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Technical Report S-151

A COMPARISON OF SELECTED GEMINAL AND VICINAL
INGREDIENTS FOR USE IN PROPELLANTS (U)

by

J. A. Lovinger

October 1967

U. S. ARMY MISSILE COMMAND
Redstone Arsenal, Alabama 35809

Contract
DAAH01-67-C-0655

ROHM AND HAAS COMPANY
REDSTONE RESEARCH LABORATORIES
HUNTSVILLE, ALABAMA 35807

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FOREWORD

The work described in this report was performed under Contract DAAH01-67-C-0655 for exploratory development of propellants for missiles and rockets. It was part of these Laboratories' program to develop high-energy solid-propellant formulations based on an NF system. The work was under the technical cognizance of the Solid Propellant Chemistry Branch of the Army Propulsion Laboratory and Center, Research and Development Directorate, U. S. Army Missile Command.

(C) ABSTRACT

This report contains a compilation of data comparing geminal and vicinal difluoramino-containing plasticizers and copolymers. The plasticizers studied are 1,2,3-tris[1,2-bis(difluoramino)ethoxy]-propane and 1,2,3-tris[2,2-bis(difluoramino)propoxy]propane. The copolymers are acrylic acid copolymers of both 2,3-bis(difluoramino)-propyl acrylate and 2,2-bis(difluoramino)propyl acrylate. Data are presented for the monomeric materials, copolymers, binders, and propellants.

The data indicate that the vicinal and geminal materials behave similarly in many respects. The major disadvantage of the geminal NF-containing materials is their greater impact sensitivity. The main area in which the geminal materials show an advantage is seen in those tests related to storage stability. These tests include vacuum gas evolution and adiabatic self-heating. Data on fissuring time show that the geminal copolymers are as good as, if not better than, the best vicinal copolymers made to date. The geminals also have higher burning rates than the corresponding vicinals; however, the increase observed in the propellant is small.

(U) CONTENTS

(U) FIGURES

(U) TABLES

Section I. (C) INTRODUCTION

Over the past several years, Rohm and Haas Company's Redstone Research Laboratories have been involved in an effort to develop propellants containing difluoramino compounds. A recent milestone was the firing of an 80-pound motor containing a binder and a plasticizer each containing difluoramino groups. The binder was a copolymer of 2,3-bis(difluoramino)propyl acrylate (NFPA) and acrylic acid plasticized with 1,2,3-tris[1,2-bis(difluoramino)-ethoxy]propane (TVOPA). The propellant was a standard composition chosen for detailed study (RH-SE-103).

Early efforts to improve the shelf life of the propellant showed that the products formed by initial dehydrofluorination of the difluoramino compounds could in turn lead to gaseous products (1)[1]. These gaseous products are probably a major cause of the short shelf-life originally measured for this class of propellants as evidenced by fissuring-time and other tests. Much effort has been expended to improve the storage characteristics of RH-SE-103 propellant. Methods of purifying materials have been developed; new processing routes have been devised. Today, based on accelerated aging tests, RH-SE-103 propellants have a projected shelf life about the same as that for composite double-base propellants.

Another way to improve the storage life of difluoramino-containing propellants revolves around the possibility of preventing the decomposition chain of reactions which lead to gas formation. TVOPA and NFPA both have difluoramino groups attached to carbons which are bonded to hydrogens. The dehydrofluorination then can proceed according to Equation 1.

$$
\begin{array}{ccc}
\mathrm{NF_2} & & \mathrm{NF} \\
| & & \| \\
-\mathrm{C}- & \longrightarrow & -\mathrm{C}- \;+\; \mathrm{HF} \\
| & & \\
\mathrm{H} & &
\end{array}
\qquad\qquad \text{Eq. 1}
$$
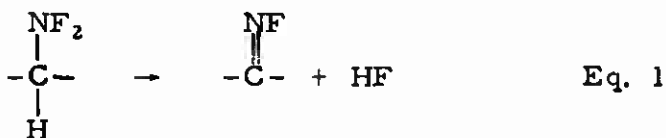
In the geminal compounds studied for this report, there are no hydrogens attached to the carbons to which the difluoramino groups

---

[1] Numbers in parentheses refer to references listed at the end of the report.

are attached. Thus, there is no easy way to initiate the dehydro-
fluorinat reaction. This resistance to dehydrofluorination by
geminal materials is illustrated by the drastic conditions necessary
to hydrolyze geminal compounds for analysis as compared with the
conditions necessary for vicinal compounds (2).

The purpose of this report is to present, in a unified manner,
data which can be used to compare directly the geminal and vicinal
systems so as to determine areas of further study of geminal materials
and to aid in deciding whether further scale-up of geminal production
should be made at this time. The report draws on our extensive
experience with the vicinal system and gives a selection of some of
the "best" current data. For the geminal system, the major work is
still on the bench scale; however, a small pilot plant to make geminal
monomer has been placed in operation. The preparation of the geminal
plasticizer used in this study is still on the laboratory scale. The
geminal data are thus based on a minimum of experience and represent
the earliest stages of development.

Section II. (C) MATERIALS

(U) The materials discussed in this report are identified in this section. The symbol used to represent each material is placed in the left margin to aid in later identification.

NFPA   1. (C)   <u>2,3-bis(difluoramino)propyl acrylate (C)</u>

$$CH_2=CH-\underset{\displaystyle \overset{O}{\|}}{C}-O-CH_2-\overset{\displaystyle \overset{NF_2}{|}}{CH}-\overset{\displaystyle \overset{NF_2}{|}}{CH_2}$$
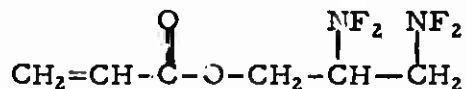
(U) A liquid acrylic monomer which contains vicinal NF_2 groups. Its preparation and some of its properties have been reported (3,4).

AA   2. (U)   <u>acrylic acid</u>

(U) Acrylic acid is copolymerized with NF_2-acrylates to give cross-linking sites in the copolymer.

PPAA   3. (C)   <u>vicinal-NFPA copolymer (C)</u>

(C) A copolymer of NFPA and AA formed by batch-free radical polymerization. A number following the symbol, i.e., 4 in PPAA-4, indicates a particular copolymer formulation. The polymerization characteristics and some properties of the copolymer system have been described (3).

PPAA-4E   4. (C)   <u>incremental-addition vicinal-NFPA copolymer (C)</u>

(C) A copolymer of NFPA and AA formed by free-radical polymerization. Instead of a batch process, the monomers are added in increments during the polymerization (5). This incremental-addition method has led to higher-molecular-weight material, and it is believed that the molecular-weight distribution is narrower than in the case of the simple batch process.

TVOPA   5. (C)   <u>1,2,3-tris[1,2-bis(difluoramino)ethoxy]propane (C)</u>

$$
\begin{array}{c}
\quad\quad\quad\; \overset{\displaystyle NF_2}{|} \;\; \overset{\displaystyle NF_2}{|} \\
H_2C-O-CH-CH_2 \\[2mm]
\quad\quad\quad\; \overset{\displaystyle NF_2}{|} \;\; \overset{\displaystyle NF_2}{|} \\
HC-O-CH-CH_2 \\[2mm]
\quad\quad\quad\; \overset{\displaystyle NF_2}{|} \;\; \overset{\displaystyle NF_2}{|} \\
H_2C-O-CH-CH_2
\end{array}
$$
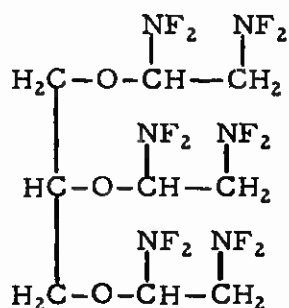
(U) A liquid plasticizer containing vicinal NF_2 groups. Preparation methods have been described (6).

MY   6. (C)   <u>2,2-bis(difluoramino)propyl acrylate (C)</u>

$$
\begin{array}{c}
\quad\quad\quad\; \overset{\displaystyle O}{\|} \quad\quad\quad\quad \overset{\displaystyle NF_2}{|} \\
H_2C=CH-C-O-CH_2-C-CH_2 \\[2mm]
\quad\quad\quad\quad\quad\quad\quad\quad\; \underset{\displaystyle NF_2}{|}
\end{array}
$$
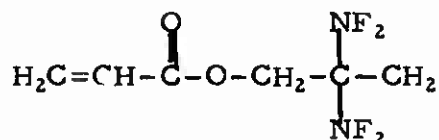
(C) A liquid acrylate containing geminal NF_2 groups. Synthesis methods are similar to those used for NFPA. The synthesis method for the intermediate has been described (7).

PY   7. (C)   <u>geminal-NFPA copolymer (C)</u>

(C) A copolymer formed by the copolymerization of MY and AA. The polymerization characteristics of this system are under study and will be reported shortly (8). Preliminary evidence is that this system polymerizes more slowly than does the NFPA-AA system.

TGAP   8. (C)   <u>1,2,3-tris[2,2-bis(difluoramino)propoxy]propane (C)</u>

$$\begin{array}{c} \text{NF}_2 \\ | \\ \text{H}_2\text{C}-\text{O}-\text{CH}-\text{C}-\text{CH}_2 \\ | \\ \text{NF}_2 \\ \\ \text{NF}_2 \\ | \\ \text{HC}-\text{O}-\text{CH}-\text{C}-\text{CH}_2 \\ | \\ \text{NF}_2 \\ \\ \text{NF}_2 \\ | \\ \text{H}_2\text{C}-\text{O}-\text{CH}-\text{C}-\text{CH}_2 \\ | \\ \text{NF}_2 \end{array}$$
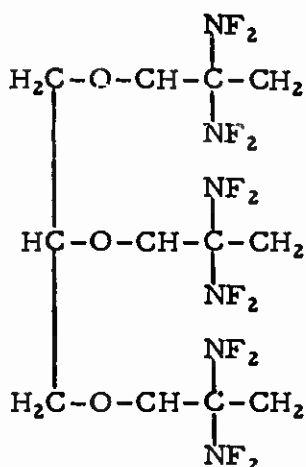
(U) A liquid plasticizer containing NF_2 groups. Its preparation has been described (9).

RH-SE-103 9. (C) <u>vicinal propellant (C)</u>

(C) A standard propellant formulation contained the following:

Material	Wt. %
PPAA	13
TVOPA	26
Ammonium Perchlorate	46
Aluminum	15
Diepoxide[a] (added) (approximately 1.5 gram diepoxide per 100 grams of propellant)	$1.5 \dfrac{\text{equivalents}}{\text{equivalent of AA}}$

[a] Unox® Epoxide 221 - Trademark of Union Carbide Corporation, New York, New York.

(U) Details of the formulation are included, in some cases, by use of additional letters and numbers in the code name. The first number after the "103" corresponds to the copolymer formulation. For this report, the letter "E" will be used after the

-5-

copolymer formulation number to designate that
the copolymer used in the propellant had been made
by the incremental additon process. Numbers
thereafter are batch numbers.

RH-Y-1   10. (C)   <u>geminal copolymer - vicinal plasticizer propellant (C)</u>

(C) A propellant formulation identical to RH-SE-103
except that PPAA is replaced by PY.

RH-Y-2   11. (C)   <u>geminal copolymer - geminal plasticizer propellant (C)</u>

(C) A propellant formulation similar to RH-SE-103
in which the vicinal materials have been replaced by
geminal materials as follows:

Material	Wt. %
PY	13
TGAP	26
Ammonium Perchlorate	46
Aluminum	15
Diepoxide (added)	$1.5 \dfrac{\text{equivalents}}{\text{equivalent of AA}}$

(U) The letters "G" and "V" in brackets distinguish
between the geminal [G] and vicinal [V] materials.
In those cases where both copolymer and plasticizer
are used, the first letter refers to the copolymer
and the second to the plasticizer.

Section III. (C) PHYSICAL PROPERTIES OF NF COMPOUNDS

The two monomers and the two plasticizers are clear, colorless liquids at room temperature. The monomers each have sharp odors. Table I lists a few common physical properties. The infrared spectra of the materials are shown in Figures 1 and 2. Some viscosity values at various stages of propellant formulation are listed in Table II.

Table I. (C) Physical Properties of NF Materials (U)				
Property/Compound	vic-NFPA	My [G]	TVOPA	TGAP
Density, g/cc at 25°C	1.350	1.325	1.54	1.458
Index of Refraction, n_D^{20}	1.4070	1.4012	1.3892	1.4031
Boiling Point, °C (torr)	43. (.3)	54°(4.2) 40° (2.4)		
Viscosity, Centipoise	2.7 (30°C) 3.5 (25°C)	2.0 (30°C)	32.4 (30°C)	51 (30°)

Table II. (C) Selected Viscosities at Various Stages of Formation (U)	Incremental Addition Copolymer, Vicinal	Batch Process Copolymer, Vicinal	Batch Process Copolymer, Geminal
	Polymer		
Intrinsic Viscosity[a]	0.41	0.21	0.14
	Binder-TVOPA Plasticizer		
Viscosity, Kp at 100°F	0.51	0.11	.09
	Propellant-TVOPA Plasticizer		
Slurry Viscosity, Kp at 100°K	4.8	2.0	1.5

[a] In acetone solution at 30°C.
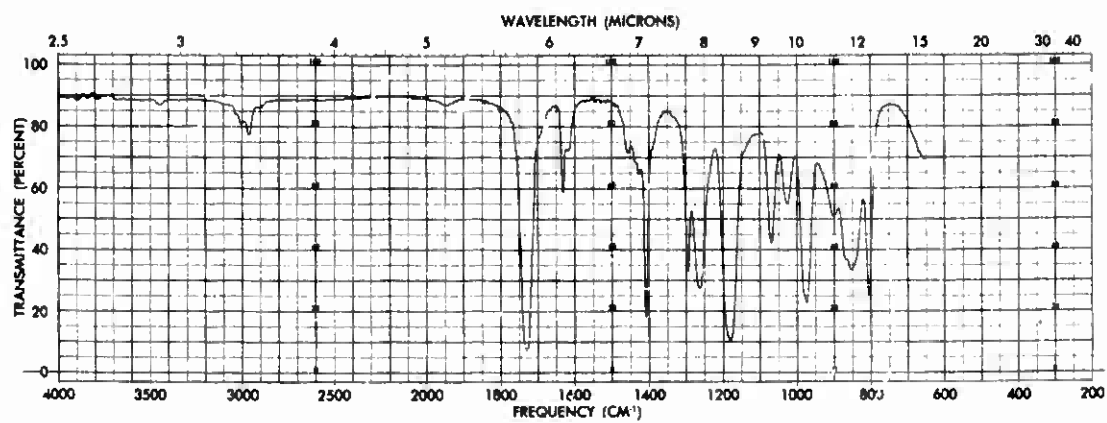
2, 3-Bis(difluoramino)propyl acrylate
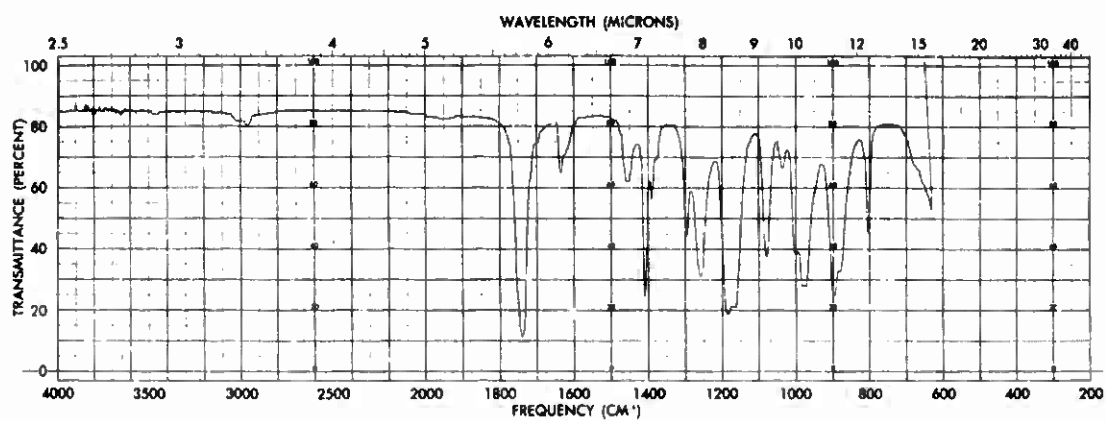
2, 2-Bis(difluoramino)propyl acrylate

FIGURE 1. (C) INFRARED SPECTRA OF THE TWO MONOMERS (U)

-8-
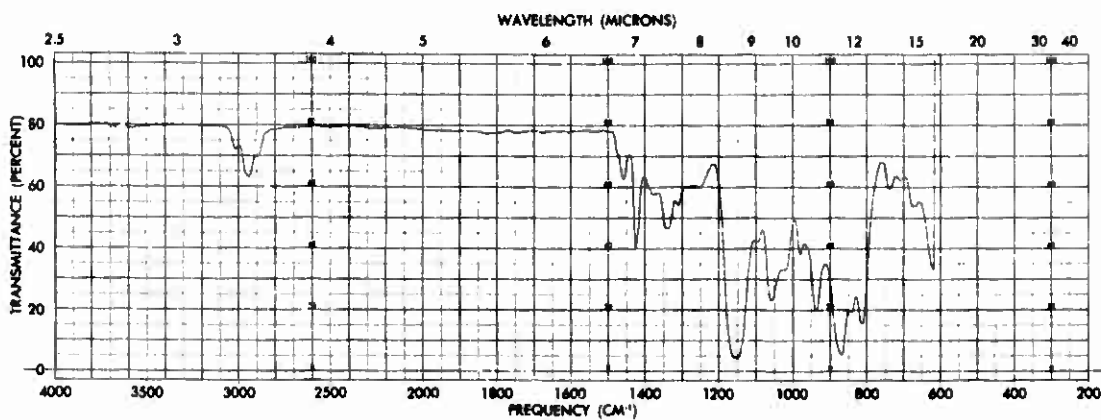
1, 2, 3-Tris[1, 2-bis(difluoramino)ethoxy]propane
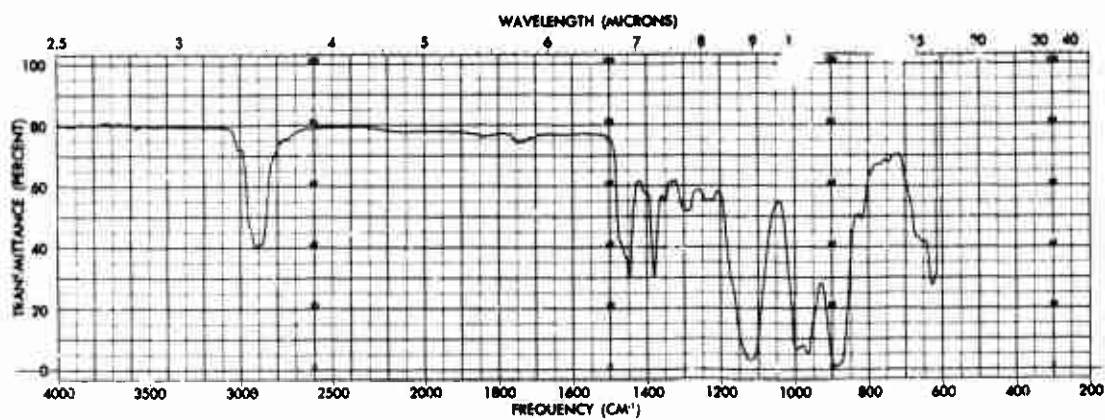
1, 2, 3-Tris[2, 2-bis(difluoramino)propoxy] propane

FIGURE 2. (C) INFRARED SPECTRA OF THE TWO PLASTICIZERS (U)

Section IV. (U) GLASS-TRANSITION TEMPERATURE OF NF PLASTICIZERS AND POLYMERS

The glass-transition temperatures (T_g) of the copolymers, plasticizers, and mixtures have been measured with a Perkin-Elmer Company Differential Scanning Calorimeter, Model DSC-1. The T_g's were chosen from the experimental curves at the inflection points. For the calculated values, mixtures of the polymer-plasticizer pairs were made and the T_g's measured. The T_g of the plasticizer was then calculated from the empirical equation (9)

$$1/T_{g(mixture)} = w_1/T_{g(polymer)} + w_2/T_{g(plasticizer)}$$

where w_1 and w_2 are the weight percentages of polymer and plasticizer. The values of T_g are listed in Table III. The data show that the geminal polymer has a higher T_g than the vicinal polymer. The geminal polymer would therefore be expected to be somewhat inferior to the vicinal polymer insofar as low-temperature mechanical properties of a response nature are concerned. The T_g's of the two plasticizers are very close, and the order reverses for measured and calculated values.

Table III. (U) Glass-Transition Temperatures of Geminal and Vicinal Materials		
Materials	Measured T_g, ^0C	Calculated T_g, ^0C
poly-vic-NFPA (homopolymer)	−11	-
poly-gem-NFPA (homopolymer)	12	-
TVOPA [V]	−76	−80
TGAP [G]	−83	−75

Section V. (U) MECHANICAL PROPERTIES OF NF PROPELLANTS

The mechanical properties, as measured by stress-strain experiments, have been measured at three different temperatures for the three propellant systems containing TVOPA as plasticizer. The data in Table IV, although favoring the incremental-addition process PPAA-4E (RH-SE-103-4E) and the geminal PY-1 (RH-Y-1) propellant binders, are not sufficiently different to allow a clear choice to be made. The number of variables in a propellant composition is sufficient to allow any of the binders tested to be used as far as mechanical properties are concerned.

Stress-strain properties of a propellant containing PY-1 and TGAP, RH-Y-2, have not yet been measured. However, equilibrium Young's moduli, E, have been measured for RH-SE-103 and RH-Y-2. The data were obtained using a simple beam-bending test at low rates of loading. The experimental technique consisted of centrally loading an end-supported beam of propellant (1/4-in. x 1/4-in. x 1 1/2-in.) in a device attached to an Instron* universal tester. The data, Table V and Figure 3, show that RH-SE-103 enters the transition region (brittle range) at a lower temperature than does RH-Y-2. Hence, the failure properties of RH-SE-103 would be expected to be slightly superior in the low-temperature region to those of RH-Y-2.

Table IV. (U) Stress-Strain Data for Propellants[a]			
	Tensile Strength, psi Elongation, %		
Propellant	-40^0F	77^0F	140^0F
RH-SE-103-4E	646/24	90/33	63/27
RH-SE-103-4	364/20	61/33	40/30
RH-Y-1-4	563/26	71/30	49/27

[a] Rohm and Haas Company No. 2 tensile specimen at 2-in./min. crosshead.

* Instron Corporation, Canton , Massachusetts.

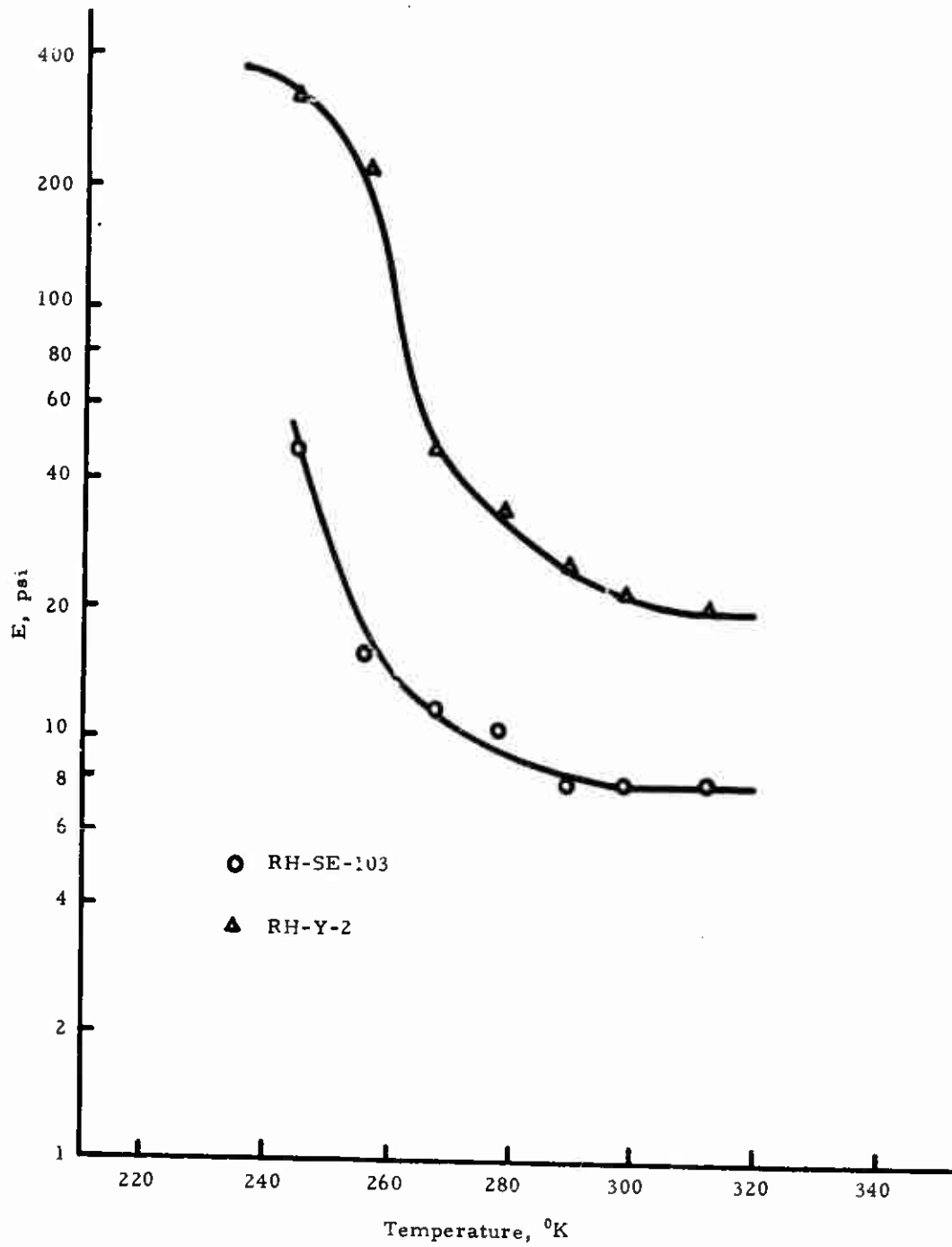| Table V. (U) Equilibrium Young's Moduli for Propellants		
	Young's Modulus, E, psi	
Temperature, ^{0}K	RH-SE-103	RH-Y-2-4
311	8.1	20.4
298	.	21.6
289	7.0	24.7
278	10.3	34.4
267	11.	47.9
255	16.0	219.5
244	46.4	332.5

FIGURE 3. (C) EQUILIBRIUM YOUNG'S MODULI FOR RH-SE-103
[V, V] AND RH-Y-2 [G, G]

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Section VI. (U) FISSURING-TIME TEST

The fissuring-time test is used in these Laboratories as an accelerated aging test. The method and some early results are described in a previous report (11). The fissuring-time is a complex function of many variables in the propellant which is dependent on such things as 1) gas evolution rate, 2) gas diffusion rate, 3) type of gases evolved, and 4) mechanical properties of the binder. The results reported herein are for two-inch cubes heated at $80^{\circ}C$.

In the past few years the stability of RH-SE-103 [V, V] propellants, as measured by this test, has been greatly increased. Propellants now being made with batch-process copolymer PPAA-4 [V] have a fissuring time of 400 hours. This can be compared with early results when the fissuring times were of the order of 24 hours. The use of copolymer made by the newer incremental-addition process, PPAA-4E [V], has increased fissuring-times for propellant to more than 1500 hours. Values of this magnitude mean that the cube probably never will fissure and also that there is probably no auto-catalytic reaction which will ignite the sample. This lack of an auto-catalytic decomposition reaction in RH-SE-103 can be contrasted to the auto-catalytic decomposition of double-base propellants.

The propellant, RH-Y-1 [G, V] has a fissuring time in excess of 1500 hours and is still being tested. As yet, no tests have been made on propellant containing both geminal copolymer and geminal plasticizer. Changes in the test procedure, such as increased cube size, will be necessary to distinguish between propellants using PPAA-4E and those using PY-1.

Section VII. (U) VACUUM GAS EVOLUTION

An important factor in the determination of the shelf life of a propellant is the amount of gas evolved by the propellant as a function of time. The vacuum gas evolution test, in which the amount of gas formed after 25, 50, and 150 hours of storage at 80^0C is measured, is described in a previous report (11).

Data obtained from the copolymers, binders, and propellants discussed in this report, are contained in Table VI and illustrated in Figures 4, 5, and 6. The data show that vicinal copolymer made by the incremental-addition process, PPAA-4E, has a lower gas evolution rate than does the copolymer made by the batch process. This difference does not seem to be carried over significantly to the binders since after 150 hours the batch process binder evolved 1.10 cc of gas compared with 1.08 cc for the incremental-addition material. The geminal copolymer produced slightly more gas after 50 hours than did PPAA-4E, but after 150 hours the geminal material tested slightly better. In the binder, the improvement using the geminal copolymer was apparent after 25 hours and was quite significant at 150 hours.

The gas evolution was also less for those propellants in which PY-1 was used in place of PPAA, with at least a 100% improvement evident. The difference caused by replacing TVOPA [V] by TGAP [G] is not significant in the samples tested (RH-Y-1 [G, V] and RH-Y-2 [G-G]).

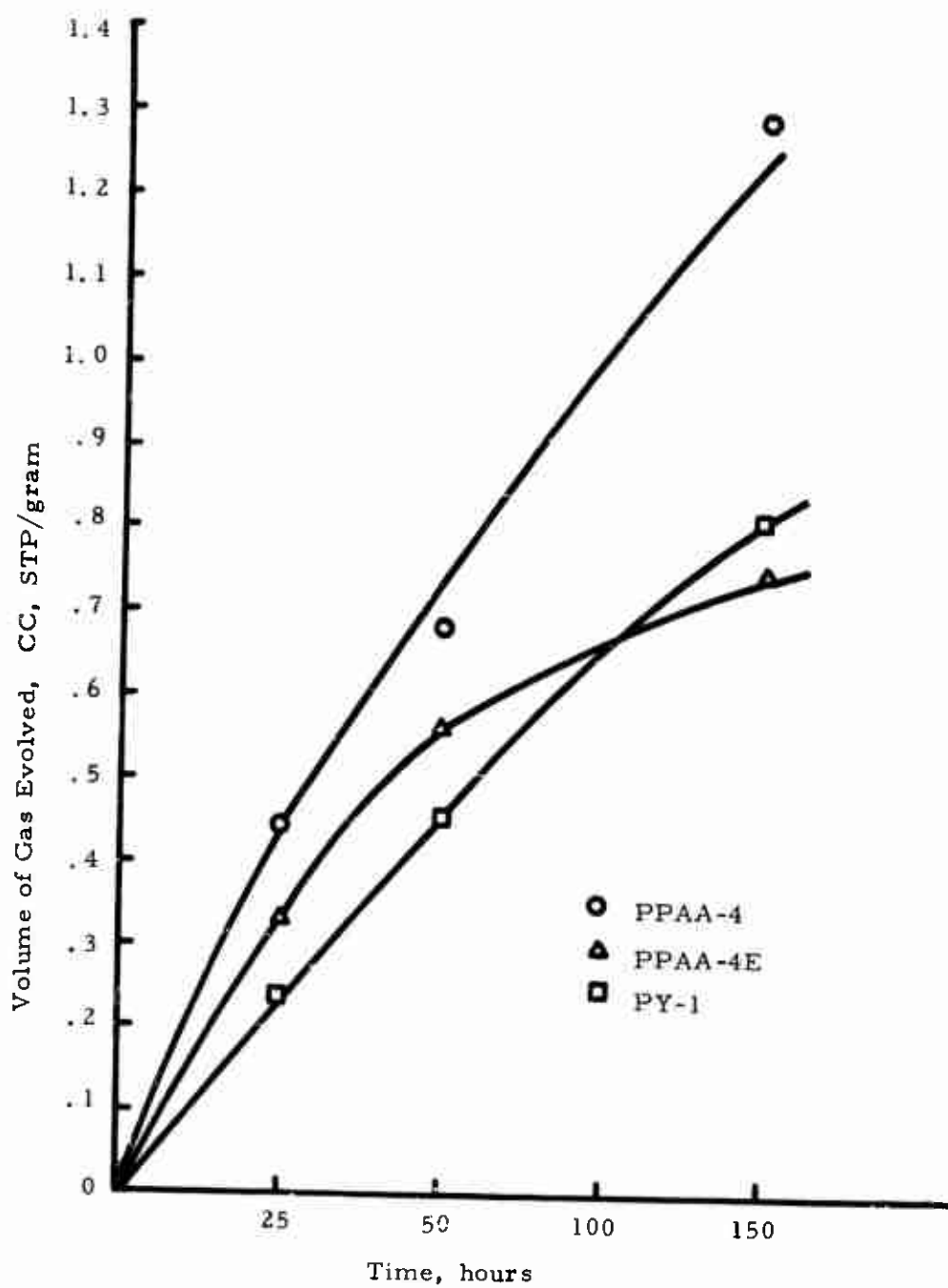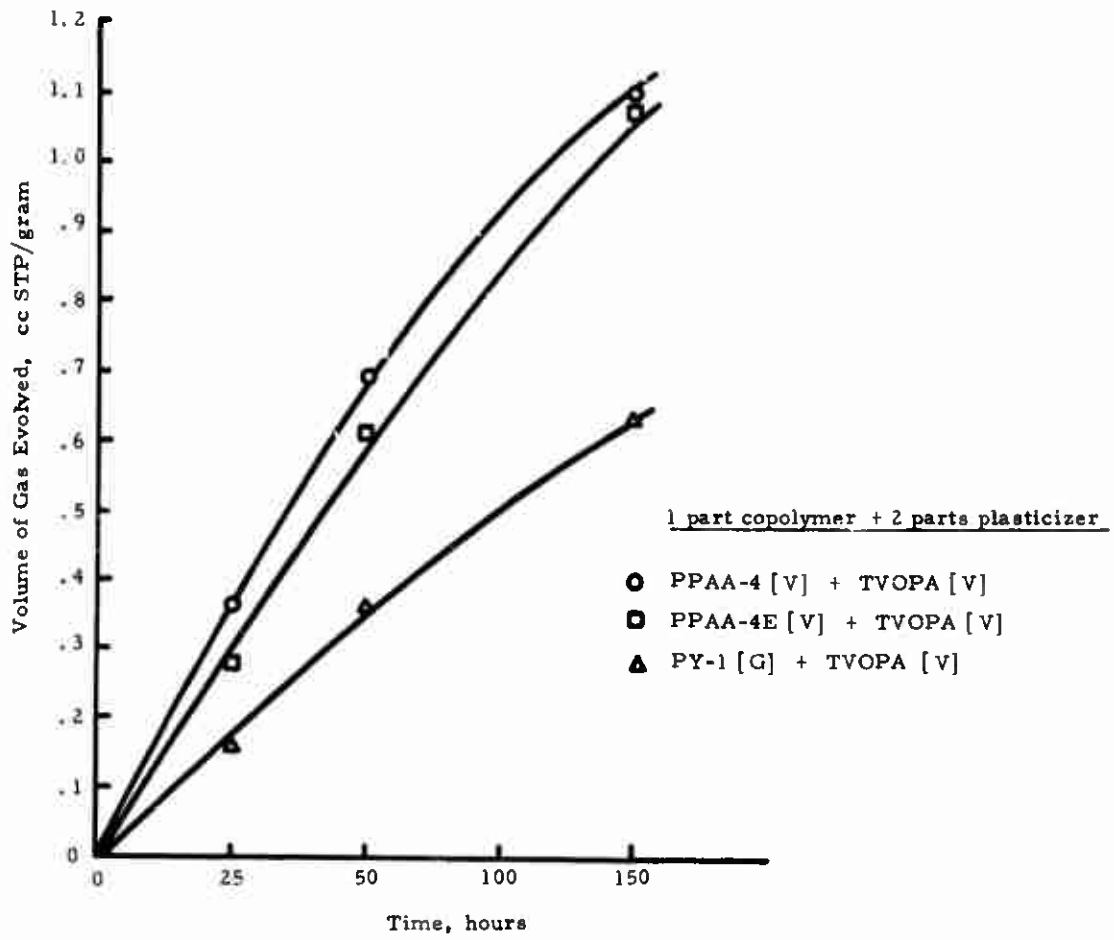| Table VI. (U) Gas Evolution of Selected Materials at 80°C in cc STP/gm			
Copolymer			
	25 hrs.	50 hrs.	150 hrs.
PPAA-4 [V]	.44	.68	1.29
PPAA-4E [V]	.24	.45	.81
PY-1 [G]	.33	.56	.74
Binder			
	25 hrs.	50 hrs.	150 hrs.
PPAA-4 [V] + TVOPA-[V]	.36	.69	1.10
PPAA-4E-[V] + TVOPA-[V]	.28	.61	1.08
PY-1 [G] + TVOPA [V]	.16	.36	.63
Propellant			
	25 hrs.	50 hrs.	150 hrs.
RH-SE-103	.18	.37	.78
RH-Y-1 [G, V]	.11	.19	.35
RH-Y-2 [G, G]	.14	.22	.33

FIGURE 4. (U) GAS EVOLUTION OF NF COPOLYMERS

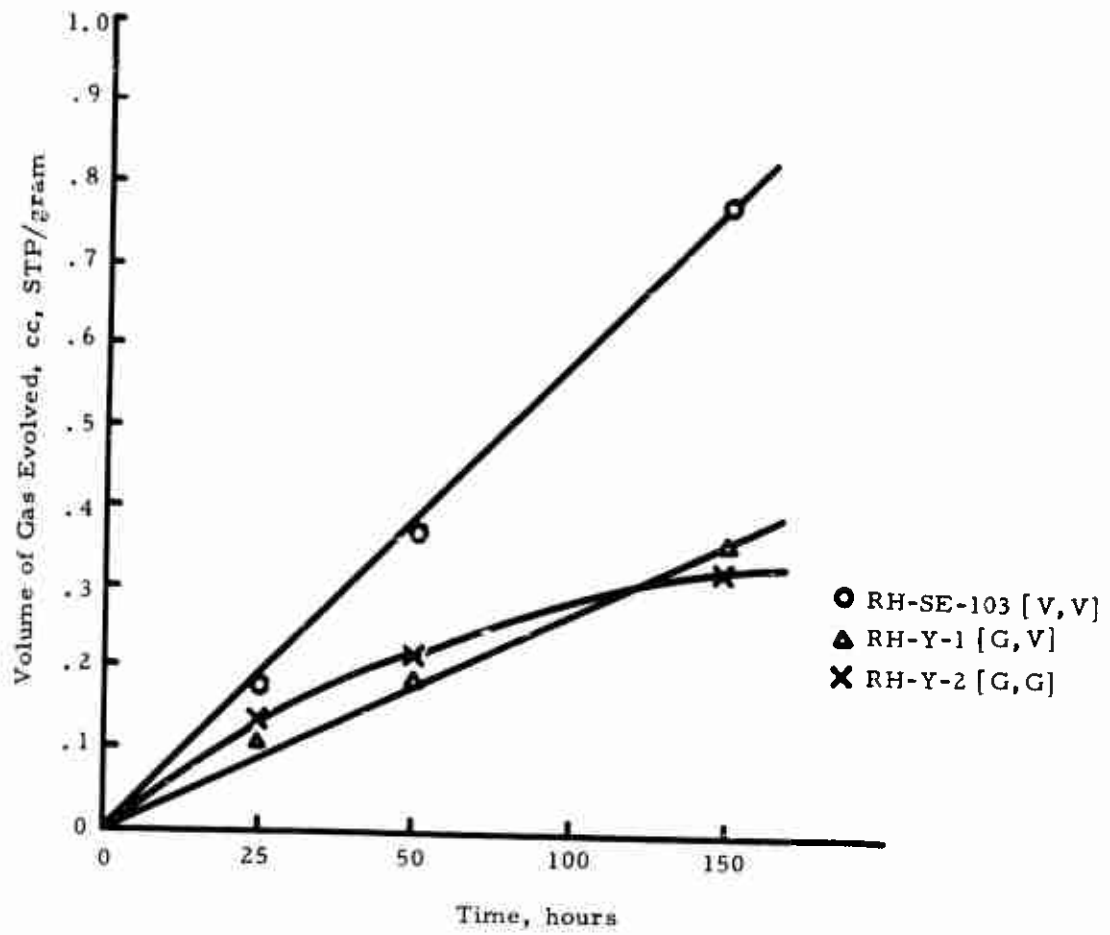FIGURE 5. (U) GAS EVOLUTION OF SOME NF BINDERS

FIGURE 6. (U) GAS EVOLUTION OF THREE NF-CONTAINING
PROPELLANTS

Section VIII. (U) ADIABATIC SELF-HEATING RATE

The adiabatic self-heating rate (ASHR) tests have been used in our Laboratories as an accelerated aging test to evaluate new propellant formulations and ingredients and as a quality-control test. The apparatus (12) is essentially an adiabatically shielded oven assembly with associated control and measuring equipment. The sample is first heated to a given temperature, and then the oven is adiabatically controlled at the sample temperature so that, as the sample self-heats due to exothermic decomposition, the furnace temperature changes correspondingly. The use of this equipment as a quality-control instrument and as an aid in determining instabilities quickly will be described more fully in a forthcoming report (13).

The ASHR for geminal copolymer, PY-1, is very low, as expected. In fact, the rate is too low to be measured under the standard conditions adopted to test the vicinal materials. It was necessary to heat the sample to a starting temperature of 160^0 C instead of 121^0 C before decomposition started. Extrapolating the results to standard starting conditions, the rate is calculated to be less than 0.1×10^{-3} cal/gm-sec at 143^0C, the standard reference temperature used for vicinal materials.

Recent batches of vicinal copolymers have had ASHR's of 14×10^{-3} (PPAA-4) and 19×10^{-3} cal/gm-sec (PPAA-3). These results are among the better ones for vicinal copolymers. Thus, the geminal copolymers (PY) have an ASHR about 150 times smaller than the better PPAA [V] now being produced at these Laboratories.

The binder systems containing two parts plasticizer to one part copolymer have also been studied using both types of copolymers together with TVOPA [V]. The average values of the ASHR's of binders using vicinal made by different methods and with different ratios of NFPA [V] to AA range from $2.5 \pm 1.3 \times 10^{-3}$ to $3.8 \pm 1.4 \times 10^{-3}$ cal/gm-sec. The binders using geminal copolymer containing 4% AA and TVOPA [V] plasticizer have had ASHR's of $1.6 \pm 0.4 \times 10^{-3}$ cal/gm-sec. Thus, in the binders, the replacement of the vicinal copolymer (PPAA) with the geminal copolymer (PY-1) has reduced the ASHR of the binder even when two-thirds of the binder is still a vicinal material. Also, the variations from sample to sample are much smaller for the geminal material than for the vicinal material. The effect of the geminal plasticizer, TGAP, on the ASHR of the binder remains to be seen.

Propellant samples differing only in type of copolymer have also been tested. The ASHR for RH-SE-103 was 1.6×10^{-3} cal/gm-sec. The corresponding propellant, RH-Y-1-7001 [G, V] made with PY-1 [G], had a rate of 1.0×10^{-3} cal/gm-sec, showing that the improvement in ASHR noted in the binder is carried over into the propellant. We can only speculate now on the effect which would be obtained if the vicinal plasticizer, TVOPA, were replaced by a geminal plasticizer such as TGAP.

The data presented in this section are tabulated in Table VII. For illustration two ASHR curves, one for PPAA-4 [V] and one for PY-1 [G] are shown in Figure 7.

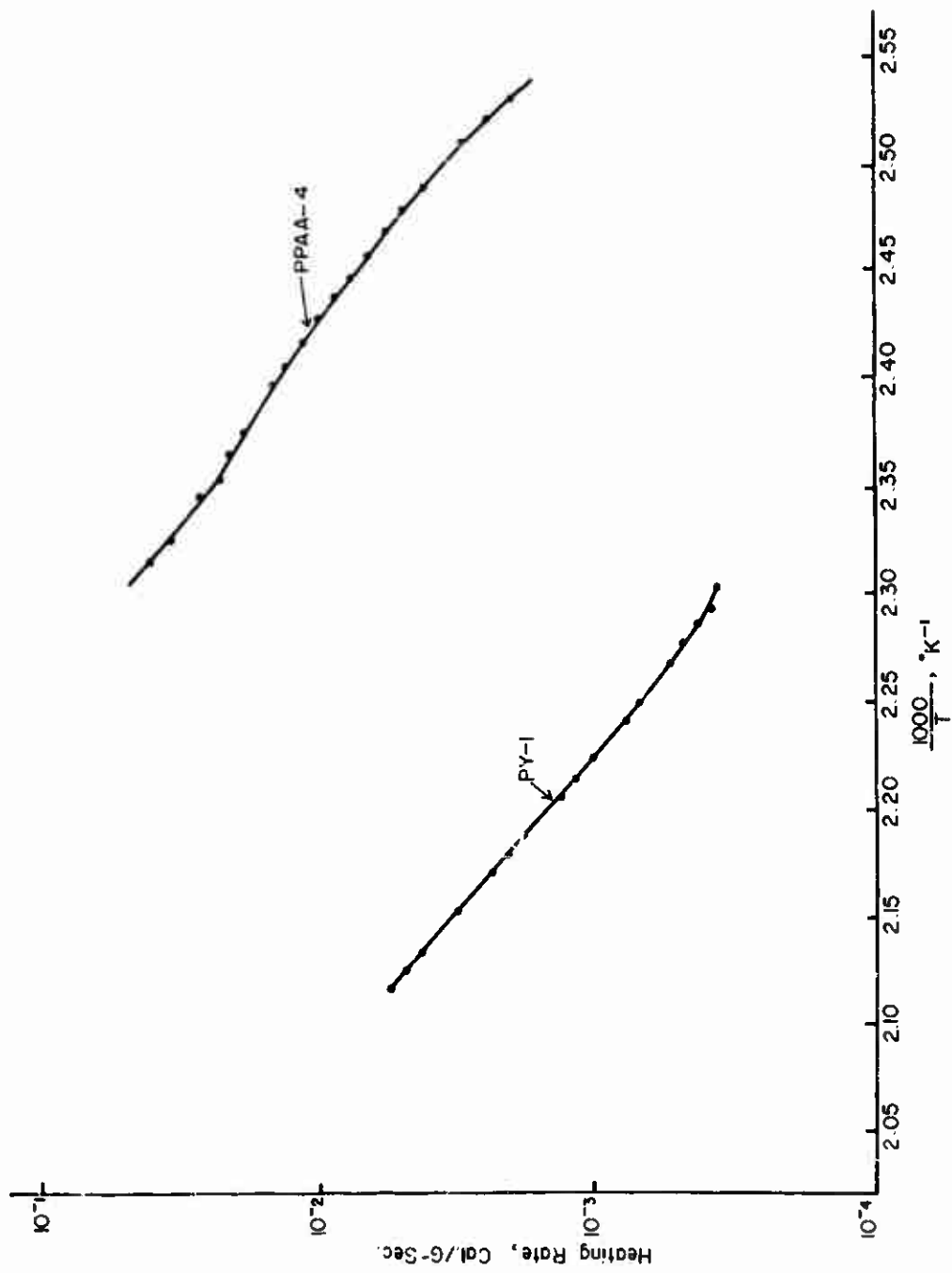| Table VII. (U) Adiabatic Self-Heating Rates of Propellant Materials	
Material	Rate at 143^0C x 10^3, cal/gm-sec
Copolymers	
PPAA-4 [V]	14.
PPAA-3 [V]	19.
PY-1 [G]	nil from 121^0C nil from 138^0C 0.1 from 160^0C
Binders (1 part copolymer + 2 parts plasticizer)	
PPAA-3 [V] + TVOPA [V]	3.8 ± 1.4
PPAA-4E [V] + TVOPA [V]	2.5 ± 1.3
PY-1 [G] + TVOPA [V]	1.6 ± 0.4
Propellants	
RH-SE-103-1149 [V, V]	1.6
RH-Y-1-7001 [G, V]	1.0 ± 0.1

FIGURE 7. (U) ADIABATIC SELF-HEATING RATES FOR PPAA-4 [V] AND PY-1 [Gj]

Section IX. (U) DIFFERENTIAL THERMAL ANALYSIS

Differential thermal analysis (DTA) has been performed on the geminal and vicinal compounds, on combinations of them, and on propellants. The apparatus used in these Laboratories has been described by Scrogham (14). The measurements reported here have been made at a scan rate of 10^0C/min with a nominal sample size of 20 milligrams. With this large size, the samples frequently ignite or even explode instead of slowly decomposing to give a simple exothermic peak. The temperatures reported herein, unless otherwise stated, are the reference temperatures corresponding to peak deflection of the samples. Figures 8 through 11 are representative of the data obtained and illustrate the peak temperatures listed in Table VIII. These values are representative of those obtained for our current "better" samples, both from the pilot plant and the laboratory.

The thermograms for the monomers are of some special interest since they show the polymerization exotherms. For vicinal NFPA, the polymerization exotherm peaks at 169^0C, being a fairly large peak (Figure 10). The major exotherm then occurs at 232^0C. The thermogram for MY [G] is shown in Figure 11. The bulk polymerization exotherm is first noted at about 160^0C. Before polymerization can proceed very far, the material begins to boil so that the boiling endotherm overcomes the polymerization exotherm. From the thermogram, the normal boiling point of MY is estimated to be about 180^0C. The small amount of material that is polymerized has a peak exotherm temperature of 264^0C.

According to the data in Table VIII, the geminal copolymer is more stable than the vicinal copolymer and this increased stability is carried over into the propellant. The plasticizers, TVOPA [V] and TGAP [G], have approximately the sam   eak DTA temperatures, although it should be noted that, in all cases   GAP samples have violently ignited at the peaks.
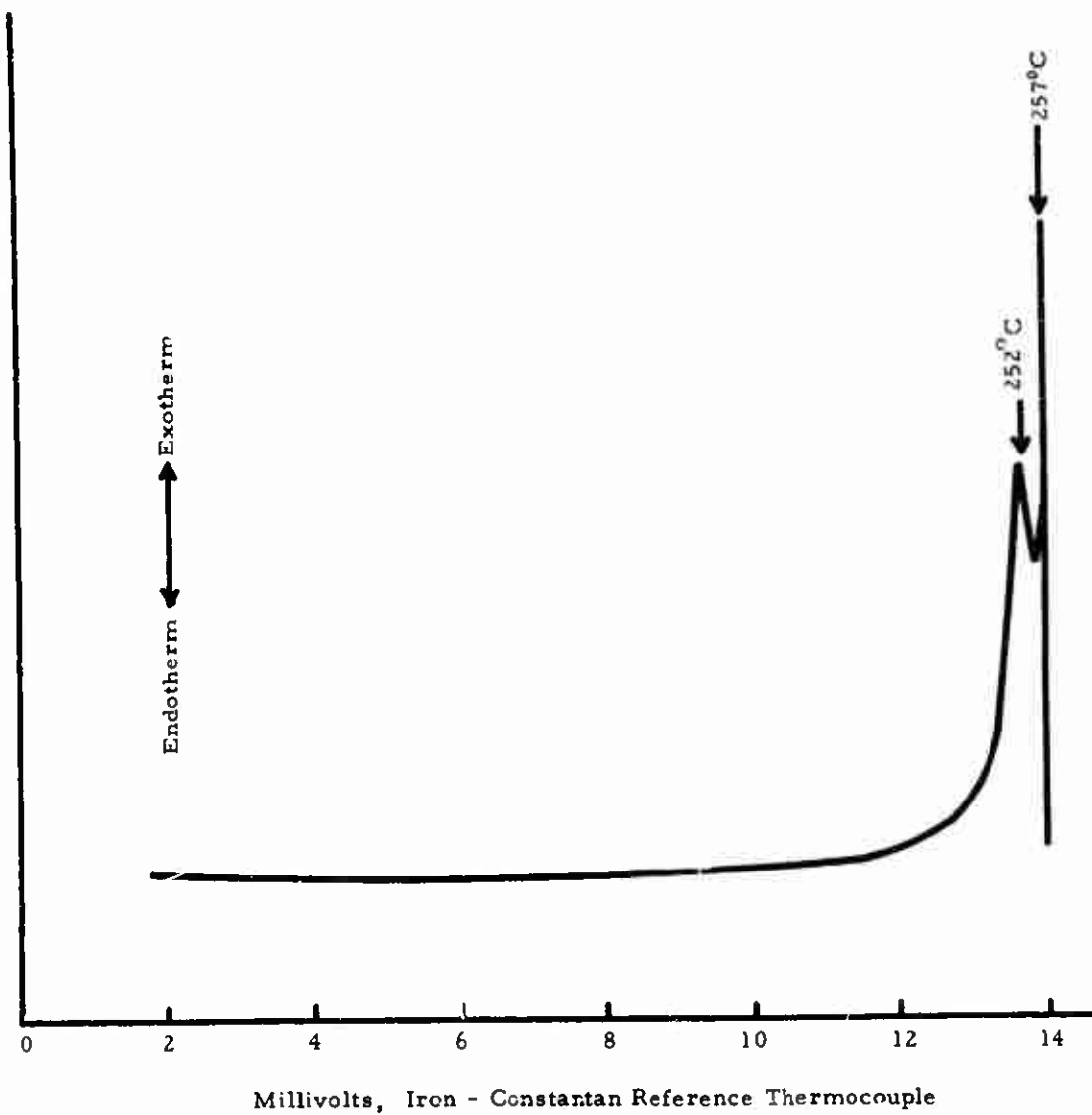
FIGURE 8. (U) THERMOGRAM OF TGAP [G]
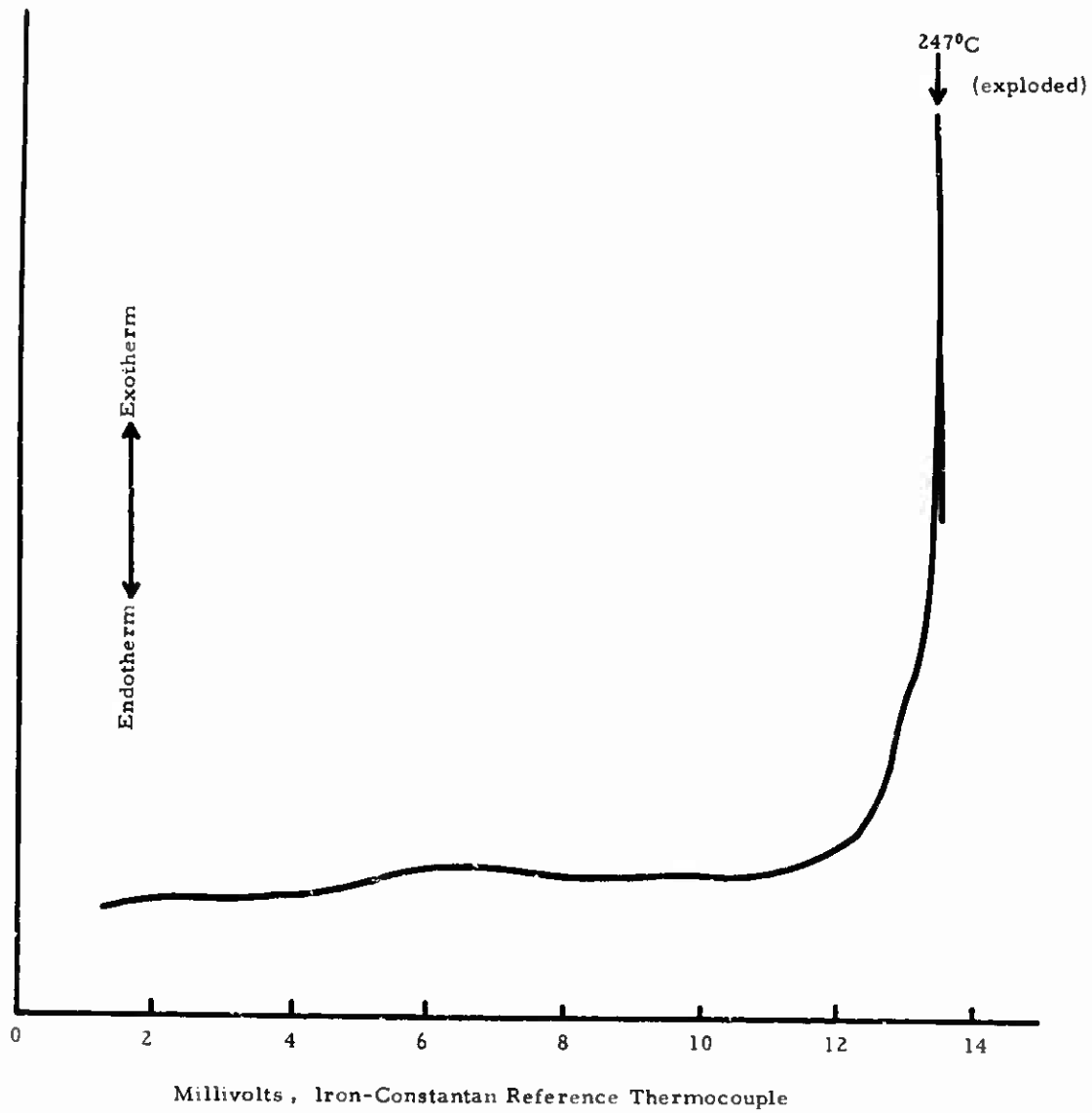
FIGURE 9. (U) THERMOGRAM OF RH-Y-2 [G,G] PROPELLANT
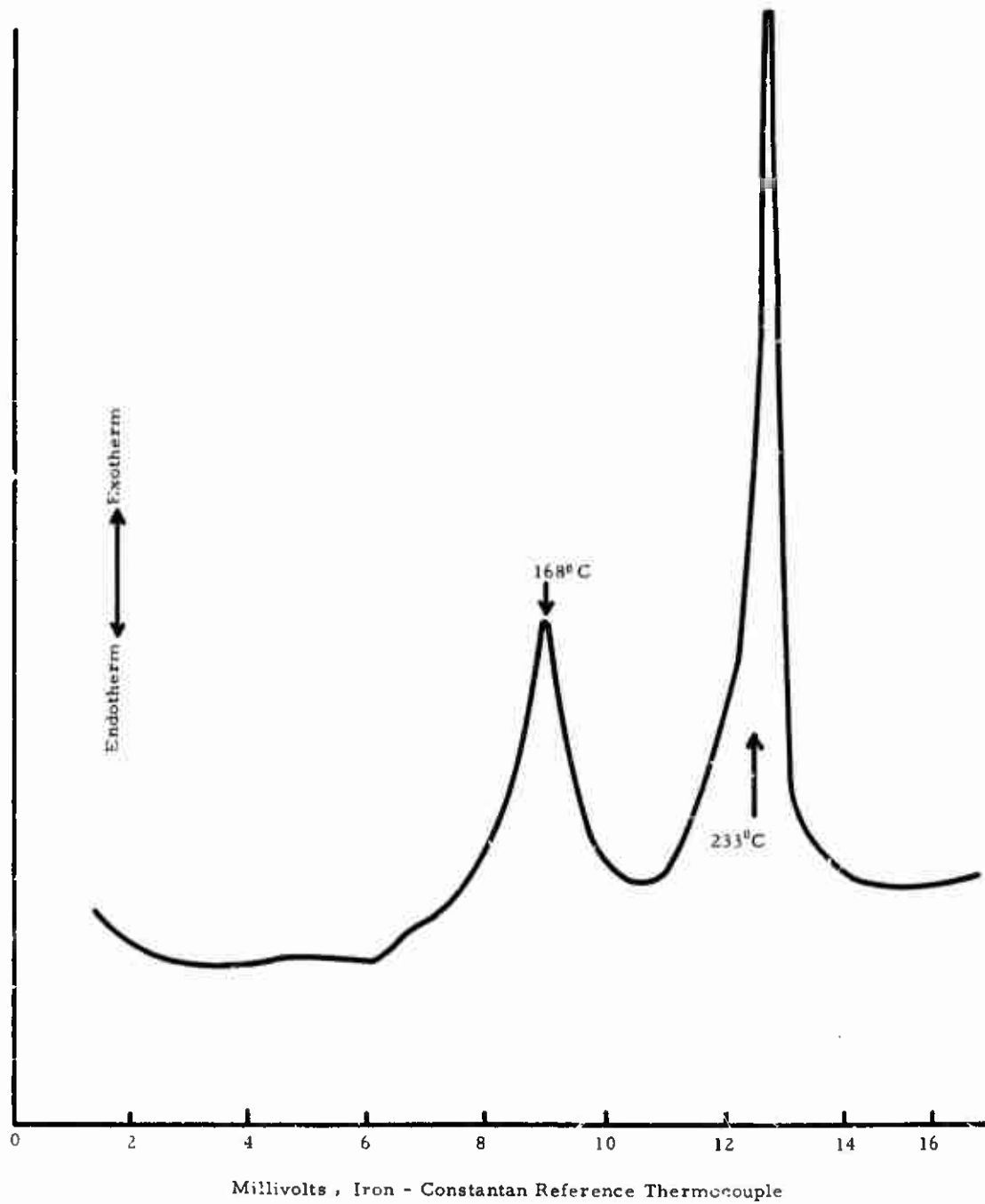
FIGURE 10. (U) THERMOGRAM OF NFPA [V]
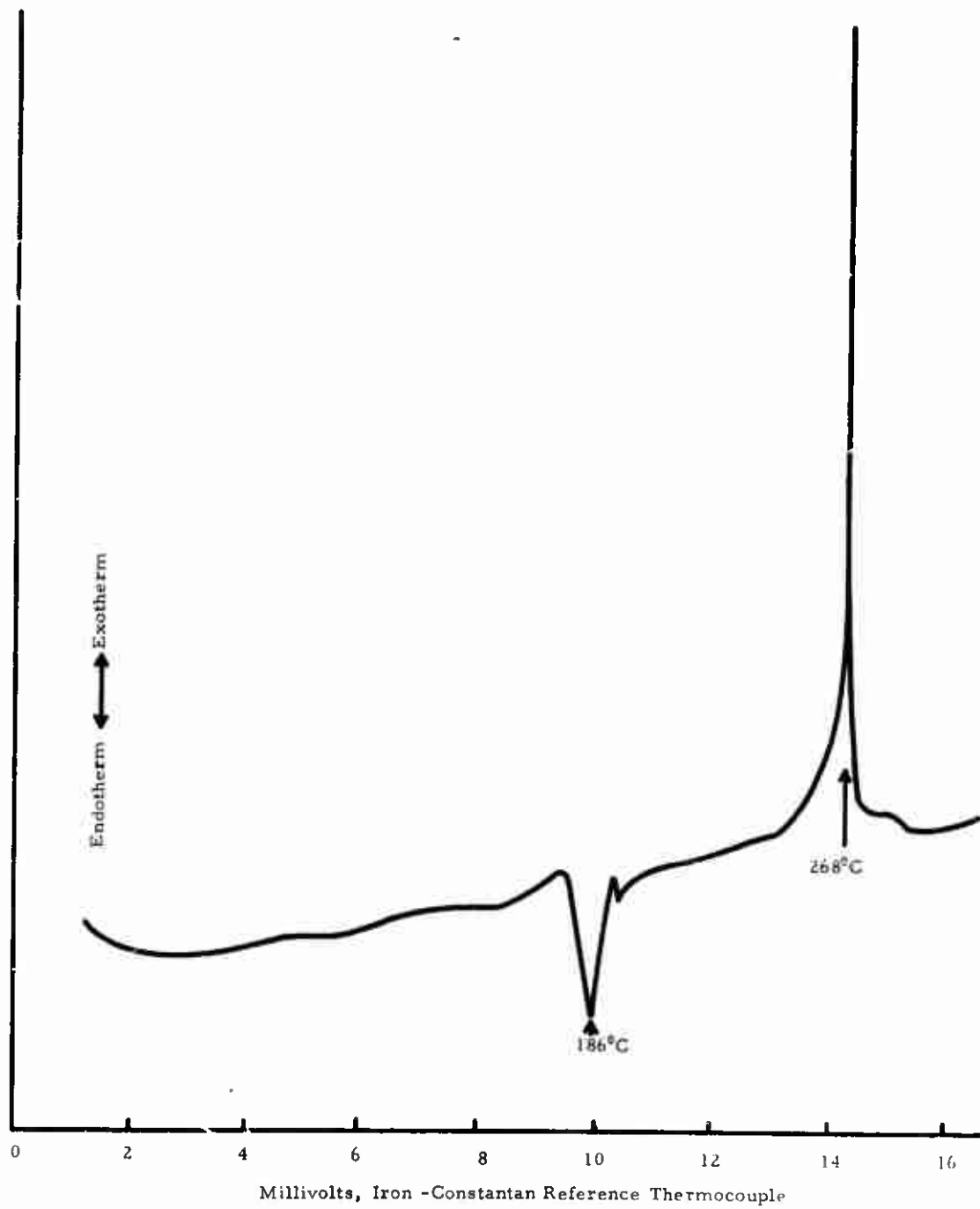
FIGURE 11. (U) THERMOGRAM OF MY [G]

Table VIII. (U) DTA Temperatures for Vicinal and Geminal Materials		
Material	Peak Exotherm Temperature, ^{0}C	Comments
Vicinal		
TVOPA	270	
NFPA (monomer)	232	polymerization exotherm peak at 170^0
homopolymer of NFPA	244	
PPAA-4	218	
PPAA-4E	215	
TVOPA/PPAA-4 (2/1)	208	ignition at peak
RH-SE-103	240	ignition at peak
Geminal		
TGAP	256	ignition at peak - shoulder peak $\sim$252^0
MY (monomer)	261	endotherm overlapping exotherm peaking at 185
homopolymer of MY	255	ignition at peak, shoulder peak $\sim$245
PY-1	255	ignition at peak
TGAP/homopolymer of MY (2/1)	256	ignition at peak
TGAP/PY-1 (2/1)	252	ignition at peak
RH-Y-2	247	ignition at peak
Geminal and Vicinal		
TVOPA/PY (2/1) (V/G)	218	ignition at peak
RH-Y-1 (G, V)	248	

Section X. (C) THERMOGRAVIMETRIC ANALYSIS[a] (U)

Thermogravimetric analyses (TGA) were performed with a Cahn RG Electrobalance, and F & M Model 240 temperature programmer, a Moseley Model 7000A XY recorder, and accessory equipment. The experiments were carried out in air with a heating rate of 10^0C/min. Two TGA graphs are shown in Figures 12 and 13.

The TGA's of the various polymers studied were very similar. Each showed a slight weight loss before entering the rapid decomposition range and then exploded, leaving a small amount of black residue in the sample pan and elsewhere in the system. The relation of the ignition temperatures to each other in these experiments is similar to those of the peak temperatures in the DTA experiments (Table IX).

The TGA's of the propellants were also very similar. All showed a slow rate of weight loss starting at about 100^0C. The samples that burned out showed the same order of stability as that indicated by DTA. Samples of RH-Y-1 and RH-Y-2 occasionally exploded instead of burning out (Table IX).

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[a] These experiments were performed at the Army Propulsion Laboratory and Center by Mr. James Burnett through the courtesy of Mr. Chester Huskins.
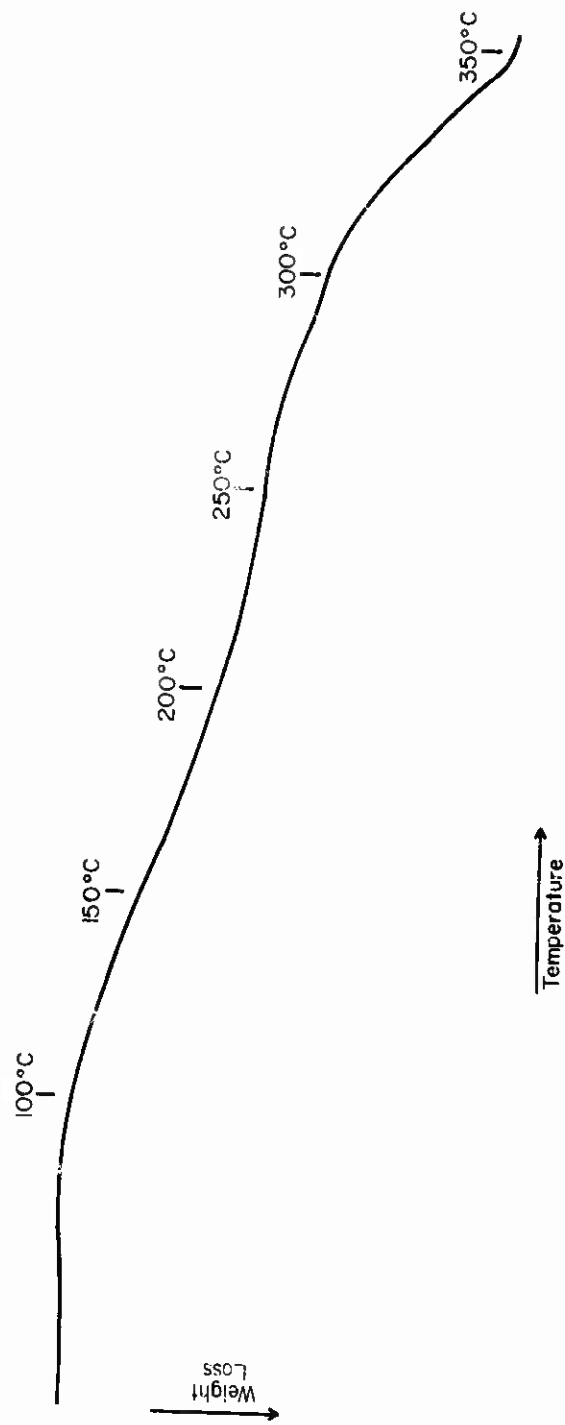
FIGURE 12. (U) THERMOGRAVIMETRIC ANALYSIS CURVE FOR
RH-SE-103 [V, V]
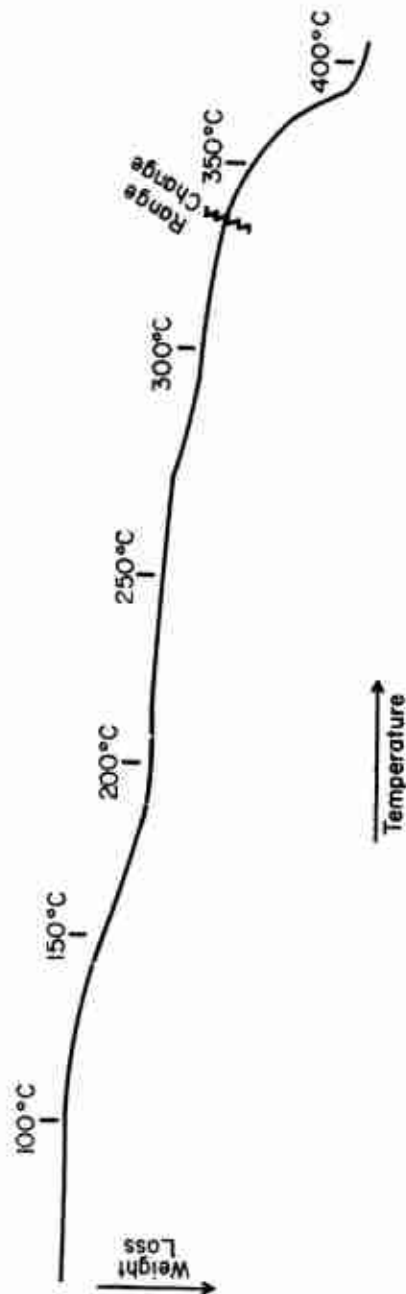
FIGURE 13. (U) THERMOGRAVIMETRIC ANALYSIS CURVE FOR RH-Y-1 [G, V]

Table IX. (C) TGA Data for Geminal and Vicinal Comparison	
Polymers	
Material	Ignition Temperature ^{0}C
poly-vic-NFPA (lab homopolymer)	240
PPAA-4-1015 (plant copolymer) [V]	220
poly-gem-NFPA (lab homopolymer)	266
PY-1 (lab copolymer) [G]	270
PY-1-7003 (plant copolymer) [G]	255

Propellants			
Material	Temperature ^{0}C beginning of wt. loss	Temperature ^{0}C 2nd wt. loss start	Comments
RH-SE-103 [V-V]	100	300	350^{0}C burned out
RH-Y-1 [G-V]	100		235^{0}C exploded
RH-Y-1 [G-V]	100	280	burned out above 350^{0}C
RH-Y-2 [V-V]	100		231^{0}C exploded
RH-Y-2 [V-V]	100		370^0 C burned out

Section XI. (C) SENSITIVITY

Sensitivities for both vicinal and geminal ingredients are measured by tests at various stages of processing. The impact test is performed on a Picatinny type of impact tester; the card-gap test is of standard design. These tests have been described in a previous report by Pratt (15). Pratt's report also contains data for other tests for the vicinal materials. His report will be updated shortly (16).

The comparison data are shown in Table X. The impact data show that the geminal materials are more sensitive than the corresponding vicinal materials. The few figures available for the card-gap test show no significant difference.

Table X. (C) Comparison of Sensitivity Data of Geminal and Vicinal Materials		
	Impact, Kg-in.	Card-Gap, in.
MY [G]	7. 7 - 9. 84	-
NFPA [V]	> 38	-
TGAP [G]	3	-
TVOPA [V]	7 - 14	-
PY-1]G]	7. 7	-
PPAA-4 [V]	21	-
PY-1 [G] solution	> 38	-
PPAA-4 [V]	> 38	-
PY-1 + TVOPA [G-V]	5. 66	.42 - .44
PY-1 + TGAP [G-G]	(1. 6)? 6. 24	-
PPAA-4 + TVOPA [V-V]	10. 1	.44 - .46
RH-SE-103 [V, V]	8. 09	-
RH-Y-1 [G, V]	5. 44	-
RH-Y-2 [G, G]	4. 9	-
RH-SE-103 slurry	-	1. 21 - 1. 23
RH-Y-1 slurry	-	1. 20 - 1. 22

Section XII. (C) BALLISTIC PROPERTIES

Strand burning rates have been measured for both binders and cured propellant by means of a strand burner described previously (17). In addition, some rates have been measured in a micro-window bomb.

At each pressure studied, the burning rates of the binders having geminal components are faster than those for the all-vicinal binders, at the same ratio of plasticizer to copolymer. At 1000 psig the rates are as follows:

> TGAP/PY-1 (2/1) [G/G]   - 1.35 in./sec
> TVOPA/PY-1 (2/1) [V/G]   - .8 in./sec
> TVOPA/PPAA-4 (2/1)[V/V] - .6 in./sec

The data are shown in Figure 14. The percentage increase from all-vicinal binder to all-geminal is considerably more than 100%.

The strand burning rates for the propellants also show the increased burning rates noted in the binders obtained by replacing the vicinal NF_2's with corresponding geminal-NF_2's at the higher pressures, but the increase is much smaller. In fact, the increase in rate is of little value and may safely be ignored. Current data with the geminal system at lower pressures (below 2000 psig) are somewhat ambiguous on the relative rates of RH-Y-1 [G-V] and RH-Y-2 [G-G]. From the strand burner, there is not enough data to locate positively the pressure-burning rate curves, and it may be that the curves for these two propellants actually cross near 1000 psig. Additional data for RH-Y-1 [G-G] are available for the low-pressure region. These points are below the high-pressure points extrapolated from the other apparatus and do not clarify the issue. In any case, both geminal-containing propellants have slightly higher burning rates than does RH-SE-103 [V-V]. The data are collected in Table XI and illustrated in Figure 15. The propellants used in this part of the study were identical in all respects except for the replacement of the vicinal materials by geminal materials on a weight-by-weight basis.

Data have also been obtained from small motor firings for propellant containing geminal copolymer[a]. The results of these firings are listed in Table XII together with data for propellants containing the vicinal copolymers made by the two different production

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[a] Rohm and Haas Company unpublished data.

methods. Here again, the burning rate of the geminal propellant is higher than that for the vicinal propellant. The measured impulse is somewhat less for the geminal and the pressure coefficient is between the two values reported for the two vicinal systems.

Table XI. (C) Strand Burning Rates for Propellants					
RH-SE-103 [V-V]		RH-Y-1 [G-V]		RH-Y-2 [G-G]	
K_{psig}	r_b in./sec	K_{psig}	r_b in./sec	K_{psig}	r_b in./sec
0.96	1.10	1.05	1.35	0.55[a]	0.92
1.52	1.43	1.69	1.81	1.09	1.14
2.33	1.96	4.06	3.85	1.15[a]	1.31
4.32	3.37	6.49	5.84	1.65[a]	1.72
6.65	5.07	11.9	9.89	2.08	2.38
13.2	8.90	18.1	13.5	2.15[a]	2.02
17.4	11.3			4.45	4.81
				9.28	9.75
				17.3	15.5

[a] Data from Polymer Chemistry Group strand burner, others from Ballistics Section burner.

Table XII. (C) Ballistic Data Comparing Geminal- and Vicinal-Copolymer Propellants			
	Propellant, type copolymer		
Property	Incremental-Addition Vicinal	Batch Vicinal	Batch Geminal
Impulse	258.5	256.8	255.2
R_{1000}, in./sec	1.14	1.10	1.26
n	0.51	0.60	0.55

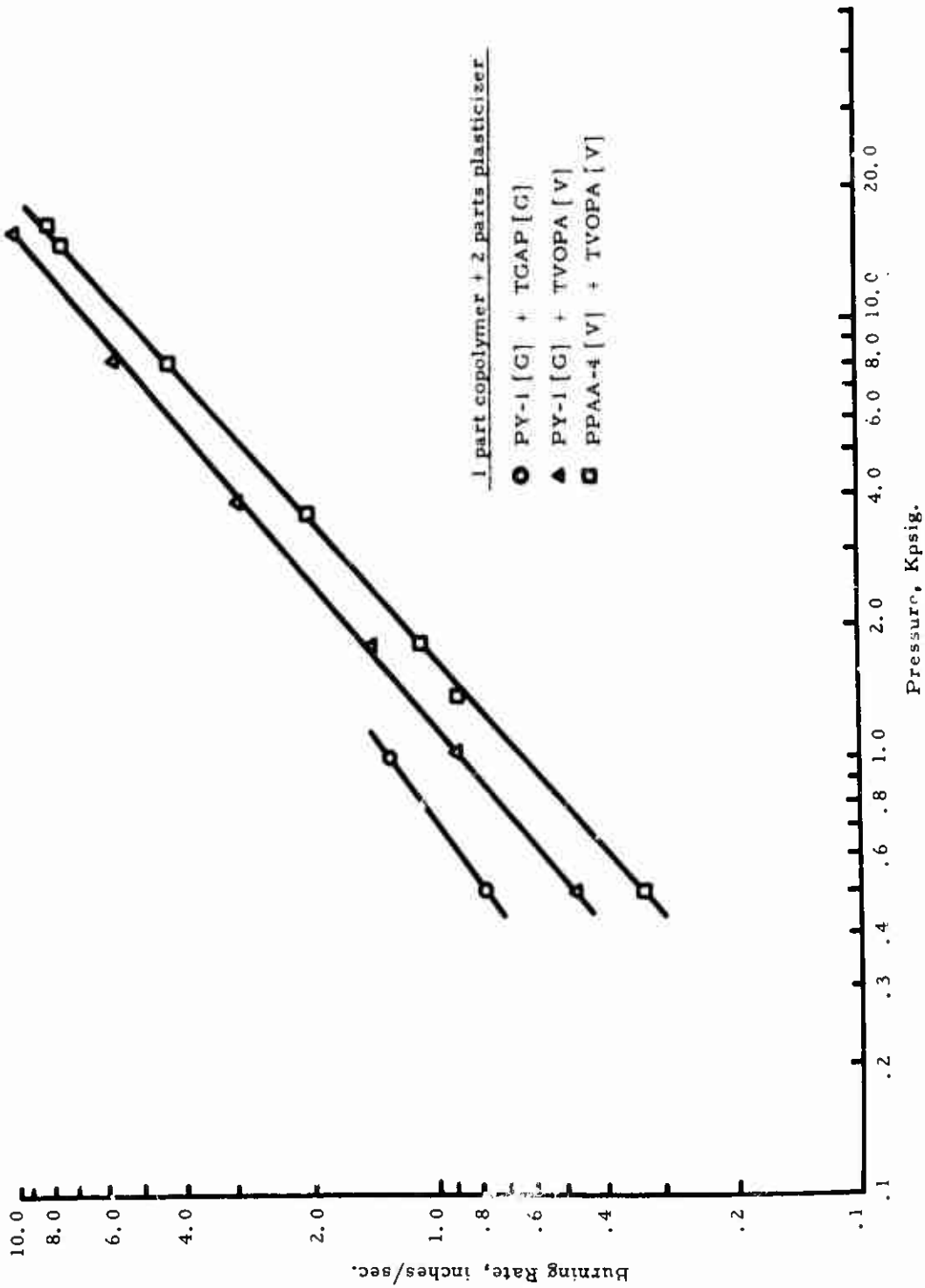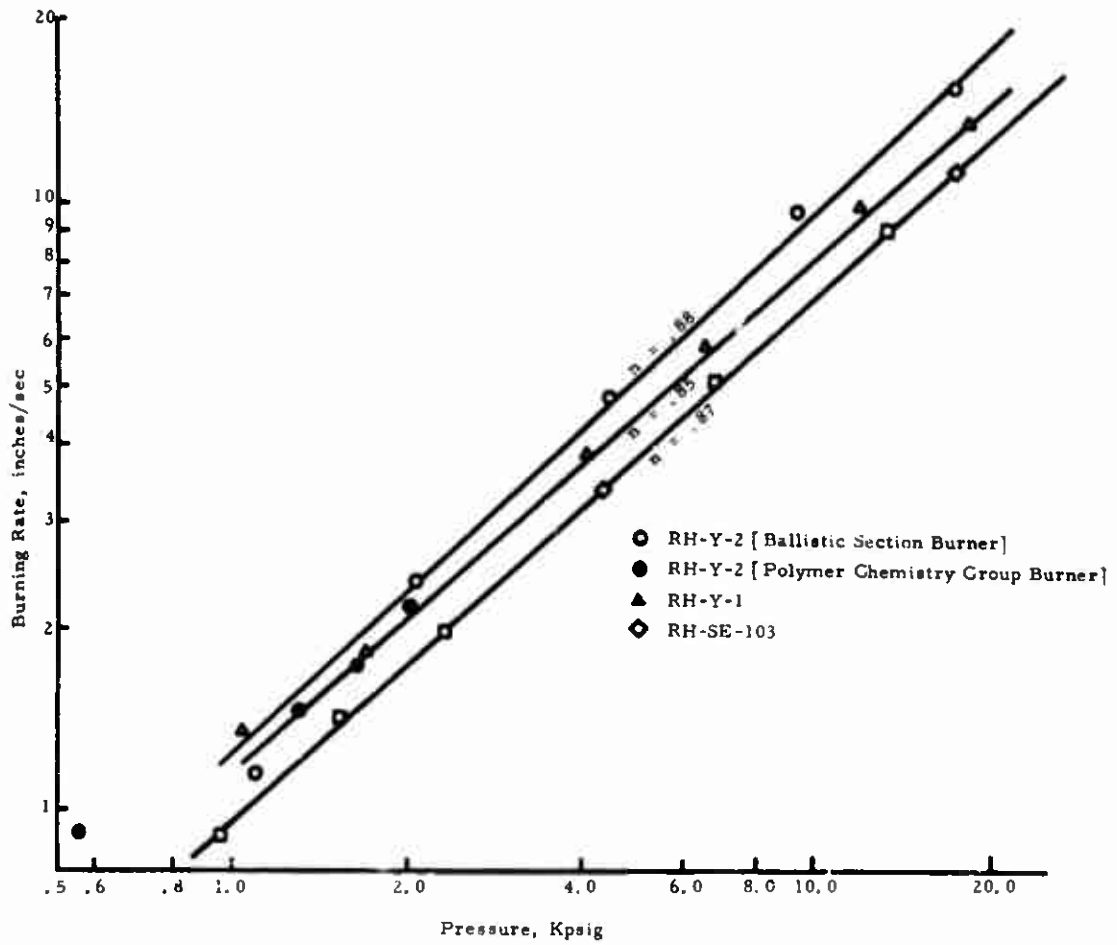FIGURE 14. (C) STRAND BURNING RATES OF BINDERS (U)

FIGURE 15. (C) STRAND BURNING RATES FOR THREE
NF-CONTAINING PROPELLANTS (U)

Section XIII. (C) SUMMARY AND CONCLUSIONS

For the properties discussed, the geminal materials studied compare favorably with their vicinal counterparts. A major drawback with the geminal materials is their increased impact sensitivity. However, card-gap, DTA, and TGA tests do not show a greater sensitivity for the geminal materials; in fact, DTA and TGA show the geminal materials, other than the plasticizer, to be more stable thermally than the corresponding vicinal materials. The burning rate increases obtained by replacing the vicinal materials with geminal, although very large in the binders themselves, are small in the propellants and do not constitute a significant improvement.

The area in which the use of the geminal materials was predicated to offer an improvement was in those factors leading to improved shelf life. The tests dealing most directly with shelf-life (the adiabatic self-heating rate tests, vacuum gas evolution tests, and fissuring-time tests) show the geminal materials to be as good as and, in some cases, much better than the best of the vicinal materials made to date.

The next area for study should be the evaluation of the all-geminal binders and propellants by the adiabatic self-heat rate test and a more stringent fissuring-time test. At the same time, the smaller range of values for the ASHR of the geminal materials compared with the vicinal materials should be checked to see if these values indicate that it is easier to produce "good" geminal material than to produce "good" vicinal material.

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13. ABSTRACT

(C) This report contains a compilation of data comparing geminal and vicinal difluoramino-containing plasticizers and copolymers. The plasticizers studied are 1,2,3-tris[1,2-bis(difluoramino)ethoxy]propane and 1,2,3-tris[2,2-bis(difluoramino)propoxy]propane. The copolymers are acrylic acid copolymers of both 2,3-bis(difluoramino)propyl acrylate and 2,2-bis(difluoramino)propyl acrylate. Data are presented for the monomeric materials, copolymers, binders, and propellants.

The data indicate that the vicinal and geminal materials behave similarly in many respects. The major disadvantage of the geminal NF-containing materials is their greater impact sensitivity. The main area in which the geminal materials show an advantage is seen in those tests related to storage stability. These tests include vacuum gas evolution and adiabatic self-heating. Data on fissuring time show that the geminal copolymers are as good as, if not better than, the best vicinal copolymers made to date. The geminals also have higher burning rates than the corresponding vicinals; however, the increase observed in the propellant is small.

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KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Difluoramino plasticizers and copolymers						
TVOPA						
TGAP						
gem-NFPA						
vic-NFPA						
Tg						
Fissuring-time tests						
Vacuum gas evolution						
Adiabatic self-heating						
DTA						
TGA						
Sensitivity						
Impact Stability						
Burning rate						
Mechanical properties						
Physical properties						