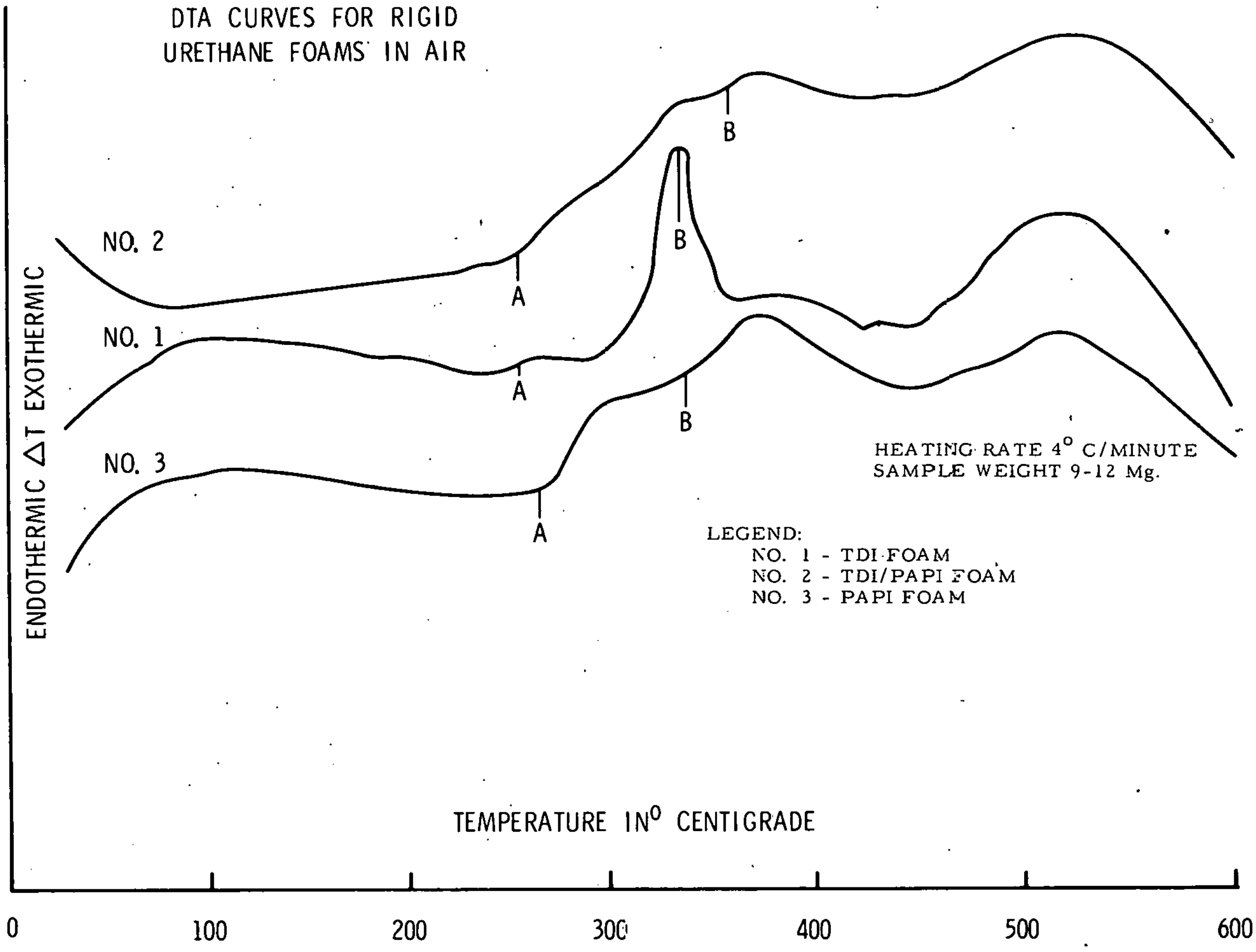

FIGURE 5

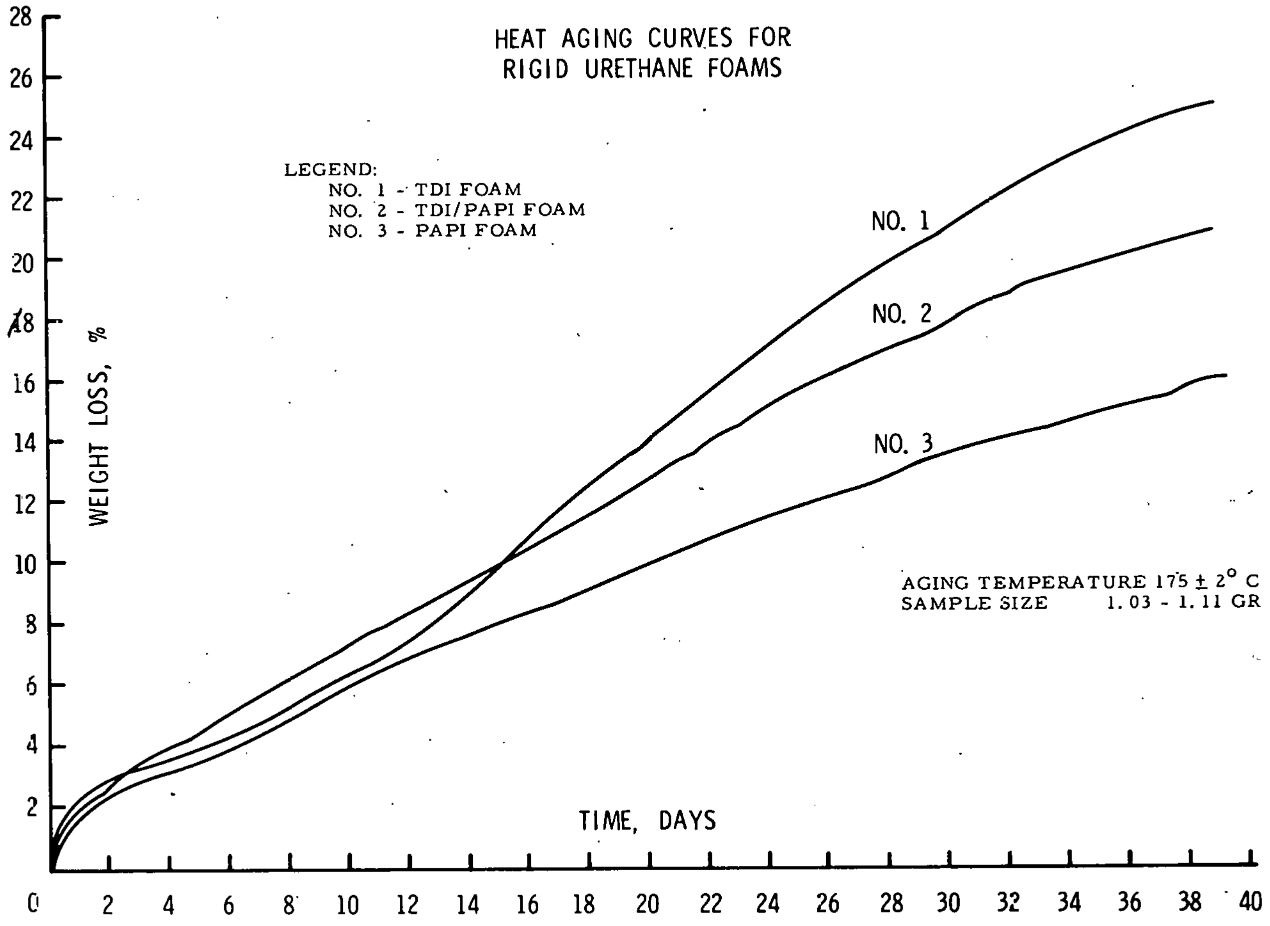

FIGURE 6

SUMMARY AND CONCLUSIONS

Rigid urethane foams are probably limited in high temperature applications, by the very nature of the thermal stability of the various components of which they are composed. The experimental data, summarized in Table V, indicates that the TDI foam (Foam 1) has little compressive strength beyond the range of 130-140°C and loses weight rapidly when heated above 225°C. The other type foams investigated (PAPI-containing materials) show improved thermal characteristics. A combination TDI/PAPI foam (Foam 2) maintains good compressive properties up to 170 - 180°C, while a foam based solely on PAPI (Foam 3) has adequate strength for many applications up to 225 - 235°C. Neither of the latter two foam systems exhibits significant weight loss below 300°C. Long-term heat-aging characteristics at 175°C for the foams investigated also indicate that the PAPI materials retain a higher percent of their original weight than the TDI foam.

The exact reason that the PAPI-based foams show good thermal stability is unknown. The nitrogen analysis of the foams indicates that PAPI-based materials may be slightly less cross-linked than the TDI foam. However, the data presented here shows this is not necessarily the sole criteria for good thermal properties. Many other facets must be taken into consideration, especially in regard to the PAPI foam. The bulkiness of the PAPI molecule, the increased aromatic content provided by its presence, the steric hindrance (protection of linkages) afforded by its size, or even the symmetry of this isocyanate could conceivably contribute to the increased thermal stability properties found for the rigid urethane foams based on this material. However, further investigation would certainly be necessary to verify these speculations.

TABLE IV

NITROGEN CONTENT FOR RIGID URETHANE FOAMS

Foam Number	Nitrogen Content, %
1. (TDI)	8.42
2. (TDI/PAPI)	7.35
3. (PAPI)	7.12

TABLE V

THERMAL CHARACTERISTICS FOR RIGID URETHANE FOAMS

	Foam 1 (TDI)	Foam 2 (TDI/PAPI)	Foam 3 (PAPI)
Property	(Approximate Temperature Limitation °C)		
Compressive Strength	130-140	170-180	225-235
Significant Weight Loss	225	300	300
Heat Aging at 175°C	Poor	Fair	Good

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ACKNOWLEDGEMENTS

The author expresses his sincere thanks to: J. M. Griffin for his help in preparing the foam test specimens; Department 213 for the physical and thermal testing and interpretation of these tests results; The Bendix Corporation, Kansas City Division, for allowing the presentation of this paper.