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NASA CR-
147791

"OPEN CELL FIRE-RESISTANT FOAM"

FINAL REPORT

Contract No. NAS 9-14717

July 1, 1975 to February 16, 1976

by

Horizons Incorporated
23800 Mercantile Road
Cleveland, Ohio 44122

Authors

James E. Thompson
Joseph W. Wittmann
Kennard A. Reynard

to

National Aeronautics and Space Administration
Lyndon B. Johnson Space Center
Houston, Texas 77058

April 1976



HORIZONS RESEARCH INCORPORATED

23800 MERCANTILE ROAD • CLEVELAND, OHIO 44122

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ABSTRACT

Candidate polyphosphazene polymers were investigated to develop a fire-resistant, thermally stable and flexible open cell foam. The $[(C_6H_5O)_2PN-(4-C_2H_5C_6H_4O)_2PN]_n$ copolymer was prepared in several mole ratios of the substituent side chains and a (nominal) 40:60 derivative was selected for formulation studies. The $[(C_6H_5O)_2PN-(4-\underline{S}-C_4H_9C_6H_4O)_2PN]_n$ also was prepared but eliminated from consideration on the basis of slightly less thermal stability as compared to the former copolymer. Preparations of $[(C_6H_5O)_2PN-(n-C_4H_9O)_2PN]_n$ and $[(4-ClC_6H_4O)_2PN-(n-C_4H_9O)_2PN]_n$ were not entirely successful.

Synthesis of the polymers involved solution polymerization of hexachlorophosphazene to soluble high molecular weight poly(chlorophosphazene), followed by derivatization of the resultant polymer in a normal fashion to give polymers in high yield and high molecular weight. Small amounts of a cure site were incorporated into the polymer for vulcanization purposes. The poly(aryloxyphosphazenes) exhibited good thermal stability and the first polymer mentioned above exhibited the best thermal behavior (TGA) of all the candidate polymers studied.

Efforts were devoted to evaluation of methods for formation of low density open cell foams. The $[(C_6H_5O)_2PN-(4-C_2H_5C_6H_4O)_2PN]_n$ (40:60 mole ratio with 2.5 mole % unsaturated pendant groups) polymer was used for this development effort. Foams of 3.5 to

9 lbs/ft³ density were produced with chemical blowing agents and peroxide curing agents using methods similar to those used industrially for the production of open cell sponge. For the intended application adequate physical properties, except for resilience, were obtained and thermal aging performance was superior. Further compounding efforts are expected to improve resilience.

Limiting Oxygen Index values of 35 to 38 were obtained. NBS smoke density values of 81 to 172 were found. In general, smoke chamber results were much better for the poly(aryloxyphosphazenes) than for currently used materials which often employ halogen. Further improvement in flame retardant properties is expected with further work.

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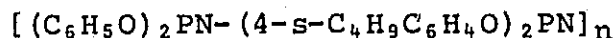
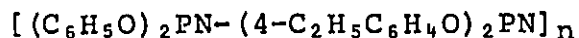
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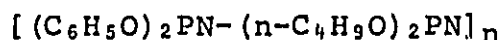
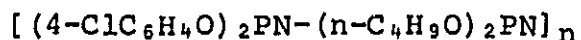
1.0 INTRODUCTION

In prior work [Ref. 1] supported by the Navy, a closed cell poly(aryloxyphosphazene) foam was investigated to develop fire-resistant and thermally stable thermal insulation for marine applications. These closed cell foams were desirable to minimize hazards associated with fire aboard ship. Thermal stability of the low density closed cell foam was demonstrated in long term aging tests at 300°F. Poly(aryloxyphosphazenes) remained flexible after 408 hours with little change in density, while other commercial fire-retardant foam materials shrank and embrittled. Considering other physical property data, these foams either meet or exceed the requirements of MIL P-0015280F for thermal insulation.

With this background in mind, the poly(aryloxyphosphazenes) were chosen by National Aeronautics & Space Administration as candidates for fire-resistant, low smoke, thermally stable, highly resilient open cell flexible foams. These foams are intended for use in seat cushions in manned spacecraft and commercial aircraft.

The following candidate polymers were investigated to meet contract objectives:





The first polymer was prepared successfully in several mole ratios of the substituent groups. The second polymer was prepared but was eliminated from consideration because of lower thermal stability as compared to $[(\text{C}_6\text{H}_5\text{O})_2\text{PN}-(4\text{-C}_2\text{H}_5\text{C}_6\text{H}_4\text{O})_2\text{PN}]_n$. The last two polymers could not be prepared under the reaction condition employed.

2.0 SUMMARY

Hexachlorophosphazene (I) can be polymerized successfully in 1,2,4-trichlorobenzene to give soluble polymer. Polyphosphoric acid (PPA, 1%) was effective at 200-210°C. High molecular weight poly(dichlorophosphazene) (II) was obtained in 22-33% conversion for derivatization purposes.

Polymers (II) were derivatized normally at 123-130°C to give polymers in high yields and high molecular weight. A "cure site" was incorporated in small amounts for vulcanization purposes. The $[(\text{C}_6\text{H}_5\text{O})_2\text{PN}-(4\text{-C}_2\text{H}_5\text{C}_6\text{H}_4\text{O})_2\text{PN}]_n$ polymer (III), 40:60 mole ratio, exhibited good thermal behavior (by TGA) with initial weight loss beginning to occur well above 400°F (204°C) for the gum stock in air. Long term thermal aging in air (500 hours) at 300°F (149°C) showed a weight loss of $\pm 1\%$ for the gum stock.

The polymer (III) which contains phenoxy and 4-ethylphenoxy substituents in a nominal mole ratio of 40 to 60 and includes 2-1/2 mole percent unsaturated pendant groups for effective crosslinking was selected as the candidate for open cell foam production. This polymer was chosen on the basis of its high degree of fire retardancy without the presence of halogen and its elastomeric character.

Foams were formulated using a combination of chemical blowing agents: Polyzole A7DN, Celogen RA, and sodium bicarbonate. The curing system was a combination of peroxides: benzoyl peroxide and VulCup 40KE. Physical properties obtained approached the desired ranges except for resilience. Further work is expected to improve that property also.

The methods used to produce $[(C_6H_5O)_2PN-(4-C_2H_5C_6H_4O)_2PN]_n$ (VI) foams, though carried out on a laboratory scale, are similar to methods used industrially for the production of open cell sponge. No major problems in scaling up laboratory processing techniques to meet production requirements are anticipated.

3.0 SYNTHESIS AND CHARACTERIZATION

3.1 Synthesis of Poly(dichlorophosphazenes) (II)

Hexachlorophosphazene (I) was obtained in high purity and was polymerized as received. All solvents used were of reagent grade or good quality, and were dried over 4A molecular sieves

prior to use. All other starting materials were either of good quality as received or purified by distillation prior to use.

Polyphosphoric acid (PPA), catalyst, was prepared by mixing 9 parts of the original acid (MCB, $H_6P_4O_{13}$) with 1 part of P_2O_5 while heating and stirring on a hot plate until a fluid and well dispersed mixture was obtained. All polymerizations were conducted in solution under nitrogen.

Hexachlorophosphazene (I) and 1,2,4-trichlorobenzene were heated until the trimer (I) dissolved, followed by the addition of PPA (1%). In general, polymerization mixtures were heated to 200-210°C for periods as given in Table I. Conversions to polymer were determined by weighing out 3-5 g of the polymerization mixture, extracting unpolymerized oligomers with petroleum ether, 3 times, drying the residual polymer in a vacuum oven at 25-35°C and weighing polymer to calculate conversion as a function of time.

When suitable conversion to polymer was obtained (20-30%), the polymerization mixture was cooled to approximately 130°C and 2 liters of dry heptane were added. The polymer does not precipitate at this stage. The mixture was transferred to a larger container and 6 liters of dry petroleum ether were added to the stirred mixture in order to precipitate the polymer from solution, followed by 2 washings with 1 liter each of dry petroleum ether. Organics were decanted and 4 liters of dry benzene were added to dissolve the polymer.

TABLE I
 Polymerizations Involving Hexachlorophosphazene (I) to Polymer [Cl₂PN]_n (II)

Run No. Design.	Amounts (g)	Temperature (°C)	Time (hrs)	1,2,4-Cl ₃ C ₆ H ₃ (mls)	Catalyst (g)	[η] (φH, 30°C)	Conversion (%)	Refer to Table II Run No. Entry
1 2044-29	300	200	66	220	polyphosphoric acid, PPA 3.5	0.93	23	1
2 2044-35	2000	212-215	45	1400	PPA 20.6	1.10	18	7
3 2044-42	2000	200	90	1400	PPA 20.7	0.70	24	2
4 2422-01	300	210	29	206	PPA 3.5	1.51	22	3
5 2422-05	2000	200-203	45.5	1390	PPA 28.4	0.62	31	5
6 2044-47	2000	200	140	1400	PPA 16.0	0.72	30	4
7 2422-07	2000	200 210	46.5 44.5	1400	PPA 20.0	1.15	30	6
8 2422-12	300	200	95	206	PPA 3.0	1.17	25	
9 ^a 2422-14	200	200	24	140	PPA 40.0	0.77	32	
10 2422-17	2000	200	79	1400	PPA 21.0	0.95	27	8

^a After 25.5 hours at 200°C, polymer gelled. Stirrer stopped overnight.

TABLE I (continued)

Run No. Design.	Amounts (g)	Temperature (°C)	Time (hrs)	1,2,4-Cl ₃ C ₆ H ₃ (mls)	Catalyst (g)	[η] (φH, 30°C)	Conversion (%)	Refer to Table II Run No. Entry
11 2436-22	2000	195-204	142	1400	PPA 21.3	0.68	23	9
12 2411-10-12	200	197-205	22	140	P ₂ O ₅ 4.0	0.30	67 46 ^b	14
13 2436-32	2000	199-209	94	1400	PPA 22.5	6.69	26	12
14 2422-20	2000	200	92	1400	PPA 21.0	0.71	28	10
15 2422-22	2000	200	67.5	1390	PPA 20.5	0.79	30	11
16 2436-43	2000	183-212	89	1400	PPA 22.7	0.75	33.5	13

^a After 25.5 hours at 200°C, polymer gelled. Stirrer stopped overnight

^b Conversion to isolated polymer.

The solids content of the polymer solution is determined by withdrawal of a weighed sample which is freeze dried under vacuum overnight, weighed, and proper amounts of polymer calculated.

High molecular soluble polymers (II) were obtained in 22-33% conversions. Data for polymerization of (II) is presented in Table I. Note that P_2O_5 (2%) as catalyst gave a lower molecular weight polymer at higher conversions (Run 12).

3.2 Derivatization of Poly(dichlorophosphazene) (II)

In order to prepare derivatives of polymer (II), reactions between the sodium salt(s) of the desired alcohol(s) and (II) were carried out in solution. A typical reaction employed:

Sodium methoxide (10 equivalents, 10 mole % excess over P-Cl (II) equivalents)

Phenols (11 equivalents, total of 20 mole % excess over P-Cl (II) equivalents only when phenols are used. When a phenol is used with butanol, then 5 equivalents of the phenol are used.

n-Butanol (12 equivalents, 140 mole % excess over P-Cl equivalents)

Eugenol (0.27 equivalent, 2.5 mole % of total phenol content)

Poly(dichlorophosphazene) (II) (9 equivalents)

Diglyme, bis(2-methoxyethyl)ether (9 liters)

Benzene (3 liters) for azeotroping.

Any significant variation of the above amounts are given in Table II.

TABLE II
Preparation of Polymers [(4-RC₆H₄O)₂PN-(R'O)₂PN]_n

Run No., Designation, Polymer and Mole Ratio Charged	Temp. (°C)	Time (hrs)	[η] (cH, 30°C)	Yield (%)	Analyses			NMR 4-RC ₆ H ₄ O/R'O Mole %	Refer to Table I Run No. Entry	Remarks
					% C	% H	% N			
1										
2044-32	25	288	1.72	83 (total)	56.87	6.64	6.64	0	4	One half of reaction mix- ture used. Method A work- up. Rubber.
R=H, R'=n-C ₄ H ₉ ^{a, b} (VI) (5:6)					50.95	7.06	7.39	2.29		
	25	288	1.56	83 (total)	56.87	6.64	6.64	0	4	
	95	45.5			52.75	7.17	7.27	0.04		
2										
2044-44	25	1.5	0.52 ^d	43	57.33	6.60	-	0	6	Difficult to isolate polymer. Workup A. Substantial loss of butyl groups observed. Rubber.
R=H, R'=n-C ₄ H ₉ ^c (VI) (5:6)	95	25			49.55	5.38		0.51		
3										
2411-01	25	66	1.47	90	49.00	5.63	5.82	13.39	7	One half of reaction mix- ture used. Workup by washing with H ₂ O (3X) and precipitating with CH ₃ OH. Rubber.
2422-01					46.01	5.40	6.00	15.00		
R=Cl, R'=n-C ₄ H ₉ ^{a-c} (V) (5:6)	25	66			49.00	5.63	5.82	13.39	7	
	102	3	1.13	87	46.20	5.49	5.76	13.64		

^a No cure site

^b (II), 0.91-0.94 equivalent

^c Glyme-benzene (5:3)

^d THF

TABLE II (continued)

Run No., Designation, Polymer and Mole Ratio Charged	Temp. [°C]	Time (hrs)	[η] (% H ₂ O)	Yield (%)	Analyses			NMR 4-RC ₆ H ₄ O/R'O Mole %	Refer to Table I Run No. Entry	Remarks
					% C	% H	% N			
4 2044-50 R=Cl, R'=n-C ₄ H ₉ C, e (V) ³ (1:1)	59-62	42	1.28	61	54.68 43.65	3.46 3.22	-	12.98 19.39	9	Difficult to isolate polymer. Workup A. Substantial loss of butyl groups observed. Plastic.
5 2421-05 2422-05 R=H, R'=4-S-C ₆ H ₄ C ₆ H ₅ F (IV) (1:1)	130	55	1.20	20	66.96 66.79	6.30 6.00	4.86 4.30	0 0.47	8	Workup B. Rubber.
6 2422-10-15 R=H, R'=4-S-C ₆ H ₄ C ₆ H ₅ F (IV) (3:2)	130	50	1.21	38	-	-	-	0 0.37	10	Workup B. Rubber.
7 2044-37 R=H, R'=4-C ₆ H ₄ C ₆ H ₅ F (III) (1:1)	125	58	1.65	88	65.00 64.86	5.42 5.61	5.38 5.37	0 0.05	5	Workup A. Flexible thermoplastic.
8 2422-13 R=H, R'=4-C ₆ H ₄ C ₆ H ₅ F (III) (40:57.5)	123-128	71	1.36	38	65.25 64.15	5.61 5.39	-	0 0.33	13	Workup B. Rubber.

³ n-C₄H₉OH/4-C₆H₄C₆H₅OH = 1/1 (molar charge) I Glyme-benzene (5:1)

TABLE II (continued)

Run No., Designation, Polymer and Mole Ratio Charged	Temp. (°C)	Time (hrs)	[η] (cH, 30°C)	Yield (%)	Analyses Calculated/Found			NMR 4-RC ₂ H ₄ O/R'O Mole %	Refer To Table I Run No. Entry	Remarks
					% C	% H	% N & Cl			
2436-29-31 R=H, R'=4-C ₂ H ₅ C ₆ H ₄ (III) (40:57.5)	123-126	50	1.26	90	65.25 62.89	5.61 5.45	- 1.20	46/54	14	Workup B. Rubber.
10 2422-20-21 R=H, R'=4-C ₂ H ₅ C ₆ H ₄ (III) (40:57.5)	128	52	1.19	85	65.25 65.15	5.61 5.55	- 0.40	46/54	17	Workup B. Rubber.
11 2422-22-23 R=H, R'=4-C ₂ H ₅ C ₆ H ₄ (III) (40:57.5)	127-129	41	1.38	93	65.25 64.61	5.61 5.50	- 0.34	47/53	18	Workup A. Rubber.
12 2436-34-36 R=H, R'=4-C ₂ H ₅ C ₆ H ₄ (III) (40:57.5)	123-126	40	0.97	77	65.25 60.95	5.65 5.11	- 3.23	47/53	16	Workup A. Rubber.
13 2436-46-47 R=H, R'=4-C ₂ H ₅ C ₆ H ₄ (III) (40:57.5)	123-126	44	1.46	81	65.25 64.73	5.61 5.38	- 0.94	45/54	19	Workup A. Rubber.

F Glyme-benzene (5:1).

TABLE II (continued)

Run No., Designation, Polymer and Mole Ratio Charged	Temp. (°C)	Time (hrs)	[η] (SH, 30°C)	Yield (%)	Analysis			NMR 4-RC ₆ H ₄ O/R'O Mole %	Refer to Table I Run No. Entry	Remarks	
					% C	% H	% N				
I4 2411-10-12 R=H, R'=4-C ₂ H ₅ C ₆ H ₄ 9 (III) (40:57.5)	129	47	0.76	79	65.25	5.61	-	0	46/54	15	Precipitated in CH ₂ Cl ₂ , centrifuged and precipi- tated from THF with water. Rubber.

9 (II), 1.60 equivalents; NaOCH₃ (1.4M).

The sodium alcoholates were prepared by the interchange reaction between sodium methoxide and the corresponding hydroxyl containing materials followed by azeotropic distillation with benzene of the methanol formed. Approximately 2 liters of distillate were collected at 70-103°C as the temperature of the reaction mixture was raised to 126°C. Completion of the interchange reaction was checked by a refractometer. At the end of the reaction, the polymer-benzene solution (10%, 9 equivalents) is added with stirring in a thin stream to the solution which is maintained at 125-130°C for 3 to 4 hours as the approximate 5 liters of benzene are distilled. Generally, the reaction is maintained at 125-130°C over a period of 2 to 3 days. When a mixed alkoxy-aryloxy polyphosphazene is prepared, the addition of the polymer solution generally is conducted at room temperature over 4 to 5 hours. Temperature is raised to 95-100°C for 3 to 4 hours to complete the reaction.

When there is no further change in base concentration in the reaction mixture, purification by either of two methods is employed. Data obtained for the polymers are presented in Table II.

Method A. The polymer was precipitated by pouring the reaction mixture into 20 liters of stirred methanol and stirred overnight. Liquid was decanted from polymer and polymer was stirred with 4 liters of methanol for 3 hours, followed by two washings with 12 liters of water-methanol mixture (2:1 by volume). The last washing was allowed to stir overnight. Polymer was dissolved in 4 liters

of tetrahydrofuran (THF) and was precipitated by adding 8 liters of distilled water to the polymer-THF solution. This procedure was conducted twice and only small quantities of chloride ion were found in the supernatant liquid. Polymer was dried under vacuum at 35-40°C.

Method B. Polymer was precipitated from the reaction mixture and washed as described in Method A. The polymer was wash-milled for 20-30 minutes to remove most ionic chloride. The polymer was stirred in distilled water overnight and dried under vacuum at 35-40°C. On occasion the polymer then was dissolved in 4 liters of THF and was reprecipitated by adding 8 liters of distilled water to the polymer-THF solution and vacuum dried.

Small amounts (2.5 mole %) of eugenol as a cure site were incorporated in the polymers. Generally, good yields of high molecular weight rubbery polymers were obtained. Structures for these polymers were confirmed by IR, NMR, and elemental analyses. Data are presented in Table II.

Some redistribution of pendant groups on the backbone of the polymer may have occurred during reaction. Therefore the substituent ratio may not necessarily reflect the initial charged ratio. The sensitivity of NMR, IR, and elemental analyses generally is not sufficient to detect this scrambling within the limit of experimental error. However, NMR analyses gave consistently slightly higher ratios of phenoxy to p-ethyl-phenoxy than originally charged. Any property variation of the above polymers could well be a

function of the above mentioned scrambling, branching, and/or molecular weight or its distribution.

In runs 2 and 4, lower yields of the polymer were obtained due to degradation of the polymer and concomitant loss of butyl group during reaction. This observation was confirmed by spectral and elemental analyses. In run 3, some polymer degradation occurred when the polymer mixture was heated to an elevated temperature as evidenced by a decrease in viscosity.

We believe the polymers, as presented in Table II, to be fully substituted except for the polymers isolated from runs 1, 9, and 12, which gave weak silver nitrate chloride ion tests. In runs 5 and 13, reprecipitating the polymers reduced their 0.47 and 0.94% chlorine content to 0.06 and 0.07, respectively. This result indicates the by-product salt (NaCl) was not completely removed from the polymer during purification.

Gum stocks of polymers $[(C_6H_5O)_2PN-(4-C_4H_7C_4H_7O)_2PN]_n$ (III), 40:57.7 mole ratio, and $[(C_6H_5O)_2PN-(4-g-C_4H_7C_4H_7O)_2PN]_n$ (IV), 1:1 mole ratio, possess good thermal stability and initial weight loss begins to occur well above 400°F (204°C) in air (Figures 1 and 2). TGA comparisons of the foam (III), 40:57.5 mole ratio (Figure 3) with its gum stock (Figure 1) indicates the gum stock is more thermally stable than the foam. On the basis of the data outgassing of the foam is not expected to pose a problem if this material encounters a heat flux typical of a fire scenario.

FIGURE 1. TGA ON GUM STOCK (VI), 40:57.5 MOLE RATIO IN AIR AT 10°C/MINUTE

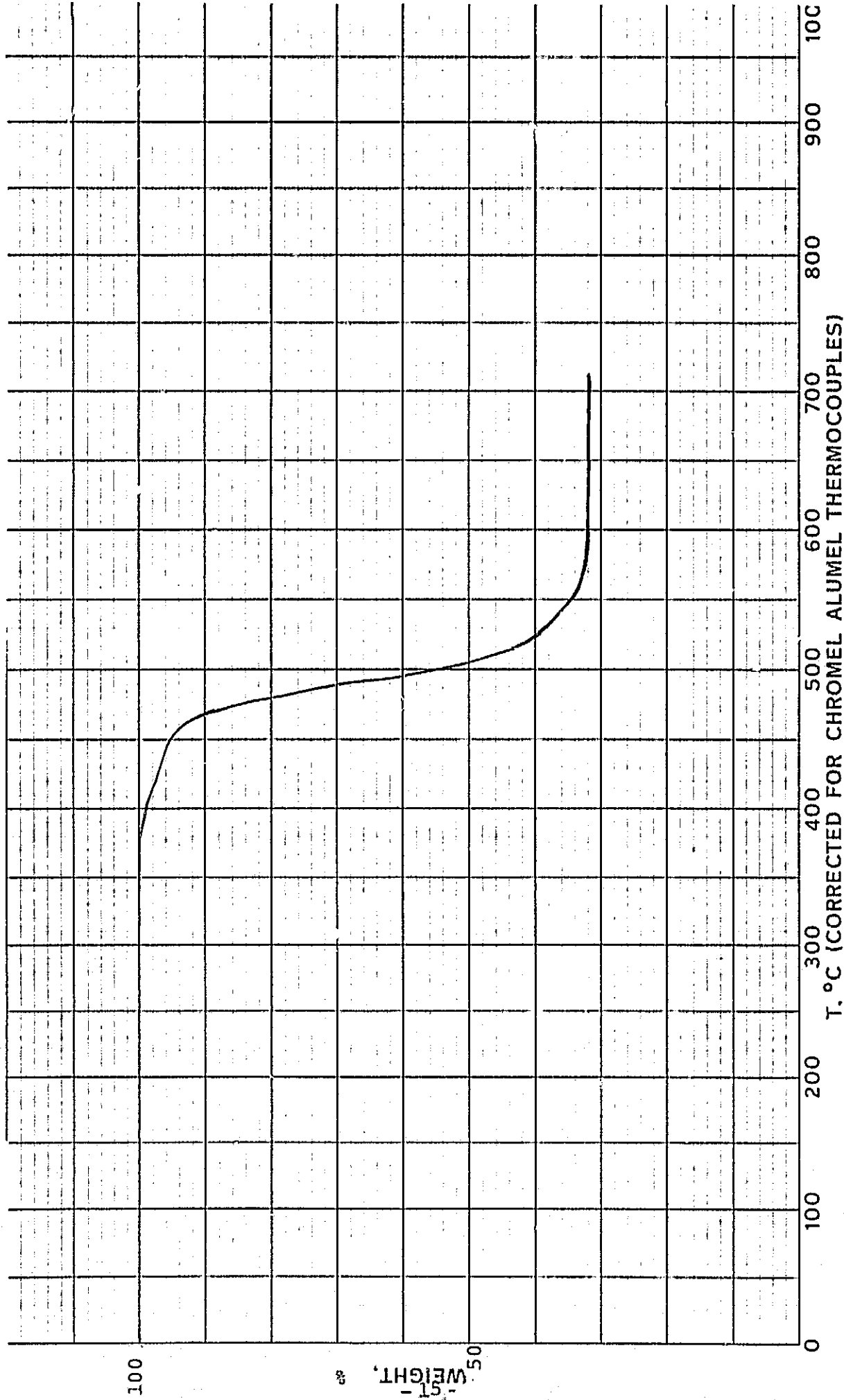
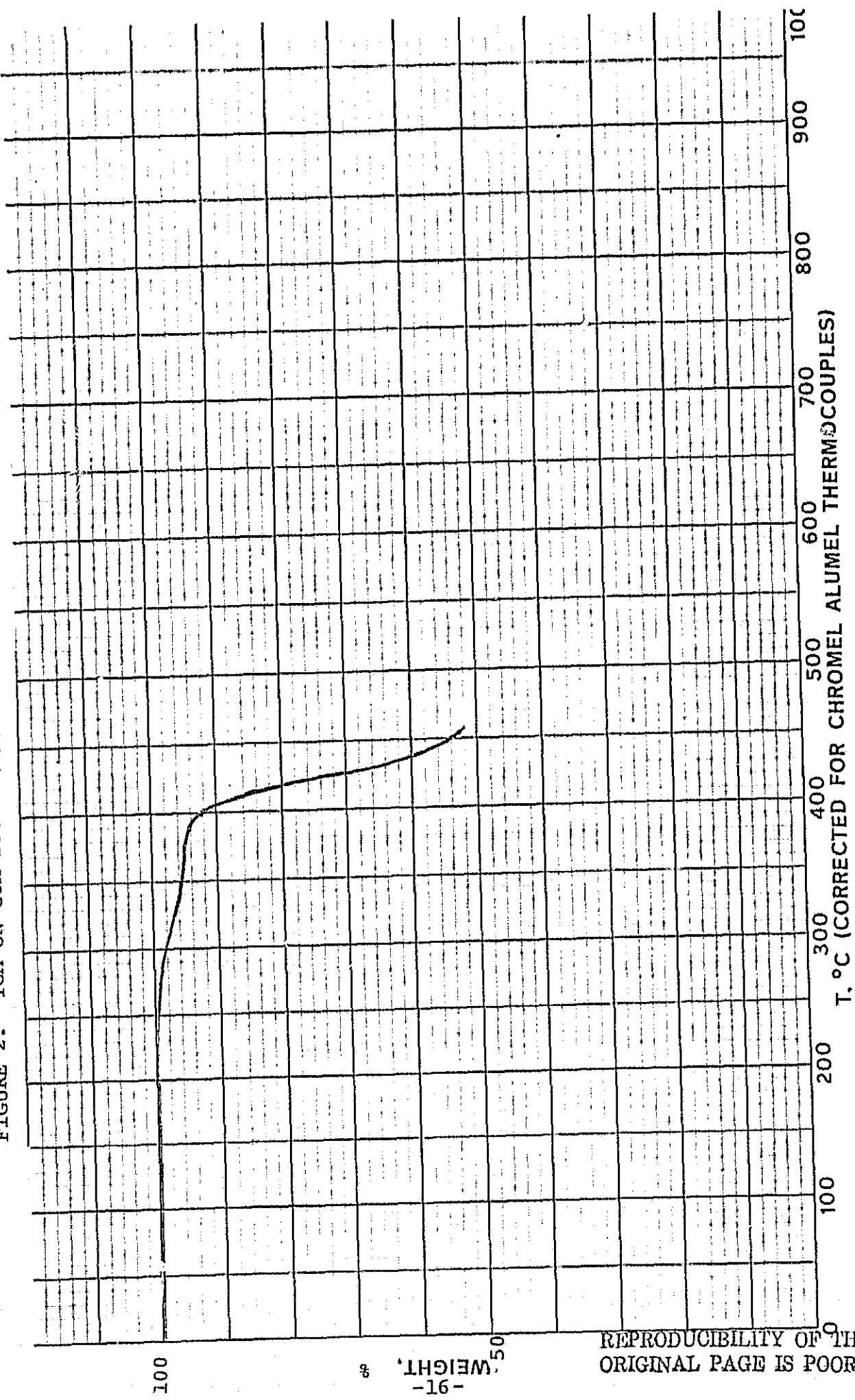


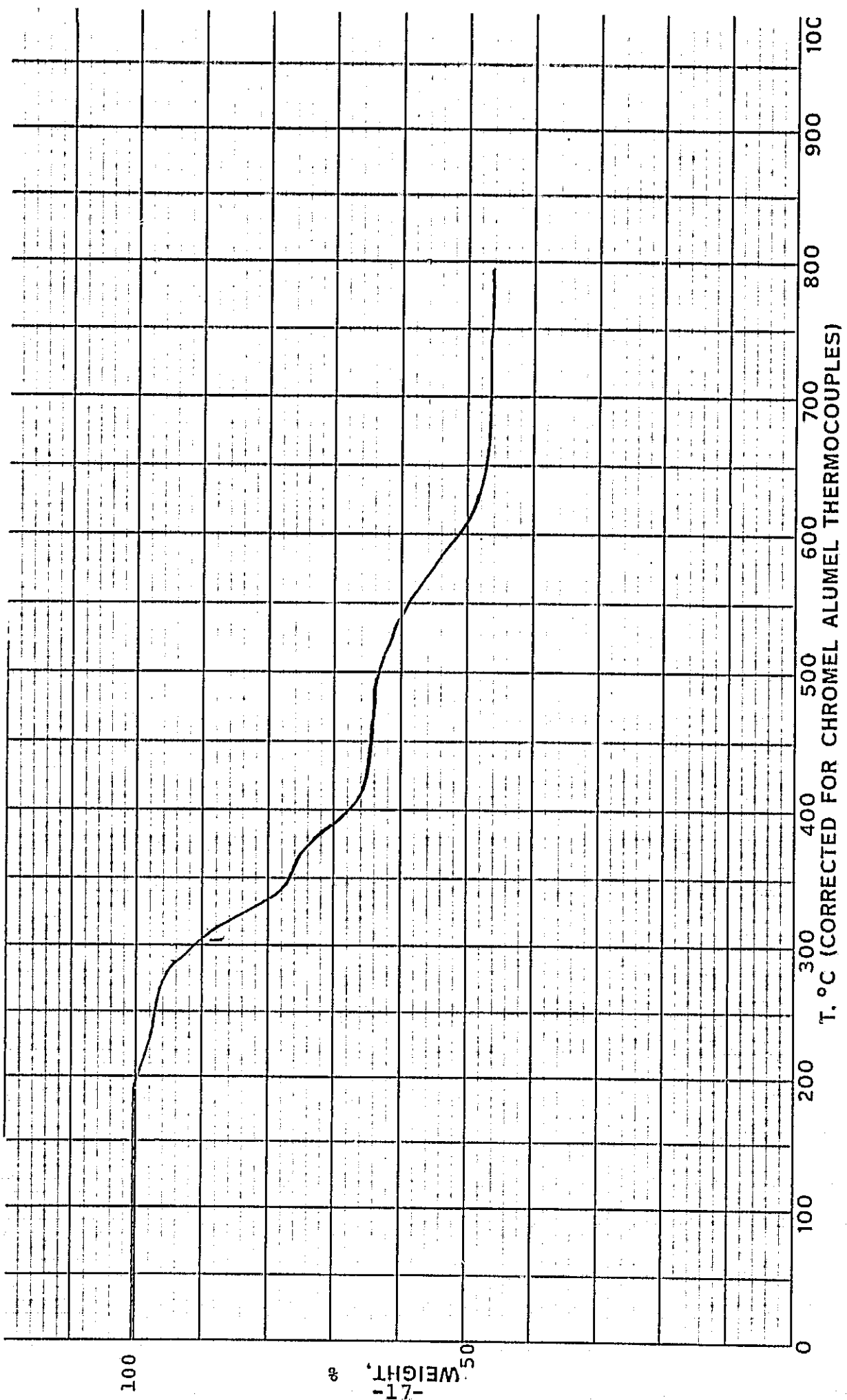
FIGURE 2. TGA ON GUM STOCK (V), 1:1 MOLE RATIO, IN AIR AT 10°C/MINUTE



100
% WEIGHT
-91-
50

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FIGURE 3. TGA ON FOAM (VI), 40:57.5 MOLE RATIO, IN AIR AT 10°C/MINUTE



Long term thermal air aging results (Table III) on the gum stock of (III), 40:57.5 mole ratio, indicates oxidative cross-linking occurs.

TABLE III

Air Aging at 300°F on Polymer (III)

<u>Time (hrs)</u>	<u>Weight Loss (%)</u>	<u>% Insoluble</u>
24	0	80
100	0.31	95
200	0.27	97
400	0.73	98
500	0.97	99

During the 500 hours, the rubber transformed from a soft to a hard solid.

Based upon preliminary physical data obtained on foamed candidate polymers, the 40-phenoxy/57.5 4-ethylphenoxy/2.5 cure site polymer was selected as best suited to meet the contract goals. A complete evaluation of this polymer as a foam is given in Section 4. Approximately 11 lbs. of this polymer were prepared for this evaluation.

4.0 PREPARATION OF FOAMS AND THEIR PROPERTIES

4.1 Candidate Polymer Evaluation

A standard foam formulation was chosen to compare polymers and to provide for selection of the candidate for more complete development. The formulation was based on previous knowledge of poly(aryloxyphosphazene) closed cell foam formulations [Ref. 1]. The base formulation is shown in Table IV.

TABLE IV

Standard Formulation for Comparing Candidate Polymers

Polymer	100 phr
Hydral 710	100
ZnO	15
Varox powder	4
Benzoyl peroxide	1.5
Celogen AZ130	10
BIK	5

Flammability properties, retention of resilience, and thermal stability were of primary interest in screening of polymers. Although measurements were made on unoptimized foam samples, we assumed these properties would allow relative ranking of gum stocks. Of course, changes in formulation would change foam properties but the likelihood of a reversal in order for these properties

was minimal. Polymers evaluated are listed in Table V. Each polymer had 2.5 mole % unsaturated pendant groups for effective crosslinking. The $[(C_6H_5O)_2PN-(4-C_2H_5C_6H_4O)_2PN]_n$ polymer showed a higher limiting oxygen index and better retention of resilience after air aging than other candidate polymers. The 2:3 mole ratio $[(C_6H_5O)_2PN-(4-C_2H_5C_6H_4O)_2PN]_n$ polymer was more elastomeric than the 1:1 mole ratio polymer and was chosen as best suited to meet the contract goals. As shown in Table V, no difference in LOI or thermal aging was seen between the 1:1 and 2:3 mole ratio $[(C_6H_5O)_2PN-(4-C_2H_5C_6H_4O)_2PN]_n$ polymers.

TABLE V
Evaluation of Candidate Polymers in Standard Formulation

<u>Polymer^a</u>	<u>Copolymer Composition</u>	<u>LOI</u>	<u>Retention of Resilience^b at 300°F in Air (days)</u>
2044-39 [(C ₆ H ₅ O) ₂ PN- (4-C ₂ H ₅ C ₆ H ₄ O) ₂ PN] _n	1:1	32	>12
2436-47 [(C ₆ H ₅ O) ₂ PN- (4-C ₂ H ₅ C ₆ H ₄ O) ₂ PN] _n	2:3	32	>12
2411-06-08 [(C ₆ H ₅ O) ₂ PN- (4- <u>S</u> -C ₄ H ₉ C ₆ H ₄ O) ₂ PN] _n	1:1	30	2
2422-15 [(C ₆ H ₅ O) ₂ PN- (4- <u>S</u> -C ₄ H ₉ C ₆ H ₄ O) ₂ PN] _n	3:2	30	2
2044-50 [(n-C ₄ H ₉ O) ₂ PN- (4-ClC ₆ H ₄ O) ₂ PN] _n	1:1	would	not cure

^a Polymers contain 2.5 mole % unsaturated pendant groups.

^b Qualitative.

These samples were molded in a 3/4" x 1-1/2" x 1/8" mold at 110°C for 10 minutes and expanded in a forced air oven for 30 minutes at 150°C.

4.2 Processing Methods

Open cell foam formulations were processed on standard rubber mixing equipment including a C. W. Brabender Prep Center and a two-roll rubber mill. Foam formulations were free blown in a forced air oven at 110°C for 30 minutes and subsequently post cured in a forced air oven at 125-150°C for an additional 30 minutes. The mixer and mill were used at ambient temperatures and heating caused by mechanical shear was minor. Formulations generally were used immediately after mixing, though some formulations used after 5 days appeared as useable as freshly prepared stock.

4.3 Formulation of Open Cell [(C₆H₅O)₂PN-(4-C₂H₅C₆H₄O)₂PN]_n Foams (General Considerations)

Open cell foams were formulated to meet the physical property requirements of urethane seat cushioning material and to possess superior fire retardancy and smoke properties. Desired values are listed in Table VI.

The general approach to obtaining a poly(aryloxyphosphazene) open cell foam was to develop formulations and processing methods which gave an open celled foam in the desired density range. Then physical properties were evaluated and formulations improved to bring physical property values into desired ranges. Considerable effort was expended in order to prepare low density

TABLE VI

Desired Property Values of Open Cell Foams

<u>Test</u>	<u>Method</u>	<u>Desired Value</u>
Density	ASTM D-1564 Suffix W, Sect. 69-74	2.5 lbs/ft ³
Tensile strength and Elongation	ASTM D-1564 Suffix T, Sect. 82-88	Tensile \geq 12 psi Elongation \geq 80%
Tear resistance	ASTM D-1564 Suffix G, Sect. 75-81	Tear resistance \geq 1 lb/in.
Fatigue	ASTM D-1564 Proc. B, Sect. 61-68	Loss \leq 20% at 65% deflection
Indentation load deflection (ILD)	ASTM D-1564 Method A, Sect. 19-25	\leq 25-35 lbs/50 in ² at 25% indentation \leq 65-90 lbs/50 in ² at 65% indentation
Compression set	ASTM D-1564 Method B	\leq 7% at 50% deflection \leq 12% at 90% deflection
Steam autoclave loss of compression load deflection	ASTM D-1564 Condition B Sect. 5-11	\leq 20%
Corrosion	Fed. Test Method Standard 151 Method 811	No corrosive effect on aluminum for \geq 14 days
Odor	1 hr/71 \pm 5°C	No objectionable odor
Dry heat	ASTM D-1564	Tensile strength
Tensile strength	Suffix A, Sect. 45-51	Tensile strength loss \leq 20%
Resilience	ASTM D-1564 Suffix R, Sect. 89-95	\geq 55%
Flammability Oxygen index Smoke density	ASTM D-2863 NBS smoke chamber	LOI \geq 40 D _{max} of 50-70
Chemical properties thermal stability corrosive or toxic by-product	NASA's TGA	400°F minimize or eliminate

(3-6 lbs/ft³) open cell foams and as a result physical properties have not yet been fully optimized. Lower densities are believed possible. Resilience in particular is lower than desired, though most other properties approach contract goals. Representative formulations are shown in Table VII, and physical test results are given in Table VIII.

Production of open cell foams involves simultaneous expansion and cure of a mixture of polymer and fillers. Three variables, rate of cure, rate of expansion and viscosity must be balanced to produce a foam with desired porosity, physical properties, and density. Balance between the rate of cure and rate of expansion is controlled by judicious choice of curing agent and blowing agent. Plasticizers are added to reduce compound viscosity.

4.4 Plasticizer Evaluation

Plasticizers normally used in the rubber industry include various oils or phosphates. Phosphates smoke badly when burned, though they are fire retardant. Hydrocarbon oils free from halogen are very flammable. Several plasticizers were evaluated, as listed in Table IX. Phosphate plasticizers resulted in excessive smoke generation in the finished foams. Oils prepared from reaction of hexachlorophosphazene with a 1:1 mole ratio mixture of sodium phenoxide and 4-ethylphenoxide acted similarly to phosphate plasticizers in production of higher smoke densities.

Silicone oils provided the best plasticizing action for the amount of plasticizer used and were chosen as a primary plasticizer in the final formulations. When used at levels below 20 phr

TABLE VII

Representative Foam Formulations

Sample No.	<u>2435-40</u>	<u>2435-41</u>	<u>2435-42</u>	<u>2435-43</u>	<u>2435-45C</u>	<u>2435-46</u>	<u>2435-50</u>
Polymer	100	100	100	100	100	100	100
Hydral 710	150	150	150	150	150	150	150
Dow Silicone Fluid 704	20	-	5	10	10	20	10
Diglyme	10	20	30	30	30	10	30
Polyzole AZDN	15	15	20	25	25	15	25
NaHCO ₃	10	10	10	10	10	10	10
Celogen RA	5	4	4	4	4	4	4
VulCup 40KE	-	2	2	2	3	2	3
VulCup R	2	-	-	-	-	-	-
Benzoyl Peroxide	-	5	6	8	9	5	8
Luperco ANS-50	8	6	2	2	-	-	-
Density, lbs/ft ³	8	7	5.3	3.5	4	9	5.5

TABLE VIII

Physical Properties of $[(C_6H_5O)_2PN-(4-C_2H_5C_6H_4O)_2PN]_n$

Sample No.	2435-45C	2435-46	2435-50
Density, lbs/ft ³	4	9	5.5
Tensile strength, psi	5.7	11	7.5
Elongation, %	50	40	44
Tear resistance, ppi	0.35	0.45	0.4
ILD, lbs/50 in ²			
at 25% deflection	6.1	17	18
at 65% deflection	13.6	40	80
Compression set, C _T , %			
at 50% deflection	13 ^a	12 ^b	17
at 90% deflection	70 ^a	70 ^b	65
Steam autoclave, loss of compression load deflection	130% gain	85% gain	50% gain
Odor	none	none	none
Dry heat tensile strength	30% gain	10% gain	70% gain
Resilience, % at 25°C	3 ^c	5 ^c	6 ^c
LOI	36	36	35

^a 12% at 50% deflection and 19% at 90% deflection obtained from samples autoclaved 5 hrs/120°C.

^b 4.5% at 50% deflection and 16% at 90% deflection obtained from samples autoclaved 5 hrs/120°C.

^c At 70°C resilience increases to 15-20%.

TABLE IX
Plasticizer Evaluation

<u>Plasticizer</u>	<u>Result</u> ^a
Tricresylphosphate	ESG
Tri (butoxyethyl) phosphate	ESG
Tri-n-butylphosphate	ESG
Silicone oils:	
200 fluid	Incompatible with polymer
510 fluid	Incompatible with polymer
704 fluid	Reduced LOI
710 fluid	Reduced LOI
Trimer oil	ESG

^a Excessive smoke generation on ignition = ESG.

compatible silicone oils do not drastically reduce LOI values. Diglyme solvent also was tried as a plasticizer. This solvent is readily compatible with the polymer and evaporates at the higher temperature (150°C) employed for the final free expansion. The most effective plasticizing action was achieved with a combination of diglyme and silicone oil.

In the course of formulation studies using sodium bicarbonate and acid as the blowing system, some acids were found to cause a reduction in viscosity and caused foam formation without the use of sodium bicarbonate. This effect is thought to be due to a reaction of the acid with the polymer. Foams produced by this method had poor physical properties and high density.

Though silicone oils have proven effective as plasticizers both in processing and in final foam properties, other suitable plasticizers for the poly(aryloxyphosphazenes) should be sought. Previously, we ascertained a certain amount of milling was necessary to produce a good closed cell foam [Ref. 1]. This phenomenon is due largely to a reduction in molecular weight. Molecular weight is related to the need for plasticizers to reduce compound viscosity. The relationship between physical properties of the foams and polymer molecular weight has not yet been defined clearly. A more complete study of the relationship of polymer molecular weight to foam properties and processing may reduce the need for plasticizers while improving fire retardant and physical properties.

4.5 Curing Systems

Reducing viscosity beyond a certain level results in enlarged pores, rather than lower density. To avoid this condition the foam must be blown and cured simultaneously. A curing system which gradually increases the viscosity after blow is initiated will allow the formation of small, uniform cells which retain their shape until full cure is achieved and cell walls are ruptured to produce open cells. Combinations of curing agents were investigated to determine optimum levels for a particular blowing system to provide lowest density and good physical strength.

A two-part peroxide system with benzoyl peroxide as low temperature peroxide and VulCup as higher temperature peroxide was developed as shown in formulations in Table VII. VulCup R (crystal) and VulCup 40KE (40% VulCup R on clay filler) were both effective as higher temperature peroxides, though VulCup 40KE was preferred due to ease of handling. Two to four parts of VulCup 40KE were sufficient for good cure of the foam.

Benzoyl peroxide in a dry granular form was used in a number of formulations. Dry benzoyl peroxide was difficult to disperse in the formulations, but was added easily if dispersed in diglyme before addition. Lupercos ANS-50 (50% benzoyl peroxide and 50% phthalate plasticizer) was used in a number of formulations and dispersed readily, though the plasticizer no doubt contributes to flammability.

4.6 Blowing Systems

A number of chemical and physical blowing agents were investigated. The most effective blowing system producing open cell foams of low density was Polyzole AZDN at levels of 15 to 25 phr with 10 phr NaHCO_3 and 4 phr Celogen RA, as shown in formulations in Table VII. Other systems tried produced either closed cell or high density foams.

Polyzole AZDN is a low temperature blowing agent which produces good closed cell foams. Addition of NaHCO_3 and Celogen RA provides for breaking of cell walls at a late stage in the cure so that cells have been efficiently formed before walls are broken and internal pressure is lost. Polyzole AZDN also functions as a vinyl polymerization catalyst and probably contributes to crosslinking. Furthermore, the peroxide curing agents are thought to initiate decomposition of the blowing agent at lower temperatures. The search for an appropriate balance between blowing and curing systems for effective foam formation was the challenge addressed during this compounding effort. Much success has been realized although more remains to be done.

4.7 Physical Properties

Results of physical property testing of poly(aryloxyphosphazene) open cell foams are listed in Table VIII. Tests were conducted according to methods listed in Table VI. Physical properties approach the desired values except for resilience.

Aging tests, dry heat and steam autoclave, show an increase in physical properties of 10 to 69% for tensile strength and 50 to 130% for compression load deflection. This gain in physical properties indicates a continuation of cure after final oven cure. High compression set values also indicate continued crosslink formation at test temperature (70°C). Two samples, 2435-45C and 2435-46, Table VIII, were tested for compression set after autoclaving for 5 hours at 120°C. The reduction in compression set from 13% to 12% at 50% deflection and from 70% to 19% at 90% deflection for sample 2435-45C, and from 12% to 4.5% at 50% deflection and from 70% to 16% at 90% deflection for sample 2435-46 indicates a general improvement in physical properties can be expected from further evaluation and optimization of factors influencing crosslink density. Increases in resilience for these same samples after autoclaving (from 3% to 5% for 2435-45C and from 5% to 11% for 2435-46) indicate improvements in resilience can be expected with continued crosslinking. When the foam was heated to 70°C, resilience values increased from 45% to 15 to 20%. This increase is thought to be due to a crystal transition at 40 to 60°C. Crystal transitions in this temperature range have been reported for similar polyphosphazenes [Ref. 2]. Lowering of this crystal transition temperature is possible by alteration of mole ratios of substituent moieties on the polymer backbone, by addition of large free volume side chains or by judicious use of plasticizers [Ref. 3].

An improvement in resilience is expected with the lowering of this transition temperature.

Increases in physical properties are readily attainable by the use of reinforcing fillers or silane treatment of nonreinforcing fillers. Smaller particle size fillers, in general, improve strength and resilience, though some loss of elongation is experienced. Improvement of physical properties is attainable with a continued compounding effort.

4.8 NBS Smoke Tests

NBS smoke test values were obtained for several formulations to determine the effect of compounding ingredients. Results are listed in Table X for the flaming condition.

TABLE X

NBS Smoke Test (Flaming) for
Poly(aryloxyphosphazene) Open Cell Foams

	<u>2435-41A</u>	<u>2435-45C</u> ^a	<u>2435-46</u>	<u>2435-50</u> ^a
D _{mc}	81	125	172	165
T _{0.9} , min.	4.73	6.06	5.57	5.69
T _{D16} , min.	0.68	0.47	0.40	0.46
SON ₄ (min. ⁻¹) ^b	48	67	92	84
Limiting Oxygen Index	38	36	36	35

^a ≈1-2 sq. ft. foam specimens of each formulation supplied to NASA for evaluation.

^b SON₄ - average rate of smoke generation, first four minutes.

Formulation 2435-41A has the lowest smoke density value and would be the starting point for further work. A foam sample of this formulation was not supplied to NASA because physical properties were less than desired and smoke data was not available at the time when formulations were supplied (2435-45C and 2435-50). Thermogravimetric analysis for these foams are given in Figures 4 and 5.

The higher value of smoke density for 2435-45C, 2435-40 and 2435-50 compared with 2435-41A is due to the inclusion of a phenylated silicone oil and a higher level of Polyzole AZDN. No smoke reducing agents are present (other than the alumina filler) in any of the formulations and appropriate additions of commercially available smoke reducing ingredients such as magnesium hydroxide filler, a higher level of hydrated alumina or a combination of fillers should reduce smoke densities to $D_{MC} \leq 70$.

5.0 CONCLUSIONS

Results obtained thus far have demonstrated the capability to produce acceptable low density open cell foams. Further reduction in density is desirable and probably can be achieved. When low density open cell foams were obtained, attention was turned to development of acceptable physical properties. Values close to contract goals were achieved in all cases but resiliency. Continuing improvement in physical properties of the foams at elevated temperatures indicates improved properties can be expected as cure conditions are optimized. Resilience values of

FIGURE 4. TGA on Foam 2435-45C in Air at 10°C/Minute

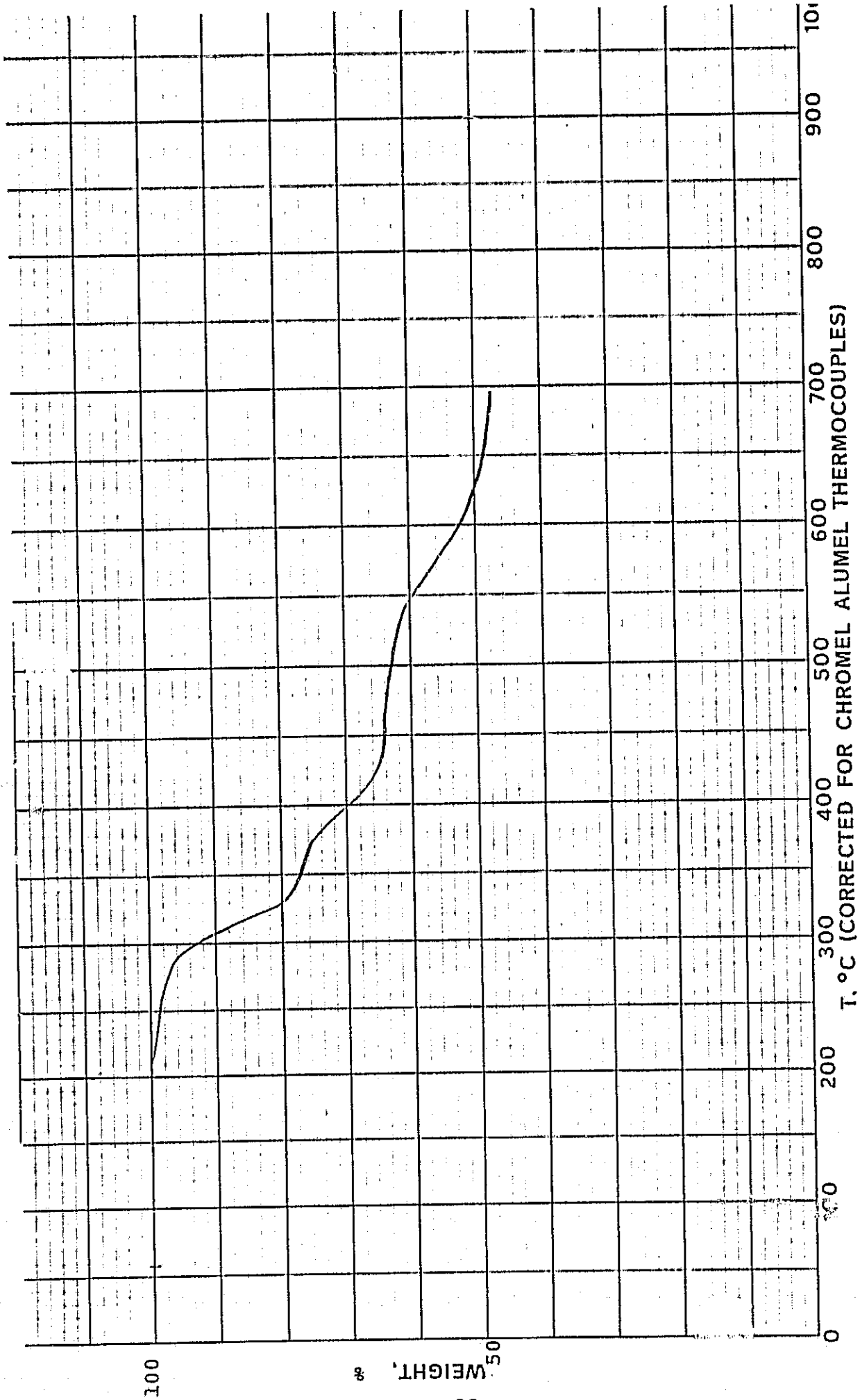
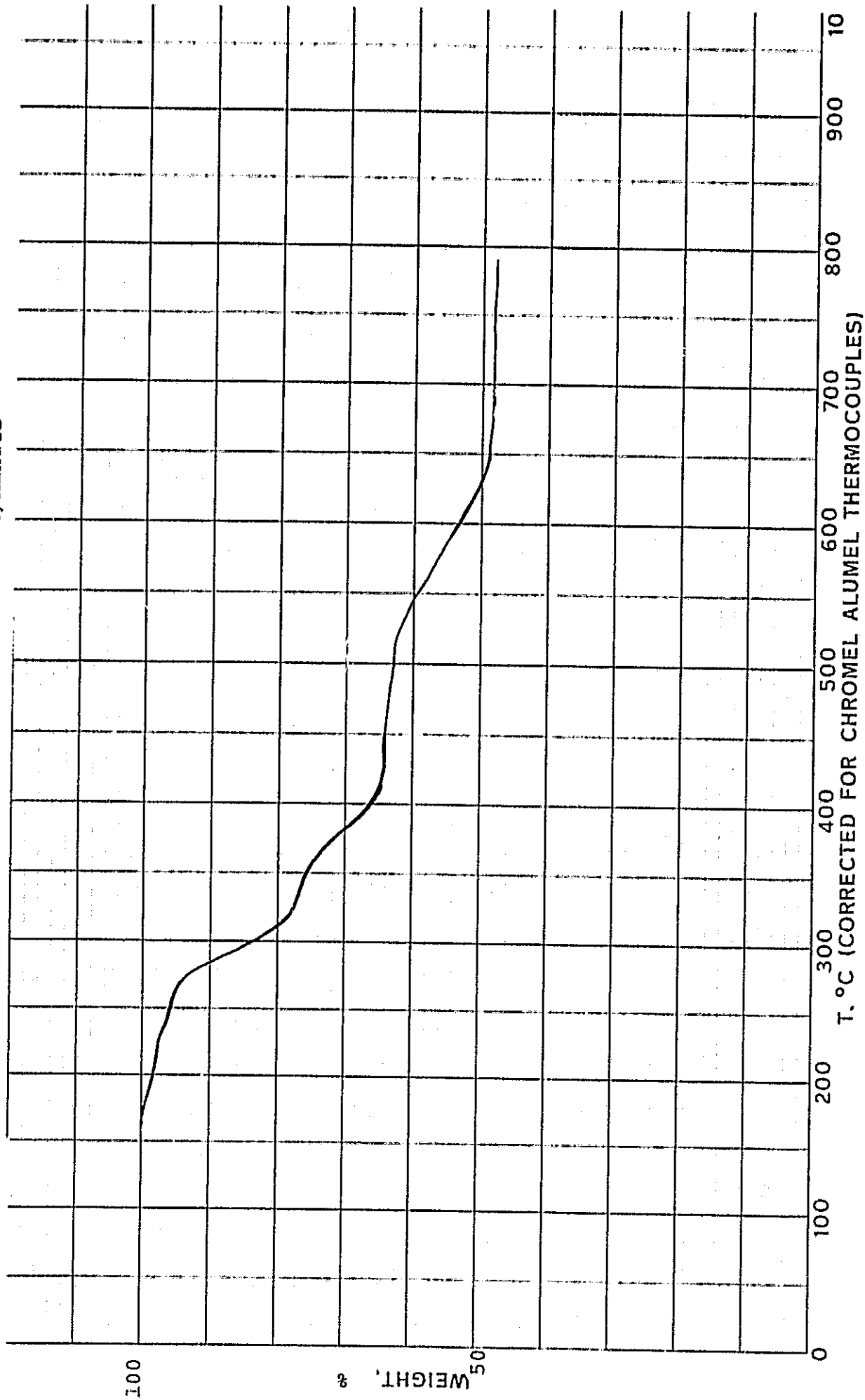


FIGURE 5. TGA on Foam 2435-50 in Air at 10°C/Minute



thermally aged foams are almost double the original values, though still too low to meet contract requirements. With continued compounding effort and possibly minor alteration of polymer composition, all physical properties should meet contract goals. A comparison of desired property values and the range of properties obtained is included in Table XI. Foams have not been tested for fatigue at this point since further improvements in other physical properties will improve fatigue. The foam can be mass produced with existing equipment and technology.

TABLE XI
Comparison of Desired Foam Properties
with Measured Values

<u>Property</u>	<u>Desired Values</u>	<u>Property Summary for 2435-41A, 2435-45C 2435-46^a, 2435-5U</u>
Density	2.5 lbs/ft ³	4 - 9
Tensile strength	≥ 12 psi	6 - 11
Elongation	≥ 80%	40 - 50
Tear resistance	≥ 1 lb/in.	0.35 - 0.45
Fatigue (65% deflection)	≤ 20% loss	not tested
Indentation Load Deflection		
(25% deflection)	≤ 25-35 lbs/50 in. ²	6.1 - 18
(65% deflection)	≈ 65-90 lbs/50 in. ²	14 - 80
Compression Set		
(50% deflection)	≤ 7%	4.5 - 17
(90% deflection)	≤ 12%	16 - 70
Steam autoclave loss of compression load deflection	≤ 20%	50 - 130% gain
Corrosion	No effect on aluminum for ≥ 14 days	not tested
Odor	none	none
Dry heat tensile strength	≤ 20% loss	10 - 70% gain
Resilience	≥ 55%	3 - 6%
Limiting Oxygen Index	≥ 40	35 - 38
Smoke density	D _{mc} = 50-70	81 - 165

^a Only flame retardant properties, density and compression set measured on sample 2435-46.

6.0 RECOMMENDATIONS

Continued development is recommended to optimize formulations and more closely evaluate the foams with regard to their intended use. Further compounding studies will determine the effect of various reinforcing fillers on physical properties, evaluate new plasticizers and improve smoke density and limiting oxygen index. Compounding studies are expected to be straightforward, evaluating various commercially available materials. An increase in physical properties is expected as the state of cure is optimized. A study of the factors involved in crosslink formation and methods to control crosslink density will assure optimum cure.

Since polymer molecular weight influences compound viscosity and possibly physical properties of the final foam, determination of the relationship involved will improve the foams. These data could reduce the need for plasticizers and hence increase fire retardant properties.

Finally, modification of the polymer itself to include large free volume side chains and various mole ratios of the two pendant groups may be beneficial. Materials of those types could lower the crystalline transition observed with the present material and thereby improve resilience.

7.0 REFERENCES

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8.0 GLOSSARY

Celogen RA	p-toluene sulfonyl semi-carbazide	Union Carbide
Diglyme	Diethyleneglycoldimethyl-ether	The Ansul Co.
Hydral 710	Hydrated aluminum oxide	Alcoa
Luperco ANS-50	50% Berzoyl peroxide in plasticizer	Lucidol Division Pennwalt Corp.
Polyzole AZDN	Azobisdiisobutyronitrile	National Polychemicals
Varox powder	50% active blend of 2,5-bis(tert-butylperoxy) 2,5-dimethyl hexane on inert mineral filler	R. T. Vanderbilt Co., Inc.
VulCup 40KE	40% VulCup R on Burgess KE clay	Hercules, Inc.
VulCup R	α - α' -bis(tert-butylperoxy) diisopropylbenzene	Hercules, Inc.